

**UNIVERSIDADE FEDERAL DE UBERLÂNDIA
INSTITUTO DE CIÊNCIAS AGRÁRIAS**

VINÍCIUS HENRIQUE ANDRADE COSTA

PERFORMANCE OF CITRATE-BASED EXTRACTORS FOR P-FERTILIZERS

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Trabalho de Conclusão de Curso apresentado à Faculdade de Agronomia do Instituto de Ciências Agrárias da Universidade Federal de Uberlândia como requisito parcial para obtenção do título de Engenheiro Agrônomo.

Orientador: Wedisson Oliveira Santos

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Banca Examinadora:

Fabiane Carvalho Ballotin
Membro da Banca

Aline de Almeida Vasconcelos
Membro da Banca

Prof. Dr. Wedisson Oliveira Santos
Orientador

ABSTRACT

The use of P extractors is significant to obtain a better efficiency in crop productivity, being important to understand which extractor is the most suitable to be used. Our objective was to evaluate the efficiency of different extractors on the recovery of available P forms in fertilizers with variable solubility. An experiment was carried out using a 2×4×18 factorial scheme, being two forms of extraction: heating or agitation; four extractors: Citric Acid pH 1.4 (AC), Acid Ammonium Citrate pH 3 (AAC pH 3), Acid Ammonium Citrate pH 5 (AAC pH 5) and Neutral Ammonium Citrate, pH 7 (NAC); and eighteen sources of P from different solubility. The experiment was carried out in a randomized block design, with three replications. To evaluate the extractive method capacity and relate them to yield of matter and P content absorbed by the crops, a test was carried out in a greenhouse, with sequential cultivation of corn (single hybrid BM 709 PRO 2) and soybean (BMX IPRO BONUS). The treatments were generated by the combination of an 8 × 2 factorial, with eight phosphate fertilizers with different solubilities (SSP, TSP, PAPER Araxá, PAPER Patos, Araxá PR, Salitre PR, Morocco PR and Daoui PR), and two doses of P (125 and 250 mg dm⁻³). The experimental design was carried out in randomized blocks, with four replications. Although there are exceptions, the combination of data demonstrates that agitation was the most effective extraction operating procedure for most P sources or extractors, and that AAC pH 3 and AAC pH 5 extractors presented similar ability to extract P, independent of the extraction procedure, except for Daoui PR shake form. In addition, the pH 3 acid ammonium citrate extractor showed a high correlation, and can be considered equal to the traditional extraction methods used to estimate the amount of P available both in natural sources and in more soluble sources, such as partially acidulated phosphate rocks and fully acidulated phosphate fertilizers.

Keywords: Fertilizers. Testing. Methods. Extractors. Plant response.

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1. INTRODUCTION

The crop's productivity is highly dependent of P availability in the soil, being responsible for 90 % of phosphate rocks extracted consumption (Pantano et al., 2016). In order to define the doses of fertilizers to be applied, and also to meet legislation, the use of phosphate fertilizers extractors is essential. These methods of extraction indicate P availability for plant nutrition, once it recovers nutrients amount that closely correlates with the amount absorbed and accumulated by plants (Bray, 1948, Binh and Zapata, 2002).

Phosphate rocks present great variation in physical, chemical and mineral properties, affecting their solubility and reactivity, as well as the characteristics of the phosphate fertilizers produced. Furthermore, to predict the recovery of phosphorus by the plant, there are recommendations of extractors for each type of phosphate. For example, for natural phosphate, citric acid is the reference extractor in Brazil.

In Brazil, neutral ammonium citrate (NAC) extractor is recommended for superphosphates, ammonium phosphates and partially acidulated P fertilizers (PAPR), while 2 % citric acid is used for phosphates rock (PRs) and thermophosphates (Brazil, 2016). In Europe and USA, 2 % formic acid and NAC are used for PRs, respectively (Binh and Zapata, 2002; Chien and Hammond, 1978). However, the existence of several methods for P sources extraction, has motivated studies in the sense of establishing a more universal one. Also, in the cases which fertilizers contains sources of P with different solubility, as NPK mixtures, and even in the PAPRs, is still not consolidated which are the more adequate chemical extractor to be used (Braithwaite et al., 1989; Chien, 1993; Santos et al., 2018).

