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Cellulose acetate film containing layered double hydroxide: a new method for determination of soil phosphorus availability

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ABSTRACT: Soil nutrient availability and interpretations of nutrient contents are based on the results obtained from specific extraction methods used in routine testing laboratories. The development of new extraction methods and new extractants with better accuracy is particularly important to determine the correct fertilizer rates to be applied. For this purpose, this study aims to synthesize, characterize and evaluate the predictive capacity of cellulose acetate film containing calcinated layered double hydroxide (CAF-LDH-c), as a new extractant and a new method of P extraction in soils. Different analyses techniques were used to characterize the CAF-LDH-c sample, including X-ray diffraction, attenuated total reflectance Fourier transform infrared spectroscopy, and scanning electronic microscopy. Soils were collected from twelve areas with different management and initial availability of P. The soils were subjected to six rates of P and were cultivated with plants. The predictive capacity of CAF-LDH-c, as a new extractant of P in different soils, was evaluated and compared to Mehlich-1 (M-1), Mehlich-3 (M-3), and Mixed Exchange Resin (MER) extractants. Chemical analyses performed on CAF-LDH-c showed that LDH in powder form was incorporated into the cellulose acetate film. There was a linear relation between P uptake by plants and extractable soil P in the soil by CAF-LDH-c, M-1, M-3, and MER extractants. The significant correlations between extracted P in the soil and P uptake by plants for CAF-LDH-c showed the efficacy of the new extractor and the newly proposed method for different types of soils. The results from the present study confirm the possibility of using CAF-LDH-c extractant as a new methodology to evaluate the availability of P in the soil for plant cultivation.

Keywords: layered double hydroxide, available phosphorus, bioassay, cellulose acetate polymer.

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INTRODUCTION

The demand for Phosphorus (P) by soils and plants to support current agricultural production requires high phosphate fertilizer applications. The massive consumption of phosphate fertilizers in agriculture is responsible for the reduction of good-quality phosphate rock deposits around the world, increasing the cost of fertilizer extraction and production (Pantano et al., 2016). Thus, effective soil fertility assessment, which is correlated with a good prediction of the availability of P in the soil, can lead to the rational recommendation for the use of phosphate fertilizers in agriculture with the application of the most effective rates of P.

For P, numerous extraction methods are used to evaluate the availability of this nutrient, whose efficiency is influenced by the soil properties and management (Beegle, 2005; Novais et al., 2007; Freitas et al., 2013), and usually, the quantity of P extracted from the soils does not show a good correlation with plant uptake (Silva and van Raij, 1999; Oliveira Júnior et al., 2011; Freitas et al., 2013; Simonete et al., 2015).

Mehlich-1 (M-1) extractant is the most extensively used in Brazil, and numerous studies have validated it as an appropriate extractor of available P in soils (Farias et al., 2009; Simões Neto et al., 2009; Steiner et al., 2012; Vieira et al., 2015; Valadares et al., 2017; Reis et al., 2020). It is noteworthy that the acid dissolution of M-1 extractant (solution pH = 1.2) can lead to the extraction of P-Ca forms, overestimating the quantity of P extracted in the soil (Alcântara et al., 2008; Freitas et al., 2013; Camêlo et al., 2015; Reis et al., 2020).

The use of Anion Exchange Resin (AER), Mixed Exchange Resin (MER), or Mehlich-3 (M-3) extractants in routine testing laboratories can be an alternative to the use of M-1. The procedure with AER and MER presents some operational difficulties, making them little used in soil chemical analysis laboratories (Mumbach et al., 2018). Nevertheless, most laboratories prefer to use MER, probably because of the possibility of extraction of cations (e.g., Ca) and P simultaneously, in the same routine analysis of soil fertility. Thus, MER can be sensitive to the P-Ca forms, making it possible to overestimate the P availability for plants, similarly for M-1 extractants (Freitas et al., 2013). Regarding M-3, data obtained through research, such as correlation and calibration studies, are still incipient (Mumbach et al., 2018), making it difficult to validate the M-3 as a soil-available P extractant (Valadares et al., 2017).

Due to the problems presented by the conventional extractants of P, further research is needed with a focus on developing new methods that present more efficiency and better predictive detection of P in different soils submitted to different managements. In this sense, nanostructured materials, such as Layered Double Hydroxides (LDHs), can offer an alternative as a new P extractant. The LDHs are inorganic solid materials characterized by a layered structure similar to brucite mineral [$Mg(OH)_2$]. In the LDH structure, the partial substitution of trivalent by divalent cations results in layers positively charged, which is compensated by the presence of the anions in the interlamellar spaces. The general formula of these materials is $[M^{2+}_{(1-x)}\ M^{3+}_{x}\ (OH)_2]\ (A^{n-})_{x/n}zH_2O$, in which M^{2+} and M^{3+} are the divalent and trivalent metal ions, respectively, A^{n-} are the intercalated anion, and z is the number of the water molecules. Especially in agriculture uses, the LDHs are intercalated with anionic molecules such as pesticides, herbicides, and plant growth hormones, as well as nutrients such as borate, nitrate, and phosphate, which serve as slow-release matrices (Ghormade et al., 2011; Berber et al., 2014; Silva et al., 2014; Bernardo et al., 2018; Castro et al., 2018a,b,c; Castro et al., 2020).

The LDHs are nanomaterials synthesized in powder form, and these materials could be difficult to separate from the soil samples during routine laboratory analysis. In this way, the need to work with a very fine texture material stimulated the development of an organic-inorganic hybrid mixture between calcined LDH (CAF-LDH-c) and cellulose acetate, in a film shape (Castro et al., 2018a,c). The authors used the CAF-LDH-c as a new absorbent of P in solution, and also as a new method of assessing soil P availability in clayey soil exposed to increasing rates of P (Castro et al., 2018a, c). In the study using the CAF-LDH-c as an extractant of available P in clayey soil, the authors found a high Pearson's correlation coefficient between CAF-LDH-c and M-1, M-3, AER, and MER extractants, and suggested CAF-LDH-c as a new routine method for determination of P availability in the soil.

In the initial study described by Castro et al. (2018c), only a simple correlation study has been made between the available levels of P in the soil from M-1, M-3, AER, MER, and CAF-LDH-c extractants, without a correlation between P plant uptake and P in the soil. The use of the organic-inorganic hybrid material composed of LDH and cellulose acetate is an eco-friendly alternative to replace commercial extractants usually used, since LDHs can be produced by green chemical synthesis, and cellulose acetate is a biodegradable polymer.

Further research is needed to evaluate the predictive ability of this kind of material as a new P extractant in different types of soils subjected to increasing rates of P, and also with plant cultivation. For this purpose, this study aims to synthesize, characterize and evaluate the predictive capacity of the hybrid organic-inorganic films derived from the mixture of cellulose acetate and calcinate LDH as a new extractant and a new method of P extraction, in soils with different management history, with the application of increasing rates of P to the cultivation of plants.

MATERIALS AND METHODS

Synthesis of cellulose acetate film containing calcinated layered double hydroxide (CAF-LDH-c)

Magnesium (Mg) and aluminum (Al) LDH intercalated with carbonate anions (CO_3^{2-}) were synthesized by the coprecipitation method using a constant pH value. In this method, 500 mL of an aqueous solution containing 0.2137 mol L^{-1} of $Mg(NO_3)_2 \cdot 6H_2O$ and 0.0709 mol L^{-1} of $Al(NO_3)_3 \cdot 9H_2O$ was added drop by drop under into a 2500 mL solution of 0.056 mol L^{-1} of Na_2CO_3. During the synthesis, the suspension formed was kept under vigorous stirring, and the pH value was maintained at 10.0 ± 0.5 using a 2.0 mol L^{-1} of NaOH solution. After the synthesis, the solid material was washed with H_2O and dried at 25 °C, under a vacuum in a glass desiccator. All the H_2O used in the synthesis reactions and the washed process was deionized (Milli-Q® system).

After the synthesis, the LDH was calcined in a tubular furnace for 4 h at 550 °C, under an O_2 atmosphere with a constant flow of 50 mL min^{-1}, and a heating rate of 10 °C min^{-1}. The calcinated LDH was stored under reduced pressure in a glass desiccator containing silica gel. The calcinated LDH is identified as LDH-c.

Cellulose acetate film containing LDH-c was synthesized by the casting method (Soares, 1998). In this method, 3.00 g of cellulose acetate (CA) was dissolved in 30 mL of acetone and left to stand for 24 h at room temperature (25 °C). Then, 1.50 g of the LDH-c was added to the CA solution, and the mixture was stirred for 60 min with a magnetic stirrer at room temperature. The formed suspension was spread on a flat glass surface and allowed to stand for one hour for acetone evaporation. The film was named CAF-LDH-c. CAF-LDH-c was stored under reduced pressure in a glass desiccator containing silica gel.

