Chapter

Kinetic Approach to Multilayer Sorption: Equations of Isotherm and Applications

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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 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 so and the first layer s₁ is:

\[ a_1 \frac{P}{P^*} s_0 = b_1 s_1^* \exp \left( -\frac{E_1}{RT} \right) \]  (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:
\[ a_i \frac{p}{\rho^*} s^*_{i-1} = b_i s^*_i \exp \left( -\frac{E_i}{RT} \right) \]  

(2)

Being \( s^*_i \) and \( s^*_{i-1} \) 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:

\[ \frac{p}{\rho^*} = \frac{s^*_i}{s^*_{i-1}} \exp \left( -\frac{\Delta G_i}{RT} \right) \]  

(3)

where \( \Delta G_i \) is the sorption free energy of the \( i \)-layer. This development differs from the classical BET model in that \( \Delta G_i \) for all layers above the first is not considered equal to free energy of bulk liquid adsorbate, \( \Delta G_L \). 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:

\[ \Delta G_i = \Delta G_L + \Delta G_e^i \]  

(4)

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

\[ s^*_i = \omega_i s^*_{i-1} \]  

(5)

where

\[ \omega_i = \frac{p}{\rho^*} \exp \left( \frac{\Delta G_L}{RT} \right) \exp \left( \frac{\Delta G_e^i}{RT} \right) \]  

(6)

Defining

\[ h_i = \exp \left( \frac{\Delta G_e^i}{RT} \right) \]  

(7)

and given that \( P_0 = \rho^* \exp (-\Delta G_L/RT) \), it results:

\[ \omega_i = \frac{p}{P_0} h_i = x h_i \]  

(8)

being \( x = p/P_0 \). The fraction of surface occupied by 1st, 2nd, ..., \( i \)-th layer follows the relation:

\[ s^*_i = s^*_1 \prod_{j=2}^{i} \omega_j \]  

(9)

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

\[ s^*_i = s^*_1 \prod_{j=2}^{i} (x h_j) \]  

(10)

As \( s^*_1 = \omega_1 s_0 \), it results:

\[ s^*_i = h_1 s_0 x^i \prod_{j=2}^{i} h_j = C s_0 x^i \prod_{j=2}^{i} h_j \]  

(11)
where \( C = h_1 = \exp (\Delta G_1^c / RT) \) 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]:

\[
s_i^* = s_i (2i - 1)^{2-D}
\]

(12)

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

\[
s_i = C s_0 x^i (2i - 1)^{D-2} \prod_{j=2}^{i} h_j
\]

(13)

According to the BET theory, the monolayer capacity, \( N_m \), is:

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

(14)

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

\[
N_t = \frac{(2n-1)^{2-D}}{\sigma} \sum_{i=n}^{\infty} s_i = \frac{C s_0}{\sigma} (2n-1)^{2-D} \sum_{i=n}^{\infty} (2i - 1)^{D-2} x^i \prod_{j=2}^{i} h_j
\]

(15)

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

\[
N = \frac{1}{\sigma} \left[ s_1 + \sum_{i=2}^{\infty} s_i \sum_{k=1}^{i} (2k-1)^{2-D} \right] = \frac{C s_0}{\sigma} \left[ x + \sum_{i=2}^{\infty} x^i (2i - 1)^{D-2} \prod_{j=2}^{i} h_j \sum_{k=1}^{i} (2k-1)^{2-D} \right]
\]

(16)

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

\[
N = \sum_{i=1}^{\infty} N_t^i = \frac{C s_0}{\sigma} \left[ x + \sum_{i=2}^{\infty} (2i-1)^{2-D} \sum_{j=i}^{\infty} x^j (2j - 1)^{D-2} \prod_{k=2}^{j} h_k \right]
\]

(17)

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

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

(18)

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

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

(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:

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

(20)

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

(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 \((\lim_{i \to \infty} \Delta G_i^e = 0)\), \(h_2 > h_3 > \ldots > 1\) or \(h_2 < h_3 < \ldots < 1\), 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)

\[
\frac{N}{N_m} = \frac{Cx \left[ 1-(n+1)x^n + nx^{n+1} \right]}{(1-x) \left[ 1-x + Cx - Cx^{n+1} \right]}
\]

