British Journal of Applied Science & Technology
2(4): 379-389, 2012

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Experimental Determination and Modelling of the Sorption Isotherms of Kilishi

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Authors' contributions

This work was carried out in collaboration between author and National Advanced School of Engineering (University of Yaounde I). AT designed the study, performed the statistical analysis, wrote the protocol, wrote the first draft of the manuscript, managed the analyses of the study, and managed the literature searches. AT read and approved the final manuscript.

Research Article

Received 24th July 2012
Accepted 28th September 2012
Published 2nd November 2012

ABSTRACT

Sorption isotherms of kilishi have been experimentally determined at 30, 40 and 50ºC by using salt method for a range of water activity from 0,064 to 0,973. His sorption capacity increases with the temperature for a given water activity. The experimental curves obtained have been simulated by the GAB model. This model enables the representation of the whole desorption isotherms, with maximum deviation of 1.2%$kg_W.kg_{dm}^{-1}$. The water content corresponding to monolayer saturation was estimated. The isosteric heat of sorption is deduced from experimental results and empirical correlations are proposed leading to satisfactorily representation. These results can be used to predict the potential changes in kilishi stability and later for the development of a system of suitable drying.

Keywords: Kilishi; sorption isotherm; isosteric heat; GAB model; specific area.

ABBREVIATIONS

a_w	Product water activity
C	Parameter linked to monolayer heat of sorption
K	Parameter linked to multilayers heat of sorption
m	Product mass (kg)

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Q_{sorp} Sorption heat ($kJ.mole^{-1}$)
S Specific area ($m^2.m^{-3}$)
X Dry basis water content ($kg_w.kg_{dm}^{-1}$)
T Absolute temperature (K)
R perfect gas constant ($J.mol^{-1}K^{-1}$)
ρ Density ($kg.m^{-3}$)
θ Temperature (°C)

INDICES

0 Initial
dm Dry basis
eq Equilibrium
exp Experimental
mod Model
w Water

1. INTRODUCTION

The conservation of meat in the hot countries is difficult for its very perishable character. This product degrades very quickly under the climatic conditions unfavorable. Several traditional techniques of conservation are employed in Africa and in other continents like the Latin America and Asia. These techniques often combine drying with other processes such as salting and infusion for example. One leads then to various products like kilishi in Sub-Saharan Africa countries in particular.

Kilishi is a product processed using beef cutout in fine thin strap (1 to 3 mm), then dried and seasoned with local spices and of the groundnut paste. Very solicited, this product is widespread in Sub-Saharan African countries. With the movements of populations and especially the immigration of African towards Europe and America countries, this appreciated product is more requested (Musonge and Njolai, 1994). The African diaspora, relatively significant, represent a potential market for this product. The market of kilishi is thus promising in the future and will be a source of incomes for the saving in this area of Africa.

Water activity a_w of a product essentially depends on its water content X and on its temperature θ. The curve representing, for a temperature θ, the equilibrium water content X_{eq} of a product as a function of its water activity a_w (or of air relative humidity HR) is called the sorption isotherm.

The sorption isotherm enables the calculation of the equilibrium water content X_{eq} depending on air conditions. This parameter will be the limit of the product water content at the end of the drying. This equilibrium water content X_{eq} is thus an important parameter used in drying models.

The sorption isotherm gives also information on the sorption mechanism and on the interaction between adsorbate and adsorbent as pointed out by Bizot et al. (1987). The equilibrium water content of a product is one of the most important parameter to predict its behaviour during storage according to Chirife and Buera (1994); Vilades et al. (1995). Nevertheless, it has been shown by Yang and Atallah (1985) that the drying method could have an effect on the characteristics of a dried product such as: adsorption and desorption isotherms, porosity, specific area and color.

Many authors have published results about sorption isotherms studies of various products but very little information is available about sorption isotherms and drying kinetics of kilishi or meat (Ji-Hun Choi et al., 2008; Simal et al., 2003; Polignéet al., 2001; Egbunike and Okubanjo, 1999; Kalilou et al., 1998; Chang et al., 1996; Musonge and Njolai, 1994).

