American Journal of

Food Technology

ISSN 1557-4571

Academic
Journals Inc.

www.academicjournals.com

OPEN ACCESS American Journal of Food Technology

ISSN 1557-4571
DOI: 10.3923/ajft.2016.264.272

Research Article

Probing Water Desorption Mechanism of Glutinous Rice Flour with Four Theoretical Isotherm Models: A Comparative Study

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Abstract

Background: Water desorption isotherm of Glutinous Rice Flour (GFR) is necessary for processing and storage design for foods such as tangyuan (a traditional Chinese dessert). **Methodology:** The GRF was equilibrated under 10 water activity (a_w) levels at 10, 20 and 30°C. Isotherm data was modeled with four theoretical isotherm equations (GAB, GDW, Aouaini and CMMS). **Results:** The values of monolayer water content obtained from the four models differed from each other due to their different assumption. All the four models predicted endothermic interaction of water with primary adsorption sites in GRF during desorption and weakly temperature-dependent water-water interaction, but gave much different adsorption enthalpy related to the primary adsorption. Within the assumption of the GDW model, not more than 20% strongly bound water molecules became secondary adsorption sites. In the scenario of the Aouaini model, the water molecules were adsorbed in a perpendicular position to the surface of GRF solids with decreased crowdedness as temperature increased and the number of layers beyond the first layer showed a very weakly temperature-dependent behavior. **Conclusion:** Although mechanism-based isotherm models can give more details on distribution of water molecules in adsorbed layers and water-water, water-sorbent interactions, additional technical observations are required to verify the predictions of a theoretical model.

Key words: Desorption isotherm, water sorption mechanism, water activity, glutinous rice flour, interaction

Received: May 03, 2016 Accepted: August 10, 2016 Published: October 15, 2016

Citation: Hua Zhang, Yanhong Bai, Xuewei Zhao and Ruiqian Duan, 2016. Probing water desorption mechanism of glutinous rice flour with four theoretical isotherm models: A comparative study. Am. J. Food Technol., 11: 264-272.

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Competing Interest: The authors have declared that no competing interest exists.

Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

Glutinous rice (*Oryza sativa*), also called waxy or sweet rice is the staple food of Asian people. Glutinous Rice Flour (GRF) is produced by grinding the soaked glutinous rice granules into powder. Due to its low content of amylose (0~2%, w/w)[1], GRF is usually used as raw material in various processed foods such as sweets, desserts, rice cakes and baked rice crackers. In China, the main industrial application of GRF in food is to produce tangyuan, a traditional Chinese sweet. Rapid freezing is widely used for industrialization of this indigenous food. Moisture desorption properties of GRF will determine water loss during freezing, storage and retail of tangyuan and finally its quality deterioration such as fissuring.

The relationship between the total moisture content and water activity of a material, over a range of a_w values at a constant temperature and under equilibrium conditions, yields a moisture sorption isotherm. This isotherm data can be obtained in two ways: Adsorption or desorption. Such data is usually used to obtain a isotherm equation which is necessary for simulating a food process concerning water transfer[2]. Moisture sorption isotherms can also be used to study features of food products, such as specific surface area and pore size[3,4]. Additionally, thermodynamic properties, including differential enthalpy and entropy, enthalpy-entropy compensation, integral enthalpy and entropy and spreading pressure etc., are ready to be calculated from sorption isotherm data[5,6]. If a theory-based isotherm model is applied to fit the data, it will promote a better understanding of an adsorption process even at the molecular level[4,7].

A large number of equations have been reported in the literature for describing the sorption isotherms of foods. Except the well-known BET and GAB models, most of the commonly-used isotherm models in food literature are empirical or semi-empirical[8]. Just as Garcia-Perez *et al.*[9] declared an ideal sorption model would be one whose parameters have physical meaning and adequate statistical indices. Theoretical foundation of an isotherm model will allow us to better interpret and deduce information about physical adsorption of water in foods. Furmaniak *et al.*[10] gave a comprehensive review of the theoretical models describing water adsorption on carbons and divided all the models into four groups. Of the four groups of theoretical models, the GDW and CMMS models have been validated to be applicable for foodstuffs[11,12]. More recently, Aouaini *et al.*[7] developed a model (called Aouaini model in this study) by means of the grand canonical ensemble in statistical physics and it to modeling water desorption from olive leaves.

