Linearized Forms of Langmuir Equations and Its Effect on the Prediction of Biosorption of Cr (VI) On Neem Leaf Powder

Nidhin Sreekumar, K Sundar, Aswathy Udayan

Abstract*: In order to understand the biosorption mechanism of Cr (VI) on to Neem leaf powder (NLP), the experimental data needs to be fitted onto a linearized form of isotherm equations. The Langmuir isotherm has five different linearized equations, and each form is generating a different constant for adsorption equilibrium based on K_L and q_{max}. The effect of linearized forms of Langmuir isotherms (LL) is studied in this work. K_L, q_{max} was calculated using five different linearized forms of Langmuir isotherm and compared. R^2 values of these LL varied drastically between 0.577 to 0.974. From the calculated K_L and q_{max}, q_e was predicted and plotted. When these predicted values and experimental values were compared, LL4 was found to be the best suited linearized form despite not having the highest correlation coefficient. The LL2 and LL4 having highest correlation coefficient showed high overshoot for predicted values over experimental values.

Keywords* : Langmuir, Adsorption; Isotherm; linearized forms; Chromium removal, biosorption.

I. INTRODUCTION

Chromium is an industrially and commercially important heavy metal having two distinct stable oxidation states. Cr (III) is known to be an essential micro-nutrient having many therapeutic effects, but its counterpart Cr (VI) is highly toxic [1]–[3]. The upper limits of Cr (VI) permissible, as per EPA are 0.1 ppm in drinking water [4]. Cr (VI) is reported to inhibit the growth of algae over a 0.03 to 0.4 ppm, but under trace dosages, they stimulate algae growth [5]. Over 1 ppm, they can reduce photosynthesis of *Macrocystis pyrifera* (giant kelp) by 20 to 30 per cent with an exposure of 7 to 9 days. At 5 ppm, 50 per cent of photosynthesis was inhibited within 4 days. At about 1 to 2 ppm, the efficiency of bacteria could be severely affected [6]. After a 6-hour exposure to 1 ppm Cr (IV), insect cells showed inhibition in the cell division process and even chromosome aberrations [7]. Prolonged exposure may result in liver and kidney damage, dermatitis, nerve damage or even death in humans [8]. Short-term effects include stomach and skin irritation and ulceration [9]. Even with the existing strict regulations, many industrial effluents contain chromium at alarming levels and are discharged into open water bodies contaminating whole ecosystems. Cr (VI) is present in effluents of dyes, steels and alloys factories, cooling tower manufacturers, tannery industries, leather manufacturers, electroplating and also wood preservative producing industries [10]. These industries are usually small to medium and will not have access to sophisticated Cr (VI) removal technologies.

A low-cost alternative for chromium removal is adsorption. The biosorption of Cr (VI) is a hot research topic, and the hunt for the ideal biosorbent for Cr is on the rise [11]–[14]. Understanding the mechanism of biosorption is a critical step in the search for biosorbents, particularly the interactions between the adsorbate and the adsorbent surface. Adsorption properties and adsorption isotherms (equilibrium data) are established at equilibrium conditions when the amount of Cr being sorbed is equivalent to being desorbed, and as a result, the solution concentration remains constant. To compare different biosorbents, it is imperative to have a reliable isotherm form. The most common isotherm in use is the Langmuir isotherm, due to its strong theoretical basis. It has been established successfully to fit many biosorbents for the removal of heavy metals as well as dyes and other pollutants [15], [16].

Langmuir isotherm equation is derived as a nonlinear equation and solving requires the use of complex non-linear regression methods. In order to simplify the calculations, researchers often use Langmuir isotherm equation in its linearized forms (LL). However, depending on the approach of the linearization, the error distribution varies drastically [17].

In the presented work, various linearized forms of Langmuir equation has been used to calculate the parameters for isotherm and also to estimate the best-linearized form based on biosorption of Cr (VI) from aqueous solution onto neem leaf powder (NLP).

II. MATERIALS AND METHODS

A. Experimental setup

Synthetic chromium solution was prepared by dissolving 141.4 mg of dried potassium dichromate, ($K_2Cr_2O_7$) analytical reagent grade (SIGMA) in distilled water and made up to 1 litre (50 ppm Cr). Leaf samples of NLP were collected at (9°34'25.9"N, 77°40'24.0"E) and sun-dried for three days.

