CHEMICAL ENGINEERING TRANSACTIONS

VOL. 58, 2017

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Remigio Berruto, Pietro Catania, Mariangela Vallone

ISBN 978-88-95608-52-5; **ISSN** 2283-9216

DOI: 10.3303/CET1758125

Bentonite Application in the Remediation of Zinc Contamination Soil

Lúcia H. G. Chaves*, Gilvanise A. Tito, Iêde de Brito Chaves

Department of Agricultural Engineering of Federal University of Campina Grande. Avenue Aprigio Veloso, 882, CEP 58429140 Campina Grande, Paraiba State, Brazil
lhgarofalo@hotmail.com

The concern of soils contaminated with heavy metals coming from commercial fertilizers and / or irrigation with wastewater is even greater when grown with food plants. Several procedures have been proposed to reduce the concentration of heavy metals in the soil; among them, the application of materials such as bentonite, able to absorb these elements, making them less available to plants. The objective of this study was to evaluate the ability of bentonite to the remediation of artificially zinc (Zn) contaminated soils, having the radish as test plant. The experiment was conducted in a greenhouse in a completely randomized design, with four replicates. After the NPK fertilization, 250 mg kg^{-1} of Zn and bentonite (doses: 0; 30; 60 and 90 t ha^{-1}) application the loamy sand soil was conditioned in 5 kg plastic containers, irrigated to field capacity and incubated during 20 days. At the end of the incubation process the crops were seeded; after 30 days of experiment, the plants were collected separating the aerial and root part, dried, triturated and weighed for plant analyses. The cumulative amount of Zn in dry biomass of the aerial part (shoot) and roots, the translocation index, the translocation factor, the bioaccumulation factor in the plant (BFP) and in the root (BFR), were evaluated. The results were analyzed by the F test and regressions. The dry phytomass of the aerial part increased and the values of BFP and BFR of radish decreased significantly as a function of increasing doses of bentonite, indicating an increase in the adsorption of zinc in the soil, decreasing the concentration in the plant parts. However, the BFP and BFR values were higher than unity, indicating high bioaccumulation potential of radish for this metal. Based on the results, the application of bentonite to the contaminated soils favored their remediation.

1. Introduction

Most heavy metals are essential to human beings, animals and higher plants, for example, Zn, among others. This metal tends to be present in higher concentrations in the upper soil layers, which is a reflection of the element addition via atmospheric deposition, application of phosphate fertilizers, humus and also the incorporation of plants used as accumulators of metals (McBride, 1994).

Soil contamination with these metals is increasingly common and worrying because of the negative impact of these elements in the ecosystem. The main concerns about the effects of heavy metals are their participation in the food chain (Kumar et al., 2012; Marin et al., 2010), reduced agricultural productivity due to phytotoxic effects, accumulation in the soil, changes in microbial activity and contamination of water resources (Wowk and Melo, 2005).

The plants are the main entry point of heavy metals in the food chain (Guimarães et al., 2008), therefore, the availability of these metals for plants is governed by several soil factors such as pH, cation exchange capacity, organic matter content, adsorption by clays and phosphorus, calcium and the presence of other metals in the soil system (Macêdo and Morril, 2008). The mobility of zinc in plants is not large. Normally, the roots contain much more zinc than the shoot, especially if the plants are growing in soils rich in zinc (Mengel and Kirkby,1982; Kabata-Pendias and Pendias, 2010).

To reduce the availability of soil zinc to plants is necessary to remediate contaminated soils according to some technique, for example, the use of adsorbent materials, such as clay minerals (Ghorbel-Abid et al., 2010;

Please cite this article as: Chaves L., Tito G., De Brito Chaves I., 2017, Bentonite application in the remediation of zinc contamination soil, Chemical Engineering Transactions, 58, 745-750 DOI: 10.3303/CET1758125

Jiang et al., 2010; Bhattacharyya and Gupta, 2007). All of them indicate the advantages of these materials such as low cost, availability and efficiency compared with other adsorbent materials.

