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Effect of nonlinear adsorption on contaminant transport through landfill clay liners

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ABSTRACT: The influence of nonlinear adsorption behavior of clays on contaminant transport through clay liners was evaluated. Two types of contaminants, hexavalent chromium and pentachlorophenol, were studied. The batch test results show that the adsorption of these contaminants on clays follows nonlinear behavior. Nonlinear adsorption occurs due to the finite cation- or anion exchange capacity of contaminants. Organic contaminant adsorption onto clays is limited by the finite number of adsorption sites. Metallic contaminants such as Cr(VI) exist as anions in solutions and are adsorbed weakly onto clays by anion-exchange. Adsorption of such anions is affected by the presence of competitive anions such as borates and phosphates and the pH. Adsorption of organic contaminants can be significant depending on the organic content of the clay liner. The contaminant transport models grossly overpredict retardation of contaminants at high solute concentrations by assuming linear adsorption; therefore, it is important to incorporate nonlinear adsorption in these models to determine accurate contaminant transport through the liner systems.

1 INTRODUCTION

The prediction of contaminant transport through clay liners is required for the design of effective landfill liners. It is important to accurately determine the breakthrough times and concentrations for contaminant fronts to comply with regulations safeguarding groundwater quality. Landfill design typically incorporates a leachate collection and removal system to prevent leachate head build-up above the liner. Although this leachate head is generally less than one foot, there is a potential for the migration of contaminants through the liner.

The Illinois Environmental Protection Agency (IEPA) has developed specific regulations to ensure that the groundwater quality in the vicinity of a landfill is not affected by entry of contaminants from the bottom of the landfill (IEPA, 1992). Per design standards for Illinois municipal solid waste landfill liners (35 IAC 811.306), a leachate collection system is necessary, the maximum allowable leachate head is one foot, and the compacted soil liner thickness should be a minimum of 5 feet. If however a 60-mil geomembrane is used above the compacted soil liner, the minimum soil liner thickness is 3 feet. The hydraulic conductivity of the soil liner should be less than 10^{-7} cm/sec. In addition, contaminant transport modeling must be performed to demonstrate that the design ensures the concentrations of pollutants outside of the zone of attenuation to be less than the applicable groundwater quality standards within 100 years of closure. The zone of attenuation is 100 feet from the landfill or the property boundary, whichever is less. USEPA (federal) regulations provide two options in designing landfill liner systems (USEPA, 1991). They stipulate that a 2 feet compacted soil liner, with hydraulic conductivity less than 10^{-7} cm/sec, is necessary when a geomembrane is used in conjunction, else they offer flexibility in designing the liner system provided it is demonstrated that the contaminant concentration in the groundwater is less than the allowable constituent concentration at the relevant point of compliance.

In order to optimize liner design and to meet the regulatory requirements, one-dimensional contaminant transport models are generally employed to determine the breakthrough times and concentrations of the contaminants through liners (e.g., Rowe and Booker, 1985). These models account for primarily three migration mechanisms, namely, advection, diffusion, and adsorption. Advection accounts for movement of contaminant along with the flowing water and is associated with the seepage velocity of the water. Diffusion is the migration of contaminant from a high concentration zone to a low concentration zone. Adsorption accounts for removal of the contaminant by the clay thereby retarding the migration of the contaminant front.

The contaminant transport models generally incorporate linear adsorption of contaminants to the clay liners. Employing linear adsorption in calculating the breakthrough times has an important underlying assumption that the clay liner has infinite adsorption capacity. While linear adsorption may be appropriate to model dilute pollutant concentrations in leachate, most pollutants possess nonlinear adsorption characteristics at high solute concentrations (Reddy et al., 1995; Johnson, 1994). Nonlinear adsorption occurs due to the finite cation- or anion exchange capacity of contaminants. Organic contaminant adsorption onto clays is limited by the finite number of adsorption sites. At high solute concentrations, saturation of adsorption sites is achieved faster. This nonlinear adsorption of contaminants can significantly affect the breakthrough times of contaminant fronts. This paper provides adsorption test results for hexavalent chromium (Cr(VI)) and pentachlorophenol (PCP) and then discusses the effects of linear and nonlinear adsorption isotherms on the contaminant breakthrough times for a typical landfill liner system.