(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     | \[ \frac{N}{N_m} = \frac{Cx}{1-x(Cx)} \] (22) | [1] |
| \(k\) | \[ \frac{N}{N_m} = \frac{Cxk}{1-(1-k)x(1-Cx)} \] (23) | [27] |
| \(i-1\) | \[ \frac{N}{N_m} = \frac{Cx(1-x)}{(1-x)(1-Cx)} \] (24) | [28] |
| \(i\) | \[ \frac{N}{N_m} = \frac{Cx}{1-x(Cx)} \] (25) | [28] |

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

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

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:

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

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

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.
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, \( \alpha \), of the total adsorbing
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]:

\[
\frac{N}{N_m} = \frac{C_x(1 - \alpha x^n)}{(1-x)(1-x+Cx)}
\]  

(32)

In Figure 2, data of champignon mushroom and its fit using Eqs. (32) and (29) for different temperatures are presented.
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)     |     |     |           |      |     |     | [55]       |
| (Agaricus bisporus)         |     |     |           |      |     |     |            |
|                             | 30  | 2.42| 20.28     | 0.8478 | 1.41 | 0.19|            |
|                             | 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)                  |     |     |           |      |     |     | [51]       |
| Casein (d)                  |     |     |           |      |     |     |            |
| Coffee (a)                  |     |     |           |      |     |     |            |
| Dextrin (a)                 |     |     |           |      |     |     |            |
| Potato starch (a)           |     |     |           |      |     |     |            |
| Anis (a)                    |     |     |           |      |     |     | [32]       |
| Avocado (a)                 |     |     |           |      |     |     |            |
| Banana (a)                  |     |     |           |      |     |     |            |
| Cardamom (a)                |     |     |           |      |     |     |            |
| Celery (a)                  |     |     |           |      |     |     |            |
| Chamomile (a)               |     |     |           |      |     |     |            |
| Emmenthal (a)               |     |     |           |      |     |     |            |
| Cinnamon (a)                |     |     |           |      |     |     |            |
| Clove (a)                   |     |     |           |      |     |     |            |
| Coriander (a)               |     |     |           |      |     |     |            |
| Eggplant (a)                |     |     |           |      |     |     |            |

**Figure 2.**

Influence of temperature on desorption isotherms of champignon mushroom (Agaricus bisporus). Solid line, Eq. (32); dotted line, Pickett Eq. (29).
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

| 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]      |

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

\[ E^\% = 100 \cdot \frac{\sum_{i=N_p}^{N_p} (N_p - N_s_i)}{N_p} \quad p: \text{predicted} \quad e: \text{experimental} \]

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

*E% = 100 \cdot \frac{\sum_{i=N_p}^{N_p} (N_p - N_s_i)}{N_p} \quad p: \text{predicted} \quad e: \text{experimental}
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.

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References

[1] Brunauer S, Emmett PH, Teller J. Adsorption of gases in multimolecular layers. Journal of the American Chemical Society. 1938;68:309-319

[2] Saadi R, Saadi Z, Fazaeli R, Fard NE. Monolayer and multilayer adsorption isotherm models for sorption from aqueous media. Korean Journal of Chemical Engineering. 2015;32(5):787-799. DOI: 10.1007/s11814-015-0053-7

[3] Zhang P, Wang L. Extended Langmuir equation for correlating multilayer adsorption. Separation and Purification Technology. 2010;70:367-371

[4] Patiha, Firdaus M, Wahyuningsih S, Nugrahaningtyas KD, Hidayat Y. Derivation and constants determination of the Freundlich and (fractal) Langmuir adsorption isotherms from kinetics. IOP Conference Series: Materials Science and Engineering. 2018;333:1-9

[5] Thomas S, Schaetzel P. Multilayer adsorption equilibrium model for gas adsorption on solids. Adsorption. 2013;19:121-129

[6] Chen S-W, Guo B-L, Wang Y-L, Li Y, Song L-J. Study on sorption of U(VI) onto ordered mesoporous silicas. Journal of Radioanalytical and Nuclear Chemistry. 2013;295:1435-1442. DOI: 10.1007/s10967-012-1998-1

[7] Cherik D, Louhab K. A kinetics, isotherms and thermodynamic study of diclofenac adsorption using activated carbon prepared from olive stones. Journal of Dispersion Science and Technology. 2017;39(6):814-825. DOI: 10.1080/01932691.2017.1395346

[8] Charoen R, Tipkanon S, Savedboworn W. Sorption isotherm study of preserved wild mangosteen (kra-thon yhee) with replacing humectants. International Food Research Journal. 2018;25(3):1258-1265

[9] Hill TL. Theory of Physical Adsorption Advances in Catalysis. Vol. 4. New York: Academic Press; 1952. pp. 211-257

