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Use of equilibrium and initial metal concentrations in determining Freundlich isotherms for soils and sediments

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Abstract

Batch equilibrium test results of Pb and Cd retention by kaolinite, humic acid and mackinawite and mixtures of these soil/sediment materials are modeled using Freundlich isotherms with the retained metal plotted as a function of the equilibrium metal concentration, C_e and as a function of the initial metal concentration, C_i. When C_i rather than C_e is used, smaller values of K_F and larger values of $1/n$ are obtained and this means the isotherm is more linear. There is no significant difference in goodness of fit for the two types of isotherms based on the coefficient of determination, r^2 and a normalized deviation, Δq. Advantages in using C_i are that no data points need to be excluded when metal is completely retained by the adsorbent and it is easier to compare the same range of metal concentrations on one graph. A unified sorption variable K_u is evaluated for each isotherm. Since K_u represents the changing slope of the Freundlich isotherm, the value of C_i or C_e needs to be specified with the value of K_u. A dimensionless form of K_u was developed so as to permit more universal application of this parameter and K_u could potentially be used in transport prediction models. r^2 and Δq together were better able to quantify goodness of fit of the data with the Freundlich isotherm than either of the two parameters separately.

Keywords: Freundlich isotherm; Dimensionless unified sorption variable; Initial metal concentration; Transport prediciton models; Goodness of fit

1. Introduction

Heavy metal industrial discharges to the environment have become a source of concern because of their potential toxicity to humans and the aquatic environment (Brown et al., 2000). Metal removal from industrial effluents has been primarily by precipitation and secondarily by adsorption, ensuring that removal to water quality guidelines can be achieved (Brown et al., 2000). Since ion exchange resins and adsorbents such as activated carbon are too expensive for widespread use, more economical materials such as peat, clay minerals, laterite minerals, calcareous soils, oxic sediments, natural zeolites, suspended particles of river water, composts and agricultural wastes have been considered (Mohammad and Najar, 1977; Ho et al., 2002).

Metals discharged to the environment are also scavenged in situ and can be naturally attenuated by sediments and soils (Mulligan and Yong, 2003). Contaminants in surface waters become sorbed to suspended particulate matter, settle, and may eventually become

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buried, while metal removal from groundwater occurs by the processes of precipitation and adsorption, when geochemical conditions are favourable (Fiorenza et al., 2000). Soils and sediments can be used to treat wastewaters and contaminated surface waters and groundwater.

Solute or contaminant uptake by an adsorbent is most often measured with batch equilibrium tests (Sparks, 2003). Varying solute concentrations are mixed with an adsorbent until equilibrium is achieved and the contaminant removed from the solution is plotted as a function of the equilibrium contaminant concentration remaining in solution (Bohn et al., 1985) or as a function of the initial contaminant concentration. The initial concentration is useful for comparing contaminant uptake by different materials or uptake of a variety of contaminants on the same graph and Chen et al. (1999) note that when the equilibrium concentration is used it is more difficult to compare different adsorbents or contaminants since the range of equilibrium concentrations may not correspond.

When partitioning of a contaminant between the solid and liquid phases is constant, adsorption is given by the following linear adsorption isotherm

$$q_e = K_d C_e \tag{1}$$

where K_d is the distribution coefficient, C_e is the equilibrium contaminant concentration and q_e is the adsorbed contaminant. The distribution coefficient is a measure of the partitioning of a contaminant and is important because it is used in transport prediction models (Yong, 2001).

Adsorption, however, is often modeled using the empirical two-parameter Freundlich isotherm and the Freundlich equation is given by

$$q_e = K_F C_e^{1/n} \tag{2}$$

where q_e is the retained metal at equilibrium (mmol/kg), C_e is the non-retained metal at equilibrium (mmol/kg), K_F is the Freundlich constant ($(\text{mmol/kg})^{1-1/n}$) and $1/n$ is a dimensionless parameter that varies between 0 and 1. The nonlinear Freundlich isotherm is widely used in geoenvironmental analysis (Chen et al., 1999) and often describes adsorption behaviour more accurately than a linear isotherm, but when the partitioning of the contaminant between the solid and liquid phases is not constant, its evaluation is more complicated (Chen et al., 1999; Yong, 2001).

