

Application of Sorption Isotherms to Extraction of Crude Caffeine from Native Kola-nut (Cola - acuminata) using Swiss Water Process.

Umeda, Uchendu¹, Puyate, Yamainian Tadaerigha¹ & Orlu, Happiness²

Department of Chemical / Petrochemical Engineering¹

Department of Chemistry²

Rivers State University, Port Harcourt, Nigeria.

umexil@yahoo.com.

Abstract

The Linear, Freundlich, and Langmuir isotherms were applied to the extraction of crude Caffeine from native Kola-nut using Flavour-Charged Water. It is shown that any of the three sorption isotherms can be used to describe the extraction process, though the Freundlich isotherm gives a maximum error of 2.65% at only one data-point. Models for predicting the quantity of crude Caffeine that can be extracted from a known quantity of native Kola-nut, and the corresponding volume of Flavour-Charged Water to be used for the extraction process, are also presented. Predictions of the models are compared with experimental data and good agreement is obtained.

Keyword: Caffeine, Extraction, Isotherms and Native Kola-nut

Introduction

Caffeine is a stimulant that may cause nervousness, irritability and insomnia. It is a major raw material in the Pharmaceutical Industries for the production of drugs and it is one of the major constituents of Kola-Nut which is obtained locally in Nigeria. (Brian and Allen, 1987). There is 1-2 % of caffeine in the fresh kola-nuts, but on drying the figure can increase to as much as 5 % or more depending on the Species (Reeling, 1999).

Sorption is a phase-transfer process describing the transfer of contaminants between liquid and a solid phase. It is a dominant process affecting almost all dissolved species in a liquid. Sorption mechanism includes all processes responsible for mass transfer such as absorption, adsorption, etc (Wu and Gschwend, 1986; Song et al., 1994). Absorption is the process whereby a chemical species is incorporated into the interior of a solid. Adsorption on the other hand, is the process whereby a chemical species is attracted to the surface of a solid body. The extent of sorption of a given constituent is often estimated using sorption isotherm.

A sorption isotherm (also adsorption isotherm) describes the equilibrium of the sorption of a material at a surface (more generally at a surface boundary) at constant temperature. It represents the amount of material bound at a surface (sorbate) as a function of the material present in the gas phase and/or in solution. Sorption isotherms are obtained in the laboratory using test which involves mixing water or any other inert solvent with the contaminant to a specific concentration of the solid medium (contaminant), and allowing the mixture to attain equilibrium. By reporting the test as varying concentrations of the constituent at the same temperature, a relation between sorbent-mass of the constituent and equilibrium concentration is obtained (Krupka et al., 1999; Sheppard et al., 1990; Inyang et al., 2000). Such isotherms may assume several shapes – linear, concave, convex, or a combination of these shapes. Theoretical equations are normally used to fit experimental data and the commonly used equations are the *Linear*, *Freundlich*, and *Langmuir* isotherms which may be defined as (Langmuir isotherm, 2019; Freundlich isotherm, 2019; Linear isotherm, 2019)

$$\text{Linear Isotherm} \quad S = K_d C \quad (1)$$

$$\text{Freundlich Isotherm} \quad S = K_f C^{1/n} \quad (2)$$

$$\text{Langmuir Isotherm} \quad S = \frac{\alpha\beta C}{1 + \alpha C} \quad (3)$$

where S is the quantity of mass sorbed on the solid surface (mg/g), C is the equilibrium concentration of the adsorbate in solution (mg/l), K_d is the slope of the linear sorption isotherm (l/g), K_f is the partition coefficient indicating the extent of sorption ($\text{mg}^{(n-1)/n} \text{l}^{1/n} \text{g}^{-1}$), n is the Freundlich exponent (ranging from 0.7 – 1.2), α is the Langmuir constant, and β is the maximum sorption capacity (or maximum amount adsorbed) as C increases.

