Ionic adsorption and characterization of biochar from discarded potatoes

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ABSTRACT: Studies aimed at mitigating environmental impacts have received attention in recent years. The use of biochar obtained from the pyrolysis is an alternative for the recovery of organic materials that usually are directly discarded in the environment. Biochar has the potential to recover nutrients from wastewater, and in the latter case, the reuse or recycling of biochar as a controlled-release fertilizer could be an option. However, the adsorption characteristics of the ions into different biochars have not been known. The aim of this study was to evaluate the ions adsorption in biochar derived from discarded potatoes, as well as to make physical and chemical characterization of the produced materials. The biochar derived from discarded potatoes was produced by pyrolysis at 450 °C under an N2 atmosphere. In order to define its ionic profile, the adsorption of $H_nPO_4^{(3-n)-}$, Ca^{2+}, Mg^{2+}, and Al^{3+} was tested in pure biochar, as well as adsorption of $H_nPO_4^{(3-n)-}$ in biochar after it was doped with Al^{3+}. The desorption of these ions was tested by washing with deionized water, and the KCl (1.0 mol·L^{-1}) and Mehlich-1 extractors. In absolute values, the adsorption order of the ions was Al^{3+} (in acid pH value) = Ca^{2+} > Al^{3+} > $H_nPO_4^{(3-n)-}$ (biochar doped with Al^{3+}) > Mg^{2+} > $H_nPO_4^{(3-n)-}$ (biochar without doping). The adsorption of $H_nPO_4^{(3-n)-}$ was positively influenced by the doping of biochar with Al^{3+}. The biochar has preferential characteristics for cations adsorption, and the doping process can aid in adsorption of anions.

Key words: eutrophic water, cation, doping, biofertilizer, anion.

INTRODUCTION

Eutrophication of water from poor use of the soil and from agricultural systems, from animal waste, and from sewage and household garbage has become an increasing problem, given its environmental impact on aquatic flora and fauna. Biochar, the product of pyrolysis of plant and animal residues (Lehmann and Joseph 2015), is an adsorbent of various chemical elements, such as nutrients for plants, heavy metals, etc. (Cui et al. 2016; Jung et al. 2015a; Takaya et al. 2016).

Biochar has potential for safe disposal of waste. The increase in recalcitrance and the stability of this waste from pyrolysis of the product is provided by fixed carbon (Agegnehu et al. 2016; Lehmann and Joseph 2015; Maurer et al. 2017; Puga et al. 2015; Smith 2016; Teichmann 2014). In addition, the application of biochar on the soil carries other benefits, such as an increase in the availability of nutrients such as N and P (Sánchez-García et al. 2016), an increase in moisture content and in soil structure (Atkinson et al. 2010), an increase in pH (Agegnehu et al. 2016), and promotion of microbial conditions (Madari et al. 2012).

Considering potato production, the waste and residues in agriculture are huge, particularly due to losses in the field, and also the lack of marketing conditions. In addition, the potatoes without commercial value that are kept in the field after harvest can be a source of pathogens (Reddy 2017; Rossmann et al. 2018). Furthermore, the manufacture of starch

from potatoes produces a lot of solid waste, which the direct disposal of this biomass into the environment can lead to environmental damage (Moreno-Piraján and Giraldo 2011). Aiming to make good use of discarded potatoes, Moreno-Piraján and Giraldo (2011) produced activated carbon from the pyrolysis of potato peel with the subsequent addition of $ZnCl_2$. The mesoporous carbon obtained presented with high surface area and pore volume which had the copper sorption capacity of 74 mg·g^{-1}. Thus, the pyrolysis of potato residues is an interesting option to reduce environmental and economic damage.

In highly weathered latosols, the high P fixing capacity in the soil Fe and Al oxyhydroxides implies competition for P among soil and plant drains (Roy et al. 2016). Furthermore, in these soils, N losses are significant, whether by leaching of nitrate or volatilization of ammonia, which cause economic and environmental disruption for their agricultural utilization. Production and use of organomineral fertilizers and controlled release aim to minimize these problems. However, the use of unstabilized organic materials maintains the original undesirable characteristics, such as a source of greenhouse gases and the presence of pests and diseases. Pyrolysis of these organic materials makes them a stable matrix for directing nutrients to plants.

Biochar, given the high presence of negative charge sites, such as carboxylic and phenolic groups, behaves like a large anion, with resultant high CEC (Cui et al. 2016). When it is subjected to a process called doping, characterized by addition of metallic cations such as Mg^{2+}, Ca^{2+}, Al^{3+}, or $Fe^{2+/3+}$ to the material of origin or after its pyrolysis (Jing et al. 2015), they act as cation bridges, and thus acquire the characteristic of anion exchange capacity (AEC), with the capacity of adsorbing anions in return (Jung et al. 2015b; Lawrinenko et al. 2017).

