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Fitting of different models for water vapour sorption on potato starch granules

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Abstract

Water vapour adsorption isotherms for native and modified potato starch were investigated. To obtain the best fit for the experimental data several models based on the BET approach were 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.

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Parameters of isothermal equilibrium sorption process for food products are very important from both scientific and practical points of view. Carbohydrate biopolymers (like starch, cellulose, hemicellulose) adsorb water vapour from air, alcohols or organic vapours easily and selectively [1,2]. These bio-based adsorbents containing different classes of chemical compounds are chemically heterogeneous. Moreover, they are also physically heterogeneous because of both crystallite and amorphous phases are present in their molecules.

In practice, equilibrium data are necessary to calculate parameters of the 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 sorption isotherms and to evaluate the utility of various adsorption models for describing water sorption on potato starch granules. The samples of native and modified by a deep freezing/thawing process (according to the procedure described by Szymońska and co-workers [3,4]) potato starch were used in this work. Water vapour adsorption isotherms were measured volumetrically at 298 K using a device for simultaneous determination of isotherms and kinetics of adsorption [5]. Before the experiment the samples were outgassed at 343 K to residual pressure about 10^{-4} mmHg.

The typical example of water sorption isotherm for potato starch granules is given in Fig. 1. The presented isotherm belongs to II type (according to the IUPAC classification) and describes the polymolecular water vapour sorption in a wide range of relative pressure. At low relative pressure water molecules penetrate the starch granule surface, where they form a monomolecular layer, while at higher pressure the

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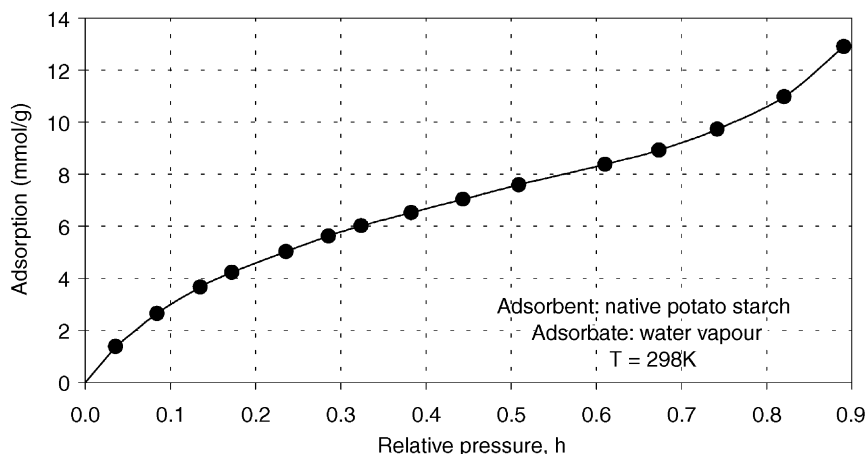


Fig. 1. Water vapour adsorption isotherms for native potato starch.

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.

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 [6,7].

In this study, we used a three-parameter equation obtained within the BET theory framework and proposed by Kats and Kutarov [8]:

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

where a is the adsorption capacity, h the relative pressure, a_m and C are the BET constants, $n = n_c + n_f$ 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 $D = 2 + n_f$ [9]. In our study, the equation parameters were obtained by non-linear regression, using minimisation of the relative deviations between the experimental and the predicted values as the objective function. The maximum relative deviations calculated by the equation do not exceed $\pm 3\%$.

Table 1 presents the parameters for all of the obtained isotherms, as well as the values of:

- the coordinates of points of monolayer h_m , calculated according to the known formulae $h_m = 1/(\sqrt{C} + 1)$,

Table 1

The parameter values obtained by application of the modified BET equation to water vapour adsorption isotherms for the potato starch samples

Sample	a_m (mmol/g)	C	D	E_1 (kJ/mol)	S_{BET} (m^2/g)	h_m
1	5.054	10.4	2.53	37.5	320	0.237
2	5.049	8.4	2.44	37.2	320	0.257
3	4.998	12.9	2.39	37.7	316	0.218
4	4.648	12.6	2.45	37.8	294	0.220
5	4.927	15.6	2.48	37.8	312	0.202
6	4.995	8.9	2.47	37.3	316	0.251
7	4.838	6.3	2.44	37.3	306	0.284
8	4.539	7.2	2.55	37.5	287	0.272
9	4.707	7.2	2.52	37.4	298	0.272
10	4.959	9.8	2.51	37.4	314	0.242

- the first heat of layer adsorption, calculated from the equation $E_1 - E_L = RT \ln C$, where E_1 is the first layer heat of adsorption, E_L the latent heat of condensation, R the gas constant, and T the absolute temperature,
- surface area of the sample, calculated from a_m values assuming that the cross-sectional area of adsorbed water molecule is equal to 0.105 nm^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 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 bound water physically on the starch surface. For all our samples we obtained the parameter C greater than 2, which is an additional confirmation that the presented isotherms could be classified as II type. It can be seen in Table 1 that adsorption energy in the first layer (E_1) has nearly the same value for all the samples, which 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. For the starch granules it can be assumed as well that water is adsorbed in two forms: 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 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 adsorbent surface irregularity. As D increases, the structure becomes more regular. Our results are in good agreement with the 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 [10].