Methodology

In the case of extraction of crude caffeine from native kola-nut using the Swiss Water Process, Flavour-Charged Water was used for the extraction process. Therefore, the sorption isotherms defined in Equations (1) - (3) will be applied only to the extraction of crude Caffeine from Kola-nut using Flavour-Charged Water. When a known mass of ground Kola-nut was added into a known volume of Flavour-Charged Water and the mixture was shaken to ensure proper mixing, the ground Kola-nut was suspended in the Flavour-Charged Water, with the extraction of crude Caffeine from the Kola-nut by the Flavour-Charged Water taking place in the suspended state. When the shaken-mixture is allowed to rest (i.e. undisturbed) for about six hours, the crude Caffeine extracted from the Kola-nut into the Flavour-Charged Water settled out to the bottom of the separating Funnel. Hence, the mass fraction of crude Caffeine obtained will be proportional to the concentration of crude Caffeine in solution with the Flavour-Charged Water in the form:

$$\frac{x}{m} \propto C \quad (4)$$

or

$$\frac{x}{m} = K_d C \quad (5)$$

which is consistent with the Linear Isotherm in Equation (1), where $S = x/m$ is the mass fraction of crude Caffeine, x is the mass of crude Caffeine, m is the mass of ground Kola-nut, $C = x/V_f$ is the mass concentration of crude caffeine in solution with Flavour-Charged Water, and V_f is the volume of Flavour-Charged Water.

Discussions

Linear Isotherm

This isotherm is given by Equation (1) or (5) above. Plotting values of S against C , gives a straight line of slope equal to K_d as obtained in Figure 1.

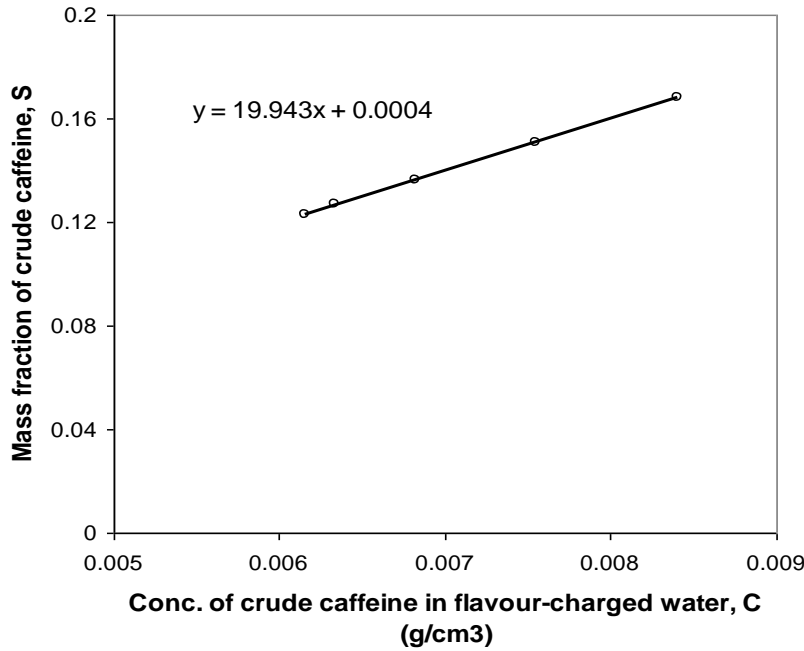


Figure 1. Plot of S against C

It may be seen from Figure 1 that $K_d = 19.943\text{cm}^3/\text{g}$ for the extraction of crude Caffeine from Kola-nut using the Swiss Water Process.

Freundlich Isotherm

This isotherm which is given in Eq. (2) is restated here for the sake of convenience as:

$$S = K'_f C_{ds}^{1/n} \tag{6}$$

where K'_f is a dimensionless partition coefficient. Since we need to take the natural logarithms of both sides of Equation (6) in order to determine K'_f and n graphically, the mass concentration (C) of crude Caffeine in solution with Flavour-Charged Water used in Equation (2) is converted into a dimensionless concentration of crude Caffeine (C_{ds}). Taking the natural logarithms of both sides of Equation (6), gives

$$\ln(S) = \ln(K'_f) + \frac{1}{n} \ln(C_{ds}) \tag{7}$$

A plot of values of $\ln(S)$ against $\ln(C_{ds})$, gives a straight line of slope equal to $1/n$ and intercept on the vertical axis equal to $\ln(K'_f)$ as obtained in Figure 2