Evaluation of the parameters in the Freundlich isotherm is accomplished by obtaining a linear form of the isotherm and the best fitting line for the data is obtained by maximizing the coefficient of determination r^2. The r^2 value indicates the goodness of fit between the data and the isotherm but other error quantifiers have also been used to evaluate the performance of adsorption models (Juang et al., 1996; Haghserrsht and Lu, 1998; Ho et al., 2002).

In this study, Pb and Cd uptake by kaolinite, humic acid and mackinawite, an iron monosulfide found in anoxic sediments and waterlogged soils, and mixtures of these three materials, is represented by Freundlich isotherms. The isotherms are given as a function of C_e and as a function of C_i and these two types of isotherms are analyzed and compared. The coefficient of determination, r^2, and a normalized deviation, Δq, used by Juang et al. (1996) and Haghserrsht and Lu (1998) are employed to evaluate the accuracy of the model in representing the data. Finally the new unified sorption variable, K_u, of Chen et al. (1999), that unites the two parameters of the Freundlich isotherm, K_F and $1/n$, is evaluated.

2. Materials and methods

2.1. Batch equilibrium tests

Batch equilibrium tests of 24 h duration were conducted at room temperature (22 °C) with Pb (as $PbCl_2$) and Cd (as $CdCl_2$) and the Pb and Cd solutions were adjusted with HCl to pH 3.6 and 3.9, respectively. The proportions of kaolinite, humic acid and mackinawite and mixtures of these materials used in the batch tests are shown in Table 1. The sediment/soil suspensions without mackinawite were initially pH adjusted while the suspensions with mackinawite were tested at their natural pH and, in each case, the initial pH value of the suspension is indicated in Table 1. The pH decreased during the batch tests and was influenced by the concentration of metal

Table 1
Solid and liquid proportions and mixtures used in batch equilibrium tests and approximate initial pH values of soil/sediment suspensions

Soil No.	Initial pH values	Kaolinite (g)	Humic acid (g)	Mackinawite (g)	Solution (mL)	Solid/solution (g/mL)
1	4.3	5			50	0.1
2	6.1	5			50	0.1
3	4.3	5	0.05		50	0.101
4	6.2	5	0.05		50	0.101
5	4.3		0.03		30	0.001
6	6.0		0.03		30	0.001
7	6.9	14		0.1	140	0.101
8	6.4	14	0.14	0.1	140	0.102
9	6.4		0.042	0.042	42	0.002
10	6.3			0.042	42	0.001

added and the amount of metal uptake occurring. The suspension pH was not maintained at a constant level as this would have introduced an additional variable and changed the amount of metal uptake.

For all the mixtures that contained mackinawite, the batch tests were conducted under anoxic conditions obtained by bubbling all solutions and suspensions with high purity nitrogen gas to reach a dissolved oxygen concentration of 0.3 mg/L. The concentration of each metal solution was maintained by replenishing the volume of distilled water lost by evaporation during de-aeration. A centrifuge tube or nalgene bottle was half filled with a soil suspension that was de-aerated before the mackinawite was added. The pH of the suspension was measured, and the bottle was filled to capacity with the de-aerated metal solution that was double the final desired metal concentration since deaerated distilled water already occupied half of the liquid volume. The bottle was sealed with parafilm, capped and placed on a roller for 24 h. The suspension was centrifuged at 6000 rpm for 10 min to separate the solid and liquid phases. Since for all the batch tests the solid and liquid phases appeared to be fully separated when the suspensions were centrifuged, there was no subsequent filtering of the liquid phases. The supernatant was acidified to pH 1 with HCl, the metal in solution was measured using a Perkin Elmer 3110 atomic absorption spectrometer, and the pH of the final suspension was measured. The mackinawite used in the batch tests was precipitated in the lab as described by Coles et al. (2000).