Novais et al. (2018a) studied biochars from chicken manure (BCM) and sugarcane biomass (BSCB), both pyrolyzed at 350 °C and subjected to doping with Al^{3+} (doping process was performed after pyrolysis of the materials). The maximum values of adsorption capacity of $H_nPO_4^{(3-n)-}$ were 701.6 mg·g^{-1} for BCM and 758.9 mg·g^{-1} for BSCB. The cationic characteristic of the nondoped biochars emerges in this study through the lack of adsorption of $H_nPO_4^{(3-n)-}$ by these materials. According to these authors, these values of adsorption for the biochars doped with Al^{3+} indicate the possibility of having a biofertilizer with 70.1 and 75.9% of P in w/w or, notably, with more than 100% P_2O_5 (161.2 and 174.6%, respectively). It is noteworthy that these biofertilizer contains Al in their composition, which is an element that is toxic to plants when present in soils with acidic pH value. Thus, the application of the biofertilizer must consider not only the P concentration but also the Al concentration and the pH value of the soil in which the fertilizer was applied, questioning the agronomic viability of applying these materials.

Therefore, in the study of Novais et al. (2018b) aiming to evaluate alternative cations for biochar doping, the BCM and BSCB were pyrolyzed at 350 and 650 °C, and the materials were subjected to predoping with Mg^{2+} (doping of materials was performed before the pyrolysis). The authors found the maximum values of adsorption of 250.8 and 163.6 mg·g^{-1} at 350 and 650 °C for BCM. For the BSCB, the maximum values of adsorption obtained were 17.7 and 17.6 mg·g^{-1} of P at temperatures of 350 and 650 °C, respectively. The authors showed a satisfactory adsorption capacity of P in biochar doped with Mg^{2+}, which may be a viable alternative to the use of Al, since Mg is considered a nutrient.

Nevertheless, Yao et al. (2012) consider that it is not clear how the application of biochar in the soil affects nutrient availability. In a study with 13 pure (nondoped) biochars from different organic materials, they noticed that most of them showed little to no ability in adsorbing nitrate or phosphate, and that 9 of them were efficient in removing ammonium from an aqueous solution. Therefore, these authors consider it essential to study the adsorption characteristics of a biochar before its agricultural use. Thus, it becomes important to know the capacity to adsorb nutrients in different pure and altered (doped) biochars so as to produce fertilizers with slow and sustainable release of nutrients or materials able to remove nutrients from eutrophized waters or wastewaters, in the latter case for the purpose of establishing an option for reuse or recycling of these nutrients.

Potato (*Solanum tuberosum* L.) is in fourth place among the main foods consumed by humans (FAO 2016). Although production is high, part of it is discarded, whether as a result of tuber diseases or because the potatoes do not meet the demands of the consumer market, thus making them a problem from the economic and environmental perspective. Different biochars may have positive or negative net surface charges (Lehmann et al. 2011). As the ionic profile of biochar from potato is not available, the aim of this study is to investigate its ionic adsorption, as well as determine its physical and chemical characteristics.

MATERIAL AND METHODS

Organic waste used

Tubers of potato (*Solanum tuberosum* L.), cultivar Agata, were used to produce biochar. First, the samples were washed in running water and maintained in a forced air circulation oven at 70 °C until the material achieved constant weight. After drying, the material was ground in a Wiley mill equipped with a 1.27-mm mesh sieve. The ground potato underwent a prepyrolysis process in a muffle furnace at 150 °C for 4 h to remove excess water. This prepyrolysis material was placed in a tubular oven for production of biochar, at a temperature of 450 °C for 4 h, with a 10 °C per min rise in temperature. An N_2 cylinder was used, with a flow of 100 $cm^3 \cdot min^{-1}$ and purity of 99.9%.

Adsorption of P, Ca, Mg, and Al

Having obtained the potato biochar, information regarding its ionic profile was sought. To do so, the adsorptions of $H_nPO_4^{(3-n)-}$, Ca^{2+}, Mg^{2+}, and Al^{3+} (this last substance under two pH conditions: controlled in an acidic range and without control) were tested in pure biochar, as well as adsorption of $H_nPO_4^{(3-n)-}$ in biochar doped with Al^{3+}. The adsorption tests consisted of addition of separate concentrations of these elements. All analyses were made in triplicate.

