Australian Journal of
Crop Science

AJCS

AJCS 13(07):1126-1130 (2019)
doi: 10.21475/ajcs.19.13.07.p1645

ISSN:1835-2707

Miscible displacement of copper in soil columns using increasing doses of bentonite

Gilvanise Alves Tito, Lucia Helena Garófalo Chaves*, Hugo Orlando Carvallo Guerra, Josely Dantas Fernandes, Jacqueline da Silva Mendes, Iêde de Brito Chaves

Technology Center and Natural Resources, Federal University of Campina Grande, Av. Aprigio Veloso, 882, Campina Grande, Paraíba, Brazil

***Corresponding author: lhgarofalo@hotmail.com**

Abstract

The objective of this research was to evaluate the effect of applying increasing doses of bentonite to the soil on the miscible displacement of copper, quantifying copper retention in the soil and elimination by leachate, in order to prevent potential risks for environmental contamination. The experiment was conducted on a laboratory using leaching columns filled by a sandy texture soil contaminated with 250 mg kg^{-1} of copper each. The experimental design was a completely randomized with four doses of bentonite, 0; 30; 60 and 90 t ha^{-1}, and three replications totalizing 12 experimental units. The leaching columns were made with PVC tubes constituted by three rings, overlaid and joined with silicone glue. Each column was filled with 4 kg of Cu contaminated soil, mixed with the doses of bentonite specified by the treatments (0; 45; 90 and 135 g). After the filling of the columns, each one received five pore volumes of distillated water, and left to percolation under a steady state flux. After percolation, the Cu concentrations in the soil and in the percolate, the breakthrough curves of the flux density and the percolation velocity were determined. The results were submitted to variance analyses using the F test and regressions. The increasing doses of bentonite until 90 t ha^{-1} increased the adsorption of copper by the soil, reducing the percolation of this element around 72%. Bentonite application to the soil decreased the flux density and flux velocity of the copper percolation, diminishing the potential risks for the environment contamination.

Keywords: copper adsorption, breakthrough curves, flux density, velocity of flux.

Abbreviations: Cu_copper; Zn_zinc; B0_soil without bentonite; B30_ soil mixed with bentonite dose 30 t ha^{-1}; B60_ soil mixed with bentonite dose 60 t ha^{-1};B90_ soil mixed with bentonite dose 90 t ha^{-1}; Pv_pore volume; r_radius; h_height; ds_soil density; dp_density of the particles; q_flow density; Q_volume of water passed in a given area; A_area;T_time; Pr_percolation velocity; P_porosity

Introduction

Contamination of the soil by heavy metals comes mainly from the disposal of urban and industrial waste and also from the increasing use of fertilizers and pesticides in agriculture, becoming a risky activity, related with the addition of heavy metals on the soil and groundwater. According to Oliveira and Marins (2011), heavy metals compromise environmental health because they are persistent, since they are not biodegradable, remaining long periods of time in the environment. The excess of heavy metals in the soil increases the possibility of their insertion in the food chain and, consequently, the contamination of the biotic members. In addition, leaching of these metals may occur with subsequent contamination of the groundwater (Machado et al., 2011).

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, oxidation (Bertol et al., 2010) and percolation velocity (Costa, 2002). Copper, due to the low mobility in the soil profile, which accentuates with increasing clay content, tends to accumulate in the superficial layer (Gomes et al., 2001), therefore, in general, have low leaching potential. However, excessive water applications (rain and or irrigation) can cause subsurface losses (Sistani et al., 2008).

To reduce the mobility of ions in the soil, several technics can be used such as, coagulation, precipitation, ion-exchange, electrochemical methods, membrane processes, extraction and adsorption. The adsorption process is carried out by adsorbent surfaces, as is the case with clay minerals. In this sense, studies by Bhattacharyya and Gupta (2007), Ghorbel-Abid et al. (2010) and Jiang et al. (2010) have pointed out the potential of clays in the retention of heavy metals in the soil matrix in order to avoid problems of contamination of groundwater.

