

# EQUILIBRIUM ISOTHERM STUDIES FOR THE SORPTION OF DIVALENT METAL IONS ONTO PEAT: COPPER, NICKEL AND LEAD SINGLE COMPONENT SYSTEMS

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**Abstract.** The sorption of three divalent metal ions – copper, nickel and lead – from aqueous solution onto peat in single component systems has been studied and the equilibrium isotherms determined. The experimental data have been analysed using the Langmuir, Freundlich, Redlich-Peterson, Toth, Temkin, Dubinin-Radushkevich and Sips isotherm models. In order to determine the best fit isotherm for each system, six error analysis methods were used to evaluate the data: the coefficient of determination, the sum of the errors squared, a hybrid error function, Marquardt's percent standard deviation, the average relative error and the sum of absolute errors. The error values demonstrated that the Sips equation provided the best model for the three sets of experimental data overall.

**Keywords:** copper, isotherm, lead, nickel, peat, sorption

## Nomenclature

- $a_F$  Freundlich isotherm constant;  
 $A_t$  Temkin isotherm constant,  $\text{dm}^3 \text{mmol}^{-1}$ ;  
 $a_L$  Langmuir isotherm constant,  $\text{dm}^3 \text{mmol}^{-1}$ ;  
 $a_{LF}$  Langmuir-Freundlich isotherm constant ;  
 $a_R$  Redlich-Peterson isotherm constant,  $(\text{dm}^3 \text{mmol}^{-1})^{b_R}$ ;  
 $a_S$  Sips isotherm constant;  
 $a_t$  Toth isotherm constant;  
 $B_D$  Dubinin-Radushkevich isotherm constant;  
 $b_T$  Temkin isotherm constant;  
 $b_R$  Redlich-Peterson isotherm exponent;  
 $C_e$  Solution phase metal ion concentration at equilibrium,  $\text{mmol dm}^{-3}$ ;  
 $E$  Mean free energy of sorption,  $\text{kJ mol}^{-1}$ ;  
 $K_L$  Langmuir isotherm constant,  $\text{dm}^3 \text{g}^{-1}$ ;  
 $K_{LF}$  Langmuir-Freundlich isotherm constant;  
 $K_R$  Redlich-Peterson isotherm constant,  $\text{dm}^3 \text{g}^{-1}$ ;



$K_t$	Toth isotherm constant;
$k_a$	Rate constant of adsorption ;
$k_d$	Rate constant of desorption;
$n_{LF}$	Langmuir-Freundlich isotherm exponent (-);
$n_S$	Sips isotherm exponent (-);
$q_d$	Dubinin-Radushkevich isotherm constant, mmol g <sup>-1</sup> ;
$q_e$	Solid phase metal ion concentration at equilibrium, mmol g <sup>-1</sup> ;
$q_m$	Langmuir monolayer saturation capacity, mmol g <sup>-1</sup> ;
$R$	Universal gas constant, 8.314 J/mol °K;
$R^2$	Statistical linear coefficient of determination (the square of the correlation coefficient, R); (-);
$T$	Absolute temperature, °K;
$t$	Toth isotherm exponent (-).

#### Greek letters

$\theta$	Fractional surface coverage (-).
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## 1. Introduction

It is now widely recognised that sorption processes provide a feasible technique for the removal of pollutants from wastewaters (McKay, 1995). The problems associated with metal ions discharged in industrial effluents are considerable, due to both their toxic and carcinogenic properties (Luckey and Venugopal, 1977; Goldstein, 1990; Freedman *et al.*, 1990). Furthermore, metal ion containing effluents are discharged from a wide range of industries, including microelectronics, electroplating, battery manufacture, dyestuffs, chemical, pharmaceutical, metallurgical and many others (Tchobanoglous and Burton, 1991; Volesky and Holan, 1995).

There is a continuing search for cheap, high capacity sorbents for metal ions because the relatively high cost of commercial sorbents such as activated carbon (Macias-Garcia *et al.*, 1993; Sasaki *et al.*, 1995; Meyer and Lieser, 1995) and ion-exchange resins (Bolto and Pawlowski, 1987) remains a major obstacle to the use of sorption processes.

Many agricultural waste products and byproducts of cellulosic origin have been tested for metal ion adsorption (Randall *et al.*, 1975; Kumar and Dara, 1981; Shukla and Sakhardande, 1991).

Several workers have studied the removal of lead by sorption processes, including the sorption of lead onto waste tea leaves (Tan and Abd. Rahman, 1988), the sorption of lead onto china clay and wollastonite (Yadava *et al.*, 1991), onto

modified groundnut (*Arachi hypogea*) husks (Okieimen *et al.*, 1991), and bagasse pith from the sugar cane industry (Aly and Daifullah, 1998). However, there is very limited accurate data available in the literature for the design of sorption systems for the removal of lead ions. The removal of copper from effluents has been studied using many sorbent materials such as biomass (Roa *et al.*, 1993; Volesky and May-Phillips, 1995), kaolinite (Spark *et al.*, 1995), dry hyacinth roots (Low *et al.*, 1994) and seafood shell waste (Findon *et al.*, 1993). In a recent review paper over one hundred copper-sorbent systems were reported (McKay *et al.*, 1999).

There is very little detailed information in the literature based on nickel removal by sorption. Coconut coir has a limited capacity (Baes *et al.*, 1996), sewage sludge has been utilised (Gao *et al.*, 1997) and various peats have been tested (Bunzl *et al.*, 1976; Zhipei *et al.*, 1984; Gosset *et al.*, 1986; Ho *et al.*, 1995; McKay *et al.*, 1998).

Sorption equilibria provide fundamental physicochemical data for evaluating the applicability of sorption processes as a unit operation. Sorption equilibrium is usually described by an isotherm equation whose parameters express the surface properties and affinity of the sorbent, at a fixed temperature and pH. Thus an accurate mathematical description of the equilibrium isotherm, preferably based on a correct sorption mechanism, is essential to the effective design of sorption systems.

Until relatively recently, for most two parameter isotherms, the accuracy of the fit of an isotherm model to experimental equilibrium data was typically assessed based on the magnitude of the coefficient of determination for the linear regression. I.e., the isotherm giving an  $R^2$  value closest to unity was deemed to provide the best fit. Such transformations of non-linear isotherm equations to linear forms implicitly alter their error structure and may also violate the error variance and normality assumptions of standard least squares (Myers, 1990; Ratkowski, 1990). Previous observations of bias resulting from deriving isotherm parameters from linear forms of isotherm equations – namely Freundlich parameters producing isotherms which tend to fit experimental data better at low concentrations and Langmuir isotherms tending to fit the data better at higher concentrations (Richter *et al.*, 1989) – appear to support this hypothesis.

Non-linear optimisation provides a more complex, yet mathematically rigorous, method for determining isotherm parameter values (Seidel and Gelbin, 1988; Seidel-Morgenstern and Guiochon, 1993; Malek and Farooq, 1996; Khan *et al.*, 1997), but still requires an error function assessment, in order to evaluate the fit of the isotherm to the experimental results.

In this study, five different non-linear error functions were examined and in each case the isotherm parameters were determined by minimising the respective error function across the concentration range studied using the *solver* add-in with Microsoft's spreadsheet, Excel (Microsoft, 1995). Four two-parameter equations – the Freundlich, Langmuir, Temkin and Dubinin-Radushkevich isotherms – and three three-parameter equations – the Redlich-Peterson, Toth and Sips isotherms – were examined for their ability to model the equilibrium sorption data.

## 2. Equilibrium Isotherms

Equilibrium isotherm equations are used to describe experimental sorption data. The equation parameters and the underlying thermodynamic assumptions of these equilibrium models often provide some insight into both the sorption mechanism and the surface properties and affinity of the sorbent. The symbols and coefficients used in the equations are defined in the Nomenclature section.

### 2.1. THE FREUNDLICH ISOTHERM

In 1906, Freundlich presented the earliest known sorption isotherm equation (Freundlich, 1906). This empirical model can be applied to nonideal sorption on heterogeneous surfaces as well as multilayer sorption and is expressed by the following equation:

$$q_e = a_F C_e^{b_F} . \quad (1)$$

The Freundlich isotherm has been derived by assuming an exponentially decaying sorption site energy distribution (Zeldowitsch, 1934). It is often criticised for lacking a fundamental thermodynamic basis since it does not reduce to Henry's law at low concentrations.

### 2.2. THE LANGMUIR ISOTHERM

In 1916 Langmuir developed a theoretical equilibrium isotherm relating the amount of gas sorbed on a surface to the pressure of the gas (Langmuir, 1916). The Langmuir model is probably the best known and most widely applied sorption isotherm. It has produced good agreement with a wide variety of experimental data and may be represented as follows:

$$q_e = \frac{q_m a_L C_e}{1 + a_L C_e} \quad \text{or, alternatively} \quad q_e = \frac{K_L C_e}{1 + a_L C_e} . \quad (2)$$

One can readily deduce that at low sorbate concentrations it effectively reduces a linear isotherm and thus follows Henry's law. Alternatively, at high sorbate concentrations, it predicts a constant – monolayer – sorption capacity.

### 2.3. THE REDLICH-PETERSON ISOTHERM

Jossens and co-workers modified the three parameter isotherm first proposed by Redlich and Peterson (1959) to incorporate features of both the Langmuir and Freundlich equations (Jossens *et al.*, 1978). It can be described as follows:

$$q_e = \frac{K_R C_e}{1 + a_R C_e^{b_R}} . \quad (3)$$

At low concentrations the Redlich-Peterson isotherm approximates to Henry's law and at high concentrations its behaviour approaches that of the Freundlich isotherm.