Characterization of materials

All synthesized materials (LDH, LDH-c, cellulose acetate film, and CAF-LDH-c) were characterized by X-ray diffraction (XRD), attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR), and scanning electron microscopy (SEM). The XRD analyses were performed using Shimadzu XRD-6000 equipment, with a graphite crystal monochromator to select Cu-Kα_1 radiation with λ = 1.5406 Å, and a step rate from 0.02° s^{-1}. The 2θ scan range was 4° and 70°. The ATR-FTIR spectra were obtained using a Jasco spectrometer, model FT/IR-4100. The wavelength range used was 4000 to 400 cm^{-1}, at 4 cm^{-1} resolution, and 256 scannings. To perform SEM analyses, the materials were deposited over a conductive double-sided adhesive tape and recovered with a thin gold film using a Quorum Q150RS. The JEOL JSM-6010LA analytical scanning electron microscope was used to analyze the morphologies of the materials. Energy dispersive spectroscopy (EDS) was also performed for the micro compositional analysis of materials.

Soils and greenhouse experiment for soil test correlation

Extractable P by CAF-LDH-c, Mehlich-1, Mehlich-3, and resin was analyzed in the soils by Reis (2016) and Reis et al. (2020). Briefly, soil samples with different textures, organic matter (OM), P availability, phosphate buffer capacity (PBC), and from areas with different soil management in Minas Gerais and Espírito Santo states, Brazil, were collected from the layer of 0.00-0.20 m. Soil samples were homogenized, sieved (2 mm), and air-dried. Soil chemical and physical properties are presented in table 1.

Table 1. Chemical and physical properties of the soils used in the study

Soil Brazilian Classification System	Soil	Soil Taxonomy	Soil management	$pH(H_2O)^{(1)}$	P	Rem-P	OM	T	V	Clay
					mg dm^{-3}	mg L^{-1}	g kg^{-1}	$cmol_c$ dm^{-3}	%	
LVd1	*Latossolo Vermelho*	Oxisol	Area without cultivation	5.15	1.0	4.3	71.1	8.84	13.0	66.6
LVd2	*Latossolo Vermelho*	Oxisol	Area with cultivation	6.92	39.4	8.3	43.5	9.94	69.6	52.3
LVd3	*Latossolo Vermelho*	Oxisol	Area with cultivation	6.78	50.9	8.9	48.7	9.96	81.2	55.7
CXbd	*Cambissolo Háplico*	Inceptisol	Area without cultivation	5.24	0.4	28.8	10.5	3.02	4.9	24.1
LVdf	*Latossolo Vermelho*	Oxisol	Area without cultivation	5.50	3.8	11.4	44.8	9.98	22.9	49.0
PVd	*Argissolo Vermelho*	Ultisol	Area without cultivation	5.14	0.5	10.8	17.7	4.17	8.0	62.0
LAd	*Latossolo Amarelo*	Oxisol	Area without cultivation	5.70	7.9	44.1	15.2	6.38	73.0	22.0
LVAd1	*Latossolo Vermelho-Amarelo*	Oxisol	Area without cultivation	6.16	0.7	12.6	15.2	4.37	39.4	55.0
LVAd2	*Latossolo Vermelho-Amarelo*	Oxisol	Area without cultivation	5.54	0.5	21.9	2.5	0.98	12.1	16.0
PVAd1	*Argissolo Vermelho-Amarelo*	Ultisol	Area with cultivation	5.91	96.5	25.0	22.4	9.38	60.7	49.1
PVAd2	*Argissolo Vermelho-Amarelo*	Ultisol	Area with cultivation	6.02	21.4	26.1	23.7	9.51	65.1	45.5
PVAd3	*Argissolo Vermelho-Amarelo*	Ultisol	Area with cultivation	5.42	11.5	27.1	26.3	8.7	39.3	40.6

(1) soil:water at a ratio of 1:2.5; P: Mehlich-1 extractant; Rem-P: remaining phosphorus; OM: organic matter; T: cation exchange capacity at pH = 7; V: base saturation. Data from Reis (2016) and Reis et al. (2020).

A factorial 12 × 6 was established with twelve soil samples (Table 1) and six rates of total P. A complete randomized block design with four replicates was used in this experiment. For this, pots with a soil capacity of 2.0 dm^{-3} were used. Lime was applied to the soil to achieve a base saturation of 50 %. Then, the soil was wetted to 80 % of field capacity (FC) and incubated for 18 days.

The soils were distributed into groups, according to remaining-P (Rem-P), correlated with the PBC, and the rates of P were calculated for each group according to Alvarez V et al. (2000). The application was made according to the levels 0.0, 0.5, 1.0, 2.0, 3.0, and 5.0 of the P calculated rate. The rate calculated for soils LVd1, LVd2, and LVd3 was 37.4 mg dm^{-3}, and 0.0, 18.7, 37.4, 74.8, 112.2, and 187.0 mg dm^{-3} of P were applied. The PVd, LVdf, and LVAd1 soils received 0.0, 16.0, 32.0, 64.0, 96.0, and 160.0 mg dm^{-3} of P, according to the rate calculated of 32.0 mg dm^{-3}. The soil LVAd2, PVAd1, PVAd2, PVAd3, and CXbd presented the rate calculated of 27.4 mg dm^{-3}, and received 0.0, 13.7, 27.4, 54.8, 82.2, and 137.0 mg dm^{-3} of P. For LAd soil, the rate calculated was 20.0 mg dm^{-3} and 0.0, 10.0, 20.0, 40.0, 60.0, and 100 mg dm^{-3} of P were applied.

A mixture of commercial Triple Superphosphate and Bayóvar Reactive Phosphate sources were used, whose proportions are 80 and 20 % of the mixture, respectively. The design of the P location fertilizer in the pots is presented in Reis (2016) and Reis et al. (2020).

Immediately afterward, seven seeds of corn (*Zea mays* L.) were sown per pot. After four and six days, seedlings were thinned to the four most uniform ones in each pot. Further liquid basal nutrients were applied according to Alvarez V et al. (1999). After 45 days of cultivation, corn plants were harvested by cutting the stems at the soil surface. Plant biomass was dried at 65 °C for 72 h, weighed to obtain dry matter (DM) and ground. Plant tissue P content was determined by nitric-perchloric digestion (3:1) and nutrient content was performed according to Braga and Defelipo (1974).

Soil samples were collected from the upper middle of the pot to obtain a composite sample between the region that received P in a localized form and the region that did not receive P. The soil sampling after corn cultivation was previously described by Reis (2016) and Reis et al. (2020). The samples were dried and sieved (2 mm). The determination of soil P availability was performed by M-1 (Mehlich, 1953), M-3 (Mehlich, 1984), and MER (van Raij et al., 2001) extractants. Additionally, the available P in the soil was extracted by CAF-LDH-c.

Extractable P by CAF-LDH-c

In Erlenmeyer flasks of 125 mL capacity were added 1.0 g of soil samples, 1.0 g of CAF-LDH-c, and 25 mL of H_2O. The films used were all kept at the same thickness of 135 ± 10 µm. The Erlenmeyer flasks were stirred for 16 h in a mechanical reciprocal shaker at 180 rpm in a closed environment. After stirring, the CAF-LDH-c were separated from the soils using a tweezer and washed with deionized H_2O to remove soil sediments that adhered to the films. Then, the CAF-LDH-c was transferred to Erlenmeyer flasks of 125 mL, and the extractant solution of ammonium chloride in hydrochloric acid (NH_4Cl 0.8 mol L^{-1} in HCl 0.2 mol L^{-1}) of 20 mL was added. This extractant solution was prepared according to the method proposed by van Raij et al. (2001). The Erlenmeyer flasks were stirred in a closed environment for one hour in a reciprocal shaker at 180 rpm. The extracts for the P determination were analyzed according to the method proposed by Braga and Defelipo (1974).

Statistical analysis

Regression analyses between soil available P by CAF-LDH-c as a function of P rates applied were adjusted. The recovery rates of P (RRP) from CAF-LDH-c in each soil were also obtained through the linear coefficient of these regression equations. The critical levels of P (CLP) for each soil were calculated by replacing the recommended rates of P

(Table 3) in the regression equations between available P by CAF-LDH-c as a function of the rate of P applied to each soil.

Pearson's correlation coefficient between P uptake by plants and extracted P from all extractants was performed for each soil, as well as a general Pearson's linear correlation between soil-available P by M-1, M-3, MER, and CAF-LDH-c extractants for all soils. The R environment was used in the statistical analysis (R Development Core Team, 2016).

RESULTS

The diffractograms of LDH, LDH-c, cellulose acetate film, and CAF-LDH-c are presented in figure 1. The diffractogram of LDH (Figure 1a) shows diffraction basal peaks (00*l*) marked as (003), (006), and (012), with 2*θ* degree values at 11.4, 22.9, and 34.6, respectively. The LDH-c XRD shows basal peaks marked as (111), (200), and (220) (Figure 1b), with 35.2, 43.1, and 62.6 2*θ* degree values, respectively. The cellulose acetate film diffractogram (Figure 1c) presents two centered peaks with lower crystallinity at 2*θ* degree values of 9.5 and 17.3. The diffractogram of CAF-LDH-c shows diffraction peaks marked as +(003) and #(111), with 2*θ* degree values at 11.3 and 35.1, respectively (Figure 1d).