2 CONTAMINANT TRANSPORT PROCESS AND THEIR RELATIVE SIGNIFICANCE

The major contaminant migration processes through the liner systems are advection, diffusion and adsorption. Advection of a pollutant is associated with the seepage velocity of the leachate and calculated using the Darcy's law given in equation (1) :

$$V_s = \frac{ki}{n} \tag{1}$$

The contaminant breakthrough time if only advection is considered can be calculated using equation (2):

$$t = \frac{H}{V_s} \tag{2}$$

In above equations, k= hydraulic conductivity, i= hydraulic gradient, n =effective porosity, V_S=seepage velocity, H=liner thickness, and t=contaminant breakthrough time. Because k, n, i and H are known with good accuracy, V_s and t can be easily calculated.

Diffusion of contaminant molecules from regions of high concentration to regions of low concentration is modeled using the Ficks' law as illustrated by equation (3):

$$F = -D_m \frac{\partial C}{\partial z} \tag{3}$$

where, F= mass of contaminant per unit area per unit time, D_m= diffusion coefficient, C= contaminant concentration, and z= depth. The diffusion coefficient does not vary significantly for different contaminants and soil types and can be determined by laboratory experiments (Shackelford and Daniel, 1991).

Adsorption of contaminants is a function of solute concentration and in general form is given by equation (4):

$$S = f(C) \tag{4}$$

where, S= amount of contaminant adsorbed to the soil, and C= solute concentration. Generally, batch tests are performed to determine S versus C and the plot of S versus C yields an adsorption isotherm. For linear adsorption, S and C are related by equation 5:

$$S = K_d C \tag{5}$$

K_d is known as distribution coefficient and is constant in the above linear adsorption isotherm.

The contaminant migration is modeled using 1-D flow and transport equation given by:

$$R\frac{\partial C}{\partial t} = D_m \frac{\partial^2 C}{\partial z^2} - V_s \frac{\partial C}{\partial z} \tag{6}$$

where, R is the retardation factor calculated using the following equation (7).

$$\frac{U}{V_s} = R = 1 + \frac{\rho_d K_d}{n} \tag{7}$$

where, U= average retarded velocity, V_S= seepage velocity, ρ_d= dry density of liner soil.

The relative significance of advection, diffusion and adsorption are illustrated for a typical landfill liner system shown in Figure 1. Analytical solution of 1-D contaminant transport equation given in Eqn.(6) was used to determine 1% concentration front (C_e/C_0=0.01) breakthrough time through the liner (Javandel et al., 1984). Analyses were performed for the cases of (I) advection only, (ii) diffusion only, (iii) advection and diffusion, and (iv) advection-diffusion-adsorption. All these analyses were performed assuming that a linear adsorption isotherm is valid. A constant leachate head of 1 foot and the following clay liner properties were assumed: hydraulic conductivity of 1 x 10^{-7} cm/sec, diffusion coefficient of 1x 10^{-5} cm²/sec, porosity of 0.3, dry density of 2.12 g/cm³ and a distribution coefficient of 0.1 cm³/gm. The analysis results for three different liner thicknesses (3, 5, and 10 feet) are shown in Figure 2. From Figure 2 it is clear that diffusion is the major contaminant migration process followed by advection. The combined effect of advection and diffusion results in a breakthrough time far less than that of either mechanism alone. Adsorption increases the breakthrough time by retarding the front migration velocity. The retardation factor used for this analysis was based on a K_d from a linear adsorption isotherm.

