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Simulation of the Errors in Equilibrium Correlations Using the Langmuir and BET Isotherms

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ABSTRACT

This paper considers methods of processing sorption equilibrium data so that the errors of derived information, such as maximum sorption capacity, can be calculated. The models considered in this study are the Langmuir and BET isotherms. In both cases the data are rearranged and correlated, on a standard spreadsheet, with a linear and quadratic function, respectively. Several estimates of the constants in the functions can be obtained by omitting data points in a consistent manner. These estimates can be statistically analyzed to give the mean and standard deviations of the constants. In obtaining the correlations on a spreadsheet, the coefficient of correlation (R^2) is obtained. Analysis of a large series of data would indicate that the value of R^2 does not give any information as to the variance of the coefficients in the correlating polynomial. The statistical analysis is finally illustrated with some examples.

INTRODUCTION

The determination of the equilibrium isotherms for a particular compound and sorbent has many applications in process and environmental engineering. Examples include the removal of water vapor on silica gel, sorption of organic contaminants from water using activated carbon, and softening of water with ion-exchange resins. The equilibrium data obtained are needed to design the process and to size items of equipment. The success of this type of activity rests on having good data for the isotherms and that, in particular, means obtaining accurate equilibrium data. The error analysis on isotherm data is not

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usually carried out, so this paper will examine methods of obtaining this type of data. In particular, the Langmuir and BET isotherm models will be considered in this work, and the methodology presented can be clearly extended to other models.

There does not seem to be any other previous study in the literature about errors associated with isotherm determinations. However, the reviewer of this paper was kind enough to point out some previous work in the field of electrophoresis (1, 2). The equations which are used to correlate sorption isotherms, in particular the Langmuir model, have a similar form to those used in electrophoresis. These workers have used Monte Carlo methods to model the errors associated with obtaining the binding coefficients needed for electrophoresis measurements. The fact that a completely divorced field from sorption isotherms was cited indicates that the problem of error analysis in many fields of environmental technology has been, for the most part, completely neglected.

THE LANGMUIR ISOTHERM

The Langmuir isotherm is a favorite one used by many workers to correlate sorption equilibrium data. The form of the correlation is given as

$$y_i = \frac{CK_\mathrm{d}x_i}{C + K_\mathrm{d}x_i} \tag{1}$$

where y_i and x_i are data points which refer to the equilibrium concentrations for the ith reading on the solid and fluid phases, respectively, C is the capacity of the sorbent for the particular pollutant under study, and K_d is the slope of the isotherm when the concentrations x_i and y_i are small. To determine these two parameters, the data rearranged so that

$$r_i = \frac{x_i}{y_i} = \frac{1}{K_\mathrm{d}} + \frac{1}{C}x_i \tag{2}$$

The Langmiur constants can be found by a linear correlation of the r_i and x_i values using a spreadsheet or a graphical package, both of which are available on most desktop computers.

The typical correlation package available on a PC gives the best fit for the data in the form $r_i = a + bx_i$, where a and b are the parameters obtained by linear interpolation using the spreadsheet. One of the problems with this simple correlation is that the errors in the Langmuir constants cannot be determined directly. Most correlation packages give the coefficient of correlation (R^2) only, and this cannot be related to the errors directly. To carry out this analysis an extensive body of data accumulated here has been analyzed and simulated to obtain a model for error estimation.

The sorbents used to obtain the data analyzed in this paper were pillared clays and synthetic hydrotalcites. For the sake of completeness, a few remarks will be made about them. Pillared clays (3) are modified smectite minerals and have a number of applications in sorption and catalysis. They are prepared by exchanging the charge compensating cations (usually Na^+) between the smectite clay layers with a high molecular weight complex cation such as alumina gel. This cation is called a pillaring agent. After firing in an oven, the "pillars" expand the spacing of the clay layers, enabling them to sorb molecules of high molecular weight. Hydrotalcite (4) is a naturally occurring mineral found in very small quantities in nature. For general use these materials must be manufactured. The structure of these compounds is very similar to a clay. However, the silica sheet is replaced by a magnesia one (MgO), and this makes them anionic exchangers.