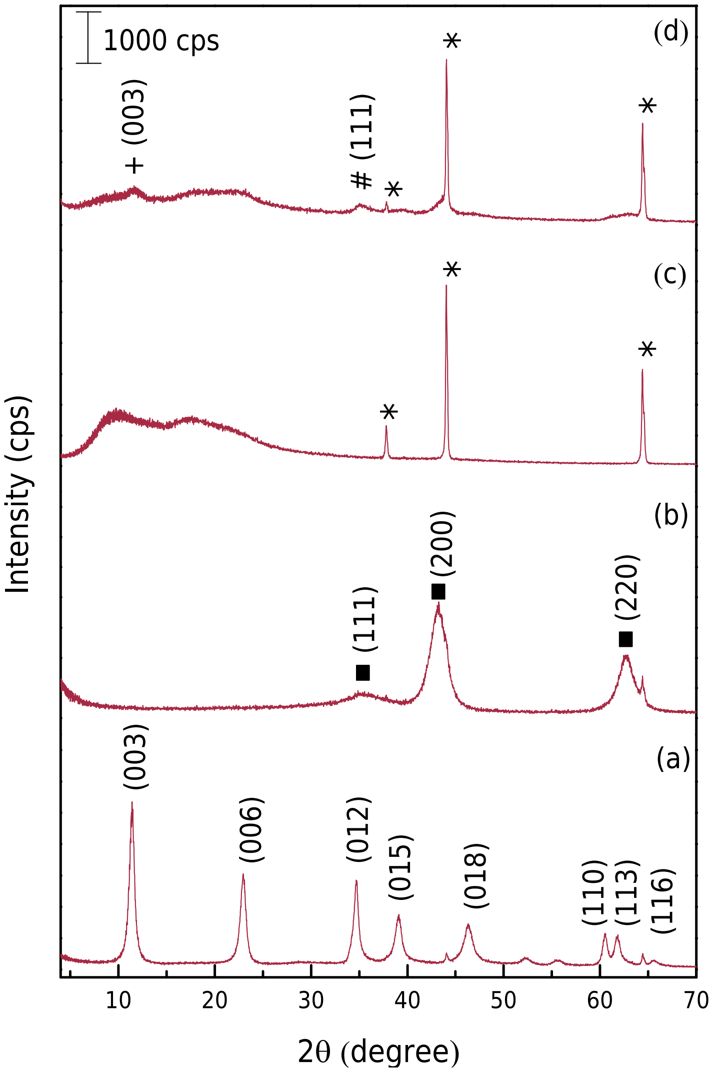

Figure 1. Diffractograms of (a) LDH, (b) LDH-c, (c) cellulose acetate film, and (d) CAF-LDH-c. *: Al signal of the sample holder; #: MgO signal; +: LDH signal; ■: peaks referring to the presence of MgO.

The ATR-FTIR spectra of LDH, LDH-c, cellulose acetate film, and CAF-LDH-c are shown in figure 2. The LDH presented bands in the wavenumber at 3400, 1650, 1360, 850, and 630 cm^{-1} (Figure 2a). For LDH-c, the spectrum shows bands at 850 and 670 cm^{-1} (Figure 2b). The ATR-FTIR spectra of cellulose acetate film presented peaks at 3400, 1748, 1360, 1249, and 1032 cm^{-1} (Figure 2c). Similar to cellulose acetate film, the CAF-LDH-c presented bands in the wavenumber of 3400, 1748, 1360, 1249, and 1032 cm^{-1} (Figure 2d).

The morphologies of the LDH, LDH-c, cellulose acetate film, and CAF-LDH-c were analyzed by SEM images (Figure 3). The LDH presented shaped agglomerated particles, such as hexagonal platelets, similar to rose sand (Figure 3a). For LDH-c there are hexagonal platelets and also densely packed particles (Figure 3b). The surface morphology of CAF-LDH-c showed the LDH-c uniformly spread on the polymeric film of cellulose acetate (Figures 3c and 3d).

As expected, the extractable P by CAF-LDH-c increased with the increase of P rates applied in the soils (Table 2). Extractable P by CAF-LDH-c had a positive linear relationship as a function of applied P rates to each soil (Table 3). The coefficients of the linear regression models show the influence of the buffer capacity of soils on extractable P by CAF-LDH-c, from 0.0564 in LVd1 (the highest P buffer capacity) to 0.4636 in PVAd3 (the lowest P buffer capacity).

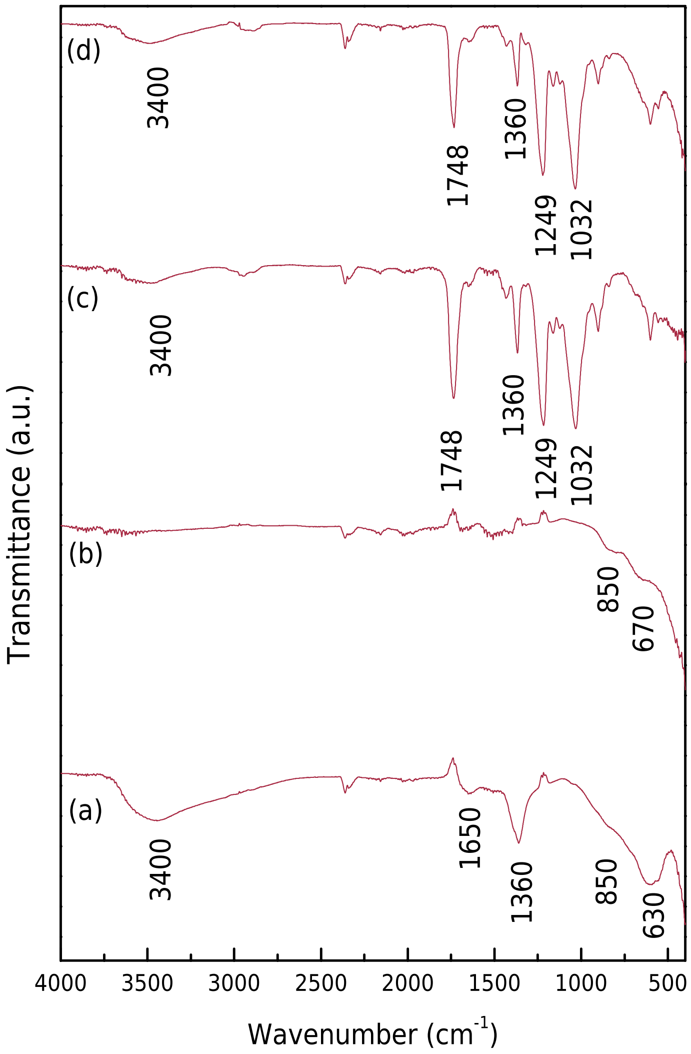

Figure 2. Attenuated total reflectance Fourier transform infrared spectroscopy spectra of LDH (a), LDH-c (b), cellulose acetate film (c), and CAF-LDH-c (d).

