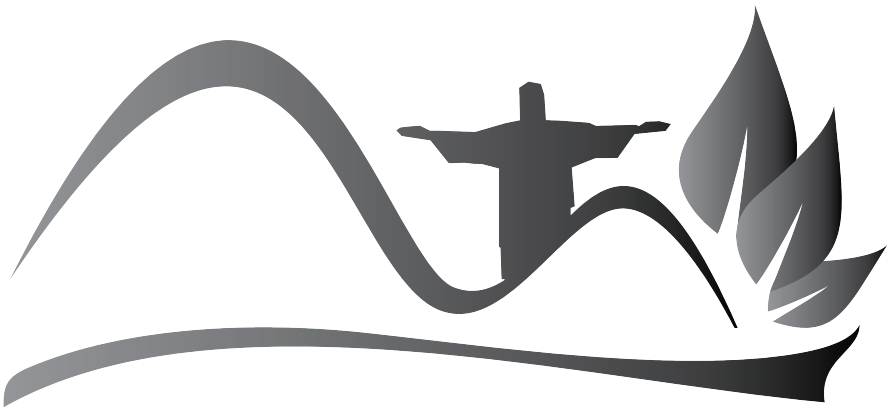
16th WORLD FERTILIZER CONGRESS OF CIEC

TECHNOLOGICAL INNOVATION FOR A SUSTAINABLE TROPICAL AGRICULTURE

PROCEEDINGS

International Scientific Centre of Fertilizers (CIEC)



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PROCEEDINGS

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SORPTION OF PB/CD BY FIVE TYPES OF PHOSPHATE FERTILIZERS

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Introduction

A great number of areas are contaminated with toxic metals in Brazil and in many cases they affect the health of the local population. The municipality of Santo Amaro da Purificação, Bahia state, has another old Plumbum plant which operated for 33 year, until 1993. High levels of Pb and Cd in blood and their toxic effects were observed in children and adults who lived nearby (Carvalho et al. 2003). Measures to reduce the solubility and bioavailability of metals in environmental samples have been proposed as a means of reducing the impact of their contamination on human populations and ecosystems. Some authors have shown that the remediation of contaminated soils using phosphates is efficient in the transformation of more soluble chemical forms of Pb (non-residual) into less soluble forms (residual). The objective of this study was to evaluate the efficiency of immobilization of Pb and Cd in remediation of soils contaminated with five types of commercial phosphate fertilizers: mono ammonium phosphate (MAP), simple superphosphate (SSP), reactive natural phosphate (RNP), thermophosphate (TP) and triple superphosphate (TSP).

Materials and methods

Characterization of phosphate fertilizer samples

The concentrations of Pb and Cd in the fertilizers were determined with the 3051a method (USEPA, 2007). Approximately 0.5 g of fertilizer sample were weighed in 100-mL tubes in triplicate and digested with a mixture of 9 mL of nitric acid (HNO_3, 70%, ultra pure, Vetec) and 3 mL of hydrochloric acid (HCl, 32%, ultra pure, Vetec). The samples were transferred to a Multiwave 3000 Anton Paar microwave apparatus programmed to raise the sample temperature to 175 °C at 16 atm in 5.3 min, hold time of 4.3 min, and reduce the temperature and pressure in 10 min. The extracts were cooled and centrifuged in a FANEM centrifuge (Model 206 - R) and the volumes were completed to 30 mL with distilled water and filtered with a paper filter. The concentrations were determined by ICP-OES (Perkin Elmer OPTIMA 3000).

The percentage of P_2O_5 in the samples of the five phosphate fertilizers was obtained by measurement with molybdophosphoric acid in a Femto 600s spectrophotometer (Brazil, 2006).

Sorption experiment

The generic term “sorption” has been used here to indicate the retention of soluble sorbates by the solid phase due to the difficulty in distinguishing the different processes involved (Violante et al. 2013). Sorption was conducted in a batch-type experiment using 1 g of sample of each fertilizer and 40 mL of Pb and Cd mono- and bimetallic solutions in polyethylene tubes. The mixtures were agitated horizontally at 150 rpm at room temperature. The experiment was conducted following Pierangeli (2001) with duration of 72 h and alternate agitation and rest every 12 h. The solutions were prepared with $Pb(NO_3)_2$ and $Cd(NO_3)_2.4H_2O$ in the following concentrations: 50, 100, 200, 500, 800, 1000 mg L^{-1}. After centrifuging the samples for 15 min at 3000 rpm, the supernatants were filtered with paper filter, the samples were diluted to 0.25% with HNO_3 and analyzed by ICP-OES (Perkin Elmer, OPTIMA 3000).

