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Differential model of the kinetics of water vapour adsorption on maize starch particles

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Abstract. An understanding of the kinetics of water vapour sorption allows for the prediction of the stability of food in the management of transport and storage processes, it also facilitates the optimization of drying processes, and the rationalization of the methods of studying sorption statics. The present study aimed to determine an appropriate model of the kinetics of water vapour sorption on the surface of maize starch particles, which could prove useful in describing kinetic curves as well as allowing for the determination of the time required to reach a state of equilibrium. Experimental data was obtained through the continuous measurement of the increase in sample mass. The model was developed by matching the simulation results to the experimental results. Its parameters were identified by minimizing the mean square error between the time courses of the simulation and the experimental results, which allowed for the avoidance of problems concerning data processing and the loss of information. Two methods were deployed in order to minimize the occurrence of error: multi-start and gradient ones. The proposed model provided an appropriate description of the kinetics of water vapour adsorption by maize starch, regardless of the mass of the samples used and the physical state of their particles. The time required for a state of equilibrium to be attained was significantly shorter than the usually assumed period of 30 days.

Keywords: sorption kinetics, two-component model, sorption, storage management

INTRODUCTION

Among all of the phenomena affecting the mobility of a substance, its transfer from a mobile phase (liquid or gas) to a solid phase is a universal phenomenon. For this reason, the "isotherm", *i.e.* the curve that comprehensively describes the retention of a substance on a solid body, is the main tool used to describe and predict the mobility of this substance in the environment. The phenomena of the retention or release of a substance, leading to an equilibrium state which may be described by isotherms, are sometimes kinetically controlled to a significant extent. Hence, it is important to extend our knowledge concerning sorption isotherm dependence in a timely manner (Limousin *et al*., 2007).

The simplest method used to obtain the sorption data of foods is by storing a weighed sample in a closed container maintained at an established relative humidity, at a constant temperature, and reweighing it after equilibrium has been reached. Theoretically, at equilibrium the water activity of the sample is the same as that of the surrounding environment. However, in practice equilibrium is never attained because that would require an infinitely long time. Therefore, the sample is weighed systematically during this process. When the difference between the subsequent weight measurement results of the sample becomes less than the sensitivity of the balance being used, it is accepted that equilibrium has been reached. The moisture content of the sample is then determined (Sahin and Sumnu, 2006).

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Currently, investigations into adsorption kinetics have inspired considerable interest primarily due to their importance in the assessment and use of adsorbents, for example, in wastewater treatment (Qiu *et al*., 2009) or air drying in industrial processes (Mittala *et al*., 2020). The more complicated models developed in studies of this type take into account both the adsorption mechanism as well as the diffusion analysis. However, appropriate, effective software is required to solve such complex mathematical equations, which will allow these models to accurately describe the effects of a given adsorbent and to gain an insight into the adsorption mechanism (Lima *et al*., 2015).

By contrast, much less attention is being paid to the issue of the kinetics of water vapour sorption on food surfaces, which leads to a state of equilibrium and is usually described using sorption isotherms. However, investigations addressing the kinetics of water vapour sorption on the surface of food products are interesting for at least a few important reasons, namely:

1) they are of significant practical importance in predicting the storage stability of foods and add much to the information obtained in sorption statics studies (Labuza and Altunakar, 2007; Goula *et al*., 2008; Silva *et al*., 2014; Stępień *et al*., 2020);

2) they allow for the optimization of the drying process (Goula *et al*., 2008; Mrad *et al*., 2012; Zhao *et al*., 2015; Wang *et al*., 2019);

3) they allow for the determination of the efficiency of acquiring the results of research concerning sorption statics and their reliability (Kohler *et al*., 2006; Gondek and Lewicki, 2007; Silva *et al*., 2014; Ocieczek *et al*., 2015).

Therefore, the investigations which focused on the kinetics of water vapour sorption in food are expected to not only solve a theoretical problem, but also to be an important element in the management of food production and distribution processes and also in the management of food quality research.

The phenomena occurring on the surfaces of solid bodies (food), are known as sorption in the first phase, they are physical in nature and constitute the starting point for subsequent changes of a chemical, biochemical or microbiological nature, which determines the stability of these bodies (Labuza and Altunakar, 2007; Silva *et al*., 2014). Undoubtedly, the phenomenon of sorption concerns the interactions of surfaces with various substances, including primarily water (usually in the form of vapour). Water vapour is a natural environmental factor that determines, first and foremost, the storage stability and microbiological safety of food (Bonilla *et al*., 2010; Ansari *et al*., 2011; Sandle, 2016; Ahmed and Islam, 2018).

