# Isotherms for the Sorption of Lead onto Peat: Comparison of Linear and Non-Linear Methods

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### Abstract

A comparison of the linear least-squares method and a trial-and-error non-linear method of three widely used isotherms (the Langmuir, Freundlich, and Redlich-Peterson) were examined in an experiment using lead ion sorption onto peat at different temperatures. The four Langmuir linear equations are discussed. Langmuir isotherm parameters obtained from the four Langmuir linear equations using the linear method differed but they were the same when using the non-linear method. Langmuir-1 is the most popular linear form, and it had the highest coefficient of determination compared with the other Langmuir linear equations. The Redlich-Peterson and Langmuir isotherms produced higher coefficients of determination. There are two separate regions depicting the Freundlich isotherm. The results show that that non-linear method may be a better way to obtain the parameters.

### Introduction

Equilibrium relationships between sorbents and sorbates are described by sorption isotherms which give the capacity of a sorbent for a sorbate. Isotherms can be obtained by examining batch reactions at fixed temperatures. Linear regression is frequently used to determine the best-fitting isotherm. The linear least-squares method with linearly transformed isotherm equations has also been widely applied to confirm experimental data and isotherms using coefficients of determination. In recent years, several error analysis methods, such as the coefficient of determination, the sum of the errors squared, a hybrid error function, Marquardt's percent standard deviation, the average relative error, the sum of the absolute errors, and Chi-square, have been used to determine the best-fitting isotherm equation [1-3].

In this study, the linear least-squares method and a non-linear method of three widely used isotherms, the Langmuir [4], Freundlich [5], and Redlich-Peterson [6], were compared in an experiment examining lead ion sorption onto peat. A trial-and-error procedure was used for the non-linear method using the *solver* add-in with Microsoft's spreadsheet, Microsoft Excel.

### Materials and Methods

A commercially available sphagnum moss peat (Board-Na-Mona, Ireland) was used as the sorbent. The peat as supplied, dried at 100°C for 24 h and then screened though a 14-mesh sieve (1.18-mm aperture; B.S. 410/43) to remove any large non-peat solids. Stock solutions of lead(II) nitrate (1 g/dm$^3$) were prepared in distilled water. All solutions used in this study were diluted with distilled water as required.

Equilibrium isotherms were determined by shaking a fixed mass of peat (0.4 g) with 100 ml of lead(II) solutions in conical flasks. A range of lead(II) concentrations (20 to 120 mg/dm$^3$) was tested at an initial value of pH 6.0.

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Table 1. Isotherms and their linear forms.

| Isotherm | | Linear form | Plot |
|---|---|---|---|
| Freundlich | $q_e = K_F C_e^{1/n}$ | $\log(q_e) = \log(K_F) + 1/n \log(C_e)$ | $\log(q_e)$ vs. $\log(C_e)$ |
| Langmuir-1 | | $\dfrac{C_e}{q_e} = \dfrac{1}{q_m}C_e + \dfrac{1}{K_a q_m}$ | $\dfrac{C_e}{q_e}$ vs. $C_e$ |
| Langmuir-2 | $q_e = \dfrac{q_m K_a C_e}{1 + K_a C_e}$ | $\dfrac{1}{q_e} = \left(\dfrac{1}{K_a q_m}\right)\dfrac{1}{C_e} + \dfrac{1}{q_m}$ | $\dfrac{1}{q_e}$ vs. $\dfrac{1}{C_e}$ |
| Langmuir-3 | | $q_e = q_m - \left(\dfrac{1}{K_a}\right)\dfrac{q_e}{C_e}$ | $q_e$ vs. $\dfrac{q_e}{C_e}$ |
| Langmuir-4 | | $\dfrac{q_e}{C_e} = K_a q_m - K_a q_e$ | $\dfrac{q_e}{C_e}$ vs. $q_e$ |
| Redlich-Peterson | $q_e = \dfrac{A C_e}{1 + B C_e^{\,g}}$ | $\ln\left(A\dfrac{C_e}{q_e} - 1\right) = g\ln(C_e) + \ln(B)$ | $\ln\left(A\dfrac{C_e}{q_e} - 1\right)$ vs. $\ln(C_e)$ |

Initial pH adjustments were carried out by adding either a sulphuric acid or sodium hydroxide solution. After shaking the flasks for 4 h, the reaction mixtures were filtered through filter paper, and then the filtrates was analyzed for the remaining lead(II) concentration with atomic absorption spectrometry (AAS).