Bentonite is composed predominantly of smectite clay group and quartz impurities and some varieties present caulinite and illite (Sdiri et al., 2011). Because it is a solid anionic, it has a remarkable affinity to metals, particularly heavy metals in solution (Bhattacharyya and Gupta, 2008).The bentonite that does not present characteristics required by the industry is less commercialized, so, it is considered as industrial waste and known regionally (at the clay exploration site) by "bofe". Because of its low commercial value, this residue is found in large amounts in Boa Vista, State of Paraiba, Brazil. Due to its high surface area and cationic exchange capacity, when incorporated into the soil, it can be used as a soil conditioner improving the soil chemical and physical characteristics, especially of the more sandy soils, as already reported by Tito et al. (2001; 2016).

The objective of this study was to evaluate the ability of bentonite to the remediation of artificially zinc (Zn) contaminated soils, having the radish as test plant.

2. Materials and Methods

The study was carried out under greenhouse conditions at the Agricultural Engineering Department of the Federal University of Campina Grande, Paraiba, Brazil. The experiments were conducted with radish (*Raphanus sativus*) on a loamy sand soil classified as a Red Eutrophic Latosol (Embrapa 2006), collected in the municipality of Campina Grande, to a 0-20 cm soil depth, with chemically characterized according to Embrapa (1997). The following attributes were found: pH (H_2O) = 6.0; Electrical Conductivity = 0.16 (mmhos cm^{-1}); Ca = 2.10 $cmol_c kg^{-1}$; Mg = 2.57 $cmol_c$ kg^{-1}; Na = 0.06 $cmol_c$ kg^{-1}; K = 0.14 $cmol_c$ kg^{-1}; H+ Al = 1.78 $cmol_c$ kg^{-1}; organic carbon = 5.5 g kg^{-1}; P = 45.0 mg kg^{-1}. The experiments were conducted in 5 kg plastic containers for radish. Soil seeded with radish received 250 mg kg^{-1} of zinc. Nitrogen, phosphorus and potassium fertilization for radish was 1.11 g of urea, 1.25 g of potassium chloride (KCl) and 8.3 g of super phosphate (P_2O_5).

After NPK fertilization and zinc and bentonite application the soil was conditioned in plastic containers, irrigated to field capacity and incubated during 20 days. Finished the incubation process the crops were seeded and 8 days after the emergency a thinning was conducted leaving two plants per vase. Each experimental unit received four doses of bentonite: 0.0; 10.7; 21.4 and 32.1 g kg^{-1}, corresponding to 0, 30, 60 and 90 t ha^{-1}, respectively. The bentonite were low quality clays, rejected for industrial purposes, called vulgarly as "bofe", coming from a Paraiba State region. The X rays diaphactogram of the clay is shown in Figure 1. The diaphactogram picks observed are typical of the smectite (S) clays, and picks of tridymite (T), a silicate mineral and polymorph of high temperature of quartz. Picks of quartz are observed although in a low quantity.

