Effect of the bentonite application on the cadmium mobility in an Argisol

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ABSTRACT
Aiming to evaluate the effect of doses of bentonite (0, 30 and 60 t ha⁻¹) in the mobility of cadmium on an Argisol, tests of mobility in soil columns with different cadmium concentrations (50, 250 and 450 mg kg⁻¹ of soil) and steady state flux, were conducted, determining its flux density and percolation velocity. The cadmium was dislocated by pulse, the solution containing the cadmium initially infiltrated into the soil for a given time period and afterwards the soil was lixiviated with distilled water. Leachates were collected every 10 minutes during 80 minutes of water percolation. The solutions percolated, expressed in pore volumes, were 6.33, 2.28 and 1.93 for the 0, 30 and 60 t ha⁻¹ of bentonite, respectively, being one pore volume equal to 1.22 cm³. The concentration of cadmium was measured by atomic absorption spectrophotometry. At the end of the experiment, the columns were dismounted and the concentrations of cadmium in the soil at different depths (0-10, 10-20, 20-30 e 30-40 cm) were also determined. The results showed that the flux density and velocity of water percolation of the water solution were significantly reduced by the addition of bentonite to the soil. The levels of cadmium in the soil did not affect these mobility parameters. Increasing doses of bentonite favored the adsorption of cadmium in the soil.

Keywords: heavy metal, miscible displacement, clay mineral.

Efeito da aplicação de bentonita na mobilidade de cádimo em Argissolo

RESUMO
Objetivando-se avaliar o efeito da aplicação de doses de bentonita (0, 30 e 60 t ha⁻¹) na mobilidade do cádimo num Argissolo, realizaram-se ensaios de mobilidade do referido metal em colunas de solo com diferentes concentrações de cádimo (50, 250 e 450 mg de kg⁻¹ de solo) submetidas a lixiviação num regime saturado, determinando-se a densidade do fluxo e a velocidade de fluxo. O cádimo foi deslocado por pulso, isto é, a solução contendo o cádimo inicialmente infiltrou no solo por um determinado tempo quando então a lixiviação foi continuada com água destilada. Lixiviados foram coletados a cada 10 minutos durante 80 minutos de percolação. As soluções percoladas, expressas em volume de poros, foram 6,33; 2,28 e 1,93 para os tratamentos de bentonita de 0, 30 e 60 t ha⁻¹ sendo um volume de poros igual a 1,22 cm³. As concentrações de cádimo determinadas por espectrofotometria de absorção atômica. Ao final dos ensaios, as colunas foram desmontadas e as concentrações de cádimo no solo a diferentes profundidades (0-10, 10-20, 20-30 e 30-40 cm), foram também
1. INTRODUCTION

In recent years, environmental pollution has reached alarming levels causing a great concern to the society, creating a conscience of environmental preservation. One of the problems that most affect the water environment is the organic or inorganic pollution resulting from residential and industrial effluents, in which the presence of heavy metals may occur. Cadmium (Cd) is a highly toxic metal and has been described as the most dangerous of all the contaminants metals in the environment (Albertini et al., 2001; Guimarães et al., 2008). When added to soil it is absorbed rapidly increasing dramatically the accumulated level of the element (Paganini et al., 2004). According to Malavolta (1994) Cd available concentrations in the soil above 3 mg kg\(^{-1}\) are considered toxic, inadequate for the cultivation of human consumption plants.

The contaminant accumulation and transport processes in the soil depend of the soil type and the contaminant nature. The pH, the organic matter, the cation exchange capacity, the specific surface and the ionic forces are soil attributes that correlate well with the adsorption of cadmium. The composition and the properties of the cadmium contaminant are significant factors on the development of the interactions with the soil substrate. The interactions between the soil and the cadmium determine the fate and mobility of cadmium in the environment and they are the result of adsorption, complexation, dissolution, and precipitation reactions in the soil. However, although these processes occur simultaneously, the adsorption reactions are probably the one that more affect the availability of cadmium in the soil (Camargo, 2006).

