

Removal of Copper Ions from Aqueous Solution by Bentonite Clay Applied in Soil in Leaching Columns

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Abstract

The objective of this research was to evaluate the effect of bentonite applied in soil, on the removal of copper (Cu) from aqueous solutions, in leaching columns. The experiment was carried out at laboratory using leaching columns filled with 4 kg of soil mixed with bentonite according to treatments B0, B30, B60 and B90, that is, 0; 30; 60 and 90 t ha⁻¹ of bentonite. Each leaching column (experimental unit) was constituted of a PVC tube, with 0.10m of diameter and 0.50m height sectioned in two 0.20 m rings (10-30 cm and 30-40 cm) and one, on the top, of 0.10 m high, reserved for a hydraulic head of 0.08 m. The columns were placed in a vertical support and saturated with distilled water by capillary ascension. Then percolation began, passing through the column five volumes of pores (initially four liters of water contaminated with 1000 mg of Cu and afterwards one liter of distilled water). Ten leached aliquots of 0.5 volume of pores were collected and stored in polypropylene flasks in a refrigerator for quantification of copper (Cu) by atomic absorption spectrophotometry. At the end of the tests, the solid material contained in each ring was collected and the Cu concentration determined. Increasing doses of bentonite increased Cu retention in soil; Cu was more retained in the surface layer in all treatments; there was no copper leaching from the columns with 60 and 90 t ha⁻¹ of bentonite application, indicating that all copper was retained in the soil avoiding thus potential risks for groundwater contamination.

Keywords: heavy metals; water reuse; adsorption; leaching

1. Introduction

Currently, pollution of water sources, whether surface or underground, is one of the major environmental problems affecting urban centers. Among the several sources of this pollution, the excessive use of fertilizers, pesticides and other chemical substances applied to the soil that can reach groundwater by leaching (Carmo et al., 2010). Effluents, mainly industrial wastewater containing lead, copper, cadmium and chromium and others metals can be a threat to ecosystems for example can contaminate groundwater resources and thus lead to a serious groundwater pollution problem. The dangers of contamination of water by heavy metals are not only restricted to the direct consumption of this contaminated water, but also the direct consequences in the food chain when it refers to bioaccumulative toxins. According to Oliveira and Marins (2011), heavy metals compromise environmental health because they are persistent, since they are not biodegradable, remaining long periods in the environment.

The higher or lower mobility of heavy metals is determined by soil attributes, such as clay content, pH, cation exchange capacity, organic matter content and other factors influencing adsorption/desorption reactions, precipitation/dissolution, complexation and oxidation (Bertol et al., 2010) and percolation velocity (Costa, 2002). Due to the low mobility of the copper in the soil profile, which accentuates with increasing clay content, tends to

accumulate it in the superficial layer (Gomes et al., 2001), having therefore, low leaching potential. However, excessive water applications (rain and/or irrigation) can cause subsurface losses (Sistani et al., 2008).

The reuse of treated effluents has great potential for agriculture, especially in arid and semi-arid regions of the Brazilian Northeast, where there is a lack of good quality water for irrigation, allowing this water to be destined to more noble uses (Dantas et al., 2014). Many physio-chemical methods have been proposed for removal of heavy metals from effluents, or else to reduce the mobility these metals. Among these, there is the adsorption process which is currently considered to be very suitable for wastewater treatment because of its simplicity and cost-effectiveness (Yadanaparthi et al., 2009; Kwon et al., 2010). According to Gottipati et al. (2012) and Banerjee et al. (2012) adsorption is a commonly used technique for the removal of metal ions from various effluents and/or for remediation of the contaminated effluents. Among widely used adsorbents for adsorption of metal ions include clay minerals (Veli & Alyuz, 2007). Eloussaief and Benzina (2010), and Guerra and Airoldi (2008) evaluated the efficiency of clay-minerals in the removal of metallic cations present in effluents and soil, respectively. Natural materials or certain waste from industrial operation for example bentonite clay of inferior quality is one of the sources for low-cost adsorbents. Generally, these materials are easily available.

