STUDY OF SORPTION PROPERTIES AND THE DEVELOPMENT OF MATHEMATICAL MODEL FOR VARIED TEMPERATURES OF BITTER KOLA

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ABSTRACT
The physicochemical properties and sorption isotherms of Bitter kola (Garcina kola) has been studied. It was processed into powder of 500 µm. The physicochemical properties determined were moisture (52.50 %), crude protein (2.51 %), crude fiber (5.12 %), fat (4.16 %), ash (0.86 %) and carbohydrate (34.85 %) content. The sorption isotherms were determined using the static gravimetric method. The obtained data were fitted into the Brunauer-Emmett-Teller, Guggenheim-Anderson-de Boer and Oswin models using the nonlinear regression method. From the results obtained, equilibrium moisture content increased with increasing water activity at a particular temperature and decreased with increase in the temperatures studied. The water surface areas of the adsorbents were calculated and the values obtained were less than 260 $m^2.g^{-1}$*. The sorption isotherm curves obtained were sigmoidal and the models were also suitable for describing the experimental data with coefficient of determination values of approximately equal to unity. A mathematical model was developed and was fitted to the experimental data which gave the correlation coefficient of* $R^2 = 0.984992$*. The result of this work revealed that shelf life of bitter kola would be sustained by storage under lower temperatures.*

Keywords: *Bitter kola, Physicochemical, Sorption, Isotherms, Static gravimetric method*

INTRODUCTION
Background of the Study
Bitter kola which is also known as '*Garcinia kola*' is a specie of flowering plant in the Clusiaceae or Guttiferae family. It is found in Benin, Cameroon, Democratic Republic of the Congo, Ivory Coast, Gabon, Ghana, Liberia,

Nigeria, Senegal and Sierra Leone. Its natural habitat is subtropical or tropical moist lowland forests. The fruit, seeds, nuts, stem and bark of the plant have been used for centuries in folk medicine to treat ailments from coughs to fever, for dental care in the form of chewing-sticks (Adu-Tutu *et al*., 1979). It is highly used for its medicinal purposes because of its anti-viral, anti-inflammatory, nanti-diabetic, bronchio-dilator and anti hepotoxic attributes. Fruit extracts from it have proven effective at stopping Ebola virus replication in laboratory test (Okunji *et al*., 2002). It has been utilized in folklore remedies by the Igbo people of the Southern Nigeria to treat ailments associated with poisoning, liver disorders, hepatitis, diarrhoea, laryngitis, bronchitis and gonorrhea (Adesina *et al*., 1995; Iwu, 1993).

Some of the use of bitter kola depends on principles of adsorption. Bitter kola is also rich in caffeine and threo-bromine and is also believed to be an aphrodisiac. Unlike other kola nuts however, bitter kola is believed to clean the digestive system, without side effects such as abdominal problems, even when a lot of nuts are eaten (Onochie and Stanfield, 1960).

The food sorption isotherm describes the thermodynamic relationship between water activity and the equilibrium of moisture content at constant temperature and pressure. The moisture sorption isotherms are extremely important in modeling the drying process, design and optimization of drying equipment, predicting shelf-life stability, calculating moisture changes which may occur during storage and selection of appropriate packaging material. Also, the knowledge of the sorption data is essentially useful to predict microbiological, enzymatic and chemical stability of food materials (Oyerinde and Lawal, 2015). Experimental determination and modeling of sorption isotherms of food materials has attracted numerous researches because their values are used in industrial purposes. Sorption isotherms are usually classified according to their shape in five different types. The sorption isotherms for most foods are nonlinear and generally with sigmoid shape (Ricardo *et al*., 2011).

In this current study, sorption properties and the development of mathematical model for varied temperatures of bitter kola are reported. This is expected to provide information for those involved in their processing and application in fruit and drug formulation.

MATERIALS AND METHODS

Experimental Methods

Preparation of the Raw Materials

The material selected for use in this study is *Garcina kola.* This was obtained from the Botany Department of University of Uyo, Uyo and is identified as such. It was washed in water, peeled manually with a steel knife, sliced and dried using a hot air oven at 105 ^{0}C until constant weight.

