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Solubilization of Bayóvar Natural Phosphate Rock under the Drain Effect of Calcium and Phosphorus at Two Levels of Acidity

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Abstract

Natural phosphate rock (NP) solubilization in soils is dependent on the soil pH and its power to remove or drain (sink effect) P and Ca of the solution that is in equilibrium with the NP. The aim of this work was to evaluate the effect of acidity and P- and Ca-sinks on the solubilization of bayóvar reactive rock phosphate (a phosphorite). Samples of this NP in aqueous suspension were placed in a cassette (Slide-A-Lyzzer G2 Dialysis Cassette) compartment and immersed in a beaker containing 150 mL of an aqueous solution with pH adjusted at 4.5 or 6.0, where P- and Ca-sinks individually or in their combinations, were applied. The tested sinks were: Anionic Resin (AR); Cationic Resin (CR); Mixed Resin (MR: AR + CR); Goethite (Goe); Goe + AR; Goe + CR and one control (NP only) in five replicates. Beakers (experimental units) were shaken for 12 h daily, at 130 rpm, until completing 30 days of equilibrium. The suspensions were filtered to extract solution-P from the residue on the filter paper; the labile-P was extracted from this residue using 0.8 mol·L^{-1} NH$_4$Cl in 2 mol·L^{-1} HCl and, finally, the remainder P in the same residue together with the filter paper were subjected to nitric-perchloric acid digestion, to determine the P-residual in the extract. Goe caused greater solubilization of the NP, indicating that this P-sink was more effective than AR, causing similar or greater solubilization than CR. AR and CR, in a similar way, significantly restricted the trait characteristic of Goe ($p < 0.05$), at both pH values, in the solubilization of NP. Although Goe generally caused greater solubilization of the NP, it also caused the lower formation of labile-P. The CR presented, in general, the highest contents of solution-P, thus it triggered solubilization of NP without the immobilization of the solution-P, unlike the one with the AR that adsorbs

it. In the lower pH condition (4.5), the solubilization of NP tended to be higher than at pH 6.0, although in a little effective way, compared to the effects of the sinks.

Keywords

Anionic Resin, Cationic Resin, Goethite, P-Sink, Ca-Sink

1. Introduction

Natural phosphate rocks (NP), widely used in agriculture, especially in soils with an advanced weathering degree, are an option for the great soil P adsorption power (soil-sink), which, due to its gradual and progressive release, provides P and Ca, favoring the plant-sink [1]. The variable contents of P and Ca in the soil solution are in equilibrium with their NP sources and are dependent on attributes such as pH and soil cationic or anionic sinks. These attributes, as well as the balance between source and solution, govern the dissolution of NP, and the withdrawal of some of these products will generate a shift of the balance in the direction of greater solubilization of NP [2] and [3].

Under natural conditions, Ca- and P-sinks tend to be quite exclusive, such that in soils with higher CTC and higher Ca-sink, there is consequently a smaller P-drain. Thus, in soils with a lower degree of weathering and a higher negative charge density, there is a higher solubilization of the NP by the greater Ca-sink, which displaces the equilibrium in the direction of dissolution [4] [5] [6] [7].

[8] found a much more effective P supply for plants when using NP in organic soils (high Ca-sink effectiveness) when compared to its use in mineral soils (lower effectiveness of this sink), suggesting that P-sink in tropical soils is not as effective as that of younger, lower weathered soils, in terms of P availability to plants. However, such mechanisms of solubilization can come from both soil- and plant-sinks, but what is not conveniently clear in the literature is how these sinks are complementary or antagonistic: the generation of a greater solubilization of NP, caused by soil attributes, does not necessarily imply in a condition for greater plant growth [9]. In one hand, Ca removal through soil-sink, via ionic exchange not competitive with the plant [5], differs from P removal from the soil solution by covalent adsorption, converting it to a non-labile form unfavorable to the plant [10]. Therefore, the Ca-sink of the plant causes solubilization of NP, with return of the benefit to the plant, while the P-sink of the soil has similar practical effect (solubilization of NP), however with immobilization of the P drained in a non-available form to plants.