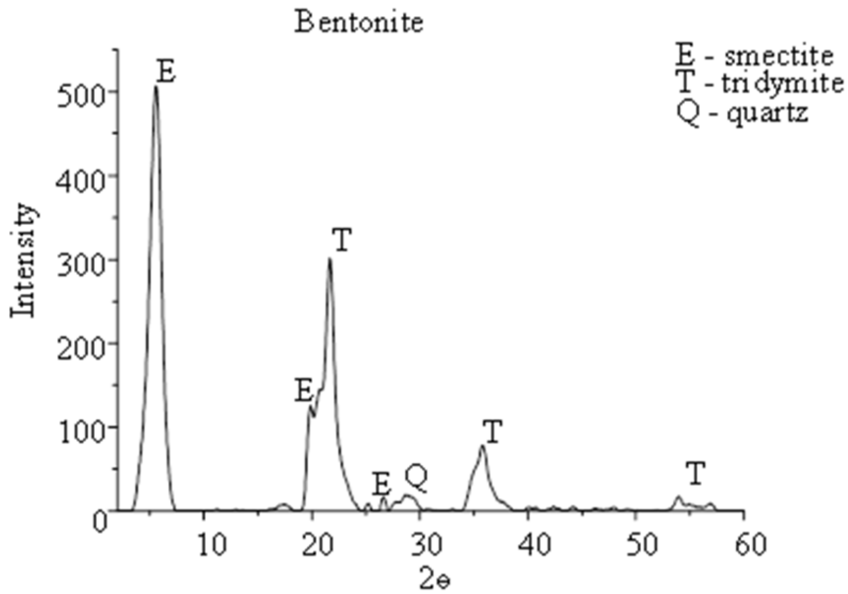

Figure 1. Diffractogram of bentonite obtained by X-ray Diffraction

The irrigation was conducted using tap water maintaining the soil to field capacity. At the 30th day of experiment, the plants were collected separating the aerial and root part, washed with distillated water, conditioned in paper sacks and dried in forced air stove at 65°C during 48 hours. After drying, the plants were triturated and weighed for foliar analyses. Zinc determination was conducted after nitroperchloric digestion, according to Embrapa procedures (Embrapa,1997), using a spectrometer of optical emission with plasma - ICP OES, as described by Oliva et al. (2003).

The cumulative amount of Zn in dry biomass of the aerial part (shoot) and roots (mg / pot) was calculated by the expression Zn accumulated shoot or Zn accumulated root = {Dry Biomass of shoot or Dry Biomass of root (g) x element concentration (mg kg^{-1})} / 1000. The translocation index (TI) was determined by using the follow expression (Abichequer and Bohnen, 1998): (Zn accumulated shoot/ Zn accumulated in the complete plant) x 100. The translocation factor (TF) gives the leaf/root zinc concentration and depicts the ability of the plant to translocate the metal species from roots to leaves (shoot) at different concentrations. This index was calculated by the relationship: TF = (zinc concentration in the aerial part of the plant (mg kg^{-1}) (shoot)/ zinc concentration in the root (mg kg^{-1})) (Gupta et al., 2008).

The bioaccumulation factor (BF), an index of the plant ability to accumulate a particular metal with respect to its concentration in the soil substrate (Ghosh and Singh, 2005), was calculated as follows: BFP = zinc concentration in the complete plant (mg kg^{-1}) / zinc concentration in the soil (mg kg^{-1}), or, to calculate metal bioaccumulation only in the root was: BFR = zinc concentration in the plant root (mg kg^{-1}) / zinc concentration in the soil (mg kg^{-1}). SISVAR statistical program (Ferreira, 2011) was employed to analyze the obtained results, by using the F test and regression polynomials, which were used to adjust the data when significant.

3. Results and discussion

With the exception of the root dry biomass of the radish, the shoot dry biomass, the Zn concentration and bioaccumulation factor in shoot and root, were significantly affected by the bentonite application to the soil (Table1). The bentonite didn´t affect the translocation index and factor.

Table 1. Summary of the analyses of variance for the dry biomass, zinc concentration and bioaccumulation fator of zinc in shoot and root of the radish cultivated on soil contaminated with zinc for the different bentonite treatments.

Source of Variation	DF	Mean Square					
		Dry biomass		Concentration		Bioaccumulation factor	
		shoot	root	shoot	root	plant	root
Bentonite	3	1.609**	0.134ns	198640.92*	146273.85**	4.981**	2.096**
Linear	1	4.136**	0.189ns	527475.2*	357527.17**	13.248**	5.123**
Quadratic	1	0.128ns	0.0002ns	2.56 **	40672.80ns	0.133ns	0.583ns
Error	12	0.208	0.067	71649.74	11629,39	0.691	0.167
VC (%)		18.2	19	18.4	7.37	14.65	7.37
Mean		2.50	1.37	1452.95	1464.03	5.67	5.54

DF= Degree of Fredom, ^{ns}, * and ** no significant, significant to the 5 and 1% level, respectively.VC = Variation Coefficient.