Revised Manuscript Received on December 05, 2019

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The dried leaves were powdered and sieved to get uniform sizes. Alkali treatment was performed to enhance the adsorption capacity of the biomass with NaOH, one of the strongest base catalysts, the effectiveness of pre-treatment using NaOH is substantiated by a greater degree of enzyme hydrolysis than with any other alkaline pre-treatments [18], [19]. Chromium estimation after biosorption was carried out by di-phenyl carbazide method [20]. Optimum biosorption conditions of pH (6), dosage (2 g/L), mixing (150 rpm) and contact time (30 mins) were adopted from previous works. The experiments were performed in duplicates, and OD values were taken twice for concurrence.

The amount of Cr (VI) adsorbed per adsorbent at equilibrium time (q_e) [21], [22]:

$$q_e = \frac{C_i - C_e}{x} \quad (1)$$

where, C_i and C_e (mg/L) are the concentrations of Cr (VI) in the liquid phase at initial and at equilibrium time, respectively. x is the adsorbent dosage (g/L), (2 g/L).

B. Langmuir isotherm

The mathematical expression of Langmuir isotherm is derived based on the assumption that uniform energy of adsorption for all particles and no transmigration of adsorbate is occurring in the plane of the surface [23], [24]:

$$q_e = \frac{q_{max} K_L C_e}{1 + K_L C_e} \quad (2)$$

where, q_e is the amount of Cr (VI) adsorbed on adsorbent at equilibrium (mg/g); C_e is the concentration of Cr (VI) in the solution at equilibrium (mg/L); q_{max} is a constant related to biosorption capacity, the amount of Cr (VI) adsorbed as a monolayer on adsorbent at equilibrium (mg/g); and K_L is the equilibrium constant related to the affinity of the binding sites and energy of adsorption (L/mg). This non-linear form can be linearized into five different forms, as follows [24].

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \quad form\ 1 \quad (3)$$

$$\frac{1}{q_e} = \frac{1}{q_{max} K_L}\frac{1}{C_e} + \frac{1}{q_{max}} \quad form\ 2 \quad (4)$$

$$q_e = \frac{-q_e}{K_L C_e} + q_{max} \quad form\ 3 \quad (5)$$

$$\frac{q_e}{C_e} = -K_L q_e + K_L q_{max} \quad form\ 4 \quad (6)$$

$$\frac{1}{C_e} = K_L q_{max}\frac{1}{q_e} - K_L \quad form\ 5 \quad (7)$$

In this work, each of these forms is fitted with the experimental data and compared with one another to estimate the best linearized Langmuir form (LL) to be utilized for the biosorption of Cr (VI) on to NLP.

III. RESULTS AND DISCUSSION

The experimental values for the biosorption of Cr (VI) on NLP were fitted with linear isotherm (q_e vs C_e), as in Fig. 1(a). The equilibrium constant for linear isotherm was obtained as 0.0392 L/g, with a correlation coefficient, R^2 = 0.8836. The experimental data are fitted with various forms of linearized Langmuir isotherm models and plotted as in Fig. 1(b-f).

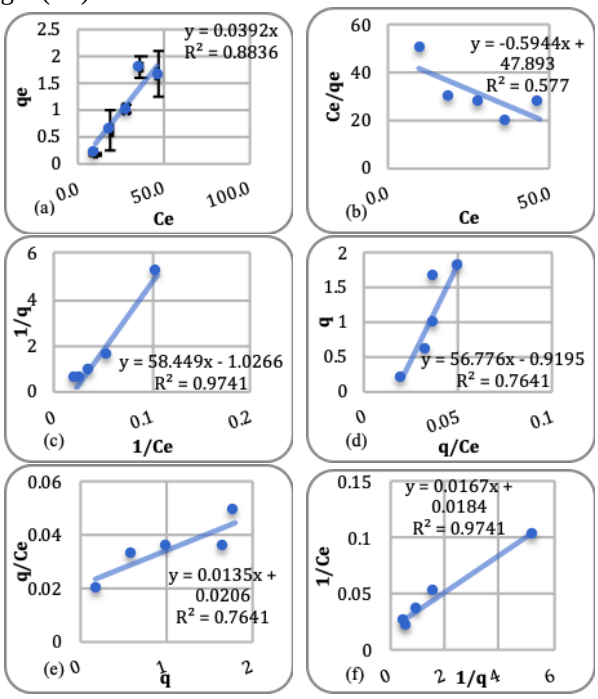

Fig. 1. Linear isotherm (a) and linearized Langmuir isotherm forms 1-5 (b-f)

The values of maximum adsorption capacity, q_{max} and the adsorption equilibrium constant K_L (rate constant) were calculated from the linearized forms of Langmuir isotherms by plotting C_e/q_e versus C_e (Fig. 1b), $1/q_e$ versus $1/C_e$ (Fig. 1c), q_e vs. $-q_e/C_e$ (Fig. 1d), q_e/C_e vs. q_e (Fig. 1e) and $1/C_e$ vs. $1/q_e$ (Fig. 1f) respectively for form 1 to 5 (Equations 3-7). The calculated values of, q_{max}, K_L and coefficient of correlation, R^2 for each of the five forms are given in Table 1.