Moisture sorption isotherms for rice flour have been determined and net isosteric enthalpy of sorption has been estimated[13-15]. While, the events occurred at molecular level during water desorption remains unclear. The objective of this study is to explore desorption behavior of water in GRF using four theory-based isotherm equations at molecule level and compare the their results in terms of monolayer water content, water-solid and water-water interactions, density of receptor sites, number of molecules per site and number of absorbed water molecule layers.

MATERIALS AND METHODS

Materials: Glutinous rice flour was purchased from local market with the composition of 8.08% (dry base, d.b.) protein, 1.11% (d.b.) lipids, 0.92% (d.b.) fiber, 0.90% (d.b.) ash and 88.99% (d.b.) carbohydrate (by difference). The GFR was mixed with water to a final moisture content of 45% (wet base) and conditioned for 3 h before desorption experiments.

Determination of desorption isotherms: Equilibrium moisture content of GRF was determined by a gravimetric technique at 10 water activity levels. About 5 g of GRF was placed in desiccators containing different saturated salt solutions as shown in Table 1 to maintain the specified water activity inside the desiccators[16]. A test tube containing thymol was placed inside the desiccators with a_w>0.75 to prevent mold growth during storage. The desiccators were placed in temperature-controlled cabinets maintained at 10, 20 and 30°C (±1°C) and the samples were allowed to equilibrate until there was no discernible weight change (±0.001 g). The equilibrium moisture content was determined by drying in an oven at 105°C until constant weight. All measurements were done in triplicate.

Modeling the isotherms: In this study, four theory-based sorption isotherm equations were used to fit moisture adsorption data.

The GAB (Guggenheim anderson and de Boer) model (Eq. 1) is the most commonly used theoretical isotherm

Table 1: Ten salts used for produce saturated solutions and their corresponding a_w at three temperatures

	10°C	20°C	30°C
LiBr	0.0714	0.0661	0.0616
LiCl	0.1130	0.1130	0.1130
CH_3COOK	0.2338	0.2311	0.2161
$MgCl_2$	0.3347	0.3307	0.3244
K_2CO_3	0.4320	0.4320	0.4320
$Mg(NO_3)_2$	0.5736	0.5438	0.5140
KI	0.7211	0.6990	0.6789
NaCl	0.7567	0.7547	0.7509
KCl	0.8677	0.8511	0.8362
K_2SO_3	0.9817	0.9789	0.9730

equation for moisture sorption of foods. The assumption of the GAB model states that the first shell of water evenly covers the sorbent surface and is very tightly bound in a monolayer and that the sorption state of the sorbate molecules in the layers beyond the first is the same, but different to the pure liquid state[17]:

$$M_e = \frac{M_0 C K_G a_w}{(1-K_G a_w)(1-K_G a_w + C K_G a_w)} \tag{1}$$

where, M_e is equilibrium moisture content expressed as kilogram water/kilogram dry solid, M_0 is monolayer water content, a_w is water activity. The C and K_G are the kinetic constants related to the sorption in the first layer and multilayer sorption, respectively.

$$C = C_0 \exp\left(\frac{E_m - E_n}{RT}\right)$$

and:

$$K_G = K_{G0} \exp\left(\frac{E_v - E_n}{RT}\right)$$

where, E_m and E_n are enthalpy of sorption of monolayer and multilayer water, E_v is vaporization energy of one adsorbed mole of water molecules, C_0 and K_{G0} are pre-exponential entropic factors related to C and K_G, respectively, R is general gas constant and T is temperature.

The GDW (generalized D'Arcy and Watt) model was proposed by Furmaniak *et al.*[18] and next was successfully applied to description of water sorption on foodstuffs[11,12,19]. The model assumes the existence of the primary sorption centers where the mechanism of Langmuir sorption occurs. Water molecules bounded to those centers convert into the secondary centers where the mechanism follows the Dubinin and Serpinsky[20] scenario. The model has the following Eq. 2:

$$M_e = \frac{M_0 K a_w}{1+K a_w} \times \frac{1-k(1-w)a_w}{1-k a_w} \tag{2}$$

where, M_0 is the maximum sorption value on primary centers, w is a parameter determining the ratio of molecules bonded to primary centers and converted into the secondary ones, K and k are the kinetic constants connected with sorption on primary and secondary centers, respectively.

$$K = K_0 \exp\left(\frac{E_K - E_v}{RT}\right),\ k = k_0 \exp\left(\frac{E_k - E_v}{RT}\right)$$

where, E_K and E_k is enthalpy of sorption related to the primary and secondary sorption sites, K_0 and k_0 are pre-exponential entropic factors related to K and k, respectively.

