ESTIMATING RETARDATION FROM THE FREUNDLICH ISOTHERM FOR MODELING CONTAMINANT TRANSPORT

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Summary

Being able to model leachate migration from landfills is needed to protect the public and the environment. The distribution coefficient K_d has been used to estimate the retardation factor used in modeling contaminant transport but this K_d assumes linear adsorption which may only be realistic at low contamination levels. At high contamination levels this approach could result in contaminant transport being significantly underestimated. The unified sorption variable, K_u of the Freundlich isotherm could be a more appropriate parameter for estimating contaminant retardation and lends itself well to approximating nonlinear adsorption.

Keywords
Freundlich isotherm, retardation coefficient, unified sorption variable, contaminant transport

1. Introduction

A concern with landfills, and especially older unlined landfills, is the migration of leachate into groundwater that supplies water bodies supporting aquatic organisms, wildlife and humans. There is a reduced risk of off-site leachate migration at newer, lined landfills with leachate collection systems but the underlying soil may still be expected to offer some protection.

Contaminants transported in groundwater may be attenuated when they bind and react with the soil. One type of laboratory measurement of this bonding employs batch equilibrium tests with adsorption being represented by isotherms that are typically linear at low contaminant concentrations and nonlinear at higher contaminant concentrations.

In order to model transport of contaminants through the subsurface a linear adsorption isotherm is usually used because of its simplicity (Sharma and Reddy, 2004). With increasing contaminant concentration an initial linear increase in sorption is followed by a slowing and nonlinear rate of sorption increase as the capacity of the sorbent becomes exhausted.

The distribution coefficient, K_d is the slope of the line of linear sorption or the ratio of the equilibrium sorbed contaminant to the solution contaminant (Sharma and Reddy, 2004; Martinez et al., 2006). Since this ratio can be significantly smaller at higher contaminant concentrations, if K_d is employed for concentrations outside of the linear range then contaminant migration will be underestimated (Yong, 2001).

Soil sorption experiments have been widely modeled with the empirical nonlinear Freundlich isotherm for which the equation is

$$q_e = K_F C^{1/n} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

where q_e is the adsorbate divided by the adsorbent, K_F is the Freundlich constant and $1/n$ depends on the linearity of the isotherm and varies between 0 and 1. Only when $1/n = 1$ and the isotherm is linear does $K_F = K_d$.

In equation (1) C is usually the contaminant in solution at equilibrium, C_e, although it may also be the initial contaminant concentration of the solution, C_i (Ziper et al., 1988; Yong, 2001). Though less used, there can be advantages to plotting adsorption as a function of the initial contaminant concentration (Chen et al., 1999; Coles and Yong, 2006).

The one dimensional general transport equation for a contaminant plume is given by

$$\frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2} - V_S \frac{\partial C}{\partial x} - \frac{\rho_d}{\eta} \frac{\partial q_e}{\partial t} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

where t is time, D_L is the diffusion-dispersion coefficient, x is distance, V_S is the seepage velocity, ρ_d is the dry density, η is porosity and the other terms are as already defined. The first, second and third terms respectively represent diffusion, advection and adsorption (Yong, 2001; Sharma and Reddy, 2004; Martinez et al., 2006) although this equation neglects radioactive decay and storage (Yong, 2001).

Adsorption results in slower contaminant transport and when adsorption is linear ($q_e = K_d C$) the soil retardation coefficient, R is given by

$$R = 1 + \frac{\rho_d}{\eta} K_d \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

When R = 1 no retardation occurs and when R > 1 the contaminant velocity is slower than the seepage velocity (Sharma and Reddy, 2004; Matinez et al., 2006). Substituting $q_e = K_d C$ into the transport equation (2) and rewriting this equation in terms of R gives the transport equation as

$$R \frac{\partial C}{\partial t} = D_L \frac{\partial^2 C}{\partial x^2} - V_S \frac{\partial C}{\partial x} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

For the Freundlich isotherm the slope or partition coefficient can be given by (Zheng and Bennett, 2002)

$$\frac{\partial q_e}{\partial C} = K_F \frac{1}{n} C^{1/n-1} = K_d \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

In this case the retardation coefficient is given as (Sharma and Reddy, 2004)

$$R = 1 + \frac{\rho_d}{\eta} K_F \frac{1}{n} C^{1/n-1} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

To more accurately estimate retardation and contaminant transport other than the use of a single value is required. However, defining transport in terms of a retardation coefficient based on nonlinear adsorption could be complicated (Yong, 2001). The Freundlich model is one of the more widely used models for describing contaminant sorption, but there are ideological problems associated with the use of K_F (Chen et al., 1999). The objective of this paper is to examine how the Freundlich model can be used to predict retardation by presenting a more simple way of accounting for nonlinear adsorption and by employing a more appropriate parameter than the Freundlich constant.

