

Biosorption thermodynamics of cadmium on coconut copra meal as biosorbent

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Abstract

Coconut copra meal, a waste product of coconut oil production was investigated for its potential use as a biosorbent for cadmium ions from an aqueous solution. A comparison of linear least-squares method and a trial and error non-linear method of three widely used isotherms, Langmuir, Freundlich, and Redlich–Peterson, were examined. Langmuir isotherm parameters obtained from the four Langmuir linear equations by using linear method were not similar, but were the same when non-linear method was used. The best-fitting isotherms were Langmuir and Redlich–Peterson isotherms. Langmuir isotherm is a special case of Redlich–Peterson isotherm when constant g is unity. In addition, various thermodynamic parameters, such as ΔG° , ΔH° , and ΔS° , were calculated. The biosorption process is a spontaneous and exothermic process.

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1. Introduction

The presence of heavy metals in both surface and ground water has led to increased environmental concern by both scientists and engineers. One of such heavy metal of concern is cadmium. As a non-essential metal for human consumption, cadmium has an extremely long biological half-life (>20 years) and it is listed by the US-EPA as one of the 126 priority contaminants and as a known carcinogen by the International Agency For Research on Cancer [1]. Cadmium has various applications in a variety of industrial processes and operations and is released through natural processes such as volcanic activities [2]. It directly meets water bodies through the effluent of industries causing a marked increase in its concentration. The major sources of cadmium release into the environment by waste streams are electroplating, smelting, alloy manufacturing, pigments, plastic, battery, mining, and refining processes [3]. The toxic effects of cadmium are well documented. Diseases such as renal damage [4], anemia [5], hypertension [6], and itai-itai [7] are associated with excess cadmium. Therefore their removal

from wastewater before there are discharged into surrounding water bodies is of importance.

A number of agricultural waste and by-products of cellulosic origin such as spent grain [8], and tree ferns [9] has been studied in literature for their capacity to remove cadmium from aqueous solutions. Table 1 shows the results of several studies that have been performed using activated carbon prepared from various agricultural wastes for the removal of cadmium from aqueous solutions.

Coconut copra meal (or pellets) is what remain after oil is extracted from coconut copra. As a result of processing, waste material disposal becomes an issue, especially with the husk and copra meal. Copra meal produced in large amounts has every little application apart from its use as animal feeds due to its high protein and fiber content. To the best of our knowledge, there is no information in literature on the use of coconut copra as a biosorbent.

In this work, the potentials for the use of copra meal as a biosorbent for cadmium ion removal from solution was investigated and the resulting isotherm compared using the linear least-squares method and a trial and error non-linear method of three widely used isotherms, Langmuir, Freundlich, and Redlich–Peterson, were examined.

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2. Materials and methods

Coconut was obtained from the open market in Benin City, Edo State of Nigeria. The fruits were dehusked, split, and sun dried until the meat (endosperm) reaches 5% moisture content. The copra was sliced and crushed in a food processing blender and the oil extracted with hot water. The copra meal was then washed several times with hot water to remove excess oil, sun dried, and sieved to obtain particles of size less than 250 μm . The sieved copra meal was soaked in 0.02 mol/dm³ HCl overnight to dissolve lignin and other plant materials. The acid solution was filtered off, and the copra meal was washed with distilled water until the pH of the wash became neutral. The copra meal was dried at 373 K for 24 h and stored in an air-tight container. The stock solution of cadmium(II) (1000 mg/dm³) was prepared in distilled water using cadmium nitrate salt (BDH); all working solutions were prepared by diluting the stock solution with distilled water.

2.1. Effect of biosorbent dose

The effect of biosorbent dose on the equilibrium uptake of cadmium ions was investigated with biosorbent masses of 0.5, 0.7, 1.0, 1.5, 2.0, 2.5, and 3.0 g. The experiments were performed by adding known weights of copra meal to six 500 ml beakers containing 100 ml of 128 mg/dm³ cadmium solution. The flasks were shaken at 150 rpm and 297 K for 2 h.

