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Research Article
Adsorption Isotherm, Non-solvent Water and Heat Sorption of *Spirulina platensis*

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Abstract

Background and Objective: Spirulina powder, rich in proteins and polysaccharides, is characterized by a high hygroscopity. Its stability depends on water behavior during storage. The aim of this study is to investigate the sorption isotherm and thermodynamic properties in order to determine non-solvent water and optimal storage conditions. **Materials and Methods:** Water sorption isotherm of *Spirulina platensis* was assessed by gravimetric method at 25 and 40°C. Guggenheim-Anderson-de Boer (GAB) equation parameters were determined by direct non-linear regression. Non-solvent water was evaluated using sorption isotherm curve. Clausius-Clapeyron equation was used to study the variation of isosteric heat versus water content. **Results:** The values of monolayer moisture content of *Spirulina platensis* determined at 25 and 40°C were respectively 6.06 and 3.94%. The maximum non-solvent water bound by Spirulina powder was 0.135 g H_2O/g. The maximum value of isosteric heat of sorption was evaluated at 60 kJ mol^{-1}. The values of parameter ΔH_1 which are 6.86 kJ mol^{-1} at 25°C and 27.34 kJ mol^{-1} at 40°C confirm that water molecules are strongly bound to proteins molecules. **Conclusion:** The results of this study letus to conclude that *Spirulina platensis* powder could be stored properly at water activity of 0.33 and moisture content of 6%.

Key words: *Spirulina platensis*, adsorption, non-solvent water, thermodynamics, heat of sorption

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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

Microalgae *Arthrospira platensis* is known under the common name *Spirulina platensis* is cultivated in many world regions for its importance in food[1-4]. In Algeria, Spirulina is cultivated actually at small-scale with a production evaluated approximately at 200 Kg/year. The physico-chemical and microbiological stability depend on moisture content of dried food and storage conditions[5-8]. Sorption isotherms are known as being a good tool for the study of the behavior of water status during the drying and storage of foods[9-12].

Studies realized on the sorption kinetic have revealed that the water adsorption is done in two stages, the first corresponds to superficial adsorption by interaction of Wander Waal type. When at this stage the adsorbed water concentration increase the second stage appears with the setup of hydrogen bonds between the water and the polar groups of the macromolecules such that proteins and polysaccharides. The water being known to be an effective solvent for ionic molecules and polar molecules, its ability to dissolve these substances decrease dramatically and even disappears when it is adsorbed. So this diminution of water solvent power was confirmed for the yeast cells and the starch[13,14]. On the other hand, Guilbot and Lindenberg[13] applied these adsorbed water properties to determine successfully the relationship between the water solvent power and the characteristics of the sorption curve. These researchers have therefore pointed out the importance of the critical point which corresponds to the optimal water content and the water activity where all the alteration reactions are inhibited during food storage. In regard to works carried out on the isotherm sorption of spirulina platens is include those of Desmorieux and Decaen[15] who have concluded that Spirulina powder is characterized by high hygroscopity and these of Oliveira *et al.*[16] who have reported that the isotherm of sorption is enthalpy controlled. As there are little or no studies carried out on the determination of non solvent water and the optimal storage conditions for Spirulina powder. The objective of this study is to determine these two parameters using the curve of sorption isotherm with the evaluation of thermodynamic properties and isosteric heat of sorption respectively by Guggenheim-Anderson-de Boer (GAB) and Clausius-Clapeyron equations.

MATERIAL AND METHODS

Vegetable materials: *Spirulina platensis* named locally HT am is produced in the region of Ouargla (31°56' 57" N, 5°19' 30" E) located at southern Algeria.

Preparation of sample: After harvesting the Spirulina at moisture content of 90% undergoes filtration and solar drying. At Ouargla region, the solar radiation was estimated at 8557 Wh/m^2 during the month of June[17]. The moisture content of dried Spirulina was evaluated approximately at 8%.

Experimental procedure: The experimentation of this study was carried out during two months on 2016. The moisture sorption isotherms at 25 and 40°C were determined by static gravimetric method[18].

