

Isothermal and Batch Adsorption Studies of the Use of *Borassus Aethiopium* and *Cocos Nucifera* for Wastewater Treatment

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Abstract

The study was aimed at comparing the adsorption of heavy metal ions (Pb^{2+} and Cd^{2+}) using activated carbon from *Borassus aethiopum* (seed shells) and *Cocos nucifera* (shells). *Borassus aethiopum* seed shells (BASS) and *Cocos nucifera* shells (CONS) collected within Zaria and its environs were crushed into particle size of about 300-450 μ m and used as adsorbents for wastewater. The Langmuir and Freundlich isotherm models were used to represent experimental data. Both models were found to fit well based on the high values of the coefficient of regression R^2 . The monolayer adsorption capacity, Q_o for Pb (II) was found to be 12.19 mg/g and 24.39 mg/g and 10.20 mg/g and 25.797 mg/g for Cd (II) for activated BASS and CONS respectively. The suitability of the Pseudo-first and second order kinetic models for the sorption of Pb^{2+}/Cd^{2+} onto activated BASS/CONS was also examined. The Pseudo-second order kinetic model provided best correlation and was found to be more statistically significant than the Pseudo-first order kinetic model. In conclusion, it was established that activated CONS had a higher monolayer adsorption capacity for Pb^{2+}/Cd^{2+} than activated BASS.

Introduction

Environmental pollution is becoming a more serious problem, and so the need for activated carbon from low cost and easily available materials (especially agricultural residual materials) for use especially in wastewater treatment is rising. These materials are versatile adsorbent because of their good adsorption properties. Conversely, conventional means used for treatment of wastewater contaminated with heavy metal ions are very expensive and advanced in technology. Thus, the need to source for cheap, economical and locally available alternatives which will suit our local needs and enhance environmental sustainability becomes necessary. Many reports have revealed the development of low cost activated carbon from cheaper and readily available materials (Bailey et.al., 1999 and Oboh et.al., 2009).

Studies on the adsorption of heavy metals by activated carbon from various low-cost materials have been reported in literature. These include; activated carbon prepared from peat, coconut shells coal (Paajanen et.al, 1997); coconut shell (optimization using response surface methodology), (Gratuito et.al., 2007); kaolinite, (Yavuz et.al, 2003); coirpith, (Kadirvelu and Namasivayan, 2003); bambara nut and rice husk, (Ajmal, et.al, 2003); Almond shells, Olive and peach stones (Ferro-Garcia et.al., 1998); hazelnut shell activated carbon (Cimino et.al, 2000; Demirbas 2003; Koby, 2004). Others include modified sugarcane bagasse, (Osvaldo et.al. 2006); chemically treated periwinkle shell (Okuo and Ozioko, 2001); *Arachis hypogea* shell (Gimba and Bahogo, 2004); modified cassava fiber (Oku and Oviawe, 2007) as well as pistachio nut shell (Abe, et.al, 1990), sawdust (Xiongzun et.al, 1986); orange peels (Agbonighale and Ugbesia, 2005)

There are many basic Isotherm models, which include, Langmuir, Freundlich, Crombie-Quilty, and Mcloughin (activated sludge); BET, Nerst, and activated sludge Isotherms (Oke et.al. 2008); Gile's classification Isotherm (Esmaili et.al, 2005; Toth, 1983; Moon et.al., 1989) and several others

Materials and Methods

Materials

To be able to carry out the experiment, Mortar, Pestle, Sieves (British Standard; 150-300 μ m), Muffle furnace (S30 2AU), pH meter (CRISON micro pH 2000), Orbital shaker (Scigenics Biotech Orbitech), weighing balance (Mettler H31), Electric oven, Atomic Absorption Spectrophotometer (Shimadzu AA6800), and Desiccators are required. Other apparatuses used were Test tubes, watch glasses, polythene bags, crucible, measuring cylinders, spatula, conical flask, volumetric flask and plastic containers. Reactions were carried out using Standard methods (APHA, 1995).

Methods

Adsorption Isotherms

Isotherm data are basic requirements for the design of adsorption reactors. Moreover, analysis of adsorption Isotherm is an important thing in environmental pollution control, the key thing is to develop an equation which will accurately represent the result and which can be used for design purposes, (Volesky, 2001 and Aksu, 2002). Langmuir, Freundlich, Temkin and Redlich-Peterson Isotherms are some Isotherms used commonly in engineering. However, for the purpose of the study, emphasis is restricted to the use of Langmuir and Freundlich models.

Langmuir Adsorption Isotherm (Model): The model represents one of the first theoretical treatments of non-linear sorption and suggests that uptake occurs on a homogenous surface by monolayer sorption without interaction between adsorbed molecules. This physically plausible isotherm, which was developed from theoretical consideration based on three assumptions; adsorption cannot proceed beyond monolayer coverage, all surface sites are equivalent and can accommodate at most one adsorbed atom; and the ability of a molecule to adsorb at a given site is independent of the occupation of neighboring sites; at equilibrium there is no net change in surface coverage.

The rate change of concentration due to adsorption should be equal to the rate of concentration due to desorption. As a result, the Langmuir Isotherm is as expressed in equation (1).

$$q_e = \frac{a_l b_l C_e}{1 + a_l C_e} \quad (1)$$

Rearranging equation (1), to give equations (2) and (3), makes the equation linearized, from which values of a_l and b_l can be determined from the slope and intercept respectively of the plot of C_e/q_e versus C_e .

$$\frac{1}{q_e} = \frac{1 + a_l C_e}{a_l b_l C_e} \quad (2)$$

$$\frac{1}{q_e} = \frac{1}{Q_o} + \frac{1}{b Q_o} \times \frac{1}{C_e} \quad (3a)$$

Equation (3a) could also be rewritten as expressed in equation (3b)

$$\frac{C_e}{q_e} = \left[\frac{1}{(b)Q_o} + \frac{1}{Q_o} C_e \right] \quad (3b)$$

Where Q_o and b are Langmuir constants.

q_e , is amount of solute removed or adsorbed at equilibrium.