The Cooperative Multi-Molecular Sorption (CMMS) model was proposed by Malakhov and Volkov[21] to describe the adsorption of alcohols on polymers. It assumes that the sorption process follows the scenario of cooperative filling of channels (interrelated nanovoids) of the sorbent and this process is combined with the growth of associates of sorbed molecules within the sorbent bulk. Comparing to the GAB and GDW, the basic differences in the CMMS model are caused by the behavior of water molecules sorbed on two adjacent sites. This model was successfully applied to description of water sorption on foodstuffs by Furmmaniak *et al.*[11] and has the following Eq. 3:

$$M_e = \frac{M_0 K_0 a_w}{(1-K_{as} a_w)(K_0 a_w + \omega^2 (1-K_{as} a_w))} \tag{3}$$

Where:

$$\omega = \frac{1}{2}\left(1 - \frac{K_1 a_w}{1-K_{as} a_w} + \sqrt{\left(1 - \frac{K_1 a_w}{1-K_{as} a_w}\right)^2 + \frac{4K_0 a_w}{1-K_{as} a_w}}\right)$$

where, M_0 is the maximum amount of the water in the channels ("Monolayer"). The K_0 and K_1 are equilibrium constants for sorption of the central and side unit on the primary side, respectively and K_{as} is the equilibrium constant for sorption of the site associate:

$$K_0 = K_{0,0} \exp\left(\frac{E_{K0} - E_v}{RT}\right),\ K_1 = K_{1,0} \exp\left(\frac{E_{K1} - E_v}{RT}\right),\ K_{as} = K_{as,0} \exp\left(\frac{E_{Kas} - E_v}{RT}\right)$$

where, E_{K0}, E_{K1} and E_{Kas} are energy of sorption of the central, side unit on the primary sites and of site associate, respectively, $K_{0,0}$, $K_{1,0}$ and $K_{as,0}$ are pre-exponential entropic factors related to K_0, K_1 and K_{as}, respectively.

Ben Lamine's group took a statistical physics treatment successfully to study solid-liquid and solid-gas adsorption systems[22]. This treatment is based on the grand canonical partition function[23]. With assumption of first layer with receptor site desorption energy $-\epsilon_1$ and N_2 number of layers with receptor site desorption energy $-\epsilon_2$. Aouaini *et al.*[7] derived the following isotherm equation and applied it to model vapor desorption isotherms of olive as in Eq. 4:

$$M_e = nN_M\left(\frac{f_1 + 2f_2 - f_3 + f_4}{1 + f_1 + f_2}\right) \tag{4}$$

Where:

$$f_1 = \left(\frac{a_w}{a_1}\right)^n,\ f_2 = \frac{\left(\frac{a_w}{a_1}\right)^n \left(\frac{a_w}{a_2}\right)^n \left(1-\left(\frac{a_w}{a_2}\right)^{nN_2}\right)}{1-\left(\frac{a_w}{a_2}\right)^n},$$

$$f_3 = \frac{\left(\frac{a_w}{a_1}\right)^n \left(\frac{a_w}{a_2}\right)^n \left(\frac{a_w}{a_2}\right)^{nN_2} N_2}{1-\left(\frac{a_w}{a_2}\right)^n},\ f_4 = \frac{\left(\frac{a_w}{a_1}\right)^n \left(\frac{a_w}{a_2}\right)^{2n} \left(1-\left(\frac{a_w}{a_2}\right)^{nN_2}\right)}{\left(1-\left(\frac{a_w}{a_2}\right)^n\right)^2}$$

where, n is number of molecules per sorption site, N_M is mass of adsorbed molecules per kilogram of dry sorbent material when only one water molecule is adsorbed in one site. Then $n{\cdot}N_M$ is equal to the monolayer water content, a_1 and a_2 are dimensionless parameters related to the adsorption energy in the first layer, beyond layers, respectively.

$$a_1 = \exp\left(-\frac{E_{a1}-E_v}{RT}\right),\ a_2 = \exp\left(-\frac{E_{a2}-E_v}{RT}\right)$$

where, E_{a1} and E_{a2} are desorption energy at the first and beyond layers, respectively.