#### 2.4. THE TEMKIN ISOTHERM

The derivation of the Temkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic, as implied in the Freundlich equation (Aharoni and Ungarish, 1977). The Temkin isotherm has generally been applied in the following form (Aharoni and Sparks, 1991):

$$q_e = \frac{RT}{b_T} \ln(A_T C_e) . \quad (4)$$

#### 2.5. THE DUBININ-RADUSHKEVICH ISOTHERM

This isotherm is generally expressed as follows (Dubinin, 1960):

$$q_e = q_D \exp \left( -B_D \left[ RT \ln \left( 1 + \frac{1}{C_e} \right) \right]^2 \right) . \quad (5)$$

Radushkevich (1949) and Dubinin (1965) have reported that the characteristic sorption curve is related to the porous structure of the sorbent. The constant,  $B_D$ , is related to the mean free energy of sorption per mole of the sorbate as it is transferred to the surface of the solid from infinite distance in the solution and this energy can be computed using the following relationship (Hasany and Chaudhary, 1996):

$$E = \frac{1}{\sqrt{2B_D}} \quad (6)$$

#### 2.6. THE TOTH ISOTHERM

Derived from potential theory, this isotherm (Toth, 1962) has proven useful in describing sorption in heterogeneous systems such as phenolic compounds on carbon. It can be represented by the following equation:

$$q_e = \frac{K_t C_e}{(a_t + C_e)^{1/t}} \quad (7)$$

It assumes an asymmetrical quasi-Gaussian energy distribution with a widened left-hand side, i.e. most sites have a sorption energy less than the mean value.

## 2.7. THE SIPS, OR LANGMUIR-FREUNDLICH ISOTHERM (Sips, 1948)

Langmuir also considered the case of a molecule occupying two sites, e.g. for the dissociative sorption of hydrogen on platinum. In such cases a derivative of the original Langmuir isotherm can be determined assuming that the rates of adsorption and desorption are proportional to  $(1 - \theta)^2$  and  $\theta^2$ , respectively, where  $\theta$  is the fractional surface coverage. Therefore, the rate equation becomes:

$$\frac{d\theta}{dt} = k_a C (1 - \theta)^2 - k_d \theta^2 . \quad (8)$$

Generalising to  $m (= 1/n)$  sites and assuming equilibrium produces the Sips sorption isotherm:

$$q_e = \frac{q_m (a_s C_e)^{n_s}}{1 + (a_s C_e)^{n_s}} . \quad (9)$$

Or, in the Langmuir-Freundlich form:

$$q_e = \frac{K_{LF} C_e^{n_{LF}}}{1 + (a_{LF} C_e)^{n_{LF}}} . \quad (10)$$

The Langmuir-Freundlich name derives from the limiting behaviour of the equation. At low sorbate concentrations it effectively reduces to a Freundlich isotherm and thus does not obey Henry's law. At high sorbate concentrations, it predicts a monolayer sorption capacity characteristic of the Langmuir isotherm.

## 2.8. DETERMINING ISOTHERM PARAMETERS BY LINEARISATION

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 linear regression. The experimental results are shown in Figure 1 with the Langmuir and Freundlich linear regression curves.

Although a linear analysis is not possible for a three-parameter isotherm, a trial and error procedure has previously been applied to a pseudo-linear form of the Redlich-Peterson isotherm to obtain values for the isotherm constants (McKay *et al.*, 1984). The method is based on the following equation:

$$\ln \left( K_R \frac{C_e}{q_e} - 1 \right) = b_R \ln(C_e) + \ln(a_R) , \quad (11)$$

and involves varying the isotherm parameter,  $K_R$ , to obtain the maximum value of the correlation coefficient for the regression of against. Figure 2 shows the coefficient of determination,  $R^2$ , as a function of  $K_R$  for lead.

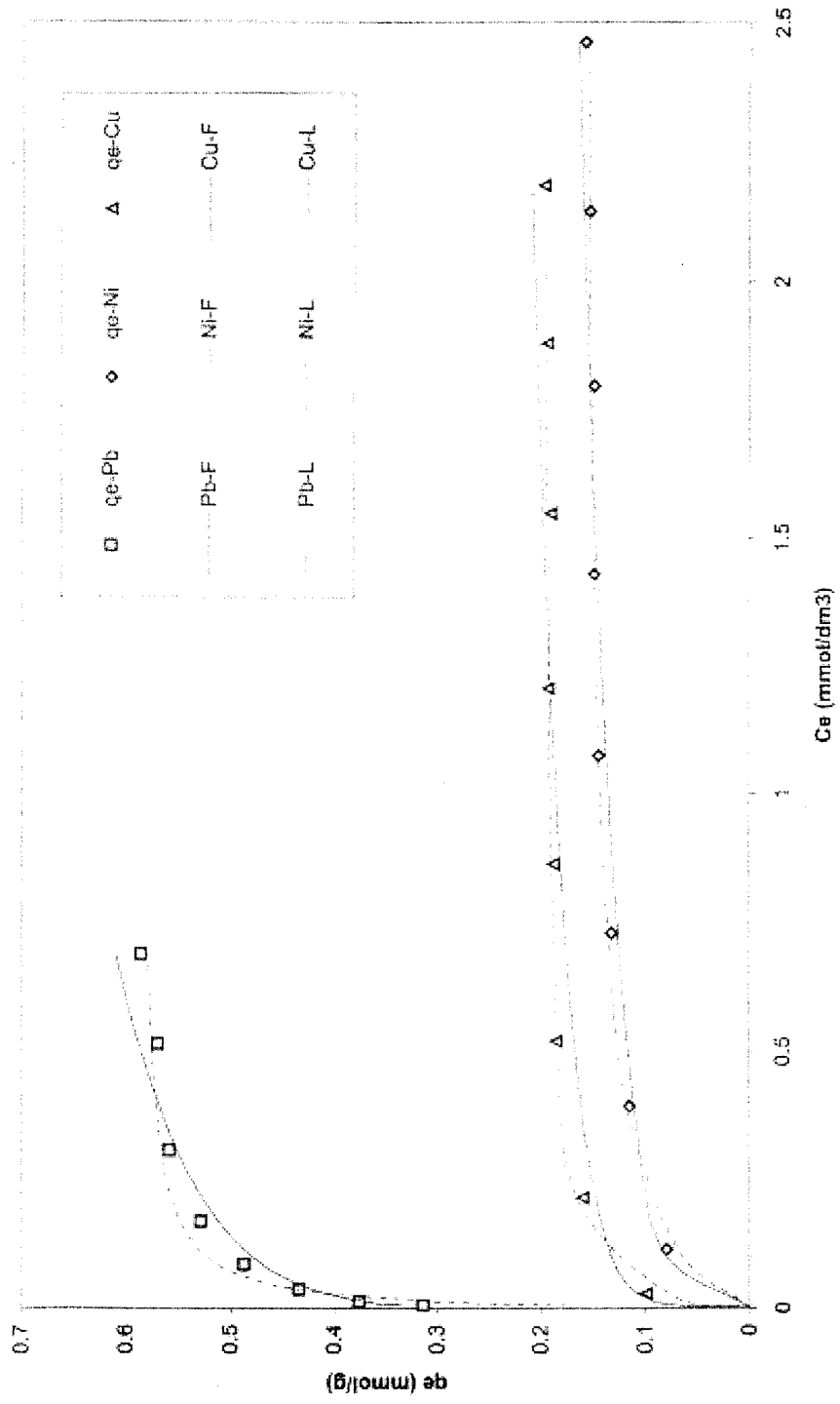


Figure 1. Linear Freundlich and Langmuir isotherms for lead, nickel and copper on peat.

TABLE I  
Isotherm constants for two-parameter models by linear regression

Isotherm	Transformed		Slope	Intercept
	X-values	Y-values		
Langmuir	$C_e$	$C_e/q_e$	$a_L/k_L$	$1/K_L$
Freundlich	$\text{Ln}(C_e)$	$\text{Ln}(q_e)$	$b_F$	$\text{Ln}(a_F)$
Temkin	$\text{Ln}(C_e)$	$q_e$	$R.T./b_T$	$R.T.\text{Ln}(A_T)/b_T$
Dubinin-Radushkevich	$(\text{Ln}(1 + 1/C_e))^2$	$\text{Ln}(q_e)$	$-B_D R^2 T^2$	$\text{Ln}(q_D)$

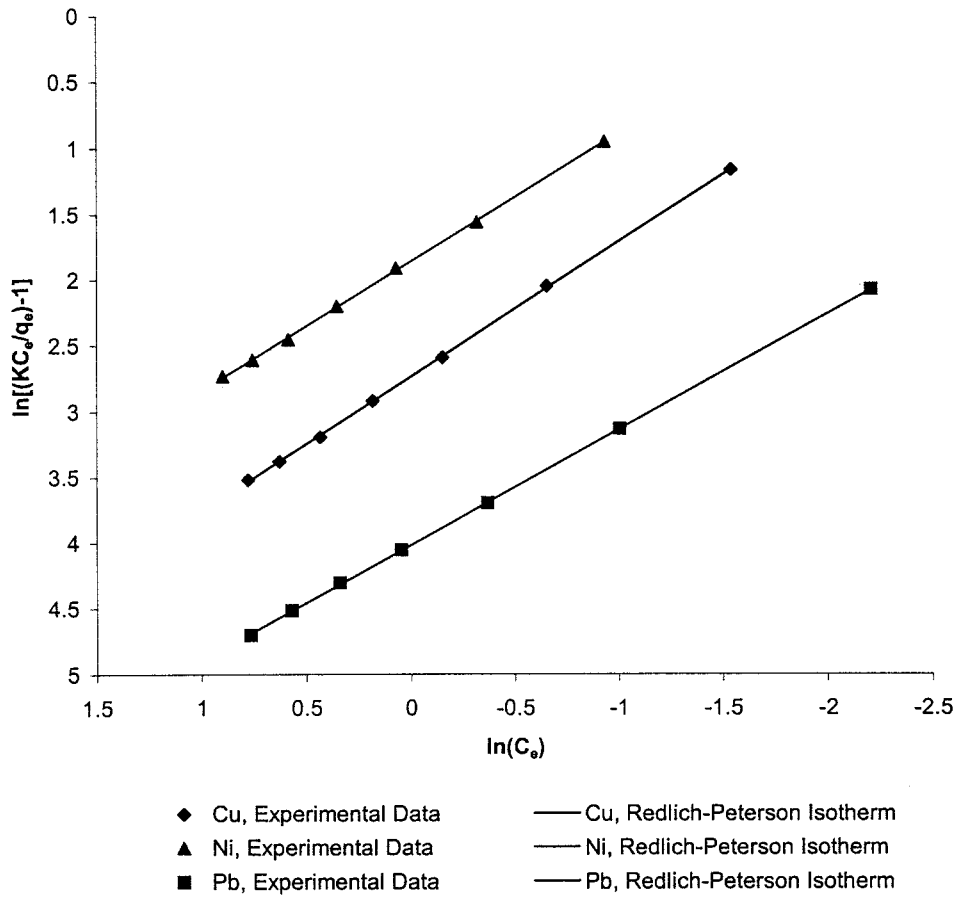


Figure 2. Redlich-Peterson equation isotherms of metal ions sorbed on peat.