For P, the method of determination of remaining P (Alvarez et al. 2000) was applied, which, in soil fertility, refers to a measure of buffering capacity or P capacity factor of soils (Novais and Smyth 1999). They are remaining-P concentrations in solution, obtained after shaking of 60 $mg \cdot L^{-1}$ of $H_nPO_4^{(3-n)-}$ in a 10 $mmol \cdot L^{-1}$ $CaCl_2$ solution with the biochar sample at a biochar:solution ratio of 1:10 (w/v) for 5 min at 200 rpm.

For adsorption of Ca^{2+}, Mg^{2+}, and Al^{3+}, the procedures were similar to those adopted for P, but these were at the concentration of 100 $mg \cdot L^{-1}$ in their chloride forms ($CaCl_2 \cdot 2H_2O$, $MgCl_2 \cdot 6H_2O$, and $AlCl_3 \cdot 6H_2O$) in aqueous solution, without the addition of $CaCl_2$. In the case of Al^{3+}, the procedure was carried out in two manners, under the supposed need to preserve the pH of the solution acidic to maintain the solubility of the Al3+.

For Al^{3+}, in addition to the objective of determining the magnitude of its adsorption, a biochar sample was subjected to what is called doping by this cation so as to develop and/or increase the AEC of the material and make it adsorbent of phosphate. To do so, after contact of the Al^{3+} solution with biochar, 0.1 $mol \cdot L^{-1}$ HCl was added until the pH stabilized in an acidic condition, with a value of around 4.5, in which Al remains in its ionic form (Al^{3+}), since raising pH above 5.2–5.5 causes its complete hydrolysis, with formation of the precipitate aluminum hydroxide (Greenland 2015). After shaking and resting, the biochar, at this stage doped, was filtered and recovered. Under this condition, its remaining P was measured, as was also done beforehand for its nondoped condition, to find how much the AEC of this material increased.

After shaking of each standard solution prepared with biochar, all were left to rest for 16 h, after which they were filtered and washed once with deionized water, using a laboratory wash bottle, to remove any excess that may have remained on the biochar structure or in the filter and which was not truly adsorbed. The concentrations of P, Ca^{2+}, Mg^{2+}, and Al^{3+} were determined in each standard solution, in the extract after filtering, and in the deionized water after washing. The sum of the amount of the element of the extract with the filtrate indicated the amount that was not adsorbed. The difference between the initial amount placed under shaking with the biochar and the sum of the extract and of the filtrate resulted in the amount adsorbed in the biochar in weight/weight.

Desorption of P, Ca, Mg, and Al

To assess the stability of adsorption of elements in the biochar, after the biochar was washed once with deionized water, as described above, successive extractions were performed. For the cations Ca^{2+}, Mg^{2+}, and Al^{3+}, the extractant KCl (1 $mol \cdot L^{-1}$) was used, whereas for $H_nPO_4^{(3-n)-}$, the extractant of available P of the soil, Mehlich-1, was used. The procedures used were similar to those for determination of their exchangeable and available forms in the soil (Donagema et al. 2011; Tedesco et al. 1995).

Accordingly, after washing with deionized water, the biochar samples with the adsorbed elements, still on the filter paper so as not to lose part of the biochar sample retained on it and not measurable, were transferred to Erlenmeyer flasks and subjected to extractions and determinations of the elements in the filtrate. Further extractions were performed, similar to the first, until the amounts of the elements extracted were no longer detectable.

Control of pH of the solutions

So as to evaluate the behavior of the pH of the solutions and the buffering level of the biochar, the pH was read throughout the process. Before shaking, the pH value of the suspension (initial pH) was measured. After shaking, the suspension was left to rest for 16 h, after which the pH (final pH) was measured. After that, the solution was filtered with the use of fast filtering quantitative filter paper, followed by reading the pH of the filtrate (pH of the extract). The material was washed while still on the filter paper with deionized water, and the pH (pH after washing) was determined.

Total concentrations of the elements in the material

Nitric perchloric digestion of the prepyrolysis potato and of the biochar were carried out to determine the total concentrations of P, Ca, Mg, and Al in this raw material, as well as the influence of pyrolysis on these concentrations.

Characterization of the materials

Samples of the prepyrolysis potato, of the pure biochar, and of the biochars after being treated with $H_nPO_4^{(3-n)-}$, Ca^{2+}, Mg^{2+}, and Al^{3+} were characterized physically and chemically by means of the techniques of X-ray diffraction (XRD), attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy, and scanning electron microscopy (SEM).

The XRD analyses were made on Shimadzu XRD-6000 equipment, using a graphite crystal as monochromator to select the radiation of the Cu-Kα1 with λ = 1.5406 Å and a step of 0.02° s⁻¹, with scanning angle (2θ) from 4 to 70°.

