Nonlinear Kinetic and Equilibrium Adsorption Isotherm Study of Cadmium (II) Sorption by *Dacryodes edulis* Biomass

*L. C. Overah

Department of Chemistry, Faculty of science, Delta State University, Abraka, Nigeria
[*Corresponding Author: E-mail: overahrubyisaac@yahoo.com; ☎ : +2348166185591]

ABSTRACT
The kinetics and equilibrium adsorption isotherm of cadmium (II) adsorption onto *Dacryodes edulis* (native peer seed) biomass was studied using a nonlinear approach, which is unpopular but proven in some literature to be more reliable and easier. In optimizing the process, about 98% removal of the cadmium ion was achieved within five minutes at pH 7 by contacting just 30 mg of the *Dacryodes edulis* seed biomass with the adsorbate solution of a concentration of 100 mg/L. Non-linear investigation of the kinetics and adsorption isotherms of the process was done using the R console statistical and computing software. The results indicated that the Elovich mechanism and the Freundlich adsorption isotherm most suitably described the kinetics and adsorption isotherm, respectively, of the process as provided by their least values of the sum of squared residuals (SSR). This outcome implied a chemical adsorption (chemisorption) mechanism and a multi-layer coverage by the cadmium ions on heterogeneous active sites of the biomass surface with a Freundlich constant or capacity factor, K_f of 27.83 mg g-1, heterogeneity factor, $1/n$ of 0.2614 and Elovich constants, α and β of 7.0 mg g^{-1} s^{-1} and 1.0 g mg-1, respectively. These findings indicate that *Dacryodes edulis* seed biomass has a good potential for cadmium (II) adsorption.
Keywords: *Dacryodes edulis,* Elovich kinetic model, Freundlich isotherm, Langmuir isotherm, Nonlinear.

INTRODUCTION
Heavy metals in water result mainly from rapid industrialization and technology advancement and is a global environmental palaver demanding quick and careful attention because of their toxicity and bioaccumulation ability. The metals of most concern are cadmium, uranium, chromium, mercury, zinc, selenium, lead, gold, copper, silver, arsenic and nickel. These metals may emanate from the disposal of sludge, ore refining, radioactive materials processing, fly ashes produced from incinerators, metal plating and the production of things like electrical equipment, alloys, paints, batteries, preservatives and pesticides. In the past decades, the methods commonly used to remove or reduce the levels of these metal ions in aqueous systems are namely: coagulation, chemical precipitation, ion exchange, solvent extraction and reverse osmosis (Rich and Cherry, 1987). However, these conventional methods have their various setbacks such as much time consumption, high energy and reagent requirement, high cost and generation of secondary wastes, which require even more careful treatment and disposal. This has necessitated the search for cheaper and eco-friendly methods for treatment of aqueous solutions and effluents containing these metals. Biosorption is this alternative method which is based on the capacities of different materials of biological origin (including microorganisms like fungi, algae and bacteria) to bind metal ions (Volesky, 1990). Apart from its cheapness, greater efficiency and minimization of the issue of secondary pollution, biosorption has a special advantage of regeneration of biosorbent, which makes it possible to recover the metal and reuse the biosorbent for more adsorption cycles (Volesky, 1999).

Two phases exist in the biosorption process; a liquid phase usually the adsorbate solution bearing the metal ions and a solid phase which is the biosorbent material. The affinity of the adsorbent for the adsorbate causes attraction and bonding of the adsorbate to the adsorbent by one of the various mechanisms such as ion

exchange, micro precipitation, complexation or chelation. The binding process proceeds until equilibrium is attained between the amounts of the sorbate bound on the adsorbent and that remaining in the solution. Thus, the sorbate ions are distributed between both phases and the extent of distribution is dependent on the degree of the adsorbent's affinity for the adsorbate.