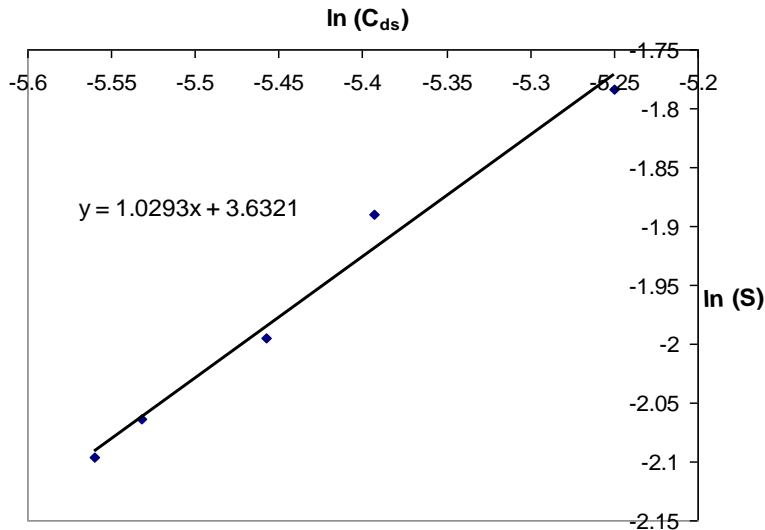


Figure 2. Plot of $\ln(S)$ against $\ln(C_{ds})$

It may be seen from Figure 2 that, Slope of graph = $1.0293 = \frac{1}{n}$, to give $n = \frac{1}{1.0293} = 0.97$

The obtained value of n in the Freundlich isotherm lies within the stipulated range of 0.7 – 1.2. Thus, for the extraction of crude Caffeine from native Kola-nut using the Swiss Water Process, the corresponding value of n is 0.97. Also, the intercept of the straight line in Figure 1 on the vertical axis equals 3.6321, such that:

$$\ln(K'_f) = 3.6321$$

to obtain:

$$K'_f = e^{3.6321} = 37.79$$

Langmuir Isotherm

This isotherm which is defined in Equation (3) is restated here for the sake of convenience as:

$$S = \frac{\alpha\beta C}{1 + \alpha C} \quad (8)$$

Taking the inverse of both sides of this equation, gives

$$\frac{1}{S} = \left(\frac{1}{\alpha\beta}\right)\frac{1}{C} + \frac{1}{\beta} \quad (9)$$

A plot of $1/S$ against $1/C$ gives a straight line of slope equal to $(1/\alpha\beta)$ and intercept on the vertical axis equal $(1/\beta)$, as obtained in Figure 3.

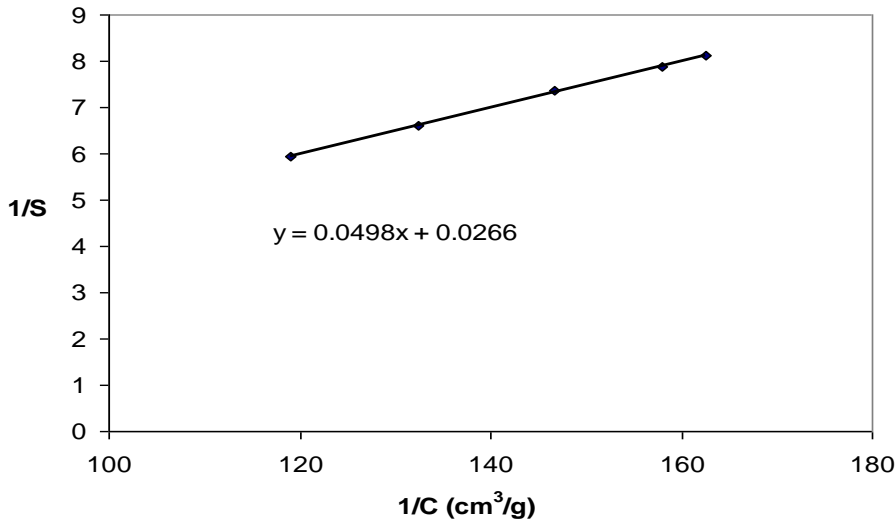


Figure 3. Plot of 1/S against 1/C

Equation (9) is often erroneously called the Hanes-Woolf regression. The Hanes-Woolf regression was proposed for fitting the Michaelis-Menten equation, which is similar in form to the Langmuir equation. Nevertheless, Langmuir proposed this linear regression technique and it should be referred to as the Langmuir linear regression when applied to adsorption isotherm (Langmuir Equation, 2019). It may be seen from Figure 3 that:

