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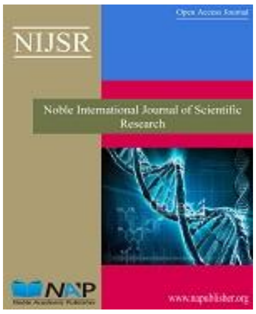

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Comparison of Linear and Non-Linear Methods of Freundlich and Langmuir Isotherm Models for the Adsorption of Lead Using Sugarcane Bagasse

Ibrahim Umar Salihi[a*], Nura Bala[b], Nasiru Danlami[c], A.Y Abdulfatah[d]
[a*,b,c,d]Department of Civil Engineering, Bayero University, Kano, Nigeria

Abstract: Linear least-square method and non-linear method of Freundlich and Langmuir were studied in an experiment for the adsorption of lead onto sugarcane bagasse using different temperatures. Isotherm parameters obtained from non-linear method was the same but differed when using linear least – square method. Highest coefficient of determination was obtained from Langmuir-1 compared other linear equations from Langmuir. Non – linear method of Freundlich model exhibits a higher coefficient of determination compared with linear least – square method.

Keywords: Sugarcane Bagasse, Lead, Isotherm, Temperature.

1. Introduction

In the effort to discover unique adsorbents in obtaining a superb adsorption process, it is very important to determine the best suitable equilibrium adsorption relationship [1]. This is often essential for excellent projection of adsorption variables and also as quantitative assessment of adsorbent performance for various adsorbent processes (and even different experimental situations) [2, 3]. In the standpoint, equilibrium relations, commonly called adsorption isotherms, explain the way contaminants relate with the materials used as an adsorbent. Hence, are crucial for enhancement of the pathways of adsorption mechanism, the assertion of the adsorbents capacities, surface properties, and successful design of the adsorption systems [4, 5].

On the other hand, the method of linear least square is a conventional linearly modified technique adopted widely to identify parameters that defined an isotherm model or the best-suited model, mainly of best fit when subjected to experimental data. The magnitude of the of regression correlation (R^2) defines the model best fit as it approaches unity [6]. However, in recent time considerable constraints associated to the expression of the linearized isotherm form has lately been described, which generate a substantial amount of various results, which absolutely change the error configuration, infringe the error deviation and standard least square normality presumptions, resulting in adsorption data disposition[7, 8].

Based on the way upon which the adsorption equation is linearized, distribution of the error changes to worse. This has confirmed the use of non-linear models in combination with other numerous statistical approaches [9, 10]. Several methods of error analysis, including sum of squared error, the coefficient of determination, the sum of absolute error, the Chi-square, and the average relative error, were used in obatining the best- fitting for isotherm equation. In this study, batch studies data obtained from the adsorption of lead into sugarcane bagasse were used. The data was analyzed using linear least square and non-linear models of Freundlich and Langmuir isotherm and the results were compared.

2. Materials and Method

2.1. Preparation of Adsorbent

Sugarcane bagasse was obtained from a local outlet at Bandar Seri Iskandar, Malaysia. The bagasse was manually cut to an average size of 10 cm and washed with tap water to remove dirt and impurities. It was later washed several times with distilled water to further purify the material. The bagasse was dried in an oven at 105°C for 24 hours until all moisture evaporated and a constant weight was achieved. The dried material was made into fine powder size of about 150 µm. The powdered bagasse was immersed in a weak sulphuric acid (0.5%, pH 4.25) overnight. Finally, it was filtered and dried under room temperature. The dried sample was stored in a desiccator before use.

2.2. Preparation of Stock Solution

A stock solution was prepared by dissolving calculated weight of lead (II) chloride salt in 1L of distilled water to give a concentration of 1000 mg/L. To obtain further required concentrations, the stock solution was diluted appropriately. The chemical employed are of analytical grade, obtained from Merck (Germany).

2.3. Experimental Procedure

Adsorption experiments were carried out using 1.0 g sugarcane bagasse in 100 mL synthetic lead (II) solutions with predetermined metal ion concentrations in a series of 250 mL Erlenmeyer flasks. The flasks were agitated using an orbital water bath shaker (Si-600R Benchtop shaker) at 150 rpm at selected temperatures. At the end of scheduled agitation times, the mixtures were separated using Whatman's glass microfiber filters paper (GF/C). Filtered solutions were analyzed for residual copper (II) concentration using an Atomic Absorption Spectrometer, AAS (Model AA 6800 Shimadzu).

Experiments were conducted to investigate the effect of varying initial lead (II) concentrations and varying temperatures at fixed bagasse dosage and pH. Initial concentrations of lead (II) were varied from 10 – 100 mg/L and temperatures (293 K, 313 K, 333K and 353 K). Initial pH of 6.0 and bagasse dosage of 1.0 g were kept constant. Solution pH was adjusted using either 2.0N Hydrochloric acid or 1.5N Sodium hydroxide.

2.4. Data Analysis

Linear - least square and nonlinear isotherm models of the two most widely used (Freundlich and Langmuir) isotherms are employed in this study. The isotherms in their linear and non-linear forms are presented in Table 1.

