

Sorption equilibrium of mercury onto ground-up tree fern

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Abstract

The sorption behavior of mercury at different temperatures onto ground-up tree fern was investigated. The experimental results were fitted to two two-parameter isotherms, the Freundlich and Langmuir isotherms, as well as to two three-parameter isotherms, the Redlich–Peterson and Sips isotherms to obtain the characteristic parameters of each model. A comparison of best-fitting was performed using the coefficient of determination and Chi-square test. Both the Langmuir and Redlich–Peterson isotherms were found to well represent the measured sorption data. According to the evaluation using the Langmuir equation, the saturated monolayer sorption capacity of mercury ions onto ground-up tree fern was 26.5 mg/g at 298 K. It was noted that an increase in temperature resulted in a higher mercury ion loading per unit weight of the tree fern. In addition, various thermodynamic parameters, such as ΔG° , ΔH° , and ΔS° , were calculated and compared with the sorption of mercury by other sorbents.

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1. Introduction

Understanding the sorption of metal ions from aqueous solutions is important in water pollution control. The application of low-cost sorbents including carbonaceous materials, agricultural products, and waste by-products has been investigated. In recent years, agricultural waste materials and by-products of cellulosic origin have been widely studied in the literature for their capacity to remove mercury from aqueous solutions. These include peat [1], bark [2], cellulose [3], lignite [4], coconut husks [5], rice husks [6], Sugi wood [7], flax shive [8], bagasse pith [9], moss [10], vegetables [11], carbonised coirpith [12], rice-husk ash [13], tea leaves, and coffee beans [14]. Several extensive studies have also been performed using activated carbon prepared from agricultural wastes for the removal of mercury from aqueous solutions such as peanut hull carbon [15], olive stones [16], and Sugi wood [17]. In addition, chemically treated sorbents including coconut husks [18], bagasse pith [19], bark [20], and polyacrylamide-grafted banana stalks [21], have been used in attempts to enhance the mercury sorption performance. Most of this work has shown that agricultural products and waste by-

products can be good sorbents for heavy metals. Many of these natural sorbents remove metals more by ion exchange than by adsorption.

The structure of tree fern is cellulose based [22], and the surface of the cellulose in contact with water is negatively charged [23]. All chemical sorbents have polar functional groups (alcohols, aldehydes, ketones, acids, phenolic hydroxides, and ethers) for chemical binding [24]. The tree fern is highly polar and has been used as a specific sorbent to remove metals such as lead [25], copper [26], cadmium [27,28], and zinc [29], as well as dye [30]. In addition, the sorption of sodium ions by tree fern showed a lower sorption capacity [23]. However, arsenical anions cannot be removed from solution because of the negative charge of the surface of tree fern material.

Several sorption isotherms have recently been studied for metal removal such as Langmuir [31], Freundlich [32], Dubinin–Radushkevich [5], Frumkin [33], van Bemmelen–Freundlich [34], Sips [35], Ideal Adsorption Solution Theory [36], BET [37], Redlich–Peterson [29], Henry [38], and Tóth [39]. The goal of the present work was to study the possibility of utilizing ground-up tree fern for the sorption of mercury ions from aqueous solutions and the effect of temperature on its sorption of mercury. In this study, Chi-square test was used, and the isotherm parameters were determined using the method of least squares. Two two-parameter isotherms, the

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Freundlich and Langmuir isotherms, as well as two three-parameter isotherms, the Redlich–Peterson and Sips isotherms, were examined for their ability to model the equilibrium sorption data. A comparison of linear and non-linear correlation analyses of these four isotherms was applied by using the sorption of mercury by ground-up tree fern.

2. Materials and methods

2.1. Materials

Raw tree fern material was dried in an oven at 100 °C for a period of 24 h, and then ground-up and screened through a set of sieves to obtain a geometrical size of 61–74 μm. This produced uniform material for the complete set of sorption tests; this material was stored in an air-tight plastic container for use in all investigations. Analytical grade reagents were used in all cases. Stock solutions of mercury(II) (1000 mg/dm³) were prepared in distilled water using mercury HgCl₂. All working solutions were prepared by diluting the stock solution with distilled water.