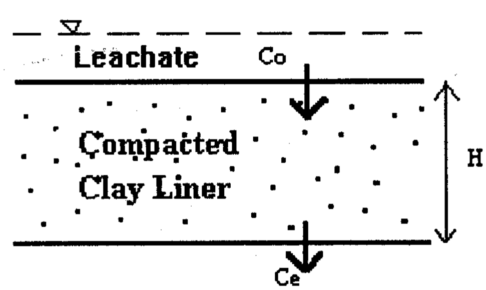

Figure 1. Typical landfill liner system

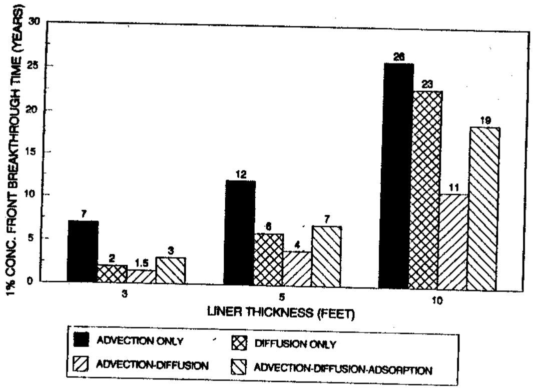

Figure 2. Relative significances of transport processes

The breakthrough time due to combined advection, diffusion and non-linear adsorption will be greater than that of advection and diffusion, but lower than that of advection, diffusion and linear adsorption illustrated in Figure 2. Further, different contaminants adsorb in differing amounts to the same adsorbate. For instance, the adsorption of inorganic contaminants is primarily dependent on the cation- or anion exchange-capacity of the clay. Further different clays have different adsorption mechanisms. Smectite groups develop a double layer via which adsorption occurs (Drever, 1988). Kaolin groups have surface groups directly involved in adsorption (Drever, 1988). Hence even in linear adsorption different K_d values are possible leading to different breakthrough times for different contaminants. Figure 3 illustrates the relationship between varying diffusion coefficients and K_d values on the breakthrough time of a contaminant front. A constant leachate head of 1 foot and the following clay liner properties were assumed: hydraulic conductivity of 1 x 10^{-7} cm/sec, diffusion coefficient of 1x 10^{-5} cm^2/sec, porosity of 0.3, dry density of 2.12 g/cm^3 and a distribution coefficient of 0.1 cm^3/gm and a constant liner thickness of 5 feet. Three different distribution coefficients of 0.01, 0.1 and 1.0 cm^3/gm were assumed.

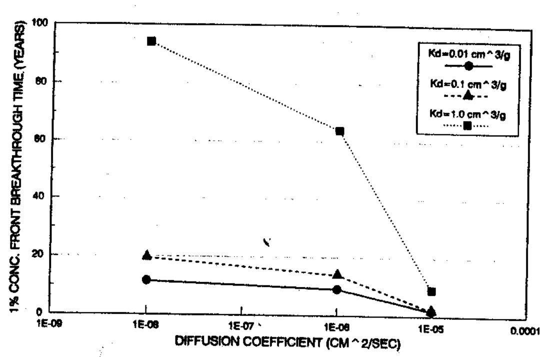

Figure 3. Effect of diffusion and distribution coefficients

Adsorption of the contaminant onto the clay surface retards the migration of the contaminant front through the liner. If the clay liner does not adsorb the contaminant then the contaminant front will migrate with a velocity equal to the seepage velocity of the leachate and the breakthrough time is a function of the liner thickness and the seepage velocity as illustrated by Equation (2). In general, most compacted clay liners adsorb contaminants both organic and inorganic. The presence of organic matter in the soil further enhances the adsorption of organics such as PCP (Warith et. al., 1993). Overall adsorption will result in retarding V_S. The degree of retardation is a function of the adsorption of the contaminant. The linear adsorption isotherm is generally valid when the contaminant concentrations are low. However. at high concentrations experimental observations of adsorption phenomenon have shown that the amount of contaminant retained by the clay bears a non-linear relationship to the solute concentration, due to the finite number of adsorption sites. This necessitates the use of nonlinear adsorption isotherm in contaminant migration analysis.