The acid ammonium citrate pH 3 extractor (AAC pH 3) presented a superior efficiency in the P prediction availability of the phosphate fertilizers for plants than official methods (Chien and Hammond, 1978; Santos et al., 2018). For PR, the P soluble in AAC pH 3 presented the highest correlation between the amount of dissolved P and the crop response in the greenhouse and field experiments (Chien and Hammond, 1978). This extractor was also efficient to extract natural phosphates of different origins and partially or fully acidulated fertilizers, as demonstrated by Santos et al. (2018).

The composition of the extracting solution influences the amount of P solubilized. Mackay et al. (1984) studied the increase of CA concentration from 2, 5 and 15 %, which were able to extract 21, 44 and 59 %, respectively, of P in the PR. This occurs due to the influence of free carbonates decreasing with the extractants strength, consuming part of the chemical reagents, especially weak extractants such as NAC (Gholizadeh et al., 2009). The pH also influences the extractor capacity of the methods.

In this context, the objective of this study was to evaluate the efficiency of different extractors to recover P available forms in fertilizers with variable solubility.

2. MATERIALS AND METHODS

2.1 Characterization of P sources

In this research, we used P sources of different solubilities: two non-reactive PRs (Araxá PR and Patos PR), as well as their partially acidulated phosphate rocks (PAPRs) (PAPR Araxá and PAPR Patos); five reactive PRs (Bayóvar PR, Daoui PR, Morocco PR, Lagamar PR, Serra do Salitre PR); six full acidulated phosphate fertilizers (FAPF) (diammonium phosphate - DAP, monoammonium phosphate - MAP, single superphosphate - SSP, and triple superphosphate - TSP); and three pattern (P-monocalcium - P-monoCa, P-dicalcium - P-diCa, and P-tricalcium - P-triCa).

Prior to conducting the chemical analysis and assay, the samples were ground and passed through a 75 sieve. The total content of P in the fertilizers were measured as described by the Brazilian Ministry of Agriculture, Livestock, and Food Supply, Normative Instruction No. 28 (Brazil, 2007). The total P content on the samples is shown in Table 1.

2.2 Assay of extraction

The predictive ability of a method depends on the extractor solution composition, such as the buffering of this solution and the concentration of its reagents, and also on the use of heat or agitation. So, in order to evaluate the influence of these factors, an experiment using a 2×4×18 factorial scheme was carried: two forms of extraction (heating or agitation); four extractors: citric acid pH 1.4 (CA), acid ammonium citrate pH 3 (AAC

pH 3), acid ammonium citrate pH 5 (AAC pH 5) and neutral ammonium citrate, pH 7 (NAC); and eighteen P sources of different solubility (Table 1). The trial was performed in a randomized block design, with three replicates.

The extractor CA was prepared by dissolving 180 g of citric acid in 1 000 mL of distilled water. For the preparation of AAC pH 3 and AAC pH 5, 180 g of citric acid were first dissolving in 500 mL of distilled water. Then, the pH solution was adjusted for 3 or 5, using the concentrated ammonium hydroxide, and the volume was complete to 950 mL with distilled water. When necessary, the solutions pH were re-adjusted and brought to a volume of 1000 mL. Already the NAC extractor, it was prepared by dissolving 370 g of citric acid in 1.5 L of distilled water and adding 350 mL of the ammonium hydroxide. The pH of this solution was adjusted to 7.0 with ammonium concentrated hydroxide or 2% citric acid.

The heating extraction, were carried out in 125 mL Erlenmeyer flasks containing 0.5 g of fertilizer samples and 25 mL of the extractor according to the target treatments. The material was kept in heating, using hot plate, for 25 min. Then, the materials were transferred to 100 mL volumetric flasks and the volume was gauged. For the shaking extraction, 0.5 g of samples was placed in 50 mL centrifuge tube, containing 30 mL of extractor. The material was kept in agitation, in circular shaker over 60 min.