[10] Pickett G. Modification of the Brunauer–Emmett–Teller theory of multimolecular adsorption. Journal of the American Chemical Society. 1945;67:1958-1962

[11] Bashiri H, Orouji H. A new isotherm for multilayer gas adsorption on heterogeneous solid surfaces. Theoretical Chemistry Accounts. 2015;134:1594-1600. DOI: 10.1007/s00214-014-1594-2

[12] Anderson RH. Modification of the BET equation. Journal of the American Chemical Society. 1946;68:689-691

[13] de Boer JH. The Dynamical Character of Adsorption. 2nd ed. Oxford: Clarendon Press; 1968. 217 p

[14] Guggenheim EA. Application of Statistical Mechanics, Chap. 11. Oxford: Clarendon Press; 1966

[15] Arthur E, Tuller M, Moldrup P, Greve MH, Knadel M, de Jonge LW. Applicability of the Guggenheim–Anderson–Boer water vapour sorption model for estimation of soil specific surface area. European Journal of Soil Science. 2018;69:245-255. DOI: 10.1111/ejss.12524

[16] van den Berg C. Vapour sorption equilibrium and other water-starch interactions; A physico-chemical approach [PhD thesis]. Wageningen: Agricultural University; 1981

[17] Knani S, Aouaini F, Bahloul N, Khalfouzi M, Hachicha MA,
Ben Laminea A, et al. Modeling of adsorption isotherms of water vapor on Tunisian olive leaves using statistical mechanical formulation. Physica A. 2014;400:57-70

[18] Staudt PB, Tessaro IC, Marczak LDF, Soares RDP, Cardozo NSM. A new method for predicting sorption isotherms at different temperatures: Extension to the GAB model. Journal of Food Engineering. 2013;118:247-255

[19] Zou L, Gong L, Xu P, Feng G, Liu H. Modified GAB model for correlating multilayer adsorption equilibrium data. Separation and Purification Technology. 2016;161:38-43

[20] Van den Berg C, Bruin S. Water activity and its relation in food systems: Theoretical aspects. In: Rockland LB, Stewart GF, editors. Water Activity: Influences on Food Quality. London: Academic Press; 1981

[21] Droste-Hansen W. Structure of water near solid interfaces. Industrial and Engineering Chemistry. 1969;61(11): 10-47

[22] Fripiat JJ. Flow and porosimetry. In: Avnir D, editor. The Fractal Approach to Heterogeneous Chemistry. Surfaces, Polymers. Chichester/New York/Brisbane/Toronto/Singapore: John Wiley & Sons; 1990

[23] Vajda P, Felinger A. Multilayer adsorption on fractal surfaces. Journal of Chromatography A. 2014;1324: 121-127

[24] Bashiri H, Shajari A. Theoretical study of fractal-like kinetics of adsorption. Adsorption Science & Technology. 2014;32:623-634

[25] Xu YF, Matsuoka H, Sun DA. Swelling characteristics of fractal-textured bentonite and its mixtures. Applied Clay Science. 2003;22:197-209

[26] Aguerre RJ, Viollaz PE, Suarez C. A fractal isotherm for multilayer adsorption in foods. Journal of Food Engineering. 1996;30:227-238

[27] Blahovec J, Yanniotis S. ‘Gab’ generalised equation as a basis for sorption spectral analysis. Czech Journal of Food Sciences. 2010;28(5): 345-354

[28] Aguerre RJ, Suarez C, Viollaz PE. New BET type multilayer sorption isotherms. Part II: Modeling water sorption in foods. Lebensmittel-Wissenschaft und-Technologie/FST. 1989;22:192-195. ISSN: (0023-6438)

[29] Sawhney IK, Sarkar BC, Patil GR. Moisture sorption characteristics of dried acid casein from buffalo skim milk. LWT- Food Science and Technology. 2011;44:502-510

[30] Donnarumma D, Tomaiuolo G, Caserta S, Gizaw Y, Guido S. Water evaporation from porous media by dynamic vapor sorption. Colloids and Surfaces A: Physicochemical and Engineering Aspects. 2015;480:159-164

[31] Aouaini F, Knani S, Ben Yahia M, Bahloul N, Kechaou N, Ben Lamine A. Application of statistical physics on the modeling of water vapor desorption isotherms. Drying Technology: An International Journal. 2014;32(16): 1905-1922. DOI: 10.1080/07373937.2014.924131