In the Paraíba State, there exists one of the most important Brazilian deposits of bentonite clays. This clay is predominantly composed of argilominerals of the group of smectite or montmorillonite and impurities of quartz. In some varieties are also kaolinite and illite (Menezes et al., 2009). Its 2:1 structure allows a greater capacity of water adsorption and ion exchange. Bentonite clay, being an anionic solid, has a remarkable affinity with metals, particularly heavy metals in solution (Bhattacharyya & Gupta, 2008), for example, copper. This element especially adsorbed by clays due to their higher surface area and Fe/Mn/aluminum oxides contents (Acosta et al., 2009; Bi et al., 2013; Huang et al., 2014), moves slowly in the soil, usually as an organic complex, and remains on the surface of the soil (Paganini et al., 2004).

Considering the above, it is proposed in this work, to evaluate the effect of bentonite applied in soil, in the removal of copper (Cu) from aqueous solutions, in leaching columns.

2. Materials and Methods

The study was conducted at the Irrigation and Salinity Laboratory of Federal University of Campina Grande located in Campina Grande, Paraíba State, using a Typic Quartzipsamment soil and bentonite clay. This soil, from the city of Lagoa Seca, Paraíba State, Brazil, was collected in the 0-20 cm deep layer, air dried, sieved through a 2.0 mm mesh sieved and chemically and physically characterized according to the methodology of Embrapa (2011) with the following results: pH (H₂O) = 5.0; Ca = 0.51 cmol_c kg⁻¹; Mg = 0.20 cmol_c kg⁻¹; Na = 0.05 cmol_c kg⁻¹; K = 0.18 cmol_c kg⁻¹; H + Al = 0.56 cmol_c kg⁻¹; OM = 2.0 g kg⁻¹; P = 5.4 mg kg⁻¹; Cu = 6.05 mg kg⁻¹; sand = 845.6 g kg⁻¹; silt = 47.2 g kg⁻¹; clay = 107.2 g kg⁻¹.

The bentonite clay was collected at the Primavera deposit located in the Boa Vista County, Paraíba State. The bentonite samples analyzed through the X-ray fluorescence, using the EDX 720 equipment had the following constituents: SiO₂ = 76.784%; Al₂O₃ = 13.339%; Fe₂O₃ = 6.347%; MgO = 2.225%; CaO = 0.759%; other oxides = 0.545%. According to the X-ray diffractogram of bentonite, the characteristic peaks are of smectite or montmorillonite mineral clay, the main component of bentonite, tridimite peaks (it is a silicate mineral and a high temperature quartz polymorph), as well as the presence of a lesser amount of quartz. The cation exchange capacity (48 meq/100 g) and the specific area (375 m²/g) of the bentonite were determined by the methylene blue method (Ferreira et al., 1972).

A completely randomized test with four doses of bentonite, 0; 30; 60 and 90 t ha⁻¹, and three replications was established totaling 12 experimental units. The soil column experimental unit, constructed in PVC with a diameter of 0.10m and 0.50m height was constituted by two 0.20 m rings and one 0.10 m superior ring, were overlaid and joined with silicone glue. To allow water percolation, at the bottom of the column was placed a PVC cap with a drain on its center. On the cap was placed a nylon fabric grid to support the solid material.

The soil and the doses of bentonite (0; 0.45; 0.90 and 1.35 kg) denoted by B0; B30; B60 and B90, respectively, were mixture and incubated for 30 days allowing a probable reaction between them. After this period, each column was filled with 4 kg of this mixture leaving at the top of column, an space of 0.10 m to maintain an hydraulic head of 0.08 m.

The columns were placed in vertical support and saturated with distilled water by capillary ascension. Then the Mariotte bottle containing water contaminated with 250 mg L⁻¹ of Cu (CuSO₄·5H₂O) was connected. Keeping a constant water depth of 0.08 m, percolation began, passing through the columns five volumes of pores (one liter

of distilled and four liters of water contaminated (1000 mg of Cu). Ten leached aliquots of 0.5 volumes of pores were collected. The pore volume of each column was determined by Equation (1):

$$P_v = \pi r^2 h (1 - ds/dp) \quad (1)$$

where, P_v : pore volume (cm^3); r : column radius (cm); h : column height (cm); ds : soil density; dp : density of the particles.