The natural tendency of any system to reach a state of maximum disorder and minimal energy results in the achievement of an equilibrium (Dutkiewicz, 1998, Atkins, 2003), this has been addressed in many papers (Bejar *et al*., 2012; Akoy *et al*., 2013; Igbabul *et al*., 2013; Stępień *et al*., 2022). However, the dynamic process that leads to the achievement of an equilibrium state, and is referred to as sorption kinetics, has been explored far less frequently (Kohler *et al*., 2006; Gondek and Lewicki, 2007; Szulc and Lenart, 2012; Machado *et al*., 2012; Ocieczek *et al*., 2015).

Hence, it seemed worthwhile to undertake a study aimed at developing a model of the kinetics of water vapour sorption on the surface of organic powders, which: 1) will prove useful in describing the course of the curves, 2) will allow for the establishment of the time required to reach a state of dynamic equilibrium, and 3) will allow for the investigation of the relationship between the physical state of the particles of the examined material and the sorption kinetics.

MATERIALS AND METHODS

The study material used was maize starch (MS), it is also referred to as mazein. Native maize starch (NMS) was produced under industrial conditions from the endosperm, whereas micronized maize starch (MMS) was obtained under laboratory conditions from the native maize starch by disintegration (micronization) using a WŻ-1 laboratory grinder (Zakład Badawczy Przemysłu Piekarskiego, Bydgoszcz, Poland) with a rotational speed of 1 000-17 000 rpm. The micronization of NMS to produce MMS took a relatively short time, *i.e.* 60 seconds at the maximum rotational speed, and aimed to modify the physical state of the NMS particles primarily to make the particles constituting the sample mixture more homogenous.

The analysed samples of NMS and MMS were in the form of white powders, these were devoid of taste and aroma, and their chemical composition was as follows (based on the data provided per unit package): fat – 0 g, including saturated fatty acids – 0 g, carbohydrates – 86.8 g, including sugars – 0.9 g, protein – 0.2 g, dietary fibre – 1.7 g, and salt – 0.01 g.

After micronization, both types of starch samples were analysed to determine the differences in their physical properties, this was based on:

1) the distributions of selected particle size parameters (diameter, sphericity, convexity, elongation, aspect ratio, and solidity) – using an automatic Morphology G3 analyser (Malvern Instruments);

2) the water content before and after adsorption – using a MAC 50 moisture analyser (RADWAG);

3) the water activity before and after adsorption – using an AquaLab 4TE meter version AS4 2,14.0 2017 (Decagon Devices, Inc.), with an accuracy of ±0.0003, at a temperature of 293 K (20°C) ± 2.5 K.

The differences in the particle size parameters were compared based on the minimal, maximal and mean values with standard deviations, these were obtained as a result of the instrumental analysis of 151 549 NMS particles and 271 677 MMS particles. In turn, the differences in water content and activity were identified on the basis of three parallel determinations, which were then subjected to ANOVA analysis and a post-hoc Tukey test. The experimental data used to develop the kinetic model was obtained through the continuous measurement of the increase in NMS and MMS sample mass, which was due to water vapour adsorption. Analyses were carried out in an atmosphere of chemically-pure water vapour (a_w=1). Mass changes were observed in the NMS and MMS samples which had various initial masses, namely *ca.* 10, 15, and 20 g. The data were registered for over 5 days. The results of the measurements were registered with a frequency of 1 measurement per 1 minute, which allowed for the achievement of over 6 000 results for each of the six analysed samples. The model was developed by matching the simulation results to the experimental results.

Mass measurements of the tested samples were performed with the use of a tensometric force sensor (strain gauges) connected to a universal 4-channel transducer for ADT 42-U bridge strain gauges (WObit). This allowed for the determination of the time courses for the mass increase of the tested samples under the influence of water adsorption. The choice of this type of solution was driven by the ready-made software and stable operation of the device. Measurements were conducted at a stable ambient temperature of 20°C±1°C.

The model parameters were determined by means of a direct identification method, which consisted of minimizing the mean square error between the time courses of the simulation and the experimental results. This approach allows for the avoidance of potential problems related to data processing and information loss. Two methods were deployed in order to minimize error: multi-start and gradient ones. The multi-start method begins the search for a solution by randomly generating initial solutions, which in turn allows for the avoidance of local minima. Also, the use of the gradient method serves to facilitate the rapid location of the minimum. This combination of methods yields favourable results.