Survey on which of the two sinks—Ca or P—is the most effective in NP solubilization has indicated to be Ca-sink the most effective, and, both, are more effective than acidification [11] [12]. Thus, a less significant NP solubilization should occur in tropical dystrophic soils, with a low effective CEC (condition for lower Ca-drain effectiveness), than in those less weathered ones, with a high effective

CEC, a condition for greater Ca-sink condition [13]. [5] observed higher P solubilization (solution-P) when the soil pH, initially alkaline, was reduced to 6.5 and then to 5.5. In addition, these authors observed a higher increase of P concentration in the soil solution when using a mixed resin (cationic and anionic), compared to the anionic resin, indicating the high effectiveness of Ca-sink in the equilibrium displacement. Similarly, [13] observed an increase of 39% to 65% of P in solution when using mixed resin instead of anionic. Finally, one can think about P-sink behavior leading to the development of non-labile forms [10], thus disfavoring the plant, such as soil-sink promoted by Fe and Al oxyhydroxides. In contrast, it is possible to consider the development of a reversible form, as labile-P, by the use of an AR as a P-sink, which resembles the absorption by the plant. [7], in a multivariate analysis, in order to identify the factors that influence NP solubilization, found as the first main component soil texture, accounting for 41% of the variable. The second component, which accounts for 31% of the variable, concerns to soil acidity followed by the third and last component accounting for 22% of the variable, which refers to the Ca- and P-sinks. The objective of this work was to verify the effects of acidity and P- and Ca-sinks on the solubilization of the reactive NP of bayóvar.

2. Material and Methods

2.1. Phosphorus Source

The P source used at this work was a sample of the natural phosphate rock (NP) of bayóvar, a sedimentary origin phosphorite, with high isomorphic substitution of phosphate by carbonate and fluorine by hydroxyl, presenting high specific surface, purchased from Heringer Fertilizer Company (Brazil). The sample was passed through a 100 mesh (0.254 mm) sieve and oven dried at 70°C. The total P content of this material (17% of P) was determined by spectrophotometry in an acid digestion extract with 3:1 (V/V) ratio of nitric-perchloric acid.

2.2. Sinks

In order to evaluate the NP solubilization of 100 mg subsamples, three sinks were used, individually or in their combinations, suspended in aqueous solution: Anionic Resin (AR)-Amberlite-400 IRA (P-sink); Cationic Resin (CR)-IRA Amberlite-120 (Ca-sink); Mixed Resin (MR)-50% AR and 50% CR-(P- and Ca-sinks); Synthetic Goethite from Sigma-Aldrich® (Goe) (P-sink) and combinations Goe + AR (P-sinks) and Goe + CR (P- and Ca-sinks). Resins preparation followed the protocol used by [14]. The suspensions had the acidity of the aqueous solution medium adjusted at pH 4.5 or 6.0 with 0.1 mol·L^{-1} HCl or 0.1 mol·L^{-1} NaOH.

2.3. Experimental Units

The treatments were arranged in a completely randomized block design, according to the factorial $[(6 + 1) \times 2]$, with six sinks and one control containing only the

NP, each treatment under two acid levels (pH 4.5 and 6.0) and five replicates. Cassette dialysis membranes (Slide-A-Lyzzer G2 Dialysis Cassette), with 3 mL capacity, internally containing the NP sample and, externally, the drains, were placed in 200 mL capacity beakers, containing 150 mL of the solution, with pH adjusted at 4.5 or 6.0. These beakers, with the cassettes containing the NP, immersed in aqueous solution with the different sinks and pH adjusted values, were kept under agitation for 12 h daily, in a horizontal shaker at 120 rpm, for 30 days, at 25°C.

2.4. Phosphorus Fractions

After equilibration time, the aqueous suspensions with the drains were filtered on slow Whatman filter paper, determining the P-solution in the filtrate. The residue left on the filter paper was washed with 0.8 $mol \cdot L^{-1}$ NH_4Cl in 2.0 $mol \cdot L^{-1}$ HCl, used in the protocol for P extraction from resins and suitable for the extraction of available forms of P, according to [14], which was denominated in this work as labile-P. This same residue, together with the filter paper, was subjected to nitric-perchloric acid digestion with 3:1 (v/v) nitric and hydrochloric acid for determination, in the extract, what was denominated residual-P. The values sum (solution-P, labile-P and residual-P) were denominated total-P, determined in the extracts of the treatments applied in the beakers. The P of unsolved NP and still within the dialysis cassettes was not determined. In all cases, the extracted P was analyzed by spectrophotometry [15].