ANALYSIS FOR THE LANGMUIR ISOTHERM

The basis of this method is to carry out a series of correlations with the data in which one or more of the data points are omitted. In this way a series of straight line correlations can be obtained and, in particular, a series of a and b values. The mean and standard deviations of these values can be obtained in the normal manner, and from this the errors in C and K_d calculated. Even with only five points of data, quite a number of permutations are possible. First, one of the points is omitted, then two, and so forth. It can be shown that the number of permutations is given from the coefficients in the binomial series $(1 + x)^N$ where N is the number of data points. Thus,

$$(1 + x)^N = 1 + \sum B_N^M x^M \tag{3}$$

In this expression B_N^M is the number of permutations possible if M points are omitted in each series. For example, if there are six data points, six permutations are possible if one data point is omitted, 15 with two, 20 with three, and 15 with four left out in each set.

Evaluation of all the possible sets of data can thus be quite time-consuming. Hand calculations were performed in the initial stages of this investigation to calculate the standard deviations (SDa and SDb) for a series of experiments as a function of the number of points omitted. The results of these calculations are given in Fig. 1 in the forms SD$a/\bar{a}$ and SD$b/\bar{b}$ as a function of the number of points left out (M) in each set. In these last two expressions the symbols with the bar above then denote the mean of the constants a and b. From this graph it can be clearly seen that the standard deviation increases when M increases. This means that the standard deviation of the correlation when all the data points are considered will be smaller than that obtained from the series when one of the points is left out. However, there is no firm theoretical basis

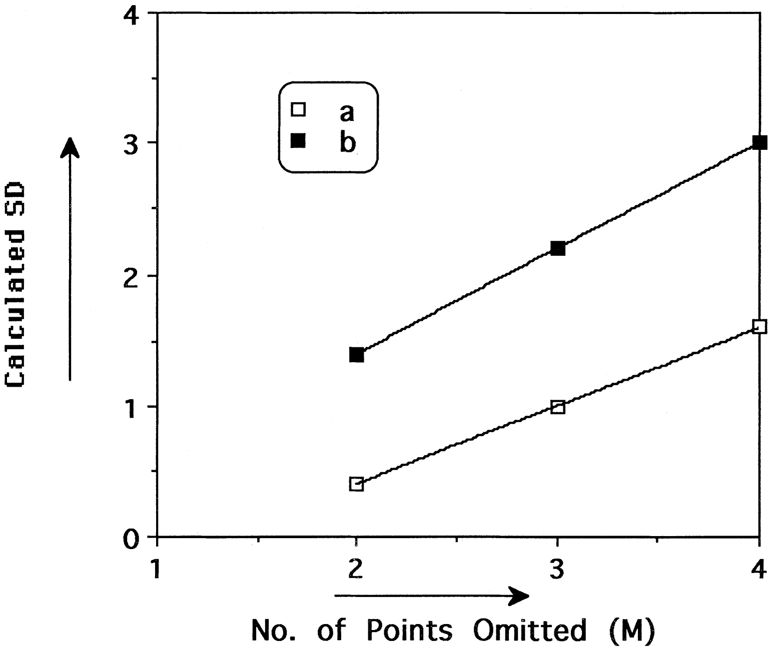

FIG. 1 Standard Deviation calculated as a function of the number of data points omitted.

for interpolating the data to obtain this value. It can reasonably be said that the standard deviation obtained from the set with one point omitted is an upper bound for the true value.