C_e , is equilibrium concentration of mixture.

Thus, Q_o , b and the squared of the regression coefficient (R^2), are adsorption parameters estimated by Langmuir model, which are used to suggest whether the adsorption of a metal ion can be modeled by Langmuir Isotherm.

It has been well documented that the essential characteristic of the Langmuir Isotherm may be expressed in terms of the dimensionless parameter (R_L). R_L has been defined as Isotherm shape that predicts if an adsorption system is favourable or unfavourable. R_L is considered as a reliable indicator of the adsorption process. Mamdouth et al (2004); Saswati and Ghosh (2005), stated that R_L indicates the Isotherm shape according to the following assumption characteristics:

$R_L > 1$ (is unfavorable); $R_L = 1$ (linear adsorption); $0 < R_L < 1$ (is favorable);

R_L , is as expressed in equation 4

$$R_L = \frac{1}{1 + b_1 C_o} \quad (4)$$

Where, C_o , is the initial concentration of the mixture.

Freundlich Adsorption Isotherm (Model): The Freundlich Isotherm is an empirical relationship which often gives a more satisfactory model of experimental data (Tebutt, 1991 and Oke 2008). The Freundlich model can be applied onto heterogeneous surfaces involving multilayer sorption. It can be expressed as in the equations 5 and 6.

$$K_f C_e^{1/n_f} \quad (5)$$

However, the linearized Freundlich adsorption isotherm can be expressed in the form; $\log_{10} q_e = \log_{10}(K_f) + \frac{1}{n} \log_{10} C_e$ (6)

C_e , and q_e , are equilibrium concentration, and adsorption capacity at equilibrium stage. While K_f and n are Freundlich constants which incorporates all factors affecting the adsorption process (adsorption capacity and intensity). Values of K_f and n can be obtained from the intercept and slope of a plot of adsorption capacity, q_e against equilibrium concentration C_e . Both parameters K_f and 'n' affect the adsorption Isotherm. The larger the K_f and 'n' values, the higher the adsorption capacity. Furthermore the magnitude of the exponent n gives an indication of the favourability of the adsorption process.

Adsorption Kinetics: The Pseudo-first-order and second-order kinetic models were tested at different concentrations in this study to determine which model is in good agreement with experiment q_e (adsorption capacity) value, thus suggesting which model the sorption system follows. The Pseudo-first-order-model can be expressed as in equation 7.

$$\log_e(q_e - q_t) = \log_e(q_e) - \frac{K_1 t}{2.303} \quad (7)$$

Where, q_e , q_t (mg/g) are the mass of the metal ion adsorbed at equilibrium (adsorptive capacity), and mass adsorbed at any time 't', K_1 , (min^{-1}) is the equilibrium constant of the Pseudo-first-order adsorption. The value of K_1 and q_e are determined respectively from the slope and intercept of the plot of $\text{Log}(q_e - q_t)$ versus t . The Pseudo-second-order model, is expressed thus,

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad (8)$$

Where, K_2 ($\text{gmg}^{-1} \text{min}^{-1}$), t , and q_e , are the Pseudo-second-order rate constant, time, and adsorption capacity at equilibrium respectively. The value of the q_e is determined from the plot of t/q_t versus t .

Determination of Level of Performance of Kinetic Models

Three different statistical expressions were used to evaluate the performance of the model. Model estimate values were compared with observed experimental values. These statistical expressions are; Total error (Err^2), Chi squared (χ^2), and Root Mean Square Error (RMSE).

- a. **Total error (Err^2):** Total error (within the context of this work) is the sum of the squares of the error between the obtained adsorption capacity and the expected adsorption capacity (for the kinetic models), which can be interpreted as a measure of variation in value expected left unexplained by the values obtained. The lower the value of total error obtained, the higher the accuracy, validity and good fitness of the method (model).

$$\text{Err}^2 = \sum_{i=1}^n (Y_{\text{obt}} - Y_{\text{exp}})^2 \quad (10)$$

Where n , Y_{obt} , Y_{exp} , are the number of data points, obtained experimental adsorption capacity values, and computed adsorption capacity value respectively (for the kinetic models).

- b. **Chi squared (χ^2):** Chi squared (within the context of this work) is the sum of the squares of the relative errors between the obtained adsorption capacity and the expected adsorption capacity (for kinetic models) and can be interpreted as a measure of variation in the values expected left unexplained by the values obtained. The lower the value of χ^2 , the higher the accuracy, validity and fitness of the model.

$$\chi^2 = \sum_{i=1}^n \left\{ \frac{(Y_{obt} - Y_{exp})^2}{Y_{obs}} \right\}; \tag{11}$$

Where n, Y_{obt} , Y_{exp} , are the number of data points, obtained experimental adsorption capacity values, and computed adsorption capacity value respectively (for the kinetic models)

- c. **Root Mean Square Error (RMSE):** Root Mean Square Error, RMSE, is used as a predictive capability of a model. It is known to be descriptive when the prediction capability among predictors is compared. As in total error, the lower the RMSE value, the higher the accuracy, validity and good fitness of the method (model).

$$RMSE = \frac{1}{n} \sqrt{\sum_{i=1}^n (Y_{obt} - Y_{exp})^2} \tag{12}$$

Where n, Y_{obt} , Y_{exp} , are the number of data points, obtained experimental adsorption capacity values, and computed adsorption capacity value respectively (for the kinetic models)

Results and Discussion

Isothermal Studies

- a. **Langmuir Isotherm:** The experimental data for the uptake of Pb^{2+}/Cd^{2+} by activated BASS/COSS over the studied concentration range of 2.5-20mg/L were processed using the Langmuir adsorption Isotherm model. The adsorption data are conveniently represented by adsorption Isotherms (which correspond to the relationship between the mass of the solute per unit mass of adsorbent q_e and the solute concentration for the solution at equilibrium C_e) according to Figs. 1 to 4.