2.5. Statistical Analysis

Initially, the normality of the errors and the homogeneity of the variance were verified. After that, the results were submitted to analysis of variance and the pH effect was evaluated by the F test. The sink effect and their combinations on the solubilization of the NP were evaluated by the Tukey test at 5%.

3. Results and Discussion

The highest solubilization of bayóvar-total-P (Table 1 and Table 2) was caused by goethite (Goe), individually or by its combinations with the anionic (AR) and cationic (CR) resins, especially at pH 6.0, contrary to that observed in other works [4] [11] [12], which indicates similar importance between the two sinks. Thus, very weathered tropical soils, with high oxyhydroxide contents, should cause large solubilization of NP, although with lower labile-P contents, as observed in this work. This observation characterizes the effective NP solubilization under these conditions, without, however, favoring the plant, as emphasized by [16]. Under this condition, the intense solubilization caused by Goe causes rapid labile-P formation, followed by equally rapid non-labile-P formation, which is not easily accessible to plants [17]. Among resins, AR, as a P sink only, caused, at pH 4.5, solubilization (total-P) similar to that of CR, indicating that the P-sink is similar to the Ca-sink as a NP solubilizing agent, contrary to the

Table 1. Phosphorus fractions content in the beaker, out of the dialysis cassettes: solution-P, labile-P, residual-P and total-P (sum of the previous fractions), after 30 days of equilibrium with the natural bayóvar phosphate with P- and Ca-sinks, at two pH values.

Sink	Solution-P		Labile-P		Residual-P		Total-P	
pH	4.5	6.0	4.5	6.0	4.5	6.0	4.5	6.0
	--------------------mg·L^{-1}----------------------							
Anionic Resin (AR)	0.042 c	0.052 d	1.56 ab	0.674 c	16.2 b	12.1 c	17.8 cd	12.9 c
Cationic Resin (CR)	2.21 a	1.76 a	1.06 abc	0.244 d	9.35 b	8.75 d	12.6 c	10.7 c
Mixed Resin (AR + CR)	0.463 b	0.062 d	4.04 a	3.58 a	13.91 b	16.1 c	18.4 c	19.7 c
Goethite	0.676 ab	0.162 c	0.040 e	0.738 c	2014 a	3138 a	2014.7 a	3138.9 a
Goethite + AR	0.036 c	0.088 cd	1.85 a	1.10 b	471.1 a	543.9 ab	472.9 b	545.1 b
Goethite + CR	1.62 a	0.592 b	0.665 cd	1.33 b	464.9 a	454.2 b	467.2 b	456.1 b
Control	1.94 a	0.460 b	0.638 d	0.186 e	0.046 c	0.321 e	2.62 de	0.97 d
CV %	13.5	9.7	11.9	7.3	6.7	2.3	5.4	4.6

P-solution: P in suspension containing the sinks; labile-P: P after extraction with 0.8 mol·L^{-1} NH$_4$Cl in 2 mol·L^{-1} HCL; residual-P: P after acid digestion of the material retained in the filter paper; and total-P (sum of these fractions). Results in the same column, followed by the same letter, do not differ statistically by the Tukey test at 5%.

Table 2. Phosphorus fractions content, in percentage, in the beaker, out of the dialysis cassetes: solution-P, labile-P, residual-P and total-P (sum of the previous fractions), after 30 days of contact with the bayóvar natural phosphate with P- and Ca-sinks, at two pH values.