CORRELATION RESULTS

From this preliminary investigation a standard protocol was used to analyze some of the data. This was to obtain values of *a* and *b* for the cases where all the points were used in the correlation and for the set where one point was left out at a time. This gives $N + 1$ calculated values from which the means ($\bar{a}$ and $\bar{b}$) and standard deviations (SD*a* and SD*b*) can be calculated. The parameters $\Lambda_a = \mathrm{SD}a/\bar{a}$ and $\Lambda b = \mathrm{SD}b/\bar{b}$ were plotted as a function of R^2, the coefficient of correlation obtained from the regression with all data points taken into account. It is reasonable to assume that the values of Λ_a and Λ_b will increase as the value of R^2 decreases.

The results of this analysis are given in Figs. 2 and 3 for the two sets of data. In Fig. 2 the results for Λ_a are given. The graph consists of a series of scattered points and there is a suggestion that there is a lower limit on Λ_a for R^2 greater than 0.92. However, even if R^2 is close to unity, the values of Λ_a may be as high as 0.5. The obvious conclusion is that the value of Λ_a cannot be estimated by an analytical function involving the coefficient of correlation (R^2). This

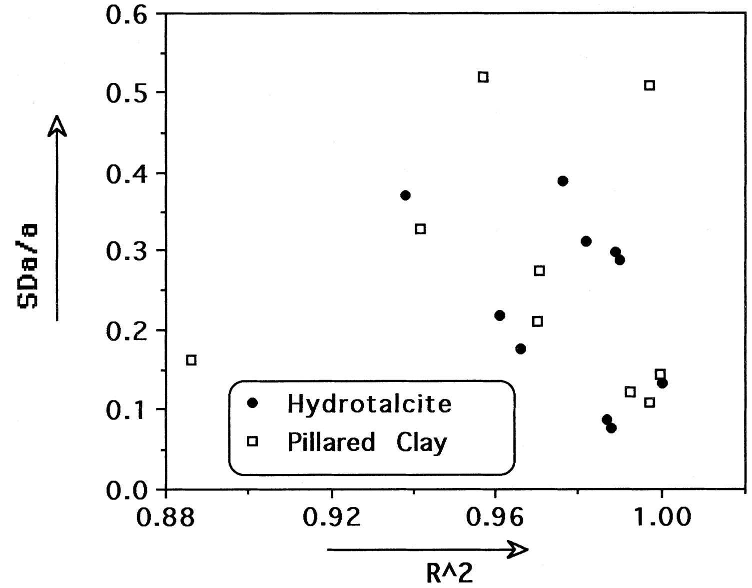

FIG. 2 Statistical analysis of the *a* Parameter.

also means that the error of measuring the reciprocal of a or the K_d values is liable to be a very considerable error. Results for Λ_b are given in Fig. 3 and it can be seen that there is a correlation between Λ_b and R^2. The data points are still somewhat scattered, so any determination of an analytical function to pre-

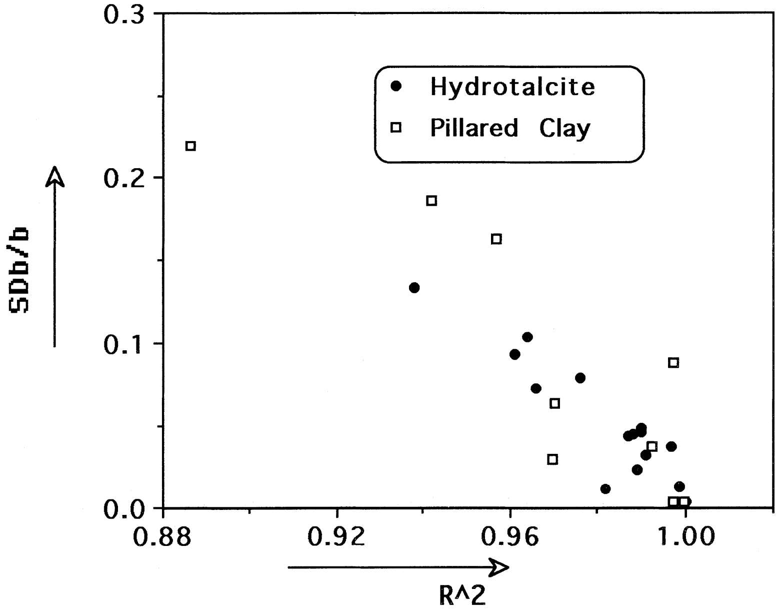

FIG. 3 Statistical analysis of the *b* Parameter.

dict Λ_b would have a considerable error term associated with it. The general values of Λ_b are less than those of Λ_a.

