POTENTIAL USE OF A CHEMICAL LEACHING REJECT FROM A KAOLIN INDUSTRY AS AGRICULTURAL FERTILIZER(1)

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SUMMARY

The industrial refining of kaolin involves the removal of iron oxides and hydroxides along with other impurities that cause discoloration of the final product and depreciate its commercial value, particularly undesirable if destined to the paper industry. The chemical leaching in the industrial processing requires treatments with sodium hyposulfite, metallic zinc, or sulfuric and phosphoric acids, in order to reduce, dissolve and remove ferruginous compounds. To mitigate the environmental impact, the acidic effluent from the leaching process must be neutralized, usually with calcium oxide. The resulting solid residue contains phosphorous, zinc, and calcium, among other essential nutrients for plant growth, suggesting its use as a macro and micronutrient source. Samples of such a solid industrial residue were used here to evaluate their potential as soil fertilizer in an incubation greenhouse experiment with two soil samples (clayey and medium-textured). The small pH shift generated by applying the residue to the soil was not a limiting factor for its use in agriculture. The evolution of the concentrations of exchangeable calcium, and phosphorous and zinc extractability by Mehlich-1 extractant during the incubation period confirms the potential use of this industrial residue as agricultural fertilizer.

Index terms: industrial residue, fertilizer, kaolin refining.

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RESUMO: *USO POTENCIAL DO RESÍDUO QUÍMICO LIXIVIADO DUMA INDÚSTRIA DE CAULIM COMO ADUBO DE TERRAS AGRÍCOLAS*

O beneficiamento industrial do caulim envolve a remoção de óxidos e hidróxidos de ferro e outras impurezas, que conferem coloração indesejável ao produto final e depreciam seu valor comercial, particularmente se destinado à indústria de papel. A lixiviação química, na linha de processamento industrial, pode ser feita com tratamentos com hipossulfito de sódio, zinco metálico e ácidos sulfúrico e fosfórico, para redução, solubilização e remoção de compostos ferruginosos. A fim de minimizar o impacto ambiental, o efluente ácido, procedente da etapa de lixiviação, deve ser inicialmente neutralizado, usualmente por óxido de cálcio. O resíduo sólido resultante contém fósforo, zinco e cálcio, entre outros nutrientes, o que sugere seu uso como fonte de macro e micronutrientes. O principal objetivo do presente estudo foi avaliar o uso do resíduo sólido como fertilizante agrícola, em experimentos de incubação em casa de vegetação, em amostras de dois solos: um de textura média e outro argiloso. A pequena alteração do pH do solo, em função da aplicação do resíduo, não constitui fator limitante à sua aplicação na agricultura. A evolução das concentrações de cálcio trocável, e fósforo e zinco extraíveis por Mehlich-1, em função do tempo de incubação, confirmam a potencialidade de uso do resíduo industrial como fertilizante agrícola.

Termos de indexação: resíduo industrial, fertilizante agrícola, beneficiamento do caulim.