2.2. Methods

Batch sorption experiments were performed at the desired temperatures (10, 15, 20, and 25 °C) on a rotary shaker at 100 rpm using 125-ml capped conical flasks. In each set of experiments, a range of initial metal ion concentrations was used of from 55 to 145 mg/dm³, and 0.25 g of ground-up tree fern was thoroughly mixed into 50 ml of the mercury solution. After shaking the flasks for 12 h, the tree fern material was separated by centrifugation, and the remaining mercury concentration of the solution was analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-AES).

3. Equilibrium isotherms

Sorption equilibria provide fundamental physicochemical data for evaluating the applicability of sorption processes as a unit operation. The sorption equilibrium is usually described by an isotherm whose parameters express the surface properties and affinity of the sorbent at a fixed temperature. In order to investigate the sorption isotherms, four equilibrium models frequently applied to the sorption of metals from aqueous solution were fitted to the experimental results. These included two two-parameter isotherms, the Langmuir and the Freundlich isotherms, as well as two three-parameter isotherms, the Redlich–Peterson and the Sips isotherms.

The equilibrium sorption capacity is obtained by using a mass balance equation:

$$q_e = \frac{(C_0 - C_e)V}{m_s}; \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentration, respectively (mg/dm³), V is the volume of solution used (dm³), and m_s is the sorbent mass (g).

3.1. Langmuir isotherm

The saturated monolayer Langmuir isotherm [40] can be represented as:

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e}. \quad (2)$$

The constants q_m and K_a are the characteristic of the Langmuir equation and can be determined from a linearised form of Eq. (2), represented by

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

A plot of C_e/q_e versus C_e should indicate a straight line of slope $1/q_m$ and an intercept of $1/(K_a q_m)$, or alternatively

$$\frac{1}{q_e} = \left(\frac{1}{K_a q_m} \right) \times \frac{1}{C_e} + \frac{1}{q_m} \quad (4)$$

which is a straight line with a slope of $1/(K_a q_m)$ and an intercept of $1/q_m$ when plotting $1/q_e$ versus $1/C_e$; where C_e is the equilibrium concentration (mg/dm³), q_e is the amount of mercury sorbed (mg/g), q_m is q_e for a complete monolayer (mg/g), and K_a is the sorption equilibrium constant (dm³/mg) [29].

3.2. Freundlich isotherm

The Freundlich isotherm [41] is expressed by the following equation:

$$q_e = K_F C_e^{1/n}. \quad (5)$$

The equation may be linearised by taking the logarithm of both sides

$$\log(q_e) = \frac{1}{n} \log(C_e) + \log(K_F) \quad (6)$$

which produces a straight line with a slope of $1/n$ and an intercept of $\log(K_F)$ when plotting $\log(q_e)$ versus $\log(C_e)$.

3.3. Redlich–Peterson isotherm

The Redlich–Peterson isotherm [42] contains three parameters and involves features of both the Langmuir and the Freundlich isotherms. It can be described as follows:

$$q_e = \frac{A C_e}{1 + B C_e^g}. \quad (7)$$

Taking the natural logarithm of both sides results in

$$\ln \left(A \frac{C_e}{q_e} - 1 \right) = g \ln(C_e) + \ln(B). \quad (8)$$

Although, a linear analysis is not possible for a three-parameter isotherm, three isotherm constants, A , B , and g , can be evaluated from the pseudo-linear plot represented by Eq. (8) using a trial and error optimization method. A general trial and error procedure which is applicable to computer operations was developed to determine 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 .