A computer program was subsequently written to carry out the analysis outlined previously. This proved to be quicker to use than the manual method of using a spreadsheet. In this program the C and K_d values were calculated directly and not from the a and b values determined in the linear spreadsheet regression. All the data for the hydrotalcite work were analyzed, and the general distribution of the calculated results was plotted using the parameters θ_c and θ_{K_d} which are defined as

$$\theta_c = \frac{C_i - \overline{C}}{\mathrm{SD}C} \tag{4}$$

where C_i is a calculated value of C for one of the iterations, $\overline{C}$ is the mean value of C for the particular isotherm determination, and SDC is the standard deviation for that determination. For K_d,

$$\theta_{K_\mathrm{d}} = \frac{K_{\mathrm{d}i} - \overline{K}_\mathrm{d}}{\mathrm{SD}K_\mathrm{d}}$$

The terms in the last equation are defined in a similar manner to those in Eq. (4).

The results of these calculations are shown in Figs. 4 and 5. Data for the uptake of the following anions were plotted on the graphs. These ions are sulfate,

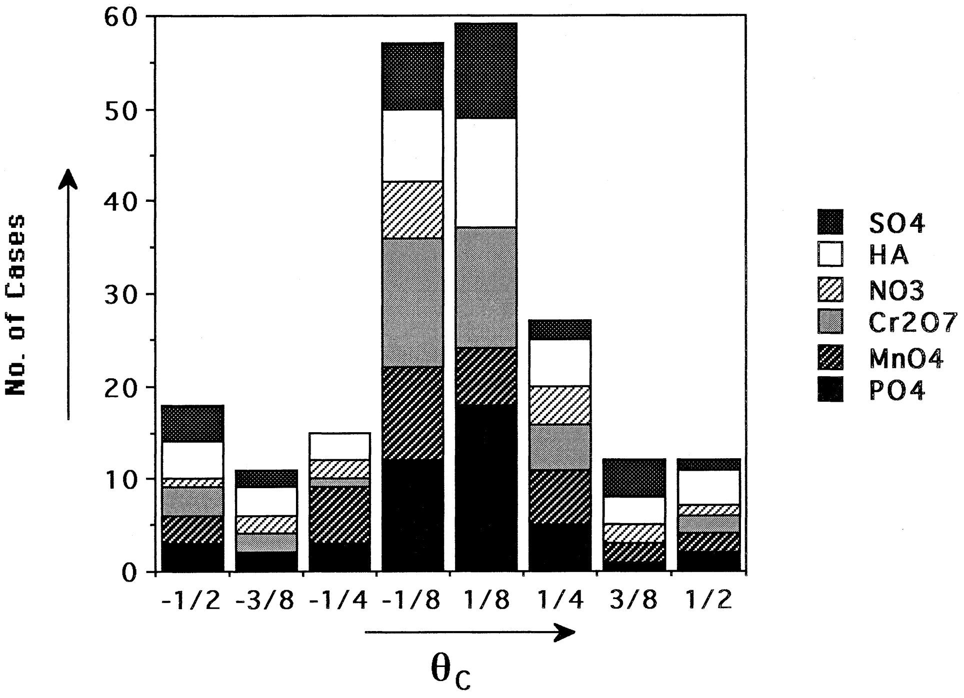

FIG. 4 Distribution of C values.