## 2.9. DETERMINING ISOTHERM PARAMETERS BY NON-LINEAR REGRESSION

Due to the inherent bias resulting from linearisation, alternative isotherm parameter sets were determined by non-linear regression. This provides a mathematically rigorous method for determining isotherm parameters using the original form of the isotherm equation (Seidel and Gelbin, 1988; Seidel-Morgenstern and Guiochon, 1993; Malek and Farooq, 1996; Khan *et al.*, 1996). Most commonly, algorithms based on the Levenberg-Marquardt or Gauss-Newton methods (Edgar and Himmelblau, 1989; Hanna and Sandall, 1995) are used.

The optimisation procedure requires the selection of an error function in order to evaluate the fit of the isotherm to the experimental equilibrium data. The choice of error function can affect the parameters derived – error functions based primarily on absolute deviation bias the fit towards high concentration data and this weighting increases when the square of the deviation is used to penalise extreme errors. This bias can be offset partly by dividing the deviation by the measured value in order to emphasise the significance of fractional deviations.

In this study, five non-linear error functions were examined and in each case a set of isotherm parameters were determined by minimising the respective error function across the concentration range studied. The error functions employed were as follows:

1. The Sum of the Squares of the Errors (ERRSQ):

$$\sum_{i=1}^p (q_{e,meas} - q_{e,calc})_i^2 \quad (12)$$

2. A Composite Fractional Error Function (HYBRD):

$$\sum_{i=1}^p \left[ \frac{(q_{e,meas} - q_{e,calc})_i^2}{q_{e,meas}} \right]_i \quad (13)$$

3. A Derivative of Marquardt's Percent Standard Deviation (MPSD) (Marquardt, 1963):

$$\sum_{i=1}^p \left( \frac{q_{e,meas} - q_{e,calc}}{q_{e,meas}} \right)_i^2 \quad (14)$$

4. The Average Relative Error (ARE) (Kapoor and Yang, 1989):

$$\sum_{i=1}^p \left| \frac{q_{e,meas} - q_{e,calc}}{q_{e,meas}} \right|_i \quad (15)$$

### 5. The Sum of the Absolute Errors (EABS):

$$\sum_{i=1}^p |q_{e,meas} - q_{e,calc}|_i \cdot \quad (16)$$

As each of the error criteria is likely to produce a different set of isotherm parameters, an overall optimum parameter set is difficult to identify directly. Hence, in order to try to make a meaningful comparison between the parameter sets, a procedure of normalising and combining the error results was adopted producing a so-called 'sum of the normalised errors' for each parameter set for each isotherm. The calculation method for the 'sum of the normalised errors' was as follows:

- (a) select one isotherm and one error function and determine the isotherm parameters that minimise that error function for that isotherm to produce the isotherm parameter set for that error function;
- (b) determine the values for all the other error functions for that isotherm parameter set;
- (c) calculate all other parameter sets and all their associated error function values for that isotherm;
- (d) select each error measure in turn and ratio the value of that error measure for a given parameter set to the largest value of that error from all the parameter sets for that isotherm; and
- (e) sum all these normalised errors for each parameter set.

The parameter set thus providing the smallest normalised error sum can be considered to be optimal for that isotherm provided:

- There is no bias in the data sampling – i.e. the experimental data are evenly distributed, providing an approximately equal number of points in each concentration range; and
- There is no bias in the type of error methods selected.

## 3. Materials and Methods

### 3.1. ADSORBENT

The experiments were conducted with sphagnum moss peat sourced from New Zealand. The peat was washed and then dried at a temperature of  $105 \pm 5$  °C for 8 hr and finally screened to obtain a particle size range of 500–710  $\mu\text{m}$  before use.

TABLE II  
Metal concentrations in sphagnum peat moss

Metal	Concentration ( $\mu\text{g g}^{-1}$ of peat)	Metal	Concentration ( $\mu\text{g g}^{-1}$ of peat)
Iron	890	Cadmium	1.1
Aluminium	660	Potassium	<1
Sodium	285	Chromium	<1
Manganese	24	Copper	<1
Zinc	19	Mercury	<1
Lead	13.5	Silver	<1
Nickel	5.5	Zirconium	<1

### 3.2. ADSORBENT CHARACTERISATION

An elemental analysis was carried out on the peat and the results, on a dry mass basis, were: carbon, 57.2%; hydrogen 5.7%; oxygen 36.0%; nitrogen 0.7%; and sulphur, 0.4%. The BET (Brunnauer, Emmelt and Teller, nitrogen isotherm) surface area was determined to be  $26.5 \text{ m}^2 \text{ g}^{-1}$  and the pore volume  $0.73 \times 10^{-6} \text{ m}^3 \text{ g}^{-1}$ . The absolute density, measured in paraffin oil, was found to be  $1220 \text{ kg m}^{-3}$ .

The metal content of the peat was determined by digesting it by heating in nitric acid and filtering. The metal ion concentrations were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The results are shown in Table II.

### 3.3. REAGENTS

Analytical grade reagents supplied by Aldrich Chemicals were used in all experiments. Stock solutions of copper (II) sulphate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ), nickel (II) sulphate ( $\text{NiSO}_4 \cdot 5\text{H}_2\text{O}$ ) and lead (II) nitrate ( $\text{Pb}(\text{NO}_3)_2$ ) were prepared in deionised water. All solutions used in this study were diluted with deionised water as required.

### 3.4. EXPERIMENTAL SYSTEM

The sorption experiments for the three systems were carried out in a thermostatically controlled shaking water bath using capped  $0.125 \text{ dm}^3$  Erlenmeyer conical flasks maintained at  $25 \pm 1 \text{ }^\circ\text{C}$ . In the sorption isotherm tests,  $0.055 \text{ g}$  of peat was thoroughly mixed with  $0.1 \text{ dm}^3$  of the metal ion solution. The concentration ranges studied for each system are shown in Table III.

As previous contact time studies indicated equilibrium was reached in two hours under similar experimental conditions (Allen, 1987; Ho *et al.*, 1994, 1995), the mixtures were agitated for three hours to ensure that equilibrium was achieved.

TABLE III  
Sorption systems studied

Metal	Mass of peat (g)	Test solution volume (dm <sup>3</sup> )	Metal concentration range (mg dm <sup>-3</sup> )
Pb	0.055	0.100	35–210
Cu	0.055	0.100	5–150
Ni	0.055	0.100	10–150

TABLE IV  
Final pH values at various initial metal ion concentrations

Initial concentrations (C <sub>o</sub> mg dm <sup>-3</sup> )	25	50	75	100	150	200	209	250	300	309	410	504
Copper solutions	3.60	3.50	3.40	3.30	3.20	3.15		3.10	3.05			
Nickel solutions	3.60	3.45	3.40	3.35	3.30	3.25		3.22	3.22			
Lead solutions				5.38			5.19			4.80	4.63	4.42

At the end of the experiment, the samples were filtered (Whatman No. 1) and the filtrates were analysed for the respective metal ion concentrations using ICP-AES. The initial and final solution pH values were measured. Initial pH values were set at  $4.50 \pm 0.10$  and final pH values appeared to show some variation with initial solution concentration. The values are given in Table IV.

Although significant pH changes were observed for several of the systems, none resulted in precipitation (Ho, 1995).

## 4. Results and Discussion

### 4.1. THE FREUNDLICH ISOTHERM

The linear Freundlich isotherm plots for the sorption of the three metals onto peat are presented in Figure 3. Examination of the plot suggests that the linear Freundlich isotherm is a good model for the sorption of lead but not for nickel or copper. Table V shows the linear Freundlich sorption isotherm constants, coefficients of determination ( $R^2$ ) and error values.