The dry biomass of the aerial part (shoot) of the radish was adjusted to a linear model as a function of increasing doses of bentonite (Figure 2) ranged from 1.824 g (0 t ha^{-1} bentonite) to 3.183 g (90 t ha^{-1} bentonite), corresponding to an increase of 74.51% in the highest dose compared to control. On the other hand, the root dry biomass had a small growth, 33.76% in the highest dose compared to control, but was not significant.

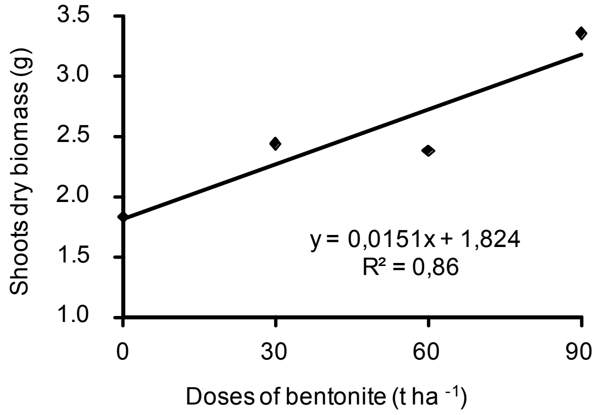

Figure 2: Dry biomass of the shoots for radish cultivated in soil contaminated with zinc for the different bentonite treatments

The positive effect of bentonite addition on plant growth may be due to its positive effect on the water retention capacity (Iskander et al., 2011) and the growth of surface area, increasing the metal cation adsorption capacity present in the soil (Tito et al., 2011) and consequently decreasing the concentration in the plant parts.

The zinc concentration in the shoot and in the roots of radish was significantly influenced to the 5% and 1% probability, respectively, by applying bentonite soil (Table 1). The linear behavior of the zinc concentration in all the parts of plants, shows the decrease of the same with increasing doses of bentonite ranging from 1696.6 to 1209.40 mg kg^{-1} in the shoot (Figure 3A) and ranging to 1664.6 to 1263.47 mg kg^{-1} in the roots (Figure 3B) occurring a decrease of 28.72% and 24.09%, respectively, the control regarding the higher dose.

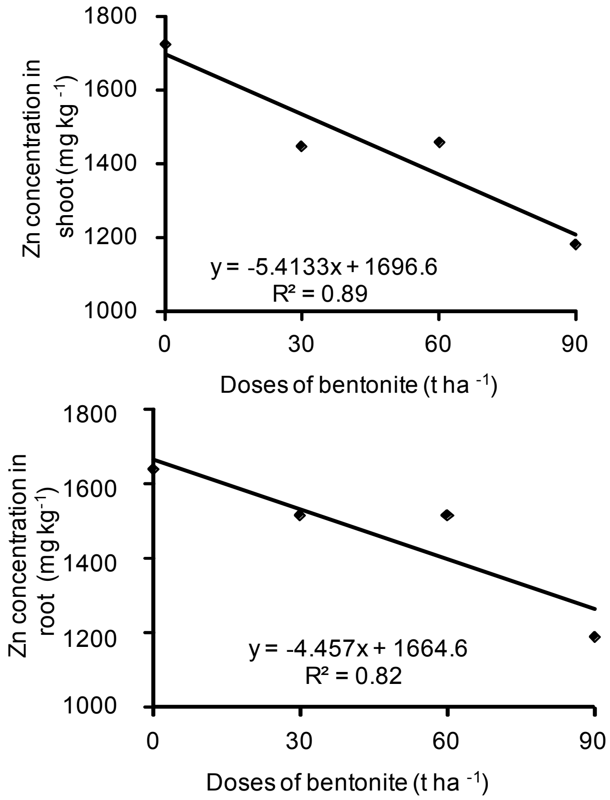

Figure 3: Zinc concentration in the shoots (A) and roots (B) of radish cultivated in the soil contaminated with zinc for the different bentonite treatments

The reduction of Zn concentration in this plant indicates a possible decrease in the availability of the element in the soil, due probably to its adsorption by bentonite.