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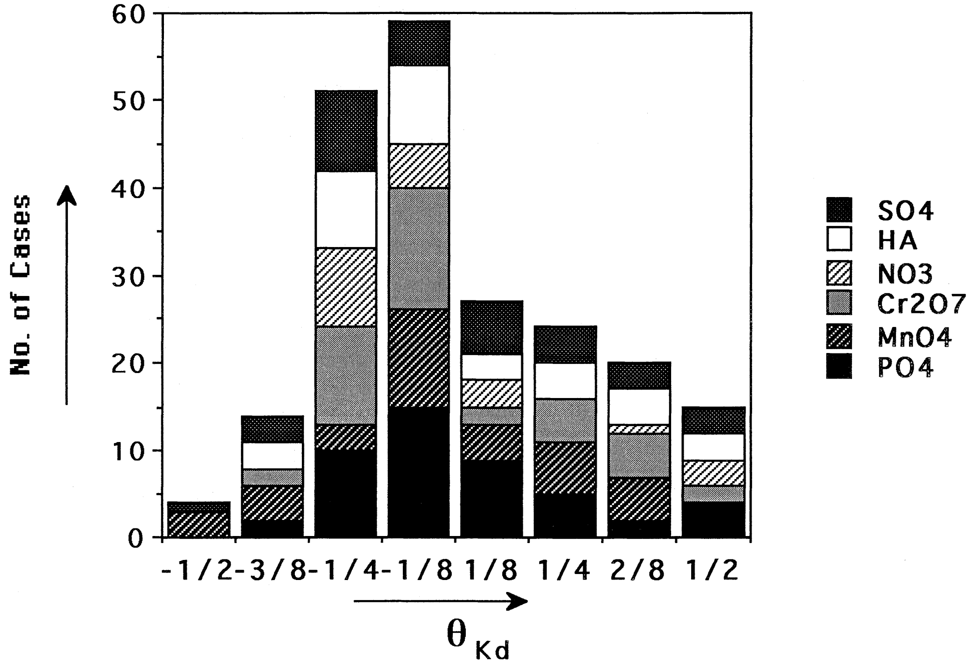

FIG. 5 Distribution of K_d values.

humic acid (HA), nitrate, chromate, permanganate, and phosphate. The data in these graphs are plotted as a cumulative stack as a function of the θ values. The stack labeled 1/8 shows the number of times the θ value was between 0 and 1/8, and the stack labeled 3/8 shows the number of times the θ value was between 1/4 and 3/8, and so on. The data for the distribution of the *C* data, which is shown in Fig. 4, display a symmetrical distribution like a normal one. However, the data in Fig. 5 for the spread of the K_d values have a distinctly skewed distribution. This would complicate the estimation of errors for this parameter.

CORRELATION OF THE BET ISOTHERM

Often data cannot be correlated by the simple Langmuir isotherm and, in more complicated situations, where, for example, two different ions are being exchanged, the BET isotherm is used. This takes the form

$$y_i = \frac{Ax_i}{(C - x_i)(1 + Bx_i)} \tag{5}$$

The method of finding the values of *a*, *b*, and *c* is more complex than it is for a Langmuir isotherm, so it will be outlined next. Rearranging the last expression gives

$$r_i = \frac{x_i}{y_i} = \frac{C}{A} + \left[\frac{BC - 1}{A}\right] x_i - \frac{B}{A} x_i^2 \tag{6}$$

Therefore, plotting r_i as a function of x_i will yield a quadratic function for which the computer correlation package will yield,

$$r_i = \frac{x_i}{y_i} = a + bx_i - cx_i^2 \tag{7}$$

a, b, and c are all positive quantities. Comparison of the last two equations and rearrangement gives

$$b = \frac{A^2ac - 1}{A}$$

So the value of A is the positive root of the quadratic equation

$$A^2ac - Ab - 1 = 0 \tag{8}$$

and the values of B and C are given by

$$B = Ac \qquad \text{and} \qquad C = Aa \tag{9}$$

Equation (5) can be rearranged by partial fractions to give

$$y_i = \frac{A}{(1 + BC)} \left\{ \frac{Bx_i}{1 + Bx_i} + \frac{x_i}{C - x_i} \right\} \tag{10}$$

