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Biodegradation and transport of phenols through compacted clay liners: experiments and modeling

Biodégradation et transport des composés phénoliques par un recouvrement d'argile compactée: expérimentation et modélisation

C.Rabozzi & M. Manassero
Dipartimento. di Ingegneria del Territorio, dell'Ambiente e delle Geotecnologie , Politecnico di Torino, Turin, Italy

ABSTRACT

The one-dimensional transport of phenolic contaminants through compacted clay liners has been simulated in this study using the advection-dispersion equation form which includes the biodegradation sink term. Laboratory tests were performed in order to evaluate the transport parameters of phenolic compounds through compacted clay samples. An appropriate numerical solution of the advection dispersion transport equation was then developed for the interpretation of the laboratory test results. The adopted numerical model is able to consider two different kinds of degradation kinetics and the appropriate boundary conditions for the laboratory equipment used in the test program.

RÉSUMÉ

Le transport unidimensionnel des contaminants phénoliques par les recouvrements d'argile compactée a été simulé dans cette étude en utilisant l'équation d'advection-dispersion avec un terme de biodégradation. Essais en laboratoire ont été exécutées afin d'évaluer les paramètres de transport des composés phénoliques par les échantillons d'argile compactée. Une appropriée solution numérique de l'équation de transport a été développée pour l'interprétation des résultats d'essai en laboratoire. Le modèle numérique adopté peut considérer deux genres différents de cinétique de dégradation et des conditions de frontière appropriées pour l'équipement de laboratoire utilisé dans le programme d'essai.

1 INTRODUCTION

In recent years, research has been devoted to a better understanding and application of microbial degradation of groundwater pollutants, for example, the treatments of polluted sub soils, based on biodegradation phenomena, have recently been set up and applied (see for instance the permeable reactive barriers, PRB, described in Malusis and Shackelford, 1997). Moreover, increasing attention has been paid to the improvement in performance of passive barriers for organic pollutant containment due to the attenuation phenomena that occurs in clayey soils (Shackelford, 1999).

A laboratory test program was carried out, in particular with reference to passive containment barrier performance, in order to assess the concentration trend versus time of some phenol compounds passing through a mineral barrier used for lining one of the most important hazardous waste landfills in northern Italy.

Attention was paid to the numerical model for the test interpretation. Several mathematical expressions are available in the literature for the description of contaminant biodegradation but the most suitable seems to be the Monod (1942) expression, and its first-order approximation.

A description of the materials, equipment and procedures related to the laboratory tests is reported in the paper. Thereafter, the interpretation results, in terms of transport parameters for the considered phenol compounds, are discussed in light of the main features of the proposed interpretation model.

2 MATERIALS AND METHODS

Two series of laboratory tests were performed. The first one was carried out to investigate the transport and degradation phenomena of a phenol solution permeating through compacted clayey-silt samples. The second series of tests employed a nitro derivate of phenol (2-nitrophenol) as the solute and the same kind of clayey-silt samples. The physical-chemical characteristics of the clayey silt used for the experimental program (Crescentino clay) are shown in Table 1.

Initially, the soil was air dried, rewetted to a water content of 19.5% (i.e. 3% wet of optimum) and compacted using the standard Proctor procedure.

The clayey specimens were then firstly saturated and later permeated with deionized water. During this phase, a preliminary assessment of the hydraulic conductivity of the soil samples was carried out using flexible wall permeameter equipment and referring to the ASTM D5084 procedure.

After about two pore volumes of flow with deionized water, the inlet reservoir was filled with the phenolic solutions (at initial concentration of $c_0=62$ ppm) starting, at the same time, with measurements of the phenol compound concentrations at the sample entrance and exit lines.

The volumetric flow of the solution was monitored at the same time in order to assess the possible variations of the hydraulic conductivity of the soil samples due to the chemical interaction of the solid skeleton with the solutes.

More details on the permeant sampling procedures, chemical analyses and related equipment can be found in Rabozzi (2003).

Table 1. Clay characteristics.

