



Adsorptive Properties of Biobased Adsorbents

LESZEK CZEPIRSKI* AND EWA KOMOROWSKA-CZEPIRSKA

AGH–University of Science and Technology, Faculty of Fuels and Energy, 30-059 Cracow, Poland

czepir@uci.agh.edu.pl

JOANNA SZYMOŃSKA

Department of Chemistry, Agriculture University, 30-059 Cracow, Poland

Abstract. Water and methanol vapor adsorption isotherms for native and modified potato starch were investigated. For obtaining the best fit for the experimental data several models based on the BET approach was evaluated. The hypothesis that water is adsorbed on the starch granules at the primary and secondary adsorption sites as well as a concept considering the adsorbent fractality were also tested. It was found, that the equilibrium adsorption points in the examined range of relative humidity (0.03–0.90) were most accurately predicted by using a three-parameter model, proposed by Kats and Kutarov (1998). For methanol a good representation of experimental data was obtained using model proposed by Talu and Meunier (1996).

Keywords: bio-based adsorbents, water and alcohols adsorption, BET model, fractal dimension

1. Introduction

Parameters of isothermal equilibrium sorption process for food products are very important both from scientific and practical point of view. Carbohydrate biopolymers (like starch, cellulose, hemicellulose) easily and selectively adsorb water vapor from air, alcohols or organic vapors (Beery and Ladisch, 2001; Ladisch, 1997; Anderson et al., 1996). These biobased adsorbents containing different classes of chemical compounds are chemically heterogeneous. Moreover, they are also physically heterogeneous because of both crystallite and amorphous phases present in their molecules.

In practice, the equilibrium data are necessary for calculating the parameters of processes like drying and packaging, which depend mainly on the product water activity. In many cases, the obtained isotherm can represent, with reasonable accuracy, the sorption data for the whole range of water activities.

The aim of this study was to determine the water, methanol and ethanol sorption isotherms and to evalu-

ate the utility of various adsorption models for describing its sorption on potato starch granules.

2. Material and Methods

The sample of native potato starch and samples modified by deep freezing/thawing process were used in this work (Szymonska et al., 2000; Krok et al., 2000).

Water and alcohols vapour adsorption isotherms were measured volumetrically at 298 K using a device for simultaneous determination of isotherms and kinetic of adsorption (Ciembroniewicz and Komorowska-Czepirska, 1985). Before the experiment samples were outgassed at 343 K to residual pressure about 10^{-4} mmHg.

3. Results and Discussion

The representative examples of water and alcohols sorption isotherm for potato starch granules are given in Fig. 1.

Water isotherm belongs to the II type (according to the IUPAC classification) and describes the

*To whom correspondence should be addressed.

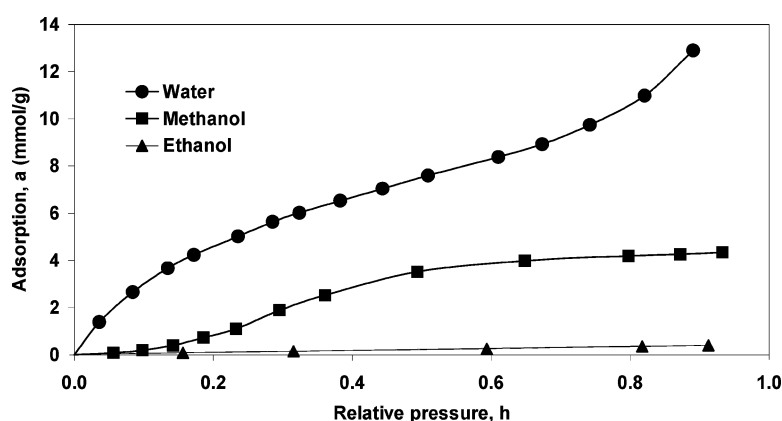


Figure 1. Water, methanol and ethanol adsorption isotherms for potato starch.

polymolecular water vapor sorption with strong adsorbate—adsorbent interactions. At low relative pressure water molecules penetrate the starch granule surface, where they form a monomolecular layer, while at higher pressure the multilayer formation takes place onto the monolayer of adsorbed water. Thus, the isotherm is the result of unrestricted monolayer—multilayer adsorption on heterogeneous substrate and its characteristic features are influenced by the relative magnitude of the adsorbent—adsorbate and adsorbate—adsorbate interactions.