Determination of optimal storage conditions: Moisture sorption characteristics of *Spirulina platensis* were studied using the method reported by Guilbot and Lindenberg[13], which consists in determination of optimal storage conditions and non solvent water of foods using isotherm curve. Sorption curve used for determination of optimal conditions. The curve is constituted of three parts . The first part of isotherm curve (OA) corresponds to the monolayer where the molecules of water are strongly bound by numerous hydrogen bonds on the primary sites absorption. In this phase, the mol of water have a very low mobility and, consequently, cannot participate at any biochemical reaction. These water molecules are considered as on integral solid phase.

The second part (AC) which is close to linear corresponding to multilayer water retained by bond hydrogen more or less strong. Their mobility remains low and consequently their participation to biochemical reaction is very limited. From critical point C appears the third phase corresponding to solvent water. The point B corresponds to the maximal quantity of non-solvent water.

Mathematical modeling and data analysis: The equation of Brunauer *et al.*[19] (BET) is described by the following Eq. 1:

$$\text{EMC} = \frac{\text{Xm} \times \text{C} \times \text{aw}}{\left[(1-\text{aw}) \times (\text{C}-1) \times \text{V2}\right]} \quad (1)$$

and its modified version GAB described by Labuza *et al.*[20] is written as following Eq. 2:

$$\text{EMC} = \frac{\text{Xm} \times \text{C} \times \text{K} \times \text{aw}}{\left[(1-\text{Kaw})(1-\text{Kaw}+\text{CXKaw})\right]} \quad (2)$$

where, EMC is Equilibrium moister content (%), aw is water activity, X_m is monolayer moisture content, C is energy constant related to sorption heat and k is related to multilayer heat of sorption are related to temperatures effects by the following relation Eq. 3 and 4:

$$C = Co \exp \Delta H_1/RT \quad (3)$$

$$K = Ko \exp \Delta H_2/RT \quad (4)$$

where, T is temperature in °K, R is the universal gas constant (8.314 J/mol/K) and ΔH_1 and ΔH_2 are functions of the heat of sorption water: ΔH_1 = Hm-Hn and ΔH_2 = Hl-Hn, Co and Ko are constants, Hm and Hn are respectively heats of sorption of the mono and multilayer and Hl is the heat of condensation of water (43 kJ mol^{-1}) at 25°C. Evaluation of the parameters Xm, Co, ΔH_1, Ko and ΔH_2 have been carried out using the nonlinear regression of Tsami *et al.*[21] by the Quasi-Newton technique. Mean relative percentage deviation (MRD, which indicates the precision of the residual value is written as following Eq. 5:

$$MRD = \frac{1}{n}\sum_{i=1}^{n}\left[\frac{Xi,calc - Xi,exp}{Xi,exp}\right] \quad (5)$$

Isosteric heat of sorption: Isosteric heat of sorption which is the amount of energy required to change unit mass of a product from liquid to vapor at a particular temperature and water activity is determinate using Eq. 6 of Clausius-Clayperon:

$$In\left(\frac{aw1}{aw2}\right) = -\frac{Qst}{R}\left[\frac{1}{T1} - \frac{1}{T2}\right] \quad (6)$$

where, Qst is isosteric heat of sorption (kJ mol^{-1}), a_{w1} and a_{w2} are respectively water activity at temperatures T_1 and T_2 (°K) and R is the universal gas constant. The net isosteric heat of sorption (qst) is the difference between the total heat of sorption (Qst) and the heat of vaporization of water (Δho):

$$qst = Qst - \Delta Ho$$

RESULTS AND DISCUSSION

Adsorption isotherms: The sorption isotherms of Spirulina powder at 25 and 40°C are shown in Fig. 1. The adsorption isotherms have sigmoidal shape at both temperatures.

The projection carried out from the point A, C and B (Fig. 2) on the axis ordinate gave the values corresponding respectively to monolayer water content, beginning of solvent water and maximal quantity of non-solvent water. On the other hand, the segment of curve in the region of water activities 0.06 and 0.45 is a portion of straight line which intersect the y-axis in a point to 0.032 g H_2O/g of spirulina powder. Equation 7 characterizing this straight line is:

$$M = 0.105 \times a_w + 0.032 \quad (7)$$

where, M is number of grams of bound water by gram of *Spirulina platensis*.