3.4. Sips isotherm

The Sips [43] or Langmuir–Freundlich isotherm also contains three parameters. The isotherm can be represented as

$$q_e = \frac{A_S C_e^{C_S}}{1 + A_S C_e^{C_S}}; \tag{9}$$

or, in the Langmuir–Freundlich form:

$$q_e = \frac{q_m K_a C_e^{K_{LF}}}{1 + K_a C_e^{K_{LF}}}. \tag{10}$$

The equation may be linearised by taking the natural logarithm of both sides:

$$\ln\left(\frac{q_e}{q_m - q_e}\right) = K_{LF} \ln(C_e) + \ln(K_a). \tag{11}$$

Three isotherm constants, q_m , K_{LF} , and K_a , can be evaluated from the pseudo-linear plot represented by Eq. (11) using a trial and error optimization method. A general trial and error procedure which is applicable to computer operations was developed to determine the coefficient of determination, r^2 , for a series of values of q_m for the linear regression of $\ln(C_e)$ on $\ln[q_e/(q_m - q_e)]$ and to obtain the best value of q_m which yields a maximum ‘optimized’ value of r^2 .

3.5. Error analysis

In the single-component isotherm studies, the optimization procedure requires an error function to be defined in order to be able to evaluate the fit of the isotherm to the experimental equilibrium data. In this study, linear coefficients of determination and non-linear Chi-square test were examined.

The Chi-square test statistic is basically the sum of the squares of the differences between the experimental data and data obtained by calculating using the models, with each squared difference divided by the corresponding data obtained by calculating using the models. The equivalent mathematical statement is

$$\chi^2 = \sum \frac{(q_e - q_{e,m})^2}{q_{e,m}}; \tag{12}$$

where $q_{e,m}$ is the equilibrium capacity obtained by calculating using the model (mg/g) and q_e is the experimental data of the equilibrium capacity (mg/g). If data from a model are similar to the experimental data, χ^2 will be a small number, and if they are different, χ^2 will be a big number. Therefore, it is necessary to also analyze the data set of the Chi-square test to confirm the best-fit isotherm for the sorption system.

4. Results and discussion

The simplest method to determine isotherm constants for two-parameter isotherms is to transform the isotherm variables so that the equation is converted to a linear form and then to apply a

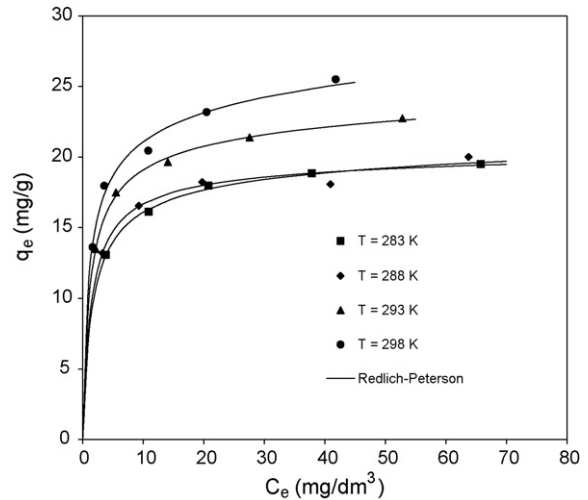


Fig. 1. Redlich–Peterson isotherms for the sorption of mercury ions using ground-up tree fern at various temperatures.

linear regression. Least square is the most common method for fitting a straight line through experimental results. The principle behind least squares is to find the line that optimizes the coefficient of determination, r^2 , or correlation coefficient, r , between the experimental points and the straight line.

Sorption isotherms of mercury ions onto ground-up tree fern at various solution temperatures are shown in Fig. 1. The Langmuir (K_a and q_m) and Freundlich (K_F and $1/n$) constants were calculated from the plots of C_e/q_e versus C_e and $\log q_e$ versus $\log C_e$, respectively, using a linear least squares fitting (Table 1). For the three-parameter isotherm, Redlich–Peterson and Langmuir–Freundlich constants were also obtained by a trial and error method using the plots of $\ln(C_e)$ versus $\ln[A(C_e/q_e) - 1]$ and $\ln(C_e)$ versus $\ln[q_e/(q_m - q_e)]$, from the linear isotherm forms of Eqs. (8) and (11), respectively. Fig. 2 shows the different isotherms for sorption of mercury onto ground-up tree fern. Comparison of the linear regression coefficient of determination, r^2 , and the non-linear Chi-square analysis, χ^2 which were calculated by Eq. (12), are shown in