The use of low quality irrigation water, the application of sewage sludge as source of nutrients for plants and the indiscriminate use of agrotoxics are dangerous sources of pollution, especially of heavy metals. According to Costa et al. (2007), the impact of heavy metal contamination should not be evaluated only by its soil total content, but by their bioavailability, which is a property related to its mobility in soil and uptake by plants.

One of the procedures proposed to reduce the mobility and bioavailability of metals, is the use of adsorbent materials, such as clay minerals (Rodrigues et al., 2004; Chui, 2005; Lacin et al., 2005). The sorption of cations can cause a real transfer of pollutants from the liquid to the solid phase. The mobility of solutes in soil is inversely related to the adsorption of the soil and the environmental conditions that favor chemical precipitation (Matos et al., 2001; Chaves et al., 2008).

The bentonite is a clay mineral constituted mainly of smectite, usually known as montmorillonite. Expansive and predominantly negative charged shows a high cation exchange capacity (CEC). In general, clay minerals are considered to be the active part of the soil, influencing the retention and movement of soil water, adsorption and ion exchange (Meurer, 2004), the latter being the most important mechanism for adsorption of inorganic pollutants such as heavy metals. Due to its sorbent properties, its low cost and feasibility to obtain it (the State of Paraiba is currently the largest bentonite producer in Brazil) studies have been conducted to evaluate the properties of the bentonite as a sorbent for heavy metals (Santos et al., 2002; Rodrigues et al., 2004; Lacin et al., 2005). Thus, the present study aimed to evaluate the effect of bentonite on the mobility of cadmium in soil columns, determining...
the flux density and velocity of the solution, and the amount of Cd leached and remaining in the soil columns after application of different pore volumes of water.

2. MATERIALS AND METHODS

The experiment was conducted at the Agricultural Engineering Department in Campina Grande, Paraiba State, Brazil using a dystrophic Argisol. The bentonite clay used was collected at a deposit (Primavera) located in the city of Boa Vista, Paraiba, Brazil. The clay was analyzed by X-ray diffraction using the XRD 6000 equipment with a radiation of Kα Cu (40 kV/30 mA). Figure 1 shows the X-ray diffractogram of the bentonite showing characteristic peaks of the smectite clay mineral, the main component of the bentonite, as well as the presence, in minor amount, of silicon oxide peaks. The X-ray analysis was conducted at the Ceramics Laboratory of the Materials Engineering Department, Federal University of Campina Grande-PB.

![Diffractogram of bentonite obtained by X-ray diffraction.](image)

X-ray fluorescent analysis of the clay were also conducted at the Ceramics Laboratory of the Materials Engineering Department, Federal University of Campina Grande-PB, with the EDX 720, being quantified: SiO$_2$ = 76.09%; Al$_2$O$_3$ = 14.51%; Fe$_2$O$_3$ = 5.21%; MgO = 2.22%; CaO = 0.76%; TiO$_2$ = 0.55%; BaO = 0.19%; K$_2$O = 0.18%; MnO = 0.028%; Cr$_2$O$_3$ = 0.023%; SrO = 0.008%; ZnO = 0.004% and calcined residues = 0.23%.

The soil sample was air dried, passed through a 2 mm mesh opening sieve and analyzed with respect to their physical and chemical characteristics (Table 1).