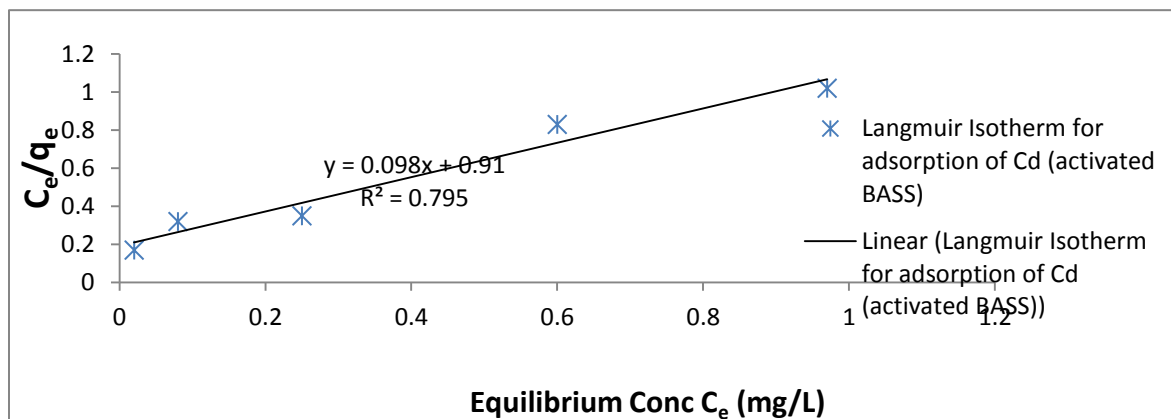


Fig. 1: Langmuir Isotherm for adsorption of Pb^{2+} using activated BASS

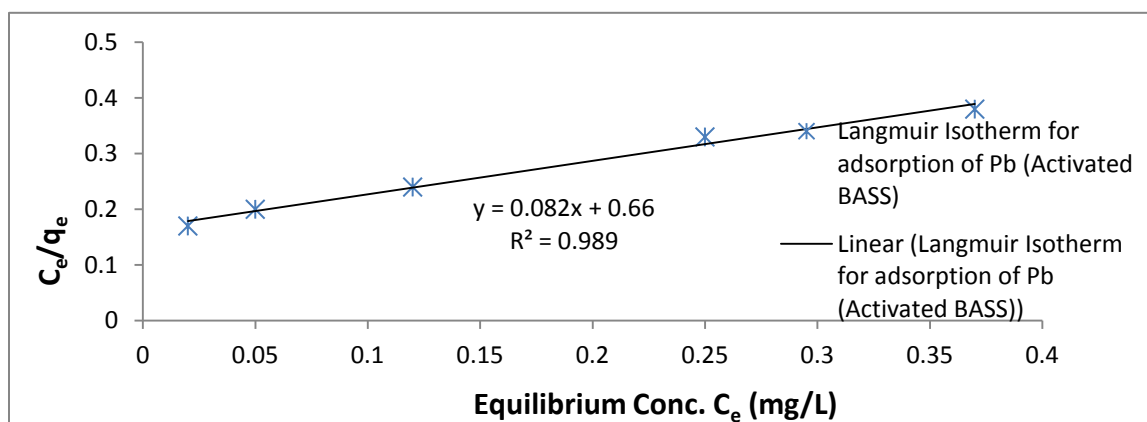


Fig 2: Langmuir Isotherm for adsorption of Cd^{2+} using activated BASS

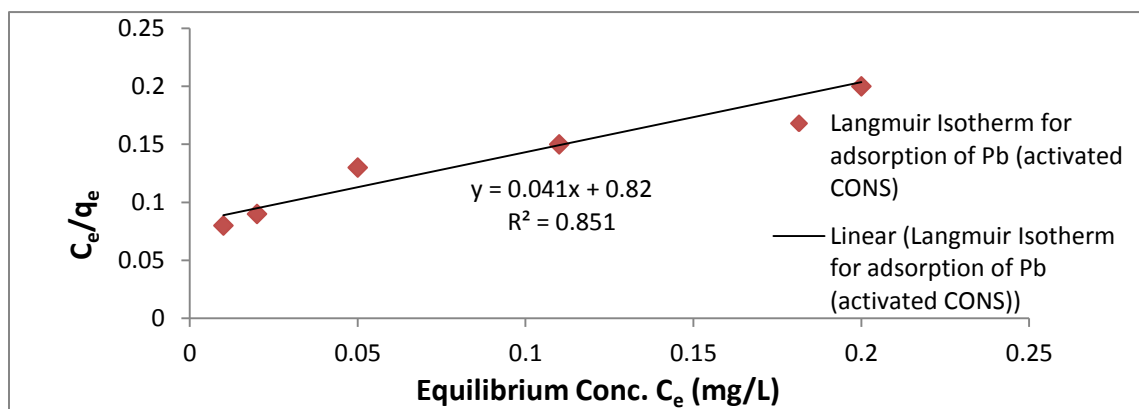


Fig 3: Langmuir Isotherm for Adsorption of Pb²⁺ using Activated CONS

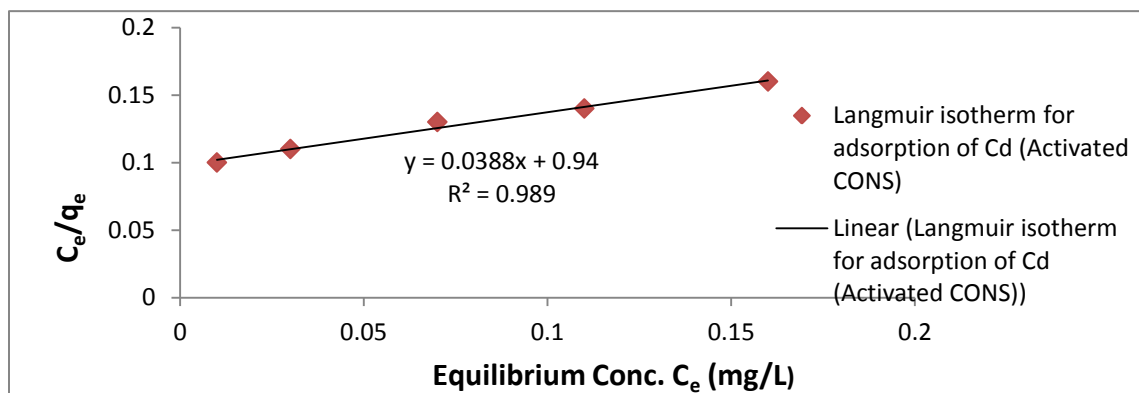


Fig 4: Langmuir Isotherm for Adsorption of Cd²⁺ using Activated CONS

The equilibrium data for Cd²⁺ and Pb²⁺ adsorption on activated BASS/CONS fitted to Langmuir equation (equation 2.3b) as applied to equilibrium adsorption assuming monolayer adsorption onto surface with a finite number of identical sites. Linear plots of C_e/q_e vs. C_e (Figs 1- 4) were employed to determine the values of Langmuir constants Q_o (mg/g) and b (L/mg) from the slope and intercept of the plots respectively. The values obtained and the correlation coefficients are listed in Table 1.

Table 1: Langmuir Isotherm Parameters and Coefficient of Regression (R²) for Pb²⁺

Parameter	Activated BASS		Activated CONS	
	Pb ²⁺	Cd ²⁺	Pb ²⁺	Cd ²⁺
Q _o (mg/g)	12.19	10.20	24.39	25.77
b (L/mg)	0.12	0.11	0.081	0.041
R ²	0.989	0.795	0.851	0.989

From Table 1 it was observed that activated CONS had a higher value for Q_o (mg/g) than activated BASS for both metal ions. Whereas activated BASS had a higher value for b (L/mg), (related to energy/rate of adsorption) than activated CONS for both metal ions. However, the Isotherm parameters together with the correlation coefficients (R²) of the Langmuir equation for the adsorption of Cd²⁺ and Pb²⁺ on both adsorbents shows that the Langmuir equation gives a good fit to the adsorption Isotherm.