Proximate Analysis

Moisture, crude protein, fibre, fat, lipid, ash and carbohydrate contents were determined according to Association Official of Analytical Chemists (AOAC, 1990); Owuamanam *et al*., 2010 and Nwanekezi *et al*., 2010.

Fabricated Air Tight Hermetic Container

The container served as an air tight apparatus that can carry the raw material and salt solution. The fabrication involved the use of nine (9) plastics with cylindrical shape, polyvinyl chloride pipes (2 cm diameter) and aluminum crucibles, cut into circular shape of 4 cm diameter and a lid to cover the container.

Preparation of Saturated Salt Solution

Nine saturated saline solutions which include; Lithium Chloride (LiCl), Sodium Chloride (NaCl), Magnesium Chloride ($MgCl_2$), Sodium Bromide (NaBr), Strontium Chloride ($SrCl_2$), Potassium Chloride (KCI), Potassium Carbonate(K_2CO_3), Potassium Iodide (KI) and Pottasium Sulphate (K_2SO_4) were used, these were enclosed in hermetic containers and had a_w values that varied between 0.113 and 0.970 (Kiranoudis *et al*., 1993; Julius, 1998; Lewis, 1976). 3 g of *garcina kola* were introduced into each hermetic container with the corresponding saline solution. Each analytical grade salt was mixed with distilled water (approximately 100 ml) until a solution with excess crystals was formed. The saturated salt solutions were poured into the hermetic containers to a depth of 1 cm.

The adsorption isotherms were determined using a temperature controlled cabinet (Hot Pack, US); with an accuracy of ±1 ^oC at the selected temperatures of 30 ^oC to 60 ^oC using the static gravimetric method, according to the COST 90 project. Thymol was placed into the containers with saline solutions that had a_w values higher than 0.65 to prevent microbial growth. The samples were periodically weighed until a constant weight was achieved, to ensure equilibrium between the samples and the saline solutions. The adsorption experiments for each temperature were performed in triplicate.

Sorption Isotherm

The relationship between the equilibrium moisture content and the water activity of the product was predicted by using the equations representing the models commonly used in foodstuff. These models which incorporate the temperature effect have been adopted as standard equations by the ASAE for the description of sorption isotherms (ASAE, 1997). In this study, the three isotherm models used to fit the experimental data are presented in Table 1.

Table 1: Isotherm models and their equations

Name of Model	Range of a_w	Mathematical Expression
BET (Brunauer-Emmett-Teller)	$0.05<a_w<0.35$	$\frac{M}{M_0} = \frac{Ca_w}{(1-a_w)(1-a_w+Ca_w)}$
GAB(Guggenheim-Anderson-de Boer)	$a_w<0.95$	$M = \frac{M_o\, G\, Ka_w}{(1-Ka_w)(1-Ka_w+GKa_w)}$
Oswin	$0.10<a_w<0.80$	$M = A\left[\frac{a_w}{1-a_w}\right]^B$

Source: Tabulated by researcher (2021)

The constants were estimated by fitting the mathematical model to the experimental data, using a non-linear regression analysis with Microsoft Excel 2013 software.

The quality of the fitting of different models was evaluated by calculating the correlation coefficient (R^2), the mean relative percentage deviation modulus E in percentage (%) and the root mean square error (RMSE) between the experimental and predicted equilibrium moisture content (Boquet *et al.*, 1978 and Basu *et al.*, 2006). The deviation modulus and root mean square error and correlation coefficient are expressed as Equations 1 through 3.

$$E = \frac{100}{N} \sum_{i=1}^{N} \frac{|X_{eq,exp} - X_{eq,pre}|}{X_{eq,exp}}$$

Equation 1

$$RMSE = \left[\frac{1}{N} \sum_{i=1}^{N} \frac{(X_{eq,exp} - X_{eq,pre})^2}{X_{eq,exp}}\right]^{\frac{1}{2}}$$

Equation 2

$$R^2 = \frac{(X_{eq,exp})}{X_{eq,exp} + X_{eq,pre}}$$

Equation 3

Where N is the number of observations; $X_{eq,exp}$ and $X_{eq,pre}$ are the experimental and predicted values of the equilibrium moisture content, respectively.