The first expression is a normal Langmuir relationship to which a nominal capacity (the monolayer value M) can be assigned in the case where x_i is large, and this is

$$M = \frac{A}{(1 + BC)} \tag{11}$$

The second is a "reverse Langmuir" component where y_i tends to infinity at values of x_i close to C. Finally, the K_d value for the BET isotherm is its slope when x_i is small and is given by

$$K_\mathrm{d} = A/C \tag{12}$$

ERROR ANALYSIS FOR THE BET ISOTHERM

This is quite a complex analysis. The main aim here is to determine the standard deviations of M and K_d, which are the main parameters that determine the sorption properties of the material. To illustrate the procedure, some actual data will be considered. The raw data are shown in Fig. 6, and seven data points were measured for the determination of the isotherm. These points were obtained for the sorption of permanganate ion on magnesium hydrotalcite at room temperature. The data have the typical sigmoidal shape that is normally associated with the BET isotherm. From the position of the point of inflection of the data, a monolayer capacity of about 45 mg/g is suggested. In Fig 7 these

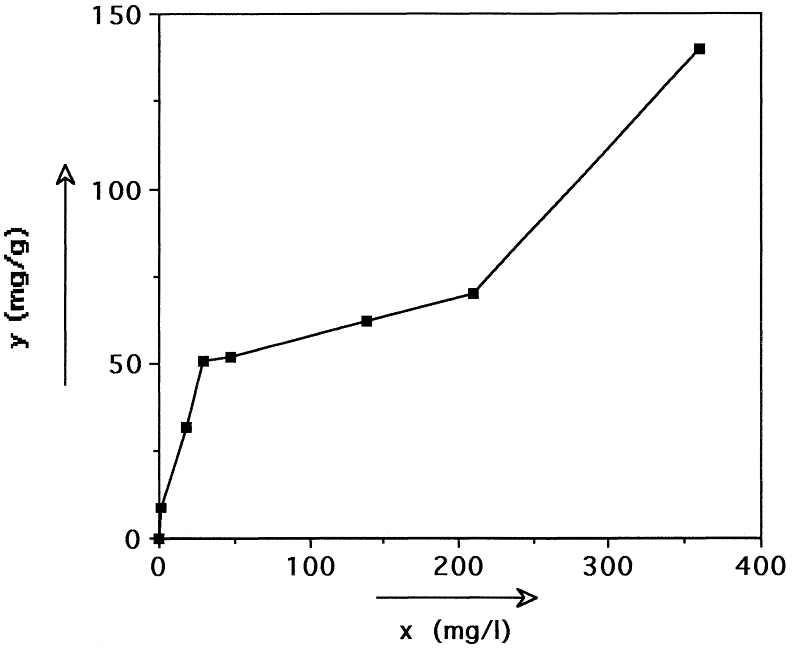

FIG. 6 Sample BET data.