The ATR-FTIR analyses were performed in a Jasco spectrometer, model FT/IR-4100. The spectra were obtained in a wavelength range from 4000 to 400 cm⁻¹, resolution of 4 cm⁻¹ and 256 scans.

For SEM analyses, the samples were held on double-sided thermal conductive adhesive tape and covered with a fine gold film. The morphology of the materials was analyzed using a scanning electron microscope (SEM) Zeiss EVO 50.

Statistical analysis

The pH values and the concentrations of the elements in the solutions, the amounts adsorbed, and the total concentrations of the elements in the pre- and postpyrolysis potato underwent descriptive statistical analysis, in which the measure of mean dispersion adopted was the standard error. Adsorption of $H_nPO_4^{(3-n)-}$ (doped and nondoped biochar) and Al^{3+} (with and without correction of pH) were compared by the F test at the level of 1% significance. The SPEED Stat software was used[4]. The results of XRD and ATR-FTIR were plotted on the OriginPro 8.5 software.

RESULTS AND DISCUSSION

Potato biochar exhibits preferential adsorption of the cations (Ca^{2+}, Mg^{2+}, and Al^{3+}) in relation to $H_nPO_4^{(3-n)-}$ (Table 1), confirming statements in diverse studies that biochar represents, in general, a *large anion* (Cui et al. 2016; Jing et al. 2015). The much lower retention of $H_nPO_4^{(3-n)-}$ (0.14 mg·g⁻¹ or 0.014 % in w/w) suggests the involvement of physical adsorption of

$H_nPO_4^{(3-n)-}$ as a consequence of diffusion of this element in micropores and fractures that exist in this material, as cited in the literature (Atkinson et al. 2010; Lehmann et al. 2006; Sizmur et al. 2017). Certainly, a similar mechanism occurred to the cations under study by the effect added to their adsorptions in the electronegative environment that exists in these empty spaces.

Table 1. Values related to adsorption* of $H_nPO_4^{(3-n)-}$, Ca^{2+}, Mg^{2+}, and Al^{3+}, in potato biochar.

Element	Concentration of the element				Total adsorbed
	Expected	Found	Extract	Washing (H$_2$O)	
	·········· mg·L^{-1} ··········				Mg·g^{-1}
P	60	56.1	28.36 ± 1.52	14.18 ± 1.07	0.14 ± 0.02
Ca	100	103.2	8.15 ± 0.71	4.77 ± 0.43	0.90 ± 0.01
Mg	100	98.0	57.90 ± 3.08	14.75 ± 3.21	0.25 ± 0.06
Al	100	106.0	12.48 ± 1.23	17.71 ± 3.85	0.76 ± 0.04
[1]Al$_{4.5}$	100	106.0	5.60 ± 4.07	10.10 ± 7.11	0.90 ± 0.11
P ([2]BB-Al)	60	56.1	0.01 ± 0.10	0.13 ± 0.03	0.56 ± 0.01

*Mean ± standard error. [1]Al$_{4.5}$: pH controlled at 4.5. [2]BB-Al: Potato biochar previously doped with Al. Source: Elaborated by the authors.

The adsorption found for Al^{3+} with the initial pH value adjusted to 4.5 (Table 1), of 0.90 mg·g^{-1}, indicates the greater adsorption for this cation, similar to that of Ca^{2+} and, finally, Mg^{2+}, approximating the classic lyotropic series of sequential priority of cation adsorption: higher energy of adsorption for cations of higher valence, followed by those of the same valence, and, for these, as a priority, by those of greater ionic radius and, consequently, smaller hydrated radius (Novais and Mello 2007), explaining lower adsorption of Mg^{2+}. Thus, this result suggests the predominant involvement of ionic and noncovalent bonds as a mechanism of adsorption of these cations in the biochar, which also explains the opposite sequential results regarding the desorption of these same cations (Table 2).

Table 2. Values related to desorption* of $H_nPO_4^{(3-n)-}$, Ca^{2+}, Mg^{2+}, and Al^{3+} in potato biochar subjected to three successive extractions.

Element	Concentration of the element			Residual adsorbed after three extractions
	1st Extraction	2nd Extraction	3rd Extraction	
	·········· mg·L^{-1} ··········			Mg·g^{-1}
[1]P	1.15 ± 0.03	0.74 ± 0.08	0.32 ± 0.10	0.12 ± 0.02
[2]Ca	6.29 ± 0.06	7.41 ± 0.39	8.76 ± 0.15	0.68 ± 0.03
[2]Mg	11.63 ± 0.55	9.85 ± 0.17	1.12 ± 0.54	0.03 ± 0.01
[2]Al	12.95 ± 0.24	5.41 ± 0.32	2.62 ± 0.15	0.55 ± 0.03
[2]Al$_{4.5}$	4.87 ± 0.08	2.45 ± 0.02	1.10 ± 0.02	0.82 ± 0.07

*Mean ± standard error. Extractants: [1]Mehlich-1 (P) and [2]1 mol·L^{-1} KCl (Ca^{2+}, Mg^{2+}, and Al^{3+}). Al$_{4.5}$: value of pH adjusted to 4.5. Source: Elaborated by the authors.