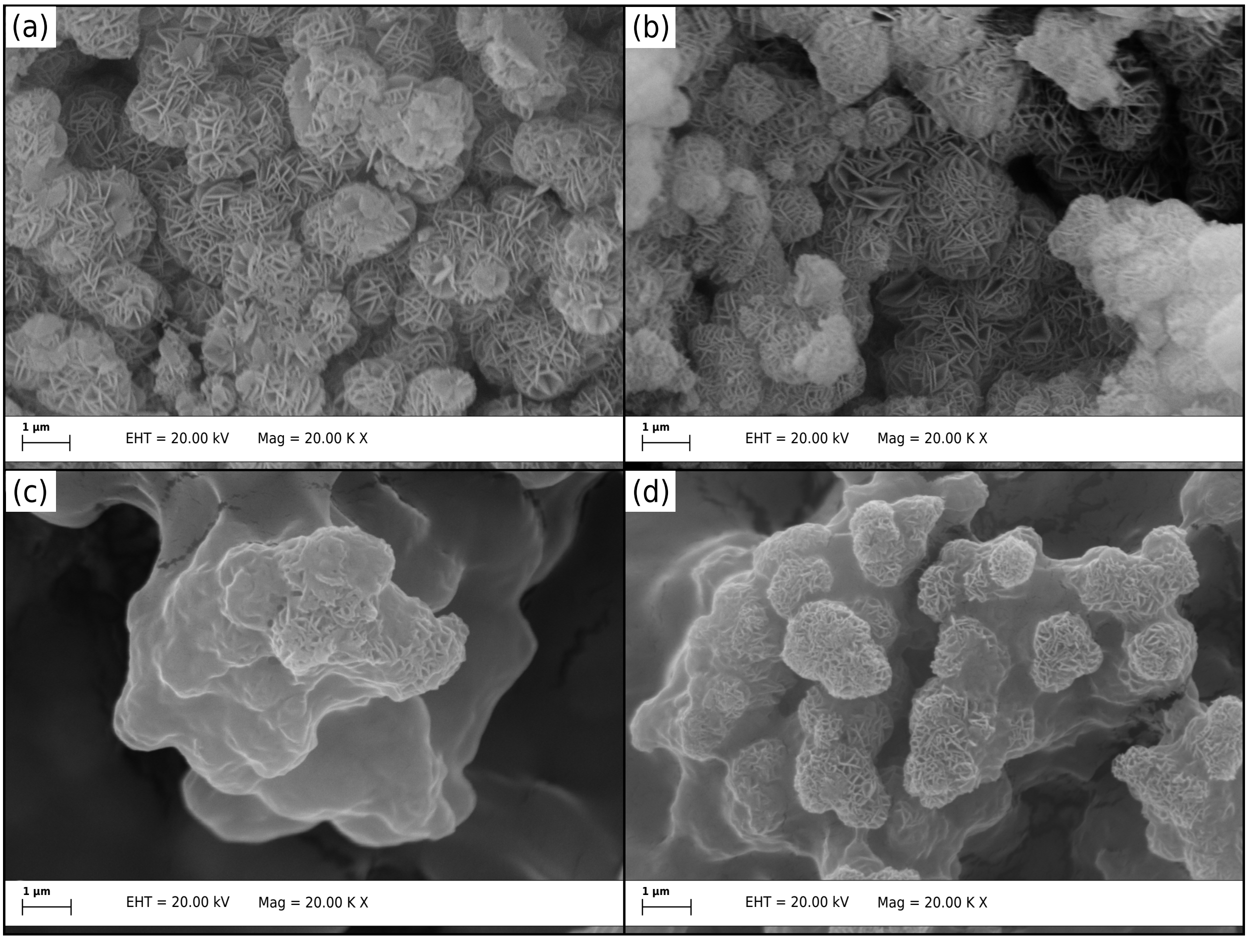

Figure 3. Representative images of SEM of LDH (a), LDH-c (b), and CAF-LDH-c (c and d).

The RRP and critical level of P (CLP) from CAF-LDH-c extractant are presented in table 3. The RRP average for all soils considering CAF-LDH-c extractant was 24.1 %. The lowest RRP value was 5.6 %, obtained for the LVd1 soil which is considered the most buffered soil (Rem-P of 4.3 mg L^{-1} – Table 1). However, the highest RRP from CAF-LDH-c was for PVAd3, LAd, and PVAd2 soils, with values of 46.4, 33.6, and 30.5 %, respectively. These soils have a lower phosphate buffer capacity, Rem-P of 27.1, 44.1, and 26.1, respectively for PVAd3, LAd, and PVAd2 soils (Table 1). When the cultivated and uncultivated soils were grouped separately, the average RRP from CAF-LDH-c of the cultivated soils was higher than the soils from uncultivated areas (29.7 and 20.1 %, respectively).

The CLP from CAF-LDH-c extractant was estimated by regression equations (Table 3). The CLP for this extractant ranged from 13.20 mg dm^{-3} (LVd1 soil) to 46.37 mg dm^{-3} (PVAd1 soil) (Table 3). In general, the higher CLP was obtained in soils collected in cultivated areas with higher initial soil-available P (LVd3 – 50.9 mg dm^{-3} of P, PVAd1 – 96.5 mg dm^{-3} of P, PVAd2 – 21.4 mg dm^{-3} of P, and PVAd3 – 11.5 mg dm^{-3} of P). The CLP values for LVd3, PVAd1, PVAd2, and PVAd3 soils were 38.27, 46.37, 30.50, and 34.17 mg dm^{-3}, respectively.

Pearson's linear correlations between shoots P uptake and soil extractable P for each soil from CAF-LDH-c extractant were performed to evaluate the predictive capacity of the CAF-LDH-c as a new extractant (Table 4). The linear relationship between P uptake and soil extractable P in the soil by CAF-LDH-c was verified by the positive Pearson's correlation coefficient, in which for all soils the coefficients ranged from 0.66 ($p<0.05$) for LVd2 soil to 0.99 ($p<0.05$) for PVd and CXbd soils.

Additionally, Pearson's linear correlation between shoot P uptake and soil extractable P from CAF-LDH-c extractant for all soils and respective P rates applied were achieved

Table 2. Soil extractable P from CAF-LDH-c extractant as a function of applied rates of P to each soil in the respective levels of P

Soil	Level of P						
	0.0	0.5	1.0	2.0	3.0	5.0	Mean
	mg dm^{-3}						
LVd1	3.4	4.3	6.4	9.9	11.5	13.5	8.2
LVd2	22.0	23.9	37.1	43.6	54.0	66.0	41.1
LVd3	27.7	30.5	33.6	37.6	58.9	63.8	42.0
CXbd	1.8	3.7	5.7	8.5	10.5	28.2	9.7
LVdf	5.8	6.9	9.9	14.8	20.8	30.4	14.8
PVd	1.4	4.7	8.2	10.8	18.3	50.7	15.7
LAd	4.7	5.0	8.4	13.5	16.0	39.2	14.5
LVAd1	2.3	7.1	14.2	18.4	28.4	37.8	18.0
LVAd2	3.2	5.8	7.6	9.9	21.1	24.4	12.0
PVAd1	44.7	51.1	55.9	59.8	62.3	84.3	59.7
PVAd2	14.6	18.8	28.4	34.8	46.1	55.7	33.0
PVAd3	5.5	9.1	10.8	16.5	24.3	72.7	23.1
Mean	11.4	14.2	18.8	23.1	31.0	47.2	24.3

The P rate of the soils LVd1, LVd2, and LVd3 was 37.4 mg dm^{-3}. PVd, LVdf, and LVAd1 was 32.0 mg dm^{-3}. LVAd2, PVAd1, PVAd2, PVAd3, and CXbd was 27.4 mg dm^{-3} and LAd was 20.0 mg dm^{-3}. The application was made according to the levels 0.0, 0.5, 1.0, 2.0, 3.0, and 5.0 of the calculated rate.

Table 3. Regression equations between extracted P by CAF-LDH-c and rates of P applied to each soil, the recovery rate of P, and critical level of P

Soil	Equation	R^2	RRP %	CLP
				mg dm^{-3}
LVd1	$\hat{y} = 4.12 + 0.0564^{**}x$	0.92	5.6	13.20
LVd2	$\hat{y} = 23.80 + 0.2416^{***}x$	0.96	24.2	23.80
LVd3	$\hat{y} = 26.81 + 0.2123^{**}x$	0.91	21.2	38.27
CXbd	$\hat{y} = 0.25 + 0.1805^{**}x$	0.92	18.1	18.76
LVdf	$\hat{y} = 5.05 + 0.1585^{***}x$	0.99	15.9	20.86
PVd	$\hat{y} = -2.16 + 0.2908^{**}x$	0.91	29.1	26.94
LAd	$\hat{y} = 1.56 + 0.3363^{**}x$	0.93	33.6	19.75
LVAd1	$\hat{y} = 4.53 + 0.2202^{***}x$	0.97	22.0	28.61
LVAd2	$\hat{y} = 3.36 + 0.1648^{**}x$	0.93	16.5	19.06
PVAd1	$\hat{y} = 45.96 + 0.2611^{***}x$	0.95	26.1	46.37
PVAd2	$\hat{y} = 17.03 + 0.3049^{***}x$	0.96	30.5	30.50
PVAd3	$\hat{y} = -1.20 + 0.4636^{**}x$	0.87	46.4	34.17

RRP: Recovery rate of P. CLP: Critical level of P. ** and *** indicate significant effect at 1 % and 0.1 %, respectively.

and compared to M-1, M-3, and MER extractants. The Pearson's correlation coefficient for CAF-LDH-c, M-1, M-3, and MER extractants were 0.74 ($p<0.05$), 0.81 ($p<0.05$), 0.82 ($p<0.05$), and 0.62 ($p<0.05$), respectively (Figure 4). Furthermore, a general Pearson's linear correlation was also performed between the soil extractable P from all extractants considering all soils and levels of P applied. There was a high Pearson's correlation coefficient between extracted P by M-1, M-3, MER, and CAF-LDH-c extractants (Table 5). The Pearson's correlation coefficients were 0.87 ($p<0.001$) for CAF-LDH-c and M-1, 0.89 ($p<0.001$) for CAF-LDH-c and M-3, and 0.84 ($p<0.001$) for CAF-LDH-c and MER (Table 5).

Table 4. Pearson's correlation coefficients between P uptake by plants and extracted P by M-1, M-3, MER, and CAF-LDH-c extractant according to soils

Soil	M-1$^{\#}$	M-3$^{\#}$	MER$^{\#}$	CAF-LDH-c
LVd1	0.98***	0.98***	0.98***	0.97**
LVd2	0.82*	0.81*	0.83*	0.66*
LVd3	0.85*	0.86*	0.80*	0.83*
CXbd	0.93**	0.92**	0.87*	0.99*
LVdf	0.92*	0.92*	0.86*	0.91**
PVd	0.94**	0.96**	0.97**	0.99*
LAd	0.98***	0.96**	0.96**	0.97**
LVAd1	0.97**	0.99***	0.98***	0.96**
LVAd2	0.97**	0.99***	0.97**	0.98***
PVAd1	0.87*	0.93**	0.96**	0.96*
PVAd2	0.97**	0.96**	0.95**	0.88*
PVAd3	0.98***	0.98***	0.92**	0.98***

*, **, and *** indicate significant effect at 5 %, 1 %, and 0.1 %, respectively. $^{\#}$: Data from Reis (2016) and Reis et al. (2020).