$$\frac{1}{\beta} = 0.0266, \text{ to give } \beta = \frac{1}{0.0266} = 37.59$$

The slope of the straight line in Figure 3 is 0.0498, such that

$$\frac{1}{\alpha\beta} = 0.0498$$

to give

$$\alpha = \frac{1}{0.0498 \times \beta} = \frac{1}{1.872} = 0.534 \text{ cm}^3/\text{g}$$

The various parameters estimated above for the Linear, Freundlich, and Langmuir isotherms on the extraction of crude Caffeine from native Kola-nut using the Swiss Water Process are summarized in Table 1 below

Table 1. Estimated Parameters of Sorption Isotherms for the Extraction of Crude Caffeine from Native Kola-nut using Swiss Water Process.

Isotherm	Parameters				
	K_d (cm ³ /g)	K'_f	n	α (cm ³ /g)	β
Linear	19.943	-	-	-	-
Freundlich	-	37.79	0.97	-	-
Langmuir	-	-	-	0.534	37.59

Comparison between experimental data and sorption isotherms.

Table 2 shows the comparison between experimental data and predictions of the three sorption isotherms using the estimated values of the parameters in the isotherms presented in Table 1. The information in Table 2 is shown graphically in Figure 4, indicating that both the Linear and Langmuir isotherms give very good fit of the experimental data at all data-points. Predictions of the Freundlich isotherm also compared well with the experimental data except

at only one data-point with an error of 2.65 %. Note in Table 2 that values of C and other parameters in the Linear and Langmuir isotherms were used to calculate predictions of these two isotherms, while values of C_{ds} , K'_f and n were used to calculate predictions of the Freundlich isotherm.

Table 2. Comparison between Experimental Data and Sorption Isotherms

C (g/cm ³)	C_{ds}	Values of S			
		Experiment	Linear	Freundlich	Langmuir
0.0084	0.00525	0.168	0.168	0.170	0.168
0.00615	0.00385	0.123	0.123	0.124	0.123
0.00633	0.00396	0.127	0.126	0.127	0.127
0.00755	0.00455	0.151	0.151	0.147	0.151
0.00682	0.00426	0.136	0.136	0.137	0.136

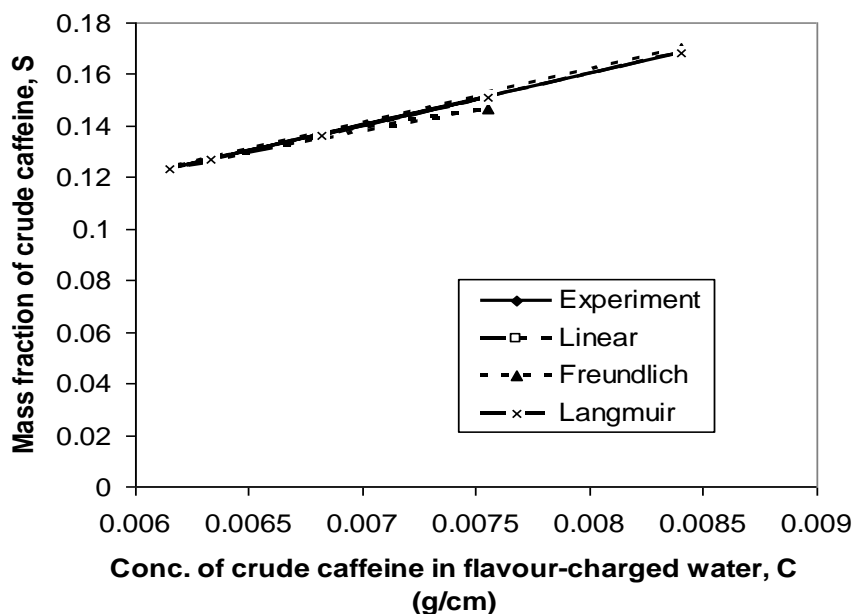


Figure 4. Comparison between experimental data and sorption isotherms.