Surface area

The specific surface area plays an important role in determining the water binding properties of particulate products. It is represented by Equation 4.

$$S_a = X_m \frac{1}{M} A N_A = 3.53 \times 10^3 X_m$$

Equation 4

Where S_a is the product surface area ($m^2.g^{-1}$), X_m is the monolayer moisture content ($kg.kg^{-1}$ dry basis), M is the molecular weight of water (18 $g.mol^{-1}$), N_A is the Avogadro's number (6×10^{23} $molecules.mol^{-1}$) and A is the area of one water molecule ($1.06 \times 10^{-19}\ m^2$). Where S_a is the product surface area ($m^2.g^{-1}$), X_m is the monolayer moisture content ($kg.kg^{-1}$ dry basis), M is the molecular weight of water (18 $g.mol^{-1}$), N_A is the Avogadro's number (6×10^{23} $molecules.mol^{-1}$) and A is the area of one water molecule ($1.06 \times 10^{-19}\ m^2$).

Development of Mathematical Models

Literatures had established that the non – linear regression (or equation) technique could be used to develop a model which takes care of many variables (Khazei and Daneshmandi, 2007; Maisnam *et al.*, 2017).

For the development of the correlation in this study, The BET model equation was considered as shown in Table 1. The Moisture content (M) depends directly on the monolayer moisture content (M_o), net heat of sorption (C) and water activity (a_w). Based on this assertion, the relationships of M with the adsorption parameters are presented in Equations 5 through 7.

$$M \propto M_o$$

Equation 5

$$M \propto C$$

Equation 6

$$M \propto a_w$$

Equation 7

For the development of the proposed moisture ratio correlation for adsorption of the product (bitter kola), the following parameters, namely: monolayer moisture content, net heat of sorption and water activity. In other words, the moisture ratio is expressed as a function of the mentioned parameters in Equations 8.

$$M = f\ (M_o,\ C,\ a_w)$$

Equation 8

Equations 5 through 7 can be expanded in the basic form of nonlinear multivariable algebraic expression as given in Equation 9.

$$M = \beta_o({M_o}^{\beta_1} \, . \, C^{\beta_2} \, . \, {a_w}^{\beta_3})$$

Equation 9

Alternatively, Equation 14 can also be expressed as Equation 10.

$$M = \beta_o\left[{M_o}^{\beta_1} \times C^{\beta_2} \times {a_w}^{\beta_3}\right]$$

Equation 10

Where β_o is the adsorption coefficient while β_1, β_2 and β_3 are exponential constants of the drying parameters.

The variables β_o, β_1, β_2 and β_3 could be determined iteratively using multivariable numerical optimization method. To determine these variables, existing literature indicates that, there are several approaches to performing this iterative estimation, namely; Gauss-Newton, the Marquardt-Levenberg, the Nelder-Mead, the steepest descent, General Reduced Gradient (GRG) protocol (Wei, 2013; Smyth, 2015; Pashaie *et al.*, 2016; Okon *et al.*, 2015).

To estimate the variables in the Equation 15 iteratively, these parameters were obtained experimentally. Then the unknown coefficient (β_o) and the exponential constants β_1, β_2 and β_3 were solved iteratively using GRG protocol in the Microsoft Excel SOLVER. To validate the correlation, its prediction was compared with the experimental data and some authors' correlation predictions. Also, the closeness of the correlation's predictions and experimental data were established using coefficient of determination (R^2) and other error functions.

RESULTS AND DISCUSSION

Proximate Analysis of *Garcina Kola*

Table 2 shows the moisture, crude protein, crude fibre, fat, ash and carbohydrate contents of *garcina kola*. This material possess high moisture content, a property of any fruit that can make it viable to microbial attack and this accounts for most biochemical and physiological reactions in plants.

Fibre plays a more important role in human nutrition than its functionality in the digestive system. It contributes to bowel movement and has been used by people with gastro intestinal disorder. This implies that *garcina kola* will serve better for this purpose.