Four kilograms of soil were mixed with 0.00; 0.45 and 0.90 kg of bentonite, corresponding to the doses of 0 (B0), 30 (B30) and 60 (B60) t ha$^{-1}$. These mixtures were left to rest during 30 days, allowing the reaction between soil and bentonite. After this period, the mixtures were again air dried and passed through a 2 mm sieve. A cadmium solution, prepared from CdCl$_2$. H$_2$O, was added to the soil to obtain equivalent concentrations of 50, 250 and 450 mg kg$^{-1}$ of soil.
The experimental design was a completely randomized in a 3 x 3 factorial arrangement (three doses of bentonite and three cadmium concentrations), with three replicates, totaling 27 experimental units. Each experimental unit consisting of a PVC column, 500 mm height and 100 mm in diameter filled with 4 kg of soil plus bentonite. The columns were constructed of five rings 100 mm in height superimposed and joined with silicone glue. These rings facilitate the removal of samples of solid material at different depths at the end of experiment. At the bottom of the column was placed a cap with a PVC tube adapted in its center to drain.
the percolated solution (Figure 2). Over the cap was placed an screen filter paper to support the solid material. The columns were filled with the soil bentonite mixture compacting with a socket each layer applied in order to provide uniformity in the density throughout the soil column. The columns were connected to a Mariotte bottle containing distilled water and saturated by capillary rise, then the columns were submitted to a constant flux maintaining a constant water level of 80 mm above the soil surface.

**Figure 2.** Set up utilized for mobility tests with three plastic columns filled with soil and bentonite.

After stabilization of the flow, the water supply at the top of each column was stopped and allowed to drain one pore volume of solution. At the end of the drainage, the bottom of the columns were closed and on top of them added a pore volume of metal solution equivalent to 50, 250 and 450 mg kg\(^{-1}\) cadmium concentrations allowing to stand during 24 hours to facilitate the reactions among the soil mixture and the cadmium. After this period, the drains were opened again, and the supply of mineral water restarted and the percolation reinitiated, keeping the hydraulic charge of 80 mm of water. The percolation lasted 80 minutes removing leachates every 10 minutes. The solutions percolated, expressed in pore volumes, were 6.33, 2.28 and 1.93 for the 0, 30 and 60 t ha\(^{-1}\) of bentonite.

The soil column pore volume was determined using the following equation:

\[
PV = \pi r^2 h (1 - \frac{ds}{dp})
\]

where:

- \(PV\) is the pore volume (cm\(^3\)), \(r\) the column ratio (cm), \(h\) the column length (cm), and \(ds\) and \(dp\) the soil density and particle density, respectively. The pore volume of the soil column was 1.22 cm\(^3\).

To determine the cadmium content in the percolates, the solution samples collected were placed in polypropylene bottles, identified and stored in refrigerator until preparation for
quantification of the metal by atomic absorption spectrophotometry. At the end of the tests, the columns were dismounted separating the rings that composed it. The solid material contained in each ring was left to air dry, weighed and sieved to 2 mm mesh. The concentration of cadmium in the soil was determined using the normally used Mehlich extraction solution (Embrapa, 1997). The standard EPA procedures, very used in the laboratories, were not adopted; although the procedures of digestion and removal of metal are more efficient according with Silva et al. (2007) the EPA method has limitations to determine nickel and cadmium in the soil, because does not solubilizes the precipitated or occluded metals. For this, it would be necessary to conduct the extraction with fluorhidric acid, which is highly corrosive, of dangerous handling and responsible for damage to the instruments that conduct the analysis.

The mobility parameters of the cadmium in the soil (flux density and velocity) were determined using the DISP software developed at the Agricultural Engineering Department of the Federal University of Viçosa, by Borges Júnior and Ferreira (2006). The computational soft DISP calculates the parameters of soil solute transport equations, based on adjustment of theoretical models to observed data, as well as performs simulations for the space and temporary variations of the concentration and balance of the solute mass in the soil profile. The DISP uses the least-squares method to obtain the diffusion-dispersion coefficient and retardation factor parameters. Comparative tests between DISP and the program CXTFIT, relative to the calculations of the Peclet number and retardation factor parameters, pointed out equivalence between both programs, however the graphic interface in DISP makes its use more feasible in relation to CXTFIT. The CXTFIT 2.0 program provides a convenient way of solving direct and inverse problems for one-dimensional solute transport during steady water flow. PHREEQC and HYDRUS 1D, 2D, 3D models were not necessary to use. The input parameters for the DISP were the observed absolute cadmium concentrations (C) for different pore volumes, soil water content (equal to saturation because the flux was under saturated conditions), soil density, column length, initial and final cadmium concentration.