The aim of the present study is to determine, by experience, the sorption isotherms of kilishi. The results can be used particularly for the development of a system of suitable drying.

2.MATHEMATICAL MODELS

Sorption isotherms of a material have been described by various mathematical models with two or more parameters as presented by Van der Berg and Bruin (1981). Nevertheless, models with more than three parameters lead to not easy use and physical interpretation. The model presented by Brunauer, Emmet and Teller (1938) known as “BET model”, and its modified version from Guggenhein, Anderson and Boer (GAB) as described by Bizot et al. (1987) have been successfully used by many authors such as Talla et al. (2005) for modelling sorption isotherms. These models include parameters which have physical meaning.

2.1 GAB Model

Contrary to BET model that allows the study of the phenomena of water molecules adsorption and desorption, the GAB model enables a representation of sorption isotherms for the whole values of water activity a_w. Moreover, the GAB model takes into account the temperature effect. Its mathematical expression is the following:

$$\boldsymbol{X_{eq}} = \frac{X_m C K a_w}{(1-Ka_w)[1+(C-1)Ka_w]} \quad (1)$$

X_m: water content corresponding to monolayer ($\mathrm{kg_w \cdot kg_{dm}^{-1}}$)
C: constant linked to monolayer sorption heat
K: constant linked to multi-layer sorption heat.

$$\boldsymbol{C} = C_0 exp\left(\frac{H_w-H_m}{RT}\right) \text{and} \boldsymbol{K} = K_0 exp\left(\frac{H_w-H_q}{RT}\right) \quad (2)$$

With H_w, H_m, H_q, respectively, condensation heat of pure water, total sorption heat of the monolayer and total sorption heat of other layers
T: absolute temperature (K) and
R: perfect gas constant (8.314 $J.mol^{-1}K^{-1}$).

With the hypothesis of an initial homogeneous monolayer filling of the product surface, one can calculate its area. Supposing that monolayer is recovered with aligned water molecules, it could easily be shown that its area can be calculated by formula (Brunauer et al., 1938):

$$S_m = \frac{\sqrt{3}\sqrt[3]{2}}{2}\left(\frac{N}{M\rho_w^2}\right)^{1/3}\rho_{dm}X_m \qquad (3)$$

S_m: monolayer area or specific area ($m^2 \cdot m^{-3}$)
N: Avogadro number = $6.023.10^{23}$
M: absorbing material molecular mass ($kg \cdot mol^{-1}$)
ρ_w: water density ($kg \cdot m^{-3}$)
ρ_{dm}: solid matrix density ($kg_{dm} \cdot m^{-3}$)
The value of the specific area of a product may give information about its rehydration and its internal structure.

2.2 Isosteric Sorption Heat

A heat whoequals to the sum of phase change latent heat L_v and of sorption heat Q_{sorp} is necessary to evaporate one kilogram of water. The sorption heat may be calculated from the curves representing, for a constant water activity, product activity as a function of temperature, these curves are called the (water) sorption isosters. The equation of these curves is given by Clausius-Clapeyron formula:

$$ln(a_w) = -\left(\frac{Q_{sorp}}{R}\right)\left(\frac{1}{T}\right) + Constant \qquad (4)$$

In a two-dimensional diagram where $\ln(a_w)$ is represented as a function of 1/T, the sorption isosters are straight lines according to the relation:

$$\left[\frac{\partial ln\,(a_w)}{\partial\left(\frac{1}{T}\right)}\right]_{X=constant} = -\frac{Q_{sorp}}{R} \qquad (5)$$

The isosteric sorption heat can be deduced from the slope of sorption isosters representing $\ln(a_w)$ as a function of 1/T for each product water content X, and then the curve $Q_{sorp}= f(X)$ can be plotted. It is an important parameter whose values show at the end of the drying it cannot be neglected in energy balance since it has the same order of magnitude as the vaporization latent heat.