In this paper the nonlinear relationship of S and C is investigated. Increasing solute concentrations (C) result in increasing S values in nonlinear form until all of the adsorption sites are occupied. Once the adsorbing medium is saturated, no adsorption takes place. Because of nonlinear adsorption, the retardation factor (R) decreases with increasing solute concentration and finally becomes equal to one. This will result in U approaching V_S and the contaminant breakthrough times drastically reduce.

3 METHODOLOGY

In order to evaluate the effect of non-linear adsorption on contaminant transport through landfill clay liners, batch test results which define adsorption isotherms of two contaminants, Cr(VI) (inorganic) and PCP (organic), was utilized. Adsorption data for Cr(VI) with glacial till and PCP with organic clay were obtained from Reddy et al. (1995) and Warith et al. (1993), respectively.

The adsorption test data for Cr(VI) and PCP was mathematically represented by the linear isotherm given in Equation (5) and also using the following different nonlinear isotherms (Fretter, 1993; Johnson, 1994):

<u>Freundlich Adsorption Isotherm:</u>

$$S = kC^n \tag{8}$$

where, k and n are constants.

<u>Langmuir Adsorption Isotherm:</u>

$$S = \frac{\alpha \beta C}{1 + \alpha C} \tag{9}$$

where, α and β are constants.

Exponential Adsorption Isotherm:

$$S = a(1 - e^{-bC}) \tag{10}$$

where, a and b are constants. The detailed adsorption isotherms are presented in Table 1.

Table 1. Adsorption Isotherms

Type of Isotherm	Cr(VI)	PCP
Linear S=	$1.82x10^{-3}C$	0.311C
Langmuir S=	(0.0026C)/(1+0.01C)	(0.606C)/(1+0.07C)
Freundlich S=	$0.01638C^{0.3924}$	$0.318C^{0.5244}$
Exp. S=	$0.2186(1\text{-}e^{-.0096C})$	$0.95(1\text{-}e^{-.318C})$

Figures 4 and 5 compare these different isotherms with the experimental data for Cr(VI) and PCP, respectively. It can be seen that the linear isotherm is valid for low concentration range, while the non-linear isotherms can incorporate the experimental data for low and high concentration ranges.

To illustrate the effect of nonlinear adsorption on contaminant transport through clay liners, a typical landfill clay liner system which meets the regulatory requirements of the Illinois Environmental Protection agency as shown in Figure 1 was selected. It should be mentioned that analytical solutions to the contaminant transport equation which incorporate nonlinear adsorption are not available and even the numerical