INTRODUCTION

Kaolin is a clay consisting essentially of minerals of the kaolinite (ideal formula, $Al_4(Si_4O_{10})(OH)_8$) group. It is white, fine-grained, chemically inert, and appropriate for paper, rubber, ink, and pottery manufacturing (Patterson & Murray, 1975). Its association to ferruginous compounds such as hematite (ideal formula, αFe_2O_3), which impart unwanted colors to the final product, depreciates its commercial value if it is to be used, for instance, in the paper industry. Physical or mechanical methods, such as dispersion or magnetic separation, to remove iron oxides and hydroxides are not always economically convenient, depending on the destination of the final product, while the efficiency is related to some kaolin characteristics. Generally, these methods are less efficient than differential dissolution treatments, as for example by leaching the ore chemically with sodium hyposulfite or metallic zinc and sulfuric and phosphoric acids in the industrial processing (Trawinski, 1980). This is the procedure adopted by Caolin Azzi Ltda, a mining industry located in the city of Mar de Espanha (21 ° 52 ' 02 " S, 43 ° 00 ' 35 " W), state of Minas Gerais, Brazil. The acidic effluent generated in this chemical leaching process is extremely harmful to the natural environment. The percolation of this material down the soil profile could significantly affect the chemical composition of the soil solution and cause a number of different and complex chemical processes such as pH variations with consequent releasing of hazardous elements to the environment. At Caolin Azzi Ltda, the acidic effluent from the leaching process is however initially neutralized with calcium oxide, in order to mitigate these hazardous effects, following the procedure described by Silva (1997). This produces a suspension that is disposed in ponds in the surroundings of the industrial plant and left to evaporate under open sky, without any further treatment or environmental protection, as those recommended by Cameselle et al. (1995). The drying process results in a solid residue that is rich in a large variety of chemical elements. The high levels of zinc, calcium, sulfur, and phosphorous, resulting mainly from the leaching and neutralization processes, suggest the possibility of using this industrial waste in agriculture. This would not only represent an economically interesting alternative but also a cleaner destination, regarding the entire natural ecosystem. In Brazil, most arable lands are highly weathered tropical soils, particularly Oxisols and Ultisols. The low agriculture potential is mainly conditioned by the intrinsic natural acidity and related factors (Rao et al., 1993). Soil acidity results from a complex set of interrelated factors, all or most of them detrimental to plant growth. Many crop plants grow best in a pH range close to neutral (6.2–7.5, approximately) (Kellogg, 1966). The main purposes of this study were (i) to carry out soil tests to evaluate the potential of this industrial residue as nutrient source for agricultural purposes and (ii) to indirectly evaluate the environmental impact, when used as soil fertilizer in agricultural areas.

MATERIAL AND METHODS

The solid residue used for this study was collected from a one-year-old deactivated dried pond in the production area of Caolin Azzi Ltda. The collected material was first prepared in the laboratory and characterized as described by Ribeiro et al. (2002). Kaolinite, lepidocrocite (ideal formula, γFeOOH), gypsum ($CaSO_4.2H_2O$), goethite (αFeOOH), and hematite accounted for the highest proportion of this solid residue, as revealed by powder X-ray diffraction (XRD), thermogravimetry, differential thermal techniques, and Mössbauer data. The material was found to be relatively rich in iron (5.50 mass % Fe_2O_3), sulfur (9.63 mass % SO_3), calcium (4.48 mass % CaO), phosphorus (3.99 mass % P_2O_5), silicon (21.10 mass % SiO_2), and aluminum (24.50 mass % Al_2O_3) (Ribeiro et al., 2003). Two soil types were used for the incubation tests: a medium-textured (collected from a sampling site near João Pinheiro, state of Minas Gerais, Brazil; soil A) and a clayey soil (from near Sete Lagoas, state of Minas Gerais, Brazil; soil B) (Table 1). A more detailed description of these soils is given by Oliveira et al. (1999).

After addition of the industrial solid residue at increasing mass proportions (0, 200, 600, 1,800, 5,400, and 16,200 kg ha^{-1}), the soil samples were watered to field capacity and kept in a greenhouse for 20 days. For the evaluations in a completely randomized design, soil sub-samples were collected after 5, 10, and 20 days of incubation. The pH values of the soil:water mixtures were determined at a mass ratio of 1:2.5. Phosphorous, potassium, and other elements (Cd, Cu, Cr, Co, Fe, Mn, Ni, Pb, Ti, and Zn) were extracted with Mehlich-1 extractant (Mehlich, 1953). Phosphorous was quantified by spectrophotometry (725 nm) by comparison with a standard curve and potassium was quantified by flame photometry as well as by comparison with a standard curve. Calcium, aluminum, and magnesium were extracted with KCl 1 mol L^{-1} solution. Aluminum was quantified by titration with NaOH solution. The macro and micronutrients calcium, magnesium, copper, iron, manganese, and zinc, and some heavy metals (Cr, Co, Ni, Cd, Ti, and Pb) were quantified by atomic absorption spectrometry (AAS). Another parameter, (H + Al), was quantified by titration with NaOH solution after extraction of soil sub-samples with calcium acetate 0.5 mol L^{-1} solution, all according to the procedure described by Ribeiro et al. (2002). The residue doses were correlated with the measured variables by numerical regression analysis.