2.2. Effect of pH on cadmium biosorption

The effect of solution pH on the equilibrium uptake of cadmium ions was investigated at pH 3, 4, 5, 6, and 7. The experiments were performed by adding a known weight copra meal to five 500 ml beakers containing 100 ml of 128 mg/dm³ cadmium solution and the pH of the solution pH adjusted using 0.1 mol/dm³ HCl or NaOH. The flasks were shaken at 150 rpm and 297 K for 2 h and the amount of cadmium adsorbed determined.

2.3. Isotherm studies

A volume of 100 ml of cadmium solution with concentrations ranging from 10.5–201 mg/dm³ was placed in a 500 ml polypropylene flask. Two grams of the copra meal was then shaken with the cadmium solutions at a constant speed of 150 rpm in a shaker water bath with temperatures of 299, 311,

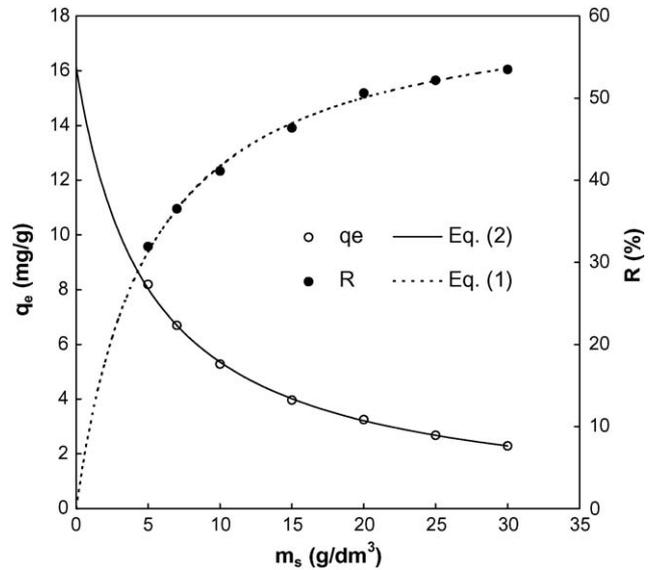


Fig. 1. Effect of biosorbent dose on percentage cadmium removal, R , and biosorption capacity, q_e , from solution.

323, and 333 K, respectively. After shaking the flasks for 2 h, the copra meal was separated by filtration. The filtrate was analyzed for the residual cadmium concentration by atomic absorption spectrophotometer (AAS).

3. Results and discussion

3.1. Composition of copra meal

The percentage proximate composition of copra meal on dry weight basis was: moisture 8.90%, protein 26.7%, crude fibre 10.0%, ash 3.90%, lipid 12.1%, and carbohydrate 38.4%.

3.2. Effect of copra meal dose

The effect of varying the coconut copra meal dose, m_s , is shown in Fig. 1. The percentage of cadmium removed increased with the copra meal dosage. As one expected, for a fixed initial cadmium concentration, the percentage of cadmium removal increased with the increasing amount of copra meal which provides greater surface area and increased number of active sites. The data in Fig. 1 can be used to derive a mathematical relationship (using the boundary conditions $m_s = 5.0$ – 30 g/dm³). The linear relationship, which has a coefficient of determination as high as 1.000 is:

$$R = \frac{m_s}{7.97 \times 10^{-2} + 1.60 \times 10^{-2} m_s} \quad (1)$$

The biosorption capacity curve in Fig. 1 indicates that biosorption capacities decreased from 8.20 to 2.29 mg/g when the copra meal dose was increased from 5.0 to 30 g/dm³. The relationship between biosorption capacity, q_e , and the copra meal dose, m_s , was also found to have an extremely high coef-

Table 1
A number of agricultural by-products available for sorption of cadmium ions

q_m	Material	Reference
2.7 mg/g	Almond-shell carbon	[26]
93.2 mg/g	Carbonized coirpith	[27]
89.4 mg/g	Peanut hull carbon	[28]
53.6 $\mu\text{mol/g}$	Olive stone carbon	[26]
29.1 $\mu\text{mol/g}$	Peach stone carbon	[26]