Table 1. Linear and non-linear forms of the isotherm models

Isotherm	Non-linear form	Linear form	Plot
Langmuir-1	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$	$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_L q_m}$	C_e/q_e vs C_e
Langmuir-2		$\frac{1}{q_e} = \left(\frac{1}{K_L q_m}\right)\frac{1}{C_e} + \frac{1}{q_m}$	$1/q_e$ vs $1/C_e$
Langmuir-3		$q_e = q_m - \left(\frac{1}{K_L}\right)\frac{q_e}{C_e}$	q_e vs q_e/C_e
Langmuir-4		$\frac{q_e}{C_e} = K_L q_m - K_L q_e$	q_e/C_e vs q_e
Freundlich	$q_e = K_F C_e^{1/n}$	$\log(q_e) = \log(K_F) + \frac{1}{n}\log(c)$	log q_e vs log C_e

The coefficient of determination (r^2) was considered as the target object to test the isotherm that fits best. The coefficient of determination is in the form of equation (1).

$$r^2 = \frac{\sum\left(q_m - \bar{q}_e\right)^2}{\sum\left(q_m - \bar{q}_e\right)^2 + \sum\left(q_m - q_e\right)^2} \quad (1)$$

where, r^2 is the coefficient of determination, $q_{m,}$ is the maximum adsorption capacity acquired from the model (mg/g), q_e is the maximum adsorption capacity acquired from the experiment and $\bar{q}_e$ is the average experimental maximum adsorption capacity.

In the event of non-linear approach, the process of trial and error was used, which is applicable to computer operation. This process was developed to determine the adsorption parameters. Solver add-in with Microsoft spreadsheet, Microsoft excels was employed in the process. The coefficient of determination (r^2) was set as the target objective to maximize its value. Isotherm constants were set as changing variables subject to the constraint that they will never be negative.

3. Results and Discussion

3.1. Linear Regression Approach

Table 2 represents constant values of Langmuir equilibrium constant $K_{L,}$ model uptake capacity $q_{m,}$ Freundlich constant $K_{F,}$ and coefficient of determination r^2, obtained from Freundlich and Langmuir linear least square plots. Langmuir isotherm model indicates a higher value of correlation of determination (r^2) compared with Freundlich isotherm model. The high r^2 value in Langmuir is an indication that the adsorption of lead into sugarcane bagasse is described by the model.

Table 2. Isotherms parameters obtained from linear approach

Langmuir and Freundlich Linear equations				
Isotherm	T (K)	293 K	313 K	333 K
Langmuir-1	q_m (mg/g)	4.8	4.92	5.5
	K_L	0.602	0.996	1.566
	r^2	0.9982	0.9986	0.9976
Langmuir-2	q_m (mg/g)	8.09	1.25	2.34
	K_L	4.10	4.66	5.10
	r^2	0.9883	0.9798	0.9896
Langmuir-3	q_m (mg/g)	2.16	3.26	2.46
	K_L	0.22	0.213	0.197
	r^2	0.9639	0.9894	0.987
Langmuir-4	q_m (mg/g)	6.53	3.8	2.23
	K_L	1.43	0.81	0.43
	r^2	0.9735	0.9849	0.9869
Freundlich	$1/n$	0.4559	0.4039	0.3845
	K_F	1.35	1.0	1.32
	r^2	0.9885	0.9865	0.9862

Analysis of adsorption data with dissimilar linear methods of Langmuir models has considerably affected the values of Langmuir constant parameters. The outcomes of isotherm constants and adsorption capacity obtained from the linear plots of Langmuir differed among themselves. Based on r^2 value obtained, Langmuir-1 fits better into the experimental data. The same sets of experimental data were used in analyzing the Freundlich isotherm model by plotting log q_e against log C_e. Langmuir-1 was more suitable for the experimental data when compared with Freundlich isotherm model. However, Freundlich isotherm model fitted the experimental data better when compared with langmuir-2, Langmuir-3 and Langmuir-4 linear models, respectively. This suggests that coefficients from linear regression methods cannot be used appropriately to compare best- fitting isotherm. The result obtained is in consistency with the result reported by Ho and McKay [11].

3.2. Non-Linear Approach

Isotherm parameters obtained using the non-linear approach of Freundlich and Langmuir isotherm models are shown in Table 3. The Langmuir isotherm parameters of all the three different temperatures obtained through non-linear approach are the same. However, Langmuir isotherm parameters obtained from non-linear approach differed with linear least – square approach. Ho Yuh-Shan suggested that it is not appropriate to compare the best-fit solution of different linear regression isotherms using the coefficient of determination [8].

Table 3. Isotherm parameters obtained from non-linear approach

Langmuir and Freundlich Non-linear equations				
Isotherm	T (K)	293 K	313 K	333 K
Langmuir-1	q_m (mg/g)	4.72	4.98	4.93
	K_L	0.666	0.704	0.721
	r^2	0.9989	0.9989	0.9999
Freundlich	*1/n*	0.2973	0.312	0.3468
	K_F	1.4559	1.4581	1.4556
	r^2	0.9999	0.9999	0.9999

The Freundlich isotherm parameters obtained from the non-linear approach of the various temperatures have yielded the same results. The non-linear approach gave higher r^2 values compared to the linear least-square approach. However, when the two models are compared, Freundlich isotherm model have a high correlation of determination than Langmuir model. All the constant parameters were found to be the same.

4. Conclusion

Adsorption parameters obtained from different linear least square methods of Langmuir isotherm model yield different coefficient values. The coefficient of determination obtained from linear regression analysis cannot be used to equate the best fitting solution of different isotherms. Non –linear method of obtaining isotherm parameters using experimental data is the most suitable approach. Langmuir-1 is more suitable to fit experimental data compared with other Langmuir linear models.

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