Based on the  $R^2$  values, the linear form of the Freundlich isotherm appears to produce a reasonable model for sorption in all three systems, with the lead and

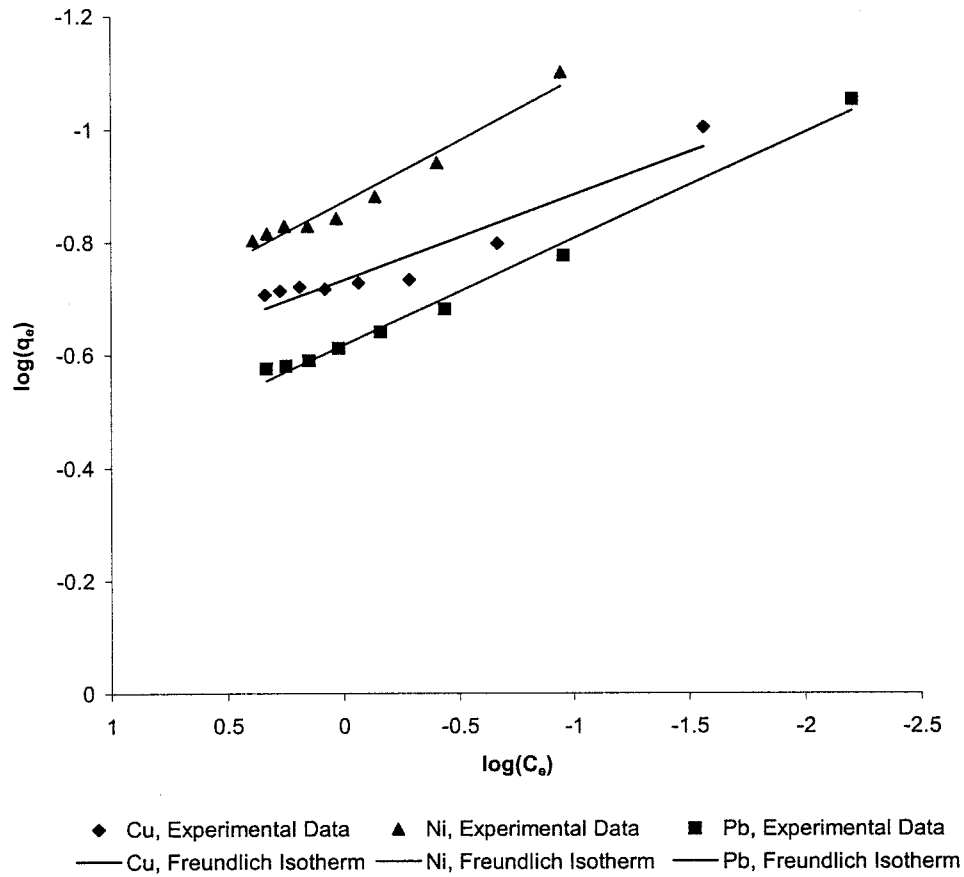


Figure 3. Freundlich equation isotherms of metal ions sorbed on peat.

TABLE V  
 Linear Freundlich isotherm parameters

	Lead	Nickel	Copper
Freundlich: $a_F$	0.639589	0.135100	0.185859
Freundlich: $b_F$	0.125618	0.215808	0.150492
Correlation coefficient $R^2$	0.972028	0.961755	0.915671
Sum of errors <sup>2</sup>	0.002143	0.000233	0.000871
Hybrid error function	0.004477	0.001755	0.005069
Marquardt's PSD	0.009927	0.013889	0.030982
Average relative error	0.260984	0.321260	0.450704
Sum of absolute errors	0.122768	0.041996	0.076003

nickel isotherms seeming to fit the experimental data better than copper. The error function values do not support this assertion, however.

The Freundlich isotherm constants determined by non-linear regression are shown in Table VI. The results demonstrate that the values of the constants –  $b_F$  and especially  $a_F$  – obtained by non-linear regression are remarkably consistent and quite similar to the linear transform values from Table V.

In each case the MPSD parameters are closest to those obtained by linearisation, typically within 2%, and these provide either the second or third best fit to the experimental data, based on the sum of the normalised errors. On this basis it would thus seem that the linear Freundlich model does give a reasonable approximation to the optimum parameter set found by non-linear regression. The minimum error occurs for the constants determined using the HYBRD error measure in the cases of copper and nickel and those determined using the ERRSQ measure for lead. The values for most error measures suggest that the Freundlich isotherm produces a better fit to the nickel data than it does for lead or copper.

#### 4.2. THE LANGMUIR ISOTHERM

The sorption data were analysed according to the linear form of the Langmuir isotherm. The plots of specific sorption ( $C_e/q_e$ ) against the equilibrium concentration ( $C_e$ ) for copper, nickel and lead are shown in Figure 4 and the linear isotherm constants –  $a_L$ ,  $q_m$ ,  $K_L$  – and the error values are presented in Table VII. These isotherms were found to be linear over the whole concentration range studied with extremely high coefficients of determination (Table VII). The  $R^2$  values suggest that the Langmuir isotherm provides a good model of the sorption system. The sorption constant,  $K_L$ , and sorption capacity,  $q_m$ , for lead are higher than those for copper and nickel. The same sorption capacity order has been reported for metal cation sorption on a modified coconut coir as  $\text{Pb(II)} > \text{Cu(II)} > \text{Ni(II)}$  although the order of  $K_L$  was given as  $\text{Cu(II)} > \text{Pb(II)} > \text{Ni(II)}$  and this was interpreted as meaning that not all inorganic sites may be available for copper(II) binding (Baes *et al.*, 1996).

The Langmuir data from the other five error analysis methods are presented in Table VIII. The individual constants,  $K_L$  and  $a_L$ , are significantly different, although the ratios give monolayer saturation capacities very close to those obtained by the linear error analysis approach.

In all cases, all the error values for any parameter set are lower than the same errors determined for the linear form of the isotherm. The only parameter values that are even close to those obtained by linearisation are the EABS set for nickel. Considering the comparative magnitudes of the error values together with the range of variation in the isotherm parameters suggests that the Langmuir isotherm does not provide a particularly good model for the sorption of lead on peat. Lastly, the HYBRD parameter set produces the best overall fit for both nickel and lead whereas

TABLE VI  
Non-linear Freundlich isotherm parameters

	Method/error function (parameter set)				
	ERRSQ	HYBRD	MPSD	ARE	EABS
Copper					
Freundlich: $a_F$	0.185265	0.185031	0.184987	0.179765	0.185279
Freundlich: $b_F$	0.131816	0.143146	0.152419	0.163444	0.094257
Sum of errors <sup>2</sup>	<b>0.000736</b>	0.000776	0.000864	0.001272	0.001215
Hybrid error function	0.005108	<b>0.004780</b>	0.004981	0.007168	0.011342
Marquardt's PSD	0.038883	0.031566	<b>0.029834</b>	0.040634	0.109226
Average relative error	0.430381	0.427924	0.427502	<b>0.416427</b>	0.449630
Sum of absolute errors	0.066189	0.069557	0.072452	0.075044	<b>0.056134</b>
Sum of normalised errors	3.224603	<b>3.199412</b>	3.307742	3.930186	4.703244
Nickel					
Freundlich: $a_F$	0.135381	0.134985	0.13476	0.135255	0.135255
Freundlich: $b_F$	0.198179	0.208052	0.216674	0.172131	0.172112
Sum of errors <sup>2</sup>	<b>0.000204</b>	0.000214	0.000236	0.000274	0.000275
Hybrid error function	0.001792	<b>0.001700</b>	0.001765	0.002874	0.002875
Marquardt's PSD	0.017113	0.014508	<b>0.013829</b>	0.032076	0.032092
Average relative error	0.308700	0.31496	0.321143	<b>0.292270</b>	0.292274
Sum of absolute errors	0.037656	0.039998	0.042113	0.031409	<b>0.031406</b>
Sum of normalised errors	3.756599	<b>3.751730</b>	3.903084	4.654606	4.655863
Lead					
Freundlich: $a_F$	0.630586	0.634548	0.638871	0.647390	0.642898
Freundlich: $b_F$	0.118623	0.122366	0.125919	0.124467	0.118531
Sum of errors <sup>2</sup>	<b>0.001936</b>	0.001994	0.002156	0.002558	0.002684
Hybrid error function	0.004517	<b>0.004367</b>	0.004493	0.005369	0.006278
Marquardt's PSD	0.011321	0.010217	<b>0.009897</b>	0.012227	0.016016
Average relative error	0.242862	0.254818	0.264773	<b>0.232601</b>	0.246093
Sum of absolute errors	0.110567	0.118135	0.124669	0.109142	<b>0.108842</b>
Sum of normalised errors	<b>3.951712</b>	3.986851	4.136891	4.325719	4.802496

the EABS produces the best fit for copper based on the sum of the normalised errors.

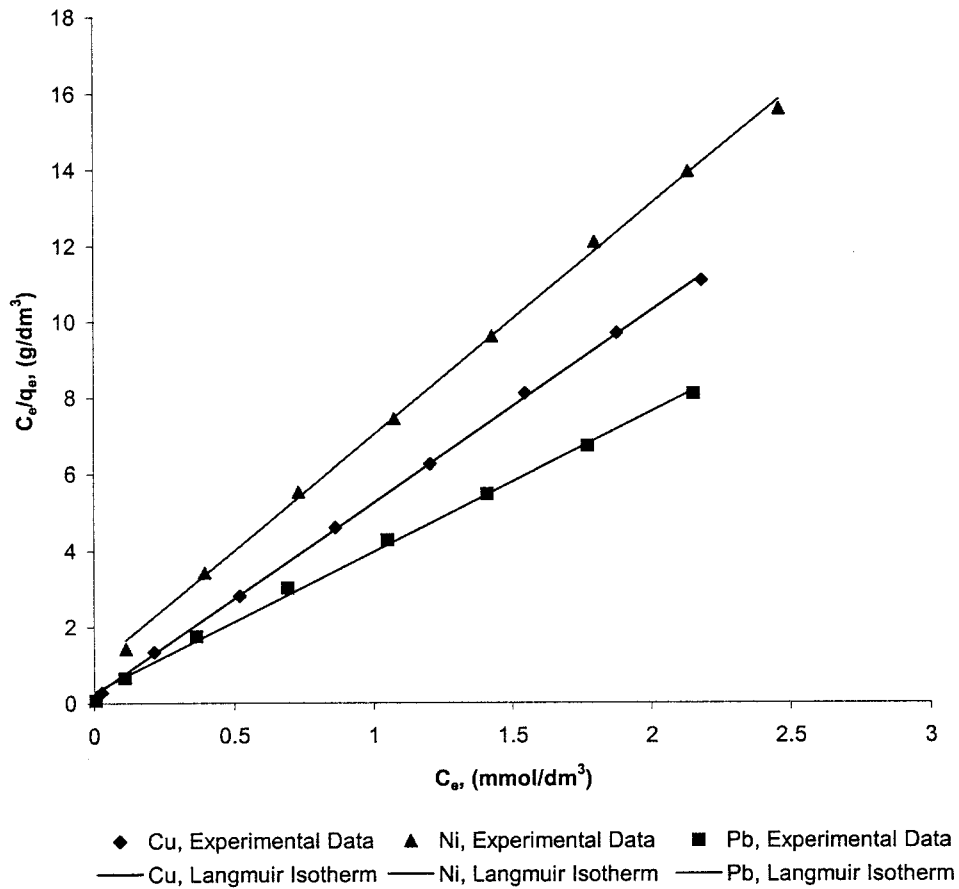


Figure 4. Langmuir equation isotherms of metal ions sorbed on peat.