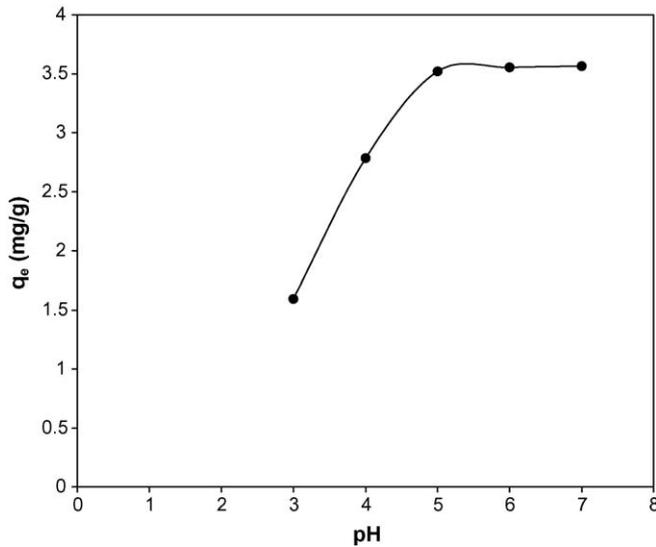


Fig. 2. Effect of pH on cadmium biosorption on copra meal.

coefficient of determination (1.000) and to have the form:

$$q_e = \frac{1}{6.20 \times 10^{-2} + 1.25 \times 10^{-2} m_s} \quad (2)$$

Similar simulation equations were presented for the sorption of copper and nickel ions from aqueous solution by sphagnum moss peat [10,11]. When the dose of the dried copra meal was increased from 20 to 30 g/dm³, the biosorption capacity of copra meal showed less significant difference. Thus, 20 g/dm³ of dried copra meal was chosen for the study on the effect of pH.

3.3. Effect of initial pH on cadmium biosorption

The biosorption capacity was found to be affected by equilibrium pH, although it is not easy to control the equilibrium pH at the end of reaction. The equilibrium pH is influenced by initial pH of the solution therefore the effect of initial pH on cadmium biosorption was employed to discuss the effect of pH. The pH value of the solution is an important controlling parameter in the biosorption process, and the initial pH value of the solution has been shown to have more influence than the final pH [12]. The biosorption capacity of copra meal was low at the initial pH 3, but increased and remained almost constant over the initial pH ranges of 5–7 (Fig. 2). The biosorption capacity of copra meal was not significantly altered when the initial pH was increased from 5 to 7. Therefore, pH value of 6 was chosen for the study on the effect of contact time.

At low pH, copra meal ligands are closely associated with the hydronium ions (H₃O⁺) and the surface of the copra meal becomes positively charged. With an increase in pH, the negative charge density on the copra meal surface increases due to deprotonation of the metal binding sites and thus increase metal biosorption. The initial pH values investigated were lower than 7.0 since insoluble cadmium hydroxide starts precipitating from the solutions at higher pH values, which makes true biosorption studies impossible.

Table 2
Langmuir linear forms

	Linear form	Plot
Langmuir-1	$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_a q_m}$	C_e/q_e vs. C_e
Langmuir-2	$\frac{1}{q_e} = \left(\frac{1}{K_a q_m}\right) \frac{1}{C_e} + \frac{1}{q_m}$	$1/q_e$ vs. $1/C_e$
Langmuir-3	$q_e = q_m - \left(\frac{1}{K_a}\right) \frac{q_e}{C_e}$	q_e vs. q_e/C_e
Langmuir-4	$\frac{q_e}{C_e} = K_a q_m - K_a q_e$	q_e/C_e vs. q_e

3.4. Isotherm studies

3.4.1. Langmuir isotherm [13]

At constant temperature, cadmium ions held onto the copra meal will be in equilibrium with cadmium ions in bulk solution.

The saturated monolayer isotherm can be represented as:

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \quad (3)$$

where C_e is the equilibrium concentration (mg/dm³); q_e the amount of metal ion sorbed (mg/g); q_m is q_e for a complete monolayer (mg/g); K_a is biosorption equilibrium constant (dm³/mg).

The Langmuir isotherm can be linearized into four different forms (Table 2), and simple linear regression will result in different parameter estimates [14,15]. The more popular linear form used are Langmuir-1 and Langmuir-2, and the best fitting is obtained by using Langmuir-1 because of the minimized deviations from the fitted equation resulting in the best error distribution [14].