2. Discussion

Although the nonlinear Freundlich isotherm is widely used, a problem associated with the use of the Freundlich constant concerns its units and for this reason Chen et al. (1999) proposed a unified sorption variable, K_u. The units for the Freundlich constant are $mg^{1-1/n} kg^{-1} L^{1/n}$ or $mmol^{1-1/n} kg^{-1} L^{1/n}$ and so Freundlich constants with different $1/n$ values are not strictly comparable. When Freundlich isotherms are linearized the slopes of the Freundlich isotherms with different $1/n$ values will intercept and so a greater value of K_F may not mean a greater adsorption (Coles and Yong, 2006). Tharayil et al. (2006) solved this problem in comparing selected Freundlich isotherms by using a "concentration-dependent sorption coefficient" K_d which they calculated at two discrete equilibrium concentrations.

The unified sorption variable is the changing slope of the Freundlich isotherm and is calculated in terms of C or q_e from either of the two below equations.

$$K_u = \frac{K_F}{C^{(n-1)/n}} \dotfill (7)$$

$$K_u = \frac{K_F^n}{q_e^{n-1}} \dotfill (8)$$

The agreement between equations (7) and (8) will reflect the goodness of fit between the data and the Freundlich isotherm (Chen et al., 1999; Coles and Yong, 2006). K_u has the same units as K_d but if C is given in mg/kg rather than mg/L (allowing that 1 L of water weighs 1 kg) then K_u is dimensionless. For the nonlinear Freundlich isotherm ($1/n < 1$), the slope of the isotherm or K_u decreases as the contaminant concentration increases (Chen et al., 1999; Coles and Yong, 2006) and this is well illustrated by Marchi et al. (2006).

Although either equation (7) or (8) can be used, equation (7) could be preferable as C (C_e or C_i) is the independent variable. However, if the Freundlich curve of best fit is used in place of the actual data then the values calculated from equations (7) and (8) are identical. Plotting K_u (on the y-axis) as a function of C_e, (on the x-axis) Marchi et al. (2006) obtained an approximately L-shaped curve that showed an initially rapid decrease in K_u followed by a more moderate decrease. Their values for K_u ranged from > 500 L/kg to < 50 L/kg and from approximately 250 L/kg to 25 L/kg for two sets of data, respectively. Since there is an order of magnitude variation in K_u, using a single value of K_d will generally underestimate contaminant transport.

Assuming linear adsorption is a simple though possibly unsafe approach. On the other hand, using the constantly changing slope of the Freundlich isotherm or K_u is complicated. However, if the change in the slope of the Freundlich isotherm as a function of the contaminant concentration is approximated

with straight line segments, the lowest value of K_u for each segment may be conservatively used to represent the ratio of sorbed contaminant to solution contaminant. This approximation could significantly improve the predictive capacity of contaminant transport without being unduly cumbersome.

3. Numerical Example

A practical example is presented. Batch equilibrium tests were conducted in duplicate on an artificial soil of 5 g of kaolinite and 0.05 g of humic acid that was spiked with 50 mL solutions of $CdCl_2$ at concentrations of 50, 100, 250, 500, 750, 1000, 1500, 2000 and 2,500 ppm (0.445, 0.890, 2.22, 4.45, 6.67, 8.90, 13.4, 17.8, and 22.2 mmol/L). These concentrations of Cd tested and the amounts of Cd adsorbed are shown in Table 1. More details of the laboratory procedure can be found in Coles and Yong (2006).

Batch Test	Initial Cd concentration, C_i (mmol/L)	Adsorbed Cd, q_e (mmol/kg)	Calculated adsorbed Cd, q_e (mmol/kg)	Unified sorption variable, K_u (L/kg)	Range of C_i (mmol/L)	K_u values for estimating R (L/kg)
1	0.445	3.59	3.87	8.70	0 – 0.445	8.00
2	0.890	5.51	5.20	5.84	0.445 – 0.890	5.80
3	2.22	7.88	7.68	3.46	0.890 – 2.22	3.40
4	4.45	9.98	10.3	2.32	2.22 – 4.45	2.30
5	6.67	13.3	12.3	1.84	4.45 – 6.67	1.50
6	8.90	14.1	13.9	1.56	6.67 – 8.90	1.50
7	13.4	17.4	16.5	1.23	8.90 – 13.4	0.90
8	17.8	16.0	18.6	1.05	13.4 – 17.8	0.90
9	22.2	21.1	20.5	0.923	17.8 – 22.2	0.90

Table 1 Batch experiment sorption results, sorbed Cd calculated using the Freundlich equation, unified sorption variables calculated from the Freundlich isotherm and approximate values of K_u for straight line segments representing the Freundlich isotherm

The Freundlich isotherm represented in equation (1) can be rewritten in the form of a straight line equation as

$$\log q_e = \log K_F + (1/n) \log C \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(9)$$

and if the logs of the data are plotted on arithmetic paper, Microsoft Excel can be used to obtain the line of best fit, its slope (which equals 1/n) and its y-intercept (the antilog of which equals K_F). The Freundlich equation obtained for the data in Table 1 is $q_e = 5.466\, C_i^{0.4261}$ and it is plotted in Figure 1 with the actual data points also shown.