The bentonites, composed predominantly of argilominerals of the group of smectite or montimorilonite and impurities, are organized on octahedral gypsum slide between two tetrahedral silica slides (2: 1 clay), which allows them to have a greater capacity of water adsorption and ion exchange. They present a higher degree of plasticity when compared to 1: 1 clays, for example kaolinite, because they contain an extra layer in the chemical structure. Bentonite clay, being an anionic solid, has a remarkable affinity with metals, particularly heavy metals in solution (Bhattacharyya and Gupta, 2008).

The use of bentonite clays as adsorbents have advantages upon many other commercially available adsorbents in terms of low-cost, an abundant availability, high specific area, excellent adsorption properties, nontoxic nature and great potential for ion exchange. Tito et al. (2012), evaluating the effect of bentonite on the mobility of zinc and copper in columns of Argisol soil irrigated with contaminated water, observed that copper was strongly adsorbed by the soil / bentonite complex. The constant concern with soil and groundwater pollution has resulted in several studies of solutes displacement in soil columns. These studies are important tools to understand the transport of adsorptive and non-adsorptive solutes to the soil (Shukla et al., 2003); as well as to estimate the magnitude of the damages caused by these elements (Costa and Prunty, 2006). The objective of this research was to evaluate the effect of applying increasing doses of bentonite to the soil on the miscible displacement of copper, evaluating the amount retained by the soil and eliminated in the leachate, aiming to evaluate and prevent potential risks for the environment contamination.

Results and Discussion

Copper concentration in the soil and in the soil leachate

All treatments had a significant effect on the amount of copper (Cu) retained in the soil and present in the leachate (Table 1). The passage of distilled water through the columns promoted the displacement of Cu present in the soil of the columns, mainly in the soil without bentonite. Copper leachead 168.58; 94.84; 51.91 and 47.98 mg for the 0; 30; 60 and 90 t ha^{-1} bentonite doses, respectively (Fig 1A). This corresponded to a reduction of 0; 43.7; 69.2 and 71.5% of the leaching obtained with the dose of 0 t ha^{-1} (control). Since the amounts of copper in the leachate decreased as a function of the increasing bentonite doses, the amounts of this element retained in the soil (Fig 1B), were 837.86; 895.67; 954.90 and 977.03 mg corresponding to the doses of 0; 30; 60 and 90 t ha^{-1}, respectively. The decrease of copper in the leachate and the increase of the retained in the soil, is attributed to the application of bentonite to the soil, since it is a predominantly smectite clay, with high microporosity and specific surface (375 m^2 g^{-1}), increasing the available sites for the adsorption, favoring a great capacity of cationic exchange (48 meq/100g), corroborating Huang et al. (2014). According to these authors, the fine soil aggregates and clay minerals have a great capacity to retain heavy metals due to their great surface area, corroborating Bertol et al. (2010) and Li et al. (2018). Tito et al. (2012) observed that the incorporation of bentonite in a soil contaminated with copper, favored the adsorption of this element, avoiding the percolation and potential contamination of the groundwater.

Copper concentration in the leachate related to the volume of water applied

According to the analysis of variance, the volume of water percolated in the soil columns (in pore volumes) had a significant effect on the concentrations of copper in the leachate in all the leaching columns, that is, in all treatments, whose best regression model was the quadratic one (Fig 2).

It is observed that the copper concentrations in the percolates after applying one pore volume of distilled water in the columns with the treatments B0, B30, B60 and B90 were 63.31; 37.12; 22.17 and 19.66 mg L^{-1}, respectively (Fig 2). The higher copper concentration in the percolate related to the treatment B0, soil without bentonite, was due to the fact that the copper was few retained in the soil and thus remaining susceptible to leaching. After application of two, three, four and five pore volumes of distilled water in all columns, copper concentrations decreased.