3.4.2. Freundlich isotherm [16]

The empirical Freundlich isotherm, based on sorption on heterogeneous surface, can be derived assuming a logarithmic decrease in the enthalpy of sorption with the increase in the fraction of occupied sites and is given by:

$$q_e = K_F C_e^{1/n} \quad (4)$$

where K_F and $1/n$ are the Freundlich constants characteristics of the system, indicating the sorption capacity and sorption intensity, respectively. Eq. (4) can be linearized in logarithmic form Eq. (5) and the Freundlich constants can be determined.

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

3.4.3. Redlich–Peterson isotherm [17]

The Redlich–Peterson isotherm contains three parameters and incorporates the features of the Langmuir and the Freundlich isotherms. The Redlich–Peterson isotherm has a linear dependence on concentration in the numerator and an exponential function in the denominator. It can be described as follows:

$$q_e = \frac{A C_e}{1 + B C_e^g} \quad (6)$$

It has three isotherm constants, namely, A , B , and g ($0 < g < 1$), which characterize the isotherm. Its limiting behavior is summarized.

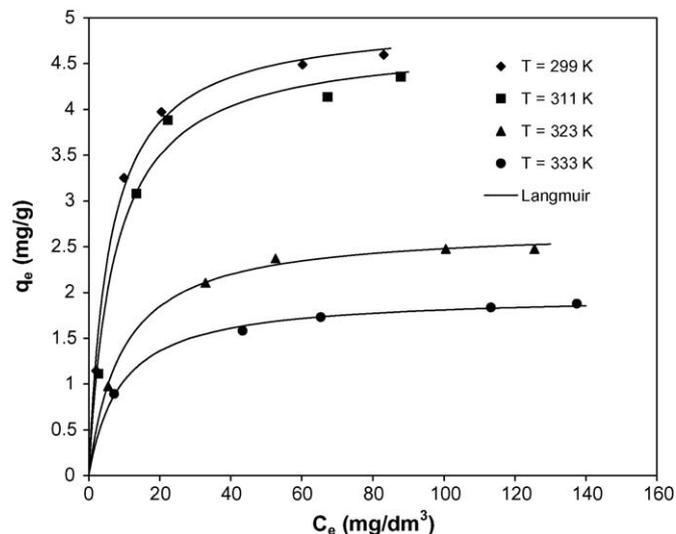


Fig. 3. Langmuir isotherm for the biosorption of cadmium ion on copra meal at different temperature (isotherm parameters are from non-linear method).

Where $g = 1$

$$q_e = \frac{AC_e}{1 + BC_e} \quad (7)$$

i.e. the Langmuir form results.

Where constants A and B are much greater than unity [18]

$$q_e = \frac{AC_e}{1 + BC_e^g} \quad (8)$$

i.e. the Freundlich form results.

Where $g = 0$

$$q_e = \frac{AC_e}{1 + B} \quad (9)$$

i.e. the Henry's Law form results.

Eq. (7) can be converted to a linear form by taking logarithms:

$$\ln\left(\frac{C_e}{q_e} - 1\right) = g \ln(C_e) + \ln(B) \quad (10)$$

Three isotherm constants, A , B , and g can be evaluated from the linear plot represented by Eq. (10) using a trial and error procedure, which is applicable to computer operation was developed to determine the isotherm parameters by optimization routine to maximize the coefficient of determination, r^2 , for a series of values of A for the linear regression of $\ln(C_e)$ on $\ln[A(C_e/q_e) - 1]$ and to obtain the best value of A which yields a maximum 'optimized' value of r^2 using the *solver* add-in with Microsoft's spreadsheet, Microsoft Excel.

The different isotherms were tested for their ability to correlate with the experimental results by comparing theoretical plots of each isotherm with the experimental data for the biosorption of cadmium ions on copra meal at different temperatures in Fig. 3. In this graph, the amount of cadmium sorbed per unit mass of copra meal, q_e , is plotted against the concentration of cadmium remaining in solution, C_e . The coefficients of determination for Freundlich, Redlich–Peterson, and four Langmuir linear isotherms (Table 2) are given in Table 3.