For the batch tests without mackinawite, no de-aeration was necessary and there was no need to ensure zero air space in the sample containers. The range of metal concentrations for the oxic batch tests was from 50 to 2500 ppm or from 0.241 to 12.0 mmol/L for Pb and from 0.445 to 22.0 mmol/L for Cd. For the anoxic batch tests the range of metal concentrations was from 100 to 2500 ppm or from 0.483 to 12.0 mmol/L for Pb and from 0.890 to 22.0 mmol/L for Cd. Slightly higher minimum metal concentrations were tested with the suspensions containing mackinawite because at lower concentrations the metal was completely retained by the adsorbent. A greater number of data points were obtained for the oxic batch tests than for the anoxic batch tests. No electrolytes other than $PbCl_2$ or $CdCl_2$ were added to the batch tests and, therefore, the ionic strengths of the suspensions were a function of the metal concentrations only.

Flat D kaolinite was obtained from the Dry Branch Kaolin Company in Dry Branch, Georgia. It was crystalline, 75% of its particles were larger than clay sized, its background metal concentrations were negligible, it had a cation exchange capacity of 1.97 meq/100 g, a zero point of charge at approximately pH 2.6, and it appeared to be relatively free of impurities (Coles and Yong, 2002).

The humic acid was extracted from a compost/topsoil in Montreal according to the method of Schnitzer and Preston (1986) except that the ash removal step was not undertaken. The humic acid contained 33.9% ash, had a pH 7 cation exchange capacity of 436 meq/100 g on an ash free basis, and a zero point of charge below pH 0.5. The oxygen-containing functional group content of the humic acid was typical and indicated the presence of both poorly and more fully decomposed fractions (Coles, 1998).

2.2. The Freundlich isotherm

The Freundlich isotherm model is considered to be appropriate for describing both multilayer sorption and sorption on heterogeneous surfaces (Ho et al., 2002). The Freundlich isotherm is linear if $1/n = 1$ and, as $1/n$ decreases, the isotherm becomes more nonlinear. The units for q_e and C_e should be consistent if parameters are to have any practical application (Yong, 2001). Since units for K_F depend on the value of $1/n$, K_F parameters are only comparable when their $1/n$ parameters are the same, and therefore K_F is not analogous to the distribution coefficient K_d (Chen et al., 1999).

Generally researchers have expressed q_e in mg/kg, C_e in mg/L and K_F in units of $mg^{1-1/n}\ kg^{-1}\ L^{1/n}$ or alternately q_e in mmol/kg, C_e in mmol/L and K_F in units of $mmol^{1-1/n}\ kg^{-1}\ L^{1/n}$. The use of different units, however, has made it difficult to compare values of K_F (Chen et al., 1999).

A linear form of the Freundlich isotherm can be obtained by taking the log of each side of the Freundlich equation to give

$$\log q_e = \log K_F + (1/n)\log C_e \tag{3}$$

and when $\log C_e$ is plotted on the x-axis against $\log q_e$ on the y-axis, $\log K_F$ becomes the intercept of the line and $1/n$ becomes the slope of the line. Investigators have tried to link the Freundlich parameters K_F and $1/n$ to mechanisms of adsorption (Sparks, 2003).

In this study, units of mmol/kg are assigned to both the ordinate (q_e) and the abscissa (C_e) reducing the units of K_F to $(mmol/kg)^{1-1/n}$. This means that only the actual metal and soil contents are taken into account. Although the authors have observed small differences in metal uptake during batch tests when different volumes of the liquid phase are used, even when the ratio of adsorbate to adsorbent remains the same, these differences related to the exact volume of the liquid component are neglected here.

Batch test results are usually plotted with the equilibrium contaminant concentration (C_e) against the retained concentration and occasionally are plotted with the initial concentration of contaminant (C_i) against the retained concentration (Ziper et al., 1988; Yong, 2001). Adsorption isotherms, on the other hand, have usually been expressed in terms of the equilibrium contaminant concentration. This research will investigate the application of both the equilibrium and the initial metal concentrations in the Freundlich isotherm model.