RESULTS AND DISCUSSION

The differences in the physicochemical properties of both types of analysed samples (NMS and MMS) are shown in Figs 1 and 2. Tables 1 and 2 present the particle size characteristics of the analysed samples, whereas Table 3 shows the results of the determinations of their water contents and water activities.

The NMS crystals (Fig. 1) formed clusters-lumps that resembled bunches of grapes. After micronization, these clusters were partially defragmented, multiple single crystals appeared, and the analysed material became more homogenous (Fig. 2).

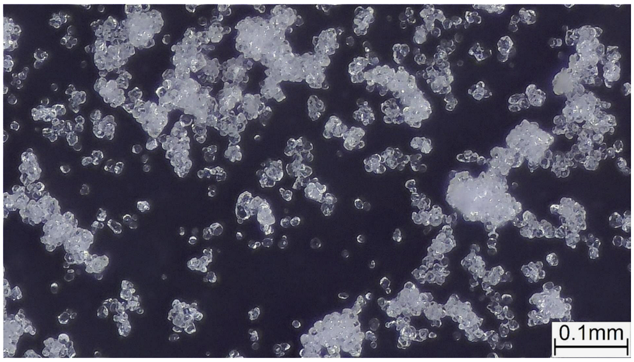

Fig. 1. Native maize starch (NMS).

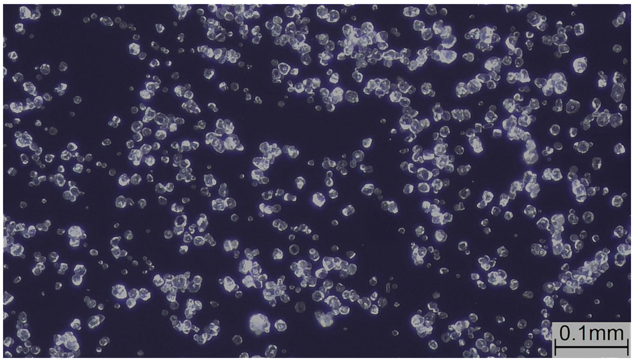

Fig. 2. Micronized maize starch (MMS).

Table 1. Selected physical characteristics of native maize starch (NMS)

Numerical distribution	Parameter					
	Min.	Max.	Mean ± SD	D(n, 0.1)	D(n, 0.5)	D(n, 0.9)
	NMS (particle number n=151.549)					
Diameter (μm)	1.090	234.71	16.81 ± 10.90	6.270	14.160	30.020
Sphericity (–)	0.037	1.000	0.797 ± 0.183	0.515	0.854	0.973
Convexity (–)	0.378	1.000	0.961 ± 0.062	0.860	0.970	0.997
Elongation (–)	0.000	0.921	0.244 ± 0.148	0.068	0.218	0.454
Aspect ratio (–)	0.079	1.000	0.756 ± 0.148	0.544	0.779	0.930
Solidity (–)	0.125	1.000	0.946 ± 0.075	0.824	0.954	0.997

Min. – minimum value, Max. – maximum value, Mean ± SD – average value ± standard deviation, D(n, 0.1) – 10% of the particles are smaller than this diameter, D(n, 0.5) – half of the particles are smaller than this diameter, and half are longer, D(n, 0.9) – 90% of the particles are smaller than this diameter.

Table 2. Selected physical characteristics of micronized maize starch (MMS)

Numerical distribution	Parameter					
	Min.	Max.	Mean ± SD	D(n, 0.1)	D(n, 0.5)	D(n, 0.9)
	MMS (particle number n=271.677)					
Diameter (µm)	1.090	152.41	11.08 ± 5.190	4.590	10.640	17.440
Sphericity (–)	0.024	1.000	0.847 ± 0.184	0.540	0.933	0.981
Convexity (–)	0.352	1.000	0.973 ± 0.062	0.835	0.988	0.998
Elongation (–)	0.000	0.914	0.214 ± 0.143	0.055	0.179	0.429
Aspect ratio (–)	0.086	1.000	0.786 ± 0.143	0.569	0.818	0.942
Solidity (–)	0.109	1.000	0.963 ± 0.075	0.812	0.986	0.998

Min. – minimum value; Max. – maximum value; Mean±SD – average value±standard deviation; D(n, 0.1) – 10% of the particles are smaller than this diameter; D(n, 0.5) – half of the particles are smaller than this diameter, and half are longer; D(n, 0.9) – 90% of the particles are smaller than this diameter.

The image obtained through the performance of a microscopic examination was improved upon using the results of particle size analyses, which showed that micronization made the diameters of the particles constituting the sample mixture smaller and more uniform (Tables 1 and 2).