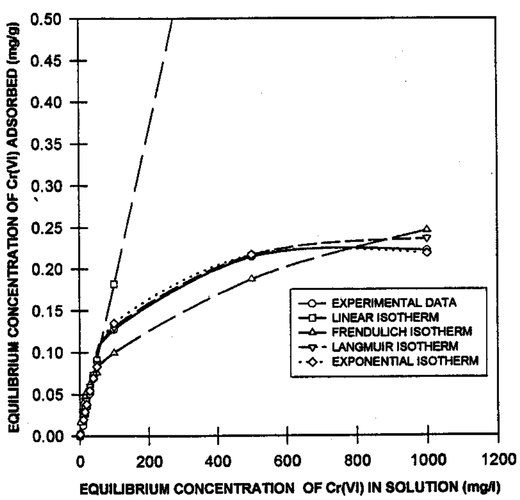

Figure 4. Cr(VI) adsorption isotherms

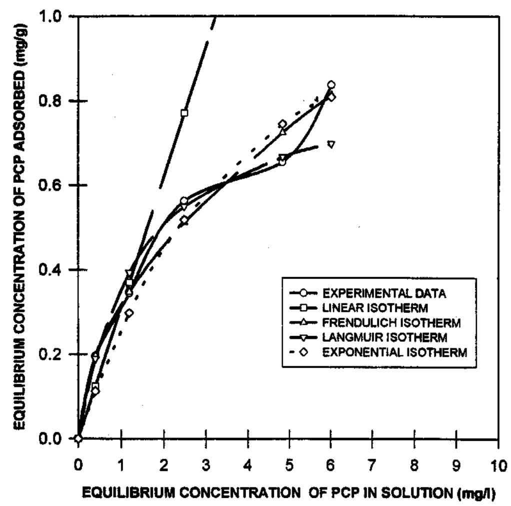

Figure 5. PCP adsorption isotherms

methods to solve such problems are limited. Since the purpose of this paper is to show the significance of nonlinear adsorption, only 1-D contaminant transport which incorporates advection and adsorption was considered. The diffusion of the contaminants is very significant and must be incorporated for field simulations. The seepage velocity of the contaminant can be calculated by using equation (1), and the adsorption retards this velocity as given by equation (7). In equation (7), K_d is constant in case of linear adsorption isotherm assumption; however, K_d value is a function of solute concentration in case of any nonlinear adsorption isotherm assumption. The K_d values can be calculated by taking the derivative of isotherm equations given in Table 1. The breakthrough time for the contaminant was then calculated by dividing the clay liner thickness by the retarded velocity (U). In calculations of breakthrough times, a constant leachate head of 1 foot and the following clay liner properties were assumed: constant liner thickness of 5 feet, hydraulic conductivity of 1×10^{-7} cm/sec, porosity of 0.3 and dry density of 2.12 gm/cm^3.

The nonlinear adsorption behavior of inorganic and organic contaminants and the contaminant breakthrough times for the selected liner system are discussed in detail in the next section.

4 RESULTS AND DISCUSSION

Figure 4 clearly demonstrates the overprediction of Cr(VI) adsorption by the linear adsorption isotherm. The adsorption experimental data can be best-fit either as an exponential or a langmuir isotherm. At high equilibrium solution concentrations of 400 mg/L of Cr(VI), the overprediction of adsorption by the linear isotherm is as high as a factor of 3, or greater. This overprediction results in erroneous retardation factors that will significantly affect the contaminant transport through the liner systems. Further, it is important to identify the adsorption mechanism responsible for the adsorption of Cr(VI). Adsorption of Cr(VI) is a typical anion - exchange mechanism. Unlike ligand exchange of certain oxyanions which is a form of chemisorption, anion-exchange of Cr(VI) is a physisorption mechanism. In the presence of competitive anions such as borates and phosphates, that possess a higher shared charge and are more electronegative, Cr(VI) will be exchanged by clay surface groups such as Si-OH and Al-OH. Smectite groups of montmorillonite clays may exhibit stronger Cr(VI) adsorption via a double layer adjacent to the clay surface. Another factor that will significantly affect adsorption of contaminants onto clay liners is the pH of the leachate. Acidic conditions of pH below the PZC (point of zero charge, i.e., the isoelectric point at which the cation exchange capacity equals the anion exchange capacity), are conducive to adsorption of Cr(VI) by anion exchange. At pH values higher than the PZC, Cr(VI) adsorption onto clays will be decrease and is virtually zero at a pH of 8.4 (Griffin et. al., 1976). Overall Cr(VI) adsorption onto clays is a weak anion-exchange mechanism that does not follow a linear adsorption isotherm at high concentrations. Models employing linear adsorption of Cr(VI) onto clay liners will severely overpredict the distribution coefficient (K_d) and the retardation factor (R). For accurate prediction of contaminant transport through liners, models which account for the complex adsorption behavior discussed above and incorporate aspects such as non-linear adsorption, effect of pH and competitive anions, should be used.