In the soil columns without bentonite (B0) and with the treatments B30, B60 and B90 it was necessary to apply 4.66; 3.73; 3.61 and 3.72 pore volumes of water to reduce the copper concentrations in the percolates to a practically constant value, 7.82; 5.48; 1.63 and 1.91 mg L^{-1}, respectively. With the application of 60 and 90 t ha^{-1} bentonite the elution curves were similar and the copper concentrations in the percolates were lower than in the other treatments because of the higher retention of copper in the soil making it less susceptible to leaching.

Percolation velocity and flux density of copper in the leaching columns

The flux density and the copper percolation velocity in the soil columns were significantly influenced at the 5% probability level by the addition of bentonite (Table 2). As the flux density and percolation velocity are influenced mainly by porosity of the soils, and since the soil in the present study was loamy sand with a high percentage of macropores, before the application of bentonite the soil had a high drainage capacity, 68.24 cm h^{-1}. By increasing the microporosity, due to the application of bentonite clay, the percolation rate was reduced to 48.27; 35.87 and 31.02 cm h^{-1} for the bentonite doses of 30; 60 and 90 t ha^{-1}, a reduction of 29.3; 47.4 and 54.4 %, respectively, when compared to the treatment B0, without bentonite (Fig 3).

The flux density in the leaching column without bentonite was 26.62 cm h^{-1}, while in the columns receiving doses of bentonite 30; 60 and 60 t ha^{-1}, were 18.79; 13.84; 11.77 cm h^{-1}, which corresponded to a reduction of the flux of 29.4; 48.0 and 55.8%, respectively (Fig 3).

Besides the increase of porosity with the bentonite application, the reduction of the percolation velocity and flux density can also be due, according to Churchman et al. (2006), to the fact that bentonites are negatively charged minerals with a high cation exchange capacity and high specific surface area, making them very effective in adsorbing cations in the soil solution. This is in agreement with Bertol et al. (2010) who observed that the nature and clay content, together with other factors, influence the adsorption / desorption reactions, the precipitation / dissolution, complexation and oxidation. Menezes et al. (2016), studying the mobility of Cu and zinc (Zn) in three types of soil, verified that the low flux density affected the contamination front displacement of the evaluated elements, allowing a great contact time of the displacing solution with the soil matrix promoting adsorption of Cu and Zn.

Table 1. Summary of the analyses of variance for the amount of copper retained in the soil and leached in the columns, with increasing doses of bentonite

		Mean Square	
Source of Variation	DF	Leachate	Soil
Bentonite	3	9411.46**	13401.00**
Linear Regression	1	24568.93**	38516.80**
Quadratic Regression	1	3655.43**	1564.08ns
Deviation	1	10.02ns	122.12ns
Error	8	81.85	948.29
VC (%)		9.96	3.37
Mean (mg)		90.83	913.87

(**), (ns): ($p \leq 0.01$) and not significant respectively. DF= Degree of Freedom. VC = Variation Coefficient.

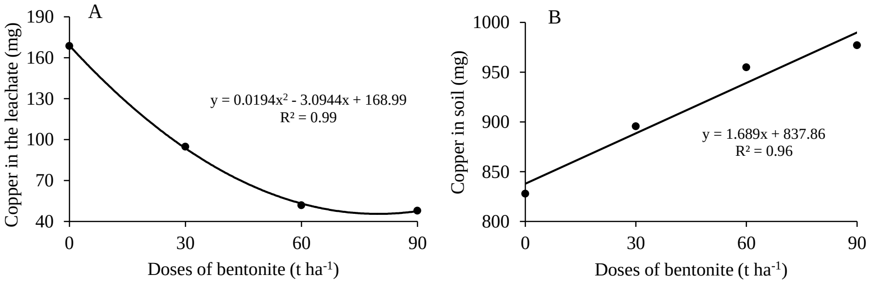

Fig 1. Amount of copper present in the leachate (A) and in the soil (B) as a function of increasing doses of bentonite.