Regression and statistical analysis: A statistics package statistic for windows (Version 6.0) was used to conduct non-linear regression process. The goodness of the fitting of each model to the experimental equilibrium moisture content and water activity data was evaluated based on statistical indices such as the coefficient of determination (R^2), residual sum-of-squares (RSS), standard error of estimate (SEE) and Mean Relative Deviation (MRD)[8].

The RSS is defined as Eq. 5:

$$RSS = \sum_{i=1}^{m} (M_e^i - \overline{M}_e^i)^2 \quad (5)$$

where, m is the number of samples, M_e^i and $\overline{M}_e^i$ are the experimental and calculated value of equilibrium moisture content, respectively.

The SEE shows the deviation of the dependent variable and is given by Eq. 6:

$$SEE = \sqrt{\frac{\sum_{i=1}^{m} (M_e^i - \overline{M}_e^i)^2}{d_f}} \quad (6)$$

where, d_f is freedom degree of fitting equation.

The MRD gives an idea of the mean departure of the measured data from the predicted data. It is expressed as Eq. 7:

$$MRD = \frac{100}{m} \sum_{i=1}^{m} \frac{\left|M_e^i - \overline{M}_e^i\right|}{M_e^i} \quad (7)$$

The SEE value represents the fitting ability of a model in relation to the number of data points. The fitted equation giving the smallest SEE value for the same set of experimental data yields the best results. The MRD is used to describe the goodness-of-fit of an equation. Therefore, the smaller the MRD value, the better the goodness-of-fit.

RESULTS AND DISCUSSION

Sorption isotherms modeling: The GAB, GDW, CMMS and Aouaini models were fitted to experimental data through non-linear regression analysis. The resulting statistical parameters for the four models are collected in Table 2.

Table 2 shows that, the GAB equation posed the lowest value of R^2 and highest values of RSS, MRD and SEE in a_w range of 0~0.97 at the three temperatures except the MRD at 30°C. It can be concluded that the GAB model led to the poorest fit within the studied a_w and temperature ranges. Van den Berg[24] pointed out that the GAB model is applicable to water activities up to about 0.9. When a_w was limited to <0.9, as can be seen from Table 2, the GAB model became the best model. As a whole, the GDW model provided the

Table 2: Statistical indices for the four models fitted to the isotherm data of glutinous rice flour at 10, 20 and 30°C

	GAB	GAB	GDW	Aouaini	CMMS
			10°C		
a_w	0~0.98	0~0.87	0~0.98	0~0.98	0~0.98
R^2	0.9830	0.9996	0.9979	0.9927	0.9841
RSS	0.0019	0.0000	0.0002	0.0008	0.0002
MRD	7.7068	0.9752	3.6190	5.6961	6.6553
SEE	0.0309	0.0030	0.0088	0.0143	0.0244
			20°C		
a_w	0~0.98	0~0.85	0~0.98	0~0.98	0~0.98
R^2	0.9885	0.9994	0.9991	0.9955	0.9884
RSS	0.0011	0.0000	0.0000	0.0004	0.0001
MRD	8.0743	0.8387	2.9327	5.3828	6.0830
SEE	0.0239	0.0034	0.0054	0.0106	0.0177
			30°C		
a_w	0~0.97	0~0.84	0~0.97	0~0.97	0~0.97
R^2	0.9916	0.9992	0.9992	0.9962	0.9933
RSS	0.0007	0.0000	0.0009	0.0003	0.0001
MRD	7.5137	1.4476	8.1011	5.5918	8.1805
SEE	0.0189	0.0035	0.0174	0.0090	0.0150