Figure 5 illustrates the various adsorption isotherms that were used to fit the experimental PCP adsorption data. Linear adsorption of PCP ceases to exist at high solution concentrations of PCP. The experimental data closely followed the exponential and langmuir isotherms. The maximum adsorbed concentration was approximately 0.8 mg/g. Typically adsorption of organics such as PCP will be much higher in soils containing organic matter. In the case of PCP adsorption, the mechanism may be a combination of both physisorption and chemisorption. The adsorption reduces at high concentrations due to a finite number of adsorption sites available to adsorption. The adsorption of PCP will be further reduced in the presence of competing adsorbates such as other organics, cations and anions. From Figure 5 it is clear that the amount of PCP adsorbed could easily be overestimated using a linear adsorption isotherm. Non-linear adsorption of PCP significantly affects the distribution coefficient (K_d) and retardation factor. At high solution concentrations of PCP, the K_d value decreases and ultimately approaches a negligible value. These results suggest that at high solution concentrations of PCP, the retardation factor (R) will be equal to one. Most models used to predict the migration of contaminants through liners do not incorporate this heterogeneity in contaminant adsorption. These models typically assume linear adsorption and account for high retardations; therefore, overpredict contaminant breakthrough times.

Figure 6 illustrates the contaminant front breakthrough times in years for Cr(VI) for the landfill liner system shown in Figure 1. Breakthrough time predicted using the linear adsorption isotherm was 167 years for a leachate concentration range of 10 to 1000 mg/L. The contaminant breakthrough times predicted by employing the various linear and non-linear adsorption isotherms are summarized in Table 2. The breakthrough time predicted by linear adsorption was independent of the solute concentrations. Overall the breakthrough times predicted by employing non-linear adsorption revealed a relationship with the solute concentrations. At high solute concentrations of 100 to 1000 mg/L, the breakthrough times predicted by considering non-linear adsorption, were below 100 years. At a Cr(VI) leachate concentration of 1000 mg/L, the breakthrough time was overestimated by linear adsorption by a factor of approximately 8, or greater.

Table 2. Cr(VI) front breakthrough times (years)

Conc. (mg/L)	Linear	Langm.	Freund.	Exp.
10	167	196	147	175
100	167	68	46	81
1000	167	14	20	12

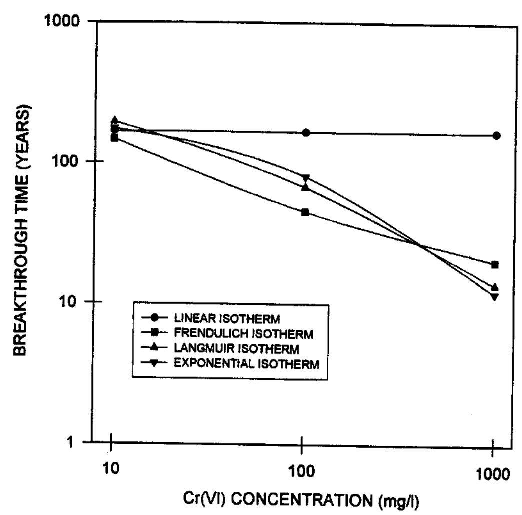

Figure 6. Cr(VI) front breakthrough times

Figure 7 illustrates the concentration front breakthrough times for PCP for the same liner system shown in Figure 1. Detailed breakthrough times predicted by employing the various linear and non-linear adsorption isotherms are shown in Table 3. It is evident that the use of a linear adsorption isotherm grossly overestimates the contaminant front breakthrough time. For instance, a breakthrough time of approximately 28,800 years was obtained using linear adsorption data for a PCP solute concentration of 100 mg/L. For the same PCP solute concentration breakthrough times of 23 years and 12 years were obtained using non-linear Langmuir and exponential isotherms. The use of linear adsorption in estimating the breakthrough times of PCP grossly overpredicts PCP retardation by a factor of approximately 2000.