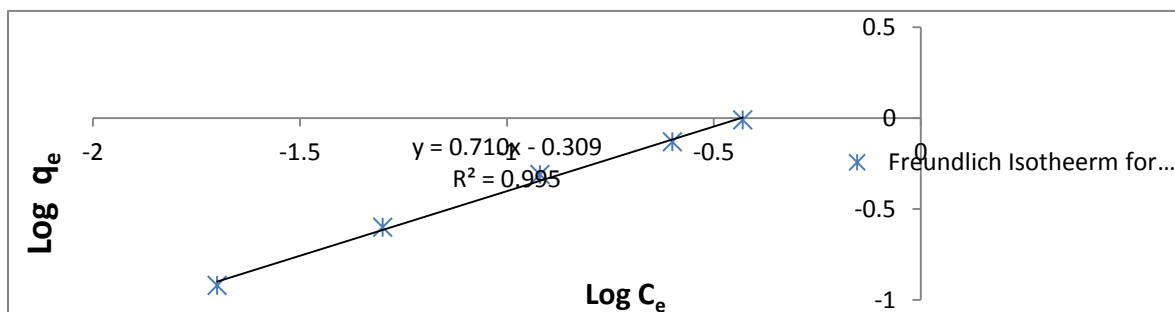
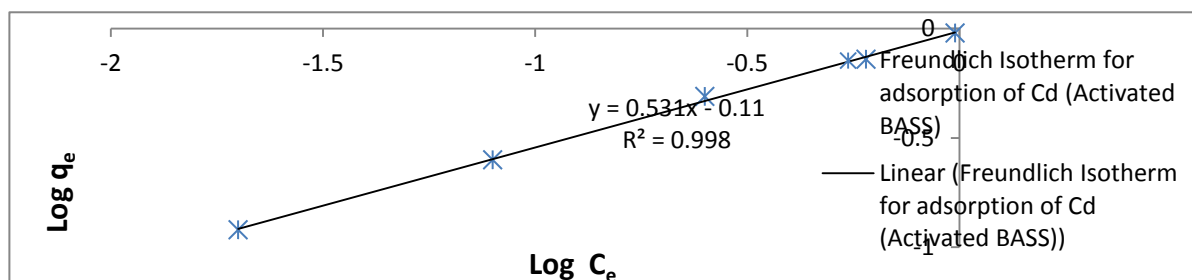
Furthermore, Weber & Chakraborti (1975), Mamdouth et.al, (2004) and Saswati & Gosh (2005), expressed the essential characteristics and feasibility of the Langmuir Isotherm in terms of a dimensionless constant separation factor or equilibrium parameter R_L , as defined in equation (2.4). Table 2 represents separation factor (R_L) values obtained activated BASS and CONS for different initial concentration of Pb²⁺/Cd²⁺.

Table 2: Separation Factor (R_L) of Activated BASS/CONS at Different Initial Concentration of

Initial conc.(mg/L)	Activated BASS (R_L)		Activated CONS (R_L)	
	Pb ²⁺	Cd ²⁺	Pb ²⁺	Cd ²⁺
2.50	0.77	0.81	0.83	0.90
5.00	0.63	0.65	0.71	0.82
10.00	0.45	0.48	0.55	0.70
15.00	0.36	0.38	0.45	0.61
20.00	0.29	0.31	0.35	0.54

According to McKay, et al (1982), Mamdouth et.al., (2004) Saswati and Gosh,(2005), R_L values between 0 and 1 indicate favourable adsorption. From Table 2, separation factor R_L of activated BASS/CONS at different initial concentrations of Pb²⁺/Cd²⁺ lie between $0 < R_L < 1$. Thus the data represents a favourable adsorption for both adsorbents.

- a. *Freundlich Isotherm*: The experimental data for the adsorption of Pb²⁺/Cd²⁺ by activated BASS/CONS over the studied concentration rang (2.5-20mg/L) were equally processed in accordance with Freundlich adsorption Isotherm model. The adsorption data are conveniently represented by Freundlich adsorption isotherms as shown in Figs 5- 8.