TABLE VII  
 Linear Langmuir isotherm parameters

	Lead	Nickel	Copper
Langmuir: $K_L$ ( $\text{dm}^3 \text{g}^{-1}$ )	45.75918	1.035939	4.652902
Langmuir: $a_L$ ( $\text{dm}^3 \text{mmol}^{-1}$ )	77.53212	6.260953	23.34904
Saturation capacity: $q_m$	0.590197	0.165460	0.199276
Coefficient of determination, $R^2$	0.999392	0.998830	0.999640
Sum of errors <sup>2</sup>	0.026728	0.000160	0.000550
Hybrid error function	0.080102	0.001823	0.005296
YMarquardt's PSD	0.242729	0.021504	0.051826
Average relative error	0.784015	0.232811	0.309219
Sum of absolute errors	0.286497	0.023962	0.037545



TABLE VIII  
Non-linear Langmuir isotherm parameters

	Method/error function (parameter set)				
	ERRSQ	HYBRD	MPSD	ARE	EABS
Copper					
Langmuir: $K_L$	6.84352	7.10994	7.28845	7.49222	7.29922
Langmuir: $a_L$	35.0648	36.5389	37.5613	38.3845	37.3742
Saturation capacity: $q_m$	0.195168	0.194585	0.194041	0.195189	0.195301
Sum of errors <sup>2</sup>	<b>0.000194</b>	0.000198	0.000205	0.000217	0.000207
Hybrid error function	0.001250	<b>0.001217</b>	0.001233	0.001323	0.001266
Marquardt's PSD	0.008370	0.007648	<b>0.007511</b>	0.008101	0.007805
Average relative error	0.170779	0.163665	0.161987	<b>0.130987</b>	0.139412
Sum of absolute errors	0.026442	0.026625	0.027298	0.02309	<b>0.02254</b>
Sum of normalised errors	4.808365	4.679145	4.723174	4.580714	<b>4.48369</b>
Nickel					
Langmuir: $K_L$	1.22088	1.27775	1.32445	1.40764	1.15011
Langmuir: $a_L$	7.55792	7.96428	8.30854	8.80566	7.02848
Saturation capacity: $q_m$	0.161537	0.160435	0.159408	0.159856	0.163636
Sum of errors <sup>2</sup>	<b>0.000109</b>	0.000113	0.000122	0.000148	0.000119
Hybrid error function	0.000967	<b>0.000925</b>	0.000953	0.001167	0.001171
Marquardt's PSD	0.009183	0.008006	<b>0.007720</b>	0.009351	0.012281
Average relative error	0.210910	0.206782	0.20498	<b>0.181438</b>	0.210351
Sum of absolute errors	0.024842	0.025414	0.026105	0.023992	<b>0.023133</b>
Sum of normalised errors	4.260104	<b>4.158057</b>	4.239416	4.537514	4.687898
Lead					
Langmuir: $K_L$	100.5017	107.7296	114.5102	91.47266	88.29985
Langmuir: $a_L$	181.1768	196.1349	210.7899	165.1662	154.6331
Saturation capacity: $q_m$	0.554716	0.549263	0.543243	0.553822	0.571028
Sum of errors <sup>2</sup>	<b>0.006893</b>	0.007061	0.007561	0.007247	0.008019
Hybrid error function	0.015684	<b>0.015278</b>	0.015648	0.017421	0.019851
Marquardt's PSD	0.037471	0.034543	<b>0.033672</b>	0.044517	0.051284
Average relative error	0.465177	0.465526	0.466953	<b>0.456389</b>	0.463050
Sum of absolute errors	0.208822	0.213802	0.219476	0.201928	<b>0.196249</b>
Sum of normalised errors	4.327903	<b>4.294782</b>	4.387715	4.546698	4.885809

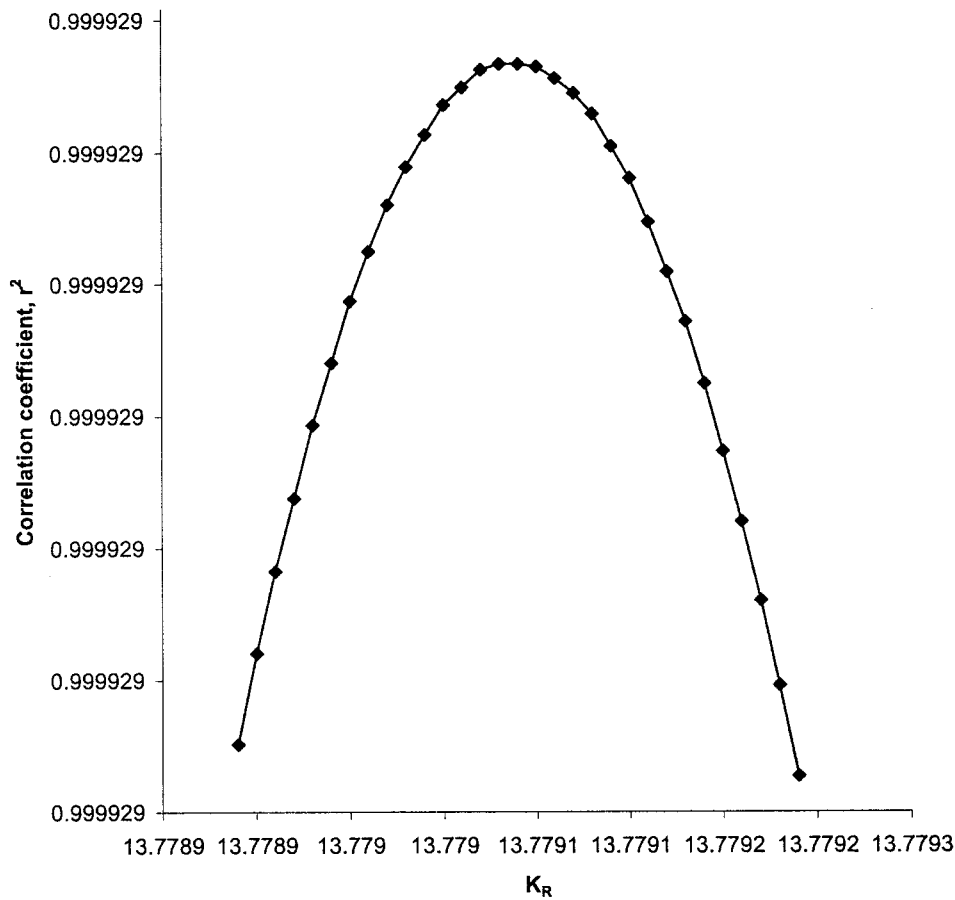


Figure 5. The coefficient of determination as function of  $K_R$  for sorption of lead onto peat.

#### 4.3. THE REDLICH-PETERSON ISOTHERM

The Redlich-Peterson isotherm plots for sorption of the three metals onto peat are presented in Figure 2. Examination of the plot shows that the Redlich-Peterson isotherm accurately describes the sorption behaviour of copper, nickel and lead on peat over the concentration ranges studied. The Redlich-Peterson isotherm constants –  $K_R$ ,  $a_R$  and  $b_R$  – and the coefficients of determination are presented in Table IX. Since the method used to derive the isotherm parameters maximises the linear correlation coefficient, it is unsurprising that in all cases the Redlich-Peterson isotherms exhibit extremely high  $R^2$  values – indicating, superficially at least, that it produces a considerably better fit compared to the preceding two parameter isotherms. Figure 5 shows the coefficient of determination,  $R^2$ , as a function of  $K_R$  for lead.

TABLE IX  
 'Linear' Redlich-Peterson isotherm parameters

	Lead	Nickel	Copper
R-P: $K_R$	288.6086	2.027348	9.475487
R-P: $a_R$	470.4830	13.55103	49.22798
R-P: $b_R$	0.913060	0.906189	0.952612
Coefficient of determination, $R^2$	0.999939	0.999716	0.999821
Sum of errors <sup>2</sup>	0.00029589	3.02328E-05	7.17191E-05
Hybrid error function	0.00055725	0.00021183	0.00039820
Marquardt's PSD	0.00106101	0.00149554	0.00222289
Average relative error	0.07899636	0.08610689	0.10518300
Sum of absolute errors	0.04095156	0.01209342	0.01903796

The non-linear error analyses are shown in Table X. Similar to the non-linear Freundlich analysis, the Redlich-Peterson isotherm constants are very consistent across the range of error methods and the actual parameter values derived by non-linear regression are very close to those obtained using the linear analysis – particularly those determined using the MPSD error measure. In several cases the error values determined by non-linear regression are greater than those for the linear isotherm parameters. This indicates that the linear equation analysis method may be a suitable approach to use for this three parameter isotherm.

The lowest sums of normalised errors are obtained using the EABS parameter set for copper and nickel and the HYBRD parameter set for lead.

