Cadmium Transport Parameters in a Clayey Residual Soil with Different Values of Contaminant pH

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Abstract. Pollutants containing metals are an important source of environmental impact. The contaminant’s pH and the soil are factors that influence the migration in the subsurface. The determination of parameters through analytical solutions is fundamental to predict contaminant subsurface migration in porous media. The objective of this study was to analyze the cadmium (Cd) transport parameters present in solutions with different pH ranges in a clayey residual soil from Southern Brazil. Column tests were carried out with residual soil and contaminant solutions containing the following pH values: 1.35 and 4.50. The transport parameters $R$, $k_d$, and $D_h$ were determined. It was possible to verify that the magnitude of the parameters was increased with a higher pH, a favorable factor for contaminant attenuation.

Keywords: column tests, residual soil, retardation factor, heavy metals, pH effect.

1. Introduction

Soil contamination by metals is a great environmental concern in many parts of the world due to fast industrialization, growing urbanization, the modernization of agricultural practices and inadequate waste disposal methods (Lestan et al., 2008). Brazil and developing countries still need further studies, particularly on the determination of contamination transport parameters in residual soils.

Waste containing metals originates mostly from solid urban and industrial waste; accidental leaks and spills; electroplating activities; mining and foundry; synthetic agricultural fertilizers and pesticides; atmospheric deposition of pollutants originated from volatilized phytosanitary products; vehicle emissions; waste incineration and transport; industrial processes and energy production processes; agricultural waste and sludge from effluent and sewage treatment plants (Bermea et al., 2002; Renella et al., 2004; Soares, 2004; Walker, 2006; Yong et al., 1992).

The main destination of solid waste is the soil. When these solid wastes have metallic constituents and they are disposed on the soil, they may contaminate not only the soil itself, but also, superficial waters (through superficial drainage) and groundwater (through migration to the subsurface). When the metals are present in the environment in concentrations many times higher than the natural ones, they can cause toxicity problems in exposed organisms such as plants, animals and humans. This is because they can penetrate in the food chain, due to their mobility in different environmental compartments (Nordberg et al., 2005; Repetto, 1995).

There are much researches being developed in Brazil and other countries about migration of contaminants in soils. However, studies capable of simulating the movement of contaminants in residual soils in Brazil still are necessary. This is important because they can help in the process of managing and controlling contamination of containment structures design. For these studies, it is necessary to obtain the transport parameters that characterize the physical and chemical nature of the distribution of contaminants in soils (Adebowale et al., 2006; Buszewski & Kowalkowski, 2006; Giannakopoulos et al., 2007).

The transport of metal contaminants in subsurfaces is influenced by several factors that may determine greater, smaller or no movement in the soil, depending on the nature of the mechanisms involved. All these processes are ruled by physical, chemical and biological processes (Yong et al., 1992; Shackelford, 1993; Costa, 2002; Moncada, 2004; Sharma & Reddy, 2004; Knop et al., 2008).

The pH is one of the main factors that can influence the transport of metal in soils. The acid range presents the greatest mobility, which can vary and even suffer a reduction when the pH is close to neutral and basic, as described in the literature for residual soils (Basta et al., 2001; Costa, 2002; Elzahabi & Yong, 2004; Jesus, 2004; Meurer et al., 2006; Lopes, 2009; Korf, 2011). In this study, this factor is assessed with the aim of investigating its influence on the nature of the physical and physicochemical processes involved in the transport of Cd, reproducing contaminant from a variety of sources. It was chosen Cd due to its high mobility in soils, which offers critical conditions.
The objective of this study was to analyze the Cd transport parameters present in solutions with different pH ranges in a clayey residual soil from south Brazil.

2. Material and Methods

2.1. Residual soil

The soil sample was collected at the geotechnical experimental field of the University of Passo Fundo - UPF. The coordinates of the collection location are: Longitude 363903 m, Latitude 6876922 m (Coordinates UTM - Universal Transverse of Mercator - 22S).

In the pedological classification it is an oxisol (Streck, 2002). These soils are very deep, drained and highly weathered, presenting a sequence of A-Bw and C horizons, where Bw is latossolic. These soils have little increase of clay with depth and gradual transition between the horizons. As they are very weathered, kaolinite and iron oxides predominate, resulting in low CEC (cation exchange capacity), high acidity and low nutrient stock (Streck, 2002). The geotechnical and chemical characterization of the soil from horizon B is presented in Table 1. The characterization shows low content of organic material, high content of clay, low pH, which when compared with the zero point of charge (ZPC) shows a negative predominant charge.