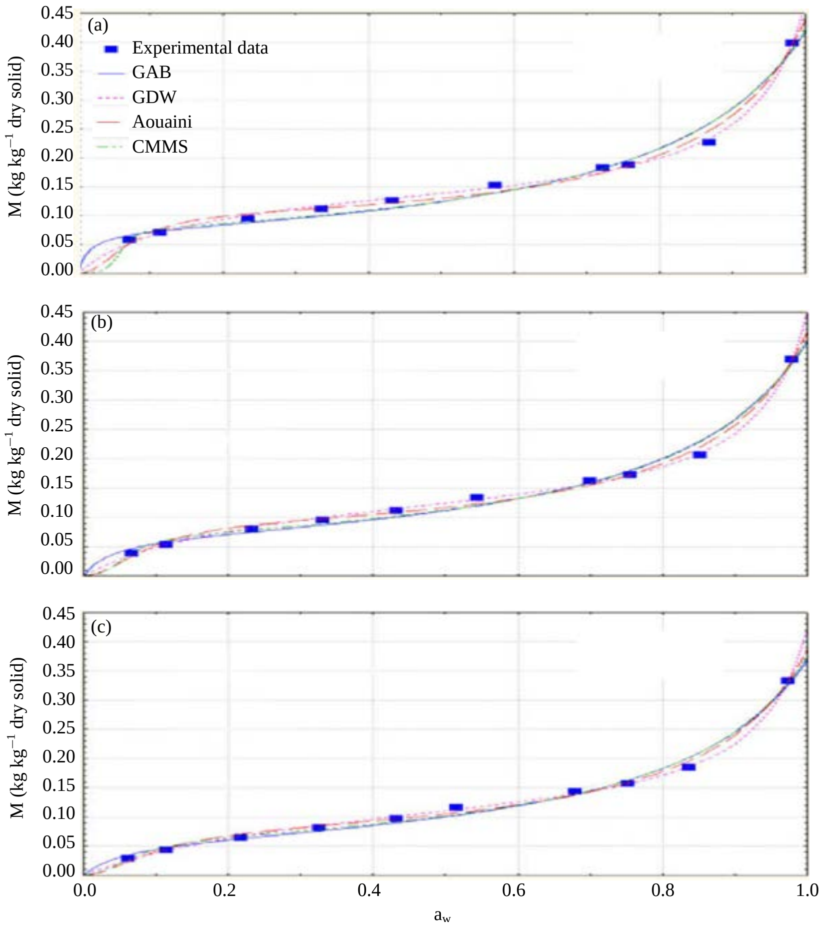

Fig. 1(a-c): Equilibrated water content of glutinous rice flour under ten water activity levels at (a) 10°C (top), (b) 20°C (middle) and (c) 30°C (bottom) and their best-fit curves obtained from the four isotherm models

best prediction in a_w range of this study, which was followed by the Aouaini model then the CMMS model. This is caused by differences in the mechanisms assumed in the three models. Among the three kinetic constants (K_0, K_1 and K_{as}) presented in the CMMS model only one (K_{as}) is responsible for the shape of isotherm in the range of medium and high a_w values. In the case of the GDW and Aouaini models there are two parameters (k and w, a_2 and N_2, respectively) influencing the shape in this a_w range. At higher temperature, the performance of the Aouaini and CMMS model improved, approaching to that of the GDW model.

The values of measured equilibrium moisture content versus water activity at 10, 20 and 30°C for GRF are shown in Fig. 1. The predicted curves from the four models are also presented. Figure 1 graphically demonstrates the difference between the measured and predicated values from the four isotherm models at various a_w values. It should be noted that the GAB curve was the result of desorption data in a_w range of 0~0.98.

The GAB model predicted more water content than that measured experimentally at lower (<~0.1) and higher (>~0.75) water activity, while less water content in medium a_w range. The GDW model gave best prediction in all the water activity and temperature levels. The CMMS model presented lower values at medium a_w range. The Aouaini model gave poor prediction at a_w lower than about 0.8. The deviation of the CMMS and Aouaini models was reduced with temperature increase. At a_w lower than about 0.1, the four models gave very different predicted values, especially at lower temperature.

The values of the obtained best-fit parameters for the four models are shown in Table 3. Because of their theoretical bases of sorption mechanism, the models can illustrate the state of water molecules in food materials even at molecular level.