#### 4.4. THE TEMKIN ISOTHERM

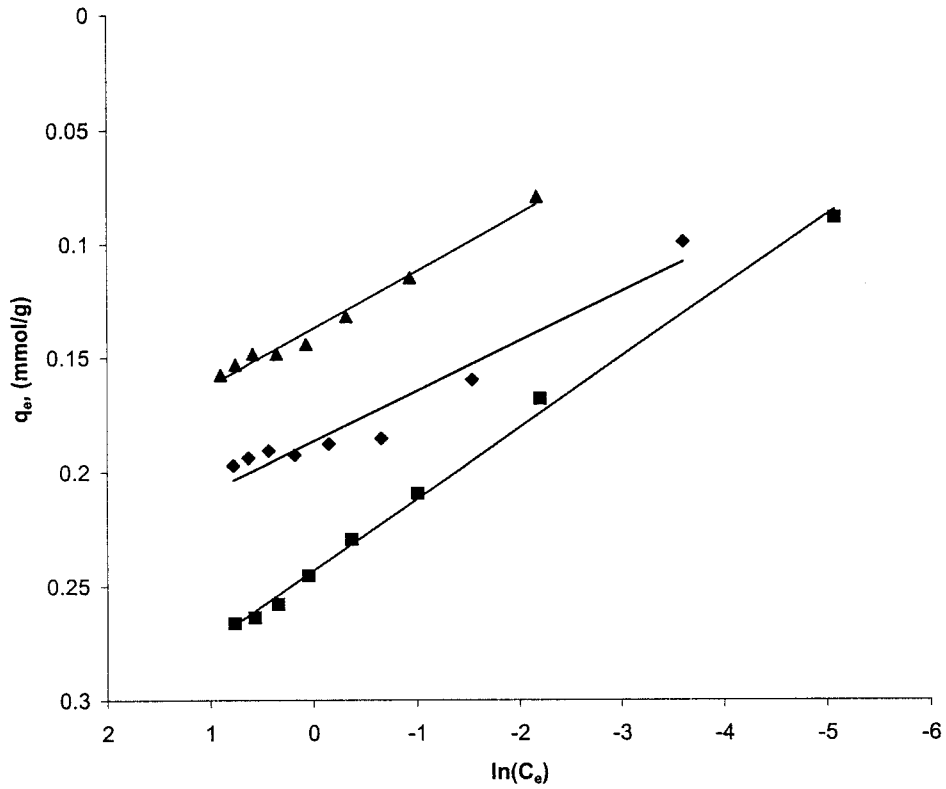
The sorption data were analysed according to the linear form of the Temkin isotherm and the linear plots are shown in Figure 6. Examination of the data shows that the Temkin isotherm provides a close fit to the lead and nickel sorption data, but the copper experimental data are not modelled as well across the concentration range studied. The linear isotherm constants and coefficients of determination are presented in Table XI and the non-linear error analyses are shown in Table XII.

Excepting the EABS parameter set for copper, the non-linear analysis methods show the  $A_T$  parameter to be quite consistent and comparable with the values derived by linearisation. The non-linear  $b_T$  parameters are less consistent, particularly for copper. For all three metals the ERRSQ parameter sets are within 1% of the linear values for this isotherm and it is quite interesting to notice that several non-linear parameter sets result in worse errors than the linear set – possibly indicating that, in this case, the linearisation method has little effect on the error assumptions

TABLE X  
Non-linear Redlich-Peterson isotherm parameters

	Method/error function (parameter set)				
	ERRSQ	HYBRD	MPSD	ARE	EABS
Copper on peat					
Redlich-Peterson: $K_R$	9.12546	9.32887	9.49796	9.22545	9.22574
Redlich-Peterson: $a_R$	47.3294	48.4361	49.3592	47.8311	47.8328
Redlich-Peterson: $b_R$	0.95609	0.953872	0.951802	0.957427	0.957424
Sum of errors <sup>2</sup>	<b>5.87048E-05</b>	5.90988E-05	6.01127E-05	5.96449E-05	5.96443E-05
Hybrid error function	0.000337	<b>0.000334</b>	0.000336	0.000344	0.000344
Marquardt's PSD	0.001957	0.001906	<b>0.001893</b>	0.001998	0.001997
Average relative error	0.087120	0.085894	0.085851	<b>0.079263</b>	0.079269
Sum of absolute errors	0.014915	0.015042	0.015273	0.013999	<b>0.013999</b>
Sum of normalised errors	4.912457	4.879921	4.910657	4.818668	<b>4.818586</b>
Nickel on peat					
Redlich-Peterson: $K_R$	1.89294	1.95122	2.00198	2.06997	2.06995
Redlich-Peterson: $a_R$	12.5524	12.9865	13.3663	13.8559	13.8558
Redlich-Peterson: $b_R$	0.915323	0.911438	0.907896	0.903325	0.903326
Sum of errors <sup>2</sup>	<b>2.92544E-05</b>	2.94452E-05	2.99284E-05	3.10E-05	3.10E-05
Hybrid error function	0.000210914	<b>0.000209141</b>	0.000210419	2.16229E-04	2.1601E-04
Marquardt's PSD	0.001549	0.001504	<b>0.00149255</b>	0.001519	0.001519
Average relative error	0.097286	0.092130	0.087992	<b>0.083206</b>	0.083208
Sum of absolute errors	0.013145	0.012672	0.012272	0.011821	<b>0.011820</b>
Sum of normalised errors	4.919283	4.798940	4.740070	4.734614	<b>4.734610</b>
Lead on peat					
Redlich-Peterson: $K_R$	265.5835	276.3955	285.7632	302.5026	271.9999
Redlich-Peterson: $a_R$	434.5717	451.5460	466.1403	498.4159	448.7846
Redlich-Peterson: $b_R$	0.916566	0.914918	0.913461	0.913740	0.918845
Sum of errors <sup>2</sup>	0.000283423	0.000286278	0.000293306	0.000438201	0.00033956
Hybrid error function	0.000556362	0.000549559	0.000554329	0.000818418	0.000662247
Marquardt's PSD	0.001115482	0.001071412	0.001060007	0.001533878	0.001308956
Average relative error	0.081038781	0.079921612	0.079218564	0.074622077	0.074886167
Sum of absolute errors	0.040161059	0.040480136	0.040839923	0.038825702	0.037307825
Sum of normalised errors	4.037198	<b>4.000696</b>	4.015261	4.871499	4.275031

of least squares. Overall, the HYBRD error analysis method gives the minimum sum of the normalised errors for all three metals.



◆ Cu, Experimental Data    ▲ Ni, Experimental Data    ■ Pb, Experimental Data  
 — Cu, Temkin Isotherm    — Ni, Temkin Isotherm    — Pb, Temkin Isotherm

Figure 6. Temkin equation isotherms of metal ions sorbed on peat.

TABLE XI  
 Linear Temkin isotherm parameters

	Lead	Nickel	Copper
Temkin: $A_T$ ( $\text{dm}^3 \text{mmol}^{-1}$ )	0.056137	0.025044	0.021799
Temkin: $RT/b_T$	59997.08	241.9233	5285.085
Temkin: $b_T$	0.041318	10.24692	0.469050
Coefficient of determination, $R^2$	0.990944	0.983955	0.943494
Sum of errors <sup>2</sup>	0.000618	7.67066E-05	0.000430
Hybrid error function	0.001317	0.000581	0.002669
Marquardt's PSD	0.003005	0.004682	0.017900
Average relative error	0.138397	0.176790	0.328875
Sum of absolute errors	0.065069	0.023040	0.053543

TABLE XII  
Non-linear Temkin isotherm parameters

	Method/error function (parameter set)				
	ERRSQ	HYBRD	MPSD	ARE	EABS
Copper on peat					
Temkin: $A_T$	0.0218325	0.022752	0.0233999	0.024103	0.016604
Temkin: $RT/b_T$	5219.68	3716.99	2991.34	2302.69	72484.2
Temkin: $b_T$	2.105586	1.49941	1.206688	0.928891	29.23967
Sum of errors <sup>2</sup>	<b>0.000408</b>	0.000422	0.000446	0.000502	0.000839
Hybrid error function	0.002545	<b>0.002425</b>	0.002480	0.002761	0.007709
Marquardt's PSD	0.017166	0.014554	<b>0.014055</b>	0.015283	0.073524
Average relative error	0.307380	0.297195	0.292891	<b>0.275246</b>	0.375712
Sum of absolute errors	0.049539	0.050282	0.051267	0.050444	<b>0.047456</b>
Sum of normalised errors	2.834586	<b>2.786959</b>	2.824536	2.880696	4.925654
Nickel on peat					
Temkin: $A_T$	0.025044	0.025509	0.025867	0.026223	0.024994
Temkin: $RT/b_T$	241.918	218.659	203.352	185.301	225.4382
Temkin: $b_T$	0.097588	0.088206	0.082031	0.074749	0.090940
Sum of errors <sup>2</sup>	<b>7.67048E-05</b>	7.83658E-05	8.18064E-05	9.03253E-05	0.00010974

TABLE XII  
(continued)

	Method/error function (parameter set)				
	ERRSQ	HYBRD	MPSD	ARE	EABS
Nickel on peat (continued)					
Hybrid error function	0.000581	<b>0.000563</b>	0.000573	0.000634	0.000793
Marquardt's PSD	0.004682	0.004193	<b>0.004089</b>	0.004477	0.005801
Average relative error	0.176788	0.174351	0.172633	<b>0.169602</b>	0.172528
Sum of absolute errors	0.023040	0.023452	0.023770	0.024086	<b>0.022996</b>
Sum of normalised errors	4.195716	<b>4.107515</b>	4.136505	4.353279	4.930682
Lead on peat					
Temkin: $A_T$	0.056136	0.056895	0.057600	0.058683	0.055292
Temkin: $RT/b_T$	60004.69	53354.24	48180.58	44731.00	70475.00
Temkin: $b_T$	0.041313	0.046462	0.051452	0.055419	0.035175
Sum of errors <sup>2</sup>	<b>0.000618</b>	0.000631	0.000664	0.000930	0.000655
Hybrid error function	0.001317	<b>0.001284</b>	0.001310	0.001746	0.001512
Marquardt's PSD	0.003004	0.002769	<b>0.002704</b>	0.003442	0.003781
Average relative error	0.138380	0.140198	0.140898	<b>0.123538</b>	0.130443
Sum of absolute errors	0.065063	0.066898	0.068112	0.060851	<b>0.060093</b>
Sum of normalised errors	4.150878	<b>4.123511</b>	4.179681	4.680385	4.378426