Recently, biosorption experiments have been carried out using agricultural materials, which are waste products or by-products from large-scale agricultural processes. For instance, activated sludge from the treatment of sewage (Hammaini *et al.,* 2007), the waste Mycelia from the fermentation process, biosolids (Sarioglu *et al.,* 2009), solid residues from olive mills (Pagnanelli *et al.,* 2001), and aquatic macrophytes (Keskinkan *et al.,* 2004). The adsorption characteristics of copper, zinc and lead on a submerged aquatic plant, *Myriophyllum spicatum,* was studied by Keskinkan *et al.* (2004). The adsorption capacities were 46.69 mg/g for lead, 15.59 mg/g for zinc and 10.37 mg/g for copper. Eyenubo and Overah (2018) studied cadmium adsorption of *Musa paradisiaca* stalk and obtained an adsorption capacity of 960 mg/g. Also, the performance of *Calotropis procera* leaf biomass was evaluated for cadmium adsorption by Babalola *et al.* (2011), and approximately 9.00 mg/g was obtained as the maximum adsorption capacity. In this study, the capacity of *Dacryodes edulis* biomass prepared from native pear seed for cadmium (II) adsorption from aqueous solution was investigated. Besides, the kinetics and equilibrium isotherms were investigated through the application of some established models to elucidate the mechanism by which the process takes place.

These models are represented by nonlinear equations, which are usually linearized and plotted accordingly to obtain a correlation coefficient that determines the fitness of the data to the model. The necessary parameters are calculated from the intercepts and slopes of such plots. However, nonlinear regression has been proved a better alternative to linear regression because it provides the most flexible functionality for curve-fitting (Ogee *et al.,* 2013). Besides, the linearization of these kinetic and isotherm equations can statistically distort the interpretation of the distributions of an experimental error (Osmari *et al.,* 2013). The implication is that the ordinary least - squares assumptions of a normal distribution of measurement or experimental errors and consistency in error variance are rendered invalid (Allen *et al.* 2003; Parimal *et al.* 2010; Osmari *et al.,* 2013). Furthermore, there are several published studies which have analysed and compared the results of using both nonlinear and linear regressions for elucidating adsorption isotherms, kinetics and thermodynamics and the general conclusion is that the former usually provides better and more accurate results (Kumar and Sivanesan 2005a,b; Parimal *et al.,* 2010 and Bolster and Hornberger, 2007).

Therefore, this work utilizes the nonlinear approach in fitting both the equilibrium and kinetic experimental adsorption data into a routine nonlinear scheme available in the R statistical computing environment. The necessary parameters are automatically generated with the plots and the fitness to a particular model is determined by examining the smallness of the residuals. To the best of our knowledge, the native pear seed has not been used for Cd (II) sorption studies except in our earlier work testing the adsorbent on Pb (II) removal and using a linear approach to study its kinetics and adsorption isotherms (Overah and Odiachi, 2017). It is hoped, therefore, that studying the applicability of *Dacryodes edulis* seed biomass, a low-cost adsorbent which in its season constitutes a great environmental nuisance, will add to the sorption data bank and that the less common nonlinear approach which proves to be a quicker, easier and yet more accurate tool for kinetic and adsorption isotherm modelling becomes a more preferable option for most researchers of similar interest than the usual and common linear approach.

MATERIALS AND METHODS

Sample Collection and Preparation

Dacryodes edulis seeds were collected from parts of Ogwashi-uku and Agbor villages both in Delta State, Nigeria. The seeds were first washed twice with tap water to rid them of sand and dirt and then thoroughly rinsed with de-ionized water. They were thereafter, air-dried for seven days, pulverized and sieved using a 100 µm mesh screen. The homogenized biomass was activated by soaking in 0.1 M HCl for 24 hours after which it was washed and filtered four times to achieve a neutral pH. The biomass was then dried again, re-powdered and stored in an airtight polythene bag.

Preparation of Stock Solution

A 1000 mg/L stock solution of cadmium (II) was prepared by weighing 2.7442 g of cadmium trioxonitrate (V) tetrahydrate ($Cd(NO_3)_2.4H_2O$) and dissolving it in de-ionized water in a large beaker. The solution was quantitatively transferred to a 1-litre standard volume flask and then further diluted to the mark with de-ionized water. The actual concentration which was determined by a Buck scientific Flame Atomic Absorption Spectrometer (FAAS) model 2004 (Germany), was used for calculations involving the serial dilutions.

Adsorption Studies

Adsorption experiments to study the kinetics of the process were carried out in batches under varied contact time from 5 minutes to 1440 minutes with 50 mL of 50 mg/L Cd (II) solution at 28 °C and pH 7 using a biosorbent dose of 30 mg. While the adsorption isotherm studies were performed also by batch experiments contacting 30 mg of the adsorbent with 25 mL Cd (II) solution whose concentration was varied from 10 to 100 mg/L for two hours at 28 °C and pH 7. After contact, the suspension was filtered using Whatman No. 1 filter paper. The residual metal ion content of the filtrates was measured by AAS. The adsorption studies were carried out at pH 7 because the cadmium speciation model showed that the precipitation of Cd (II) ions at this pH was negligible under the given experimental conditions. Moreover, prior studies had shown that the effect of pH on Cd (II) sorption onto *Dacryodes edulis* was virtually insignificant.