RESULTS AND DISCUSSION

The pH of the residue in aqueous suspension was found to be 4.6. The pH of the initial medium-textured

Table 1. Physical and chemical characteristics of soil samples used in the incubation experiment and mineralogical composition of the clay fraction, [kaolinite (Ka), gibbsite (Gb), and goethite (Gt)]. Adapted from Oliveira et al., 1999

Component/Parameter		Soil	
		João Pinheiro (soil A)	Sete Lagoas (soil B)
pH in H_2O 1:2.5		5.13	5.77
P Total$^{(1)}$/mg dm^{-3}		64.4	934.0
P Mehlich-1$^{(2)}$/mg dm^{-3}		0.17	1.90
Cation exchange composition$^{(3, 4)}$/ cmol$_c$ dm^{-3}	Al^{3+}	1.57	0.26
	Ca^{2+}	0.15	2.5
	Mg^{2+}	0.32	0.59
	H + Al	4.8	8.9
Granulometric composition$^{(5)}$/g kg^{-1}	Coarse sand	460	80
	Fine sand	170	70
	Silt	20	130
	Clay	350	720
Field capacity$^{(6)}$/kg kg^{-1}		0.18	0.37
Clay fraction mineralogical composition$^{(7)}$/g kg^{-1}	Ka	298	143
	Gb	14	101
	Gt	22	143

(1) Extractant $HNO_3/HClO_4$ (8:3) (v/v) (Brasil, 1983). (2) Extractant: Mehlich-1 (Defelipo & Ribeiro, 1981). (3) Extractant: KCl 1 mol L^{-1} (Defelipo & Ribeiro, 1981). (4) Extractant: CaOAc 1 mol L-1, pH 7.0 (Defelipo & Ribeiro, 1981). (5) Method described in Emprapa (1997). (6) Methodology described by Fernandes & Sykes (1968). (7) Methodology described by Resende et al. (1987).

soil was 5.2 and that of the clayey soil 5.8. After applying the solid residue to the soil samples, the pH of the aqueous suspension of both soils decreased by 0.6 units, as the dose of the solid residue reached 16 x 10^3 kg ha^{-1}, after 5 days of incubation (Figure 1). The pH was also influenced by the incubation period. As the experiment continued, the pH increased in both soils. In the medium-textured soil (A) the equilibrium was reached after 10 days, when the pH value was 0.1 unit higher than after 5 incubation days. For the clayey soil (B) the pH increased about 0.2 pH units, between the 5th and the 20th incubation day, although the pH increase of the first 10 incubation days was higher than from the 10th day onwards. The parameter values were fitted (Table 3) according to the algebraic model for fitted pH curves (Figure 1). The buffer capacity of the clayey was greater than of the medium-textured soil and slightly higher for lower residue doses.

A particular characteristic of acid soils with falling pH is an increasing ability to accumulate free aluminum and manganese ions (Ritchey et al., 1991). In this study, no acidity variation tended to inhibit plant growth, since no relevant content of heavy metals or other toxic elements, including aluminum, was detected in the KCl-extracted soil solution. As a general trend, free aluminum increases as soil acidity increases. For soil A, the exchangeable aluminum content decreased as the solid residue dose increased, despite the pH reduction. This effect was more evident for longer incubation times (Figure 2) and could be explained by the assumption that calcium, from gypsum dissolution, replaces exchangeable aluminum on clay mineral surfaces. The released aluminum would then precipitate as $Al(OH)_3$ or be chemisorbed on iron or aluminum oxides of the residue, and become unavailable for the extractant solution. Another possibility would be its precipitation as aluminum phosphate or basic phosphate salt. The lower clay content in soil A compared to soil B caused a higher exchangeable aluminum effect in that soil. In natural soil environments, a pH below 4.5 may represent a physiological barrier to plant growth due to the toxicity of high free aluminum or manganese, which is aggravated by deficiencies of calcium, magnesium, potassium, sodium, phosphorous, nitrogen, sulfur, zinc, or molybdenum. However, in spite of the low pH reached in soil A, the experimental results suggest that residue application could reduce aluminum toxicity, especially in low-clay soils.