Table 3. PCP front breakthrough times (years)

Conc. (mg/L)	Linear	Langm.	Freund.	Exp.
1	28831	19379	15487	20306
10	28831	890	5201	1217
100	28831	23	1773	12

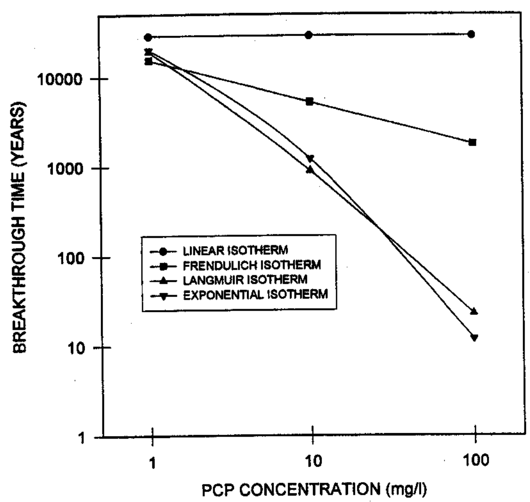

Figure 7. PCP front breakthrough times

5 CONCLUSIONS

The significance of using non-linear adsorption in predicting the breakthrough times of contaminant fronts through a clay landfill liner has been demonstrated. Batch experiments results revealed that adsorption of both Cr(VI) and PCP was non-linear. These experiments revealed that finite number of adsorption sites for organics such as PCP, and a finite anion-exchange capcity for anionic contaminants such as Cr(VI) result in non-linear adsorption of both these contaminants onto clay liners. The design of landfill liner systems must be revamped to include the above effects of non-linear adsorption on the breakthrough times of contaminant fronts.

REFERENCES

Illinois Environmental Protection Agency, Title35: Environmental Protection, Subtitle G: Waste Disposal, Part 811, Standards for New Solid Waste Landfills, 1992.

Drever, J. I., The Geochemistry Of Natural Waters, Prentice-Hall, New Jersey, 1988.

Fetter, C.W., Contaminant Hydrogeology, Macmillan, New York, 1993.

Griffin, R.A., Frost, R.R., and Shimp, N.F. ,"Effect of pH on Removal of Heavy Metals from Leachates by Clay Minerals," Residual Management By Land Disposal: Proceedings Of The Hazardous Waste Research Symposium, Tucson, Az, 1976.

Javandel, I., Doughty, C., and Tsang, C-F., Groundwater Transport: Handbook of Mathematical Models, Water Resources Monograph Series, American Geophysical Union, Washington, D.C., 1984.

Johnson, R.O. , "Nonlinear Adsorption Of Uranyl: Analytical Modeling Of Liner Migration," Ground Water, Vol. 32, No.2,1994, pp 293 - 304.

Reddy, K.R., Parupudi,U.S., Devulapalli,S., and Xu., Y.C., "Effects Of Soil Composition On Removal Of Chromium By Electrokinetics," Submitted.

Rowe, R.K., and Booker, J.R., "1-D Pollutant Migration in Soils of Finite Depth," Journal of Geotechnical Engineering, ASCE, Vol.111, No.4, 1985, pp.13-42.

Shackelford, C.D., and Daniel, D.E., "Diffusion in Saturated Soil. I. Background, II. Results for Compacted Clay," Journal of Geotechnical Engineering, ASCE, Vol.117, No.2, 1991, pp.467-506.

United States Environmental Protection Agency, "Solid Waste Disposal Facility Criteria; Final Rule," Federal Register, 40 CFR Parts 257 and 258, 1991.

Warith, M.A., Fernandes, L., and Forge, F.L., "Adsorption of Pentachlorophenol on Organic Soil," Hazardous Waste and Hazardous Materials, Vol.10, No.1, 1993, pp.13-25.