Table 3
Isotherm parameters obtained by using linear method

Isotherm	T (K)			
	299	311	323	333
Langmuir-1				
q_m (mg/g)	4.92	4.68	2.66	2.01
K_a (dm ³ /mg)	0.176	0.141	0.119	0.099
r^2	1.000	0.998	0.999	1.000
ΔG° , kJ/mol	-7.41	-7.15	-6.97	-6.66
Langmuir-2				
q_m (mg/g)	5.31	5.14	2.73	1.95
K_a (dm ³ /mg)	0.134	0.101	0.102	0.118
r^2	0.997	0.996	0.999	0.998
Langmuir-3				
q_m (mg/g)	5.12	4.94	2.72	1.96
K_a (dm ³ /mg)	0.148	0.113	0.103	0.116
r^2	0.970	0.941	0.993	0.991
Langmuir-4				
q_m (mg/g)	5.17	5.04	2.73	1.96
K_a (dm ³ /mg)	0.143	0.107	0.103	0.115
r^2	0.970	0.941	0.993	0.991
Freundlich				
$1/n$	0.362	0.378	0.305	0.257
K_F (mg/g)(dm ³ /mg) ^{1/n}	1.09	0.934	0.634	0.561
r^2	0.863	0.857	0.918	0.966
Redlich–Peterson				
g	1.000	1.000	1.000	0.937
B (dm ³ /mg) ^g	0.140	0.106	0.103	0.188
A (dm ³ /g)	0.729	0.535	0.281	0.274
r^2	0.997	0.995	1.000	1.000

Langmuir-1 had the highest coefficients of determination compared with other Langmuir linear equations. It was observed that the coefficient of determination of Langmuir-1 is higher than that of Langmuir-2 [14,18]. The coefficient of determination for both theoretical Langmuir-1 and Redlich–Peterson isotherms were higher than those obtained for Freundlich isotherm, indicating that the biosorption system is more likely monolayer coverage of the copra meal surface by the cadmium ions. Fig. 4 shows plots comparing the theoretical Langmuir isotherm, the empirical Freundlich isotherm, and the Redlich–Peterson isotherm with experimental data. The good fit of the Redlich–Peterson and Langmuir isotherms were not the same even when the coefficient of determinations was high for both isotherms.

3.5. Thermodynamic studies

Thermodynamic considerations of a biosorption process are necessary to conclude whether the process is spontaneous or not. The Gibbs free energy change, ΔG° , is an indication of spontaneity of a chemical reaction and therefore is an important criterion for spontaneity. Also, both energy and entropy factors must be considered in order to determine the Gibbs free energy of the process. Reactions occur spontaneously at a given temperature if ΔG° is a negative quantity. The free energy of a biosorption reaction, considering the biosorption equilibrium

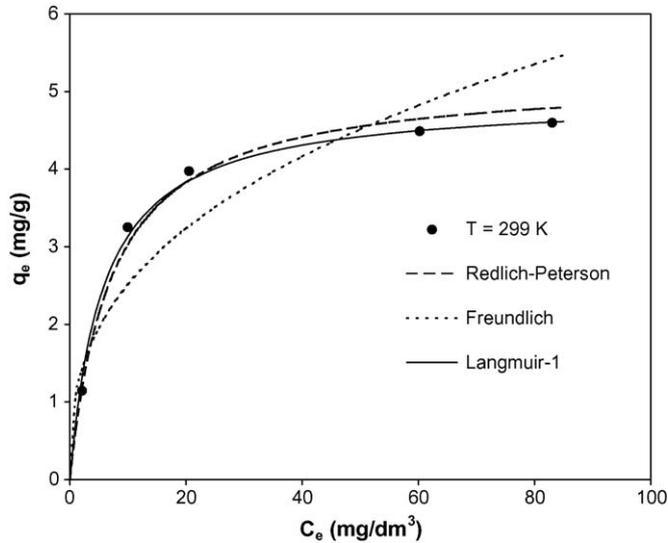


Fig. 4. Isotherms obtained by using linear method for the biosorption of cadmium using copra meal at temperature 299 K.

constant K_a is given by the following equation:

$$\Delta G^\circ = -RT \ln K_a \quad (11)$$

where ΔG° is the standard free energy change (J), R the universal gas constant, 8.314 J/mol K, and T is absolute temperature (K).