2.2. Contaminant solution

The contaminant solution contains Cd dissolved in distilled water. Its concentration was extrapolated by 100 times the Brazilian Code Intervention Value for Groundwater - CONAMA (2009) what is equivalent at 167 times World Health Organization Recommendation Values - WHO (2004), simulating a large contamination source. The concentration inserted was 0.5 mg.L$^{-1}$, which was achieved through diluting a standard solution of Cd at a concentration of 1000 mg.L$^{-1}$. The contaminant solution was prepared in the pH ranges 1.35 and 4.50.

2.3. Molding of the test samples

An undisturbed soil sample was extracted from B horizon in the shape of 0.30 m edge cubic block, from which cylindrical probes were molded with 0.05 m diameter and variable heights. Table 2 presents the physical indices and dimensions of all the tested samples.

| pH   | Test sample | Water content (%) | Height (cm) | Diameter (cm) | Specific weight (g/cm$^3$) | Void ratio | Porosity (%) | Void volume (cm$^3$) |
|------|-------------|-------------------|-------------|---------------|---------------------------|------------|--------------|---------------------|
| 1.35 | 1           | 35.27             | 9.22        | 4.93          | 1.50                      | 1.41       | 58           | 102.74              |
|      | 2           | 32.50             | 6.40        | 5.17          | 1.43                      | 1.46       | 59           | 79.85               |
|      | 3           | 34.62             | 8.66        | 4.57          | 1.51                      | 1.38       | 58           | 82.38               |
| 4.50 | 4           | 35.27             | 8.04        | 4.74          | 1.57                      | 1.29       | 56           | 80.10               |
|      | 5           | 32.50             | 10.35       | 4.82          | 1.53                      | 1.39       | 57           | 107.28              |
|      | 6           | 32.50             | 12.09       | 4.84          | 1.56                      | 1.27       | 56           | 124.06              |
The effluent was collected each time that accumulated volume was sufficient for send the contaminant to analysis. The metal concentration was determined using an atomic absorption spectrophotometer.

After determining the metal concentration in the contaminated solution that was percolated through the samples, it was possible to obtain the contaminant’s breakthrough curve. The contaminant breakthrough curve shows, on axis through curve. The contaminant breakthrough curve presented by Shackelford (2005), which defines the area of the percolated waste/initial concentration - C/C₀. Table 3 presents the hydraulic characteristics of the 6 samples tested.

2.5. Determination of the transport parameters in the column test

Retardation Factor (Rᵣ) was calculated by the method presented by Shackelford (2005), which defines the area above the breakthrough curve as the value for Rᵣ. In this case, for the curves that did not reach C/C₀ = 1, the experimental data were extrapolated by linear trend until a unitary relation was reached.

The coefficient of distribution (kᵣ) considers the linear relation between the mass absorbed by unit of solid mass and the concentration of the substance that remains in solution, after reaching equilibrium, in a saturated soil. Equation 1 presents the equation for kᵣ (Ogata & Banks, 1961). In the equation rᵣ is the specific dry mass of the soil and n is the porosity.

\[ kᵣ = \frac{Rᵣ - 1}{\rho_s} \times n \] (1)

Ogata & Banks (1961) developed an analytical solution for the model of contaminant transport in homogenous and saturated soils where there is interaction between the porous material and the contaminant. Equation 2 presents the analytical solution for a reactive solute followed by their initial and boundary conditions, where there is the occurrence of bio-physicochemical contaminant attenuation processes. In the equation Dᵣ is the hydrodynamic dispersion; C/C₀ is the relative concentration or concentration of percolated waste/initial concentration; L is the unidimensional flow distance; t is the percolation time, vᵣ is the percolation velocity and erfc is the complementary error function for analytical solution.

\[ \frac{C}{C_0} = \frac{1}{2} \left[ \text{erfc} \left( \frac{RᵣL - vt}{2\sqrt{DᵣRᵣt}} \right) + e^{\frac{vᵣL}{Dᵣ}} \text{erfc} \left( \frac{RᵣL + vt}{2\sqrt{DᵣRᵣt}} \right) \right] \] (2)

The analytical solution was used to do the adjustment of a theoretical curve obtained through the Ogata and Banks solution (Eq. 2) to the transport curve (breakthrough) originated from the column test. For the construction of the theoretical curve, the “C/C₀” values were found by fixing the parameters calculated and varying Dᵣ and time (t), until the optimization of the adjustment to the experimental curve. The best adjustment of the theoretical to the experimental curve determined, by back analysis, the value of the Dᵣ parameter.