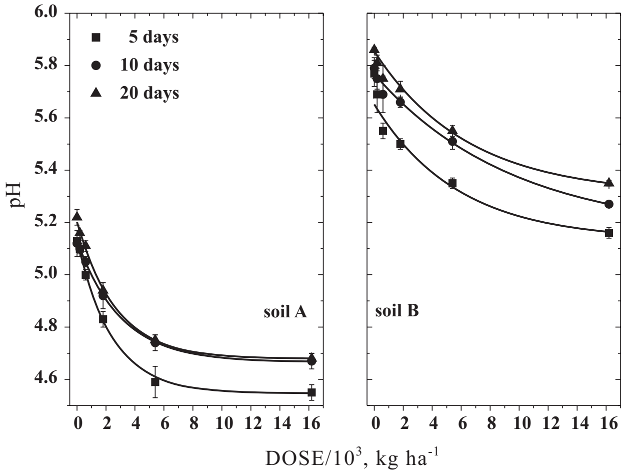

Figure 1. Evolution of soil acidity under increasing doses of solid residue in soils A and B. Table 3 shows the fitted parameter values according to the algebraic model adjusted for pH progress.

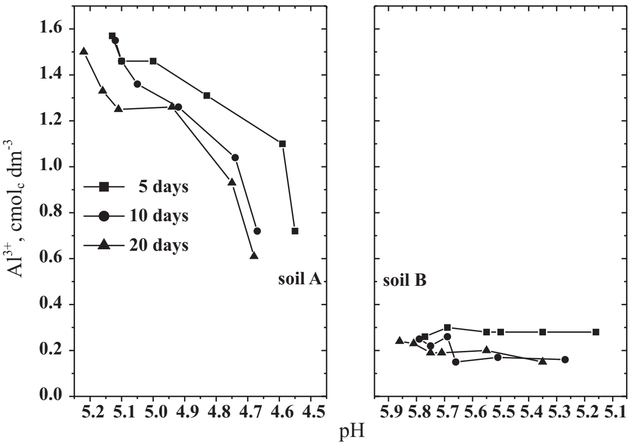

Figure 2. Exchangeable aluminum with increasing acidity in different incubation times in soils A and B.

The increased acidity and higher exchangeable aluminum in both soils, at increasing applications of solid residue, are reflected in values which approach the (H + Al)-potential acidity (Table 2).

As a general trend, the soil pH is not changed at all or increased only slightly by calcium sulfate (Malavolta, 1985). Despite the low solubility, calcium sulfate provides the soil solution with a calcium source (Ismail et al., 1993). A linear increase of exchangeable calcium was observed, particularly in the medium-textured soil (Figure 3). No similar effect was observed for the clayey soil which indicates a higher buffering characteristic of its colloidal system. Table 3 shows the fitted parameter values according to the algebraic model for fitted Ca^{2+} curves (Figure 3).

The soil pH is also assumed to greatly affect phosphorus release to the soil solution. Phosphorous availability to plants is particularly restricted at low pH and high free aluminum contents, since phosphorous tends to be fixed as aluminum phosphate, which is a relatively insoluble salt under these conditions (Rao et al., 1993). On the other hand, in soils with higher pH, phosphorus reacts with calcium and magnesium to form insoluble compounds. The optimum availability of phosphorus to plants is observed in slightly acidic to neutral conditions (Lindsay, 1979). Phosphorous extractability by Mehlich-1 extractant increased after solid residue

Table 2. Nutrients and toxic elements in the soil extracts after application of increasing doses of residue in different incubation times