## Results and Discussion

In this study the coefficient of determination, $r^2$, was used to test the best-fitting isotherm to the experimental data:

$$r^2 = \frac{\sum\left(q_m - \overline{q_e}\right)^2}{\sum\left(q_m - \overline{q_e}\right)^2 + \sum\left(q_m - q_e\right)^2} \tag{1}$$

where $q_m$ is the equilibrium capacity obtained from the isotherm model, $q_e$ is the equilibrium capacity obtained from experiment, and $q_e$ is the average of $q_e$.

### Linear Regression Method

Linear regression is frequently used to determine the best-fitting isotherm, and the method of least squares has been used for finding the parameters of the isotherms. However, the Langmuir isotherm can be linearized as four different types (Table 1), and simple linear regression will result in different parameter estimates [7, 8]. The more-popular linear forms used are Langmuir-1 and Langmuir-2, and the best fit is obtained using Langmuir-1 because of the minimal deviations from the fitted equation resulting in the best error distribution [7]. Figures 1 to 4 show the four linear Langmuir equations with the experimental data for the sorption of lead ion onto peat at various

temperatures. Values of the Langmuir constants, the saturated monolayer sorption capacity, $q_m$, and the sorption equilibrium constant, $K_a$, are presented in Table 2 for the sorption of lead ion onto peat at 283, 293, 303, and 313 K. These values of the coefficient of determinations, $r^2$, obtained from Langmuir-1, indicate that there is strong positive evidence that the sorption of lead ions onto peat follows the Langmuir isotherm. It is clear that transformations of the non-linear Langmuir isotherm equation to linear forms implicitly alter the error structure and may also violate the error variance and normality assumptions of the standard least-squares method [3]. The linear analysis using different linear forms of the Langmuir equation will significantly affect calculations of the Langmuir parameters. Figure 5 shows typical results for the sorption of lead ion onto peat at 293 K. It seems that the Langmuir
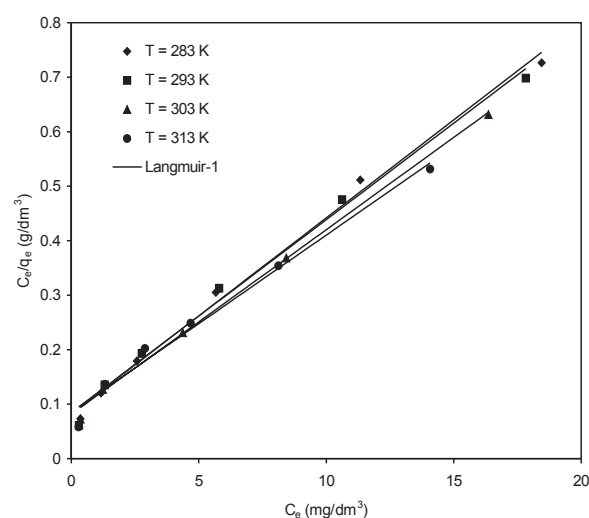


Fig. 1. Langmuir-1 isotherm obtained using the linear method for the sorption of lead(II) onto peat at various temperatures.

isotherm obtained from Langmuir-1 provided a better fit to the experimental data.

The applicability of the Freundlich sorption isotherm was also analyzed, using the same set of experimental data, by plotting $\log(q_e)$ versus $\log(C_e)$. If just the linear form of Langmuir-1 is used for comparison, Langmuir-1 was more suitable for the experimental data than was the Freundlich isotherm because of the higher value of the coefficient of determinations (Table 2). In contrast, if using the linear form of the other Langmuir equations, the Freundlich isotherm was more suitable for the experimental data than was the Langmuir isotherm in most cases, especially in the case of Langmuir-3 and Langmuir-4. The Freundlich isotherm constant, $K_F$, $1/n$, and the coefficients of determination are shown in Table 2.