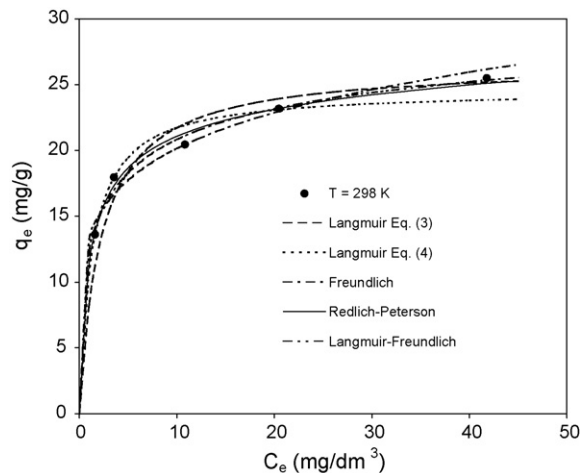


Fig. 2. Comparison of different isotherms for the sorption of mercury by ground-up tree fern.

Table 1
 Constants for Langmuir Eq. (3), Langmuir Eq. (4), Freundlich, Redlich–Peterson, and Langmuir–Freundlich isotherms

T (K)	Langmuir Eq. (3)		Langmuir Eq. (4)			Freundlich		Redlich–Peterson			Langmuir–Freundlich		
	q_m	K_a	q_m	K_a	ΔG°	K_F	$1/n$	g	A	B	K_{LF}	K_a	q_m
283	20.2	0.401	19.7	0.502	−10.9	11.2	0.142	0.950	13.6	0.837	0.738	0.601	21.0
288	20.3	0.423	19.6	0.628	−11.6	11.9	0.127	0.973	14.6	0.826	0.371	0.753	25.4
293	23.5	0.471	22.4	0.687	−12.0	12.6	0.158	0.943	21.1	1.15	0.573	0.721	25.9
298	26.5	0.454	24.6	0.762	−12.5	13.2	0.183	0.916	28.9	1.54	0.462	0.594	32.9

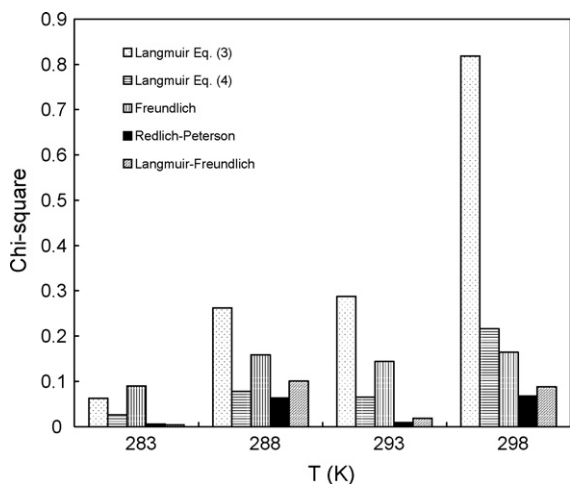


Fig. 3. Comparison of non-linear Chi-square test analysis, χ^2 .

Figs. 3 and 4. The results indicate that the three-parameter Redlich–Peterson isotherm exhibits the best-fit with the highest value of r^2 and lowest value of χ^2 . Both three-parameter isotherms of Redlich–Peterson and Langmuir–Freundlich have lower values of χ^2 than these of the two-parameter isotherms. Even though the most suitable isotherm for the data set was the Redlich–Peterson isotherm, the difference between the two linear forms of the Langmuir isotherm significantly affected the result. Values of r^2 obtained from the linear Langmuir Eq. (3)