By contrast, micronization caused no significant modifications in the shape of the maize starch particles that may be expressed by changes in their sphericity, convexity, elongation, aspect ratio, and solidity (Tables 1 and 2). Therefore, it may be concluded that the micronization process decreased the particle size and made the mixture homogeneous without causing damage to the starch granules, which may be of great importance for the interpretation of the results of kinetic analyses and also sorption statics determination. The correlations between the physical characteristics of the particles and the kinetics and statics of water vapour sorption on food surfaces have been addressed in a recent work (Peleg, 2020) exploring the sorption mechanism and the importance of models describing the state of dynamic equilibrium.

The present study also analysed the effect of micronization on water content and activity in the analysed sample mixtures (NMS and MMS) because the motion of the water in the matrix of a body is not stable and changes along with its changing content (Labuza and Altunakar, 2007; Gondek and Lewicki, 2007). Therefore, it was essential to establish whether the micronization process only modified the physical parameters of the maize particles or whether it also affected their chemical properties, *i.e.* water content and activity. This was important for the interpretation of the results of subsequent analyses. The water content of NMS reached 13.4253±0.4999 g H_2O 100^{-1} g d.m., whereas its water activity was determined to be 0.4043±0.0017. Micronization resulted in a statistically insignificant (p=0.4734) decrease in the water content of MMS to a level of 13.1953±0.0623 g H_2O 100^{-1} g d.m. This decrease was, however, accompanied by a statistically significant ($p=1.3\ 10^{-5}$) reduction in water activity to 0.3771±0.0006. The aforementioned results meant that micronization caused no significant differences between both starch types in terms of their susceptibility to the motion of water.

The content and activity of the water were also determined after water vapour adsorption, and the respective results were analysed by considering the differences resulting from both the micronization process and the sample mass (Table 3).

Table 3. Water content and activity in the analysed samples of maize starch after adsorption

Sample code	Water content (g H_2O 100^{-1} g d.m.) ± SD (n=3)	
	NMS	MMS
20	16.8927 ± 0.4998	16.8958 ± 0.0619
15	16.1881 ± 0.4998	16.0995 ± 0.0625
10	15.3494 ± 0.4999	15.2937 ± 0.0622
Sample code	Water activity (–) ± SD (n=3)	
	NMS	MMS
20	0.9628 ± 0.0005	0.9673 ± 0.0019
15	0.9648 ± 0.0008	0.9706 ± 0.0010
10	0.9655 ± 0.0013	0.9724 ± 0.0026

SD – standard deviation.

There were no statistically significant differences ($T_{crit.}=7.7086$; $T_{20M/N}=0.0001$; $T_{15M/N}=0.0927$; $T_{10M/N}=0.0368$) in the mean water contents after adsorption between the non-micronized (native) and micronized samples. By contrast, statistically significant differences were noted between the samples due to their mass. NMS was the exception, there were no statistically significant differences between the samples having a mass of 20 and 15 g and those weighing 15 and 10 g ($T_{crit.NMS} = 1.2987$, $T_{20/15NMS} = 0.7047$, $T_{20/10NMS} = 1.5433$, $T_{15/10NMS} = 0.7047$, $T_{crit.MMS} = 0.1616$, $T_{20/15MMS} = 0.7962$, $T_{20/10MM} = 1.6021$, $T_{15/10MMS} = 0.8059$). The aforementioned finding may indicate that the heterogeneity of the NMS mixture contributes to the masking of the quantitative effect of water vapour adsorption as determined by the sample size. Only a doubling of the sample size caused the difference in the final water content to became statistically significant. In turn, the homogeneity of the MMS mixture revealed the quantitative effect of water vapour adsorption as it related to the sample size. In the case of the MMS samples, even the smallest difference in their size caused a statistically significant difference in their final water content. Presumably, the heterogeneity/homogeneity of the mixture of particles should represent an important element to be considered during investigations addressing water vapour sorption on the surface of food powders, as claimed by Peleg (2020). This finding is especially important with reference to the research dealing with mathematical models of surface phenomena.