The results obtained were subjected to analysis of variance, using the SISVAR program (Ferreira, 2003).

3. RESULTS AND DISCUSSION

The flux density and velocity of the solution were significantly influenced at the 1% probability level by the bentonite treatment. The increasing concentration of Cd and the interaction between Cd concentrations and doses of bentonite, were not significant (Table 2).

Applications of 30 and 60 t ha⁻¹ bentonite compared to control (0 t ha⁻¹) reduced the flux density in 72.62 and 78.63% and the percolation rate in 76.27 and 83.00 %, respectively. The beneficial effect of bentonite application can be attributed to the fact that this clay has a large quantity of micropores which difficult the passage of water and solutes through the soil, and also because its high specific surface favors cation exchange. Water moves more quickly through the large pores and spaces in a sandy soil, as the one used on this study, than it does through the small pores in a clayey soil; thus addition of bentonite clay to the soil favors the retention of water and pollutants. A low flow velocity and a high adsorption of the pollutant by the clay reduce risks of contamination by percolation.

According Jesus (2004), the migration and retention of pollutants in the soil is influenced, among other factors, by the mineralogy and cation exchange capacity of the soil. Because the reactions among the clay and pollutants are not instantaneous, if the flow velocity is relatively high, the cations do not have chance to be retained by the soil, being percolated and contaminating the subsoil waters (Freeze and Cherry, 1979).

**Table 2. Summary of variance analysis and mean comparison test for the flow density and velocity as affected by cadmium and bentonite treatments.**

<table>
<thead>
<tr>
<th>Sources of variation</th>
<th>Degrees of Freedom</th>
<th>Flux Density Mean Square</th>
<th>Flow Velocity Mean Square</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium (C)</td>
<td>2</td>
<td>74.91 ns</td>
<td>492.47 ns</td>
</tr>
<tr>
<td>Bentonite (B)</td>
<td>2</td>
<td>11742.6**</td>
<td>77203.2**</td>
</tr>
<tr>
<td>C x B</td>
<td>4</td>
<td>132.46 ns</td>
<td>870.83 ns</td>
</tr>
<tr>
<td>Residue</td>
<td>18</td>
<td>33.76</td>
<td>221.94</td>
</tr>
<tr>
<td>CV (%)</td>
<td></td>
<td>14.00</td>
<td>14.09</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bentonite</th>
<th>Mean (cm h(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 t ha(^{-1})</td>
<td>81.67</td>
</tr>
<tr>
<td>30 t ha(^{-1})</td>
<td>22.36</td>
</tr>
<tr>
<td>60 t ha(^{-1})</td>
<td>17.45</td>
</tr>
</tbody>
</table>

Linear Regression:  
\[ Y = -30.3X + 100.9 \]  
\[ R^2 = 80.9\% \]

Quadratic Regression:  
\[ Y = 25.5X^2 - 132.2X + 185.9R^2 = 100\% \]

<table>
<thead>
<tr>
<th>Cadmium</th>
<th>Mean (cm h(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 mg kg(^{-1})</td>
<td>38.85 a</td>
</tr>
<tr>
<td>250 mg kg(^{-1})</td>
<td>40.39 a</td>
</tr>
<tr>
<td>450 mg kg(^{-1})</td>
<td>44.44 a</td>
</tr>
</tbody>
</table>

***, ns. Significant at 1% (F test) and no significant, respectively. Means followed by the same letter in column do not differ among themselves by Tukey test at 5% probability.