3. MATERIALS AND METHODS

3.1 Sorption Method

The static method of the saturated salts solutions has been used for sorption isotherms determination. It is a method where diffusion is the only way of mass transfer between the tested product and the surrounding air. The relative air humidity is fixed by contact with saturated salts solution whose water vapour pressure at a given temperature is perfectly known. This method is commonly used for product sorption isotherms determination (Jannot et al., 2006; Talla et al., 2005; Koukila et al., 2001).

The time necessary to reach equilibrium is quite long compared to the dynamic method since the diffusion rate is limitating factor.

3.2 Experimental Process

The first step is choice of salts so that a large interval of water activities could be obtained. In our experiments, ten salts have been used that covered the range 0.06 to 0.97 for water activities, these salts are: LiBr, LiCl, KCH_3CO_2, $MgCl_2$, K_2CO_3, NaBr, $CuCl_2$, NaCl, KCl and K_2SO_4. The corresponding values of water activities are given by Bizot and Multon (1978).

Kilishi is first obtained using beef cutout in fine thin strap (1 to 3 mm), then dried and seasoned with local spices and of the groundnut paste.Three samples of this product, previously dehydrated at 60ºC, were set in each of the ten recipients containing the ten saturated salts solutions. The use of three samples in each recipient aims at making sure that the results obtained could be reproduced with each experiment. Fig.1 shows the experimental device.The recipients were set in a temperature regulated chamber. Samples were weighted each 48 h until their mass variation became less than 1 mg. The oven dry mass was then measured after dehydration for 48 h at 102ºC to calculate the equilibrium water content X_{eq}.

The sorption isotherm is given by the experimental couples (a_w, X_{eq}). The experimental procedure consists in introducing the recipients in the chamber regulated to the lowest temperature value of the series (30ºC) then, when the equilibrium is reached, all the samples are weighted and the temperature is raised to the next value (40ºC). This procedure is repeated for 50ºC. During the experiments, a partial vacuum was applied inside the recipients to increase the mass transfer rate. The equilibrium water content is given by the following formula:

$$\boldsymbol{X_{eq} = 100\left(\frac{m_{eq}}{m_d} - 1\right)} \tag{6}$$

m_{eq}: sample equilibrium mass (kg); and
m_d: sample oven dry mass (kg_{dm}).

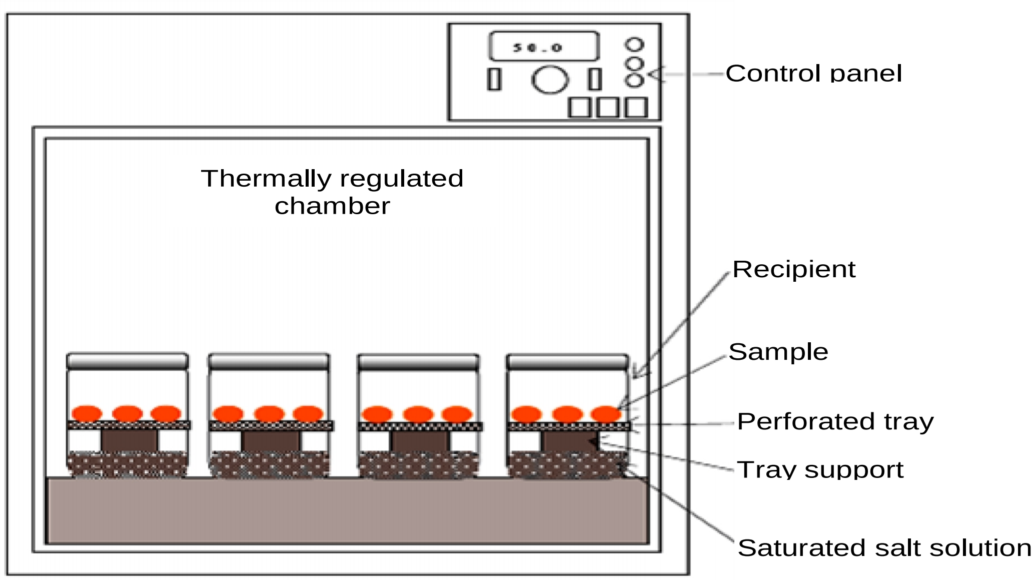

Fig. 1. Experimental device for sorption isotherm determination

4. RESULTS AND DISCUSSION

Fig. 2 represents the experimental desorption isotherms of kilishi obtained at different temperatures. The isotherms are sigmoidal as usually presented for foodstuff as done by Iglesias and Chirife (1982). For a given value of the water activity, the equilibrium water content decreases with the temperature.