2.3. Performance criteria

The coefficient of determination r^2 has been most frequently used as a measure of the goodness of fit between adsorption data and an adsorption isotherm. The better the fit the more closely r^2 approaches 1. A normalized deviation, Δq has also been used to test the fit between adsorption data and the Freundlich isotherm (Juang et al., 1996; Haghserrsht and Lu, 1998) and it is defined as

$$\Delta q=\left(\frac{1}{N}\right)\sum_{i=1}^{N}\left|\left(q_{e,i}^{calc}-q_{e,i}^{exp}\right)\right|/q_{e,i}^{exp} \tag{4}$$

where N is the number of data points and $q_{e,i}^{calc}$ and $q_{e,i}^{exp}$ are the calculated and experimentally determined retained metal concentrations. The better the fit between the model and the data, the more closely Δq approaches 0.

2.4. Unified sorption variable, K_u

One of the problems in using the Freundlich isotherm model has been related to the difficulty in trying to compare values of K_F when either the $1/n$ values are not the same, or different units of measurement have been used. Therefore, Chen et al. (1999) proposed a unified sorption variable, K_u to represent the constantly changing slope of the Freundlich isotherm ($K_u=q_e/C_e$), and in a linear system $K_u=K_d$. This new variable has the same units as K_d and can be estimated in terms of either C_e or q_e by employing either of the following two equations.

$$K_u=K_F/C_e^{(n-1)/n} \tag{5}$$

$$K_u=K_F^n/q_e^{n-1} \tag{6}$$

The more closely data fits the Freundlich isotherm, the better will be the agreement between Eqs. (5) and (6) for determining K_u. Chen et al. (1999) assigned units of L/kg to K_u but here since units of mmol/kg have been assigned to both q_e and C_e, K_u is dimensionless and in this form might have more universal application. Values of K_u are calculated and evaluated for the data in this research since K_u is a new and relatively untested variable.

3. Results and discussion

The Freundlich parameters shown in Tables 2 and 3 represent the batch test results with the metal retention as a function of the initial metal concentration, C_i and as a function of the equilibrium metal concentration, C_e and some of these isotherms are plotted in Figs. 1 and 2.

Tables 2 and 3 and Figs. 1 and 2 reveal that when the initial metal concentration is used, smaller values of K_F and larger values of $1/n$ are always obtained. With a

Table 2

Freundlich parameters K_F and $1/n$, goodness of fit parameters r^2 and Δq, and the unified sorption variable K_u for Freundlich isotherms of adsorption data plotted in terms of the initial Pb concentration C_i and the equilibrium Pb concentration C_e

No. [a]	Pb and C_i					Pb and C_e				
	K_F	$1/n$	r^2	Δq	K_u range	K_F	$1/n$	r^2	Δq	K_u range
1	1.62	0.510	0.96	0.071	1.14–0.15	3.76	0.324	0.95	0.075	10.9–0.14
2	2.17	0.457	0.92	0.085	1.63–0.17	6.95	0.183	0.96	0.027	34.3–0.12
3	1.74	0.580	0.96	0.068	1.32–0.25	5.57	0.333	0.98	0.046	28.8–0.29
4	5.79	0.335	0.90	0.025	1.28–0.26	14.2	0.142	1.00	0.005	44.6–0.32
5	28.18	0.408	0.96	0.015	1.25–0.10	112.2	0.255	0.97	0.012	14.1–0.09
6	104.7	0.302	0.74	0.017	0.66–0.12	374.2	0.161	0.58	0.020	3.3–0.10
7	10.35	0.288	0.76	0.023	1.12–0.31	32.35	0.039	0.09	0.024	1.64–0.24
8	2.84	0.678	0.95	0.019	0.98–0.51	27.25	0.240	0.90	0.026	38.9–1.19
9	6.56	0.728	0.91	0.020	1.19–0.66	523.5	0.248	0.84	0.027	242–2.27
10	41.69	0.510	0.81	0.038	1.46–0.46	1737	0.099	0.59	0.016	66.2–0.54

Units for K_F are $(\text{mmol/kg})^{1-1/n}$ and other parameters are dimensionless.

[a] Number of soil/sediment mixtures same as in Table 1.