Soil	Incubation time/Days	Dose	Al^{3+} (1)	H + Al(3)	Mg^{2+} (1)	K(2)	Fe(2)	Cu(2)	Mn(2)
		kg ha^{-1}	cmol$_c$ dm^{-3}			mg dm^{-3}			
A	5	0	1.57(9)	4.8(3)	0.32(1)	42(3)	10(2)	0.24(5)	3.2(8)
		200	1.5(2)	4.8(2)	0.33(1)	45(3)	12(1)	0.26(3)	3.2(3)
		600	1.46(0)	4.91(0)	0.33(1)	46(3)	11.3(3)	0.23(3)	3.19(8)
		1.800	1.31(7)	4.91(0)	0.33(1)	47(2)	14.2(8)	0.25(5)	3.7(3)
		5.400	1.10(2)	4.91(0)	0.35(1)	49(3)	21(1)	0.4(2)	4.7(4)
		16.200	0.72(2)	5.0(1)	0.35(3)	46(3)	42(1)	0.55(3)	5.1(2)
	10	0	1.55(9)	4.77(0)	0.34(2)	39(2)	13(4)	0.12(2)	3(1)
		200	1.5(2)	4.77(0)	0.37(2)	45(5)	12.2(8)	0.17(5)	3.2(2)
		600	1.4(1)	4.77(0)	0.36(4)	46(4)	13(1)	0.19(3)	3.3(5)
		1.800	1.26(5)	4.77(0)	0.34(1)	44(1)	16(2)	0.21(2)	3.8(4)
		5.400	1.04(6)	4.77(0)	0.34(1)	43.3(5)	22(3)	0.23(3)	4.9(4)
		16.200	0.7(1)	4.77(0)	0.35(1)	43(1)	38(3)	0.49(8)	5.4(4)
	20	0	1.50(7)	4.77(0)	0.34(1)	46(5)	16(4)	0.23(3)	3(1)
		200	1.3(1)	4.77(0)	0.33(1)	46(3)	14.7(9)	0.23(2)	3.3(3)
		600	1.25(0)	4.77(0)	0.33(1)	49(4)	15(2)	0.25(1)	3.3(6)
		1.800	1.26(4)	4.77(0)	0.33(1)	49(3)	17.3(8)	0.21(4)	3.7(2)
		5.400	0.9(2)	4.77(0)	0.35(1)	48(2)	24(1)	0.27(4)	4.7(3)
		16.200	0.61(7)	4.6(3)	0.36(1)	46(2)	42(3)	0.48(6)	5.0(2)
B	5	0	0.26(2)	8.9(2)	0.59(3)	70(4)	30(11)	0.6(1)	34(7)
		200	0.30(5)	9.0(3)	0.64(2)	70(3)	36(9)	0.56(5)	38(5)
		600	0.28(0)	9.4(2)	0.62(1)	65(3)	34(8)	0.51(6)	35(9)
		1.800	0.28(0)	9.3(2)	0.65(2)	68(1)	38(10)	0.49(4)	36(7)
		5.400	0.28(0)	9.46(7)	0.61(3)	69(2)	53(5)	0.66(8)	45(2)
		16.200	0.28(0)	9.29(8)	0.61(3)	69.8(5)	48(6)	0.64(6)	42(3)
	10	0	0.25(2)	8.5(2)	0.54(1)	61(2)	32(8)	0.35(6)	34(5)
		200	0.22(2)	9.0(2)	0.62(2)	66(1)	38(15)	0.3(1)	37(6)
		600	0.26(5)	8.94(0)	0.63(1)	69(2)	34(15)	0.34(8)	38(6)
		1.800	0.15(0)	8.94(0)	0.67(4)	67(3)	39(10)	0.4(1)	37(6)
		5.400	0.17(2)	8.94(0)	0.67(2)	69(2)	33(4)	0.39(6)	38(2)
		16.200	0.16(2)	8.94(0)	0.66(4)	70(5)	41(6)	0.41(6)	41(4)
	20	0	0.24(0)	8.94(0)	0.54(2)	61(1)	35(8)	0.39(4)	30(7)
		200	0.23(2)	8.94(0)	0.62(3)	68(2)	38(11)	0.61(3)	34(7)
		600	0.19(2)	8.94(0)	0.62(2)	71(2)	38(13)	0.59(9)	31(8)
		1.800	0.19(2)	8.94(0)	0.64(2)	69(4)	38(12)	0.49(7)	31(8)
		5.400	0.20(0)	8.94(0)	0.61(3)	72(4)	42(5)	0.49(5)	38(4)
		16.200	0.15(0)	9.13(8)	0.60(5)	73(3)	44(5)	0.49(5)	41(3)