**Fig 5: Freundlich Isotherm for Adsorption of Pb²⁺ using activated BASS****Fig 6: Freundlich Isotherm for Adsorption of Cd²⁺ using Activated BASS**

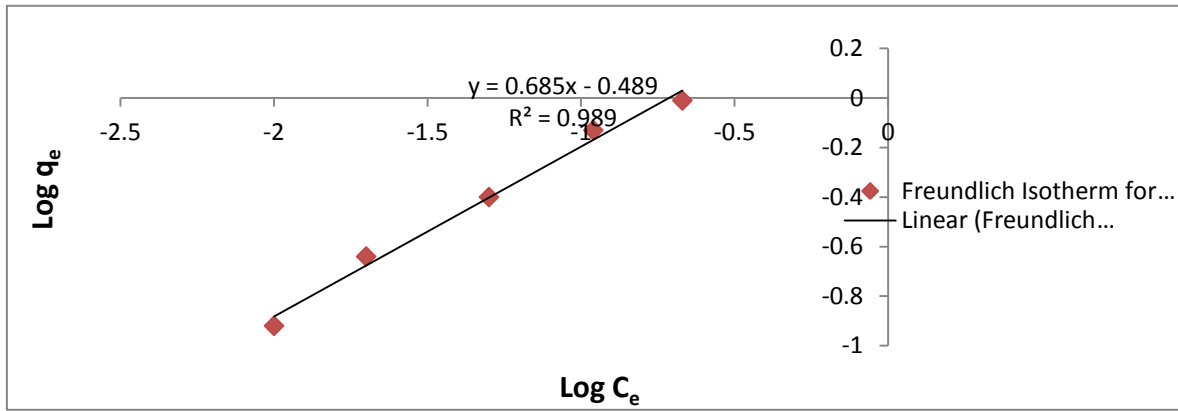


Fig 7: Freundlich Isotherm for Adsorption of Pb²⁺ using Activated CONS

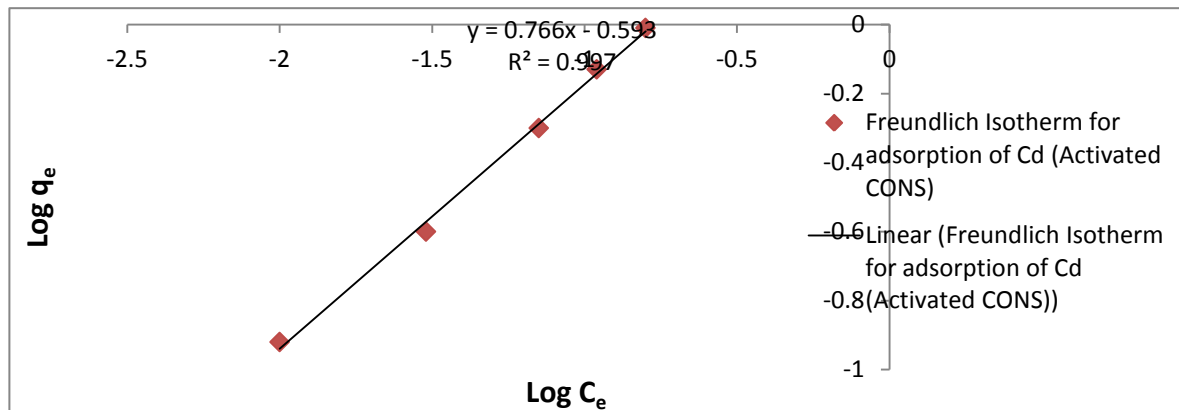


Fig 8: Freundlich Isotherm for Adsorption of Cd²⁺ using Activated CONS

The Freundlich isotherm parameters K_f and n which are constants incorporating all factors affecting the adsorption process; adsorption capacity (K_f) and intensity of adsorption (n) were calculated from the Freundlich Isotherms based on equation (6). Values are listed in Table 3.

Table 3: Freundlich Isotherm Parameters and Coefficient of Regression (R^2) for Lead and Cadmium

Parameter	Activated BASS		Activated CONS	
	Pb ²⁺	Cd ²⁺	Pb ²⁺	Cd ²⁺
K_f (mg/g)	0.49	0.78	0.32	0.26
n (L/mg)	1.41	1.88	1.46	1.31
R^2	0.995	0.998	0.989	0.996

According to Treybal (1980), Zoubolis,et.al, (2002), values of n (which reflects the intensity of adsorption) ranging between 1 and 10; represents favourable adsorption. It was observed in Table 3 that for both adsorbents,(activated BASS and CONS), was within the range of 1 to 10; hence the adsorption process of both metal ions (Pb²⁺/Cd²⁺) using activated BASS/CONS was favourable.

Adsorption Kinetic Studies

The study of the adsorption kinetics describes uptake rate (of adsorbate) and evidently, this rate controls the residence time of the adsorbate uptake at the solid-solution interface including the diffusion process. In this study, the Pseudo-first and second order kinetic models were studied from the plots of time versus percentage (%) removal of the metal ions (Pb^{2+} and Cd^{2+}) for the two adsorbents.

- a. *Pseudo-first-order kinetic model:* The Pseudo-first order model is as expressed in equation (2.7). The values of K_1 and q_e are determined respectively from the slope and intercept of the plot of $\text{Log}(q_e - q_t)$ versus t , as shown in Figs 9 - 12 and the values of K_1 , q_e and correlation coefficients (R^2) are tabulated in Table 4.