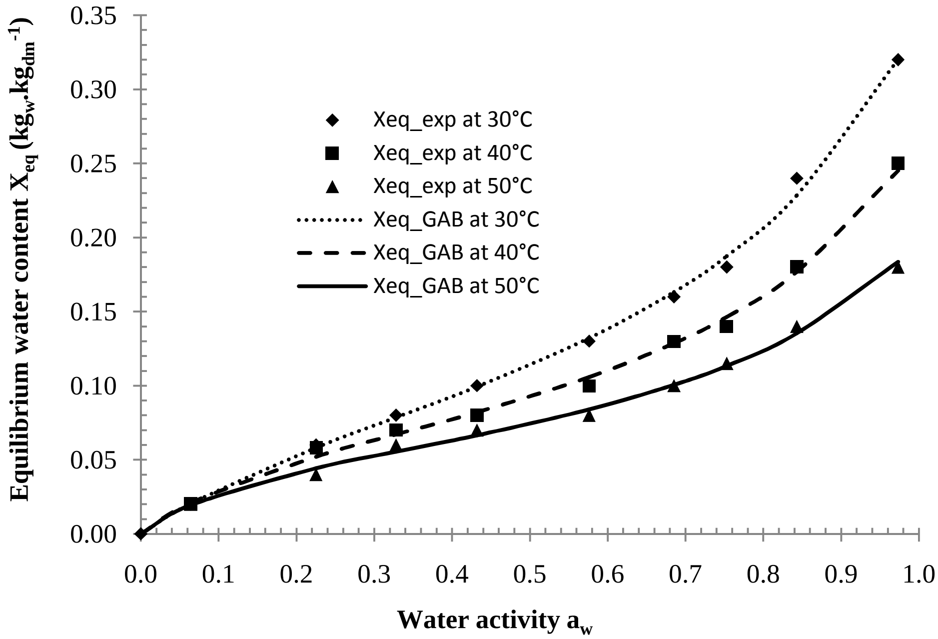

Fig. 2.Sorption isotherms of kilishi at several temperatures: simulation by the GAB model and experimental results

The constants X_m, C, K of the GAB model depend on product characteristics and on temperature. All these constants are estimated from experimental results. For each temperature, these parameters are estimated by minimizing the sum of the quadratic errors between the experimental equilibrium water contents X_{eq} and the values calculated with equation (1).

$$S = \sum_{k=0}^{n} \left(\frac{X_{exp} - X_{mod}}{X_{exp}}\right)_i^2 \qquad (7)$$

n is the number of measurements for a temperature (ten in the present case).

Table 1 resumes the whole results of the estimation for kilishi and for each temperature. Furthermore, Fig. 2 represents comparison between the experimental curves and the curves simulated by the GAB model. The parameter X_m is the water content corresponding to monolayer saturation. According to experimental results, the estimated parameters X_m and K decrease when the temperature rises since the parameter C increases with temperature (Table 1). This is in agreement with the behaviour of other products as reported by Labuza et al. (1985); Maroulis et al. (1988); Okos et al. (1992); Sopade and Ajisegiri (1994) for parameter X_m.