The studies on desorption of cations and of $H_nPO_4^{(3-n)-}$ (Table 2) indicate nondesorbed amounts retained, a probable consequence of the chemical and physical retention of Ca^{2+}, Mg^{2+}, and Al^{3+} and, in the case of P, probably only of physical retention of P. Higher desorption of Mg^{2+} is observed in comparison to the other cations (Table 2), which is due to its greater hydrated radius, and thus lower binding energy. When the pH of the Al^{3+} solution was controlled, the KCl extractant was less efficient in extracting this cation from the surface of the biochar. For P, the successive extractions practically did not remove it, reinforcing the idea of diffusion of this element in micropores and fractures that exist in this material and not of chemical adsorption on the surface (Atkinson et al. 2010; Lehmann et al. 2006; Sizmur et al. 2017).

The values of adsorption found for Al^{3+} (0.90 mg·g^{-1}) (Table 1) in the biochar doping process are much, much smaller than those found by Novais et al. (2018a): 701.6 mg·g^{-1} in chicken manure biochar and 758.9 mg·g^{-1} in sugarcane biomass biochar. The probable reason for this is the difference between the material of origin used for production of the biochars and the procedure adopted for determination of maximum adsorption capacity of Al^{3+} (MACAl) by those authors. Regarding the raw material used in biochar production, the literature abundantly shows expressive differences in ionic adsorption among materials as a variable of their origin (Jung and Ahn 2016; Jung et al. 2016; Yao et al. 2013; Zhang and Gao 2013).

Comparison of the magnitude of adsorption of $H_nPO_4^{(3-n)-}$ as a consequence of doping of biochar shows that doping leads to an increase in adsorption of $H_nPO_4^{(3-n)-}$(Table 3), which corroborates that observed by Novais et al. (2018a). However, there is a big difference in adsorption of $H_nPO_4^{(3-n)-}$ between the two biochars doped with Al^{3+}, 0.56 and 701.5 mg·g^{-1}, in this study and in Novais et al. (2018a), respectively. In their study, Novais et al. (2018a) used concentrations of Al^{3+} that ranged from 0 to 3000 mg·L^{-1}, so as to have MACAl by the Langmuir isotherm. The present study used only 100 mg·L^{-1}. This low concentration used was for the purpose of simply assessing the hypothesis of cationic adsorption prevailing over anionic adsorption. Therefore, in the study of Novais et al. (2018a), the biochar was doped with the maximum amount of Al^{3+} obtained by means of the isotherm and, in our study, with a concentration of only 100 mg·L^{-1}. Whereas in the former study the development of positive charges for adsorption of $H_nPO_4^{(3-n)-}$ was maximum, in the latter study, it was comparatively minimum.

Table 3. Comparison between the values of adsorption of $H_nPO_4^{(3-n)-}$ without and with doping with Al^{3+}, as well as adsorption of Al^{3+}, without and with correction of pH of the solution, in potato biochar.

Adsorption of $H_nPO_4^{(3-n)-}$ (mg·g^{-1})		Adsorption of Al^{3+} (mg·g^{-1})	
$H_nPO_4^{(3-n)-}$ (biochar without doping)	0.14 b	Al^{3+} (pH without correction)	0.76 a
$H_nPO_4^{(3-n)-}$ (biochar with doping)	0.56 a	Al^{3+} (corrected pH = 4.5)	0.90 a

Means followed by the same letter in the column do not differ by the F test at the level of 1% probability. Source: Elaborated by the authors.

From the lack of statistical difference between the values found for the concentration of Al^{3+} in the extract with pH not corrected and that with pH of 4.5, it can be questioned whether there is the need to stabilize initial pH in the doping process in an acidic range, as suggested by Novais et al. (2018a), and not alkaline, like the pH originally found in the biochar (Table 4).

Table 4. Values of pH of the $H_nPO_4^{(3-n)-}$, Ca^{2+}, Mg^{2+}, and Al^{3+} solutions* subjected to shaking in contact with potato biochar.