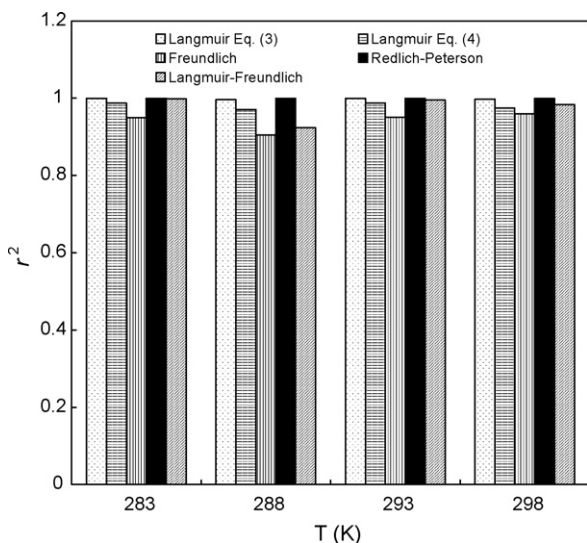


Fig. 4. Comparison of linear regression coefficients of determination, r^2 .

were consistently higher than these of Langmuir Eq. (4). However, the value of χ^2 shows that the Langmuir Eq. (4) produced a better fit than Eq. (3). This denotes that a different axis setting would alter the results of a linear regression and hence influence the determination process. Unlike the linear analysis, different forms of the equations would significantly effect r^2 and impact the final determination, whereas the non-linear Chi-square analysis is a method which avoids such errors [44].

Values of χ^2 were compared to determine the appropriate type of two-parameter isotherm for mercury sorption. χ^2 values for the fitting of mercury to the theoretical Langmuir Eq. (4) isotherm were lower than the values for the empirical Freundlich isotherm, as shown in Fig. 3. Hence, the Langmuir isotherm agrees well with the experimental data, assuming that all of the sorption sites have equal energy [40].

The effect of the isotherm shape can be used to predict the favorableness or unfavorableness of a sorption system in batch processes.

The effect of the isotherm shape can be used to predict if a sorption system is ‘favorable’ or ‘unfavorable’ in batch processes [45]. According to Hall et al. [46], the essential features of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter, K_R , which is defined by the following relationship:

$$K_R = \frac{1}{1 + K_a C_0}; \tag{13}$$

where K_R is a dimensionless separation factor, C_0 is the initial concentration (mg/dm^3), and K_a is the Langmuir constant (dm^3/mg). The parameter K_R indicates the shape of the isotherm according the following table

Values of K_R	Type of isotherm
$K_R > 1$	Unfavorable
$K_R = 1$	Linear
$0 < K_R < 1$	Favorable
$K_R = 0$	Irreversible

The relationship between the parameter K_R and C_0 was reported as a figure [29]. The values of K_R for mercury are given in Fig. 5. The K_R values indicate that sorption is more favorable for the higher initial mercury concentrations than for lower ones. Referring to Fig. 5, it is obvious that ground-up tree fern is a good sorbent for mercury. The sorption is more favorable at higher temperatures.

The monolayer coverage, q_m , obtained from the Langmuir isotherm for each temperature increased with increasing temper-

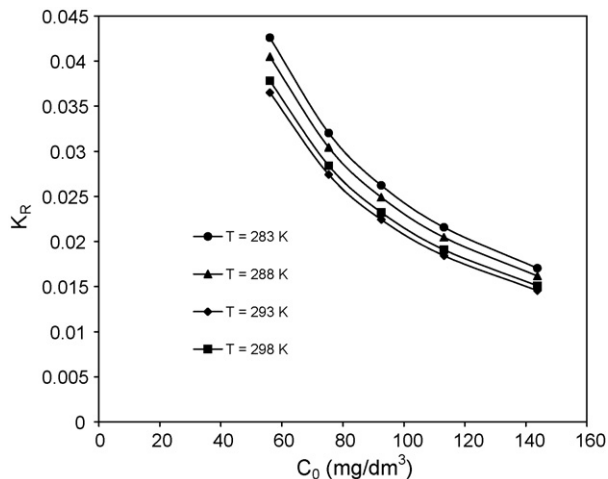


Fig. 5. Plot of K_R against initial mercury ion concentration at various temperatures.