Table 1. Estimated values of the parameters of the GAB model

¯ (°C)	X_m ($kg_w.kg_{dm}^{-1}$)	C	K	S_m ($m^2.m^{-3}$)	$X_0{}^{\circ}{}_{dm}/S_m$ ($kg_w.m^{-2}$)
30	0.095	5.140	0.748	$4.299\times10^{+10}$	8.968×10^{-08}
40	0.071	7.799	0.745	$3.196\times10^{+10}$	1.206×10^{-07}
50	0.055	10.384	0.732	$2,481\times10^{+10}$	1.554×10^{-07}

Moreover, the specific area is directly proportional to the water content at the saturation of monolayer. The decreasing of the specific area S_m with temperature increasing can be explained by the decrease of porosity as an effect of the thermal expansion of the solid matrix leading to pores shrinkage. Table 1 also indicates the values of $X_0\rho_{dm}/S_m$, which represents, at the initial state, the water content filling the pores by unit of specific area and so has the dimension of a water thickness. The density of solid phase measured, was 1285 $kg.m^{-3}$. This value has been used in our calculation. This parameter decrease when the temperature rises and may indicate that Kilishi will be easier to dry on high temperature. This prediction is in agreement with the results of Talla et al. (2005) for tropical fruits.

The representation of the residues on Fig. 3 shows higher deviation for high values of water activities. The maximum deviation for this product is lower than 1.5% for a water activity of 0.843. The mean relative deviation of the GAB model using the values of Table 1 compared to the all experimental points is 3.5% for this product. Nevertheless, the deviation is quite low (maximum 0.6%) for water activities lower than 0.35 and is thus interesting for drying modelling since final water content around 0.15 $kg_w.kg_{dm}^{-1}$ is generally recommended. The relatively low deviations lead to the conclusion that the GAB model represents the sorption isotherm of kilishi quite satisfactorily.

The sensitivity of the GAB model to the parameters X_m, C, and K is deduced from equations (8) to (10).

$$\frac{\varepsilon}{100}\boldsymbol{X_m}\frac{\partial X_{eq}}{\partial X_n} = \frac{\varepsilon}{100}\boldsymbol{X_{eq}} \tag{8}$$

$$\frac{\varepsilon}{100}\boldsymbol{C}\frac{\partial X_{eq}}{\partial C} = \frac{\varepsilon}{100}\boldsymbol{X_{eq}}\left[\mathbf{1} - \frac{CKa_w}{1+(C-1)Ka_w}\right] \tag{9}$$

$$\frac{\varepsilon}{100}\boldsymbol{K}\frac{\partial X_{eq}}{\partial K} = \frac{\varepsilon}{100}\boldsymbol{X_{eq}}\left[\frac{Ka_w}{1-Ka_w} + \frac{1}{1+(C-1)Ka_w}\right] \tag{10}$$

These three formulas represent the variation of the estimated value of X_{eq} indices by a relative variation of ε% of respectively the parameters X_m, C, and K from their nominal values. For example, Fig.4 represented this sensitivity at 50°C and shows that the GAB model is quite insensitive to parameter C: a relative variation of 10% on the parameter C has no effect on the simulated values of X_{eq}. This confirms, as pointed out by Rouquerol et al. (1999), that the simplified theoretical expression of the parameter C given by formula (2) cannot lead to reliable estimation of the total sorption heat H_m of monolayer.

The parameters C_0 and $H_w - H_m$ have not been estimated since it will not be reliable as previously pointed out. The values of estimated parameters of K calculation were:
$K_0 = 0.528$ and $H_w - H_m = 0.884$ $kJ.mol^{-1}$.