Sink	Solution-P		Labile-P		Residual-P		Total-P[1]	
pH	4.5	6.0	4.5	6.0	4.5	6.0	4.5	6.0
	-------------------%------------------------							
Anionic Resin (AR)	0.006 e	0.008 c	0.016 bc	0.007 cd	0.405 b	0.301 b c	0.427 cd	0.315 d
Cationic Resin (CR)	0.331 a	0.264 a	0.011 bcd	0.002 ef	0.234 c	0.219 c	0.575 c	0.485 c
Mixed resin (AQR + CR)	0.069 d	0.009 c	0.040 a	0.036 a	0.232 bc	0.401 b	0.938 c	0.447 c
Goethite	0.101 cd	0.024 c	0.000 e	0.007 c	50.4 a	78.4 a	50.5 a	78.5 a
Goethite + AR	0.005 e	0.013 c	0.018 b	0.011 b	11.8 a	9.1 a	11.8 b	9.2 b
Goethite + CR	0.244 ab	0.089 b	0.007 cde	0.013 de	11.6 a	11.3 a	11.9 b	11.5 b
Control	0.290 ab	0.069 b	0.006 cde	0.002 f	0.001 d	0.008 d	0.298 de	0.079 d
CV %	15.3	16.2	28.6	10.8	7.3	4.9	5.4	4.8

[1]The missing value to 100% is left in the NP sample, still inside the dialysis cassette. P-solution: P in the suspension with the sinks; P-labile: P after extraction with 0.8 mol·L^{-1} NH$_4$Cl in 2 mol·L^{-1} HCL; Residual-P: P after acid digestion of the material retained in the filter paper; and the total-P (sum of the previous fractions). Results in the same column, followed by the same letter, do not differ statistically by the Tukey test at 5%.

literature, which emphasizes the Ca-sink as the most important one, as already mentioned. The Goe + AR sink, with a double and exclusive P-sink function,

was as effective as Goe + CR, again emphasizing that the P-sink is as effective as the Ca-sink for the bayóvar solubilization. It is also interesting to note that AR and RC, similarly, strongly restricted the solubilization caused by Goe. As a hypothesis for this fact, is the AR, with its cationic profile, competing with Goe charges. A similar effect was observed for CR, as occurs with soil organic matter, blocking oxyhydroxide charges and decreasing P adsorption/retention [18].

The mixed resin (MR), with the double function of P- and Ca-sinks caused solubilization similar to AR alone. As already commented the P-sink, with apparently restricted effect as NP solubilizing agent has a behavior similar to that of the Ca-sink. MR was the sink with higher levels of labile-P, although with small NP solubilization, as already commented. It is interesting to note that CR alone tended to present the highest levels of solution-P. The probable solubilization caused by the Ca-sink did not remove P from solution as it did with the AR or with the MR, with an intermediate effect of the two resins.

The lower solution-P contents, as expected, were obtained with the AR or even with the combination of this with Goe (Goe + AR), with double effect of the sink for the solution-P, contrasting with the CR, that generates solubilization, but not effective removal (adsorption) of P-solution. On the other hand, Goe generates great solubilization as a P-sink and, at the same time, it is also an effective sink for the P-solution.

The very low labile-P content obtained with Goe, which solubilizes NP and rapidly transforms the solubilized P in non-labile-P, is increased when it joins AR (at pH 4.5). Thus, it can be imagined that the increase in OM content in soils, as in the case of the adoption of conservation management practices such as no-tillage, has the effectiveness of NP as a source of P for plants, increased by the effect of P-drain of OM, as suggested by the Goe + AR treatment, compared to Goe alone.

As for the pH effect, it is observed that the content of solution-P increased with increasing acidity (pH 4.5), with higher solubilization than that obtained at pH 6.0. For the P-labile the trend is the same, but with exceptions not explicable except for the difficulty in maintaining the pH values adjusted to those established as treatment, given the large buffer of the acidity under these conditions. For the total-P, the pH effect for the various sinks was even lower and not consistent with the expected values, due to the difficulties of adjusting its standards and the lower acidity effect in the tested range, compared to the P- and Ca-sinks, as observed in the Literature [11].

4. Conclusion

Goethite (Goe) entails, in general, outstanding solubilization of natural phosphate of bayóvar (NP), compared to the other sinks. However, this Goe solubilizing effect is limited by the presence of the two resins; yet, its greater solubilization leads to a large formation of non-labile-P. The predominant P-sink characteristic of the treatments is generally as effective as that of the Ca-sink, as a

factor of NP solubilization. The medium acidity effect on the solubilization, although it occurs, is not very effective, comparatively to the sink effects.

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