The Redlich-Peterson isotherm constants, $A$, $B$, and $g$, as well as the coefficient of determination, $r^2$, for the lead

ion sorption systems using peat were obtained using the linear form (Table 1). In all cases, the Redlich-Peterson isotherm exhibited the highest coefficient of determinations, which produced a considerably better fit compared with the Langmuir and Freundlich isotherms. It can be seen that the values of $g$ are not close to unity, which means the isotherms are approaching the Freundlich but not the Langmuir isotherm. Figure 6 shows plots comparing the theoretical Langmuir isotherm, the empirical Freundlich isotherm, and the Redlich-Peterson isotherm with the experimental data for the sorption of lead ions onto peat at a temperature of 313 K. The Redlich-Peterson and Langmuir isotherms are not the same even though the coefficients of determinations were high for both isotherms. In addition, the Freundlich isotherm coefficients were also determined at both the lower ($C_e < 4$ mg/dm$^3$) and the higher equilibrium concentration ranges ($C_e > 4$ mg/ dm$^3$). It is apparent from Fig. 7 that there are two separate regions depicting the isotherm. The sorption of lead ions onto peat using the Freundlich isotherm had a high coefficient of determination for both lower ($r^2 > 0.994$) and higher ($r^2 > 0.983$) equilibrium concentration ranges. The results suggest a decrease in the exponent at higher equilibrium concentrations.
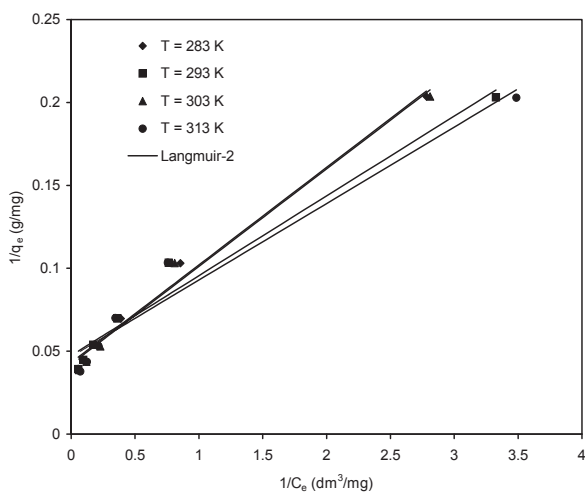
## Non-linear Method

In the case of the non-linear method, a trial-and-error procedure, which is applicable to computer operation, was developed to determine the isotherm parameters using an optimization routine to maximize the coefficient of determination between the experimental data and isotherms in the *solver* add-in with Microsoft's spreadsheet, Microsoft Excel. The abilities of three widely used isotherms, the Freundlich, Langmuir, and Redlich-Peterson isotherms, to model the equilibrium sorption data were examined. Table 3 shows the isotherm parameters obtained using the



Fig. 2. Langmuir-2 isotherm obtained using the linear method for the adsorption of lead(II) onto peat at various temperatures.
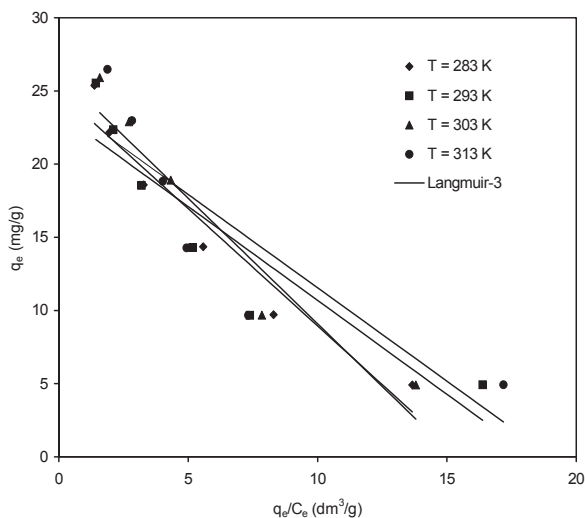


Fig. 3. Langmuir-3 isotherm obtained using the linear method for the adsorption of lead(II) onto peat at various temperatures.
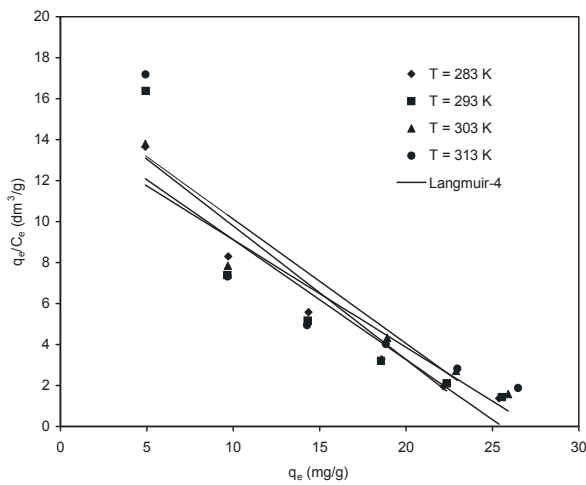


Fig. 4. Langmuir-4 isotherm obtained using the linear method for the adsorption of lead(II) onto peat at various temperatures.