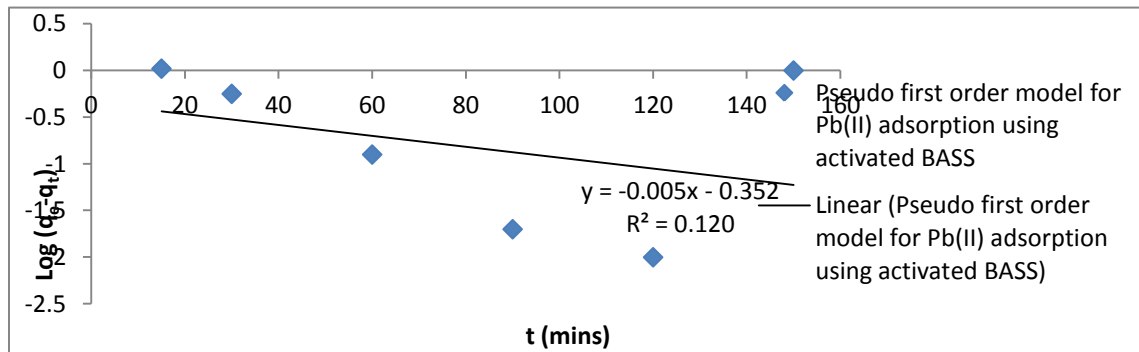


Fig 9: Pseudo-first order model for Pb^{2+} adsorption using activated BASS

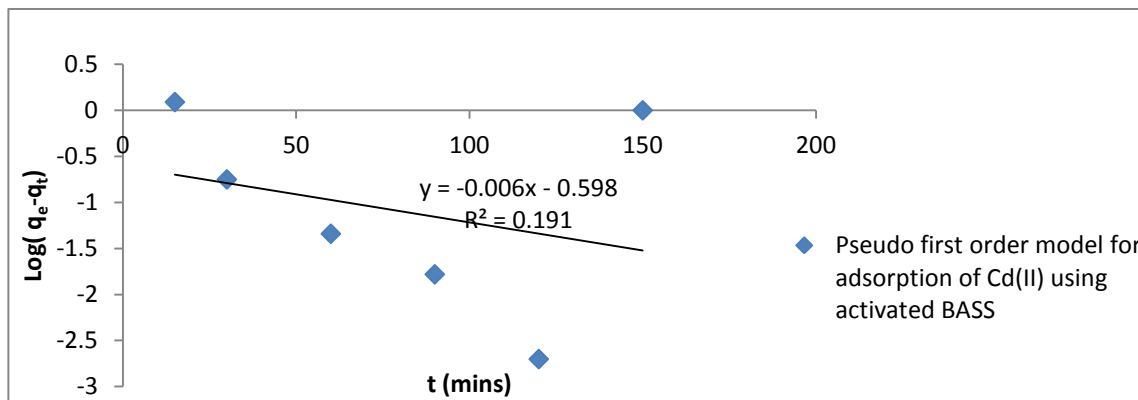


Fig 10: Pseudo-first order model for Cd^{2+} Adsorption using Activated BASS

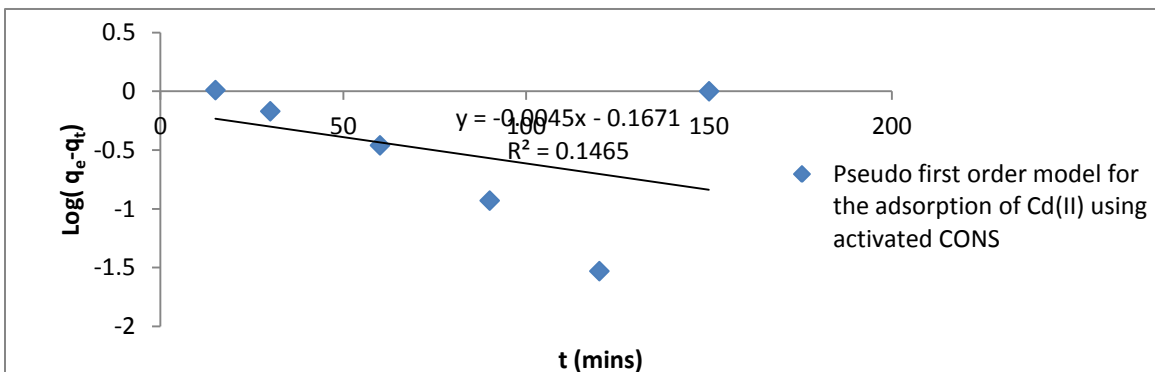


Fig 11: Pseudo-first order model for Cd^{2+} Adsorption using Activated CONS

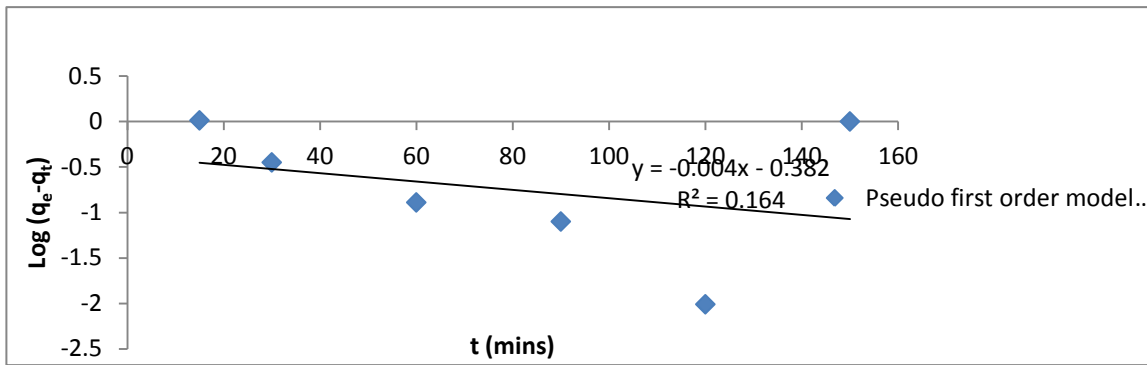


Fig 12: Pseudo-first order model for Pb²⁺ adsorption using Activated CONS

a. *Pseudo-second Order Kinetic Model:* The Pseudo-second order model equation is as expressed in equation (8). The values of K_2 (g/mg/min), and q_e , (mg/g) were determined respectively from the intercept and slope of the plot of t/q_t versus t as shown in Figs 13-16.