In all the bentonite treatments it was not detected cadmium in the percolated solutions indicating that possibly the cadmium was transformed and retained by the soil in some chemical form, corroborating the results found by Amaral Sobrinho et al. (1999), Anjos and Mattiazzo (2000), Prado and Juliatti (2003), Dal Bosco et al. (2004) and Moreira et al. (2010). One explanation for this is the possible reactions of the cadmium with the oxides present in the soil and bentonite (mainly Fe and Al oxides) as shown by the fluorescent analysis described in the Materials and Methods. Wittbroadt and Palmer (1997) working with heavy metals in soil-humic acids also reported that the presence of oxides of Fe and Al in the soil has been used to explain the absence of heavy metals in leachates of soils treated with biosolids. Same fact was observed by Nascimento et al. (2010) studying the leaching of lead and zinc in soils treated with steel waste. Another explanation for not detecting Cd in soil solution in the present study maybe because the Cd concentrations were below the limit of detection of the instrument used, in this case the atomic absorption spectrometry (0.034 mg kg\(^{-1}\)).

Figure 3 shows the distribution curves of cadmium at the 0-10, 10-20, 20-30 and 30-40 cm soil layers at the end of the experiment and after sectioning the columns.
Figure 3. Distribution of the available cadmium in the 0-10, 10-20, 20-30 and 30-40 cm soil layers of the column after the lixiviation with 7 pore volumes of distilled water, for the different cadmium levels (50; 250 and 450 mg kg\(^{-1}\)) and doses of bentonite applied to the soil (0; 30 and 60 t ha\(^{-1}\)).

It was observed that after the lixiviation with 7 pore volumes of distilled water, the highest levels of cadmium in the soil columns, regardless of bentonite concentrations, were found in the first layer of soil column (0-10cm) decreasing significantly with depth. Messias et al. (2007) evaluating the mobility of micronutrients in soil treated with sewage sludge, also found that the Cd was retained most in the first layer of soil. Juliatti et al. (2002) studying the availability and mobility of Cd in a Red Oxisol observed that the higher concentrations of total Cd were restricted only to the surface layer of the soil not existing downward movement of the element into the soil. The high concentration of Cd at the soil surface characterize an strong interaction among the cadmium and the soil, probably a high
adsorption already at the surface layer, decreasing with depth to such extent that no Cadmium was detected in the percolated solution. The same was observed by Amaral Sobrinho et al. (1999) studying the lixiviation of Pb, Zn, Cd and Ni in a Yellow Red Podzolic soil.

With respect to the bentonite dose it can confirmed on Figure 3 that the Cd adsorption increased with the addition of bentonite. These results were expected since the bentonite is a 2:1 clay mineral with a high cation exchange and adsorption capacity. Figure 4 shows the total concentration of cadmium found in the soil column after the lixiviation with 7 pore volumes of distilled water for the different bentonite and cadmium treatments studied. Although Cd was not detected in the percolated solution, the total concentration for Cd determined in the soil after the dismantling of the columns, was lower than the total quantities of Cd applied to the soil at the beginning of the experiment. In the soil with 50 mg kg\(^{-1}\) of Cd were found only 55.68, 68.85 and 89.44 % of the content initially applied to soil columns for the 0; 30 and 60 t ha\(^{-1}\) bentonite treatments, respectively.

The high Cd concentrations found in the soil column after the lixiviation with 7 pore volumes of distilled water, when compared with the initially applied to the soil can be attributed to the fact that probably the extracting solution utilized by the Mehlich method did not extract the metal in all the forms found in the soil. According to Amaral Sobrinho et al. (2009), the different forms in which heavy metals in the soil may occur (soluble, exchangeable and adsorbed form; occluded in oxides of Fe, Al and Mn form; retained in insoluble organic material form and precipitated forms) are only determined by specific extractors.

![Figure 4](image_url)

**Figure 4.** Cadmium content in the soil columns submitted to different cadmium (50; 250 and 450 mg kg\(^{-1}\)) and bentonite (0; 30 and 60 t ha\(^{-1}\)) levels.

4. CONCLUSIONS

The mobility parameters flux density and percolation velocity of the solution were reduced significantly with the application of bentonite to the sandy soil used;
The cadmium content of the soil did not affect the flux density and the percolation rate of the solution; Increasing doses of bentonite promoted the adsorption of cadmium into the soil. Practically, there was not mobility of Cd in the soil column.

5. ACKNOWLEDGMENTS

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6. REFERENCES


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