The significance of differences between the mean water activity determined after adsorption in the non-micronized and micronized samples turned out to be high ($T_{crit.}$=7.7086; $T_{20M/N}$ = 16.3452; $T_{15M/N}$ = 61.3728; $T_{10M/N}$ = 17.1533). In turn, the significance of differences in water activity between the samples differing in mass was negligible ($T_{crit. NMS}$ = 0.0025; $T_{20/15NMS}$ = 0.0020; $T_{20/10NMS}$ = 0.0027; $T_{15/10NMS}$ = 0.0007; $T_{crit.MMS}$ = 0.0050; $T_{20/15MMS}$ = 0.0033; $T_{20/10MMS}$ = 0.0051; $T_{15/10MMS}$ = 0.0018). In the case of both NMS and MMS, the statistically significant differences in the final water activity were only determined between the samples that differed by a factor of two in their mass. Thus, regardless of the degree of homogenization of the particles constituting the mixture, only a significant difference in the sample size may reveal differences in the thermodynamic state of the adsorbed water, as expressed by its activity.

The sorption of water vapour by solid bodies depends on multiple factors, the most important of which include: chemical composition, the physicochemical state of the constituents, and their physical structure. These parameters may be used to determine the volume of the adsorbed water vapour and the kinetics of water vapour sorption (Spiess and Wolf, 1986). The extent and the kinetics of water vapour diffusion are largely determined by the state at which thermodynamic equilibrium is reached. Either a loss or an increase in water vapour content occurs in one region or component of the food at the expense of another region or component in a continuous mode until a state of thermodynamic equilibrium is reached with the surrounding food components and the environment. In the case of modelling multi-domain systems, like *e.g.* food products, the formation of divisions of multiple components differing in water activity and thus in chemical potentials (different water activity values) are required, water molecules are exchanged due to the difference in chemical potentials between the components until the system ultimately reaches a water activity equilibrium in every domain (Labuza and Altunakar, 2007).

To summarize, the study results point to the complexity of the process of reaching a state of equilibrium (sorption statics) between the water vapour molecules in the surrounding environment and the water molecules on the surface of such a solid body (in the form of a powder) as maize starch. In addition, the study results indicate the important role of the size of the particles constituting the matrix of the solid body and of the mass of this solid body in reaching a dynamic equilibrium. Furthermore, they may provide answers to certain queries expressed by Peleg (2020), and constitute a starting point to further considerations concerning the attainment of a state of equilibrium and, thus, over the kinetics of the sorption process. A state of equilibrium may be attained at various water contents, depending on the size of the particles constituting the matrix of the solid body and on the mass of this solid body. The results of the present study may be important to investigations addressing sorption isotherm models and also those used to determine sorption isotherms.

The course of water vapour adsorption on the surface of maize starch particles was examined experimentally by registering changes in the sample mass over time. The first measurements revealed a rapid increase in the mass of each analysed sample because their state was far from a state of equilibrium and because the water particles initially occupied energetically-attractive sites on the surface of the maize starch granules (Fig. 3). After that, the increase in sample mass was significantly slower, and the masses of each analysed sample tended asymptotically to a certain value corresponding to the equilibrium state (m_e). The results of the research of Machado *et al.* (2012) imply that the adsorption process involves more than a single kinetic stage (or adsorption rate).

The empirical data presented in Fig. 3 has formed a theoretical foundation for developing a differential equation describing sorption kinetics, namely sample mass changes as a function of time. Eq. (1) is as follows:

$$\frac{dm}{dt} = a(m_e - m) + c(m_e - m)^n \ , \tag{1}$$

where: $\frac{dm}{dt}$ – sample mass change over time (mg min^{-1}), m – sample mass in a given moment (mg), m_e – sample mass in a state of equilibrium (mg), t – time (min), a – model constant (1 min^{-1}), c – model constant (mg^{1-n} min^{-1}), n – model constant (–).

This is a two-element equation, including a linear element – which to date has been most often applied in the description of adsorption kinetics (Ocieczek *et al.*, 2015; Noorbakhsh *et al.*, 2006; Švábová *et al.*, 2011), and a non-linear element which allows for the attainment of a good fit to the experimental data. Including the non-linear inertial element in the equation significantly improves the fit of the model to the experimental data. The non-linear element is necessary in order to describe the adsorption in the first phase of the process which is characterized by a rapid increase in sample mass. The exponent n>3 significantly increases the rate of sample mass increase when differences in the mass of the samples are large (m_e-m). In turn, the c constant points to the importance of this element. It is worth