For the very low values of water activity the value of M tends to 0.032 g H_2O/g Spirulina. This value would be considered as being adsorbed water on the ˜surface of *Spirulina platensis* macromolecules, in other words it corresponds to water monolayer. This adsorption is mostly due to surface adsorption[22]. It represents strongly bound water, a typical case is sorption of water onto highly

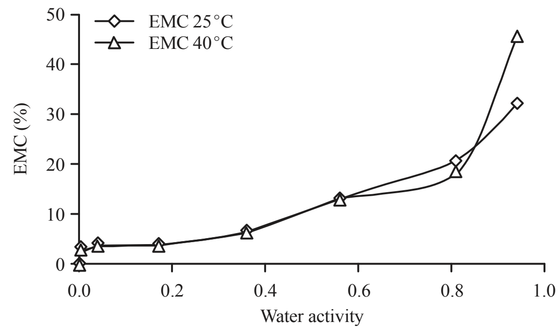

Fig. 1: Effect of temperature on Spirulina powder sorption isotherms

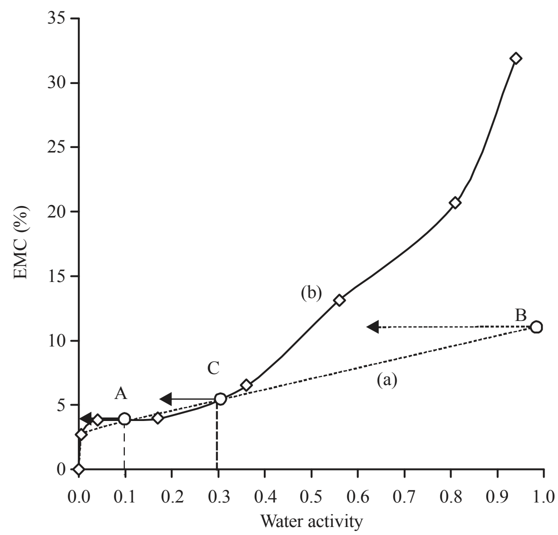

Fig. 2: Adsorption isotherm of spirulina powder at 25°C, (a) Equation $M = 0.105 \times a_w + 0.032$ and (b) Isotherm curve at 25°C

Table 1: Thermodynamic values of Spirulina determined by 5-parameters of GAB equation

T (°C)	Xm (%)	C	ΔH_1 (kJ mol^{-1})	K	ΔH_2 (kJ mol^{-1})	R^2	MRD
25	6.06	31.88	6.86	0.87	-15.738	0.98	0.097
40	3.94	1693.80	27.34	0.98	-52.590	0.99	0.075

Xm: Monolayer moisture content, ΔH_1: Hm-Hn, ΔH_2: Hl-Hn, MRD: Mean relative percentage deviation, C: energy constant related to sorption heat, K: Related to multilayer heat of sorption. R^2: Coefficient of determination

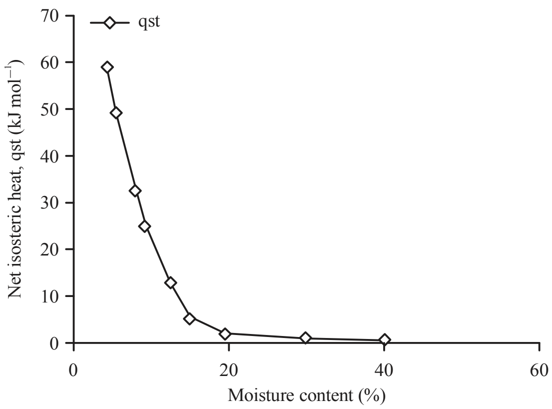

Fig. 3: Net isosteric heat of sorption of *Spirulina platensis*

hydrophilic biopolymers such proteins and polysaccharides[23]. According to Eq. 7, for water activity equal to 1, the maximum non-solvent water is 0.135 g, knowing that non solvent water is composed of primary adsorption (monolayer) and adsorption in the form of solid solution in the macromolecules (multilayer)[13].