The leachates were collected in polypropylene flasks, previously washed in 5% hydrochloric acid solution and distilled water to be decontaminated, and stored in a refrigerator until the quantification of copper (Cu) by atomic absorption spectrophotometry.

At the end of the tests, the columns were undone by separating the rings that composed them. The solid material contained in each ring was air dried and sieved in a 2 mm mesh. Then it was determined the Cu concentration present in this material according to Embrapa (2011).

The experimental data was analyzed by ANOVA using F test at 5% of significance level. In case of significant effect, it was performed regressions analyses (linear and quadratic). All the analyses were performed using the statistical software SISVAR (Ferreira, 2011).

3. Results and Discussion

Based on the analysis of variance, it was verified that the copper retained in the soil was significantly influenced at the $p < 0.01$ level by the doses of bentonite, by the depths and by the interaction between these factors (Table 1).

Table 1. Summary of the analyses of variance for the copper amount retained in the soil in two depths (D1 and D2) of the leaching columns, with increasing bentonite doses

| Source of Variation | DF | Mean Square |
|----------------------|----|-----------------------|
| | | Soil |
| Bentonite (B) | 3 | 1234.02** |
| Error | 6 | 143.25 |
| Depth (D) | 1 | 1979267.53** |
| B × D | 3 | 134429.60** |
| Error | 10 | 437.79 |
| ----- | | |
| <i>B × D1</i> | | |
| Linear Regression | 1 | 304707.76** |
| Quadratic Regression | 1 | 32468.80** |
| Deviation | 1 | 4671.07** |
| Error | 10 | 437.79 |
| ----- | | |
| <i>B × D2</i> | | |
| Linear Regression | 1 | 83731.23** |
| Quadratic Regression | 1 | 12701.01** |
| Deviation | 1 | 2044.00 ^{ns} |
| Error | 10 | 437.79 |
| ----- | | |
| CV1(%) | | 2.56 |
| CV2(%) | | 4.47 |
| Mean (mg) | | 468.37 |

Note. (**), (*), (^{ns}): ($p \leq 0.01$) and ($p \leq 0.05$) and not significant, respectively. DF = Degree of Freedom. CV = Coefficient of Variation.

The largest amounts of copper were adsorbed in the soil superficial layer (0-20 cm) of the leaching column; the behavior of the adsorption of this element varied according to the increasing doses of bentonite applied to the soil adjusting to the quadratic model.

Comparing the amount of Cu retained in the soil with the highest bentonite dose (90 t ha^{-1}), 917.43 mg, in relation to the control (0 t ha^{-1}) 489.68 mg, there was an increase of 87.35% showing the beneficial effect of

bentonite on the adsorption of this metal. This may be related to the cation exchange capacity of the bentonite clay, in whose negative electrical charges the metals are adsorbed. According to Acosta et al. (2009), Bi et al. (2013), and Huang et al. (2014) this is due to the higher specific surface area of the bentonites and Fe/Mn/aluminum oxides, characteristic of the same. According to Kemerich et al. (2013), the elements Zn, Cu, Cd and Pb have a high affinity for the colloidal fraction of the soil and clays, forming, with the reactive surfaces of the clay, stable molecules that correspond to the specific adsorption, with high binding energy and stability.

Although the bentonite was homogeneously incorporated into the soil column, it was observed that in all treatments most of the Cu was retained in the superficial layer (Figure 1), confirming its low mobility, which is in agreement with Paganini et al. (2004). Bertol et al. (2010), evaluating the mobility of P, Cu and Zn in soil columns, also observed that Cu was retained in the first layer of soil.