Table 5. Pearson's correlation coefficient between extracted P by M-1, M-3, MER, and CAF-LDH-c extractant for all soils and applied doses of P

	M-1$^{\#}$	M-3$^{\#}$	MER$^{\#}$	CAF-LDH-c
M-1	-	0.98***	0.90***	0.87***
M-3	-	-	0.91***	0.89***
MER	-	-	-	0.84***

$^{***:}$ indicate significance at 0.1 %. $^{\#}$: Data from Reis (2016) and Reis et al. (2020).

DISCUSSION

Cellulose acetate film containing calcinated layered double hydroxide (CAF-LDH-c) can be used as a measure of P extraction in soils. The diffractogram of LDH in figure 1a presents the characteristic profile of the hydrotalcite-like structure, with basal peaks (003), (006), and (012) with 2θ degrees values at 11.4, 22.9, and 34.6, respectively. The repetition of the basal peaks (003) and (006) is related to the stacking of the LDH layers (Edañol et al., 2020), and this diffraction result is expected for crystalline LDH with good structural organization and a purity phase. The basal spacing calculated by Bragg's equation ($n\ \lambda = 2d_{hkl} \sin \theta$) was 7.75 Å (Figure 1a). This value is expected for carbonate anions intercalated into MgAl-LDH (Bernardo et al., 2018; Zhang et al., 2018; Seidi et al., 2021). The LDH-c shows peaks referring to the presence of MgO, indicated in figure 1b as (111), (200), and (220). In this type of LDH, the calcination process using appropriate temperature and atmosphere may produce the crystalline MgO, and also other amorphous compounds, such as oxides and mixed oxyhydroxides (Santos et al., 2017a,b). The diffractogram of cellulose acetate film had two centered semi-crystalline peaks, matching with findings of Emam et al. (2021) and Sharma et al. (2021) (Figure c). The diffractogram of CAF-LDH-c had a low-intensity peak related to the plane (003) from LDH, and also presented a (111) peak attributed to the MgO plane. This peak occurs because of the intercalation of carbonate anions present in the air into the LDH-c interlayer present in the film. The contamination of CAF-LDH-c with CO_3^{2-} occurs due to the contact of this material with carbon dioxide in the air.

The broadband in the region of 3400 cm^{-1} from LDH, cellulose acetate film, and CAF-LDH-c (Figures 2a, 2c, and 2d, respectively) is due to the O-H stretching of the H_2O molecules and/or hydroxyl groups (Castro et al., 2018; Larosa et al., 2018; Castro et al., 2020). The intense band around 1650 cm^{-1} for LDH (Figure 2a) occurs due to the O–H stretching of the hydroxyl groups and/or H_2O molecules (Dib et al., 2021). The bands at 1360, 850, and 630 cm^{-1} presented by LDH, are associated with vibration modes of CO_3^{2-} intercalated absorbed anions (Zhang et al., 2018; Guo et al., 2020; Fajrina et al., 2021). For LDH-c (Figure 2b), the bands at 850 and 670 cm^{-1} are attributed to vibration modes of Al-O and Mg-O of Mg(Al)O (Santos et al., 2017a,b; Zhu et al., 2018). The band at 1748 cm^{-1} for cellulose acetate film and CAF-LDH-c is typical of the formation of cellulose acetate and is due to the stretching of C=O groups (Brum et al., 2012; Berber et al., 2014; Imam et al., 2020; Lee et al., 2021). The band at 1249 cm^{-1} is due to the stretching of C-O of the O-(C=O)-CH_3 (Brum et al., 2012). The region in the wavenumber range from 1360 to 1370 cm^{-1} (Figures 2c and 2d) for cellulose acetate film and CAF-LDH-c are related to C-H bending (Chen et al., 2021). The band at 1032 cm^{-1} is associated with C-O stretching (Emam et al., 2021).

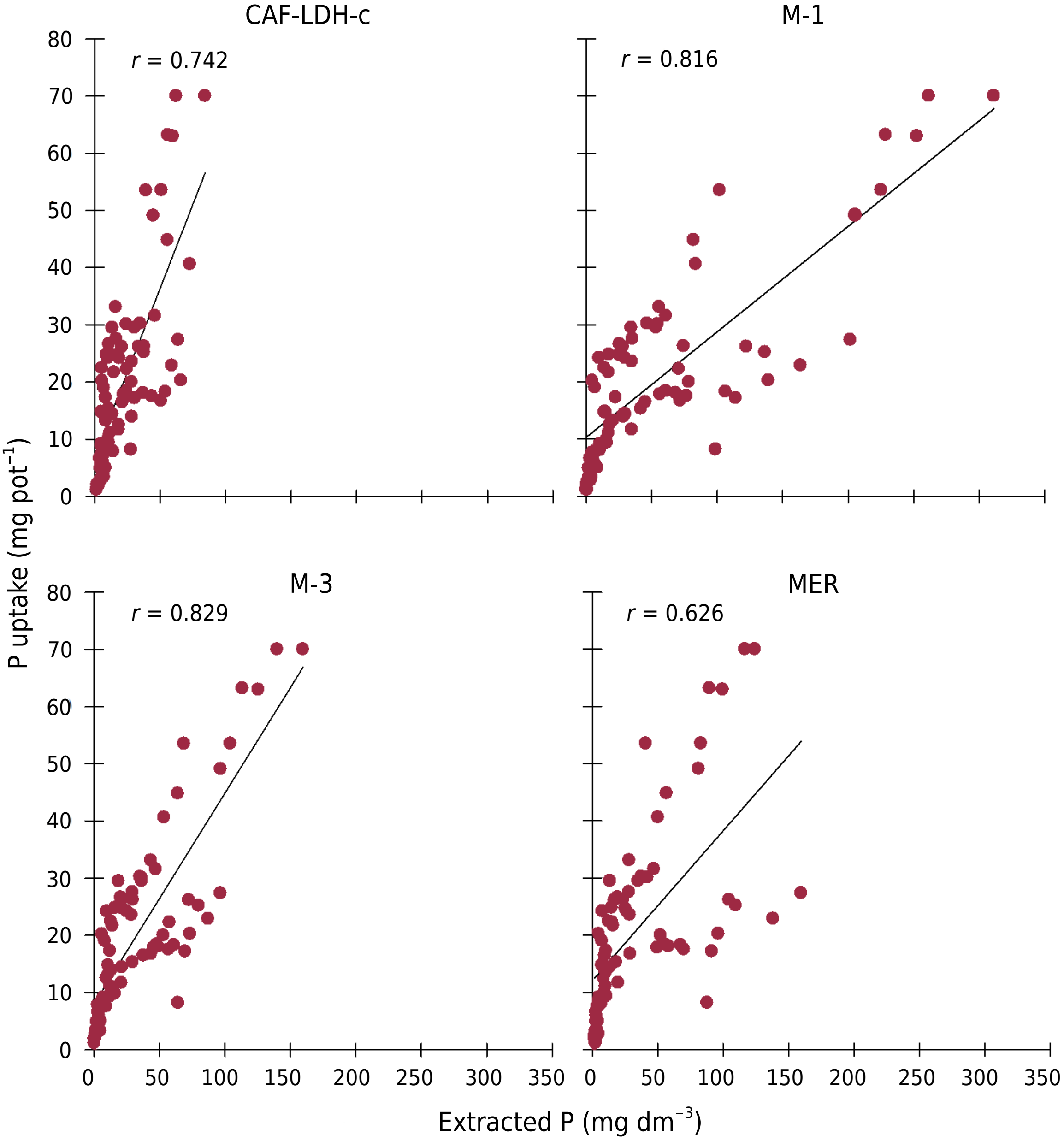

Figure 4. Pearson's correlation coefficient between extracted P by CAF-LDH-c, M-1, M-3, and MER extractants for all soils and applied rates of P and P uptake by plants. M-1, M-3, and MER: Data from Reis (2016) and Reis et al. (2020).

The agglomerated particles shaped like hexagonal platelets making the rose sand structure is typical for LDH material (Figure 3a), which agreed with the previous results from Wang et al. (2013), Yang et al. (2019), and Suescum-Morales et al. (2021). The LDH-c showed both hexagonal platelets making the rose sand structure and regions with densely packed particles, as a result of the thermal treatment applied (Figure 3b). The interaction between cellulose acetate and LDH-c showed the simultaneous presence of precursor materials in the synthesized CAF-LDH-c (Figures 3c and 3d). The CAF-LDH-c showed a coating and distribution of LDH-c in the cellulose acetate matrix, indicating the physical protection of LDH-c and the cellulose acetate polymeric net. Physical protection is important because, in the present study, the film is being used to extract P from the soil, so the film was shaken with the soil as described in the methodology. Thus, the film characteristics showed high stability after agitation with the soil. The EDS analyses from LDH and LDH-c showed a higher presence of Mg, Al, and O, as expected. Conversely, for CAF-LDH-c there is a higher presence of C, O, Mg, and Al, for which the C is due to the cellulose acetate polymeric net.