Statistical Analysis

All data obtained from the study of the effect of pH, contact time, adsorbent dose and initial Cd (II) ion concentration were analysed by making appropriate plots using the Origin 6.1 software, while the kinetic and equilibrium data analysis were done as described in the following subsections.

Nonlinear Analysis of the Kinetics of the Adsorption Process

To study the mechanism of the Cd (II) ions adsorption onto the adsorbent, four kinetic models were used to test the data from time-dependent studies namely, the pseudo first-order, pseudo second-order, intraparticle diffusion and Elovich kinetic models.

Nonlinear plots of the amount of Cd (II) adsorbed at different time intervals, q_t against time, t for the four kinetic models were made using a routine nonlinear scheme available in the 'R' statistical and computing environment. The "R" console is used to make nonlinear plots of models from which the values of the corresponding parameters are generated ("R" Development Core Team, 2011). Each of the models was assessed by the sum of squared residuals (SSR). The best-suited model was then determined by comparing the values of the SSR of the models. The smaller the value of the SSR, the better the fitness of the model to the experimental data (Hamza *et al.*, 2013). The values of the relevant kinetic parameters were generated automatically at the bottom of the R sheet.

Nonlinear Analysis of the Adsorption Isotherms

Nonlinear plots of the amount of Cd(II) adsorbed at equilibrium, q_e against the residual concentration of Cd (II), C_e for the Langmuir and Freundlich isotherm models were made and the

fit of each model was assessed by the SSR. It is important to model the concentration-dependent data because it provides information that can be used for the comparison of the capacities of different adsorbents under different conditions of operation (Rifaqat & Moonis, 2002).

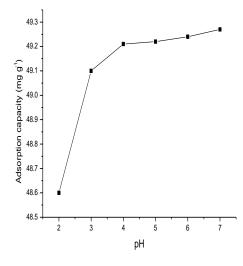The relationship between the cadmium ions concentration taken up by the adsorbent, *qe* and the concentration remaining in the solution, *Ce* at a constant pH and temperature at equilibrium is described by the adsorption isotherms. In this work, the Langmuir and Freundlich isotherms were employed. The relevant parameters to each kinetic and adsorption isotherm (Table 1) were generated automatically by the 'R' software.
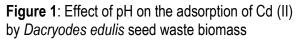
Table 1: Kinetic and adsorption isotherms models, their equations and related parameters.

KINETIC MODEL	EQUATION	PARAMETERS
Pseudo first –order	$q_t = q_e(1 - e^{-K_1 t})$	q_e, k_1
Pseudo second- order	$q_t = \dfrac{k_2 q_e^2 t}{1 + k_{2q_e} t}$	q_e, k_2
Elovich	$q_t = \dfrac{1}{\beta}\ln(\alpha\beta) + \dfrac{1}{\beta} lnt$	α, β
Intra - particle diffusion	$q_t = k_{id}(t)^{1/2} + C$	k_{id}, C
ADSORPTION ISOTHERM	**EQUATION**	**PARAMETERS**
Langmuir	$q_e = \dfrac{q_m\, b\, C_e}{1 + bC_e}$	q_m, b
Freundlich	$q_e = K_f C_e^{1/n}$	K_f, n

RESULT AND DISCUSSION
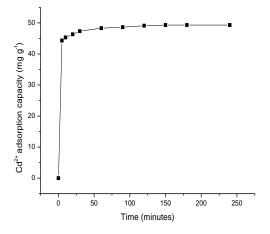
The Effect of pH

The uptake of Cd (II) by *Dacryodes edulis* at varied pH values is illustrated in Figure 1. The uptake of Cd (II) on *Dacryodes edulis* increased initially from 48.60 to 49.08 mg/g when the pH increased from 2 to 4 and only slightly (from 49.08 to 49.535 mg/g) as the pH was further increased from 4 to 7. This indicates that pH plays an insignificant role in Cd (II) uptake on *Dacryodes edulis*. However, previous studies by Eyenubo and Overah (2018) under nearly similar experimental conditions have shown that at pH 8 and above, several insoluble cadmium (II) hydroxide species begin to precipitate. Therefore, throughout the rest of this study, the pH was kept constant at 7 where the Cd (II) removal process is certainly free from the contributions from precipitation of cadmium as hydroxides.