Table 2. Isotherm parameters obtained using the linear method.

| Isotherm | $T$ (K) | 283 | 293 | 303 | 313 |
|---|---|---|---|---|---|
| Langmuir-1 | $q_m$ (mg/g) | 27.8 | 28.3 | 29.5 | 30.8 |
| | $K_a$ (dm³/mg) | 0.437 | 0.416 | 0.415 | 0.382 |
| | $r^2$ | 0.995 | 0.992 | 0.996 | 0.984 |
| | $\Delta G°$ (kJ/mol) | -10.6 | -10.9 | -11.1 | -11.4 |
| Langmuir-2 | $q_m$ (mg/g) | 23.2 | 21.1 | 23.7 | 21.4 |
| | $K_a$ (dm³/mg) | 0.733 | 0.984 | 0.718 | 1.01 |
| | $r^2$ | 0.991 | 0.969 | 0.983 | 0.959 |
| Langmuir-3 | $q_m$ (mg/g) | 25.0 | 23.5 | 26.2 | 24.3 |
| | $K_a$ (dm³/mg) | 0.623 | 0.780 | 0.583 | 0.784 |
| | $r^2$ | 0.939 | 0.837 | 0.900 | 0.775 |
| Langmuir-4 | $q_m$ (mg/g) | 25.6 | 25.0 | 27.3 | 26.7 |
| | $K_a$ (dm³/mg) | 0.585 | 0.652 | 0.525 | 0.608 |
| | $r^2$ | 0.939 | 0.837 | 0.900 | 0.775 |
| Freundlich | $1/n$ | 0.410 | 0.409 | 0.448 | 0.447 |
| | $K_F$ (mg/g)(dm³/mg)$^{1/n}$ | 8.51 | 8.58 | 8.57 | 8.75 |
| | $r^2$ | 0.970 | 0.987 | 0.973 | 0.993 |
| Redlich-Peterson | g | 0.811 | 0.703 | 0.749 | 0.608 |
| | $B$ (dm³/mg)$^g$ | 1.41 | 3.54 | 1.67 | 7.77 |
| | $A$ (dm³/g) | 22.0 | 41.1 | 24.2 | 78.7 |
| | $r^2$ | 1.000 | 0.999 | 0.997 | 0.997 |

non-linear method. In the case of the Langmuir isotherm, the results from the four linear Langmuir equations are the same. When using the non-linear method, there was no problem with transformations of non-linear Langmuir

equations to linear forms, and also they had the same error structures. The Langmuir constants obtained from the non-linear and linear methods differed even when compared with the results of Langmuir-1, which had the
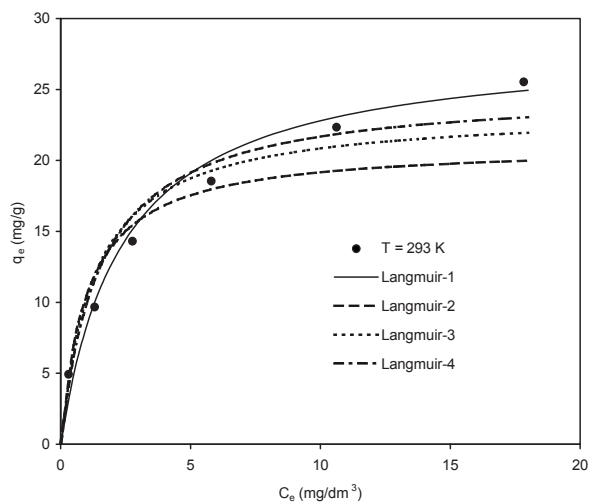