After extraction, the materials were filtered (pore size, 11 cm diameter) and P concentration was determined by molecular spectrophotometry, according to Braga and Defelipo (1974).

2.3 Greenhouse trial

To evaluate the extractive method capacity and relate them to the matter productivity and P content absorbed by the cultures, a trial was conducted under greenhouse conditions, with a sequential cultivation of corn (simple hybrid BM 709 PRO 2) and soybean (BMX BÔNUS IPRO).

A representative soil sample amount (Oxisol) was collected at layers of 0.0 - 0.3 m, and passed through a 4 mm sieve for the trial needs, and a 2 mm for chemical analyses. This soil presented low available P content (0.1 mg dm^{-3} , Mehlich 1 extractor), 75 % of clay (Claessen, 1997), a pH (H_2O) of 5.9 (at a ratio of 1:2.5 v/v), high exchangeable Ca^{2+} and Mg^{2+} , 2.92 and $0.62 \text{ mmolc dm}^{-3}$, respectively (KCl 1.0 mol L^{-1} extractor), medium

soil organic C (1.6 dag kg^{-1} , Walkley and Black, 1934), and remaining P of 8.5 mg L^{-1} , (Alvarez V. et al, 2000).

The treatments were generated by the combination of a factorial 8×2 , being eight phosphate fertilizers with different solubility (SSP, TSP, PAPR Araxá, PAPR Patos, Araxá PR, Salitre PR, Morocco PR and Daoui PR), and two P doses (125 e 250 mg dm^{-3}). The experimental units consisted of plastic pots with a capacity of 1.5 dm^3 of soil. The experimental design was performed in randomized blocks, with four replicates.

The lime requirement was calculated meeting a Ca:Mg molar ratio of 4:1, and was applied at the time of setting up the experiment, together with the P dose, in all soil volumes. Then, the five maize seeds were sown in each pot, at a depth of about 2 cm. The soil was wetted to 80 % for its field capacity, and kept in this condition during all periods of the assay. After four days of seedlings emerging, they were thinned to get the two most uniform plants per pot.

The fertilizations with other nutrients were carried out by applications in the form of nutrient solution, at 7, 14 and 21 d after planting. The total doses and sources of nutrients corresponded to 200 mg dm^{-3} of N $[(\text{NH}_2)_2\text{CO}]$, 150 mg dm^{-3} of K (KCl), 50 mg dm^{-3} of S $[(\text{NH}_4)_2\text{SO}_4]$, 1.0 mg dm^{-3} of B (H_3BO_3), 3.0 mg dm^{-3} of Zn ($\text{ZnSO}_4 \cdot \text{SO}_4$), 1.4 mg dm^{-3} of Cu ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), 3.12 mg dm^{-3} of Fe ($\text{FeC}_{13}\text{-EDTA}$), 3.6 mg dm^{-3} of Mn ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$), and 0.15 mg dm^{-3} of Mo $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}]$.

At 30 days of cultivation, the corn shoot was collected. Then, 10 days after the corn collection, five seeds of soybean were sown into undisturbed soil pots at a depth of 0.2 m. After seedlings emerged, two plants were grown in each pot and were inoculated with commercial Bradyrhizobium.

The water availability was controlled daily to maintain the soil near 80 % field capacity throughout the experimental period. At 40 days after planting, the aerial part of the soybean was collected.

The corn and soybean shoots were dried in a forced circulation oven at $65 \text{ }^\circ\text{C}$ until weight stabilization; and shoot dry matter was determined. Then, the plant material was digested in nitric-perchloric acid solution (3:1, v/v), and the concentration of P in the extract was determined by molecular absorption spectrophotometry according to Braga and Defelipo (1974) method.

The soil samples were taken at the end of the experiment, in all volumes of soil, were air-dried and passed through a 2.0 mm sieve for analysis of available P by Mehlich

3 (Mehlich, 1984). The extractor Mehlich 3 (CH_3COOH 200 mol L^{-1} + NH_4NO_3 250 mol L^{-1} + NH_4F 15 mol L^{-1} + HNO_3 13 mol L^{-1} + EDTA 1 mol L^{-1}) was added in soil (1:10, soil:solution), and the samples were shaken for 5 min, and left to rest for 16 h. After this time, the extract was filtered with slow filtering paper, then P content was determined by molecular absorption spectrophotometry according to Braga and Defelipo (1974).