Table 2: Proximate composition for *garcina kola*

Components	Percentage (%)
	Garcina Kola
Moisture content	**52.500**
Crude protein	**2.510**
Crude fibre	**5.120**
Fat content	**4.160**
Ash	**0.860**
Carbohydrate	**34.850**

Source: Computed by the researcher (2021)

Equilibrium moisture content and water activities at varied temperatures

The result of the EMC and a_w of *garcina kola* is shown in Tables 3. This was taken at temperature range of 30 to 60 ^oC. It can be clearly observed that as temperature increases, the EMC decreases for this material.

Table 3: **Summary of the Equilibrium Moisture Content and Water Activity at Varied Temperatures for *Garcina Kola***

30 ^oC		40 ^oC		50 ^oC		60 ^oC	
a_w	EMC	a_w	EMC	a_w	EMC	a_w	EMC
0.113	0.050	0.112	0.049	0.111	0.048	0.111	0.045
0.324	0.070	0.316	0.068	0.305	0.066	0.293	0.065
0.432	0.081	0.432	0.080	0.432	0.079	0.432	0.077
0.560	0.110	0.532	0.100	0.509	0.097	0.497	0.095
0.679	0.112	0.661	0.120	0.645	0.117	0.631	0.114
0.691	0.127	0.673	0.125	0.657	0.120	0.643	0.118

0.751	0.200	0.747	0.199	0.744	0.197	0.745	0.190
0.836	0.330	0.823	0.310	0.812	0.290	0.803	0.285
0.970	1.835	0.964	1.830	0.958	1.790	0.952	1.750

Source: Computed by the researcher (2021)

Moisture Sorption Isotherm of *Garcina Kola* at Varied Temperatures

The experimental data for the EMC and a_w were plugged into nonlinear regression graphs using Microsoft Excel 2013. Figures 1 through 4 are the moisture sorption isotherms for *garcina kola* at varied temperatures. The equilibrium moisture at a given water activity, decreased with increase in temperature. This is in agreement with the theory of physical sorption (Iglesias *et al.*, 1975; Hassian *et al.*, 2001). This indicates that *garcina kola* became less hygroscopic with increasing temperature. The adsorption isotherms exhibited Type II curve with a characteristic sigmoidal shape.

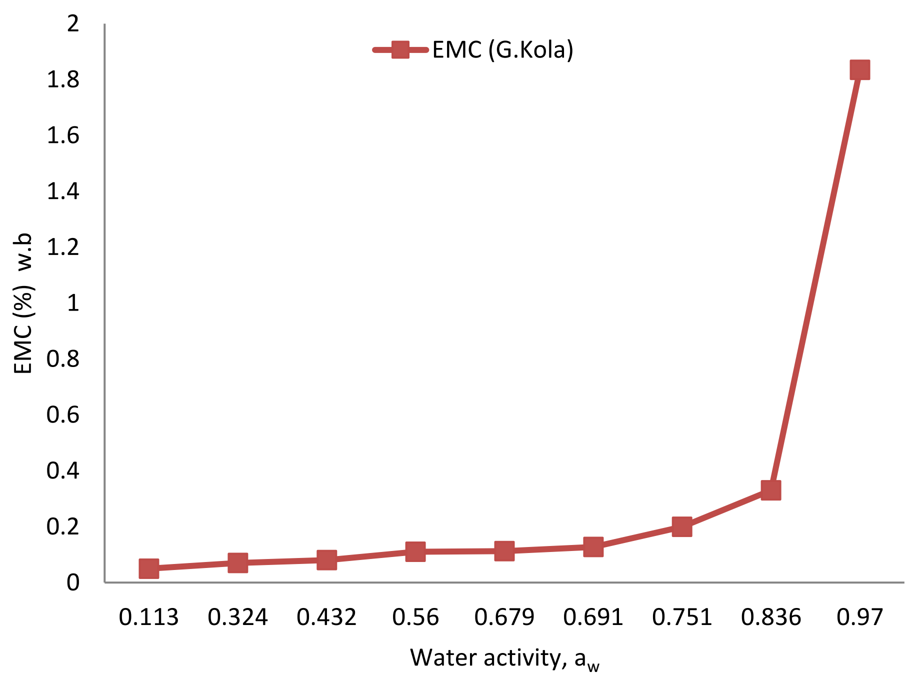

Figure 1: Adsorption isotherm of *taro* and *garcina kola* at 30 ºC
Source: Plotted by the researcher (2021).