Table 3
Freundlich parameters K_F and $1/n$, goodness of fit parameters r^2 and Δq, and the unified sorption variable K_u for Freundlich isotherms of adsorption data plotted in terms of the initial Cd concentration C_i and the equilibrium Cd concentration C_e

No.[a]	Pb and C_i					Pb and C_e				
	K_F	$1/n$	r^2	Δq	K_u range	K_F	$1/n$	r^2	Δq	K_u range
1	1.18	0.427	0.96	0.046	0.72–0.05	1.59	0.370	0.96	0.050	0.93–0.05
2	2.56	0.403	0.97	0.030	1.14–0.09	4.02	0.276	0.91	0.079	1.67–0.07
3	2.06	0.426	0.98	0.027	0.93–0.09	3.71	0.310	0.98	0.026	4.12–0.09
4	2.26	0.486	0.92	0.068	1.26–0.15	4.99	0.336	0.90	0.081	7.82–0.16
5	9.27	0.493	0.87	0.030	0.43–0.07	15.49	0.442	0.86	0.031	0.70–0.08
6	0.482	0.897	0.96	0.015	0.22–0.18	0.759	0.868	0.95	0.018	0.29–0.21
7	2.7	0.462	0.80	0.034	0.32–0.14	4.57	0.371	0.74	0.038	0.49–0.15
8	1.85	0.642	0.97	0.014	0.50–0.27	4.10	0.523	0.96	0.017	0.99–0.36
9	60.26	0.429	0.86	0.017	1.19–0.35	501.2	0.204	0.91	0.012	22.9–0.60
10	151.4	0.365	0.82	0.016	1.34–0.29	1047	0.172	0.85	0.014	27.2–0.39

Units for K_F are $(\text{mmol/kg})^{1-1/n}$ and other parameters are dimensionless.

[a] Number of soil/sediment mixtures same as in Table 1.

larger proportion of metal uptake at lower metal concentrations, the equilibrium metal concentration is smaller and the x value of the first data point is smaller, giving a larger y intercept and a flatter slope. For complete metal uptake, the equilibrium metal concentration is zero, log of zero is undefined and this data point cannot be used in the linear form of the Freundlich isotherm.

Higher values of both K_F and $1/n$ indicate that greater metal uptake is occurring. Since $1/n$ and log K_F represent the isotherm's slope and the intercept, respectively, metal uptake between isotherms with either the same value of $1/n$ or the same value of K_F is easy to compare. If both of these parameters differ, the two isotherms may intercept and plotting the isotherms may better reveal how the metal uptake differs.

The values of r^2 and Δq in Tables 2 and 3 suggest it is better to use more than a single error measurement to confirm the goodness of fit between the data and the Freundlich model, as there are instances where one parameter indicates a poor fit and the other indicates a good fit.

In Fig. 1, values of both r^2 and Δq indicate that each isotherm is a good fit for the data. In Fig. 2, one or both of the values of r^2 and Δq indicate that the isotherms are a poorer fit for the data than in Fig. 1. The functions of r^2 and Δq appear to be valid indicators because observation reveals that about 98% of the data points in Fig. 1 are well aligned with the Freundlich isotherms compared to about 74% of the data points in Fig. 2.

The top isotherm in Fig. 2b ($r^2=0.59$, $\Delta q=0.016$) appears to fit the data slightly better than the top isotherm in Fig. 2a ($r^2=0.81$, $\Delta q=0.038$) and this is predicted by the respective Δq values but is contrary to what is indicated by the respective r^2 values. The middle isotherm in Fig. 2a ($r^2=0.76$, $\Delta q=0.023$) looks comparable to the middle isotherm in Fig. 2b ($r^2=0.09$, $\Delta q=0.024$) despite the large difference in