Monolayer water content: The monolayer adsorption quantity is very important in the food industry to maximize the

Table 3: Best-fit parameters obtained by fitting four models to water desorption isotherm data of glutinous rice flour at 10, 20 and 30°C

Models	Parameters	10°C	20°C	30°C
GAB	M_0	0.1003	0.0938	0.0875
a_w<0.9	C	24.3200	14.3200	10.6600
	K_G	0.6669	0.6640	0.6567
GDW	M_0	0.1531	0.1559	0.1560
	K	7.1721	4.3709	3.1945
	k	0.9344	0.9333	0.9327
	w	0.1812	0.1824	0.1822
Aouaini	n	2.0821	1.9068	1.7527
	N_M	0.0521	0.0502	0.0484
	a_1	0.0747	0.0926	0.1058
	a_2	1.1454	1.1461	1.1509
	N_2	72.2500	76.8400	76.2700
	M_0 (= $n \cdot N_M$)	0.1085	0.0958	0.0849
CMMS	M_0	0.0704	0.0663	0.0599
	K_0	3.0306	2.1478	0.5745
	K_{as}	0.8237	0.8355	0.8410
	K_1	21.6725	15.0345	11.2019

shelf life of food[2]. It can be noted from Table 3 that the values of monolayer moisture content obtained from the GDW model were much higher than those obtained from other three models. The GAB and Aouaini models gave lower and almost equal values of monolayer water content. The CMMS model gave the lowest monolayer water content among the four models, which varied from 0.0599-0.0704 kg kg^{-1} (d.b.) with temperature decreasing from 30-10°C. The magnitude of monolayer water content predicted from different models had the following order at all the three temperatures: GDW>GAB>CMMS, which is well consistent with the result obtained by Furmaniak *et al.*[11] for semolina.

It is estimated that the monolayer moisture contents by fitting the BET (Brunauer-Emmet-Teller) model to the experimental data. The resulting values were 0.0803, 0.0721 and 0.0667 kg kg^{-1} (d.b.) at 10, 20 and 30°C, respectively, which were slightly higher than those estimated from the CMMS model. The estimated M_0 of semolina obtained by CMMS is 7.641 kg kg^{-1} (d.b.)[11]. The calculated value of $n \cdot N_M$ obtained from another statistical physics-based isotherm model for potato decreases from 0.117-0.021 kg kg^{-1} (d.b.) with temperature increase[4] from 40-60°C. The M_0 values obtained from the GDW model for GRF in this work are very close to the result for semolina (16.69% (d.b.))[11], but much higher than the results for chickpea seeds, lentil seeds and potato (6.157, 7.307 and 4.066 kg kg^{-1} (d.b.), respectively) obtained by the same model[19].

It is worthy to pay attention to relatively high values of the parameter M_0 obtained from description of experimental data by the GDW model. Those values also seem to be overestimated in comparison to expected ones from the shapes of isotherms. The much higher M_0 values should be interpreted in the context of its assumption. The M_0 in the GDW model represents the maximum sorption on primary centers. The primary centers might not be fully saturated by water molecules.

Another point to note is that the M_0 values obtained by the GAB, Aouaini and CMMS models all decreased with temperature, which has been observed in other food systems[4,19,25]. The monolayer water content decreasing with the temperature increasing reflected reduction in the number of reactive sites brought about by the temperature induced physico-chemical changes in the product and indicated the endothermic character of the desorption of water molecules from the primary sites in GRF. While, the same parameter obtained by the GDW model are almost equal at the three temperature levels. This temperature independent behavior is also a result of the basic assumptions of the GDW model.

Energetic parameters: For all the three temperature levels, the sorption kinetic constants K_G and C in the GAB model showed the same behavior: C»1 and K_G~1, indicating that the mechanism of water sorption in monolayer is different from that in multilayer region, which is not different significantly from that in outer bulk liquid water region[26]. The sorption kinetic constant for the primary sites (K) in the GDW model presented a value higher than one, which corresponds to type II isotherms of highly hygroscopic materials. The observation of K>k in the GDW model is in line with the much higher value of parameter C than K_G in the GAB model.

For both GAB and GDW models, one can notice the following regularities: The kinetic constants related to sorption on the primary site in the GDW model (K), in the GAB model (C) and in the CMMS model (K_0 and K_1) all decreased obviously with temperature increase. While the energetic parameter a_1 in the Aouaini model increased with temperature increase. Similar observation was reported by Aouaini *et al.*[7] for olive leaves. This paradoxical observation is a result of its different relationship between the kinetic parameters and temperature as compared with that of other three models.