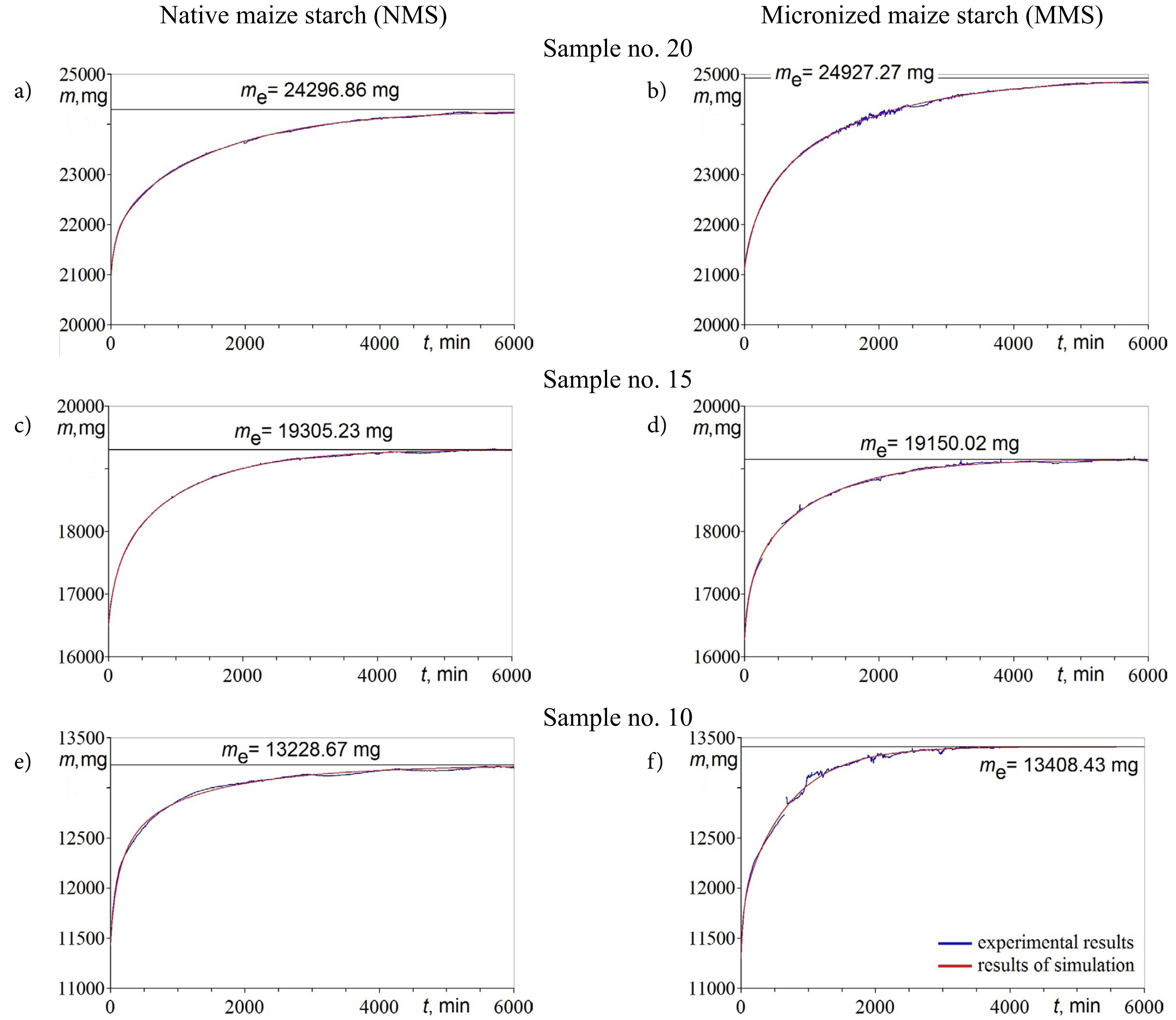

Fig. 3. Kinetic curves of water vapour adsorption on NMS samples (a, c, e) and MMS samples (b, d, f) differing in mass (Table 4).

emphasizing that the presented model is accurate enough to enable the estimation of the mass at a state of equilibrium m_e even if this state has not been reached. In addition, the proposed equation contains only four identifiable parameters, which points to its considerable degree of usefulness.

The high value of the dynamics of water vapour adsorption by maize starch, especially in the initial period of the process, is probably determined by the complex morphology of its granules (Machado *et al*., 2012; Lima *et al*., 2015). Maize starch granules have a complex structure composed of small granules, which indicates their fractal morphology (Fig. 4) (Zhou *et al*., 2014, Patindol *et al*., 2015, Chi *et al*., 2021, https://fineartamerica.com/featured/baking-flour-containing-starch-grains-dennis-kunkel-microscopy-science-photo-library.html). In addition, the real surfaces usually have a fractal nature, while the microstructures specific to them are composed of nanostructures (Patindol *et al*., 2015). Achieving larger magnifications requires the use of an electron microscope which reveals further details of starch granule morphology (https://fineartamerica.com/featured/baking-flour-containing-starch-grains-dennis-kunkel-microscopyscience-photo-library.html).