Quartz	69%
Inorganic carbon content	1.09%
Total organic carbon content	0.343%
Specific surface	0.79 m^2/g
Cation exchange capacity	6.22 meq/100g
pH	7.8
Maximum dry density (Proctor)	17.8 kN/m^3
Optimum water content (Proctor)	16.3%
Plastic limit	18.5%
Liquid limit	41.3%

3 THEORETICAL APPROACH

The one-dimensional transport of an organic compound through a barrier (e.g., mineral liner, reactive barrier) can be described using the advection-dispersion equation with equilibrium sorption and biologically active source/sink term:

$$R_d \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} - \left(\frac{\partial c}{\partial t} \right)_b$$ (1)

where R_d is the retardation factor (dimensionless), c is the solute concentration (ML^{-3}), t is the transport time (T), D is the hydrodynamic dispersion coefficient ($L^2 T^{-1}$), x is the distance in the direction of transport (L), v is the seepage velocity (LT^{-1}), and the subscript b denotes the biologically active term. Equation (1) assumes that the flow and transport are one-dimensional, the porous medium is homogeneous and incompressible, the sorption is instantaneous and reversible, and biotransformation only occurs in the aqueous phase.

As previously mentioned, the last term of Eq. (1) represents the biological degradation process of the organic pollutants within the liquid phase. Basically, this process can be modelled in the simplest way using first-order kinetics with the substrate chemical loss (concentration) given by:

$$\left(\frac{dc}{dt} \right)_b = -\lambda c$$ (2)

where λ is the first order kinetics constant and c is the contaminant concentration. A more consistent simulation of the chemical substrate loss rate can be carried out using Monod's kinetics, as described below:

$$\left(\frac{dc}{dt} \right)_b = -\frac{\mu_{max} M c}{(K_c + c)}$$ (3)

where μ_{max} (T^{-1}) is the maximum rate of the microorganism increase, M (ML^{-3}) is the total microbial concentration and K_c (ML^{-3}) is the half-saturation constant which is defined as the rate of increase in the substrate concentration that allows the constituent to increase at half the maximum specific rate.

It is immediately possible to observe that the first-order kinetics expressed by Eq. (2) represents a limit case of the Monod kinetics (Eq. 3) when $K_c/c \gg 1$.

Although a first order degradation model offers the possibility of using the closed form solutions of Eq. (1) for most boundary conditions in one dimensional transport scenarios, its suitability for describing biodegradation rates depends on the assumption that the maximum concentration of contaminant is much lower than the value of the half-saturation constant, but on the other hand, it is not possible to know the value of the half-saturation constant for a system without fitting experimental data with a Monod kinetics model. A comparison of the existing measurements of the half-saturation constant, for organic compounds, with maximum observed concentrations suggests that a first-order model is probably widely misapplied. The misuse of first-order kinetics could obscure the relative effects of a number of different factors that influence rates of natural attenuation.

In particular, first-order kinetics could provide unconservative estimates of phenol concentrations depending on the magnitude of the influent pollutant concentration, the Monod degradation constants and the microbial mass (Malusis and Shackelford, 1997).

The final one-dimensional equation for organic contaminant transport where the degradation of the contaminant (substrate concentration) follows the Monod kinetics, is obtained introducing Eq.(3) into Eq. (1):

$$R_d \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} - \frac{\mu_{max} M c}{(K_c + c)}$$ (4)

An appropriate numerical solution of Eq. (4) that describes one-dimensional chemical transport was developed considering different boundary conditions (Manassero et al., 2000).

In particular, Eq. (4) was solved discretizing the transport domain into intervals of time and space and applying a centered-in-space finite difference formulation. As a final result, the distribution of a solute concentration can be determined for a given time t over the whole transport domain of interest.

4 RESULTS AND DISCUSSION

It is well known that the influence of pore fluid chemistry on the hydraulic conductivity (HC) of clayey soils is one of the main concerns when determining the long-term performance of clay liners of waste disposals. Within contaminated soils, physicochemical interactions can occur between the solid skeleton and the chemical compounds. Due to these interactions, the physical properties and the fabric of the soil can change drastically, altering the HC of the clay liners. In particular, several researchers have shown that, with reference to chemical compatibility problems, the most important parameter is the dielectric constant of the permeant, ε (Fernandez and Quigley, 1985; Di Maio et al., 2004).