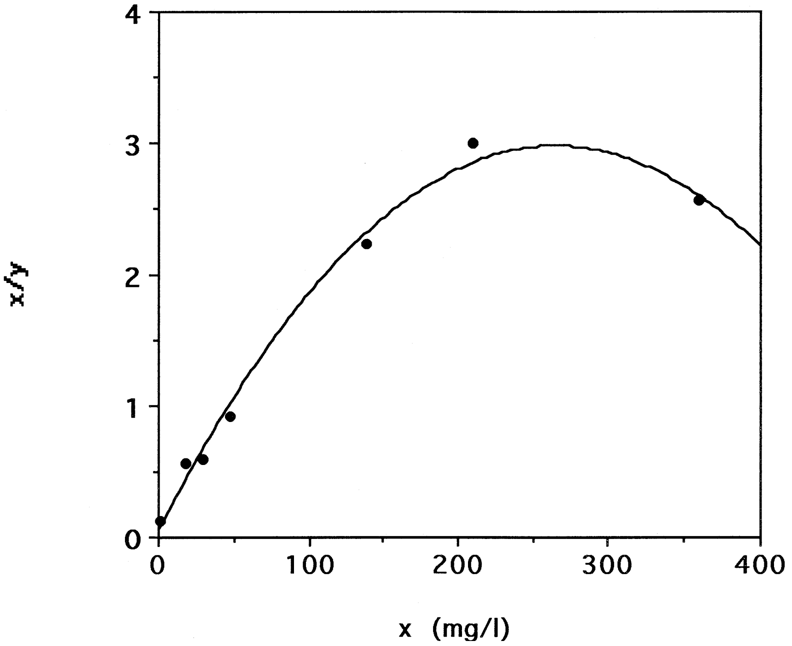

FIG. 7 BET correlation plot.

TABLE 1

Calculation no.	Value of M	Value of K_d
1	44.8	17.4
2	56.2	6.8
3	48.4	9.7
4	43.0	22.5
5	44.4	12.4
6	44.8	11.4
7	44.2	229.4
8	44.1	46.3

data are transformed to an x/y versus x plot and, following Eq. (7), this has been correlated using a quadratic function which is shown on the figure.

Visual inspection shows that the apparent fit is quite good, and an R^2 value of 0.997 was obtained for this plot. The values of a, b, and c were obtained and the algebra of the previous section was carried out to obtain an estimate of M and K_d from Eqs. (11) and (12). The process was then repeated, omitting one of the data points in turn, and the results of these calculations are shown in table 1 which refers to the calculation in which all seven points were used for the correlation.

It can be seen that the results for the values of M are reasonably consistent, and a mean value of 46.2 was obtained with a standard deviation of 4.3. The ratio of standard deviation to mean is around 0.1, so there is statistical confidence in the value obtained. However, the calculations for the K_d values show considerable scatter. There is one “rogue” result in the figures of 229.4. The mean for K_d is 44.5 and the standard deviation is greater than the mean. It should be concluded that a valid value for K_d cannot be obtained from these data.

CONCLUSIONS

The procedure outlined in this paper enables the errors inherent in an isotherm correlation to be estimated using a fairly simple routine. All the results presented here indicate that the capacities of sorbing materials can be estimated with some confidence. However, there is evidence that the initial slopes of the isotherms, which determine the K_d values, may be very difficult to calculate with any degree of certainty. This is of some concern for applications removing trace quantities of pollutants as, in this case, the removal is directly proportional to the K_d value. This means that the data must be very accurate for this determination. Further research into this problem has a basic role in sorption research.

NOMENCLATURE

a, b	linear correlation coefficients
$\bar{a}$, $\bar{b}$	mean of a and b
c	sorbent capacity
K_d	slope of isotherm when x is small
N	number of data points
R^2	correlation coefficient
SD	standard deviation
x_i, y_i	data points
Λ_a	SD$a/\bar{a}$
Λ_b	SD$b/\bar{b}$

REFERENCES

1. M. T. Bowser and M. T. Chen, “Monte Carlo Simulation of Error Propagation in the Determination of Binding Coefficients from Rectangular Hyperbolae,” *J. Phys. Chem.*, *103A*, 192–202 (1999).
2. K. L. Rundlett and D. W. Armstrong, “Examination of the Origin, Variation and Proper Use of the Expressions for the Estimation of Association Constants by Capillary Electrophoresis,” *J. Chromatogr. 721A*, 173–186 (1996).
3. R. T. Yang and L. S. Cheng, “Pillared Clays as Gas Adsorbents and Catalysts,” in *Access in Nanoporous Materials* (T. J. Pinnavia and M. F. Thorpe, Eds.), Plenum Press, New York, NY, 1995, pp. 37–91.
4. S. Miyata, “Physico-chemical Properties of Synthetic Hydrotalcites in Relation to Their Composition,” *Clays Clay Miner.*, *28*, 50–56 (1980).

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