To analyse the isotherm in the multilayer region, we applied the Frenkel–Halsey–Hill (FHH) equation in the form:

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

where B and r are the constants, the latter giving a qualitative measure of the adsorbate–adsorbent interaction strength in the multilayer region of the isotherm. It was found that the FHH plots in the 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 [11]. The correspondence between the FHH isotherm exponent and the fractal dimension is given in Fig. 2.

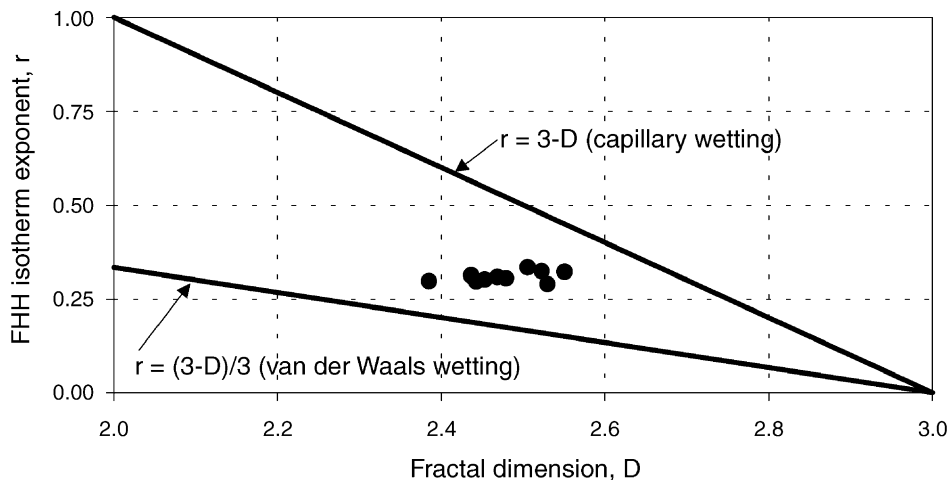


Fig. 2. FHH isotherm exponent as a function of the fractal dimension.

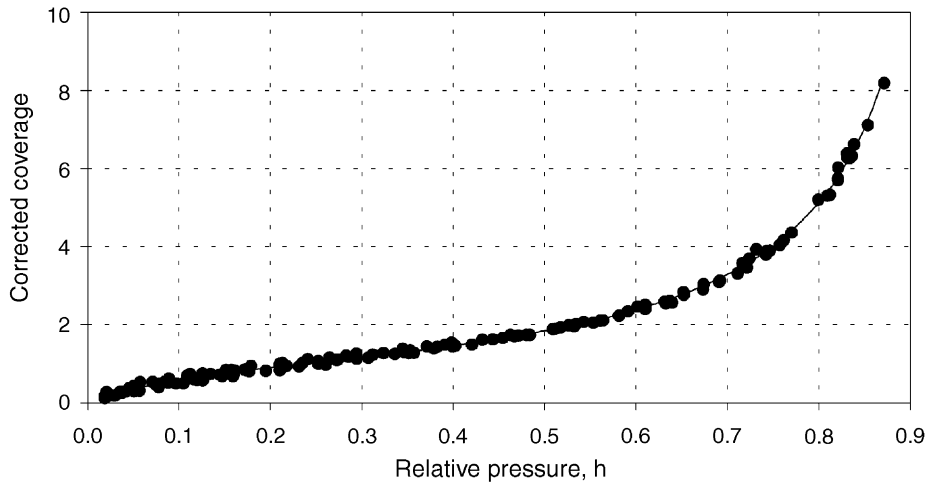


Fig. 3. Generalised water vapour adsorption isotherms for the potato starch samples.

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

In the next step, experimental isotherms were transformed to the generalised curve according to the procedure proposed and discussed in detail by Kats et al. in [12]. For this aim the isotherms were expressed in the coordinates: $\Theta_c = f(h)$, where $\Theta_c = a/a_m(1 - h^n)$ is the corrected value of coverage. According to this approach for the same values of the corrected coverage corresponding to the same values of relative pressure, adsorption isotherms could be described by one generalised curve. The individual isotherms transformed in such a way into a generalised form are presented in Fig. 3.

It should be noted that transformation of any individual isotherm has not changed its S-shape form. This approach might be considered as a starting point for the analysis of adsorption mechanism in the systems with simultaneous physical adsorption and swelling processes.

The obtained results indicate that although water adsorption on the 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 the analysis of adsorption mechanism in the case of biopolymer-type adsorbents.

A number of problems still remains to be explored to analyse the properties of these unique materials and we do hope to discuss some of them in our next work.

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