ature (Table 1). Increasing the temperature is known to increase the rate at which chemisorption and diffusion processes occur. Typical chemisorption involving valence forces through the sharing or exchange of electrons between the sorbent and sorbate, is an endothermic process, thus chemisorption may play a significant role in the sorption process. In addition, increasing the temperature may produce a swelling effect within the internal structure of the tree fern material enabling metal ions to penetrate further [47] or to the creation of some new active sites on the sorbent surface [6].

The plateau on each isotherm corresponds to monolayer coverage of the surface by the metal ions, and this value is the ultimate sorptive capacity at high concentrations which can be used to estimate the specific surface area, S , of ground-up tree fern using the following equation:

$$S = \frac{q_m N A}{M}; \quad (14)$$

where S is the specific surface area in m²/g tree fern, q_m is the monolayer sorption capacity in g metal/g tree fern, N is Avogadro's number (6.02×10^{23}), A is the cross-sectional area of metal ion in m², and M is the molecular weight of the metal. A comparison of the specific surface area for sorption of divalent metal ions was made by using the monolayer sorption capacity, q_m , which was obtained from previous work [28,29]. Therefore, the specific surface areas can be calculated by Eq. (14) for Zn²⁺, Cu²⁺, Pb²⁺, Cd²⁺, and Hg²⁺ (Table 2). The specific surface area of ground-up tree fern for the metal ions was affected by the

Table 2
Specific surface areas and saturated monolayer capacities for metals by ground-up tree fern

Metal	Ionic radius (Å)	M	A (m ²)	q_m (mg/g)	S (m ² /g)
Zn ²⁺	0.88	65.38	2.43×10^{-20}	7.58	1.70
Cu ²⁺	0.87	63.546	2.38×10^{-20}	10.6	2.39
Cd ²⁺	1.09	112.41	3.73×10^{-20}	16.3	3.26
Hg ²⁺	1.16	200.59	4.23×10^{-20}	26.5	3.36
Pb ²⁺	1.33	207.2	5.56×10^{-20}	39.8	6.43

divalent metal characteristics such as ionic radius and molecular weight. In general, the area increased with an increase in the monolayer sorption capacity and the specific surface areas except for zinc which had a lower monolayer sorption capacity and specific surface areas compared copper. The same sorption capacity order ($\text{Cu}^{2+} > \text{Zn}^{2+}$) occurred in the sorption of metals by natural zeolite [48], low-rank Turkish coals [49], and native sugar beet pulp [50]. The specific surface area of ground-up tree fern was in the order of $\text{Zn}^{2+} < \text{Cu}^{2+} < \text{Cd}^{2+} < \text{Hg}^{2+} < \text{Pb}^{2+}$.

In environmental engineering practice, both energy and entropy factors must be considered in order to determine what processes will occur spontaneously. Gibb's free energy change, ΔG° , is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if ΔG° is a negative value. The thermodynamic parameters of Gibb's free energy change, ΔG° , enthalpy change, ΔH° , and entropy change, ΔS° , for the sorption processes are calculated using the following equations:

$$\Delta G^\circ = -RT \ln K_a \quad (15)$$

and

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

where R is universal gas constant (8.314 J/mol K) and T is the absolute temperature in K.