The dielectric constant of the solutions used in the experimental program ranges between 8 and 17.3 which is rather different from the one for deionized water. Therefore, in principle, some appreciable variation of HC can be expected when the deionized pore water is progressively substituted with phenolic solutions.

The results of the tests for the evaluation of the hydraulic conductivity of Crescentino clay and possible compatibility problems with phenolic species are presented in Figure 1. In this figure, only the tests with the Crescentino clay specimens consolidated at an isotropic effective stress $\sigma'_{oct}=100$ kPa are reported as an example. In particular, the hydraulic conductivity values are plotted versus the dimensionless time parameter i.e. the pore volumes of flow (PV= v·t/L where L is the sample length).
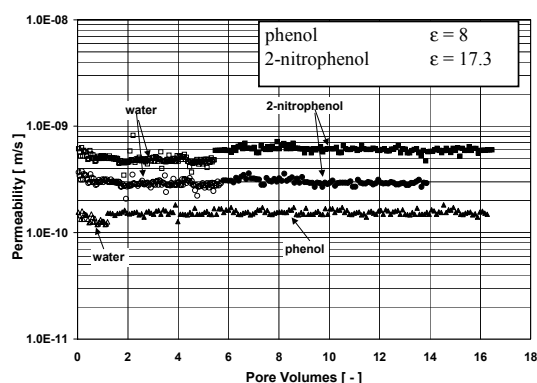

Figure 1. Hydraulic conductivity of samples permeated with deionized water and a phenolic solution.

Although some fluctuations of the hydraulic conductivity can be noted during the permeation with the contaminant solution, which may be due to some perturbations of the hydraulic

head, caused by the sampling procedure of the permeant, the hydraulic conductivity usually shows no significant alterations.

These results are due to both the low sensitivity of the compacted Crescentino clay fabric to the chemical interaction with the used phenolic solutions and to a sort of compensation of the shrinkage trend, in the presence of pore fluid with a dielectric constant that is lower than water, caused by the confinement effective stresses imposed during the tests with the flexible wall permeameter. The interpretation of the column test using the advective-dispersive-reactive equation was therefore carried out considering a constant seepage velocity of the solution through the soil samples.

Two series of column tests (with high concentrations of phenol and 2-nitrophenol) were performed to estimate the transport parameters of the phenolic compounds through compacted clay specimens (e.g. hydrodynamic dispersion coefficient, D, retardation factor, R_d, and degradation constants of phenolic compounds).

In the first step, the experimental results obtained from the column tests were interpreted assuming constant concentrations in the source reservoir and boundary conditions of the third type at the entrance and of the second type at the exit (Manassero et al., 2000). Both a first order degradation term and Monod's kinetics were adopted for comparison purposes. With reference to the input parameters for the Monod equation, a value of M = 0.2 mg/l was assumed on the basis of some literature indications for this kind of soil (Nielsen et al., 1995). Typical solute breakthrough curves, obtained permeating Crescentino clay with a solution of 2-nitrophenol, are shown in Figures 2 and 3.
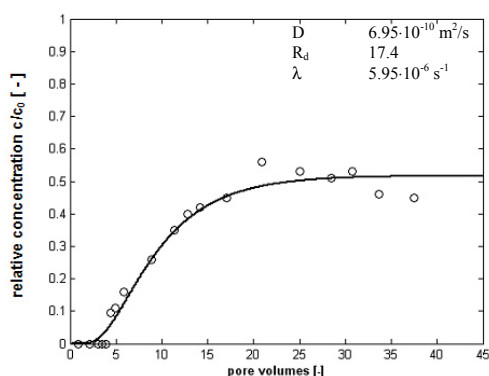
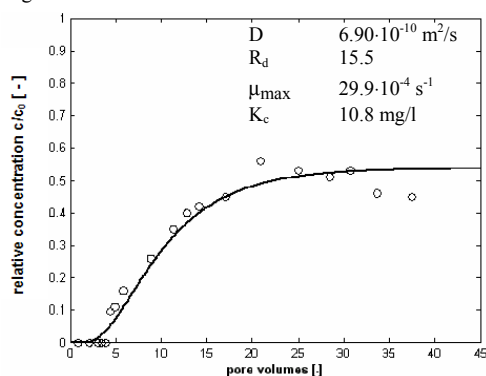Figure 2. Breakthrough curve for 2-nitrophenol obtained using first order degradation model.