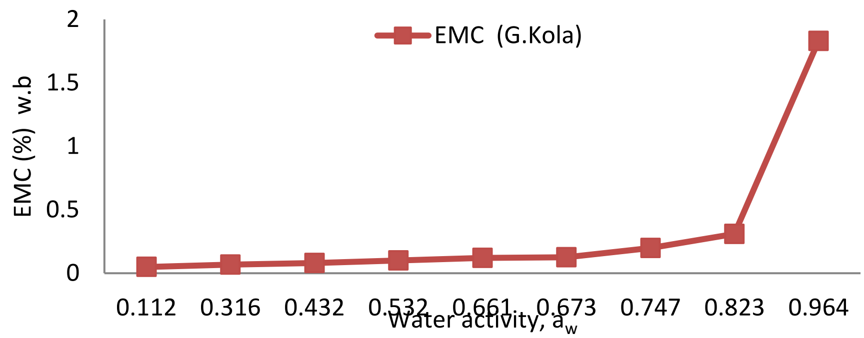

Figure 2: Adsorption isotherm of *taro* and *garcina kola* at 40 ^{o}C
Source: Plotted by the researcher (2021).

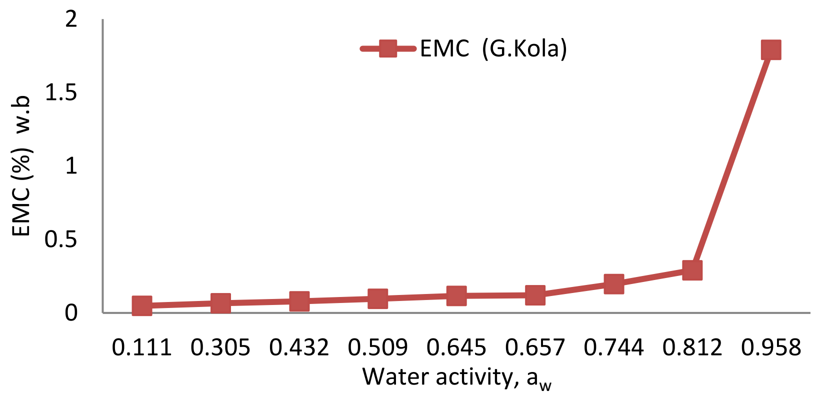

Figure 3: Adsorption isotherm of *taro* and *garcina kola* at 50 ^{o}C
Source: Plotted by the researcher (2021).

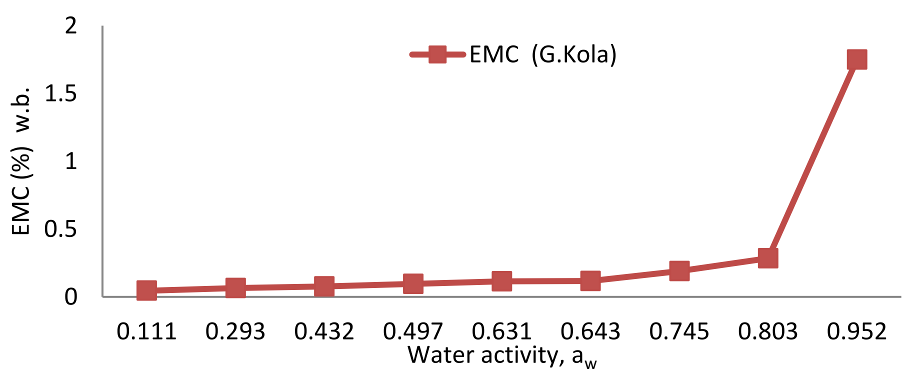

Figure 4: Adsorption isotherm of *taro* and *garcina kola* at 60 ^{o}C
Source: Plotted by the researcher (2021).

Adsorption Models

The experimental data (EMC) obtained were plugged into the adsorption models which include Brunauer-Emmett-Teller (BET), Guggenheim-Anderson-de Boer (GAB) and Oswin models. Tables 5 shows the coefficients of the models, the mean relative percentage modulus (E), the root mean square error (R.M.S.E) and the correlation coefficient (R^2). All the models presented correlation coefficients very close to unity indicating good fit to experimental data. The high values of R^2 at different temperatures revealed that the good fit of the models is independent of temperature variation.