Figure 1: Effect of pH on the adsorption of Cd (II) by *Dacryodes edulis* seed waste biomass

Effect of Contact Time

The adsorption capacity of *Dacryodes edulis* biomass for Cd (II) as a function of time (at pH 7) is displayed in Figure 2. The result shows that the biosorption of Cd (II) onto *Dacryodes edulis* is a rapid process reaching equilibrium at 150 minutes. After this time, there was only a slight increase in the amount of Cd (II) ions uptake up to 240 minutes. This implies a rapid initial rate of Cd (II) ions uptake followed by a slow rate of uptake. The slowing down of the process suggests that the active sites were being saturated with the ions.
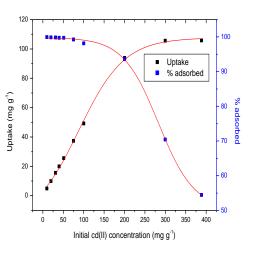

Figure 2: Effect of time on the adsorption capacity of *Dacryodes edulis* seed waste biomass for Cd(II) ions.

However, a very significant amount of Cd (II) ions (approx 45 mg/g) was adsorbed within the first 5 minutes. This probably suggests that there is a strong affinity for the adsorbate by the adsorbent. After this time, there was only an insignificant increase in the amount of adsorbed ions. Therefore, the rest of the experiment was carried out at 5 minutes. Similar results were reported by Eyenubo and Overah (2018) for Cd (II) adsorption onto *Musa paradisiaca* biomass. Cd (II) adsorption onto *Musa paradisiaca* biomass was rapid in the first ten minutes after which further extension of the time yielded an insignificant increase in the amount adsorbed. Hynda and Rachida (2008) also reported initial rapid lead adsorption onto crude and biologically

activated stems of dates. In the first ten minutes, 63.8% lead adsorption by the raw date stems was achieved while 97% was achieved using biologically activated date stems with only a slight and insignificant increase at times beyond ten and five minutes for both raw and activated biomass, respectively.

Effect of Initial Cadmium (II) Concentration

The result of the uptake of Cd (II) onto *Dacryodes edulis* biomass at varied initial metal ion concentrations is shown in Figure 3.
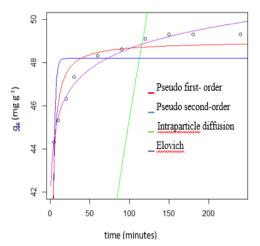

Figure 3: Effect of initial Cd(II) concentration on the uptake of the cd (II) ions onto *Dacryodes edulis* seed waste biomass.

The metal uptake increased from 4.898 to 105.81 mg g^{-1} when the initial Cd (II) concentration was increased from 10 mg/L to 400 mg/L at a constant biomass dosage of 50 mg. This increase may be ascribed to the fact that when the initial Cd (II) concentration is high, there is a strong driving force, which helps to overcome the adsorbate ions' resistance to mass transfer from the aqueous phase to the solid-liquid interface. This implies that the adsorption sites on the adsorbent in the solution with a larger concentration will reach adsorption equilibrium more readily. However, the reverse is the case for percentage adsorbed. When the initial Cd (II) concentration is increased, the percentage adsorbed decreases due to saturation of binding

sites at constant biomass dose. These trends of results have been previously reported (Babalola *et al.,* 2011; Overah, 2011; Hamza *et al.,* 2013). According to their reports, adsorption capacity or uptake increases with increase in initial metal ion concentration but percentage adsorption decreases with increasing initial metal ion concentration. This is in line with the outcome of this study.

Nonlinear Analysis of the Kinetics of Cd (II) Adsorption onto *Dacryodes edulis*

The results of the nonlinear kinetics study of the adsorption of Cd (II) onto *Dacryodes edulis* are shown in Figure 4.

Figure 4: A nonlinear comparison of the four kinetics models for Cd (II) adsorption onto *Dacryodes edulis seed waste* biomass.

It is obvious from Figure 4 that the Elovich model provides a better fit as most of the data points fall on the Elovich curve (purple line). However, more concrete support is provided by the least value of the SSR for the Elovich model compared with those of the other models shown in Table 2. The implication of this is that the process occurs through a chemisorption mechanism.