Numbers in brackets represent the error in the last significant digit, estimated as the standard deviations from the mean of 4 replications. (1) Extracted with KCl 1 mol L^{-1}. (2) Extracted with Mehlich-1 extractant. (3) Extracted with calcium acetate 0.5 mol L^{-1}.

application (Figure 4). The values of the parameters were fitted (Table 3) according to the algebraic model for P curves (Figure 4). Dose and time are therefore important factors to release phosphorus to the extractant solution. The phosphorus extractability was lower for the medium-textured (A) than for the clayey (B) soil, after applying solid residue up to 5,400 kg ha^{-1}. Upon application of 5,400 kg ha^{-1}, the response was opposite of the previously observed: in soil B, the extractable P decreased and the phosphorous availability sank with incubation time. This was probably caused by the chemisorption of phosphate ions on iron or aluminum oxides. The same effect was observed for zinc (Figure 5). Probably, even in an unfavorable pH range, the higher clay content favors phosphorous chemisorption. Nevertheless, the linear increase of the extractable fraction indicates the potential of this residue for plant phosphorus supply.

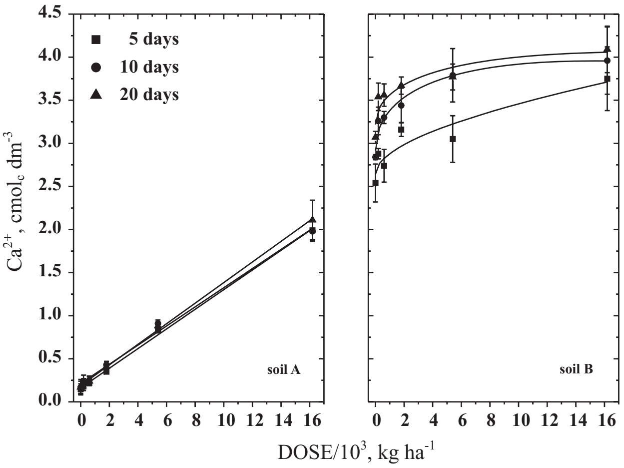

Figure 3. Exchangeable calcium under increasing doses of solid residue in soils A and B. Table 3 shows the fitted parameter values according to the algebraic model adjusted for Ca^{2+} response.

For the medium-textured soil (A), the phosphorous extractability was non-linear. This behavior supports the hypothesis of a chemical mechanism involving the precipitation of aluminum phosphate, for higher residue doses, which would explain the observed reduction in aluminum exchangeability of this soil.

Zinc is an essential micronutrient to plants and its accessibility is very closely related to the soil pH (Pierzynski & Logan, 1993). Variations in pH caused by solid residue applications to soil samples could also affect zinc extractability. In this study case, the Mehlich-1 extractable zinc contents increased linearly with the applied residue doses (Figure 5). Table 3 shows the values of the fitted parameters according to the algebraic model for adjusted Zn curves in Figure 5. In both soils, the measured zinc extractability in Mehlich-1 extractant was about the same. However, in soil B the extractability clearly decreased as the incubation time increased.

Table 3. Values of the fitted parameters A, B, and C, according to the algebraic model of each evaluated nutrient and pH, where D is the dose of the applied residue, given in kg ha^{-1}. Numbers in brackets represent the estimated uncertainty in the last significant digit