2.4 Data analysis

Data were submitted to one-way analysis of variance, regression and correlations analyses were performed using the R environment (R Core Team, 2020).

3 RESULTS AND DISCUSSION

3.1 P content in the sources

It is possible to observe that the content of P is not directly related to the solubility of the source, but rather the representation of the total in it. Solubility would affect the rate of P release, but the total content is variable among sources.

Table 1. Total P content in the sources.

Fertilizer	P	Fertilizer	P	Fertilizer	P
	---wt %---		---wt %---		--wt %--
DAP	16.67	P-monoCa	22.52	Morocco PR	12.74
MAP1	20.62	P-diCa	21.36	Lagamar PR	10.68
MAP2	22.64	P-triCa	15.63	Patos PR	11.82
SSP 1	9.04	Araxá PR	12.70	Salitre PR	11.34
SSP 2	9.27	Bayovar PR	12.12	PAPR Araxá	10.77
TSP	20.03	Daoui PR	12.00	PAPR Patos	10.21

DAP: diammonium phosphate, MAP: monoammonium phosphate, SSP: single superphosphate; TSP: triple superphosphate, P-monoCa: monoammonium phosphate, P-diCa: tricalcium phosphate, P-triCa: tricalcium phosphate. PR: phosphate rock, PAPR: partially acidulated phosphate rock. Total P in the fertilizers were measured as described by the Brazilian Ministry of Agriculture, Livestock, and Food Supply, Normative Instruction No. 28 (Brasil, 2007).

3.2 Agitation or Heating – Induced Changes in Extractable P

The proportions of total P extracted in citric acid (CA), acid ammonium citrate pH 3 (AAC pH 3), acid ammonium citrate pH 5 (AAC pH 5) or neutral ammonium citrate (NAC), using agitation or heating as extraction procedure are shown in Figure 1.

Extractable P levels were affected by the extraction procedures, as we can see by contrasting the orange and blue columns in Figure 1. In fact, for P sources whose effects of extraction methods were different, such as P-monoCa, P-triCa, MAP1, SSP1, SSP2, TSP, PAPR Araxá, Morocco PR, Daoui PR, Bayóvar PR and Lagamar PR, the agitation promoted greater extraction for most of extractors. On the other hand, for SSP 2 the extractable P levels by heating were higher in all extractors. In addition, for SSP1 source with the AAC pH 3 extractor, and the TSP source with the CA extractor, heating was more effective.

Contrasting effects of operational extraction procedures in terms of extractors were also found (Figure 1). Extractable P levels for the CA were equivalent or higher when agitation was the procedure, except only for TSP. For AAC pH 3 and AAC pH 5 extractors, the heating was more effective only for the SSP sources. When NAC was the extractor, for four P sources (22% of the sources) of different origins (Daoui PR, PAPR Araxá, SSP2 and P-triCa) the heating was more effective.

These initial data support that agitation was the most effective operational procedure both for most sources and for P extractors.

3.3 Extractable P Levels is Contrasting among Extractors

As expected, there were contrasting differences on extractable P levels among extractors and P sources (Figure 1). For the most soluble P sources (P-monoCa, P-diCa, P-triCa, DAP, MAP, SSP and TSP) when the extraction was by agitation, only for P-triCa the NAC extractor recovered less P. However, for heating, the ACC pH 3 extractor was less effective when the P sources were P-monoCa or P-triCa.

For the less soluble P sources (PAPR Araxá; PAPR Patos; Morocco PR; Daoui PR; Bayovar PR; Lagamar PR; Araxá PR; Patos PR and Salitre PR) differences among extractors were also found. Regardless of operational procedure CA extractor highlighted from the others for PAPR Patos, and the natural phosphates. In fact, for the PRs, the CA

extractor accessed the largest amount of the P (about 51 %), which was followed by AAC pH 3 (29.6 %), and this difference was significant for all sources, except Salitre PR considering agitation the best form of extraction. And for the heating, only Bayovar, Daoui, Morocco and Patos PRs presented differences between the extractors. The extractors AAC pH 3 and AAC pH 5 presented the similar capacity on P extraction, regardless of extraction procedure, except for Daoui PR agitation form.