Element	initial pH	final pH	pH extract	pH after washing
P	8.95 ± 0.10	9.62 ± 0.08	9.58 ± 0.04	9.44 ± 0.02
Ca	9.47 ± 0.02	9.86 ± 0.14	9.79 ± 0.01	9.59 ± 0.06
Mg	9.43 ± 0.04	9.60 ± 0.05	9.75 ± 0.01	9.63 ± 0.03
Al	9.09 ± 0.01	9.53 ± 0.08	9.58 ± 0.02	9.36 ± 0.03
$Al_{4.5}$	4.17 ± 0.23	9.30 ± 0.34	9.16 ± 0.33	9.10 ± 0.31

*Mean ± standard error. $Al_{4.5}$: pH adjusted to 4.5. Source: Elaborated by the authors.

The significant adsorption of Al^{3+} in the biochar, as also observed in other studies (Jung et al. 2015b; Zhang and Gao 2013), indicates that it can be successfully used in doping processes so as to develop its capacity to adsorb anions, and particularly those responsible for water eutrophication, such as phosphate and nitrate (Dodds et al. 2009; Howarth and Marino 2006). Thus, with these anions adsorbed, it can constitute a slow-release fertilizer for agriculture, as well as deepen the concept of reuse or recycling of nutrients for agricultural production (Fang et al. 2015; Jung et al. 2016; Sizmur et al. 2017).

The pH values of the solutions throughout the adsorption process are shown in Table 4. It can be seen that biochar is a material with very high basic buffering, just as cited in the literature (Novais et al. 2018a). Regardless of the solution prepared and the stage of adsorption, the biochar maintained the pH value of the medium around 9.0. Even in the case in which the pH of the Al^{3+} solution was previously corrected to 4.5, after the shaking process, it returned to 9.0.

The total concentrations of P, Ca, Mg, and Al were determined before and after pyrolysis of the tubers (Table 5). The P and Mg concentrations in prepyrolysis are similar to those found by Fernandes et al. (2011), whereas the Ca concentration is much greater. The Al concentration was not detectable. After pyrolysis, the nutrient concentrations increased, and it was also possible to detect Al concentrations (Table 5). These initial concentrations and increases were the consequence of the effect of concentration given the loss of weight of material in the pyrolysis process, as well as of the fertilization profile of the potato crop, especially in regard to the high demand for P (Fernandes et al. 2015).

Table 5. Total concentrations* of P, Ca, Mg, and Al in prepyrolysis potato (used for biochar production) and postpyrolysis (potato biochar) subjected to nitric perchloric digestion.

Element	Concentration (mg·g⁻¹)	
	Prepyrolysis potato	Postpyrolysis potato (Biochar)
P	2.75 ± 0.04	8.43 ± 0.12
Ca	4.30 ± 0.23	6.50 ± 0.38
Mg	1.45 ± 0.03	3.50 ± 0.03
Al	0.00 ± 0.00	0.42 ± 0.05

*Mean ± standard error. Source: Elaborated by the authors.

The XRDs for the samples of prepyrolysis potato (PP), potato biochar (PB), and potato biochar after contact with solution of 60 mg·L⁻¹ of $H_nPO_4^{(3-n)-}$ (PB-P); after contact with solution of 100 mg·L⁻¹ of Ca^{2+} (PB-Ca); after contact with solution of 100 mg·L⁻¹ of Mg^{2+} (PB-Mg); after contact with solution of 100 mg·L⁻¹ of Al^{3+} (PB-Al); after contact with solution of 100 mg·L⁻¹ of Al^{3+} in controlled pH (PB-Al4.5); and after doping with Al^{3+} and contact with solution of 60 mg·L⁻¹ of $H_nPO_4^{(3-n)-}$ (PB-Al+P) are shown in Fig. 1.
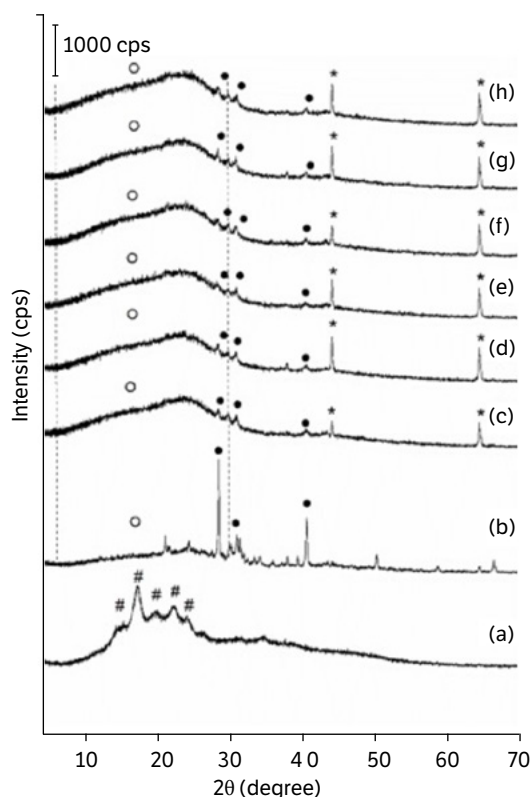
Figure 1. X-ray diffractograms for PP (a); PB (b); PB-P (c); PB-Ca (d); PB-Mg (e); PB-Al (f); PB- Al4.5 (g); and PB-Al+P (h).