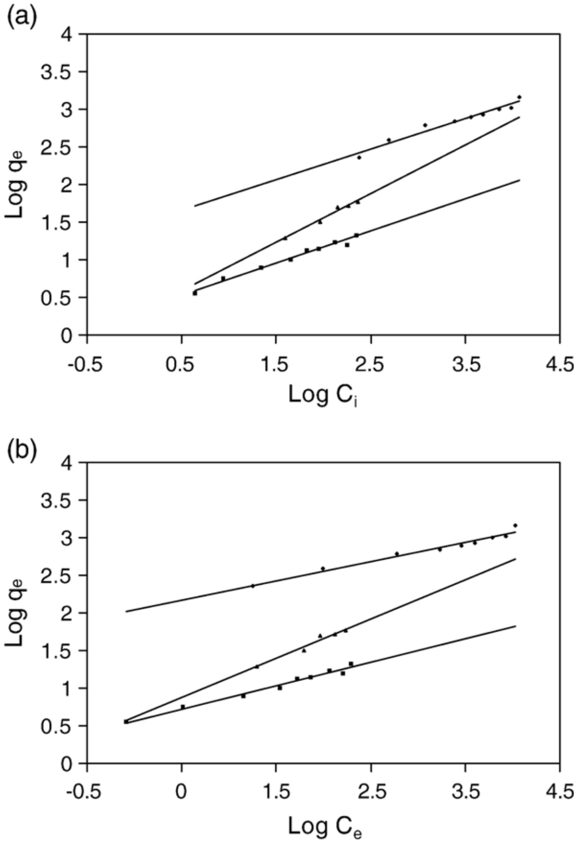

Fig. 1. Freundlich isotherms showing the retention of Pb by the pH 4.3 humic acid No. 5 (◆) and retention of Cd by the pH 4.3 kaolinite and humic acid, No. 3 (■) and the mackinawite, humic acid and kaolinite, No. 8 (□). Metal uptake is given as a function of the initial metal concentration (a) and the equilibrium metal concentration (b).

r^2 values. The top two isotherms in Fig. 2b each have one less data point than their counterparts in Fig. 2a because complete metal uptake occurred at the lowest metal concentrations and this may be the reason for the relatively low r^2 values. The need for both r^2 and Δq values in determining goodness of fit can be seen from Fig. 2.

For all of the isotherms, the average r^2 and Δq values obtained are 0.90 and 0.034, respectively, when the initial metal concentrations are used and are 0.84 and 0.031, respectively, when the equilibrium metal concentrations are used. The lower r^2 values obtained when using the equilibrium metal concentrations may be influenced by the fact that some data points are lost when complete metal uptake occurs at the lowest metal concentrations. If this discrepancy is overlooked, then overall differences in values of r^2 and Δq for the two types of isotherms may not be significant. Otherwise, there may be a slight advantage to using the initial metal concentrations for plotting the Freundlich isotherms.

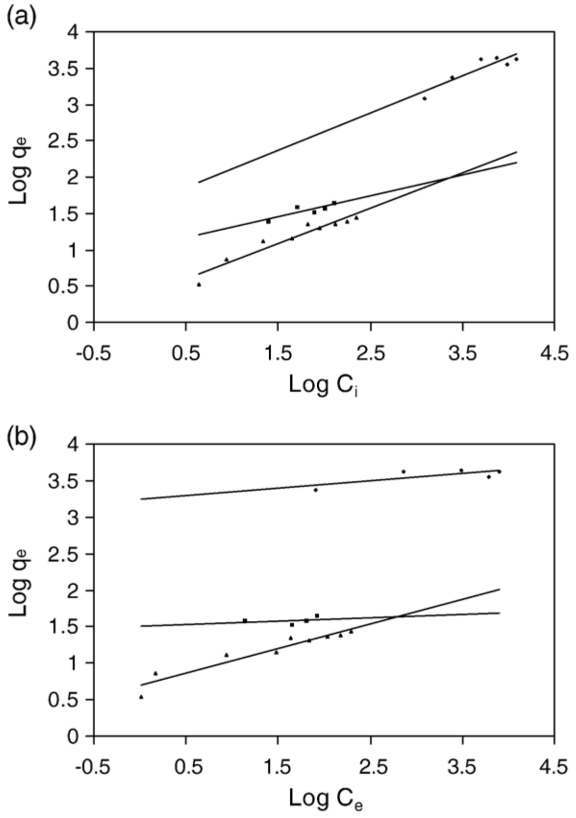

Fig. 2. Freundlich isotherms showing the retention of Pb by the mackinawite, No. 10 (◆) and the mackinawite and kaolinite, No. 7 (■) and retention of Cd by the pH 6.2 kaolinite and humic acid, No. 4 (□). Metal uptake is given as a function of the initial metal concentration (a) and the equilibrium metal concentration (b).