In the case of methanol isotherm represent type V of isotherms with mono- and multilayer adsorption plus eventual capillary condensation. It shows also the inflection point characteristic for formation of clusters via H-bonding.

Adsorption of ethanol is negligible comparing with water and methanol and in further consideration this adsorbate was not made allowance for.

Numerous theories have been developed to explain the thermodynamic and molecular interactions occurring during monolayer and multilayer formation. However, there is no isotherm with a simple mathematical form capable of representing the sorption properties of biopolymers like starch in the whole range of water activities. In general, water sorption isotherms for starch products are analysed according to the BET model or its modifications, for instance the GAB (Guggenheim—Anderson—de Boer) equation. The BET model was found to be adequate only in the lower relative pressure range (<0.4), yet the GAB model was not appropriate for the estimation of monolayer capacity (Timmermann et al., 2001; Viollaz and Rovedo, 1999).

In first step hypothesis that water could be adsorbed on starch in two forms was tested. According to BET theory it was assumed that water is adsorbed as: primary molecules (adsorption sites with high binding energy, such as hydroxyl groups) and secondary molecules (sites with lower binding energy, such as previously occupied primary and other secondary sites). The following equations were used to represent the total (a), primary (a_p) and secondary (a_s) adsorption sites:

$$a_p = \frac{a_m b_1 h}{(1 - b_2 h + b_1 h)} \quad a_s = \frac{a_m b_1 b_2 h^2}{(1 - b_2 h)(1 - b_2 h + b_1 h)}$$

$$a = a_p + a_s \quad a = \frac{a_m b_1 h}{(1 - b_2 h)(1 - b_2 h + b_1 h)} \quad (1)$$

where: b_1 , b_2 —parameters, C —BET constant; $C = b_1/b_2$.

Values of parameters are listed in Table 1, as well as, surface area of the samples S_{BET} (calculated from a_m

Table 1. The parameter values obtained by application of Eq. (1) to water vapor adsorption isotherms for potato starch samples.

Sample	a_m (mmol g ⁻¹)	b_1 (-)	b_2 (-)	C (-)	S_{BET} (m ² g ⁻¹)
1	5.122	5.567	0.527	10.56	324
2	5.134	11.158	0.854	13.06	325
3	4.808	9.887	0.765	12.92	304
4	5.070	11.490	0.730	15.75	321
5	5.003	6.236	0.680	9.17	317
6	4.989	7.379	0.732	10.08	316

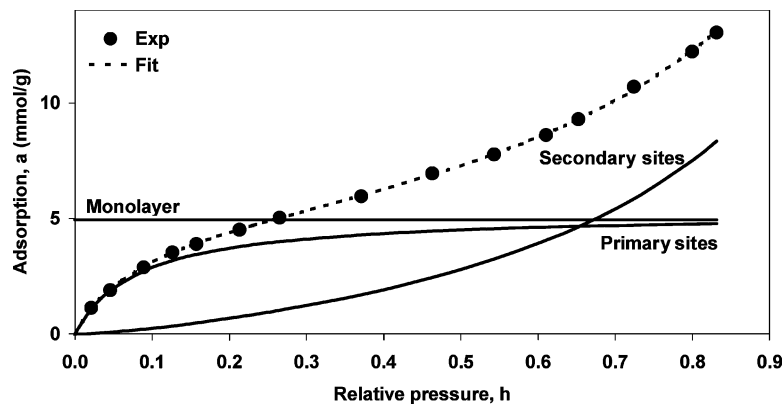


Figure 2. Water vapour isotherm for potato starch sample and modeled BET plots.

values assuming that cross-sectional area of adsorbed water molecule is equal 0.105 nm^2) is given. Figure 2 shows as an example the total isotherm and the components (monolayer, primary and secondary centers) as calculated by use the Eq. (1). The similarity between experimental isotherm and those modeled using the BET approach is evident. Over the range of relative pressures examined, model accurately predicts equilibrium adsorption points.