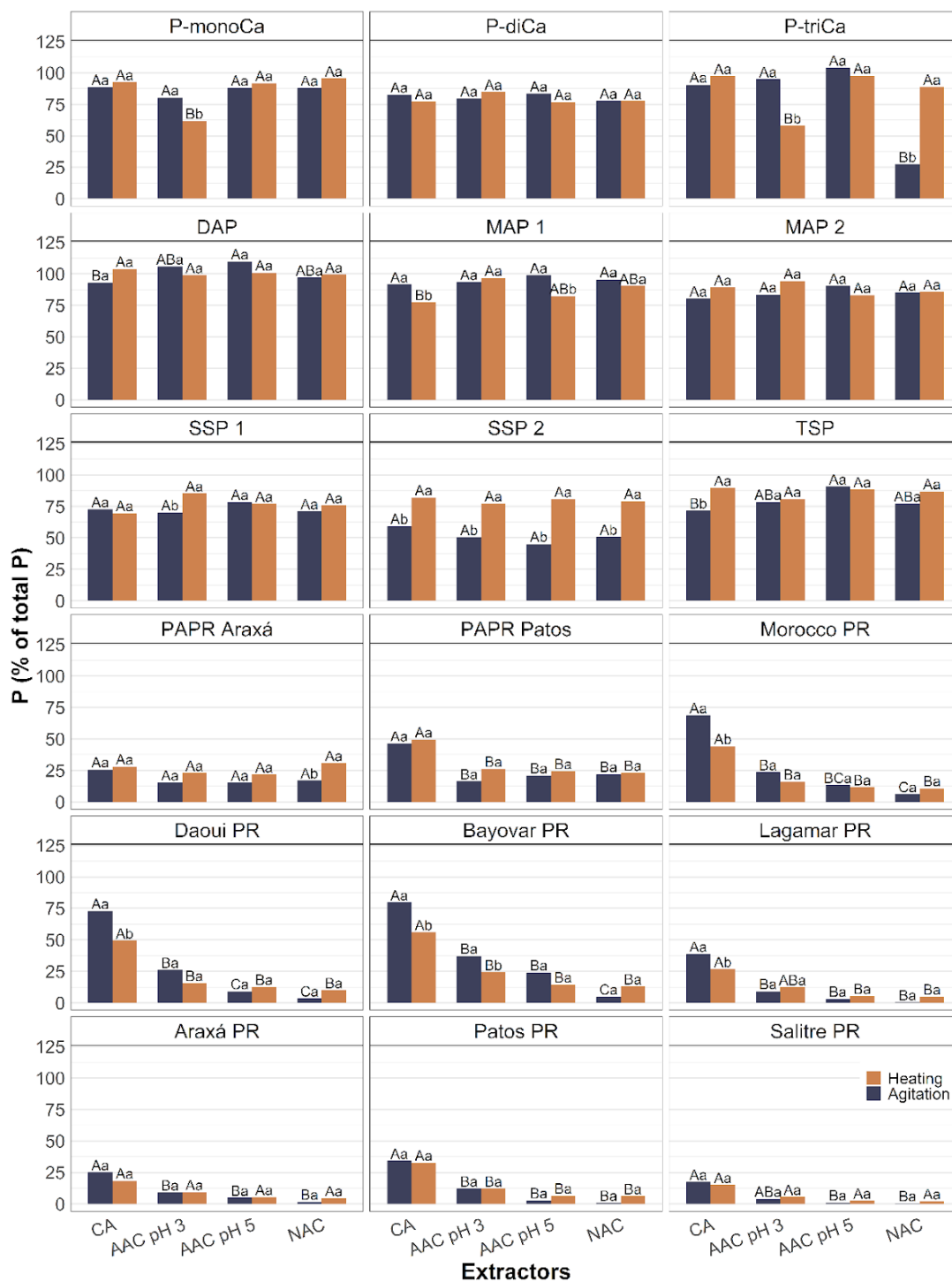


Figure 1. Extractable P level in citric acid (CA), acid ammonium citrate pH 3 (AAC pH 3), acid ammonium citrate pH 5 (AAC pH 5) and neutral ammonium citrate (NAC), using agitation or heating as form of the extraction, for phosphorus sources of varying solubility. Different letters on each bar indicate significant differences ($p \leq 0.05$), according to the Tukey test. Upper case letters compare data between extractors, for each fertilizer within forms of the extraction; and the lower letters, compare differences between forms of the extraction (agitation or heating), inside fertilizer and extractor.

3.4 Extractor's performance on plant response

In this assay, we evaluate the efficiency of the extractors in terms of plant response. We observed that with increasing P doses, we observed a linear positive for the dry matter and P uptake, for the corn, soybean and total; for both method for extraction: agitation (Table 2) and heating (Table 3); with a high statistical significance ($p \leq 0.01$). In the general, the P uptake promoted the best adjustments of the regression model than dry matter, indicating the importance this variable as indicator for the methods efficiency.

The P uptake for corn and total value, showed that P_AAC pH 3 presented higher the R² values, therefore, more predictive than P_AAC pH 5, P_NAC and P_CA, when used the heating as extraction method. While, P_CA present best adjustments in P uptake of the soybean, in the process of agitation and heating.

The inclination of the lines were very similar for the extractors used, being the same for dry matter of corn using the heating method, and P uptake for soybean, agitation; and corn and soybean, heating.