Considering the relationship between free energy and equilibrium constant, change in equilibrium constant with temperature can be obtained in the differential form as follows:

$$\frac{d \ln K_a}{dT} = \frac{\Delta H^\circ}{RT^2} \quad (12)$$

After integration, the integrated form of Eq. (12) becomes:

$$\ln K_a = -\frac{\Delta H^\circ}{RT} + Y \quad (13)$$

where Y is a constant. Eq. (13) can be rearranged to obtain

$$-RT \ln K_a = \Delta H^\circ - TRY \quad (14)$$

Let

$$\Delta S^\circ = RY \quad (15)$$

Substituting Eqs. (14) and (15), the Gibbs free energy change, ΔG° , can be represented as follows:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (16)$$

A plot of Gibbs free energy change, ΔG° , versus temperature, T , was found to be linear, Fig. 5. The values of ΔH° and ΔS° were determined from the slope and intercept of the plot. The

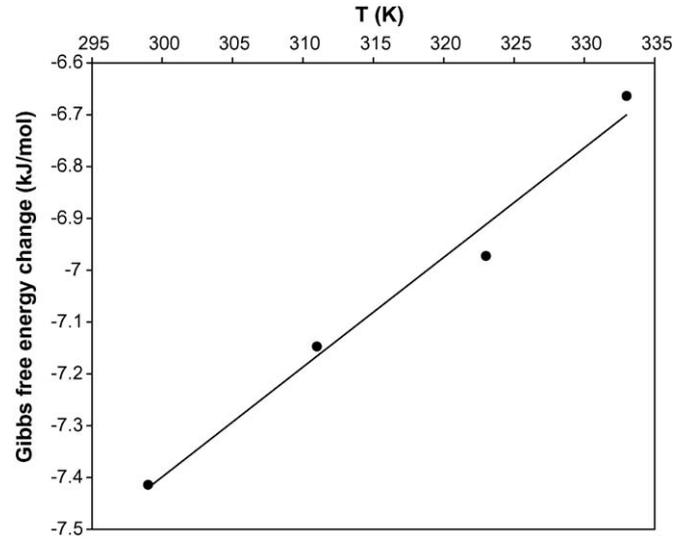


Fig. 5. Plot of Gibbs free energy change, ΔG° , vs. temperature, T .

thermodynamic parameters Gibbs free energy change, ΔG° , was calculated using Langmuir-1 constant (Table 3). The enthalpy change, ΔH° , and the entropy change, ΔS° , for the biosorption process were calculated to give the values -13.7 kJ/mol and 21.2 J/mol K, respectively. The negative values of ΔG° confirm the feasibility of the process and the spontaneous nature of biosorption with a high preference for cadmium on copra meal. In most cases, biosorption of cadmium was found to have negative values of ΔG° (Table 4). The value of ΔH° is negative, indicating that the biosorption reaction is exothermic. However not all the cadmium biosorption systems are endothermic (Table 4). The positive value of ΔS° reflects the affinity of the copra meal for cadmium and suggests some structural changes in cadmium and copra meal interaction [19]. In addition, positive value of ΔS° shows increasing randomness at the solid/liquid interface during the biosorption of cadmium ions onto copra meal. Positive values of ΔS° have also reported for the biosorption of cadmium by rice husk [20], dead *Sargassum* sp. biomass [21], and hematite [22].

The use of coefficient of determination of linear regression analysis for comparing the best fitting of different linear isotherms was found not to be appropriate [18]. Therefore, a further analysis was attempted; a trial and error procedure was used for non-linear method by using the *solver* add-in with Microsoft's spreadsheet, Microsoft Excel [23]. In this procedure, the application of computer operation was developed to determine the isotherm parameters by optimization routine to maximize the coefficient of determination between experimental

Table 4

A comparison of thermodynamic parameters for the biosorption of cadmium by different biosorbents

ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/K mol)	Material	Reference
Negative	40.14	0.14	Rice husk	[20]
Negative	-21.49	3.798	Dead <i>Sargassum</i> sp. biomass	[21]
Negative	-13.089	38.288	Hematite	[22]
Negative	14.12	-	Spent grain	[8]