On the whole, therefore, any of the three sorption isotherms may be used to describe extraction of crude Caffeine from native Kola-nut using the Swiss Water Process.

Correlations between mass of crude caffeine, mass of kola-nut and volume of flavour-charged in the Swiss Water Process

During extraction of crude Caffeine from native Kola-nut using the Swiss Water Process on a large scale, it is necessary to predict:

- ✓ The quantity of crude Caffeine that can be obtained from a known quantity of native Kola-nut, and
- ✓ The appropriate volume of Flavour-Charged Water to be used to extract the predicted quantity of crude Caffeine from the known quantity of native Kola-nut.

Model 1. Prediction of extractable quantity of crude caffeine from a known quantity of kola-nut

Plotting mass of crude Caffeine against mass of Kola-nut gives the graph shown in Figure 4. The polynomial representing the relationship between mass of crude Caffeine and mass of Kola-nut is superimposed on the experimental data-points, and the equation of the polynomial as obtained in Figure 4 is

$$M_C = -7 \times 10^{-6} M_k^3 + 0.0032 M_k^2 - 0.2972 M_k + 16.4 \quad (10)$$

where M_C is the mass of crude caffeine.

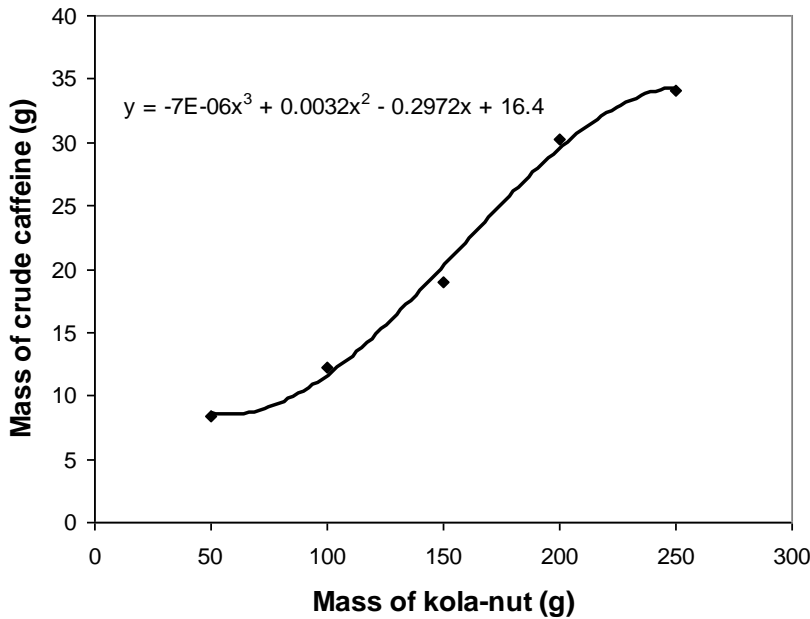


Figure 4. Plot of mass of crude caffeine against mass of kola-nut

Model 2. Prediction of volume of flavour-charged water for a known mass of kola-nut

Plotting volume of Flavour-Charged Water against mass of Kola-nut gives the graph shown in Figure 5. As may be seen from Figure 5, the equation representing the relationship between volume of Flavour-charged water and mass of Kola-nut is obtained as

$$V_f = 0.02 M_k \quad (11)$$

which can be used to estimate the volume of Flavour-Charged Water that may be used to extract the quantity of crude Caffeine predicted by eq. (10) from a known mass of Kola-nut.