Nonlinear Analysis of the Adsorption Equilibrium Isotherms

An adsorption isotherm is a mathematical model, which relates the adsorbate concentration left in the liquid phase and adsorbed on the solid phase at constant temperature and pH when both phases are in equilibrium. It is essentially a curve, which explains the retention, release, or mobility of adsorbate species from the aqueous to the solid phases at a constant pH and temperature during an adsorption process. Adsorption equilibrium is the ratio of the amount adsorbed on a surface to that remaining in the solution, while the state of equilibrium is the point at which the adsorbate ions concentrations in the bulk solution and at the liquid-solid interface are in dynamic balance with each other (Somorjai, 1993).
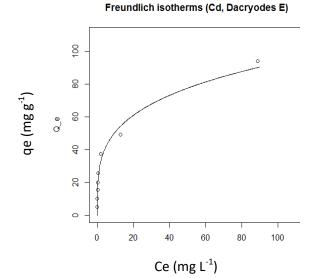
Cd (II) uptake onto *Dacryodes edulis* seed waste biomass at the temperature considered visibly followed both Langmuir and Freundlich Isotherms (Figures 5 & 6). However, the Freundlich isotherm gave a better fit. This is evident by the less value of the SSR as shown in Table 3 and suggests multilayer adsorption of the Cd (II) ions onto heterogeneous binding sites.

The value of the parameter 1/n (the measurement of surface heterogeneity) may be interpreted in a more useful way. When 1/n < 1, the amount of adsorbed material increases less rapidly than the concentration and implies a chemisorption process; and 1/n > 1, indicates cooperative adsorption (Haghseresht and Lu, 1998); and when 1/n = 1, the adsorption equation is equivalent to the distribution law. On the other hand, if 1/n approaches zero (that is becoming more heterogeneous) *qe* equals *Kf*, which amounts to the formation of a monolayer with no further adsorption (Freundlich, 1906; Foo and Hameed, 2010). In this work, 1/n is 0.2614, which further suggests that the process is a chemisorption process.
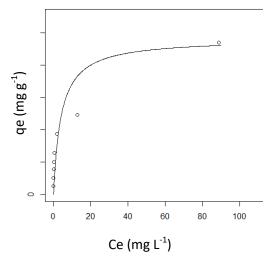
Table 2: Values estimated for the parameters of the four kinetics models tested for Cd (II) adsorption onto *Dacryodes edulis* biomass.

KINETIC/ADSORPTION ISOTHERM	EQUATION	PARAMETERS
Pseudo first-order	$q_e,$	50.00 mg
	k_1	0.2 min^{-1}
	SSR	187.0
Pseudo second-order	$q_e,$	50.00 mg
	k_2	$0.01 \text{ g mg}^{-1} \text{ min}^{-1}$
	SSR	3.957
Elovich	A	$7.00 \text{ mg g}^{-1} \text{ min}^{-1}$
	β	1.00 g mg^{-1}
	SSR	0.7010
Intra-particle diffusion	k_{id}	$1.00 \text{ mg g}^{-1} \text{ min}^{-0.5}$
	SSR	4126.726

Figure 5: Nonlinear Freundlich isotherm plot for Cd(II) adsorption onto *Dacryodes edulis* seed waste biomass**.**

Figure 6: Nonlinear Langmuir isotherm plot for Cd (II) adsorption onto *Dacryodes edulis* seed waste biomass.

Table 3. Langmuir and Freundlich isotherm parameters for the uptake of Cd (II) onto *Dacryodes edulis* biomass.

LANGMUIR			FREUNDLICH			
q_m (mg/g)	K_L	SSR	k_f (mg g^{-1})	n	1/n	SSR
96.26	0.2440	1497	27.83	3.825	0.2614	125.1

Table 4. A comparison of the q_{max} for Cd (II) adsorption onto various adsorbents.