Table 2. Summary of the analyses of variance for flow density and percolation velocity in the columns, with increasing doses of bentonite

		Mean Square	
Source of Variation	DF	Flux density	Percolation velocity
Bentonite	3	129.32*	850.26*
Linear Regression	1	356.24**	2342.50**
Quadratic Regression	1	25.69ns	168.75
Deviation	1	6.02ns	39.67ns
Error	8	24.58	161.67
VC (%)		27.79	27.80
Mean (cm h^{-1})		17.84	45.74

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

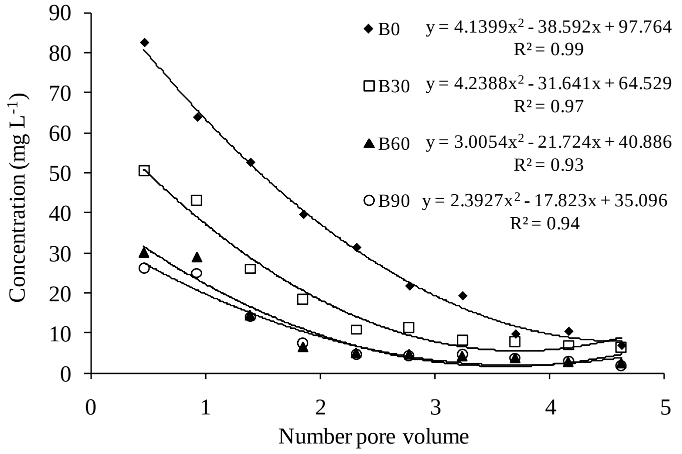

Fig 2. Copper concentration in the leachate as a function of the number of pore volumes applied, for treatments B0, B30, B60 and B90.

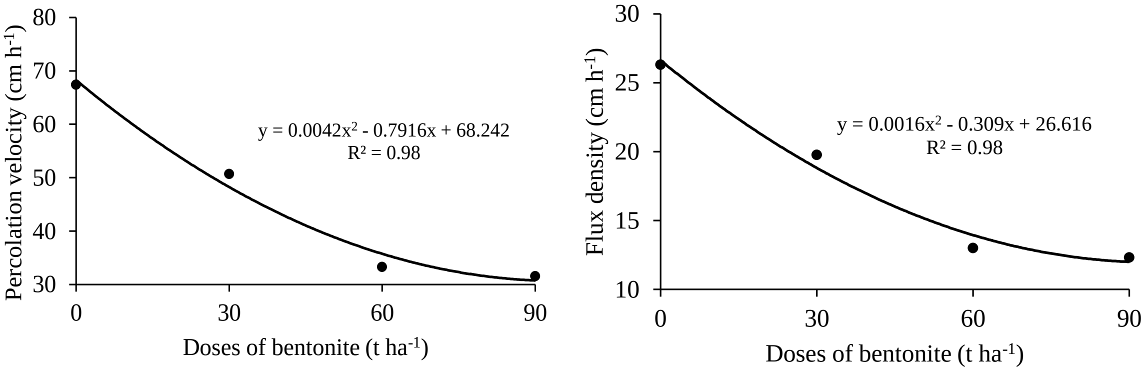

Fig 3. Percolation velocity and flux density of copper in the leach columns as a function of increasing bentonite doses.

Materials and Methods

Experimental apparatus

This study was conducted at the Irrigation and Salinity Laboratory of the Federal University of Campina Grande located in Campina Grande, Paraiba State, using lysimeter columns.

Four kg of uncontaminated air dry soil were mixture with 0; 45; 90 and 135 g of bentonite, corresponding to the doses of 0; 30; 60 and 90 t ha^{-1} denoted by B0; B30; B60 and B90. The mixtures of soil and bentonite were contaminated with 250 mg kg^{-1} of copper sulphate incubated for 30 days allowing a reaction between them. After this period the mixtures were air dried and placed into the columns leaving a 0.10m space on the top for a hydraulic head of 0.08 m.

Design and treatments

A completely randomized design with four doses of bentonite, 0; 30; 60 and 90 t ha^{-1}, and three replications was established totalizing 12 experimental units.