Figure 3. Breakthrough curve for 2-nitrophenol obtained using Monod's kinetics.

It is possible to observe, even though $K_c/c_0 < 1$, that when using both a first order degradation and a Monod equation the theoretical fitting of the experimental data is acceptable, in particular when referring to the initial part of the curves. Moreover, the difference between the transport parameters of Eq. (4), obtained from the theoretical approaches using first order degradation and Monods equation, are negligible in terms of the diffusion-dispersion coefficient and rather small in terms of

retardation factor. Therefore, referring to the materials involved in this experimental program and the given boundary conditions, it seems acceptable to simplify the Monod equation using the first order approximation to describe the biodegradation phenomena.

This conclusion has already been reached by Malusis and Shackelford (1997) who show that neglibile differences appear using either first order degradation or Monods kinetics, even in the case of $K_c/c_0 < 1$ but with $\mu_{max}M/K_c \geq 5$ day^{-1} as obtained from the fitting parameters of the considered test results.

In order to improve the theoretical fitting of the experimental data for PV higher than 20, the upper boundary condition was modified to take into account the degradation of the phenol concentration in the source reservoir (see Fig. 4). The experimental data related to the source reservoir concentration were fitted using a first order decay equation:

$$c = c_0 e^{-\eta t} \tag{5}$$

where c is the concentration of contaminant source in the resevoir at time t, c_0 is the initial concentration, η is a first order decay coefficient given by $\eta = \ln 2/T_{1/2}$, where $T_{1/2}$ is the half life for degradation of the contaminant under the condition being examined. The decay constants and the half lives are summarized in Table 2.
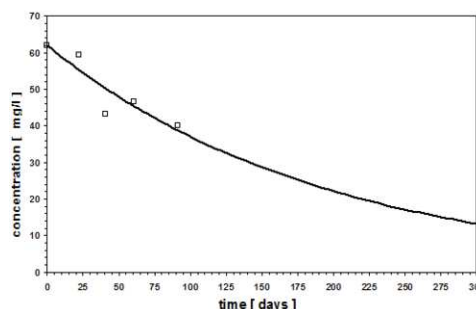
Figure 4. Concentration of the contaminant source during the test.

Table 2. First order decay coefficients for contaminant source of phenolic solutions.

	η [s^{-1}]	$T_{1/2}$ [days]
Phenol	7.95·10^{-8}	120
2-Nitrophenol	5.95·10^{-8}	135

Equation (5) was used to model the actual boundary conditions at the sample entrance in a more appropriate way resulting in the following expression:

$$\left(-D\frac{\partial c}{\partial x} + vc \right)_{x=0} = v\left(c_0 \cdot e^{-\eta \cdot t} \right) \tag{6}$$

The solute breakthrough curves, which were obtained solving the transport equation (Eq. 4) and applying the latter upper boundary condition (Eq. 6), are shown in Figures 5 and 6 for the phenol and 2-nitrophenol respectively.

The final best estimate of the transport parameters and decay coefficients, reported in Table 3, were obtained fitting experimental data with the least square method.

Table 3. Transport parameters and decay coefficients.

	D [m/s^2]	R_d [-]	μ_{max} [s^{-1}]	K_c [mg/l]
Phenol Test1	6.3·10^{-10}	9.95	9.1·10^{-5}	6.5
Phenol Test2	6.5·10^{-10}	13.1	2.8·10^{-4}	2.9
2-Nitrophenol	6.4·10^{-10}	18.6	10.1·10^{-4}	10.8