In this study, we also used a three-parameter equation obtained within the BET theory framework and proposed by Kats and Kutarov (1998):

$$a = a_m \cdot \frac{Ch(1 - h^n)}{(1 - h)(1 - h + Ch)} \quad (2)$$

where: a —is the adsorption capacity, h is the relative pressure, a_m , C are the BET constants, $n = n_c + n_f$ is the non-integer parameter in which the whole part corresponds to the real number of polylayers (n_c) and its fractional part (n_f) is defined by the adsorbent fractality as: $D = 2 + n_f$ (Kats et al., 1999).

The equation parameters were obtained by non-linear regression, using as objective function the minimisation of the relative deviations between the experimental and predicted values. The maximum relative deviations calculated by the used equation do not exceed $\pm 3\%$.

The Eq. (2) gives possibility to expand the range of applicability up to 0.9 of relative pressure and to describe experimental isotherms in multilayer region, as well as, region of clusters formation on adsorption centers.

Table 2 presents the parameters for all of the obtained isotherms, as well as, values of: the coordinates

Table 2. The parameter values obtained by application of Eq. (2) to water vapor adsorption isotherms for potato starch samples.

Sample	a_m (mmol g ⁻¹)	C (-)	D (-)	E_1 (kJ mol ⁻¹)	S_{BET} (m ² g ⁻¹)	h_m (-)
1	5.054	10.4	2.53	37.5	320	0.237
2	4.998	12.9	2.39	37.7	316	0.218
3	4.648	12.6	2.45	37.8	294	0.220
4	4.927	15.6	2.48	37.8	312	0.202
5	4.995	8.9	2.47	37.3	316	0.251
6	4.959	9.8	2.51	37.4	314	0.242

of points of monolayer h_m , calculated according to the known formulae: $h_m = 1/(\sqrt{C} + 1)$; the first the heat of layer adsorption, calculated from the equation: $E_1 - E_L = RT \ln(C)$, where: E_1 is the the first layer heat of adsorption, E_L is the heat of condensation, R is the gas constant, and T is the absolute temperature; S_{BET} —surface area of the samples. Figure 3 shows comparison of experimental points of isotherm for one of the samples under study and results of fitting using Eq. (2).

The water sorption ability of starch granules is caused by interactions of water molecules with free hydroxyl groups of the glucose units of starch. It has been also suggested that some amount of water could be adsorbed on starch granules due to capillary condensation. The monolayer capacity of such adsorbent is strongly related to the number of polar groups that are able to physically bound water on the starch surface. For all our samples we obtained parameter $C > 2$, what is an additional confirmation that presented isotherms could be classified as the II type. It can be seen from

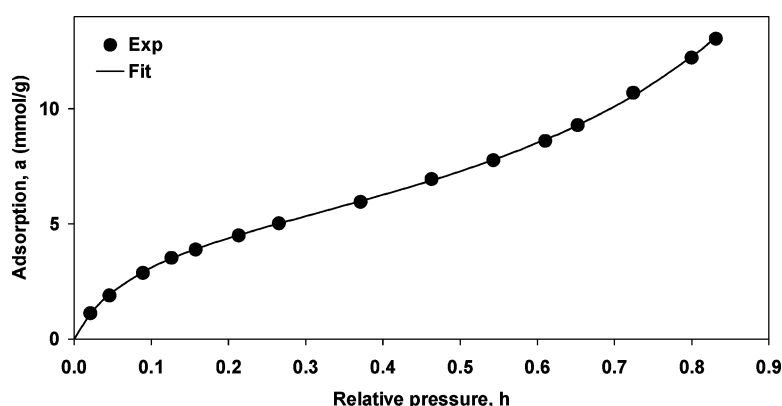


Figure 3. Water vapour isotherm for potato starch sample and fitting curve according to Eq. (2).

the Table 1, that adsorption energy in first layer (E_1) is practically of nearly the same value for all of the samples, what implies similar mechanism of water sorption in this region. Relatively high monolayer adsorption energy indicates formation of an oriented chemisorbed layer by water vapour molecules.