The CAF-LDH-c extractant was sensitive to P rates applied in all different types of soils used in this study since there was a linear increase of soil extractable P from CAF-LDH-c extractant with the increase of P rates applied (Tables 2 and 3). Furthermore, CAF-LDH-c extractant was shown to be suitable for comparing soils with high and lower initial soil available P in cultivated and uncultivated areas, respectively. This was the first step to validating the predictive capacity of CAF-LDH-c as a new extractant of P in different soils. Previous research reported by Reis et al. (2020) with the same type of soils used in the present research showed that the P rates applied influenced the available P from M-1, M-3, and MER extractants. However, the model that best fit the data was linear and quadratic for M-1 extractant, while for M-3 and MER extractants the model that best fit the data was linear (Reis et al., 2020). These results showed that M-3, MER, and CAF-LDH-c extractants were the most promising extractants to assess the availability of P in different soils subjected to increased rates of this nutrient.

Through the linear equations between the extracted P by CAF-LDH-c and rates of P applied, the RRP was obtained from the linear coefficient of the equations. The recovery rate of P by extractants can be changed by soil characteristics or management, such as phosphate buffer capacity, initial P availability, and phosphate fertilization. The recovery rates allow estimating the rates to increase the availability of nutrients in the soil (Maluf et al., 2015). Therefore, to ensure a rational recommendation of phosphate fertilizers, it is important to recognize which soil properties influence the nutrient recovery capacity of an extractant.

The RRP from CAF-LDH-c was influenced by each type of soil, phosphate buffer capacity, and the initial P availability in soils. The lowest and highest recovery rates by CAF-LDH-c were obtained in soils with higher and lower phosphate buffer capacity, respectively (Tables 1 and 3). The sensitivity of extractants to phosphate buffer capacity is not only characteristic of those whose mechanism is based on acidic dissolution, e.g., M-1 and M-3, but also of extractants that have an ion-exchange mechanism, such as MER (Novais and Smyth, 1999; Novais et al., 2007; Freitas et al., 2013; Mumbach et al., 2020). It is noteworthy that CAF-LDH-c extractant has a mechanism of extraction based on ion adsorption, which explains the sensitivity of this extractant to phosphate buffer capacity. In many cases, the adsorption process in LDH can be realized by ion-exchange reactions between intercalated anions and the anions usually present in the soil, such as phosphate, carbonates, nitrates, borates, etc. since the ion replacement can lead to better stability of the LDH structure (Miyata, 1983; Costantino et al., 2014). In addition, in the specific case of this research, the material used for phosphorus adsorption was calcinated LDH incorporated into cellulose acetate polymer. After the calcination process, the LDHs can be converted into oxyhydroxides, and the adsorption of P from soil solution is due to

"LDH memory effect" (Bendinelli et al., 2016; Bernardo et al., 2016; Cosano et al., 2016; Santos et al., 2017b).

In the soils collected in cultivated areas in which P fertilization is a common practice, there was a higher initial availability of P, therefore, in these soils, the P recovery capacity of the extractant is higher than in the soils from the uncultivated areas. When soils were grouped according to the area in which they were collected, the average RRP from CAF-LDH-c was 29.7 and 20.1 % for cultivated and uncultivated areas, respectively (Table 3). Previous studies presented by Reis et al. (2020), Souza et al. (2017), and Mumbach et al. (2018), using M-1, M-3, and MER extractants, showed that the recovery capacity of the extractants is greater in soils from cultivated areas compared to soils from uncultivated areas. Thus, the results of the present study agreed with the previous studies reported in the scientific literature and showed that the CAF-LDH-c extractant was sensitive to P recovery in cultivated and uncultivated soils since the average recovered by this extractor was higher in cultivated soils.

The critical level of P calculated for CAF-LDH-c extractant (Table 3) also showed the sensitivity of this extractant to initial soil availability of P. In general, the critical level was higher for cultivated soils with higher initial available P content. The results from the present study agreed with previous research studies presented by Souza et al. (2017) and Mumbach et al. (2018).

The approach used in the methods regarding the predictive capacity of the P availability was made by Pearson's linear correlation between the P uptake by plants and the availability of P in the soil by each extractant. This is explained because the plant's nutrient uptake is a measure that is less affected by concentration or dilution effect on the total P absorbed, due to the greater or lesser growth of the plants, as occurs with the content of P in the tissue. There was a linear relationship between P uptake and soil extractable P in the soil by CAF-LDH-c, M-1, M-3, and MER extractants (Table 4). It is important to obtain extractants whose contents of nutrients extracted from the soil correlate significantly with the plant's nutrient uptake (Simões Neto et al., 2009). Thus, all extractants used in this study had a satisfactory predictive capacity for the P availability in the soil. Specifically for CAF-LDH-c, the significant correlations between extracted P in the soil and P uptake showed the efficiency of the method for different types of soils. Wide efficiency in soils with different properties is a required design in a new extractor (van Raij and Feitosa, 1980; Simões Neto et al., 2009). Although all extractants have been efficient, the use of CAF-LDH-c is an ecologically friendly alternative to replace the commercial extractants typically used, since LDHs can be produced from green synthesis, and cellulose acetate is a biodegradable polymer. Furthermore, LDHs applied as extractors allow a faster analysis in the laboratory in comparison with MER because they do not present all the operational difficulties presented by resin extractants.

The general correlation between the P content extracted in all soils and the plant nutrient uptake gives information about the range of the extractant in relation to different types of soil. Therefore, greater correlations could mean less influence of soil properties on the extraction capacity of the nutrient by the extractant. It was observed that the highest correlation coefficients were obtained when the extractors used were M-1 and M-3, followed by CAF-LDH-c and, finally, MER (Figure 4).

Another possibility to evaluate the predictive capacity of a new extractant is to compare the total extracted in the soil with the other extractants most used in routine testing laboratories and research (Eckert and Watson, 1996). Thus, a general correlation between the P content extracted in all soils for CAF-LDH-c, M-1, M-3, and MER extractants was investigated (Table 5). The correlation between the P extracted from soil was highly significant among all extraction methods used (Table 5). The significant correlation of the P in the soil from CAF-LDH-c, with those extractants usually used by routine testing laboratories, shows the possibility of using this extractant as a new routine method.

Several studies showed only a significant correlation between the usual extractors, and also showed the correlation between plants' P uptake and P availability in the soil from extractants (Bonfim et al., 2003; Rolim et al., 2008; Farias et al., 2009; Simonete et al., 2015). In the present study, in which the aim was to evaluate a new extractor to access the availability of P in the soil, CAF-LDH-c was shown to have the predictive capacity for the P availability in the soil, P in the plant, and P recovery from other conventional extractors. Usually, in research for soil fertility, field calibration experiments are necessary after greenhouse correlations studies to validate the new extractant. Thus, additional experiments using CAF-LDH-c as an extractant of P in field conditions are being performed by the authors.

CONCLUSIONS

A new accurate method to evaluate P in soil was developed. This method has a sensitivity to the phosphate (P) buffering capacity of soils as shown through the availability of P in the soils, by the P recovery rate capacity, and the critical level of P. Significant correlations of the extractable P from CAF-LDH-c with Mehlich-1, Mehlich-3, Mixed Exchange Resin, and P uptake by plants demonstrated the possibility of using this extractant as a new methodology to evaluate the availability of P in the soil for plant cultivation.

APPENDIX A. SUPPLEMENTARY DATA

Supplementary data to this article can be found online at https://www.rbcsjournal.org/wp-content/uploads/articles_xml/1806-9657-rbcs-47-e0220140/1806-9657-rbcs-47-e0220140-suppl01.pdf.

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REFERENCES

Alcântara FA, Furtini Neto AE, Curi N, Resende AV. Extraction methods for phosphorus and their relationship with soils phosphorus-buffer capacity estimated by the remaining-phosphorus methodology – A pot study with maize. Commun Soil Sci Plant Anal. 2008;39:603-15. https://doi.org/10.1080/00103620701828395

Alvarez V VH, Novais RF, Barros NF, Cantarutti RB, Lopes AS. Interpretação dos resultados das análises de solos. In: Ribeiro AC, Guimarães PTG, Alvarez V VH, editors. Recomendação para o uso de corretivos e fertilizantes em Minas Gerais - 5ª aproximação. Viçosa, MG: Comissão de Fertilidade do Solo do Estado de Minas Gerais; 1999. p. 25-32.

Alvarez V VH, Novais RF, Dias L, Oliveira J. Determinação e uso do fósforo remanescente. Boletim Informativo da Sociedade Brasileira de Ciência do Solo. 2000;25:27-33.