3. Results and Discussion

Figure 1 presents the experimental results of the column test, along with the curve, analytically adjusted by Ogata & Banks (1961) methodology, to pH 1.35 and 4.50. The analysis of the experimental curves’ adjustments to the theoretical model, presented in Fig. 1, shows that the relation C/C₀ = 1 was reached faster for pH 1.35 than for pH 4.50. For pH 1.35, on average, the maximum retention of ions of the contaminant in the soil occurred between 100 min and 200 min (5.98 Vperc/Vv and 11.35 Vperc/Vv), respectively, after the start of the test.

The relation C/C₀ = 1 in the experimental curves occurred only with pH 1.35. For pH 4.50, only was possible reached C/C₀ = 1 through the extrapolation of the curve obtained by the analytical solution, showing an increase in the delay of the contamination plume in consonance with the pH increase.

Table 4 presents the transport parameters obtained for all the samples tested with pH 1.35 and 4.50. The table shows the average, the standard deviation and the coeffi-

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Table 3 - Hydraulic characteristics of the sample tested.

| pH  | Test | Hydraulic head (m) | Hydraulic gradient (i) | Hydraulic conductivity (m/s) | Percolation velocity (m/s) |
|-----|------|--------------------|------------------------|-----------------------------|---------------------------|
| 1.35| 1    | 1.2                | 12.98                  | 5.9 x 10⁴                    | 7.67 x 10⁻⁵                |
|     | 2    | 1.2                | 18.69                  | 3.7 x 10⁴                    | 6.83 x 10⁻⁵                |
|     | 3    | 2.0                | 23.15                  | 1.4 x 10⁴                    | 3.17 x 10⁻⁵                |
| 4.50| 4    | 2.8                | 14.23                  | 7.2 x 10⁴                    | 1.03 x 10⁻⁵                |
|     | 5    | 3.0                | 6.41                   | 1.1 x 10⁴                    | 6.83 x 10⁻⁵                |
|     | 6    | 2.7                | 9.47                   | 1.2 x 10⁵                    | 1.13 x 10⁻⁵                |
cient of variation for the results related to the samples tested
with each pH. For $R_d$ and $k_d$, the coefficient of variation was
not higher than 20%. However, for $D_h$ the value approached
35%, on average. The analysis of the variance of the differ-
ent pHs for $R_d$, $k_d$ and $D_h$ showed significance for all the re-
sponses ($p < 0.02$).

The average values of the physicochemical param-
ters for $k_d$ were $2.55 \times 10^{-3}$ m$^3$.kg$^{-1}$ with pH 1.35 and $10.85$
$\times 10^{-3}$ m$^3$.kg$^{-1}$ with pH 4.50, and for the $R_d$ parameter it was
5.83 with pH 1.35 and 23.35 with pH 4.50. When pH in-
crease from 1.35 to 4.50, it was observed a significant
increase ($p < 0.001$) in the delay parameters, by approxi-
mately 4 times. This fact was expected, once several au-
thors state that an increase in pH can favor the metals
precipitation and increase ionic exchange or changeable ad-
sorption, which is one of the main contributing mechanisms
to adsorption in soils with a predominance of variable sur-
face charges (Elzahabi & Yong, 2001; Basta et al., 2001;
Costa, 2002; Jesus, 2004; Meurer et al., 2006; Lopes, 2009;
Korf, 2011).

Yong et al. (1992) stated that the observed increase in
metal retention capacity with the pH increasing occurs when
the soil solution exceeds the zero point of charge. In this
case, there is the formation of the pH-dependent negative
charge and may also occur precipitation reaction, as reported
in the literature (e.g. Schwertmann & Taylor, 1989; Lagrega,
1994; Elzahabi & Yong, 2001; Adebowale et al., 2006).