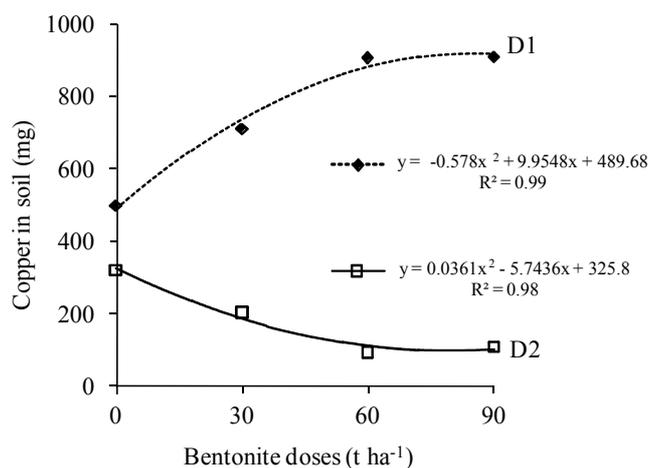


Figure 1. Copper amount retained in soil at depths D1 and D2 (0-20; 20-40 cm) of the leaching columns

Based on the analysis of variance (Table 2), it was verified that copper in the leachate was significantly influenced at the $p < 0.01$ level by the doses of bentonite, and that the data was fitted to a quadratic model (Figure 2).

Table 2. Summary of the analyses of variance for the copper in the leachate with increasing doses of bentonite

| Source of Variation | DF | Mean Square |
|----------------------|----|-------------|
| | | Leachate |
| Bentonite (B) | 3 | 42721.83** |
| Linear Regression | 1 | 27658.94** |
| Quadratic Regression | 1 | 13068.66** |
| Deviation | 1 | 1994.22** |
| Error | 8 | 103.93 |
| CV(%) | | 27.42 |
| Mean (mg) | | 37.18 |

Note. (**), (*), (^{ns}): ($p \leq 0.01$) and ($p \leq 0.05$) and not significant respectively. DF = Degree of Freedom. CV = Coefficient of Variation.

After the application of water contaminated with 250 mg L^{-1} of Cu in the columns, copper was only found in the leachates of columns filled with soil without bentonite (B0) and with B30 (30 t ha^{-1}) 140.3 and 8.3 mg, respectively. Copper was more leached in the soil without bentonite due to the presence of pores with larger diameters facilitating the percolation of the water together with the copper. The incorporation of the bentonite clay provides an increase of micropores and consequently reduces the percolation of the water facilitating the retention of the metal (Figure 2). In the case of the B30 treatment, the 30 t ha^{-1} of bentonite was not sufficient to

adsorb all copper (1000 mg L^{-1}) from the water applied to the columns. This shows that the amount of Cu present in this water was above the adsorption capacity of the bentonite at this dose (30 t ha^{-1}). However, with the 60 and 90 t ha^{-1} dose of bentonite, there was an increase in the number of exchange sites available for the bonds between metal and clay, thus favoring the adsorption of Cu; consequently, copper was not found in the leachate from columns with B60 and B90 treatments.

The high specific surface ($375 \text{ m}^2\text{g}^{-1}$) of this 2:1 clay favored the adsorption of the metal in the clay, corroborating Huang et al. (2014). According to these authors, fine soil aggregates and clay minerals have a greater capacity to retain heavy metals because of their larger surface area.

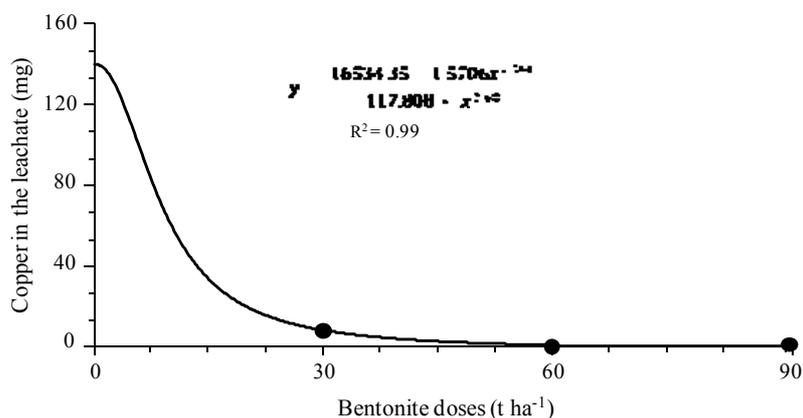


Figure 2. Amount of copper found in leachates as a function of increasing bentonite doses