The fractal dimension of the investigated samples (D) was found relatively high, approaching 3. This could indicate that water molecules are adsorbed at the inner sorption sites three dimensionally. The fractal dimension is related to the degree of the irregularity adsorbent surface. As D increases the more irregular the structure becomes. Our results are in good agreement with data of Nagai and Yano. They determined the fractal dimension of freeze-dried and ethanol treated starches and found them to be in the range 2.3–3.0 (Nagai and Yano, 1990).

For analyse of the isotherm in the multilayer region, we applied Frenkel–Halsey–Hill (FHH) equation

in the form:

$$\ln(p/p_s) = -\frac{B}{(a/a_m)^r} \quad (3)$$

where B and r are constants, the latter giving a qualitative measure of the adsorbate–adsorbent interaction strength in the multilayer region of the isotherm. It was found that FHH plots in linear coordinates show good linearity over the range of relative pressures $(0.3–0.9)p_s$. Within the framework of this theory, we discussed the relationship between FHH isotherm exponent r and the fractal dimension D , based on the analysis of Pfeifer and Liu (1997). The correspondence between the FHH isotherm exponent and the fractal dimension is given in Fig. 4.

Our results let us to conclude, that water sorption on potato starch granules is the intermediate process between two regimes: van der Waals and capillary wetting.

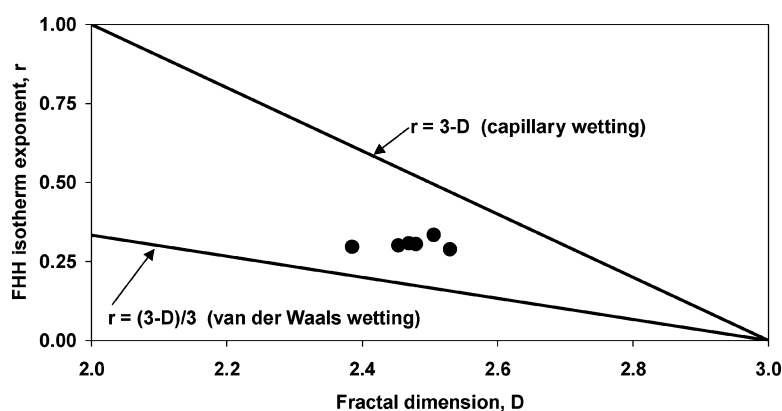


Figure 4. FHH isotherm exponent as a function of the fractal dimension.

Table 3. The parameter values obtained by application of Eq. (4) to methanol vapor adsorption isotherms for potato starch samples.

Sample	a_m (mmol g ⁻¹)	H (mmol g ⁻¹ mmHg ⁻¹)	K (-)
1	4.724	2.792	7.003
2	4.722	0.701	1.917
3	6.137	0.286	0.556
4	5.845	0.872	1.603
5	4.414	1.172	3.220
6	5.073	1.589	3.688

For methanol the approach proposed above does not give a good representation of experimental data what is probably connected with different mechanism of adsorption (as far as water is adsorbed by forming hydrogen bonds between the hydroxyl groups on the surface and water molecules, in case of methanol it can be assumed that methyl groups cause strong screening effect for methanol molecules).

In this study we undertook the attempt to use model proposed by Talu and Meunier (1996) for description of water vapor adsorption on activated carbon:

$$p = \frac{H\Psi}{1 + K\Psi} \exp\left(\frac{\Psi}{a_m}\right) \quad \Psi = \frac{-1 + \sqrt{1 + 4K\xi}}{2K}$$

$$\xi = \frac{a_m \cdot a}{a_m - a} \quad (4)$$

where: a —adsorption at equilibrium partial pressure of methanol vapor p ; a_m —saturation capacity; H —Henry's constant; K —reaction constant for cluster formation.

Parameters of Eq. (4) are listed in Table 3 and we treat it as the indicator making the possible the com-

parison of properties of different samples with respect to methanol.

The obtained results indicate that although water and alcohols adsorption on potato starch granules should not be considered as a surface phenomenon, the approach proposed in this study validates the usage of the multilayer adsorption concept in analysis of adsorption mechanism in case of biopolymer-type adsorbents.

A number of problems still remain to be explored to analyze the properties of these unique materials and we do hope to discuss some of them in future.

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