It is estimated that sorption energy parameters in the GAB, GDW, Aouaini and CMMS models and the results are listed in Table 4. Some reported values of comparable materials are also presented.

The sorption energy to primary sites in the GDW assumption (72.95 kJ mol^{-1}) was very close to the enthalpy of sorption of monolayer water in the GAB model (74.19 kJ mol^{-1}). The sorption energy at the first layer from the Aouaini model had a much lower value (54.47 kJ mol^{-1}). The sorption energy of the central unit on the primary sites in the CMMS model is 103.90 kJ mol^{-1} and of the side unit

Table 4: Sorption energy (kJ mol^{-1}) of water on receptor sites in glutinous rice flour and comparable materials obtained from the GAB, GDW, Aouaini and CMMS models[a]

Model	GAB		GDW		Aouaini		CMMS			
sorption energy	E_m	E_n	E_K	E_k	E_{a1}	E_{a2}	E_{K0}	E_{K1}	E_{Kas}	Source
GRF	74.19	44.58	72.95	44.09	31.60	43.86	103.90	76.60	43.69	Present study
Raw paddy			50.67	~44.03						Furmaniak *et al.*[27]
Oats flake			60.20	~44.46						Furmaniak *et al.*[27]
Quinoa grain	115.37	45.81	98.67	~44.03			119.18	58.90	~44.03	Furmaniak *et al.*[25]
Potato	62.77	47.75	70.22	47.97			58.86	61.15	47.54	Furmaniak *et al.*[25]
Potato	127.46	51.67	152.33	50.88						Furmaniak *et al.*[19]
Potato					47.33[b]	40.31[b]				Aouaini *et al.*[4]

[a]Value of E_v was calculated using $E_v = 6.15\times10^4 - 94.14T + 17.74\times10^{-2}T^2 - 2.03\times10^{-4}T^3$ [28], 44.03 kJ mol^{-1} at 20°C, [b]Average value at 40, 45 and 60°C. The model applied to obtain the values supposes that N_1 layers of adsorbed water molecules are formed with the first energy ($-\epsilon_1$) and the other layers are adsorbed with the energy ($-\epsilon_2$) with the condition that $\epsilon_1>\epsilon_2>0$

76.60 kJ mol^{-1}. In the scenario of CMMS, both central and side units on the primary sites provide location sites for water molecule sorption. Then the enthalpy for sorption to primary sites should be the average of sorption energies obtained from K_0 and K_1. The average enthalpy is 90.25 kJ mol^{-1}, which is higher than that from the GDW the GAB models.

No significant differences were observed in parameter k in the GDW model for the three temperatures. According to the GDW's assumption, the obtained values indicate that the kinetics of water sorption on secondary sites is similar. Same behavior of K_G (related to polymolecular sorption energy) in the GAB, a_2 (associated with sorption energy in the N_M water layers) in the Aouaini model and K_{as} (related to sorption energy of site associates) in the CMMS model was observed. The parameter a_2 keeping at an almost constant level suggests that the water-water interactions in multilayer region varied slightly with temperature.

Sorption sites: Model parameters such as number of molecules per site n and density of receptor sites N_M in the Aouaini model and w in the GDW model can give information on the sorption sites.

The parameter N_M in the Aouaini model, reflecting the receptor sites accessible to the water molecules in the first layer, decreased slightly from 0.0521 kg kg^{-1} at 10°C to 0.0484 kg kg^{-1} at 30°C. Similar behavior was observed by Aouaini *et al.*[7] for water vapor desorption of olive leaves. The N_M decreasing is probably due to inactivation of some receptor sites at higher temperature.

It can be noted from Table 3 that the parameter n decreases with temperature. The n decreasing is probably due to the more vigorous agitation of water molecules at higher temperature and some water molecules escaped from the receptor sites. According to Aouaini *et al.*[7], two possible cases of the anchoring of the adsorbed molecules can be distinguished depending on the parameter n. When n is superior to 1 (one receptor site is occupied by more than one molecule), the molecules adopt a perpendicular anchorage. When, n is lower than 1, the molecules adopt a parallel position to adsorbent surface.