Isotherm Fitting Tool (ISOFIT) and Akaike information criterion

Isotherms were used to describe the correlation between the reaction time and the adsorbate (metals) and adsorbant (phosphate fertilizers) and the con-

centration of the substances in the equilibrium solution. The type of isotherm that best represents the results was determined with the software *Isotherm Fitting Tool* (ISOFIT), which adjusts the isotherm parameters to the experimental data through the minimization of a weighted sum of squared error (Matott et al. 2008).

According to the Akaike theory (Wu et al. 1998), the most accurate method is the one with the smallest AIC (Akaike Information Criterion) or AICc (Akaike Information Criterion for a small set of samples, normally smaller than 40). Very close values of AIC (or AICc) suggest that some models may be adequate to estimate the experimental data obtained. Next, the models can be compared using the AIC, more than two distinct forms, using the ΔAIC and the weighted AIC. The ΔAIC is obtained by subtracting the AIC of the model and the AIC of the best model, that is, that which had the lowest AIC. A model is considered good when its *w* value is lower than 10% of the greatest *w* value of the set of calculated models (Mazerolle 2004).

Results and discussion

Characterization of the phosphate fertilizer samples

The analysis of the metals contained in the fertilizers showed that Pb and Cd were present in the compositions of only RNP and TP (Table 1). RNP released 33 mg L^{-1} of Cd and TP, 66 mg L^{-1} and 1.4 mg L^{-1} of Pb/Cd, respectively, when submitted to the USEPA 3051a method. Normative Instruction no. 27 (Brazil 2006) of the Ministry of Agriculture, Livestock and Food Supply sets the maximum concentrations of toxic metals in imported fertilizers and fertilizers produced in Brazil. The concentrations of Pb and Cd in the five fertilizers that were analyzed were below the regulation limits (Table 1).

Sorption experiment

The isotherms show that the sorption of Pb by the five fertilizers was rather efficient after 72 h, the sorption being complete for MAP, regardless of the fertilizer concentration. For the bimetallic solution, in general the sorption decreased, as expected, due to the competition by the two ions for the sorption sites. As a result, the isotherm calculation with the ISOFIT was not used. The data obtained corroborate the literature results that the sorption of Pb in soils or phosphate fertilizers is independent of the presence of Cd (Violante et al. 2013) and of pH variation range.

The five phosphate fertilizers had different adsorption capacity. Fertilizers TP and RNP had a greater Cd sorption capacity in all concentrations of both mono- and bimetallic solutions. The pH of the solution in equilibrium is probably related to this behavior, considering that Chen et al. (1997) reported that the sorption of Cd increased at higher pH values (close to or higher than 6).The sorption sequence for the monometallic solution was TP > RNP > TSP > SSP > MAP. For the bimetallic solution, TP continued to be more efficient than RNP and SSP, TSP and MAP did not have significant variations of sorption capacity.

ISOFIT showed that two models, the Linear and the Langmuir models, represented the experimental data the best and had the best results in nine of the ten experimental conditions (five fertilizers vs. two types of solution, mono- and bimetallic).

Conclusion

The five samples of phosphate fertilizers investigated in this study (mono-ammonium phosphate, simple superphosphate, reactive natural phosphate, thermophosphate and triple superphosphate) immobilized Pb in mono- and bimetallic (Pb/Cd) solutions efficiently. Cd was most efficiently immobilized by thermophosphate in both conditions. Without taking cost into consideration, thermophosphate is the most indicated fertilizer for the remediation of soils contaminated with Pb and Cd.

Keywords: Phosphate fertilizers, sorption, desorption, isotherm, Pb, Cd.

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set out in Annexes I, II, III, IV and V of this Instruction as regards the maximum levels permitted for phytotoxic agents pathogenic to man, animals and plants, heavy metals, pests and weeds. Official Gazette [of] the Federative Republic of Brazil, Brasilia, DF, Section 1, 2006 p.15.

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Table 1. Concentrations of P, Cd and Pb in the phosphate fertilizer samples.

Fertilizers	P_2O_5	Extraction		Limits[a]	
		Cd	Pb	Cd	Pb
	%	---------- mg kg^{-1} ----------			
MAP	56	< DL[b]	< DL	176	880
SSP	21	< DL	< DL	80	400
RNP	30	33	< DL	116	580
TP	17	1.4	66	68	340
TSP	46	< DL	< DL	180	900

[a]Maximum allowed concentration toxic metals in mineral fertilizers containing phosphorus according to Normative Instruction 27 (Brasil, 2006).
[b]Detection limits: the quantification of trace element concentration of Cd and Pb were 3 mg L^{-1} and 30 mg L^{-1}, respectively.