K_d is 3.59 ÷ 0.445 or 8.07 [L/kg] when determined using the measured data and 3.87 ÷ 0.445 or 8.70 [L/kg] when taken from the Freundlich isotherm (or the first term in the column 5 of Table 1). The unified sorption variables are the slopes at each of the data points. If the points on the Freundlich curve are used to determine the unified sorption variables, then using equation (7) or (8) yields identical results. These unified sorption variables are given in column 5 of Table 1 and the curve showing these variables plotted against the initial Cd concentrations is shown in Figure 2. It can be seen from Table 1 that the values of K_u range from 8.70 to 0.923 L/kg or almost a difference of one

order of magnitude and this variation is very similar to the variations in values of K_u that were encountered by Marchi et al. (2006).
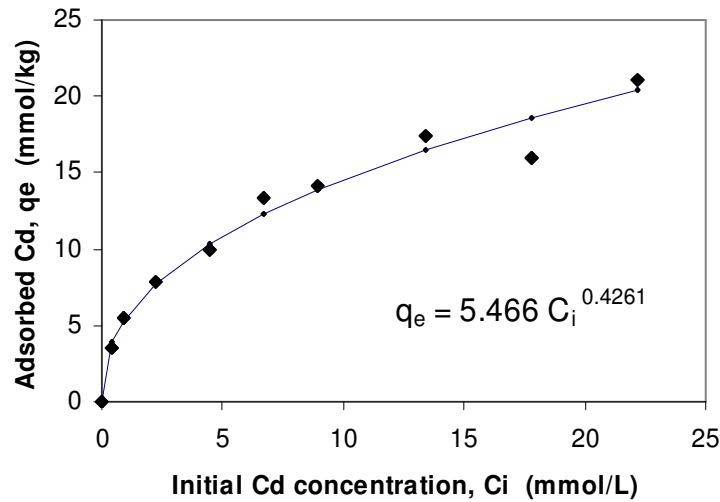

Fig. 1 Sorption of Cd as a function of the initial Cd concentration showing the batch test results and the Freundlich isotherm that best fits the sorption data

Greater adsorption means greater retardation and slower contaminant transport. Therefore, assuming a smaller value of K_u and R is conservative and provides a margin of safety since it assumes more rapid transport. Therefore one solution would be to use the lower value of K_u for a selected range of values of C (or in this case C_i). Also at the higher contaminant concentrations there is less variation in K_u and so the same value of K_u can be used over a wider range of C at the higher contaminant concentrations.
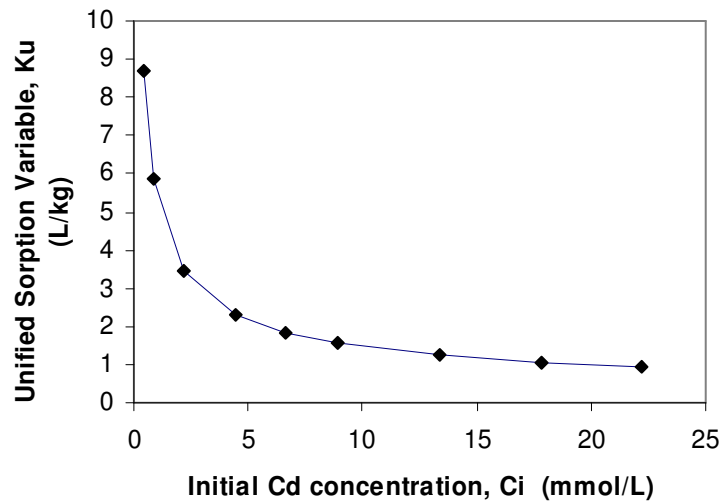

Fig. 2 Unified sorption variables calculated from the Freundlich isotherm data as a function of the initial Cd concentrations

If the curve in Figure 2 is broken into segments as indicated in column 6 of Table 1, then possible values of K_u that can be assigned to each of these segments are shown in column 7 of Table 1. These values range from 8.00 to 0.90 L/kg whereas K_d in this instance would be approximately 8.00 L/kg.

Using a fewer number of different K_u values would mean a safer and more conservative estimate of the transport of contaminants.

4. Conclusion

The linear distribution coefficient K_d has been used to calculate the retardation factor R that is used in contaminant transport equations. However, since linear adsorption is assumed the actual ratio of adsorbate to adsorbent may be smaller by a factor of about 10 at higher contaminant concentrations. Since this is not conservative it could be safer and more accurate to make use of the unified sorption variable K_u to calculate R. Since K_u changes constantly with C and using a constantly changing K_u would be complicated, one solution is to select a small number of discrete values of K_u that can be used to approximate and slightly underestimate the actual values of K_u and each of these values can be used to calculate R over the range of contaminant concentrations that they are applicable.

In the example presented here the use of a total of 6 different values of K_u are suggested but this number could be smaller if a more conservative estimate is acceptable.

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