Note. # = peaks of amylopectin chains; ○ = peaks of graphite structure; ● = peak of amorphous structure; * = peaks in reference to the Al of the sample holder. Source: Elaborated by the authors.

Diffraction peaks in the 2θ region from 15° to 25° (#) (Fig. 1a) are related to the structural organization of amylopectin chains (Gallant et al. 1997). This is part of starch composition, which is the form of sugar reserves in potato tubers (Zhao et al. 2018). The wide peak (2θ = 15°), the strong peak (2θ = 17°), and the double peak (2θ = 22–24°) are patterns of type B starch (Hizukuri et al. 2006). The basal spacing (distance between the amylopectin chains) calculated by Bragg's Law ($n\lambda = 2d_{-hkl}sen\theta$) is 3.20 Å. The diffraction peaks 2θ = 28°, 30–32°, and 42° (●) (Fig. 1b) are characteristics of the graphite

structure (Stanjek and Häusler 2004; Sun et al. 2008). These are repeated in the biochar after contact with the ions in a less intense way (Figs. 1c–h). The wide flattened peak in the 2θ position between 5° and 30° characterizes the amorphous structure of the samples (º) (Figs. 1b–h). Amorphous materials do not present a diffraction pattern of narrow peaks as in crystalline materials, but rather wide peaks, due to the irregular arrangement of the atoms (Chauhan and Chauhan 2014). The peaks 2θ = 44° and 65°, demarcated by *, are in reference to the Al of the sample holder.