Fig. 5. Langmuir isotherms obtained using the linear method for the adsorption of lead(II) onto peat at a temperature of 293 K.
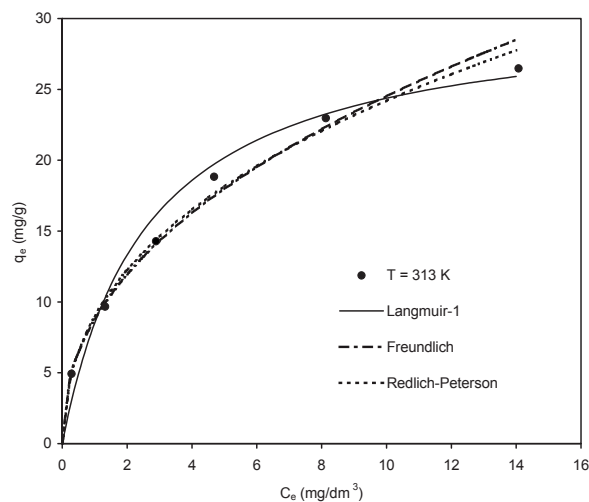


Fig. 6. Isotherms obtained using the linear method for the sorption of lead(II) onto peat at a temperature of 313 K.

Table 3. Isotherm parameters obtained using the non-linear method.

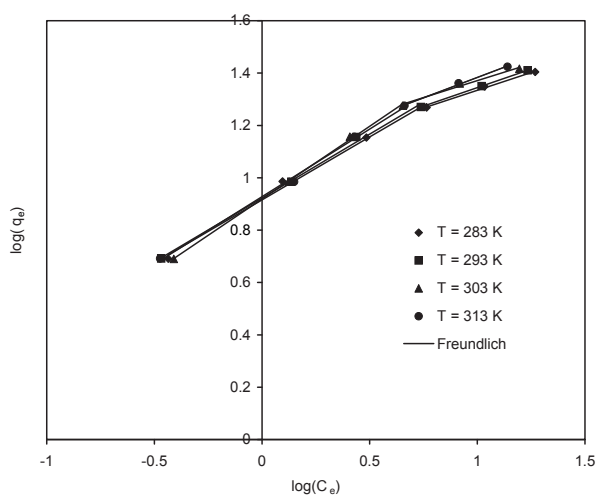| Isotherm | $T$ (K) | 283 | 293 | 303 | 313 |
|---|---|---|---|---|---|
| Langmuir | $q_m$ (mg/g) | 27.5 | 28.5 | 30.1 | 32.5 |
| | $K_a$ (dm³/mg) | 0.435 | 0.373 | 0.373 | 0.302 |
| | $r^2$ | 0.988 | 0.983 | 0.992 | 0.984 |
| Freundlich | $1/n$ | 0.356 | 0.367 | 0.387 | 0.416 |
| | $K_F$ (mg/g)(dm³/mg)$^{1/n}$ | 9.37 | 9.25 | 9.52 | 9.23 |
| | $r^2$ | 0.977 | 0.986 | 0.960 | 0.985 |
| Redlich-Peterson | g | 0.824 | 0.764 | 0.903 | 0.719 |
| | $B$ (dm³/mg)$^g$ | 1.30 | 1.90 | 0.623 | 1.77 |
| | $A$ (dm³/g) | 21.0 | 26.2 | 14.1 | 24.7 |
| | $r^2$ | 0.999 | 0.998 | 0.993 | 0.992 |