The ability of a plant to accumulate metals from soils can be estimated using the bioaccumulation potential in plant (BFP) and/or in root (BFR). These factors can be used to estimate a plant's potential for phytoremediation purposes.

The BFP and BFR of radish decreased significantly to 1% probability by increasing doses of bentonite soil (Table 1) indicating an increase in the adsorption of zinc in the soil, decreasing the concentration in the plant parts. This behavior is beneficial since clay minerals such as bentonite have a great potential to adsorb pollutants due to their large specific surface area, the layered structure, and high cation exchange capacity (Bhattacharyya and Gupta, 2008).

According to Figure 4 the BFP and BFR ranged from 6.899 to 4.451 and from 6.304 to 4.783 showing a reduction of 35.48% and 24.13%, respectively, presenting better fit in linear model. However, the BFP and BFR values were higher than unity, indicating high bioaccumulation potential of radish for this metal.

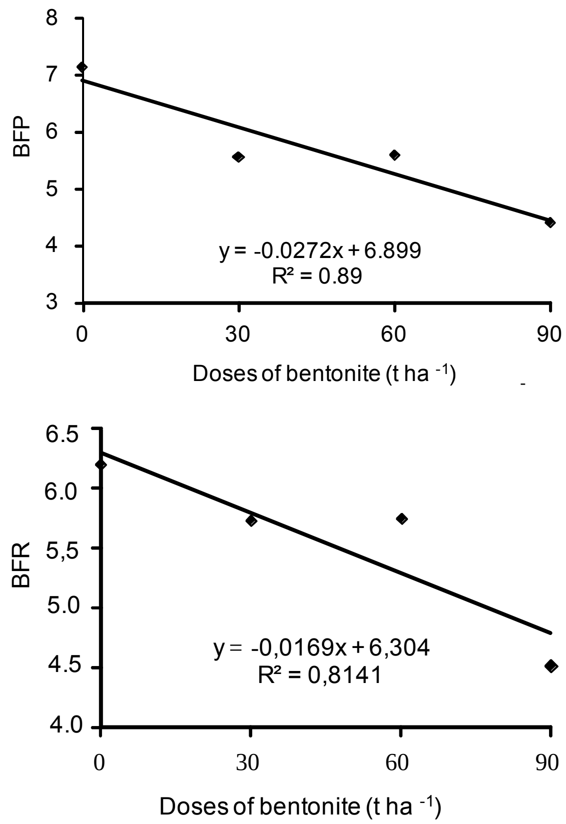

Figure 4: Bioaccumulation factor of zinc in plant (BFP) and in root (BFR) of radish depending on dose increasing bentonite.

Although the bentonite did not influence the TF of radish, the values of this factor < 1 (from 1.048 (without bentonite) to 0.989 (90 t ha^{-1})) indicated a low capacity for transporting zinc from roots to shoots which means that the radish is a suitable plant for phytoextraction for this metal. This can be confirmed by the concentration data and the amounts of zinc which were higher in the root than in the shoot. This is worrisome because the comestible part of plant is the root.

4. Conclusions

Bentonite in soil contaminated with zinc had a significant positive effect on development of shoot of radish; promoted the retention of this metal in the soil, evidenced by the reduction of the zinc concentration in the shoot and roots of radish. Bentonite favored the reduction of bioaccumulation factors of zinc thereby increasing the concentration of this element in soil in relation to the plants. The application of bentonite to the contaminated soils favored their remediation.

Acknowledgments

Special thanks to the Coordination for the Superior Level Personal Improvement (CAPES) for the scholarship granted to the second author and the National Council for Scientific and Technological Development-CNPq.

Reference

Abichequer A.D., Bohnen H., 1998, Eficiência de absorção, translocação e utilização de fosforo por variedades de trigo, Rev. Bras. Ci. Solo. 22(1), 21-26.

Bhattacharyya K.G., Gupta S.S., 2007, Adsorptive accumulation of Cd(II),Co(II),Cu(II),Pb(II) and Ni (II) from water on montmorillonite: Influence of acid actvation, J. Col. Inter. Sci. 310(2), 411-424.