Table 4
Selected distributions of K_u, calculated in terms of C_e or C_i and q_e

Pb with soil No. 4			Pb with soil No. 5			Cd with soil No. 3		
$r^2=1.00$, $\Delta q=0.005$			$r^2=0.97$, $\Delta q=0.012$			$r^2=0.98$, $\Delta q=0.027$		
C_e	K_u		C_e	K_u		C_i	K_u	
	$f(C_e)$	$f(q_e)$		$f(C_e)$	$f(q_e)$		$f(C_i)$	$f(q_e)$
0.28	42.2	47.0	18	13.0	15.1	4.41	0.87	0.97
5.36	3.36	2.83	97	3.72	3.04	8.81	0.59	0.55
14.6	1.41	1.25	593	0.96	0.81	22.0	0.35	0.34
25.3	0.89	0.87	1720	0.44	0.57	44.1	0.23	0.24
47.7	0.51	0.58	2840	0.30	0.40	66.0	0.19	0.17
69.7	0.37	0.39	3990	0.23	0.31	88.1	0.16	0.15
92.0	0.29	0.30	6220	0.17	0.18	133	0.12	0.12
			8600	0.13	0.16	176	0.11	0.13
			10600	0.11	0.06	220	0.09	0.09

Tables 2 and 3 show how the value of the unified sorption variable, K_u differs when the initial and equilibrium metal concentrations are used to determine the Freundlich isotherms. A narrower range of K_u values is obtained when metal uptake is given as a function of C_i because the value of $1/n$ tends to be larger or closer to a linear isotherm, for which a constant value of K_u or K_d would be obtained.

The values of K_u in Tables 2 and 3 were obtained by employing Eqs. (5) and (6) and taking the average. Some of the distributions obtained for the unified sorption variable in terms of Eqs. (5) and (6) separately are contained in Table 4. These examples were selected according the agreement between Eqs. (5) and (6) and this can usually be predicted by a high r^2 value. The K_u values in the left hand columns are for the isotherm with single best fit in terms of both r^2 and Δq. When the r^2 was at least 0.96 or 0.97 or was at least 0.95 with a low Δq value, agreement between Eqs. (5) and (6) was generally good. When the Freundlich isotherm was not a good fit for the data, there was significant variation in the values of K_u and in these instances the values of K_u in Tables 2 and 3 may not be as representative.

4. Conclusions

Whether the Freundlich isotherms are determined for metal uptake as a function C_i or C_e, there may not be a significant difference in the goodness of fit of the data. However, an advantage in using C_i could be that when complete contaminant uptake occurs, there is no need to exclude any of the data. Another advantage of using C_i is that a comparable range of metal concentrations for all of the batch tests could be obtained. This is not always obvious in this study since there were some differences in ratio of solid to liquid used. However, had this ratio always been the same, then similar values for C_i would have appeared in Figs. 1a and 2a. This is an area where future research could be undertaken.

Since in this research the units of mmol/kg were the same for q_e and C_e and C_i, the unified sorption variable K_u became dimensionless and in this form it could possibly have more widespread application. The similarities that exist between K_u and K_d mean that K_u could also be used in transport prediction models but the metal concentration would have to be specified since K_u changes with metal concentration.

For metal uptake as a function of C_i compared to metal uptake as a function of C_e, $1/n$ is closer to 1 or closer to a linear isotherm, and K_u is closer to being a constant value as occurs when the isotherm is linear.

Values of K_u are most accurate when the data is a good fit for the isotherm. The results suggest that an r^2 of at least 0.96 or 0.97 or an r^2 of at least 0.95 with a low Δq, will ensure reasonable agreement between the two equations used for calculating K_u. Goodness of fit was better predicted by both r^2 and Δq than by only one of theses two measurements of error.

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