[32] Wolf W, Spiess WEL, Jung G. Die Wasserdampf sorptions isothermen einiger in der Literatur bislang wehig beruck sichtiger. Lebensmittel-Wissenschaft und Technologie. 1973; 6(3):94-96

[33] Maraulis ZB, Tsami E, Marinos-Kouris D. Application of the GAB model to the moisture sorption isotherms for dried fruits. Journal of Food Engineering. 1988;7:63-78
[34] Makover B, Dehority GL. Equilibrium moisture content of dehydrated vegetables. Industrial and Engineering Chemistry. 1943;35(2): 193-197

[35] Iglesias HA. Isotermas de sorción de agua en remolacha azucarera y análisis del fenómeno de sorción de agua en alimentos [Tesis]. Buenos Aires University, F.C.E.yN.; 1975

[36] Coleman DA, Fellows HC. Hygroscopic moisture of cereal grains and flaxseed exposed to different relative humidities. Cereal Chemistry. 1955;2:275-287

[37] Hellman NN, Melvin EH. Surface area of starch and its role in water sorption. Journal of the American Chemical Society. 1950;72:5186-5188

[38] Bushuk W, Winkler CA. Sorption of water vapor on wheat flour, starch and gluten. Cereal Chemistry. 1957;34:73-76

[39] Day DL, Nelson GL. Desorption isotherms for wheat. Transactions of ASAE. 1965;8:293-297

[40] Aguerre RJ, Suarez C, Viollaz P. Moisture desorption isotherms of rough rice. Journal of Food Technology. 1983; 18:345-351

[41] Dunstan ER, Chung DS, Hodges TO. Adsorption and desorption characteristics of grain sorghum. Transactions of ASAE. 1973;16(4): 667-670

[42] Pixton SW, Henderson S. Moisture relations of dried peas, shelled almonds and lupins. Journal of Stored Products Research. 1979;15(2):59-63

[43] Pixton SW, Warburton S. The moisture content/equilibrium relative humidity relationship and oil composition of rapeseed. Journal of Stored Products Research. 1977;13:77-81

[44] Gane R. The water content of the seeds of peas, soya beans, linseed, grass, onion and carrot as a function of temperature and humidity of the atmosphere. Journal of Agricultural Science. 1948;38:81-83

[45] Iglesias HA, Chirife J. Effect of fat content on the water sorption isotherm of air dried minced beef. Lebensmittel-Wissenschaft und Technologie. 1977;10: 151-153

[46] Motarjemi Y. A study of some physical properties of water in foodstuffs. Water activity, water binding and water diffusivity in minced meat products [PhD thesis]. Lund, Sweden: Lund University; 1988

[47] Doe PE, Hashmi R, Pouler RG, Olley J. Isohalic sorption isotherms. Journal of Food Technology. 1982;17:125-134

[48] Labuza TP, Kaanane A, Chen JY. Effect of temperature on the moisture sorption isotherms and water activity shift of two dehydrated foods. Journal of Food Science. 1985;50:385-391

[49] Chau KV, Heinis JJ, Perez M. Sorption isotherms and drying rates for mullet fillet and roe. Journal of Food Science. 1982;47:1318-1328

[50] Rounsley RR. Multimolecular adsorption equation. AIChE Journal. 1961;7(2):308-311

[51] Bizot H. Using the GAB model to construct sorption isotherms. In: Jowitt R, Escher F, Hallstrom B, Meffert HPT, Spiess WEL, Vos G, editors. Physical Properties of Foods. Vol. 11. London/New York: Applied Science Publishers; 1983

[52] Zuritz CA, Singh RP, Moini SM, Henderson SM. Desorption isotherms of rough rice from 10 to 40°C. Transactions of ASAE. 1979;22:433-440
[53] Falabella MC, Aguerre RJ, Suarez C. Modelling non-isothermal sorption equilibrium data of cereal grains. Lebensmittel-Wissenschaft und Technologie. 1992;25:286-288

[54] Pantuso FS, Tolaba MP, Aguerre RJ. A BET approach to multilayer adsorption in swelling products. Journal of Food Commerce. 2014;122:68-71

[55] Shivhare US, Arora S, Ahmed J, Raghavan GSV. Moisture adsorption isotherms for mushroom. Lebensmittel-Wissenschaft und Technologie. 2004;37:133-137

[56] Iguaz A, Vírseda P. Moisture desorption isotherms of rough rice at high temperatures. Journal of Food Engineering. 2007;79:794-802