Soil/ Parameters	**João Pinheiro – pH = A + $Be^{-(D/C)}$**				**Sete Lagoas – pH = A + $Be^{-(D/C)}$**			
Time/days	**A**	**B**	**C/10^3**	**R^2**	**A**	**B**	**C/10^3**	**R^2**
5	4.55(3)	0.58(3)	2.4(3)	0.999	5.13(3)	0.52(3)	6(1)	0.963
10	4.67(3)	0.47(3)	3.0(7)	0.999	5.16(7)	0.61(6)	9(3)	0.999
20	4.68(2)	0.52(2)	2.7(4)	0.999	5.31(2)	0.55(2)	6(1)	0.998
	Ca^{2+} = A + BD				**Ca^{2+} = A + BD + $CD^{½}$**			
	A	**B/10^{-4}**		**R^2**	**A**	**B/10^{-5}**	**C/10^{-2}**	**R^2**
5	0.16(2)	1.14(3)		0.998	2.6(2)	1(1)	1.0(1)	0.881
10	0.21(3)	1.11(4)		0.995	2.9(1)	-7(2)	1.7(1)	0.969
20	0.19(1)	1.19(2)		0.999	3.2(1)	-4.5(4)	1.2(5)	0.885
	P = A + BD + CD^2				P = A + BD			
	A	**B/10^{-3}**	**C/10^{-8}**	**R^2**	**A**	**B/10^{-4}**		**R^2**
5	0.03(9)	1.51(0)	-5.02(3)	0.999	1.82(7)	8.2(3)		0.994
10	-0.03(9)	1.43(0)	-5.11(1)	0.997	1.47(7)	5.6(2)		0.992
20	-0.02(9)	1.28(0)	-3.35(4)	0.999	1.78(2)	6.2(1)		0.998
	Zn^{2+} = A + BD				**Zn^{2+} = A + BD**			
	A	**B/10^{-2}**		**R^2**	**A**	**B/10^{-2}**		**R^2**
5	0.9(3)	1.32(1)		0.999	0.87(8)	1.2(1)		0.974
10	0.6(2)	1.26(2)		0.999	0.3(2)	1.0(7)		0.982
20	0.8(4)	1.30(2)		0.999	0.5(2)	1.0(4)		0.994
	Pb^{2+} = A + BD				**Pb^{2+} = A + BD + $CD^{½}$**			
	A	**B/10^{-3}**		**R^2**	**A**	**B/10^{-4}**	**C/10^{-2}**	**R^2**
5	22(2)	1.1(2)		0.867		**no correlation**		
10	18(3)	1.7(2)		0.956	4.9(4)	-4.8(1)	8.9(2)	0.935
20	21(2)	1.2(2)		0.878	6.6(5)	5.8(7)	-	0.948

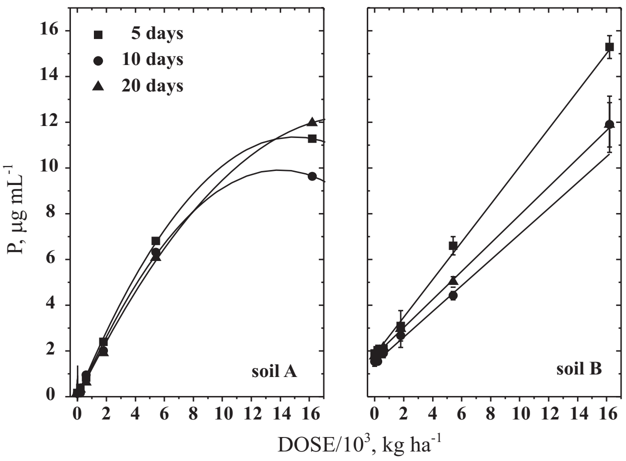

Figure 4. Phosphorous extractability under increasing doses of solid residue in soils A and B. Table 3 shows the fitted parameter values according to the algebraic model adjusted to P response.