Bentonite analysis

The bentonite clay used in this experiment was collected in the Primavera deposit located in the municipality of Boa Vista, Paraíba State. Through X-ray fluorescence, analysis, using an EDX 720 equipment, the bentonite samples were analyzed showing the following constituents: SiO_2 = 76.784%; Al_2O_3 = 13.339%; Fe_2O_3 = 6.347%; MgO = 2.225%; CaO =0.759%; other oxides = 0.545%. According to the X-ray diffractogram of bentonite, the characteristic peaks were of smectite or montmorillonite mineral clay, main component of bentonite, tridimite peaks (silicate mineral and a high temperature quartz polymorph), as well as the presence, of few amounts of quartz.

The cation exchange capacity and the specific area of the bentonite were determined by the methylene blue method (Hanger and Brindley, 1970).

Soil analysis

The characteristics of the Typical Quartzipisamment soil used in the experiment, according to the methodology of Embrapa (2011), were the following: pH (H_2O) = 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 = 845.6g kg^{-1}; silt = 47.2 g kg^{-1}; clay = 107.2 g kg^{-1}.

Conduction of study

The lysimeter columns were constructed in PVC with a diameter of 0.10m and 0.50m height formed by two 0.20 m rings and one 0.10 m high ring, overlaid and joined with silicone glue. At the bottom of the lysimeter was placed a 0.10m PVC cap with a drain adapted in its center. On the bottom of the cap was placed a screen made with nylon fabric, to support the solid material. The lysimeter was filled in such a way as to provide a uniformity soil density throughout the column.

The lysimeters were placed in a vertical support and the soil saturated by capillary ascension with distilled water. Then, a Mariotte bottle containing distilled water was connected, keeping a constant water head of 0.08 m on the soil. Afterward the percolation began, passing through the soil five pore volumes of distilled water (five liters of water), and the leachates sampling started collecting, consecutively, 10 aliquots of 0.5 pore volumes. The leachates were collected in polypropylene flasks, previously washed in 5% hydrochloric acid solution and distilled water for decontamination, and stored in a refrigerator until the quantification of copper (Cu) by atomic absorption spectrophotometry.

The pore volume of each lysimeter was determined by Equation (1):

$$Pv = \pi r^2 h(1 - ds/dp) \qquad (1)$$

where, Pv - pore volume (cm³); r - lysimeter radius (cm); h – lysimeter height (cm); ds - soil density; dp - density of the particles.

Flux density was determined using Darcy's law (1856), according to Equation (2):

$$q = \frac{Q}{At} \qquad (2)$$

where q = flux density, cm h^{-1}; Q = volume of water passed in a given area, cm^3; A = lysimeter cross-sectional area, cm^2; T = leaching time, h.

The percolation velocity was determined according to the Equation (3):

$$Pr = \frac{q}{P} \qquad (3)$$

where, Pr = percolation velocity, cm h^{-1}; q = flux density, cm h^{-1}; P = porosity, %.

The leaching dynamics of Cu in the soil lysimeters, for the treatments evaluated were analyzed by the construction of concentration curves of Cu leachate versus the number of pore volume in the collected effluents.

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

Statistical analysis

The experimental data was analyzed by the analysis of variance using the F test at 5% significance level (ANOVA). In case of significant effect, the results were submitted to regression analyses. All the analyses were performed using the statistical software SISVAR (Ferreira, 2011).

Conclusions

The increasing doses of bentonite until 90 t ha^{-1} increased the adsorption of copper by the soil, reducing the percolation of this element around 72%.

Bentonite application to the soil decreased the flux density and flux velocity of the copper percolation, diminishing the potential risks for the environment contamination.

Acknowledgement

Special thanks to the Coordination of Improvement of Higher Level Personnel - CAPES (Brazil) and National Council for Scientific and Technological Development – CNPq (Brazil) for the scholarship granted and financial support to the first author.

References

Bertol OJ, Fey E, Favaretto N, Lavoranti OJ, Rizzi NE (2010) Mobilidade de P, Cu e Zn em colunas de solo sob sistema de semeadura direta submetido às adubações mineral e orgânica. Rev Bras Ci Solo. 34:1841-1850.