Table 2. Dry matter production and P uptake by corn, soybean and total as a function of P doses extracted by citric acid (P_CA), acid ammonium citrate pH 3 (P_AAC pH 3), acid ammonium citrate pH 5 (P_AAC pH 5) and neutral ammonium citrate (P_NAC), using agitation as extraction method.

C O R N	Dry matter (g pot ⁻¹)	P_CA	$\hat{y} = -0.11 + 0.03^{***}x$	R ² = 0.41
		P_AAC pH 3	$\hat{y} = 0.21 + 0.05^{***}x$	R ² = 0.8
		P_AAC pH 5	$\hat{y} = 0.64 + 0.04^{***}x$	R ² = 0.84
		P_NAC	$\hat{y} = 0.71 + 0.04^{***}x$	R ² = 0.87
	P uptake (mg pot ⁻¹)	P_CA	$\hat{y} = -0.32 + 0.02^{***}x$	R ² = 0.42
		P_AAC pH 3	$\hat{y} = -0.01 + 0.03^{***}x$	R ² = 0.77
		P_AAC pH 5	$\hat{y} = 0.32 + 0.03^{***}x$	R ² = 0.8
		P_NAC	$\hat{y} = 0.37 + 0.03^{***}x$	R ² = 0.83

S O Y B E A N	Dry matter (g pot ⁻¹)	P_CA	$\hat{y} = 3.60 + 0.03^{***}x$	R ² = 0.38
		P_AAC pH 3	$\hat{y} = 5.00 + 0.02^{***}x$	R ² = 0.15
		P_AAC pH 5	$\hat{y} = 5.28 + 0.01^{***}x$	R ² = 0.11
		P_NAC	$\hat{y} = 5.31 + 0.01^{***}x$	R ² = 0.11
	P uptake (mg pot ⁻¹)	P_CA	$\hat{y} = 0.68 + 0.03^{***}x$	R ² = 0.67
		P_AAC pH 3	$\hat{y} = 1.73 + 0.03^{***}x$	R ² = 0.65
		P_AAC pH 5	$\hat{y} = 2.16 + 0.03^{***}x$	R ² = 0.58
		P_NAC	$\hat{y} = 2.22 + 0.03^{***}x$	R ² = 0.57
T O T A L	Dry matter (g pot ⁻¹)	P_CA	$\hat{y} = 3.49 + 0.06^{***}x$	R ² = 0.62
		P_AAC pH 3	$\hat{y} = 5.21 + 0.06^{***}x$	R ² = 0.68
		P_AAC pH 5	$\hat{y} = 5.92 + 0.05^{***}x$	R ² = 0.65
		P_NAC	$\hat{y} = 6.02 + 0.06^{***}x$	R ² = 0.66
	P uptake (mg pot ⁻¹)	P_CA	$\hat{y} = 0.36 + 0.06^{***}x$	R ² = 0.6
		P_AAC pH 3	$\hat{y} = 1.74 + 0.07^{***}x$	R ² = 0.8
		P_AAC pH 5	$\hat{y} = 2.48 + 0.05^{***}x$	R ² = 0.77
		P_NAC	$\hat{y} = 2.60 + 0.06^{***}x$	R ² = 0.78