The parameters set of Table 3 are completely consistent with most of the values reported in specialized literature (Nielsen et al., 1995; Manassero at al., 1999).
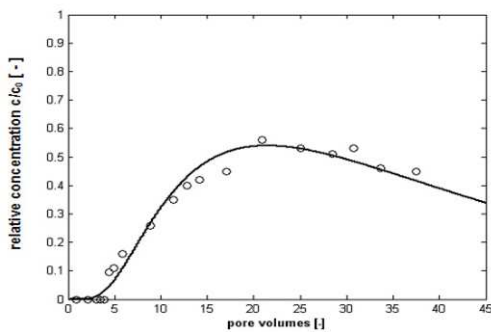

Figure 6. Breakthrough curve for the phenol obtained applying the upper boundary condition described by Eq.(6).
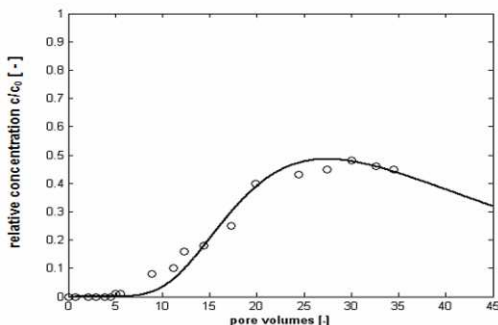

Figure 7. Breakthrough curve for the 2-nitrophenol obtained applying the upper boundary condition described by Eq.(6).

The data resulting from the experimental program were used as input parameters to simulate the one-dimensional solute transport through a composite bottom liner of one of the most important hazardous waste landfills in northern Italy. Figure 8 shows an example of the amount of the effluent concentration of the phenolic compounds in the aquifer underlying the landfill versus time.
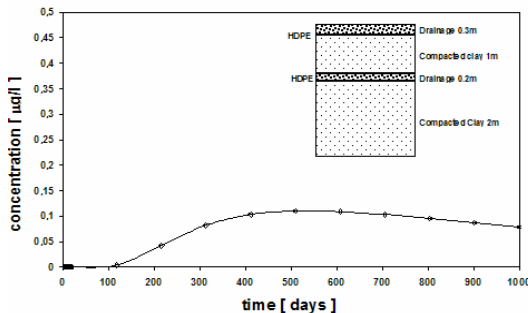

Figure 8. Effluent phenol concentration through the bottom liner of a waste landfill.

The considered initial source phenol concentration corresponds to its solubility limit i.e. 80 mg/l and the maximum allowable concentration within the aquifer must be less than 0.5 μg/l according to Italian regulation. As can be seen in Figure 8, the predictions of the theoretical model fully comply with the local regulation requirements. Moreover, these theoretical predictions were confirmed by the initial data of all the components of the comprehensive monitoring system employed to check the performances of the aforementioned landfill.

5 CONCLUSIONS

An experimental program, which includes series of column tests in flexible wall permeameter cells, has been carried out in order to investigate the influence of phenolic compounds bio-degradation on transport phenomena through mineral barriers used for pollutant control. Compacted clayey-silty soil samples were used together with phenol and 2-nitrophenol solutions.

The interpretation of the experimental results was carried out via a one dimensional transport model that is able to simulate either first-order degradation kinetics or Monod's non-linear degradation kinetics. The basic differential equation was coupled with the appropriate boundary conditions (Manassero et al., 2000) and solved using a finite difference technique that also allows the phenol compound degradation in the source reservoir to be taken in account.

Solute breakthrough curves for first-order degradation and Monod's kinetics were compared and it was observed that they are similar for the considered materials and scenarios, i.e. also in the case when influent concentration, c is comparable or smaller than K_c but in the same time, the microbial mass, M and the maximum rate of microorganisms increase, μ_{max} are large enough in such a way that $\mu_{max}M/K_c \geq 5$ day^{-1} (Malusis and Shackelford, 1997).

In order to obtain satisfactory results of experimental data fitting in the long term, it is necessary, for the considered phenolic compounds, to take into account the degradation phenomena that occur in the source reservoir besides the one in the pore space of the considered soil.

The results of the experimental study were used to assess the performances of a liner in one of the most important hazardous waste landfills in northern Italy. The phenolic compounds concentration in the underlying aquifer was predicted by a two dimensional model. The final concentration values resulted to be well below the maximum concentration limit established by the Italian regulations.

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