Bhattacharyya KG, Gupta SS (2007) Adsorptive accumulation of Cd(II), Co(II), Cu(II), Pb(II) and Ni(II) from water on montmorillonite: influence of acid activation. J Coll Inint Sci. 310:411-424.

Bhattacharyya KG, Gupta SS (2008) Influence of acid activation on adsorption of Ni(II) and Cu(II) on kaolinite and montmorillonite: kinetic and thermodynamic study. Chem Eng J. 136:1-13.

Churchman GJ, Gates WP, Theng BKG, Yuan G (2006) Clays and Clay Minerals for Pollution Control. In: Bergaya F, Theng BKG, Lagaly G (eds.) Develop Clay Sci., vol. 1, Elsevier, Amsterdam.

Costa JL, Prunty L (2006) Solute transport in fine sandy loam soil under different flow rates. Agric Water Manag. 83:111-118.

Costa POS (2002) Avaliação em laboratório do transporte de contaminantes no solo do aterro sanitário de Sauípe/BA. Rio de Janeiro: PUC, 2002. 188p. Dissertação (Mestrado em Engenharia Civil).

Embrapa, Centro Nacional de Pesquisa de Solos (2011) Manual de métodos de análise de solo, 2rd. Embrapa, Rio de Janeiro.

Ferreira DF (2011) Sisvar: a computer statistical analysis system. Ci Agr. 35:1039-1042.

Ghorbel-Abid I, Galai K, Trabelsi-Ayadi M (2010) Retention of chromium (III) and cadmium (II) from aqueous solution by illitic Clay as a low-cost adsorbent. Desalination. 256:190-195.

Gomes PC, Fontes MPF, Silva AG, Mendonça ES, André R, Netto AR (2001) Selectivity sequence and competitive adsorption of heavy metals by Brazilian soils. Soil Sci Soc Am J. 65:1115-1121.

Hange PT, Brindley GW (1970) Methylene blue adsorption by clay minerals, determination of surface area and cation exchange capacities (clay-organic studies XVIII). Clay and Clay Miner. 18: 203-212.

Huang B, Li Z, Huang J, Guo L, Nie X, Wang Y, Zhang Y, Zeng G (2014) Adsorption characteristics of Cu and Zn onto various size fractions of aggregates from red paddy soil. J Haz Mat. 264:176-183.

Jiang M, Jin X, Lu X, Chen Z (2010) Adsorption of Pb (II), Cd (II), Ni (II) and Cu (II) onto natural kaolinite clay. Desalination. 252:33-39.

Li Q, Du H, Chen W, Hao J, Huang Q, Cai P, Feng X (2018) Aging shapes the distribution of copper in soil aggregate size fractions. Env Pol. 233:569- 576.

Machado ME, Menezes JCSS, Costa JFCL, Schneider IAH (2011) Análise e avaliação da distribuição de metais pesados em um antigo aterro de resíduos sólidos urbanos “Aterro Invernadinha”. Evidência. 11:69-82.

Menezes JPC, Oliveira LFC, Generosa CM, Franco CS, Fia R, Fia FRL (2016) Mobility of heavy metals in soils of arrangement municipal solid waste. Ambiência.12: 909-919.

Oliveira RCB, Marins RV (2011) Dinâmica de metais-traço em solo e ambiente sedimentar estuarino como um fator determinante no aporte desses contaminantes para o ambiente aquático: revisão. Virt Quím. 3:88-102.

Shukla MK, Ellsworth TR, Hudson RJ, Nielsen DR (2003) Effect of water flux on solute velocity and dispersion. Soil Sci Soc Am J. 67:449-457.

Sistani KR, Mclaughlin MR, Brink GE (2008) Soil nutrient evaluation from swine effluent application to five forage-system practices. Nutr Cycl Agroecosyst. 82:265-271.

Tito GA, Chaves LHG, Guerra HOC (2012) Mobilidade do zinco e do cobre em Argissolo com aplicação de argila bentonita. Rev Bras Eng Agríc Amb.16:938-945.