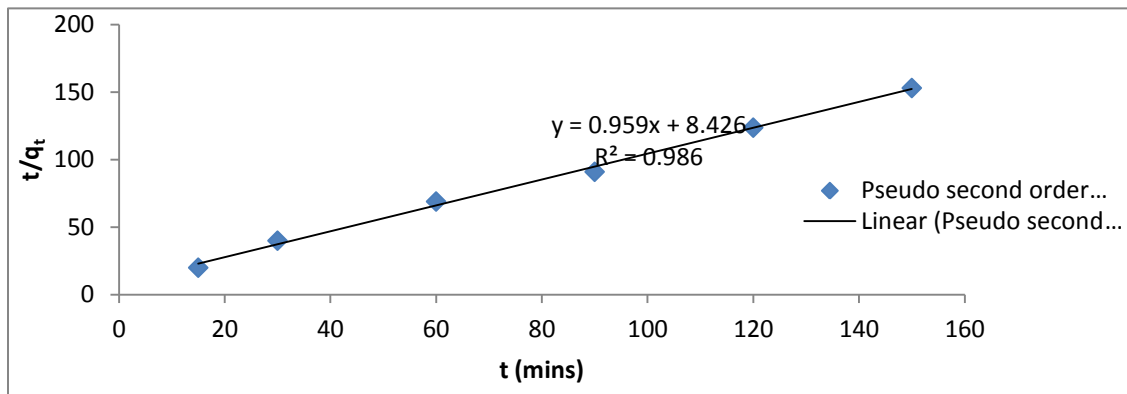


Fig 13: Pseudo-second order model for Pb²⁺ adsorption using activated BASS

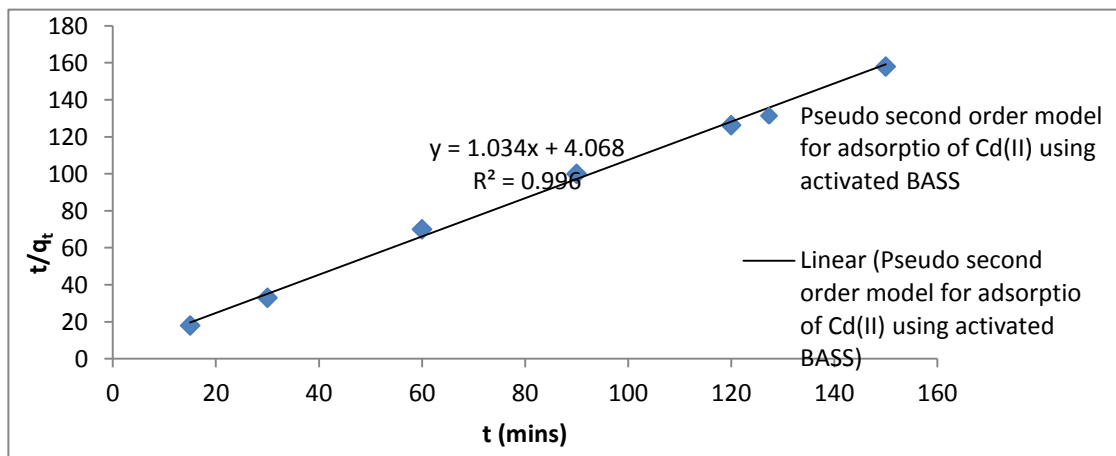


Fig 14: Pseudo-second order model for Cd²⁺ adsorption using activated BASS

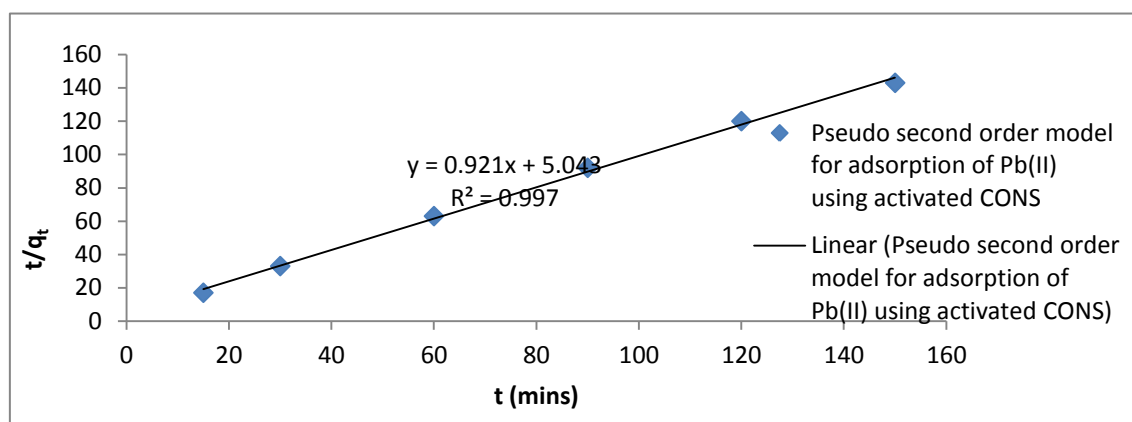


Fig 15: Pseudo-second order model for Pb^{2+} Adsorption using Activated CONS

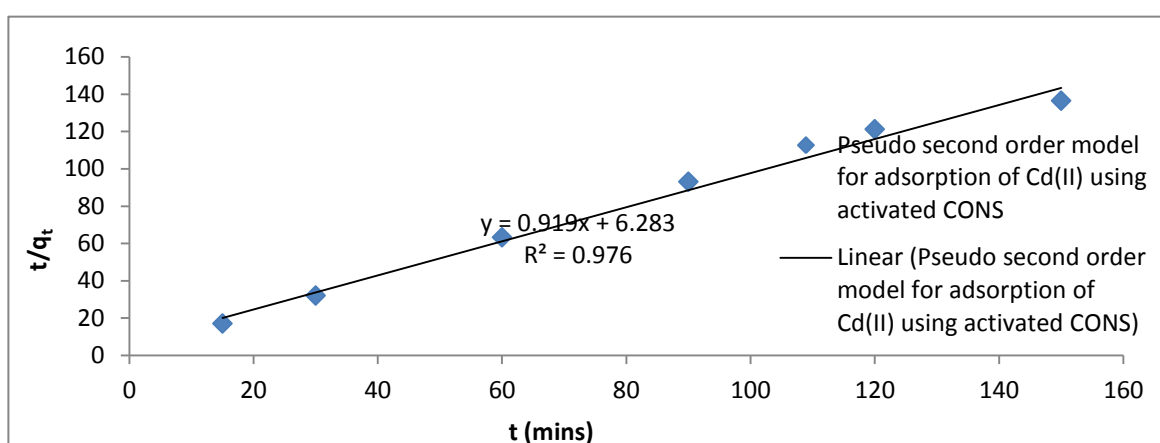


Fig 16: Pseudo-second Order Model for Cd^{2+} Adsorption using Activated CONS

Table 4: Kinetic Parameters for Adsorption of Pb and Cd using Activated BASS/CONS

Reaction order	Activated BASS		Activated CONS	
	Pb (II)	Cd (II)	Pb (II)	Cd (II)
Pseudo-first order				
(parameters)	0.980	0.950	1.050	1.100
q_e , exp (mg/g)	0.011	0.014	0.009	0.009
K_1 , (min^{-1})	0.444	0.252	0.415	0.680
q_e , cal, (mg/g)	0.120	0.191	0.164	0.146
(R^2)				
Pseudo-second order				
(parameters)	0.980	0.950	1.050	1.100
q_e exp (mg/g)	0.109	0.263	0.170	0.134
K_2 ($\text{gmg}^{-1}\text{min}^{-1}$)	1.040	0.967	1.080	1.088
q_e , cal, (mg/g)	0.986	0.996	0.997	0.976
(R^2)				

Where, $q_{e,\text{exp}}$ and $q_{e,\text{cal}}$ (mg/g) are the observed experimental values of the adsorption capacity of the adsorbent from experiment and calculated value of adsorption capacity from the Pseudo-first & second order models (plots) respectively. K_1 , (min^{-1}) and K_2 ($\text{gmg}^{-1}\text{min}^{-1}$) are the Pseudo-first order/Pseudo-second order rate constants. (R^2) is the coefficient of regression for the models.

From Tables 4, it was observed that the calculated value of adsorption capacity from the Pseudo-second order models (plots) $q_{e,\text{cal}}$ (mg/g), are in good agreement with the observed experimental values of the adsorption capacity of both adsorbent from experiment $q_{e,\text{exp}}$ (mg/g) for the adsorption of both metal ions.

This suggests that the sorption system for both metal ions using activated BASS/CONS followed the Pseudo-second order model, whereas the Pseudo-first order model was found not applicable in explaining the adsorption process/mechanism for both adsorbents.

Statistical Evaluation of Adsorption Kinetics for Cd(II) and Pb(II)

Statistical evaluation of the adsorption kinetics of both metal ions (for both adsorbents) were done using some predictive test tools like total error, Chi squared, and Root Mean Square error, as defined in equations 3.10, 3.11, and 3.12 respectively. Values are as tabulated in Tables 5.

Table 5: Statistical Evaluation of Adsorption Kinetics for Pb (II) and Cd (II) using Activated BASS/CONS