ADSORBENT	q_{max} (mg/g)	PARAMETERS	REFERENCE
Dacryodes edulis	96.26	Particle size: 100 um, Temp: 28 °C, pH: 7, agitation time: 5 minutes Adsorbent dose: 50 mg	This work
Calotropis procera	8.91	Particle size: 150 um, Temp: 27 °C, pH: 5, agitation time: 60 minutes adsorbent dose: 110 mg	Babalola *et al.,* 2011
Ficus carcia	30.31	Particle size: 150 um, Temp: 30 °C, pH: 6, agitation time: 80 minute, adsorbent dose: 500 mg	Farhan *et al.,* 2013
Maize leaf	10.18	Particle size: 5000 um, Temp: 27 °C, pH: 3, agitation time: 120 minutes, adsorbent dose: 500 mg	Babarinde *et al.,* 2007
Scolymus hispanicus L	54.04	Particle size: 100 um, temp: 25 °C, pH: 6.5, agitation time: 60 minutes, adsorbent dose: 2000 mg	Barka *et al.,* 2010
Osmundea pinnatifida	10.02	Particle size: 500 um, temp: 23 °C, pH: 5, agitation time: 60 minutes, adsorbent dose: 20 g/L	Hassouni *et al.,* 2014

Comparison of the Capacity of some Biosorbents for Cd (II) Adsorption

Several adsorbents have been employed and reported for the adsorption of Cd (II) ions from aqueous solution. A comparison of the potentials of some of these adsorbents for Cd (II) ion adsorption using the values of their respective qmax (Table 4) showed that *Dacryodes edulis* has a high potential for Cd (II). The difference in qmax for Cd (II) adsorption onto the various adsorbents may be due to different chemical make-up and surface area of the adsorbents. Besides, different experimental conditions may contribute to the difference in the adsorbent capacity of the various adsorbents for the Cd (II) ion. For example, the *Dacryodes edulis* particle size used in this study was smaller than those reported for the other adsorbents except Ficus carcia as seen in Table 4. Smaller particle sizes lead to greater surface areas and consequently, better adsorption.

CONCLUSION

Dacryodes edulis biomass is found in this work to have good prospects for cadmium (II) ion adsorption from aqueous solution. The process is rapid, Pseudo second-order and follows a chemisorption mechanism. Cadmium (II) adsorption using *Dacryodes edulis*, therefore, promises to be a feasible method for the control of the levels of cadmium ions in effluents and wastewater. It is therefore recommended that further studies be done to evaluate *Dacryodes edulis* for its potential for Cd (II) adsorption from real cadmium containing industrial effluents.

REFERENCES

Allen, S.J., Gan, Q., Matthews, R., & Johnson, P.A. (2003). Comparison of optimised isotherm models for basic dye adsorption by kudzu. *Bioresource Technology,* **88**: 143 - 152.

Babalola J.O, Overah L.C, Babarinde, A, Oninla, V.O., & Olatunde, A. (2011). Kinetic, equilibrium and thermodynamic studies on the biosorption of Cd (II) from aqueous solution by the leaf biomass of *Calotropis procera*. *Journal of Applied Science and Environmental Management,* **15** (4): 607-615.

Babarinde, N.A.A., Babalola, J.O., & Sanni S.O. (2007). Isotherm and thermodynamic studies of the biosorption of Cd (II) from solution by maize leaf. *International Journal of Physical Science,* **2**: 207–211.

Barka, N., Abdennouri, M., Boussaoud, A., & El Makhfouk, M. (2010). Biosorption characteristics of cadmium(II) onto Scolymus hispanicus L. as low-cost natural biosorbent. *Desalination,* **258**: 66–71.

Bolster, C. H., & Hornberger, G. M. (2007). On the use of linearized Langmuir equations. *Soil Science Society of American Journal,* **71**: 1796-1806.

Eyenubo, B. O., & Overah, L. C. (2018). Biosorption studies of cadmium (II) ions from aqueous solution by *Musa paradisiaca* stalk, *MAMBILLA: Journal of Sciences and Environment,* **5**(1): 102 - 109.

Farhan, A. M., Al-Dujaili, A. H., & Awwad, A. M. (2013). Equilibrium and kinetic studies of cadmium (II) and lead(II) ions biosorption onto Ficus carcia leaves. *International Journal of Industrial Chemistry*, **4**:24

Foo, K. Y., Hameed, B. H. (2010). Insights into the modelling of adsorption isotherm systems. *Chemical Engineering Journal,* **156**: 2-10.

Freundlich, H. M. F. (1906). Over the adsorption in solution. *Journal of Physical Chemistry* 57: 385-471.

Haghseresht, F., & Lu, G. (1998). Adsorption characteristics of phenolic compounds onto coal-reject-derived adsorbents. *Energy Fuels,* **12**: 1100-1107.

Hammaini, A., González, F., Ballester, A,. Blázquez, M. L., & Muñoz, J. A. (2007). Biosorption of heavy metals by activated sludge and their desorption characteristics. *Journal of Environmental Management,* **84**: 419-426.

