IMPORTANCE OF DISTRIBUTION COEFFICIENT OF THE SOIL-CONTAMINANT SYSTEM FOR STUDYING VARIOUS GEOENVIRONMENTAL ENGINEERING PROBLEMS

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ABSTRACT
Geomaterials have peculiar physical, chemical and mineralogical properties. These properties influence their interaction with the contaminants to a great extent. This interaction can be quantified by employing a parameter, “Distribution Coefficient”, $k_d$, which plays an important role for determining sorption and desorption characteristics of a contaminant when it interacts with geomaterials. As such, its determination becomes mandatory for understanding and quantifying the mechanism(s) by which geomaterials get contaminated. With this in view, $k_d$ parameter for a solution of model contaminant when it interacts with a geomaterial, was determined by conducting laboratory studies. This paper presents details of such studies and a commentary on the guidelines for determining the $k_d$ parameter, and its importance and applications in various geoenvironmental engineering problems.

INTRODUCTION
Waste disposal, due to present day industrial activities, is becoming a serious issue and threat to our society. There are various types of wastes such as Municipal, Industrial, Bio-medical and Radionuclear, which require proper handling and disposal in the geoenvironment. This issue assumes the form of a major problem due to callous approach of the industries which are responsible for dumping the waste in the geomaterial (at shallow or great depths) without its pre- and post-treatment. In most of the situations, the waste contains hazardous and toxic substances, which may leach out from the waste matrix due to hydrological conditions prevailing at the disposal or burial site, in the due course of time. The leached substance termed as ‘leachate’ contains heavy metals and its migration, if not contained, would cause pollution or contamination of the geoenvironment.

The mechanism responsible for this degradation of geomaterials is the interaction between the soil and contaminants and can be quantified by employing a mathematical term, partitioning coefficient or distribution coefficient, $k_d$. Basically, $k_d$ describes partitioning of the solute between solid (soil matrix) and liquid (pore solution) phases and using this parameter, the sorption and desorption mechanisms can be quantified.

Sorption describes how a contaminant gets attached (adhered) onto the solid phase and is primarily a chemical process, wherein the adsorbate (molecule or metal ions) enters into a substrate (surface) and forms new bonds, whereas, desorption is the leaching process, reverse of the sorption process, wherein the sorbed contaminants migrate out of the geomaterial matrix (1-5).

Incidentally, $k_d$ can be determined commonly by performing (a) batch tests (1, 6-9) (b) column tests (1, 3, 8-10), and (c) lysimeter tests (11, 12). However, these methodologies have their own strengths and limitations, as reported by the earlier researchers (9).

The objective of this paper is to elucidate some geoenvironmental engineering problems and highlight the importance of $k_d$ in their modeling and simulation. Such studies reveal that researchers have mostly employed “batch sorption experiments” for determining the sorption and desorption characteristics of the geomaterials and in particular for the reactive contaminants. However, these studies recommend different types of sorption and desorption isotherms such as linear, Langmuir and Freundlich isotherms (13) but do not bring out which isotherm is most suitable for geomaterials, in general. With this in view, detailed investigations were conducted on crushed sand stone, collected from western part of India, to evaluate the suitability of these isotherms and the resultant $k_d$ that can be used for defining the sorption and desorption characteristics of geomaterials in the most precise manner (9).
SOME GEOENVIRONMENTAL PROBLEMS

The fate and transport of reactive contaminant(s) in geomaterials, and environmental cleanup strategies of highly contaminated geomaterials depend on their sorption and desorption characteristics. Some of the real life situations where sorption and desorption characteristics play an important role are; development of an efficient remediation methodology for highly contaminated geomaterials and ground water aquifers (14, 15), selection of suitable geological formations and backfill materials for disposal of the low and high level radioactive waste (16, 17), design of barrier layers of waste containment system for domestic and industrial wastes (10, 17-20), studies related to accumulation of heavy metals and pesticides in subsoil due to indiscriminate agricultural practices and inefficient waste disposal strategies (1) etc.

DETERMINATION OF k_d

Sorption and desorption characteristics of a geomaterial mainly depend on the liquid to solid ratio, L/S, temperature, chemical composition of the (contaminant) solution such as pH and ionic strength and time of contact/interaction (21-24). k_d can be determined (both for sorption and desorption, or leaching of ions) by employing the following mathematical relationships, which are known as isotherms.

The amount of a cation (in present study, SrCl_2) sorbed on the sorbent (in present study, the sand stone) (in mg/kg), C_s, can be computed by employing the following relationship.

\[ C_s = (C_i - C_e) \times (L/S) \]  
(1)

where, C_i and C_e are the initial and equilibrium concentration of cations. Using C_s and C_i values, sorption isotherms can be developed for different geomaterials (13).