P_CA: Extractable P contents in 2% citric acid; P_AAC pH 3: Extractable P contents in acid ammonium citrate pH 3; P_AAC pH 5: Extractable P contents in acid ammonium citrate pH 5; P_NAC: Extractable P contents in neutral ammonium citrate.

Table 3. Dry matter production and P uptake by corn, soybean and total as a function of P doses extracted by citric acid (P_CA), acid ammonium citrate pH 3 (P_AAC pH 3), acid ammonium citrate pH 5 (P_AAC pH 5) and neutral ammonium citrate (P_NAC), using heating as extraction method.

C O R N	Dry matter (g pot ⁻¹)	P_CA	$\hat{y} = -0.58 + 0.04^{***}x$	R ² = 0.66
		P_AAC pH 3	$\hat{y} = 0.16 + 0.04^{***}x$	R ² = 0.91
		P_AAC pH 5	$\hat{y} = 0.46 + 0.04^{***}x$	R ² = 0.86
		P_NAC	$\hat{y} = 0.44 + 0.04^{***}x$	R ² = 0.86
	P uptake (mg pot ⁻¹)	P_CA	$\hat{y} = -0.64 + 0.03^{***}x$	R ² = 0.87
		P_AAC pH 3	$\hat{y} = -0.05 + 0.03^{***}x$	R ² = 0.82
		P_AAC pH 5	$\hat{y} = 0.18 + 0.03^{***}x$	R ² = 0.82
		P_NAC	$\hat{y} = 0.16 + 0.03^{***}x$	R ² = 0.82
S O Y B E A N	Dry matter (g pot ⁻¹)	P_CA	$\hat{y} = 3.93 + 0.02^{***}x$	R ² = 0.33
		P_AAC pH 3	$\hat{y} = 5.10 + 0.01^{***}x$	R ² = 0.13
		P_AAC pH 5	$\hat{y} = 5.18 + 0.01^{***}x$	R ² = 0.13
		P_NAC	$\hat{y} = 5.15 + 0.01^{***}x$	R ² = 0.14
	P uptake (mg pot ⁻¹)	P_CA	$\hat{y} = 0.68 + 0.03^{***}x$	R ² = 0.80
		P_AAC pH 3	$\hat{y} = 1.83 + 0.03^{***}x$	R ² = 0.63
		P_AAC pH 5	$\hat{y} = 1.99 + 0.03^{***}x$	R ² = 0.62
		P_NAC	$\hat{y} = 1.95 + 0.03^{***}x$	R ² = 0.65

T O T A L	Dry matter (g pot ⁻¹)	P_CA	$\hat{y} = 3.35 + 0.06^{***}x$	R ² = 0.77
		P_AAC pH 3	$\hat{y} = 5.26 + 0.06^{***}x$	R ² = 0.71
		P_AAC pH 5	$\hat{y} = 5.63 + 0.05^{***}x$	R ² = 0.68
		P_NAC	$\hat{y} = 5.59 + 0.06^{***}x$	R ² = 0.69
	P uptake (mg pot ⁻¹)	P_CA	$\hat{y} = 0.05 + 0.07^{***}x$	R ² = 0.81
		P_AAC pH 3	$\hat{y} = 1.78 + 0.06^{***}x$	R ² = 0.84
		P_AAC pH 5	$\hat{y} = 2.17 + 0.06^{***}x$	R ² = 0.8
		P_NAC	$\hat{y} = 2.12 + 0.06^{***}x$	R ² = 0.82

P_CA: Extractable P contents in 2% citric acid; P_AAC pH 3: Extractable P contents in acid ammonium citrate pH 3; P_AAC pH 5: Extractable P contents in acid ammonium citrate pH 5; P_NAC: Extractable P contents in neutral ammonium citrate.