Table 5
Isotherm parameters obtained by using non-linear method

Isotherm	T (K)			
	299	311	323	333
Langmuir				
q_m (mg/g)	4.99	4.76	2.71	1.97
K_a (dm ³ /mg)	0.172	0.138	0.107	0.111
r^2	0.993	0.998	1.000	1.000
Freundlich				
$1/n$	0.305	0.268	0.249	0.232
K_F (mg/g)(dm ³ /mg) ^{1/n}	1.34	1.41	0.806	0.623
r^2	0.862	0.982	0.992	0.998
Redlich–Peterson				
g	1.000	1.000	1.000	0.941
B (dm ³ /mg) ^g	0.172	0.138	0.107	0.183
A (dm ³ /g)	0.855	0.658	0.290	0.270
r^2	0.993	0.998	1.000	1.000

data and isotherms. Table 5 shows isotherm parameters obtained by using non-linear method. In the case of Langmuir isotherm, the results for the four Langmuir linear equations were similar. By using non-linear method there was no problem with transformation of non-linear isotherm equation to linear forms, and also they had the same error structures. In the case of Redlich–Peterson, the values of g are unity which is the same as the results from linear method. It can be seen that the values of g were closer to unity, which means the isotherms are approaching the Langmuir but not Freundlich isotherm. Fig. 6 shows that the Redlich–Peterson and Langmuir isotherms overlapped, and they seem to be the best-fitting models for the experiment results with the same values of coefficient of determination (Table 4). Langmuir isotherm is a special case of Redlich–Peterson isotherm when constant g is unity [24,25] and Redlich–Peterson constant B is the same as Langmuir biosorption equilibrium constant, K_a . In addition, it was reported that Freundlich isotherm is a special case of Redlich–Peterson isotherm when constants A and B

are much greater than unity [18]. Unlike the linear analysis, different isotherm forms would affect r^2 significantly, and impact the final determination of parameters while non-linear methods would prevent such errors.

The effect of temperature on the biosorption isotherm is shown in Fig. 3. The results show that the capacity of the copra meal for cadmium ions biosorption decreases with increase in temperature. The saturated monolayer biosorption capacity, q_m , was found to decrease from 4.99 to 1.97 mg/g for an increase in solution temperature from 299 to 333 K (Table 5). This is a clear indication that the biosorption of cadmium on copra meal is an exothermic process. On the other hand, the biosorption equilibrium constant, K_a , decreased from 0.172 to 0.111 dm³/mg, as temperature is varied from 299 to 333 K.

4. Conclusion

Biosorption of cadmium ions from solution by coconut copra meal is a spontaneous and exothermic process. The saturated monolayer biosorption capacity of the copra meal for cadmium ions at 299 K was calculated to be 4.99 mg/g. The biosorption process is pH dependent and maximum removal of cadmium from aqueous solution occurred at pH 6. Non-linear method of error analysis could be a better way to compare isotherm fitting. Langmuir isotherm is a special case of Redlich–Peterson isotherm when constant g is unity. Both two-parameter Langmuir and three-parameter Redlich–Peterson isotherms were the best-fitting models for the biosorption of cadmium on coconut copra meal.

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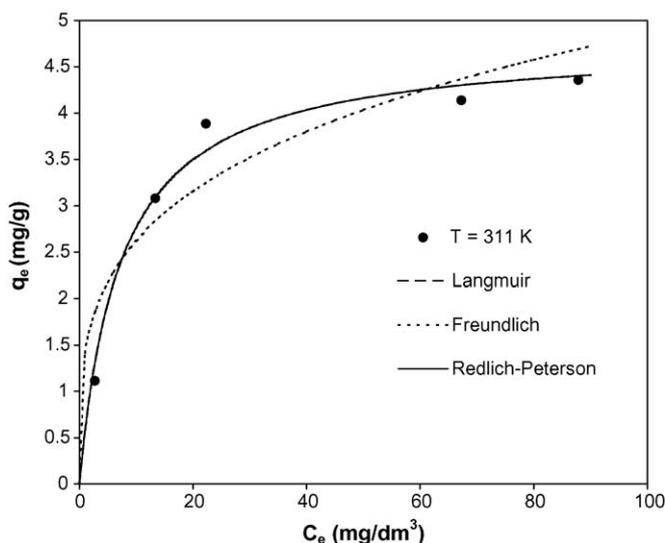


Fig. 6. Isotherms obtained by using non-linear method for the biosorption of cadmium using copra meal at temperature 311 K.

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