Fig. 7. Freundlich isotherm for the lower equilibrium concentration range of the sorption of lead(II) onto peat at various temperatures.
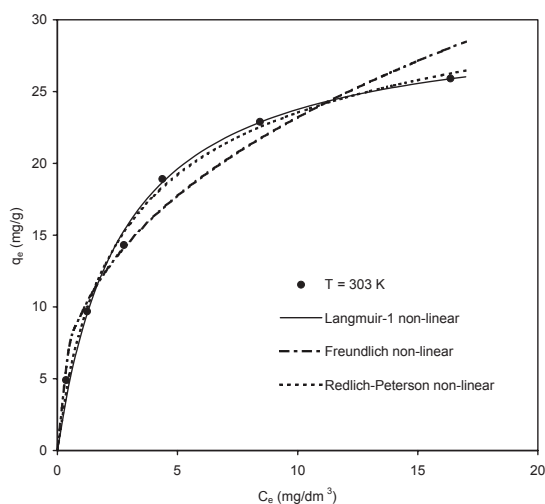
highest coefficient of determination for any Langmuir isotherm (Tables 2 and 3). It seems that the best fit was obtained by Langmuir-1 as compared with other Langmuir linear equations because it had the highest coefficient of determination and because the Langmuir constants $K_a$ and $q_m$ were both closer to those obtained using the non-linear method. Figure 8 shows that the Redlich-Peterson and Langmuir isotherms differed, but with similar coefficients of determination, they seemed to be the best-fitting models for the experiment results (Table 3). It has been reported that it is inappropriate to use the coefficient of determination of a linear regression analysis for comparing the best-fitting solution of different isotherms [3]. Linear regression has produced very different outcomes. Consequently, the Redlich-Peterson isotherm was found to be the most-suitable model for this sorption system. The Langmuir isotherm was also considered to be a suitable model with a high coefficient of determination. Unlike the
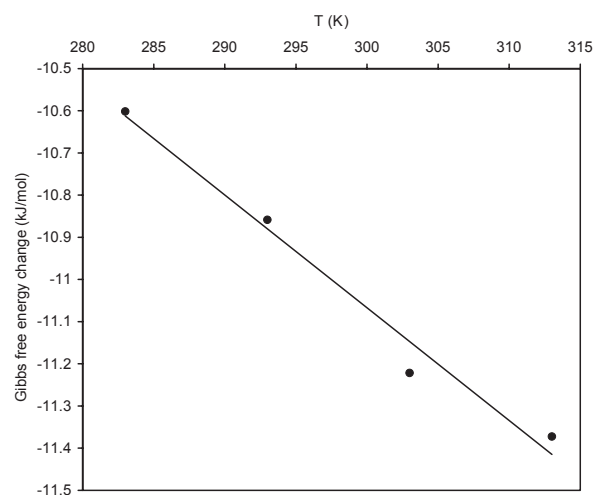


Fig. 8. Isotherms obtained using the non-linear method for the sorption of lead(II) onto peat at a temperature of 303 K.



Fig. 9. Plot of Gibbs free energy change, ΔG°, versus temperature, T.

linear analysis, a different isotherm would significantly affect the $r^2$ value and impact the final determination of parameters, where use of the non-linear method would avoid such errors.

## Thermodynamic Parameters

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, $\Delta G°$, is the fundamental criterion of spontaneity. Reactions occur spontaneously at a given temperature if $\Delta G°$ is a negative value. The thermodynamic parameters of $\Delta G°$, enthalpy change, $\Delta H°$, and entropy change, $\Delta S°$, for the adsorption processes are calculated using the following equations:

$$\Delta G° = - RT \ln K_a \qquad (2)$$

and

$$\Delta G° = \Delta H° - T\Delta S° \qquad (3)$$

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

A plot of $\Delta G°$ obtained using $K_a$ of Langmuir-1 versus temperature, $T$, was found to be linear (Fig. 9). The values of $\Delta H°$ and $\Delta S°$ were respectively determined from the slope and intercept of the plots. The thermodynamic parameter, $\Delta G°$, is shown in Table 2. $\Delta H°$ and $\Delta S°$ for the sorption process were calculated to be –3.04 kJ/mol and 26.8 J/mol K, respectively. The negative value of $\Delta G°$ confirms the feasibility of the process and the spontaneous nature of sorption with a high preference for lead(II) to sorb onto peat. The value of $\Delta H°$ was negative, indicating that the sorption reaction is exothermic. However the sorption capacity of lead(II) slightly increased with increasing temperature. A negative $\Delta H°$ was also reported for the sorption of lead(II) onto china clay, wollastonite [9], and bentonite [10]. The positive value of $\Delta S°$ shows the increasing randomness at the solid/liquid interface during the sorption of lead ions onto peat.

## Conclusions

It is not appropriate to use the coefficient of determination of the linear regression method for comparing the best-fitting isotherms. The non-linear method is a better way to obtain the isotherm parameters. Langmuir-1 is the most-popular linear form which had the highest coefficient of determination compared with other Langmuir linear equations. Both the two-parameter Langmuir and the three-parameter Redlich-Peterson isotherms had higher values for the coefficient of determination for the sorption of lead ion onto peat. The Freundlich isotherm can be applied in two separate regions of equilibrium concentrations. Thermodynamic parameters shows that the sorption of lead onto peat is spontaneous nature and exothermic.

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