Table 5: Estimated Parameters by Nonlinear Regression for BET, GAB and OSWIN Models *for Garcina Kola*

Models	Constants	Temperatures (°C)			
		30	40	50	60
BET	M_o (g/g dry solid)	0.181576	0.080867	0.041238	0.032293
	C	0.552673	0.917647	1.386102	1.706528
	R^2	0.99835	0.998261	0.997453	0.993035
	RMSE	0.02211	0.022701	0.026876	0.045547
	E (%)	12.56221	16.31022	17.69961	10.38048
GAB	M_o (g/g dry solid)	0.072897	0.050659	0.029747	0.023466
	K	0.989682	0.999365	0.974841	1.007904
	G	1.002062	1.174062	1.666545	1.796874
	R^2	0.996416	0.998076	0.997479	0.997517
	RMSE	0.032727	0.023936	0.026832	0.026348
	E (%)	16.50219	21.07163	20.83303	25.12812
OSWIN	A	0.079592	0.068519	0.065333	0.062802
	B	0.903281	0.999387	1.058778	1.114019
	R^2	0.99678	0.998234	0.99791	0.997649
	RMSE	0.030881	0.022931	0.02446	0.025406
	E (%)	11.87691	18.26048	21.06275	23.0462

Source: Computed by the researcher from calculated data (2021)

Surface Area

Table 6 presents the surface area of *garcina kola* from 30 to 60 ^{o}C. It was estimated using Equation 4 and the monolayer moisture contents of *garcina kola* were obtained by GAB model. The results indicated that, the availability of surface areas for hydrophilic binding decrease with increasing temperature. The calculated surface area values of *garcina kola* were within the range commonly obtained for food and fruits (100 - 250 $m^2.g^{-1}$) (Cassini *et al.*, 2006).

Table 6: Surface area of *garcina kola*

Temperature (^{o}C)	Adsorption S_a ($m^2.g^{-1}$)
30	257.32650
40	178.82640
50	105.00690
60	82.83500

Source: Computed by the researcher (2021)

Developed Model

Three parameters were used to develop a mathematical model that relates moisture content (M) to monolayer moisture content (M_o), net heat of sorption (C) and water activity (a_w) for the adsorption of moisture by *garcina kola* powder to which this research is established. Table 7 shows the values of the developed adsorption coefficient (β_o) and exponential constants (β_1, β_2, and β_3). These values were obtained using Microsoft Excel 2013 Solver after iteration with the General Reduced Gradient (GRG) protocol.

Table 7: Simulated values for different product using the developed model

Symbol	*Garcina Kola*
β_o	96.69954
β_1	1.80472
β_2	0.51181
β_3	10.09131

Source: Computed by the researcher (2021)

The quality of the developed model was evaluated using different statistical criteria to check for goodness of fit. The statistical variables include; correlation coefficient (R^2), root mean square error (RMSE) and sum square error (SSE). This is as shown in Table 8.

Table 8: Statistical values for different product using the developed model

Symbol	*Garcina Kola*
R^2	0.98499
RMSE	0.07039
SSE	4.63077

Source: Computed by the researcher (2021)

The empirical model developed for *garcina kola* is given as Equation 11.

$$M = 96.69954\left[{M_0}^{1.80472} \times C^{0.51181} \times {a_w}^{10.09131}\right]$$

Equation 11

Conclusion

This study has specifically provided the following information on sorption properties for varied temperature of bitter kola (*garcina kola*) and the following had been revealed:

i. The physicochemical properties and sorption isotherms of *garcina kola* powder was determined.
ii. The equilibrium moisture content of *garcina kola* decreased with increase in temperature at a given water activity (a_w), indicating that it became less hygroscopic at high temperatures giving a clear stability domain of *garcina kola* after drying leading to extensive shelf life.
iii. The results of the fit revealed that the three models accurately described all the adsorption and moisture isotherms for *garcina kola*.
iv. The mathematical model was developed and validated by fitting it into the experimental data which produced accurate result of correlation coefficient ($R^2 = 0.984992$) for *garcina kola*.

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