Beegle D. Assessing soil phosphorus for crop production by soil testing. Phosphorus: Agr Environ. 2005;46:123-43. https://doi.org/10.2134/agronmonogr46.c5

Bendinelli EV, Rocha AC, Barcia OE, Aoki IV, Margarit-Mattos ICP. Effects of lamellar reconstruction routes in the release of molybdate encapsulated in Mg-Al layered double hydroxides. Mater Chem Phys. 2016;173:26-32. https://doi.org/10.1016/j.matchemphys.2015.12.049

Berber MR, Hafez IH, Minagawa K, Mori T. A sustained controlled release formulation of soil nitrogen based on nitrate-layered double hydroxide nanoparticle material. J Soils Sediments. 2014;14:60-6. https://doi.org/10.1007/s11368-013-0766-3

Bernardo MP, Guimarães GGF, Majaron VF, Ribeiro C. Controlled release of phosphate from layered double hydroxide structures: Dynamics in soil and application as smart fertilizer. ACS Sustain Chem Eng. 2018;6:5152-61. https://doi.org/10.1021/acssuschemeng.7b04806

Bernardo MP, Moreira FKV, Colnago LA, Ribeiro C. Physico-chemical assessment of [Mg-Al-PO_4]-LDHs obtained by structural reconstruction in high concentration of phosphate. Colloids Surface A - Physicochem Eng Asp. 2016;497:53-62. https://doi.org/10.1016/j.colsurfa.2016.02.021

Bonfim EMS, Freire FJ, Santos MVF, Silva TJA, Freire MBS. Avaliação de extratores para determinação de fósforo disponível de solos cultivados com *Brachiaria brizantha*. Acta Sci Agron. 2003;25:323-8. https://doi.org/10.4025/actasciagron.v25i2.1912

Braga JM, Defelipo BV. Determinação espectrofotométrica de fósforo em extratos de solo e material vegetal. Rev Ceres. 1974;21:73-85.

Brum SS, Oliveira LCA, Bianchi ML, Guerreiro MC, Oliveira LK, Carvalho KTG. Synthesis of cellulose acetate from the bean straw using N-bromosuccinimide (NBS) as catalyst. Polimeros. 2012;22:447-52. https://doi.org/10.1590/S0104-14282012005000061

Camêlo DL, Ker JC, Novais RF, Corrêa MM, Lima VC. Sequential extraction of Phosphorus by Mehlich-1 and ion exchange resin from B horizons of ferric and Perferric Latosols (Oxisols). Rev Bras Cienc Solo. 2015;39:1058-67. https://doi.org/10.1590/01000683rbcs20140405

Castro GF, Ferreira JA, Eulálio D, Moraes ARF, Leopoldo VRC, Pinto FG, Novais RF, Tronto J. Organic-inorganic hybrid materials: Layered double hydroxides and cellulose acetate films as phosphate recovery. J Agric Sci Technol B. 2018a;8:360-74. https://doi.org/10.17265/2161-6264/2018.06.003

Castro GF, Ferreira JA, Eulálio D, Souza SJ, Novais SV, Novais RF, Pinto FG, Tronto J. Layered double hydroxides: matrices for storage and source of boron for plant growth. Clay Miner. 2018b;53:79-89. https://doi.org/10.1180/clm.2018.6

Castro GF, Ferreira JA, Moraes ARF, Cantarutti RB, Pinto FG, Tronto J, Novais RF. Cellulose acetate film and layered double hydroxide as determination method of available phosphorus in the soil. J Agric Sci Technol B. 2018c;8:420-32. https://doi.org/10.17265/2161-6264/2018.07.002

Castro GF, Mattiello EM, Ferreira JA, Zotarelli L, Tronto J. Synthesis, characterization and agronomic use of alginate microspheres containing layered double hydroxides intercalated with borate. New J Chem. 2020;44:10066-75. https://doi.org/10.1039/c9nj06042a

Chen K, Yu J, Huang J, Tang Q, Li H, Zou Z. Improved mechanical, water vapor barrier and UV-shielding properties of cellulose acetate films with flower-like metal-organic framework nanoparticles. Int J Biol Macromol. 2021;167:1-9. https://doi.org/10.1016/j.ijbiomac.2020.11.164

Cosano D, Esquinas C, Jiménez-Sanchidrián C, Ruiz JR. Use of Raman spectroscopy to assess the efficiency of MgAl mixed oxides in removing cyanide from aqueous solutions. Appl Surf Sci. 2016;364:428-33. https://doi.org/10.1016/j.apsusc.2015.12.181

Costantino U, Vivani R, Bastianini M, Costantino F, Nocchetti M. Ion exchange and intercalation properties of layered double hydroxides towards halide anions. Dalt Trans. 2014;43:11587-96. https://doi.org/10.1039/c4dt00620h

Dib M, Moutcine A, Ouchetto H, Ouchetto K, Chtaini A, Hafid A, Khouili M. Novel synthesis of α-Fe_2O_3@Mg/Al-CO_3-LDH nanocomposite for rapid electrochemical detection of p-nitrophenol. Inorg Chem Commun. 2021;131:108788. https://doi.org/10.1016/j.inoche.2021.108788

Eckert DJ, Watson ME. Integrating the Mehlich-3 extractant into existing soil test interpretation schemes. Commun Soil Sci Plant Anal. 1996;27:1237-48. https://doi.org/10.1080/00103629609369629

Edañol YDG, Poblador JAO, Talusan TJE, Payawan LM. Co-precipitation synthesis of Mg-Al-CO_3 layered double hydroxides and its adsorption kinetics with phosphate(V) ions. Mater Today Proc. 2020;33:1809-13. https://doi.org/10.1016/j.matpr.2020.05.059

Emam HE, El-Shahat M, Abdelhameed RM. Observable removal of pharmaceutical residues by highly porous photoactive cellulose acetate@MIL-MOF film. J Hazard Mater. 2021;414:125509. https://doi.org/10.1016/j.jhazmat.2021.125509

Fajrina N, Yusof N, Ismail AF, Jaafar J, Aziz F, Salleh WNW, Nordin NAHM. MgAl-CO_3 layered double hydroxide as potential filler in substrate layer of composite membrane for enhanced carbon dioxide separation. J Environ Chem Eng. 2021;9:106164. https://doi.org/10.1016/j.jece.2021.106164

Farias DR, Oliveira FHT, Santos D, Arruda JA, Hoffmann RB, Novais RF. Fósforo em solos representativos do estado da paraíba.: II - Disponibilidade de fósforo para plantas de milho. Rev Bras Cienc Solo. 2009;33:633-46. https://doi.org/10.1590/s0100-06832009000300016

Freitas IF, Novais RF, Villani EMA, Novais SV. Phosphorus extracted by ion exchange resins and mehlich-1 from Oxisols (Latosols) treated with different phosphorus rates and sources for varied soil-source contact periods. Rev Bras Cienc Solo. 2013;37:667-77. https://doi.org/10.1590/S0100-06832013000300013

Ghormade V, Deshpande MV, Paknikar KM. Perspectives for nano-biotechnology enabled protection and nutrition of plants. Biotechnol Adv. 2011;29:792-803. https://doi.org/10.1016/j.biotechadv.2011.06.007

Guo L, Wu Y, Duan P, Zhang Z. Improving sulfate attack resistance of concrete by using calcined Mg-Al-CO_3 LDHs: Adsorption behavior and mechanism. Constr Build Mater. 2020;232:117256. https://doi.org/10.1016/j.conbuildmat.2019.117256

Imam SS, Adnan R, Kaus NHM. Immobilization of BiOBr into cellulose acetate matrix as hybrid film photocatalyst for facile and multicycle degradation of ciprofloxacin. J Alloys Compd. 2020;843:155990. https://doi.org/10.1016/j.jallcom.2020.155990

Larosa C, Salerno M, Lima JS, Meri RM, Silva MF, Carvalho LB, Converti A. Characterisation of bare and tannase-loaded calcium alginate beads by microscopic, thermogravimetric, FTIR and XRD analyses. Int J Biol Macromol. 2018;115:900-6. https://doi.org/10.1016/j.ijbiomac.2018.04.138

Lee J, Moon JY, Lee JC, Hwang TI, Park CH, Kim CS. Simple conversion of 3D electrospun nanofibrous cellulose acetate into a mechanically robust nanocomposite cellulose/calcium scaffold. Carbohydr Polym. 2021;253:117191. https://doi.org/10.1016/j.carbpol.2020.117191

Maluf HJGM, Soares EMB, Silva IR, Neves JCL, Silva MFO. Disponibilidade e recuperação de nutrientes de resíduos culturais em solo com diferentes texturas. Rev Bras Cienc Solo. 2015;39:1690-702. https://doi.org/10.1590/01000683rbcs20140658

Mehlich A. Mehlich 3 soil test extractant: A modification of Mehlich 2 extractant. Commun Soil Sci Plant Anal. 1984;15:1409-16. https://doi.org/10.1080/00103628409367568

Mehlich A. Determination of P, Ca, Mg, K, Na and NH_4 by North Carolina Soil Testing Laboratories. Raleigh: University of North Carolina; 1953.