Reaction Order	Activated BASS		Activated CONS	
	Pb (II)	Cd (II)	Pb (II)	Cd (II)
Pseudo-first order				
Total error (Err^2)	0.287	0.487	0.403	0.176
Chi squared (χ^2)	0.300	0.513	0.384	0.160
Root Mean Square Error (RMSE)	0.536	0.698	0.635	0.420
Coefficient of regression (R^2)	0.120	0.191	0.164	0.146
Pseudo-second order model				
Total error (Err^2)				
Chi squared (χ^2)				
Root Mean Square Error (RMSE)	4.0Exp-3	3.0Exp-3	1.0Exp-2	1.4Exp-3
Coefficient of regression (R^2)	3.9Exp-2	3.2Exp-4	8.3Exp-4	4.4Exp-3
	0.06	0.017	0.03	0.012
	0.997	0.996	0.996	0.998

From Tables 5, it was observed that the Pseudo-second order model was found to be statistically significant (for kinetic adsorption studies of both metal ions using activated BASS/CONS) based on the higher values of coefficient of regression and lower values of total error, root mean squared error (RMSE), and Chi squared values obtained for the Pseudo-second order model compared to the values obtained for the pseudo-first order model. Generally, the lower the values of Total error, RMSE, and Chi squared, the higher the accuracy, validity and good fitness of the model. Furthermore, the linearity of the plots as depicted by higher values of coefficient of correlation (R^2) for the Pseudo-second order plots suggested its suitability as a model in describing the kinetic adsorption mechanism of the adsorption process. Consequently, the higher the value of coefficient of correlation (R^2), the better the suitability of the model.

Conclusion

This study indicated the suitability of activated BASS/CONS for the removal of Pb(II) and Cd(II) in aqueous solution through batch adsorption studies. The Langmuir and Freundlich isotherm models were used to represent experimental data. Both models fitted well with obtained experimental data based on the high values of the coefficient of correlation R^2 obtained from linear plots (Langmuir Isotherms) for both adsorbents. The monolayer adsorption capacity (Q_0) for Pb (II) was found to be 12.19 mg/g and 24.39 mg/g for activated BASS and CONS respectively. Similarly, Q_0 for Cd (II) was 10.20 mg/g and 25.797 mg/g for activated BASS and CONS respectively.

The Pseudo-second order kinetic model provided best correlation of experimental data for the adsorption of both metal ions (using activated BASS/CONS), whereas the Pseudo-first order model did not fit experimental data well. Also, the Pseudo-second order model was found to be more statistically significant than the Pseudo-first order kinetic model.

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