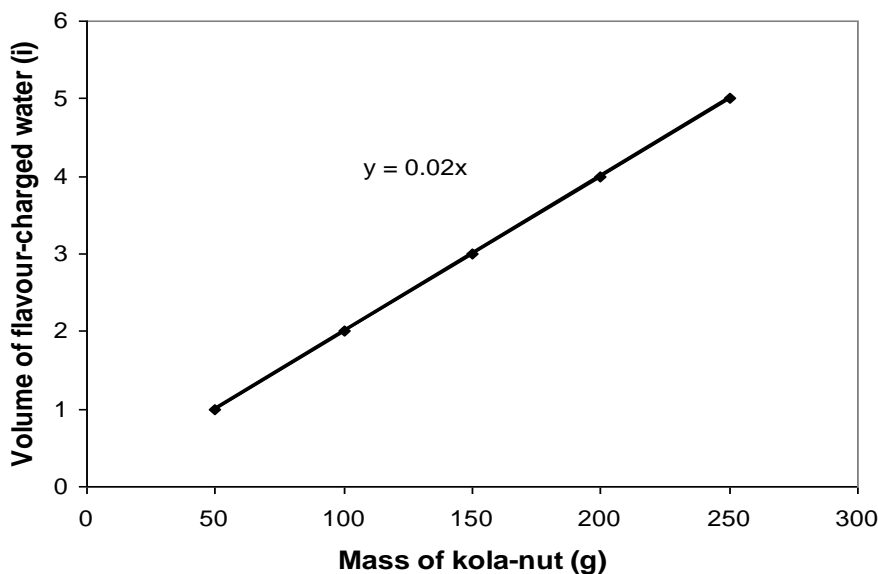


Figure 5. Plot of volume of flavour-charged water against mass of kola-nut

Table 3. Comparison between Models Predictions and Experimental Data

Mass of kola-nut (g)	Mass of crude caffeine (g)		Volume of flavour-charged water (litre)	
	Experiment	Model 1	Experiment	Model 2
50	8.4	8.67	1.0	1.0
100	12.3	11.68	2.0	2.0
150	19.0	20.20	3.0	3.0
200	30.2	28.96	4.0	4.0
250	34.1	32.72	5.0	5.0

Table 3, shows the comparison between experimental data and prediction of Models 1 and 2. It may be seen from Table 3 that predictions of the models compare reasonably well with the experimental data.

Conclusion

Three sorption isotherms (Linear, Freundlich, and Langmuir) have been fitted to experimental data on extraction of crude Caffeine from native Kola-nut using Flavour-Charged Water based on the Swiss Water Process. It has shown that all the three sorption isotherms can be used to describe the extraction process. The Freundlich isotherm gave a maximum error of 2.65 % at only one data-point.

References

- Freundlich isotherm (2019). Freundlich Equation – wikipedia, the free encyclopedia; http://en.wikipedia.org/wiki/freundlich_equation., 20, October 10, 2019
- Inyang, H. I., Daniels, J. I. & Chien, C. C. (2000). Methods of analysis of contaminant migration in barrier materials: In L. Wise, D. J. Trantolo, E. J. Cichon, H. I. Inyang and U. Stottmeister, *Remediation Engineering of Contaminated Soils*, Marcel Dekker Inc., New York, 632-635

- Krupka, K. M., Kaplan, D. L., Whelan, G., Serne, R. J. & Mattigod, S. V. (1999). Understanding variation in partition coefficient, K_d values, *United States of America Environmental Protection Agency Manual*, 1, 2-36.
- Langmuir isotherm (2019). Langmuir equation – wikipedia, the free encyclopaedia; http://en.wikipedia.org/wiki/langmuir_equ., 20, October 10, 2019.
- Linear isotherm (2019). http://wwwbr.cr.usgs.gov/projects/GW_unsat/vs2di/hlp/solute/linearisotherm.html, 20, October 10, 2019.
- Reeling, J. (1999). Therapeutic of Kola Nut. *Journal of the American Medical Association*. 5, 6-10.
- Sheppard, S. C., Sheppard, M. I. & Evenden, W. G. (1990). A novel method used to examine variation in TC sorption among 34 soils, aerated and anoxic. *Journal of Environmental Radioactivity*, 11, 215.
- Song, L., Johnson, P. R. & Elimelechi, M. (1994). Kinetics of colloid deposition onto heterogeneously charged surfaces in porous media, *Environmental Science and Technology*, 28, 1165-1166.
- Wu, S. C. & Gschwend, P. M. (1986). Sorption kinetics of hydrophobic organic compounds to natural sediments and soils, *Environmental Science and Engineering*, 20, 717-718.