Miyata S. Anion-exchange properties of hydrotalcite-like compounds. Clays Clay Miner. 1983;31:305-11. https://doi.org/10.1346/CCMN.1983.0310409

Mumbach GL, Oliveira DA, Warmling MI, Gatiboni LC. Quantificação de fósforo por Mehlich 1, Mehlich 3 e resina trocadora de ânions em solos com diferentes teores de argila. Rev Ceres. 2018;65:546-54. https://doi.org/10.1590/0034-737x201865060010

Mumbach GL, Gatiboni LC, Dall'Orsoletta DJ, Schmitt DE, Pessotto PP, Oliveira CMB. Phosphorus extraction with soil test methods affected by soil P sorption capacity. J Soil Sci Plant Nutr. 2020;20:1882-90. https://doi.org/10.1007/s42729-020-00259-1

Novais RF, Smyth TJ. Fósforo em solo e planta em condições tropicais. Viçosa, MG: Universidade Federal de Viçosa; 1999.

Novais RF, Smyth TJ, Nunes FN. Fósforo. In: Novais RF, Alvarez V VH, Barros NF, Fontes RLF, Cantarutti RB, Neves JCL, editors. Fertilidade do Solo. Viçosa, MG: Sociedade Brasileira de Ciência do Solo; 2007. p. 472-500.

Oliveira Júnior A, Prochnow LI, Klepker D. Soybean yield in response to application of phosphate rock associated with triple superphosphate. Sci Agric. 2011;68:376-85. https://doi.org/10.1590/s0103-90162011000300016

Pantano G, Grosseli GM, Mozeto AA, Fadini PS. Sustainability in phosphorus use: A question of water and food security. Quim Nova. 2016;39:732-40. https://doi.org/10.5935/0100-4042.20160086

R Development Core Team. R: A language and environment for statistical computing. Vienna, Austria: R Foundation for Statistical Computing; 2016. Available from: http://www.R-project.org/.

Reis JV. Potencial do extrator mehlich-3 na avaliação da disponibilidade de fósforo de diferentes solos [dissertation]. Viçosa, MG: Universidade Federal de Viçosa; 2016.

Reis JV, Alvarez V VH, Durigan RD, Paulucio RB, Cantarutti RB. Interpretation of soil phosphorus availability by mehlich-3 in soils with contrasting phosphorus buffering capacity. Rev Bras Cienc Solo. 2020;44:e0190113. https://doi.org/10.36783/18069657rbcs20190113

Rolim MV, Novais RF, Nunes FN, Alvarez V VH. Efeito da moagem do solo no teor de fósforo disponível por Mehlich-1, resina em esferas e em lâmina. Rev Bras Cienc Solo. 2008;32:1181-90. https://doi.org/10.1590/S0100-06832008000300026

Santos RMM, Gonçalves RGL, Constantino VRL, Santilli CV, Borges PD, Tronto J, Pinto FG. Adsorption of Acid Yellow 42 dye on calcined layered double hydroxide: Effect of time, concentration, pH and temperature. Appl Clay Sci. 2017a;140:132-9. https://doi.org/10.1016/j.clay.2017.02.005

Santos RMM, Tronto J, Briois V, Santilli CV. Thermal decomposition and recovery properties of ZnAl-CO_3 layered double hydroxide for anionic dye adsorption: Insight of the aggregative nucleation and growth mechanism of LDH memory effect. J Mater Chem A. 2017b;5:9998-10009. https://doi.org/10.1039/C7TA00834A

Seidi F, Jouyandeh M, Paran SMR, Esmaeili A, Karami Z, Livi S, Habibzadeh S, Vahabi H, Ganjali MR, Saeb MR. Imidazole-functionalized nitrogen-rich Mg-Al-CO_3 layered double hydroxide for developing highly crosslinkable epoxy with high thermal and mechanical properties. Colloids Surface A - Physicochem Eng Asp. 2021;611:125826. https://doi.org/10.1016/j.colsurfa.2020.125826

Sharma A, Mandal T, Goswami S. Fabrication of cellulose acetate nanocomposite films with lignocelluosic nanofiber filler for superior effect on thermal, mechanical and optical properties. Nano-Struct Nano-Objects. 2021;25:100642. https://doi.org/10.1016/j.nanoso.2020.100642

Silva FC, Van Raij B. Disponibilidade de fósforo em solos avaliada por diferentes extratores. Pesq Agropec Bras. 1999;34:267-88. https://doi.org/10.1590/S0100-204X1999000200016

Silva V, Kamogawa MY, Marangoni R, Mangrich AS, Wypych F. Layered double hydroxides as matrices for nitrate slow-release fertilizers. Rev Bras Cienc Solo. 2014;38:272-7. https://doi.org/10.1590/S0100-06832014000100027

Simões Neto DE, Oliveira AC, Freire FJ, Freire MBGS, Nascimento CWA, Rocha AT. Extração de fósforo em solos cultivados com cana-de-açúcar e suas relações com a capacidade tampão. Rev Bras Eng Agric Ambient. 2009;13:840-8. https://doi.org/10.1590/s1415-43662009000700005

Simonete MA, Ernani PR, Moro L, Teixeira-Gandra CFA, Gatiboni LC. Eficiência de métodos analíticos na predição da disponibilidade de fósforo para arroz irrigado em solos catarinenses. Rev Bras Cienc Solo. 2015;39:1151-60. https://doi.org/10.1590/01000683rbcs20140797

Soares NFF. Bitterness reduction in citrus juice through naringinase immobilized into polymer film. Ithaca: Cornell University; 1998.

Souza RPD, Pegoraro RF, Reis ST. Disponibilidade de fósforo e produção de biomassa de pinhão manso em solos com distintas texturas e doses de fósforo. Rev Agro@mbiente On-Line. 2017;11:1-10. https://doi.org/10.18227/1982-8470ragro.v11i1.3492

Steiner F, Lana MDC, Zoz T, Frandoloso JF, Fey R. Extraction methods and availability of phosphorus for soybean in soils from Paraná State, Brazil. Semin - Cienc Agrar. 2012;33:1005-14. https://doi.org/10.5433/1679-0359.2012v33n3p1005

Suescum-Morales D, Cantador-Fernández D, Jiménez JR, Fernández JM. Mitigation of CO_2 emissions by hydrotalcites of Mg_3Al-CO_3 at 0 °C and high pressure. Appl Clay Sci. 2021;202:105950. https://doi.org/10.1016/j.clay.2020.105950

van Raij B, Andrade JC, Cantarella H, Quaggi JA. Análise química para avaliação da fertilidade de solos tropicais. Campinas: Instituto Agronômico de Campinas; 2001.

van Raij B, Feitosa CT. Correlação entre o fósforo extraído de solos por diversos extratores químicos e o absorvido pelo milho. Bragantia. 1980;39:51-7. https://doi.org/10.1590/s0006-87051980000100007

Valadares SV, Alvarez V VH, Santos WO, Paes JLA, Lins CB, Novais RF. Sensitivity of soil P availability tests to Ca-P in Oxisols. Commun Soil Sci Plant Anal. 2017;48:1834-42. https://doi.org/10.1080/00103624.2017.1395456

Vieira RCB, Fontoura SMV, Bayer C, Moraes RP, Carniel E. Adubação fosfatada para alta produtividade de soja, milho e cereais de inverno cultivados em rotação em Latossolos em plantio direto no centro-sul do paraná. Rev Bras Cienc Solo. 2015;39:794-808. https://doi.org/10.1590/01000683rbcs20140463

Wang Q, Gao Y, Luo J, Zhong Z, Borgna A, Guo Z, O'Hare D. Synthesis of nano-sized spherical $Mg_3Al–CO_3$ layered double hydroxide as a high-temperature CO_2 adsorbent. RCS Adv. 2013;10:3414-20.

Yang Z zhu, Wei J jing, Zeng G ming, Zhang H qing, Tan X fei, Ma C, Li X cheng, Li Zhao, Zhang C. A review on strategies to LDH-based materials to improve adsorption capacity and photoreduction efficiency for CO_2. Coord Chem Rev. 2019;386:154-82. https://doi.org/10.1016/j.ccr.2019.01.018

Zhang Q, Leroux F, Tang P, Li D, Feng Y. Low molecular weight hindered amine light stabilizers (HALS) intercalated MgAl-Layered double hydroxides: Preparation and anti-aging performance in polypropylene nanocomposites. Polym Degrad Stab. 2018;154:55-61. https://doi.org/10.1016/j.polymdegradstab.2018.05.027

Zhu Y, Zhu R, Chen Q, Laipan M, Zhu J, Xi Y, He H. Calcined Mg/Al layered double hydroxides as efficient adsorbents for polyhydroxy fullerenes. Appl Clay Sci. 2018;151:66-72. https://doi.org/10.1016/j.clay.2017.10.018