In this study, three sorption isotherms; (a) linear isotherm (denoted as LR and represented by Equation 2), (b) Langmuir isotherm (denoted as LM and represented by Equation 3), and (c) Freundlich isotherm (denoted as FH and represented by Equation 4) were fitted to the experimental data, as explained in the following.

\[ C_s = K_p \times C_e \]  
(2)

\[ C_s = \frac{C_i \times b}{1 + K \times C_e} \]  
(3a)

i.e., \[ \frac{C_s}{C_e} = \frac{1}{K} \times \frac{b}{C_e} \]  
(3b)

\[ C_s = K_d \times (C_o)^n \]  
(4a)

i.e., \[ \log(C_s) = n \times \log(K_d) + \log(C_o) \]  
(4b)

where, K_p is the partition coefficient (in l/kg), K is the constant related to the binding strength of the sorbent-sorbate system (in l/kg), b is a parameter related to the maximum amount of sorbate getting sorbed on soil/rock particle, K_d is the distribution coefficient (in l/kg) and n is a constant.

Results obtained are presented in Figure 1 (and Table 1). It was observed that linear and Freundlich isotherms yield a regression coefficient, R^2, which is very close to unity (9). This indicates that linear or Freundlich isotherms should be used for defining the sorption characteristics of the geomaterial-contaminant system.

![Fig. 1. Sorption isotherms for a typical contaminant-geomaterial interaction](image-url)
Table 1. The sorption-desorption characteristics

<table>
<thead>
<tr>
<th>L/S</th>
<th>( K_e ) (l/kg)</th>
<th>( K_l ) (l/kg) ( 10^3 )</th>
<th>( K_d ) (l/kg) ( 10^{-3} )</th>
<th>( n )</th>
<th>LR</th>
<th>LM</th>
<th>FH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.29</td>
<td>6.71</td>
<td>55</td>
<td>0.11</td>
<td>0.9</td>
<td>0.99</td>
<td>0.96</td>
</tr>
<tr>
<td>20</td>
<td>2.79</td>
<td>3.24</td>
<td>73</td>
<td>0.51</td>
<td>0.9</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>50</td>
<td>5.36</td>
<td>1.36</td>
<td>142</td>
<td>1.98</td>
<td>0.9</td>
<td>0.91</td>
<td>0.99</td>
</tr>
<tr>
<td>100</td>
<td>11.7</td>
<td>7.16</td>
<td>385</td>
<td>2.03</td>
<td>0.9</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>200</td>
<td>67.31</td>
<td>1.98</td>
<td>459</td>
<td>3.85</td>
<td>1.0</td>
<td>1.0</td>
<td>0.97</td>
</tr>
</tbody>
</table>

In addition, desorption characteristics of the geomaterial were established by following the methodology as discussed below. The concentration of the sorbate after desorption phenomena (in mg/kg), \( C_{sl} \), can be computed by employing Equation 5.

\[
C_{sl} = \left( C_s - C_{el} \right) \left( L/S \right)
\] (5)

where, \( C_s \) is the equilibrium concentration of the cations of the leachate present in the solute after 2 hr. of the leaching time.

Using \( C_{sl} \) and \( C_{el} \) values, desorption isotherms for different geomaterials can be developed. To achieve this, LM, LR and FH sorption isotherms (represented by Equations 2, 3 and 4) were modified by replacing \( C_s \) with \( C_{sl} \), \( C_e \) with \( C_{el} \), \( K \) with \( K_{pl} \), \( K_l \) with \( K_{pl} \), \( K_d \) with \( K_{dl} \), \( b \) with \( bl \) and \( n \) with \( nl \), where \( K_{pl} \) is the partition coefficient for desorption mechanism (in l/kg), \( K_l \) is the constant related to the binding strength of the sorbent-sorbate system for the desorption phenomena (in l/kg), \( bl \) is a parameter related to the maximum amount of sorbate present in the desorption mechanism, \( K_{dl} \) is the distribution coefficient for the desorption mechanism (in l/kg) and \( nl \) is a constant.

Desorption isotherms for the sample of sand stone are being presented in Figure 2. Details of the fitting parameters along with the regression coefficient, \( R^2 \), are presented in Table 1. It can be observed from the results presented in Table 1 that except for the Langmuir isotherm, the other two isotherms yield \( R^2 \) that is very close to unity, for all the geomaterials. This indicates that linear or Freundlich isotherms should be used for defining the desorption characteristics of the geomaterial-contaminant system.

CONCLUDING REMARKS

The importance of \( k_d \) parameter in defining the geomaterial-contaminant interaction has been elaborated and demonstrated in this paper. It has been observed that Freundlich isotherm is the most suitable isotherm to establish sorption and desorption characteristics of all types of geomaterials.

REFERENCES