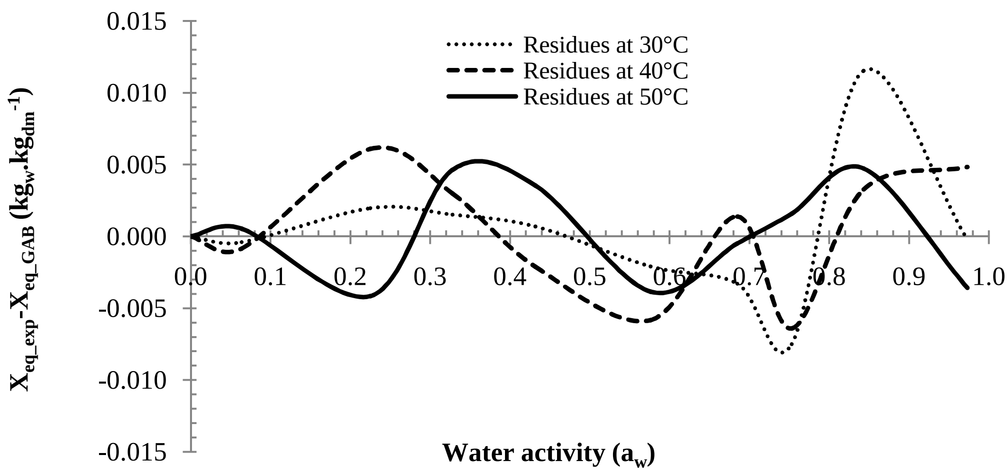

Fig. 3. Residues between experimental values of Xeq and values calculated by the GAB model for kilishi

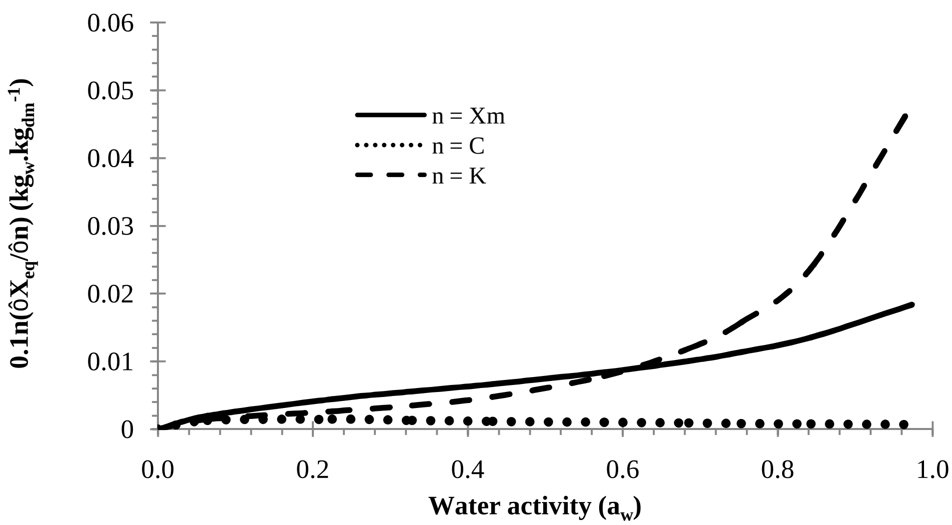

Fig. 4. Variation of Xeq induced by a relative variation of 10% of each parameter at 50ºC

The value of $H_w - H_q$ represents the mean value of sorption heat of the studied meat, which is lower than the vaporization heat of water. Fig. 5 represents, for kilishi, the sorption isosters $\ln(a_w)$ vs. 1/T that must be strainght lines according to formula (4). For each water content X, a sorption isoster has plotted and the isosteric sorption heat was calculated from its slope. For this product, the representation of Q_{sorp} vs. X has then been plotted on Fig. 6. It can be observed that the isosteric sorption heat is high for the low water content; indicating the strong link between the absorbate (water) and the adsorbent, but it is quite negligible compared to vaporization latent heat for high water content. The experimental results have been correlated satisfactorily by relation (11).

$$\boldsymbol{Q_{sorp} = 455.28 + 3994.53exp\left(-\frac{X}{0.05}\right)} \tag{11}$$

Q_{sorp}: sorption heat ($kJ.kg^{-1}$)
X: water content ($kg_w \cdot kg_{dm}^{-1}$)