Bhattacharyya K.G., Gupta S.S., 2008, Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: a review, Adv. Colloid Interface Sci. 140, 114–131.

EMBRAPA, Centro Nacional de Pesquisa de Solos, 1997, Manual de métodos de analise de solo, 2rd. Embrapa, Rio de Janeiro.

EMBRAPA, Centro Nacional de Pesquisa de Solos, 2006, Sistema brasileiro de classificação de solos, Embrapa, Rio de Janeiro.

Ferreira D.F., 2011, Sisvar: a computer statistical analysis system, Ci. Agrot., 35(6), 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 (1-3), 190-195.

Ghosh M., Singh S.P., 2005, A comparative study of cadmium phytoextraction by accumulator and weed species, Environ. Pollut. 133, 365–371.

Guimarães M.A., Santana T.A., Silva E.V., Zenzen I.L., Loureiro M.E., 2008, Toxicidade e tolerância ao cádmio em plantas, Rev. Trop.: Ci. Agr. Biol. 2(2), 58- 68.

Gupta S., Nayek S., Saha R.N., Satpati S., 2008, Assessment of heavy metal accumulation in macrophyte, agricultural soil and crop plants adjacent to discharge zone of sponge iron factory, Environ. Geol. 55, 731-739.

Iskander A.L., Khald E.M., Sheta A.S., 2011, Zinc and manganese sorption behavior by natural zeolite and bentonite, Annals of Agric. Sci. 56, 43-48.

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(1-3), 33-39.

Kabata-Pendias A., Pendias H., 2010, Trace Elements in Soils and Plants. 3rd Edition, CRC Press, Boca Raton. http://dx.doi.org/10.1201/b10158

Kumar P.S., Ramalingam S., Sathyaaselvabala V., Kirupha S.D., Murugesan A., Sivanesan S., 2012, Removal of Cd(II) from aqueous solution by agricultural waste cashew nut shell, Korean J. Chem. Engin. 29,756–768.

Macêdo L.S., Morril W.B.B., 2008, Origem e Comportamento dos Metais Fitotóxicos: Revisão da Literatura. Tecn. & Ci. Agr., 2, 29-38.

Marin A.B.P., Aguilar M.I., Ortuno J.F., Meseguer V.F., Saez J., Florenz M., 2010, Biosorption of Zn(II) by orange waste in batch and packed bed systems, J. Chem. Tech. Biotech. 85, 1310–1318.

McBride M.D., 1994, Environmental Chemistry of Soils. Oxford University, New York.

Mengel K.; Kirkby E.A., 1982, Principles of Plant Nutrition. International Potash Institute, Worblaufen.

Oliva S.R., Raitio H., Mingorance M.D., 2003, Comparison of two wet digestion procedures for multi-element analysis of plant samples, Com. Soil Sci. Plant Anal. 34, 2913-2923.

Sdiri A., Higashi T., Hatta T., Jamoussi F., Tase N., 2011, Evaluating the adsorptive capacity of montmorillonitic and calcareous clays on the removal of several heavy metals in aqueous systems, Chem. Eng. J. 172, 37-46.

Tito G.A., Chaves L.H.G., Guerra H.O.C., Soares F.A.L., 2011, Uso de bentonita na remediação de solos contaminados com zinco: efeito na produção de feijão, Rev. Bras. Eng. Agr. Amb. 15, 917-923.

Tito G.A., Chaves L.H.G., Guerra H.O.C., Vasconselos A.C.F., 2001, Bentonite application in an Ultisol. Effect on physical and chemistry soil properties, Agro-Ci. 17(1), 51-58.

Tito G.A., Chaves L.H.G., Vasconcelos A.C.F., Fernandes J.D., Guerra H.O.C., 2016, Bentonite application in the remediation of copper contaminated soil, African J. Agr. Res., 11, 1218-1226.

Wowk G.I.T.H., Melo V.F., 2005, Avaliação do nível de chumbo, em solo de várzea, proveniente da reciclagem de baterias, Rev. Bras. Eng. Agr. Amb. 9(4), 613-622.