Hamza, I. A. A. Martincigh, B. S., Ngila, J. C., Nyamori, V. O. (2013) Adsorption studies of aqueous Pb (II) onto a sugarcane bagasse/multi-walled carbon nanotube composite. *Physics and Chemistry of the Earth,* **66**: 157–166.

Hassouni, H., El, Abdellaoui, D., Hani, S. E. L, & Bengueddour, R. (2014) Biosorption of cadmium (II) and copper (II) from aqueous solution using red alga (Osmundea pinnatifida) biomass. *Journal of Material Environmental Science,* **5** (4): 967 - 974.

Hynda Y. and Rachida M. (2008). Biosorption of Lead (II) Ions From Aqueous Solutions by Biological Activated Dates Stems. *Journal of Environmental Science and Technology, 1: 201-213.*

Keskinkan, O., Goksu, M. Z., Basibuyuk, M., & Forster, C.F. (2004). Heavy metal adsorption properties of a submerged aquatic plant (Ceratophyllum demersum). *Bioresource Technology,* **92**(2):197-200.

Kumar, K.V., & Sivanesan, S, (2005a). Comparison of Linear and non-Linear Methods in Estimating the Sorption Isotherm parameters for Safranin onto Activated Carbon (Short Communication): *Journal of Hazardous Materials,* **B123**: 288-292.

Kumar K.V. and Sivanesan S, (2005b). Prediction of optimum sorption isotherm: comparison of linear and non-linear method. *Journal of Hazardous Materials.* B126: 198–201.

Ogee A., Ellis M., Scibilia B. and Cheryl P. (2013). Adventures in statistics: Curve fitting

with linear and nonlinear regression:https://blog.minitab.com/blog/adventures-in-statistics-2/curve-fitting-with-linear-and-nonlinear regression.

Osmari, T. A., Gallon, R., Schwaab, M., Elisa B., Joao, B. S. and Pinto, J.C. (2013). Statistical Analysis of Linear and Non-linear Regression for the Estimation of Adsorption Isotherm Parameters. *Adsorption Science & Technology,* **31**(5): 433 - 458.

Overah L.C. (2011). Biosorption of Cr (III) from aqueous solution by the leaf biomass of *Calotropis procera. Journal of Applied Science and Environmental Management*, **15**(1) 87- 95.

Overah L.C., & Odiachi, J. I. (2017). Evaluation of *Dacryodes edulis* (native pear)seed for Pb (II) sorption from aqueous solution. *Journal of Applied Science and Environmental Management,* **21** (1): 186 - 199.

Pagnanelli, F., Trifoni, M., Beolchini, F., Esposito, A., Toro, L., & Veglio, F. (2001). Equilibrium biosorption studies on single and multi-metal systems. *Process Biochemistry,* **37**:115-124.

Parimal, S., Prasad, M. and Bhaskar, U. (2010). Prediction of equilibrium sorption isotherm: Comparison of linear and non-linear methods *Industrial Engineering and Chemical Research,* **49**: 2882 - 2888.

Rifaqat, A. R. and Moonis A. K. (2002). Biosorption of bivalent metal ions from aqueous solution by agricultural waste: kinetics, thermodynamic and environmental effects. *Separation and Purification Technology.* 57(2):394-402.

R Development Core Team. (2011). R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria. ISBN 3-900051-07-0.

Rich, G., and Cherry, K (1987). Hazardous waste treatment technologies, Pudvan publishers, New York.

Sarioglu, M. U., Güler, A. A., & Beyazit, N. (2009). Removal of copper from aqueous solutions using biosolids. *Desalination,* **239**(1-3): 167 – 174

Somorjai, G. A. (1993). Introduction to Surface Chemistry and Catalysis, *John Wiley & Sons, Inc.,* New York 177-217.

Volesky, B. (1990). Biosorption of heavy metals in: Biosorbents and biosorption of heavy metals, Ed. B. Volesky. Boca Raton, F. L.: CRC Press 221- 238.

Volesky, B. (1999). Biosorption for the next century, Biohydrometallurgy and the Environment Toward the Mining of the 21st Century, Internat. Biohydrometallurgy Symposium Proceedings, 1999, volume B, Ballester, A. & Amils, R. (eds.) Elsevier Sciences, Amsterdam, The Netherlands: 161-170.