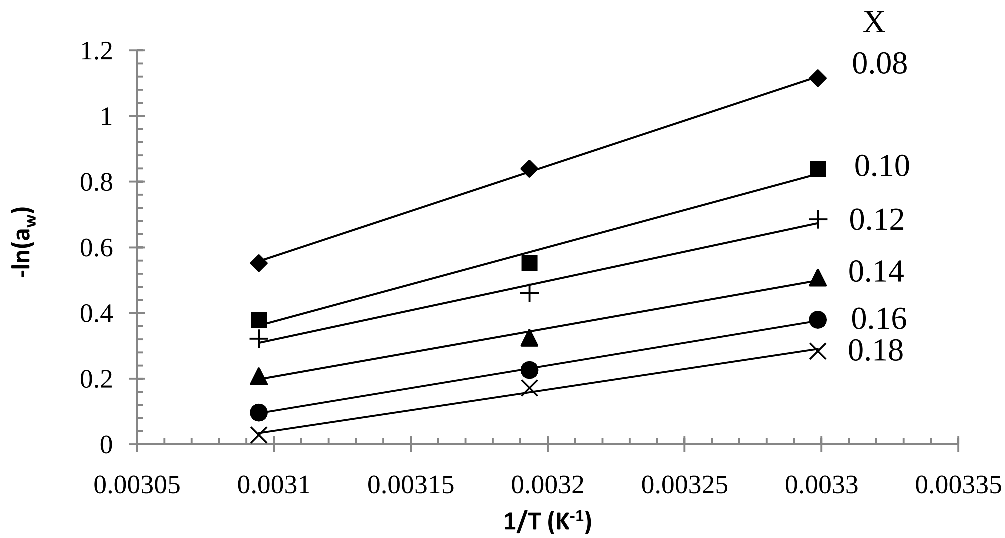

Fig. 5. Sorption isosters for kilishi

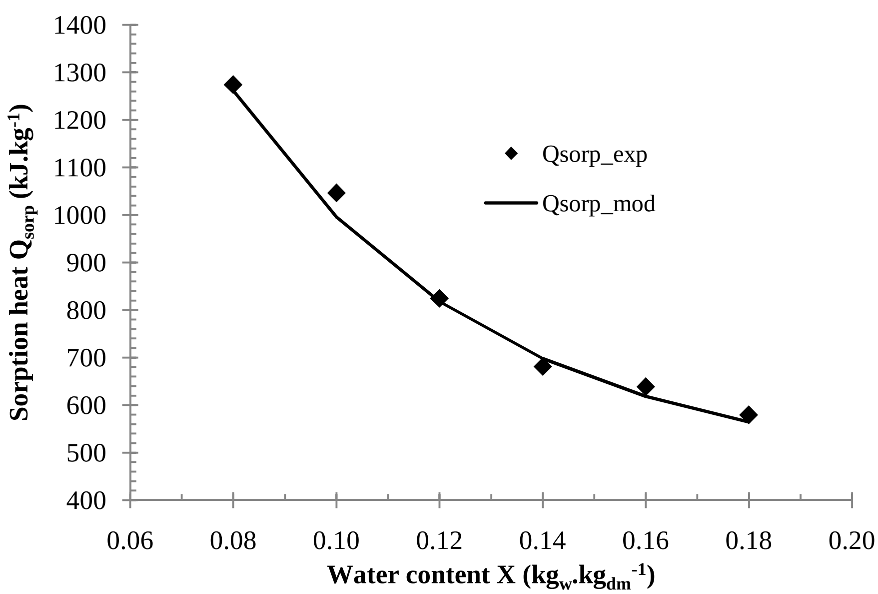

Fig. 6. Sorption heat of kilishi vs. water content

5. CONCLUSION

In this study, the desorption isotherms of kilishi have been experimentally established and modeled by GAB model. The maximal deviation between experimental results and calculated values of water content X by this model is around 0,011 $\mathrm{kg_W.kg_{dm}^{-1}}$ for X = 0.85. The GAB model also leads to the calculation of isosteric desorption heat of kilishi.

Furthermore, the curves giving the isosteric desorption Q_{sorp} heat vs. water content X have been deduced from the experimental desorption isotherms. The high values observed for low water content indicates the strong link between the adsorbate (water) and the adsorbent. Empirical relations $Q_{sorp} = f(X)$ have been established for this product.

ACKNOWLEDGEMENTS

The author expressesits sincere thanks to National Advanced School of Engineering, University of Yaounde I, for her material support.

COMPETING INTERESTS

The author has declared that no competing interests exist.

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