Considering the amount of copper applied to the soil columns through the contaminated water (1000 mg) plus the amount of this element already existing in the soil (24.2 mg), totaling 1024.2 mg of Cu, the percentages of copper remaining in the soil columns (two depths) and in the leachate were obtained. It was observed that most of the metal was retained in the soil, mainly in the superficial layer (depth of 0-20 cm, D1), that is, 489.7 ; 736.3 ; 878.9 and 917.4 mg of Cu, for the 0 ; 30 ; 60 and 90 t ha^{-1} of bentonite, respectively. The application of 30 , 60 and 90 t ha^{-1} of bentonite promoted an increase of 50.4 ; 79.5 and 87.3% , respectively, when comparing with the control, 0 t ha^{-1} (Figure 3).

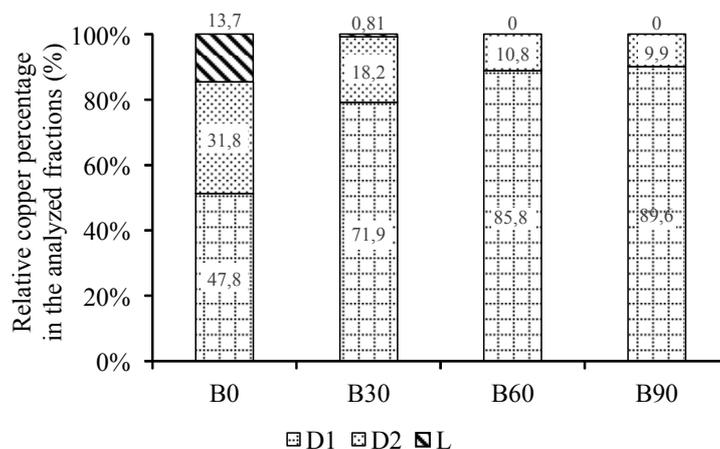


Figure 3. Copper percentage found in the three fraction analyzed (soil at two depths, D1 (0-20 cm) and D2 (20-40 cm) and in the leachate, L) as a function of the doses of bentonite, B0, B30, B60, B90

The amount of Cu retained in the soil in the 20-40 cm layer (D2) decreased as a function of the increasing doses of bentonite, that is, 325.8 ; 185.9 ; 111.1 and 101.3 mg corresponding to treatments B0, B30, B60 and B90, respectively, since the largest amount of copper had already been adsorbed in the superficial layer (D1). This

promoted a decrease of 42.9; 65.9 and 68.9%, comparing the doses of 30, 60 and 90 t ha⁻¹ of bentonite with the control, 0t ha⁻¹ (Figure 3). It can be verified that the percentages of copper adsorbed to the soil at both depths were similar between the doses of 60 and 90 t ha⁻¹.

It was observed in the leachates, 140.35; 8.35; 0 and 0 mg of copper when applied the doses of 0; 30; 60 and 90 t ha⁻¹, of bentonite in the columns, corresponding, respectively, to 13.7; 0.8; 0 and 0%. There was no copper leaching from the soil columns with 60 and 90 t ha⁻¹ of bentonite, indicating thus that all copper was retained in the soil (Figure 3).

4. Conclusions

The application of bentonite to the soil increased the removal of copper from aqueous solutions through these leaching columns

Most of the copper retention occurred in the surface layer of the leaching columns

Doses of bentonite greater than 60 t ha⁻¹, applied to the soil, could avoid potential risks of groundwater contamination in soils contaminated with 250 mg L⁻¹ of Cu.

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