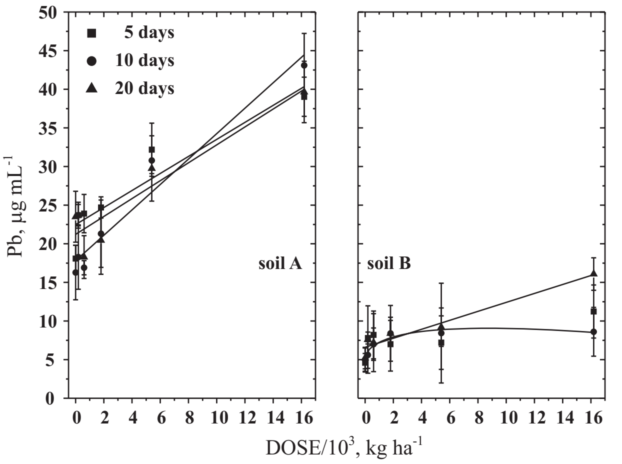

Figure 6. Lead extractability under increasing doses of solid residue in soils A and B. Table 3 shows the fitted parameter values according to the algebraic model adjusted to Pb response.

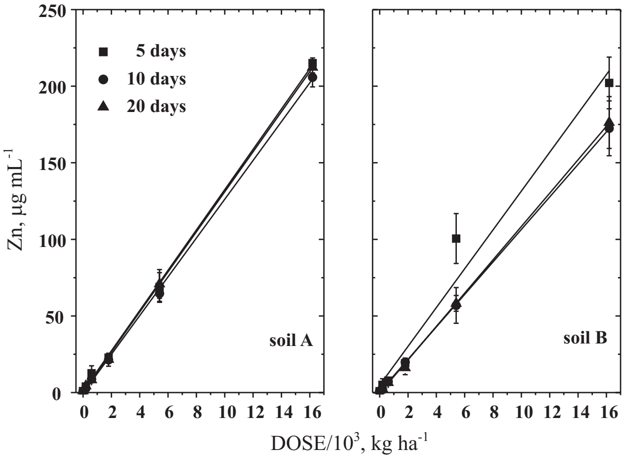

Figure 5. Zinc extractability under increasing doses of solid residue in soils A and B. Table 3 shows the fitted parameter values according to the algebraic model adjusted for Zn response.

Heavy metals, including chromium, cobalt, cadmium, nickel, titanium, and lead may also be toxic to plants. In this study, some heavy metal contents were measured in a solution extracted with the Mehlich-1 extractant, which tends to overestimate the real solubility in the soil solution. All measured elements were found to be below the limit of analytical detection, except lead (Figure 6), which was however below any critical limit to threaten plant development or mammal health, according to USPHS (1997) and Goyer (1993), even for the medium-textured soil (A), where it was higher. In fact, other tests of water solubility and sequential extraction of lead could be performed after residue application, for a more reliable evaluation of the real risk of applications of this residue to agricultural soils. However, if not even a highly acidic extractant such as Mehlich-1 was capable of increasing the lead extractability with increasing residue doses in the clayey soil (B) and very little with time duration for both tested soils, another extractant as for instance, KCl, resin, or any other, would probably not be able to perform the extraction.

The fact that lead extractability is lower in the clayey soil (B) than in the medium-textured soil (A) is also explained by the colloidal characteristics of soil B where lead would be adsorbed in aluminum or iron oxides and hydroxides, becoming stable and immobile and therefore, unavailable for the extractant solution. Table 3 shows the parameter values drawn from the fitted Pb data to the algebraic model (Figure 6).

Once the availability of heavy metals sharply decreases as pH increases, common procedures of correction of soil acidity, such as liming, could also be employed together with residue application in an attempt to reduce lead availability to even lower levels.

Although no significant variations of the magnesium and potassium contents were observed in both soils, there was a tendency of increasing iron, copper, and manganese extractability with increasing solid residue doses (Table 2).

CONCLUSIONS

1. The application of this solid residue slightly increased the acidity of both tested soil samples, but no chemical property was found that would limit its use as agricultural fertilizer. Actually, the small decrease in the soil pH value upon residue application represents no significant constraint to plant growth and does not significantly favor the release of heavy or other toxic elements to the soil solution.

2. The application of this solid residue tends to reduce the aluminum toxicity, especially in low-clay soil samples.

3. In spite of lower P_2O_5 contents, compared with the conventional single superphosphate (with 17-20 mass % P_2O_5), this solid industrial residue is an interesting nutrient source for agricultural purposes, as an elemental provider for phosphorous, calcium, magnesium, and zinc uptake from soil solution by plants.

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