The parameter $D_h$ presented a significant difference
between the pH values studied, in the order of
$1.22 \times 10^{-6}$ m$^2$/s with pH 1.35 and $5.00 \times 10^{-6}$ m$^2$/s with
pH 4.50. It was observed that the variation was approxi-
mately 4 times between the pH values studied, with the
same relation maintained for the $k_d$ and $R_d$ values. This
increase may have occurred due to the obtention of the pa-
rameter by back analysis of Eq. 2, which is influenced by
parameter $R_c$.

In comparison with literature values, $D_h$ are higher
than the ones obtained in similar studies, such as Azevedo
et al. (2005) and Lange (2002), who studied respectively,
the percolation of metals in clay soils of landfill and an

**Figure 1** - Experimental results and adjustment by Ogata & Banks (1961) methodology of the tests carried out with pH 1.35 and 4.50.
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Table 4 - Contaminant transport parameters obtained for Cd.

| pH  | Test sample | \( R_s \) (m/kg) | \( k_x \) (cm/s) | \( D_x \) (m²/s) |
|-----|-------------|------------------|-----------------|-----------------|
| 1.35| 1           | 5.00             | 2.09 x 10⁻³     | 1.50 x 10⁻⁴     |
|     | 2           | 5.50             | 2.45 x 10⁻³     | 1.50 x 10⁻⁴     |
|     | 3           | 7.00             | 3.10 x 10⁻³     | 6.67 x 10⁻⁵     |
|     | Average     | 5.8 ± 1.0        | 2.55 x 10⁻³     | 1.22 x 10⁻⁴     |
|     | Standard deviation | 1.04          | 0.51 x 10⁻¹     | 4.83 x 10⁻⁷     |
|     | Coefficient of variation (%) | 17.84          | 20.10           | 39.36           |
| 4.50| 4           | 26.00            | 12.07 x 10⁻³    | 4.67 x 10⁻⁵     |
|     | 5           | 23.04            | 10.92 x 10⁻³    | 3.67 x 10⁻⁴     |
|     | 6           | 21.00            | 9.57 x 10⁻³     | 6.67 x 10⁻⁵     |
|     | Average     | 23.3 ± 2.5       | 10.85 x 10⁻³    | 5.00 x 10⁻⁵     |
|     | Standard deviation | 2.51           | 1.25 x 10⁻³     | 1.53 x 10⁻⁴     |
|     | Coefficient of variation (%) | 10.77          | 11.53           | 30.55           |
|     | \( p^* \)   | < 0.001          | < 0.001         | 0.015           |

*p value of the variance analysis.

Table 5 - Range of the parameters proposed for Cd in residual soil (oxisol).

| pH  | Variation range | \( R_s \) | \( k_x \) (cm³/g) | \( D_x \) (cm³/min) |
|-----|-----------------|----------|-----------------|-------------------|
| 1.35|                 | 5-7      | 2.09-3.10       | 0.4-0.9           |
| 4.50| 21-26           | 9.57-12.07 | 2.2-4.0        |

oxisol and obtained values in the range of 10⁴ m²/s and 10⁻⁶ m³/s. This behavior can be explained by the difference in structures and mineral formation and direct influence of the low \( k_x \) and \( R_s \) values, which also reduced the \( D_x \) values, which have been obtained through these parameters.

The behavior described makes possible to suggest the range of transport parameters for the Cd contaminant in the clayey residual soil (oxisol). Table 5 shows the variation range suggested to be used in numerical simulations in engineering designs.

4. Conclusions

The results and analyses presented led to the following conclusions:
- Increase in the solution’s pH led to increase in the values of parameters \( k_x \) and \( R_s \).
- The pH increase led to an increase in the \( D_x \) because their obtention is related to the \( R_s \) which was influenced by the pH.
- The values of the contaminant transport parameters obtained in this study can be used as indicators in the design of engineering projects in the residual clayey soil (oxisol), when percolated by cadmium dissolved in an acid medium.

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List of Symbols

C/C₀ - Relative concentration or concentration of percolated waste/initial concentration

Dₜ - Hydrodynamic dispersion

erfc - Complementary error function

i - Hydraulic gradient

kᵣ - Coefficient of distribution

L - Unidimensional flow distance

n - Porosity

p - p value from variance analysis

R₂ - Retardation factor

CEC - Cation Exchange Capacity

SSA - Specific Surface Area

UTM - Universal Transverse of Mercator

Vperc/Vv - Percolated volume / void volume

νᵣ - Percolation velocity

rₛ - Specific dry mass of the soil

Gₛ - Specific gravity of the soil

ZPC - Zero Point of Charge