The thermodynamic parameters Gibb's free energy change, ΔG° , are calculated using K_a which is obtained from Langmuir Eq. (4) and are shown in Table 1. A plot of Gibb's free energy change, ΔG° , versus temperature, T , was found to be linear (Fig. 6). The enthalpy change, ΔH° , and the entropy change, ΔS° , for the sorption processes were obtained from the intercept and slope of Eq. (16) and found to be 18.8 kJ/mol and 0.105 kJ/mol K, respectively. The negative values of ΔG° confirm the feasibility of the process and the spontaneous nature of sorption with a high preference of mercury ions by ground-up tree fern. The decrease in the negative value of ΔG° with an increase in temperature indicates that the sorption process of mercury ions on ground-up tree fern becomes more favorable at higher temperatures [51]. In most cases, sorption of mer-

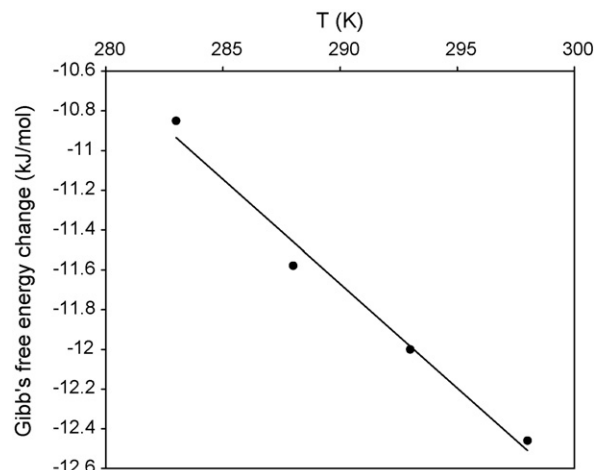


Fig. 6. Plot of Gibb's free energy change, ΔG° , versus temperature, T .

Table 3

A comparison of thermodynamic parameters for the sorption of mercury by different sorbents

Sorbent	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol K)	References
Polyurethane (PUR)	Negative	−30.7	−70.1	[56]
Activated carbon	Negative	−23.6	−20.5	[55]
Sawdust	Negative	20.9	87.4	[54]
Polyacrylamide-grafted iron(III) oxide	Negative	26.3	100	[53]
Polyacrylamide-grafted banana stalk	Negative	32.1	169	[21]
2-Mercaptobenzimidazole-clay	Negative	34.8	190	[52]
Deminerallized lignite coal	Negative	−2.6	0.024	[4]

cury was found to have negative values of ΔG° (Table 3). The value of ΔH° is positive, indicating that the sorption reaction is endothermic. However, not all the mercury sorption systems were endothermic (Table 3). Entropy has been defined as the degree of chaos of a system. A positive value of ΔS° reflects increasing randomness at the solid/liquid interface during the sorption of mercury ions on the sorbent [6,21,52]. There are consistencies in the sorption of mercury by other sorbents, for example, rice husks [6], polyacrylamide-grafted iron(III) oxide [53], 2-mercaptobenzimidazole-clay [52], sawdust [54], deminerallized lignite coal [4], and polyacrylamide-grafted banana stalks [21]. However, a negative value for ΔS° was also reported for the sorption of mercury by activated carbon derived from fertilizer waste [55] and for the sorption of Hg(II)-SCN on polyurethane foam [56]. In addition, there are two conclusions for the sorption of mercury presented in the literature. The first is that a relatively small positive value of ΔS° indicates that no significant structural change occurs in the sorbent [21,53]. The other is that the positive value of ΔS° reflects the affinity of the ground-up tree fern for mercury ions and suggests some structural changes in both the mercury and sorbent [52].

5. Conclusion

Ground-up tree fern is able to sorb mercury ions from aqueous solutions. The mercury ion binding capacity of ground-up tree fern was a function of temperature. The sorption capacity increased with increasing temperature. It is not appropriate to use the coefficient of determination of the linear regression analysis for comparing the best-fit of the Redlich–Peterson, Sips, Freundlich, and both linear Langmuir isotherms. The results from this study were extremely well described by the three-parameter Redlich–Peterson isotherm. The negative values of ΔG° indicate the spontaneous nature of sorption with a high preference of mercury ions on ground-up tree fern, and that the sorption reaction is endothermic in which there is increasing randomness at the solid/liquid interface during the sorption of mercury ions onto ground-up tree fern. The monolayer sorption capacity and the specific surface areas of tree fern for divalent metal ions were affected by the metal ionic radius and molecular weight.

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