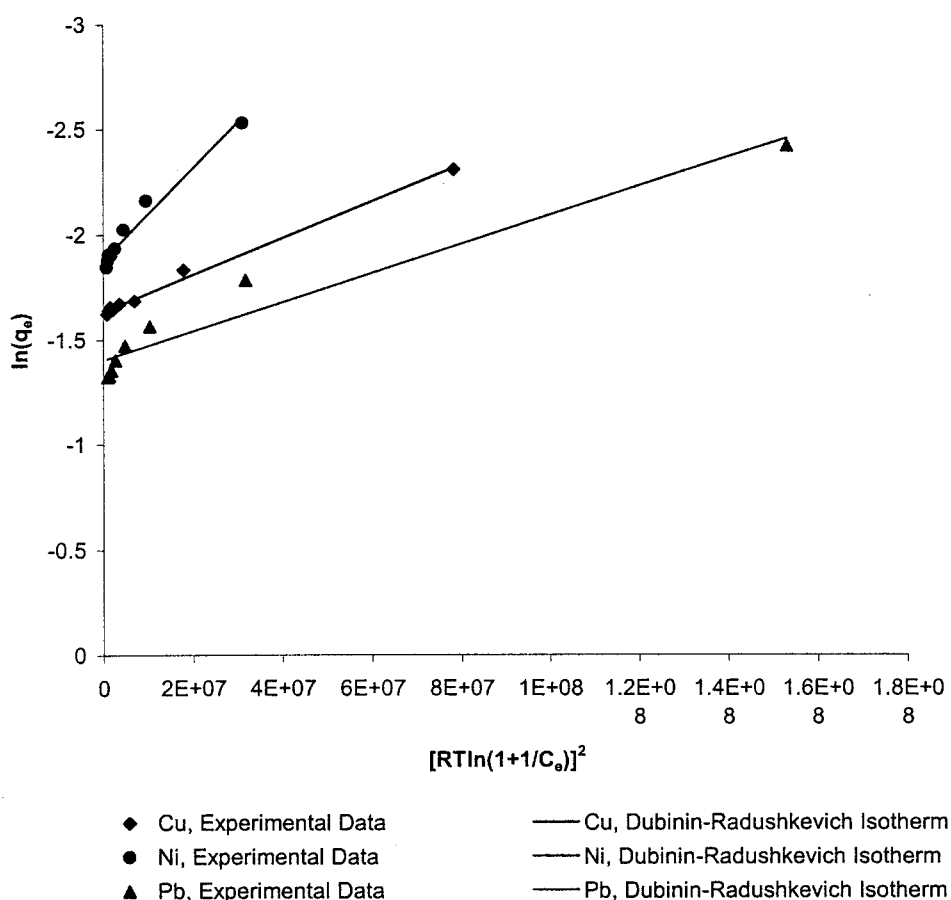


Figure 7. Dubinin-Radushkevich equation isotherms of metal ions sorbed on peat.

#### 4.5. THE DUBININ-RADUSHKEVICH ISOTHERM

The linear Dubinin-Radushkevich isotherm plots for the sorption of the three metals onto peat are presented in Figure 7 and examination of the data shows that the Dubinin-Radushkevich isotherm provides a very accurate description of the data for copper ions over the concentration range studied. However, for the sorption of lead and nickel the experimental data do not correlate as well with the Dubinin-Radushkevich equation and this is confirmed by the coefficients of determination shown in Table XIII.

The values of  $E$  calculated using Equation (6) are 7.7, 4.9 and 11.5  $\text{kJ mol}^{-1}$  for copper, nickel and lead, respectively. The typical range of bonding energy for ion-exchange mechanisms is 8–16  $\text{kJ mol}^{-1}$ , indicating that chemisorption may play a significant role in the adsorption process. The  $q_D$  values are consistent with the non-linear  $q_m$  values previously determined for the Langmuir isotherm.



TABLE XIII  
Linear Dubinin-Radushkevich isotherm parameters

	Lead	Nickel	Copper
D-R: $q_D$	0.581122	0.152386	0.194962
D-R: $B_D \times R^2 \times T^2$	0.023172	0.128840	0.051478
D-R: $B_D$	3.77071E-09	2.09657E-08	8.37683E-09
D-R: $E$ (J mol <sup>-1</sup> )	11515.25	4883.493	7725.830
Coefficient of determination, $R^2$	0.991634	0.967911	0.993349
Sum of errors <sup>2</sup>	0.000709	0.000201	7.27602E-05
Hybrid error function	0.001428	0.001532	0.000428
Marquardt's PSD	0.002945	0.012011	0.002550
Average relative error	0.131666	0.241464	0.107694
Sum of absolute errors	0.063628	0.031340	0.018612

Table XIV shows the best fit  $q_D$  and  $B_D$  parameters for the five error methods – the  $q_D$  values are remarkably consistent for each metal, with the exception of the EABS set for lead. The values are also generally close to those for the linear parameter set, particularly those determined using the MPSD error method which provides the second or third best fit of the non-linear parameter sets. Based on the sum of the normalised errors, the HYBRD parameter set produces the best fit for nickel, whereas the ARE set produces the best fit for copper and lead.

#### 4.6. THE TOTH ISOTHERM

This three parameter isotherm has been analysed by the five error methods and the values of the constants are presented in Table XV.

Once again, similar to several of the preceding isotherm results, the parameter values do not vary significantly across the range of error methods. The sums of the normalised errors indicate that the closest fits to the copper, nickel and lead experimental data are produced by the ARE/EABS, MPSD and ERRSQ parameter sets respectively.

#### 4.7. THE LANGMUIR-FREUNDLICH FORM OF THE SIPS EQUATION

Table XVI shows the values of the Langmuir-Freundlich constants using the five analysis methods.

While the three constants  $K_{LF}$ ,  $a_{LF}$  and  $n_{LF}$  are quite similar across the range of error functions, there appears to be two distinct groupings according to the parameter values obtained. This appears to be related to the form of the error function since the first three error methods (ERRSQ, HYBRD, MPSD) employ the square

TABLE XIV  
Non-linear Dubinin-Raduskevich isotherm parameters

	Method/error function (parameter set)				
	ERRSQ	HYBRD	MPSD	ARE	EABS
Copper					
D-R: $q_D$	0.195388	0.195133	0.194880	0.195526	0.195526
D-R: $B_D \times R^2 \times T^2$	0.052755	0.052014	0.051490	0.051068	0.051068
Sum of errors <sup>2</sup>	<b>6.53952E-05</b>	6.63078E-05	6.82482E-05	7.18628E-05	7.18628E-05
Hybrid error function	0.000408	<b>0.000400</b>	0.000404	0.000431	0.000431
Marquardt's PSD	0.002638	0.002459	<b>0.002422</b>	0.002597	0.002597
Average relative error	0.104990	0.099644	0.096535	<b>0.085699</b>	0.085699
Sum of absolute errors	0.016797	0.016518	0.016434	0.014994	<b>0.014994</b>
Sum of normalised errors	4.856741	4.715189	4.703748	<b>4.693398</b>	<b>4.693398</b>
Nickel					
D-R: $q_D$	0.153637	0.152857	0.152067	0.152546	0.152546
D-R: $B_D \times R^2 \times T^2$	0.138301	0.132932	0.128966	0.124010	0.124010
Sum of errors <sup>2</sup>	<b>0.000187</b>	0.000191	0.000202	0.000218	0.000218
Hybrid error function	0.001552	<b>0.0015033</b>	0.001534	0.001674	0.001674
Marquardt's PSD	0.013622	0.012280	<b>0.011972</b>	0.013065	0.013065
Average relative error	0.256926	0.246658	0.249805	<b>0.220184</b>	0.220184
Sum of absolute errors	0.031074	0.030991	0.032537	0.029555	<b>0.029555</b>
Sum of normalised errors	4.737768	<b>4.589190</b>	4.695822	4.724451	4.724451
Lead					
D-R: $q_D$	0.583958	0.582399	0.580763	0.585493	0.585494
D-R: $B_D \times R^2 \times T^2$	0.023824	0.023469	0.023164	0.023152	0.023152
Sum of errors <sup>2</sup>	<b>0.000668</b>	0.000680	0.000713	0.000794	0.000794
Hybrid errorfunction	0.001437	<b>0.001407</b>	0.001430	0.001656	0.001656
Marquardt's PSD	0.003213	0.003000	<b>0.002943</b>	0.003489	0.003489
Average relative error	0.140608	0.135813	0.132621	<b>0.117059</b>	0.117059
Sum of absolute errors	0.064213	0.063927	0.064125	0.056780	<b>0.056780</b>
Sum of normalised errors	4.629516	<b>4.527346</b>	4.546646	4.716763	4.716763

of the difference between the calculated and measured  $q$  values whereas the last two error methods (ARE, EABS) use the absolute value of the difference. For all three metal ion systems the MPSD error method produces the lowest sum of the normalised errors.