Table- I: Parameter comparison

	R^2	K_L	q_{max}	**Experimental vs. Predicted**
LL1	0.5770	0.0124	1.6824	Acceptable
LL2	0.9741	0.0176	0.9741	Overshoot
LL3	0.7641	0.0176	0.9195	Overshoot
LL4	0.7641	0.0135	1.5302	**Acceptable**
LL5	0.9741	0.0184	0.9076	Overshoot

It is infered from Table 1 that parameter values vary for each form. The maximum sorption capacity varied from 0.9076 mg/g to 1.6824 mg/g. Similarly, the values of correlation coefficient and equilibrium constant also were varying drastically. From the table, it can also be observed that linearized form 2 and form 5 are having the highest R^2 values;

hence, they may be best suited to represent Cr (VI) sorption on NLP. But it may be noted that form 1 is the most commonly used form for representing biosorption. For a better judgement as to which linearized form is best suited for representing sorption of Cr (VI) on to NLP, the K_L and q_{max} and values obtained from each of the linearized forms were substituted back into the non-linear form of Langmuir isotherm to predict the equilibrium sorption. The plots of experimental and predicted for each of the linearized forms are as in Fig. 2. From Fig. 2, it is observed that linearized form 1 and 4 closely follows the experimental value, whereas the other forms are overshooting. It may also be noted that the LL2 and LL5 produced high correlation coefficient but were producing overshooting predicted values over experimental values, hence deemed not suited for representing biosorption of Cr (VI) onto NLP.

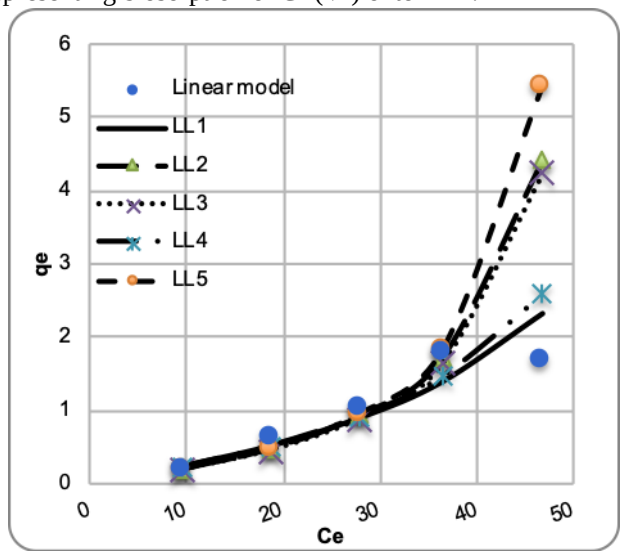

Fig. 2. Comparison of experimental and predicted values from linearized Langmuir forms

From the Table 1, linearized Langmuir form 4 (Equation 6) was best suited to represent biosorption of Cr (VI) onto NLP due to the proximity of predicted and experimental values as well as the high correlation coefficient value. These results also indicate the inadequacy of linearized forms for providing a singular solution. The variation in the error structure upon the linearizing technique of the nonlinear equation is deemed to be the cause of the generation of different outcomes for different linearized forms [25].

IV. CONCLUSION

This study was intended to asess the best suited linearized Langmuir isotherm equation that can precisely explain the experimental results of Cr (VI) biosorption onto neem leaf powder (NLP). The calculated values obtained for q_e and K_L for the different linearised forms of Langmuir isotherm model were found to vary drastically. Further, from the predicted and experimental values derived from each linear expression of Langmuir model, it was inferred that correlation coefficient; R^2 alone could not be used to judge the best suited linearized form of Langmuir equation. Even if high R^2 is produced, the linearized form may predict overshooting values. It was observed that LL form 1 provides reliable evaluates but has a low correlation coefficient. The presented results points out that it is not accurate to use the form 2, 3 and 5 equations for estimating the Langmuir isotherm parameters for the biosorption of Cr (VI) onto NLP. This inadequacy primarily is due to the variations in the error distribution while transforming a nonlinear equation to a linearized form. This inadequacy causes the calculated results to be distorted and yield unsuitable parameters.

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