The compartments between the maize starch granules and in the hollows of the surface are particularly energetically attractive for water molecules. In these regions, water molecules are strongly attracted from several sides simultaneously. Just filling these regions results in the occupation of the hydrophilic regions on the exposed surface, these are less attractive in terms of energy. This interpretation of the results is also supported by certain theoretically grounded research results that show the importance of the influence of the surface structure on the thermal effects associated with the adsorption process and in other surface phenomena. A recent study has addressed the problem of the influence of the surface microstructure on the physicochemical properties of the interface (Furmaniak *et al*., 2007).

When considering the forces of interaction between molecules and particles, and also micro-surface forces, it is important to consider the short (less than 1 nm) and long

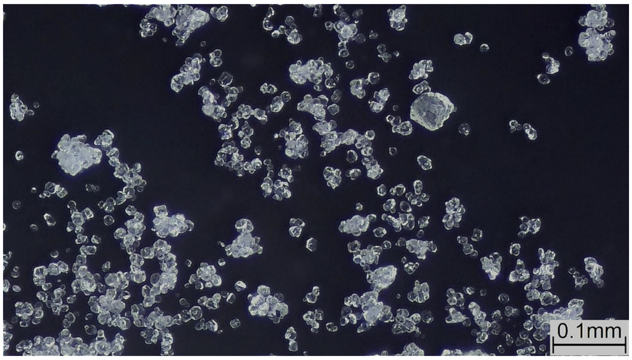

Fig. 4. Magnification of the maize starch particles: 1 – particles composed of many crystals, 2 – particles with a notable micro-roughness on the surface.

range (up to 100 nm, and sometimes larger) interactions, which not only differ in terms of energy but also in terms of variability related to distance. At the same time, the various states of aggregation are a convincing, macroscopic manifestation of the occurrence of intermolecular interaction. They explain the various chemical and physical phenomena which are observed and also the different properties of molecule clusters. The interface area is also a system that has properties which are determined by various types of intermolecular interactions related to the structure and properties of its interacting components (Dutkiewicz, 1998, Atkins, 2003). These interactions are characterized by various energy levels, which are inversely proportional to the distance (r) between the individual components of the system, these occur in different powers (from 1 to 10). This means that the interaction energy rapidly decreases with distance, which in turn depends on the type of interaction. In general terms, it may be stated that the interactions between the different individual components are responsible for the binding of the molecules in gases, liquids, and solid bodies, which are referred to as van der Waals forces. Therefore, it is the non-linearity of the van der Waals forces that causes the first layer of water to be the most powerfully attracted. Successive layers of water are only formed after the first layer has been formed, and this process may be described mainly by the linear component of the proposed equation. Similar observations regarding the general mechanism of water vapour sorption on food surfaces may be found in the work of Furmaniak *et al.* (2007), who presented them in a graphical form. These authors stated that this mechanism may be the same one used in the Guggenheim-Anderson-de Boer (GAB) or Generalized D'Arcy and Watt (GDW) models, depending on the distribution of the primary water sorption sites. If the geometrical constraints for BET clustering do not exist at the surface and if each of the primarily observed water molecules is transformed into only one secondary surface site, the mechanism may be deemed to follow the GAB scenario. In turn, for rough or porous surfaces where there are geometrical constraints with regard to the formation of secondary sites and/or when more than one secondary site arises from one primary site, the water sorption mechanism is in line with the GDW scenario.

The values of the model parameters which may be identified from the experimental results are presented in Table 4 together with the values of the determination coefficient R^2 and the residual standard deviation RSD.

A comparison of the parameters which are constants in the proposed kinetic model of water vapour sorption on starch allowed for the formulation of some general observations. Very high determination coefficient values indicate that the proposed model described the kinetics of water vapour adsorption by maize starch well, this is regardless

Table 4. Parameters of the kinetic equation of water vapour sorption on the surface of native and micronized maize starch