On the other hand, the two parts OA and AC of isotherm curve are consistent with BET equation which is agree closely with experiment for a_w less than 0.5. Using the nonlinear regression analysis, the value of Xm calculated from BET equation is 4.42% with a coefficient of correlation R = 0.98.

The point C (Fig. 2), which considered as the inflection point on the typical sigmoidal isotherm indicates the region of optimum storage because oxidation may occur at lower activity and microbial reactions occur at high humidity[24]. Consequently, the optimal storage conditions for *Spirulina platensis* powder would be approximately 6% for moisture content and 0.33 for water activity. The similar analysis of sorption curve was reported by Mathlouthi[25] who have indicated the optimal conditions of food storage versus water activity.

Fitting of isothermal sorption model to experimental data: The fitting of GAB model to experimental data at 25 and 40°C are presented in Fig. 1. A crossover of the curves can be seen for water activity of 0.8, where it is observed that the higher temperatures and the higher moisture content. The same phenomenon was observed for other high sugar and proteins content foods[20,21,26]. In this context, Berlin *et al.*[27] reported that at higher relative pressure, the water was adsorbed by small molecules and forming concentrated solution. These authors have concluded that 1 g of proteins binds about 0.5 g of water and the denaturations have a weak effect on the quantity of adsorbed water.

The results of GAB equation at 5 parameters (Xm, C, K, ΔH_1 and ΔH_2) solved by non-linear regression analysis are indicated in Table 1. The value of MRD (7.5%) and the high coefficient of determination R^2 (0.98) confirm that GAB equation has ability to predict equilibrium water content data. The values of moisture monolayer content computed using GAB equation at 25 and 40°C are respectively 6.08 and 3.84%, which decrease with increase of temperature, this decrease is explained by a reduction in sorption actives sides of macromolecules[28]. These values of moisture monolayer content (Xm) correspond to highest physico-chemical and microbiological stability of the product.

The energy required for elimination of water from *Spirulina platensis* overcomes to the heat of evaporation of pure water, the energy needed to overcome the hydrogen bonds which retain water to polyhydroxy compounds. The ΔH_1 which is the difference between the enthalpy of sorption of the monolayer and multilayer has a value of 27.3 kJ mol^{-1} at 40°C (Table 1). This value indicates existence of strong bonds between solids and monolayer water molecules. These bonds are widely stronger than those which exist between the monolayer and multilayer molecules.

Isosteric heat of sorption: The net isosteric heat of adsorption of water (qst) for Spirulina powder is indicated in Fig. 3. This curve shows the amount of heat required to remove water from food, starting from moisture content of 40 g/100 g dry basis to any moisture down to 15 g/100 g. The maximum value of isosteric heat of sorption is 60 kJ mol^{-1} at lower moisture content. However, at moisture content superior to 20% its value approaches to zero. This result is similar to those obtained by Oliveira *et al.*[16] for *Spirulina platensis*. Same results were also observed for high-protein food and protein isolates[28,29].

The results indicated that the value of non-solvent water and the optimal value of water activity and moisture content corresponding to critical point, required for conditions storage of Spirulina powder, could be determined directly on sorption isotherm curve.

CONCLUSION

The moisture adsorption isotherm of Spirulina powder at two temperatures were determined with the static gravimetric method using various sulfuric acid solutions. The inverse effect of the temperature was observed in the range of water activity 0.8 and 0.9, due to high protein content of Spirulina. The non-solvent water was determined from isotherms curve and the Eq.:

$$M = 0.105\times a_w+0.032$$

The isosteric heat of sorption was assessed using Clausius-Clapeyron equation.

SIGNIFICANCE STATEMENTS

The determination of non-solvent water from sorption isotherm curve is important for the study of behavior of food during storage. The GAB equation provide only the value of the monolayer content and enthalpy sorption, but not multilayer water content. Thus, it would be interesting to complete the results of GAB equation by the determination of non-solvent water from isotherm curve. As the non-solvent water is constituted of monolayer and multilayer water it would be possible to estimate the multilayer moisture content known for its impact on food texture, from non-solvent water content minus monolayer moisture content calculated by GAB equation. This study would help researchers in investigation of isotherm sorption of food.

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