TABLE XV  
Non-linear Toth isotherm parameters

	Method/error function (parameter set)				
	ERRSQ	HYBRD	MPSD	ARE	EABS
Copper					
Toth $K_t$	0.209239	0.210009	0.210752	0.210941	0.210941
Toth: $a_t$	0.063027	0.064388	0.065696	0.065055	0.065055
Toth: $t$	0.619460	0.607436	0.596812	0.602320	0.602320
Sum of errors <sup>2</sup>	<b>5.03443E-05</b>	5.05624E-05	5.11254E-05	5.21982E-05	5.21982E-05
Hybrid error function	0.000281	<b>0.000280</b>	0.000281	0.000289	0.000289
Marquardt's PSD	0.001583	0.001556	<b>0.001548</b>	0.001610	0.001610
Average relative error	0.089526	0.087284	0.085874	<b>0.081725</b>	0.081725
Sum of absolute errors	0.015854	0.015674	0.015568	0.014833	<b>0.014833</b>
Sum of normalised errors	4.920121	4.865674	4.853426	<b>4.848424</b>	<b>4.848424</b>
Nickel					
Toth: $K_t$	0.188969	0.190549	0.192083	0.191520	0.191520
Toth: $a_t$	0.184819	0.186288	0.187806	0.186323	0.186323
Toth: $t$	0.565458	0.552727	0.541474	0.538451	0.538451
Sum of errors <sup>2</sup>	<b>2.44437E-05</b>	2.45E-05	2.47604E-05	2.61037E-05	2.61037E-05
Hybrid error function	0.000171471	<b>0.000170654</b>	0.000171258	0.000180	0.000180
Marquardt's PSD	0.001218	0.001197	<b>0.001192</b>	0.001242	0.001242
Average relative error	0.087139	0.083659	0.080836	<b>0.077666</b>	0.077666
Sum of absolute errors	0.012056	0.011735	0.011461	0.011219	<b>0.011219</b>
Sum of normalised errors	4.871167	4.786564	<b>4.739218</b>	4.821852	4.821852
Lead					
Toth: $K_t$	0.739442	0.742158	0.743244	0.751869	0.751869
Toth: $a_t$	0.062242	0.062698	0.062885	0.064666	0.064666
Toth: $t$	0.289165	0.286650	0.285637	0.278049	0.278049
Sum of errors <sup>2</sup>	0.000132747	0.00013288	0.000133035	0.000150	0.000150
Hybrid error function	0.000270147	0.000269824	0.000269893	0.000303	0.000303
Marquardt's PSD	0.000563315	0.000561862	0.000562170	0.000633	0.000633
Average Relativeerror	0.058308	0.058791	0.058879	0.054741	0.054741
Sum of absolute errors	0.028105	0.028298	0.028329	0.026666	0.026666
Sum of normalised errors	<b>4.650009</b>	4.662527	4.666122	4.871044	4.871044

TABLE XVI  
Non-linear Langmuir-Freundlich isotherm parameters

	Method/error function (parameter set)				
	ERRSQ	HYBRD	MPSD	ARE	EABS
Copper on peat					
Langmuir-Freundlich: $K_{LF}$	2.14991	2.08274	2.02256	1.59041	1.58715
Langmuir-Freundlich: $a_{LF}$	10.3345	9.98363	9.66912	7.42852	7.40996
Langmuir-Freundlich: $n_{LF}$	0.673314	0.664207	0.656161	0.59441	0.593951
Sum of errors <sup>2</sup>	<b>3.82427E-05</b>	3.8412E-05	3.8852E-05	5.69E-05	5.67691E-05
Hybrid error function	2.14742E-04	<b>2.13607E-04</b>	2.14466E-04	3.05038E-04	3.04548E-04
Marquardt's PSD	0.0012159	0.0011946	<b>0.0011891</b>	0.0016369	0.0016340
Average relative error	0.0712637	0.0690375	0.0675713	<b>0.0604497</b>	0.0605878
Sum of absolute errors	0.0124994	0.0122898	0.0121539	0.0113882	<b>0.0113613</b>
Sum of normalised errors	4.1194485	4.0577340	<b>4.0334520</b>	4.7593535	4.7543318
Nickel on peat					
Langmuir-Freundlich: $K_{LF}$	0.592046	0.580038	0.569123	0.516854	0.516854
Langmuir-Freundlich: $a_{LF}$	3.22598	3.14329	3.06809	2.69653	2.69653
Langmuir-Freundlich: $n_{LF}$	0.662162	0.653107	0.645185	0.611076	0.611076
Sum of errors <sup>2</sup>	<b>2.3424E-05</b>	2.34948E-05	2.36756E-05	2.70E-05	2.70E-05
Hybrid error function	1.63176E-04	<b>1.62524E-04</b>	1.63004E-04	1.83503E-04	1.83503E-04
Marquardt's PSD	0.0011490	0.0011323	<b>0.0011280</b>	0.0012473	0.0012473
Average relative error	0.0845587	0.0814457	0.0789199	<b>0.0715295</b>	0.0715295
Sum of absolute errors	0.0117719	0.0114842	0.0112394	0.0103810	<b>0.0103810</b>
Sum of normalised errors	4.6767189	4.6011570	<b>4.5563464</b>	4.7277609	4.7277609
Lead on peat					
Langmuir-Freundlich: $K_{LF}$	4.170931	4.149833	4.155374	3.867534	3.867534
Langmuir-Freundlich: $a_{LF}$	5.966065	5.930056	5.940039	5.451214	5.451214
Langmuir-Freundlich: $n_{LF}$	0.380987	0.380112	0.380370	0.370238	0.370238
Sum of errors <sup>2</sup>	<b>1.25349E-04</b>	1.25375E-04	1.25389E-04	1.49E-04	1.49E-04
Hybrid error function	2.6168E-04	<b>2.61623E-04</b>	2.61644E-04	3.13E-04	3.13E-04
Marquardt's PSD	5.63066E-04	5.62975E-04	<b>5.62913E-04</b>	6.82E-04	6.82E-04
Average relative error	0.059261	0.059255	0.0592190	<b>0.054393</b>	0.054393
Sum of absolute errors	0.027873	0.027851	0.0278629	0.026122	<b>0.026122</b>
Sum of normalised errors	4.506014	4.504986	<b>4.5048663</b>	4.855024	4.855024

TABLE XVII  
Linear isotherm comparison – Sum of normalised errors<sup>a</sup>

Linear isotherm	Lead	Nickel	Copper
Freundlich	0.938344	4.608361	4.554900
Langmuir	5.000000	3.983077	3.811958
Temkin	0.455592	1.964325	2.777875
Dubinin-Radushkevich	0.446509	3.757032	0.697433
Redlich-Peterson	<b>0.266096</b>	<b>0.871335</b>	<b>0.684328</b>

<sup>a</sup> Denotes normalised across the range of linear isotherms (instead of error functions).

TABLE XVIII  
Linear isotherm comparison – Regression coefficients of determination ( $R^2$ )

Linear isotherm	Lead	Nickel	Copper
Freundlich	0.972028	0.961755	0.915671
Langmuir	0.999392	0.998830	0.999640
Temkin	0.990944	0.983955	0.943494
Dubinin-Radushkevich	0.991634	0.967911	0.993349
Redlich-Peterson	0.999939	0.999716	0.999821

#### 4.8. ERROR ANALYSIS – LINEAR SYSTEMS

Unsurprisingly, possibly because of the method used to determine its parameters, the data in Table XVII show that the three parameter Redlich-Peterson isotherm produced the best fit for all three metals based on the measured errors. For both the lead and nickel equilibrium data, the linear parameter set for the Temkin isotherm provides the second closest fit over all the error methods. For copper, the linear Dubinin-Radushkevich parameters produce the second closest fit.

The linear parameter sets providing the worst fit over all the error methods were the Langmuir, Freundlich and Freundlich isotherm parameters for the lead, nickel and copper data respectively. As Table XVIII shows, the highest coefficients of determination ( $R^2$ ) were obtained for all three systems using the Redlich-Peterson isotherm, with the Langmuir isotherm generally producing a close second.

Excepting the Langmuir and Redlich-Peterson isotherms, the  $R^2$  values appear to give a reasonable indication of the relative quality of fit of the linear isotherm based on the sums of normalised errors. A possible explanation lies in the fact that linearisation of these three remaining isotherms requires taking logarithms, introducing similar effects to the error structure. Taking logarithms may also lead

to better fits at the extremes of concentrations since linear regression implicitly minimises the sum of the squares of the errors to determine the equation parameters and thus the error in a value of  $10^3$  will have a similar weighting to the error in a value of  $10^{-3}$ .

#### 4.9. ERROR ANALYSIS – NON-LINEAR SYSTEMS

Based on the non-linear regression results, selection of the linear isotherm transformation with the highest linear regression coefficient of determination does not appear to be the most appropriate method to choose a model for sorption equilibria.

Based on any of the error measures, better fits can be obtained for most two parameter isotherms by using non-linear regression – although, except for the Langmuir and Temkin isotherms, the linear parameters do provide reasonably close estimates to the optimised non-linear solutions for all three metal ion systems. Using the normalised error criteria presented here to combine non-linear errors demonstrates that the parameters obtained by linearisation are not bad and in certain cases better than the values derived by non-linear regression.

For the four two-parameter isotherms examined, the HYBRD error measure produced the parameter set providing the lowest sum of normalised errors in nine out of the twelve systems (examining four isotherms for each of three metals) and the MPSD error measure was second best for six of the twelve systems. For the three parameter isotherms, the MPSD error measure produced the parameter set providing the lowest sum of normalised errors in four out of the nine systems with the HYBRD error measure giving the second lowest value in each case and therefore providing the next best fit isotherm constants.

The three parameter isotherms were always found to provide a better match to the experimental data than the two parameter isotherms and the incorporation of the degrees of freedom of the system – the number of data points minus the number of isotherm parameters – as a divisor in the error function did not alter this.

The Sips or Langmuir-Freundlich isotherm equation employing the parameter set derived using the MPSD error provided the best model overall for all three experimental systems.

## 5. Conclusions

A detailed error analysis was carried out to determine the best isotherm models for sets of equilibrium sorption data for three metal ions on peat. In all cases the three parameter Sips – or Langmuir-Freundlich – isotherm equation was found to provide the closest fit to the equilibrium data and the optimum parameter values were produced by non-linear regression using the MPSD error function. This optimum isotherm-error function combination was identified using the sum of normalised errors.

Regarding the results presented for the two parameter isotherms examined, several comments can be made:

- excepting the Langmuir isotherm, the order of linear coefficients of determination was observed to provide a good indication of the relative ranking of the linear isotherm fits;
- excepting the Langmuir and Temkin isotherms, the linear derived parameters produced reasonable estimates of the values derived by non-linear regression and were generally closest to those determined using the MPSD error function; and
- the HYBRD error function generally appears to produce the best fit isotherm parameter values for two parameter isotherms.

For the three parameter isotherms examined the MPSD error function generally produces isotherm parameter values that give the lowest sum of normalised errors, most often followed by the HYBRD error function.

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