Sample code	Model parameters (units)	20	15	10
NMS	$m_e \pm$ SD (mg)	24296.86 ± 0.69	19305.23 ± 0.24	13228.67 ± 0.64
	$a \pm$ SD (1 min^{-1})	$6.17\ 10^{-4} \pm 1.05\ 10^{-6}$	$8.71\ 10^{-4} \pm 1.31\ 10^{-6}$	$5.81\ 10^{-4} \pm 5.41\ 10^{-6}$
	$n \pm$ SD (–)	6.1529 ± 0.0198	4.2516 ± 0.0131	3.0783 ± 0.0144
	$c \pm$ SD ($\text{mg}^{1-\text{n}}\ \text{min}^{-1}$)	$3.67\ 10^{-21} \pm 5.69\ 10^{-22}$	$2.10\ 10^{-14} \pm 2.11\ 10^{-15}$	$1.01\ 10^{-9} \pm 1.02\ 10^{-10}$
	t_{CE} (min)	12002	7810	10425
	RSD (mg)	14.28	10.99	17.25
	R^2	0.999	0.999	0.995
MMS	$m_e \pm$ SD (mg)	24927.27 ± 1.28	19150.02 ± 0.46	13408.43 ± 0.83
	$a \pm$ SD (1 min^{-1})	$5.85\ 10^{-4} \pm 2.09\ 10^{-6}$	$8.91\ 10^{-4} \pm 2.31\ 10^{-6}$	$1.403\ 10^{-3} \pm 5.16\ 10^{-6}$
	$n \pm$ SD (–)	3.9045 ± 0.0180	4.6622 ± 0.0233	8.2766 ± 0.125
	$c \pm$ SD ($\text{mg}^{1-\text{n}}\ \text{min}^{-1}$)	$7.32\ 10^{-14} \pm 1.06\ 10^{-14}$	$1.14\ 10^{-15} \pm 2.05\ 10^{-16}$	$8.00\ 10^{-27} \pm 6.48\ 10^{-27}$
	t_{CE} (min)	11690	7613	5034
	RSD (mg)	20.64	17.53	23.09
	R^2	0.999	0.998	0.996

t_{CE} – the time required to reach a state close to dynamic equilibrium (m_e–m = 1 mg 10 g^{-1} of initial mass) in the process of water vapour adsorption on starch particles, *RSD* – residual standard deviation, R^2 – determination coefficient.

of the modification of the mass of the sample mixtures as well as the state of the particles (native, micronized) forming the mixtures of individual samples.

The differences between the kinetics of water vapour adsorption on NMS and MMS granules were insignificant. However, the final water contents of the samples with different masses differed more in the case of MMS. By contrast, the final water activity of the non-micronized and micronized samples was always significantly differentiated by the micronization process. These findings, however, do not affect the course of the adsorption process (the kinetics of water vapour sorption), but they may be important with regard to the research concerning the state of dynamic equilibrium.

Regardless of its degree of heterogeneity/homogeneity, the smaller the mass of the sample was, the more rapidly it reached an equilibrium. This finding indicates that the influence of the sample mass on the time required for its stabilization is significant, which is the essence of the investigations concerning kinetics and these play an important role in sorption statics research.

The time necessary to determine the adsorption isotherms, and thus the sorption statics analysis, can be shortened to 6 000 min (approx. 4 days) for samples weighing 10 g. A 10 g sample is suitable for determining isotherms that are undisturbed by the impact of significant noises.

On the other hand, the results produced by the study of adsorption kinetics are most reliable for samples weighing more than 10 g. Hence, it would be beneficial for the quality of the results to analyse samples with a mass of 20 to 30 g. The best fit of data was obtained for samples weighing 20 g, and the worst for those weighing 10 g.

The non-linearity of the inertial element of the equation occurred in powers from 3 to 8 for the tested samples and conditions, which confirms that the maize starch initially absorbs water vapour very rapidly. This is probably due to the interaction of the water vapour molecules with single or multiple hydrophilic groups of the matrix at the same time, which may be individuals with different properties.

Moreover, even though the sample mass differentiated the value of the non-linearity power, this effect was not found to be explicit in the case of the collected material. Therefore, no other more detailed statements may be made at this stage, and the research should be continued with other types of native and micronized starches, and then extended to include samples with larger particle sizes, *e.g.* black pepper, coffee, *etc.* The proposed kinetic model should also be tested on the basis of a more complex experimental model, which will be the subject of further work in this area.

CONCLUSIONS

1. The study results allowed for the conclusion to be reached that the time required to reach a state of dynamic equilibrium in the process of water vapour adsorption on the surface of native and micronized maize starch was significantly shorter than the usually assumed period of 30 days.

2. The fragmentation of the maize starch granules did not cause significant changes in the kinetics of the water vapour adsorption process on their surface, but it may be very important in the determination of sorption isotherms.

Conflict of Interest: The authors declare that they have no conflict of interest.

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