For the case of glutinous rice flour, the water molecules were adsorbed in a perpendicular position to the adsorbent surface. It can be seen from Table 3 that the best-fit values for n were not integers. It seems confusing that part of a molecule is located on one site. One solution for it would be considering the n as an average value of the its only two closer neighbor integers, denoted as n_1 and n_2 here. Then the relation $n = n_1.x+n_2.(1-x)$ holds, with x being the percentage of sites occupied by n_1 number of water molecules and (1-x) the percentage of sites occupied by n_2 number of water molecules. The calculated percentage of sites occupied by n_1 and n_2 number of water molecules at 10, 20 and 30°C were 91.79 and 8.21%, 9.32 and 90.68%, 24.73 and 75.27%, respectively.

In the assumption of the GDW model, the parameter w is the ratio of the molecules bonded to primary centers and converted into the secondary ones. This parameter gives information on the number of sorption sites in multilayer region. For glutinous rice flour, the value of w is considerably smaller than unity at all the three temperatures. According to the obtained values for w, not more than 20% of those strongly bound molecules become secondary adsorption sites for the next water molecules. The smaller number of created secondary centers than the number of primary centers may be due to, for example, steric effects.

The GAB and Aouaini models assume that all the sorption sites are saturated in the first layer, while the GDW and CMMS models assume that the sites on the sorbent surface may be partially occupied. After knowing monolayer water content, the sorption site number in unity of solid from the GAB and Aouaini models or maximum site number in the GDW and CMMS models can be calculated through dividing the monolayer water content by the product of mass of one water molecule and number of water molecule per sorption

Table 5: Calculated number of sorption site ($\times 10^{23}$) in per kilogram of dry glutinous rice flour at 10, 20 and 30°C

Model	10°C	20°C	30°C	Notes
GAB	33.55	31.37	29.26	Average
Aouaini	17.43	16.80	16.20	Average
GDW	51.20	52.14	52.17	Maximum
CMMS	23.54	22.17	20.03	Maximum

site. The GAB, GDW and CMMS models assume adsorption of one water molecule per site[19,29]. The resulted values are presented in Table 5. It is clearly demonstrated that the four models predict very different sorption site density. Of course, one can attribute this discrepancy to their different assumption on sorption mechanism. While, for a specified solid sorbent at a specified temperature, its sorption site density would be a defined amount which should not be depend on the model selected for fitting. So, even though more than one isotherm model can give very good prediction, only one model reveal the truth of sorption mechanism. Other criterions beside fit-goodness are needed to identify the model with correct assumption for the specified material.

Number of layers beyond the first layer: In the scenario of the Aouaini model, N_2 represents the number of layers beyond the first tightly-bound water monolayer. With temperature increase, N_2 shows a slight increase. This result is contrast to the observation of Aouaini *et al.*[7] for olive leaves during water vapor desorption. The researchers explained their finding as a result of thermal agitation, which harm the surface forces between the water molecules. Our finding may suggest that the water-water molecular interaction in the multilayer region in glutinous rice flour is so strong that the temperature increase from 10-30°C can not disrupt the association. Additionally, according to the Fig. 1 by Aouaini *et al.*[7], when N_m has higher values, its further increase will give a very slight influence on the isotherm curves at higher a_w range. So, precise estimation of N_m will depend on the precise measurement of equilibrium water contents at higher a_w levels. The sharp increase of water content with a_w in higher a_w range will make it very difficult to measure water content-a_w relation using a gravimetric technique.

CONCLUSION

The GDW model best predict the equilibrium water content of GRF within the a_w and temperature ranges involved in this study. The predicting performance of the Aouaini and CMMS models improved at higher temperature. The monolayer water content obtained by the GDW model is much higher than that obtained by the other three isotherm models, with the CMMS giving the lowest value. The desorption energy of the first water molecular layer obtained from the four models varied between 54.47 J mol^{-1} and 90.25 J mol^{-1}. The values of sorption energy in the multilayer region predicted from all the four models are close to the evaporation enthalpy of free water. With temperature increase, the primary site density and water molecule number per site as explored by the Aouaini model decrease, while marginal increase in the number of layers beyond the first is observed. Not more than 20% of the strongly bound molecules in the GDW scenario become secondary adsorption sites for the next water molecules.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the financial support of The Major Science and Technology Specific Projects of Henan Province in 2015 (151100110100) and The Major Science and Technology Specific Projects of Zhengzhou in 2015 (152PZDZX026).

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