The correlation between extractable P content for the different extractors and P uptake by corn or soybean crops under heating or agitation is shown in table 2. With the exception of CA in the form of agitation, for corn, all other data gave significant correlation values. But the highest correlations stand out, such as AAC pH3 through heating in corn, although the significance was the same for AAC Ph 5 AND NAC, under the same conditions.

Table 4. Coefficients of linear correlation between extractable P level (% of total P) for different extractors under heating or agitation and the P uptake by corn or soybean crops

Extractor	Agitation		Heating	
	Corn	Soybean	Corn	Soybean
P_CA	0.54 ^{ns}	0.75*	0.79*	0.86**
P_AAC pH 3	0.88**	0.76*	0.96***	0.74*
P_AAC pH 5	0.92**	0.73*	0.93***	0.75*
P_NAC	0.94**	0.73*	0.93***	0.77*

P_CA: Extractable P contents in 2% citric acid; P_AAC pH 3: Extractable P contents in acid ammonium citrate pH 3; P_AAC pH 5: Extractable P contents in acid ammonium citrate pH 5; P_NAC: Extractable P contents in neutral ammonium citrate. ns, *, **, ***, non-significant, and significant at 0,05; 0,01, and 0,001% by t-test, respectively. It was used as P sources (125 and 250 mg/dm³ P) DAP: diammonium phosphate, MAP: monoammonium phosphate, SSP: single superphosphate; TSP: triple superphosphate, P-monoCa: monoammonium phosphate, P-diCa: tricalcium phosphate, P-triCa: tricalcium phosphate. PR: phosphate rock, PAPR: partially acidulated phosphate rock.

The solubility test using chemical extractors is important to determine, simply and quickly, the reactivity of PRs (Gholizadeh et al., 2009). Furthermore, the analysis allows us to choose the best extractors that present correlation with the nutrient amount absorbed and accumulated by the plant, being therefore, indicative of P content available in the fertilizers.

It was observed that P amount solubilized from reactive sources was higher than the non-reactive. The difference in the dissolution rate occurred due to different crystalline structure (Gholizadeh et al., 2009). The igneous PRs presented a crystalline structure, coarser, and nonporous, what promoted a low degree of surface reactions, unlike sedimentary PRs (Chien, 1993). On the other hand, the partially acidulated phosphate rocks, presented higher solubility than in nature rock, what could be explained by the conversion of apatite minerals to more soluble P forms, possibly amorphous species of iron and Ca-phosphate, monocalcium phosphate and dicalcium phosphate, was reported by Santos et al. (2016).

The extractors with acid character usually recover more P than the neutral character, because of their high acidity (pH ~2.0) (Binh and Zapata, 2002). This factor was clearer for PRs and PAPRs, using extractors CA and AAC pH3 when compared with NAC.

In this work, we demonstrated that acid ammonium citrate pH3 extractor presented high correlation, and could be considered equal to the traditional methods of extraction used to estimate amount of P available both in natural sources and in more soluble sources, as partially acidulated phosphate rocks and fully acidulated phosphate fertilizers. These results are important because there are no official methods to determine P availability in fertilizers that contain P sources of different solubility and reactivities. Santos et al. (2018) performed greenhouse trial and showed that the extractor AAC was the best to predict agronomic effectiveness of P fertilizers of varying solubility. Chien and Hammond (1978) related that ammonium citrate pH 3 presented the highest correlation between the amounts of P they dissolve and the crop response in the greenhouse and field experiments.

4 CONCLUSION

Contrasting the biological response of corn and soybean in terms of dry matter production and P uptake as a function on P doses extracted the acid ammonium citrate pH3 extractor presented a high correlation, and could be considered equal to the traditional methods of extraction used to estimate the amount of P available both in natural sources and in more soluble sources, as partially acidulated phosphate rocks and fully acidulated phosphate fertilizers.

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