The spectra of ATR-FTIR for PP, PB, PB-P, PB-Ca, PB-Mg, PB-Al, PB-Al$_{4.5}$, and PB-Al+P are shown in Fig. 2. The band from 3600 to 3000 cm^{-1} (Fig. 2a) is attributed to stretching of the O–H bonds of the hydroxyl groups and also of H$_2$O molecules (Castro et al. 2018a; 2018b; 2020a; 2020b). These groups are present in cellulose, hemicellulose, and lignin (Zugernmaier 2008). The band of 1700 cm^{-1}, present in all samples (Figs. 2a–h), refers to the double C=O bonds, of vibration of aromatic groups (Ferreira et al. 2015). After calcination of the material, this band decreases in intensity and undergoes small variations of displacement. The intense band at 1000 cm^{-1} (Fig. 2a) refers to the stretching of C–O and the vibration of C–H of the cellulose present in the potato tuber (Ferreira et al. 2015).
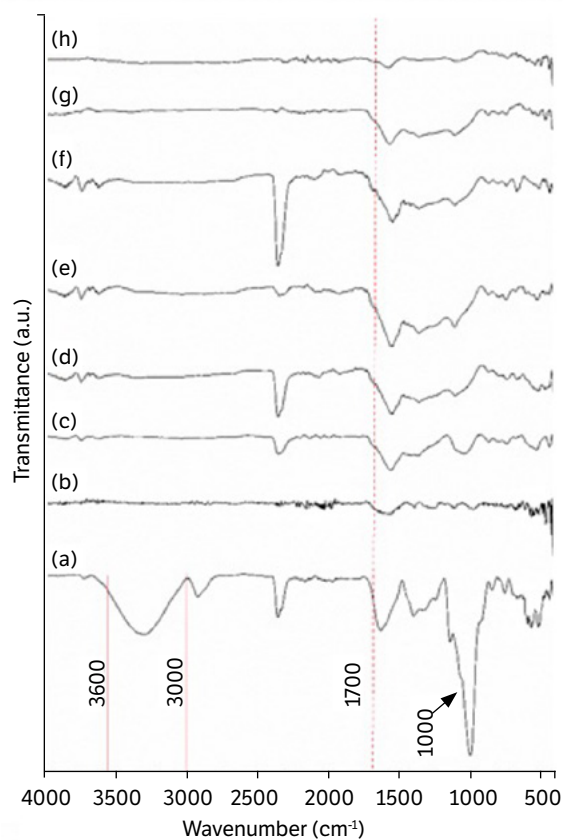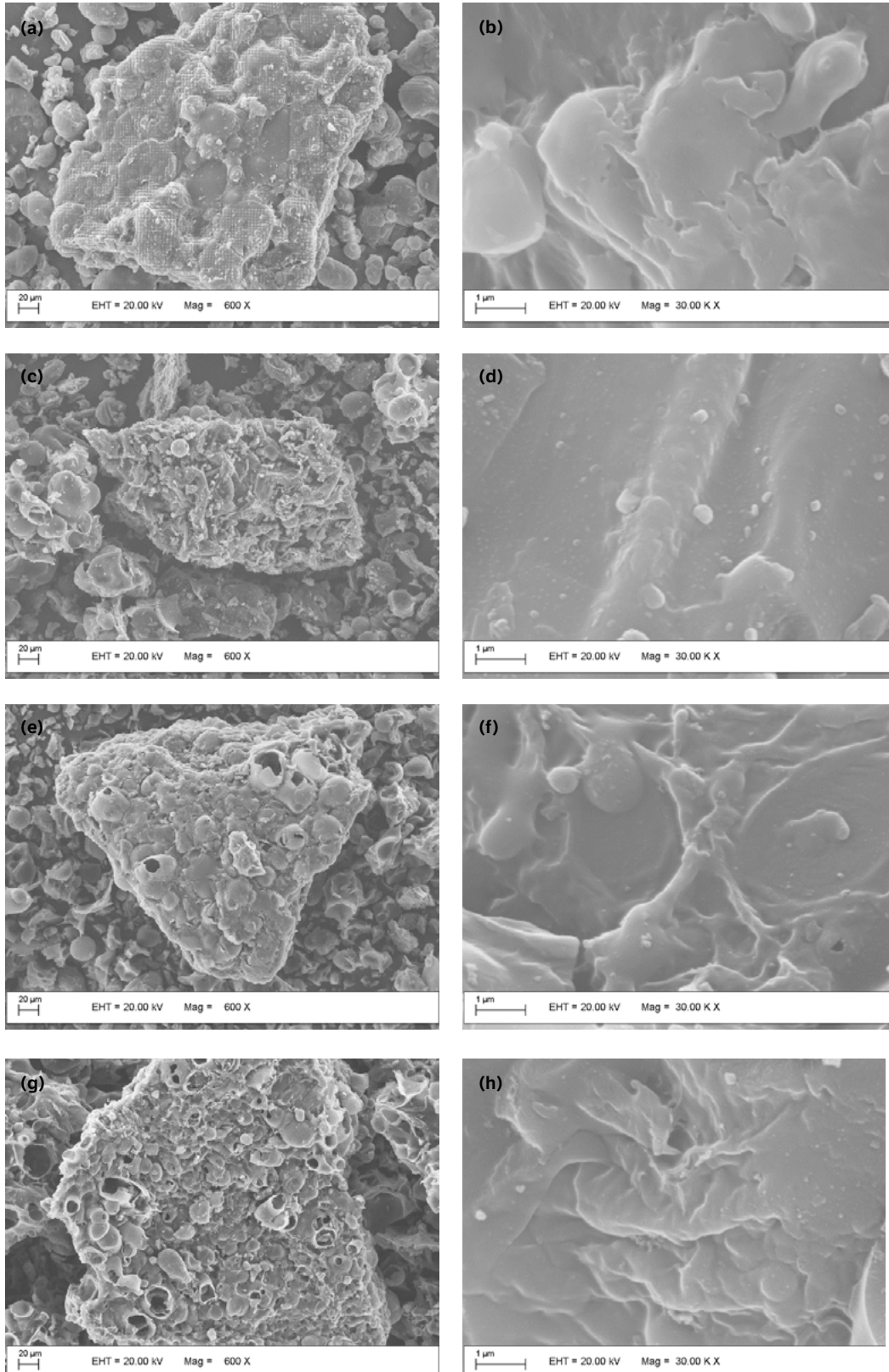

Figure 2. Spectra of ATR-FTIR for PP (a); PB (b); PB-P (c); PB-Ca (d); PB-Mg (e); PB-Al (f); PB-Al4.5 (g); and PB-Al+P (h).
Source: Elaborated by the authors.

The representative images from SEM are shown in Fig. 3. A complex, porous structure of material in pre- and postpyrolysis is observed (Figs. 3a–d). The addition of the anion (H$_n$PO$_4^{(3-n)-}$) makes the structure a little porous (Figs. 3e and f). The addition of the cations (Ca^{2+}, Mg^{2+}, and Al^{3+}) to the biochar makes its structure more porous (Figs. 3g, i, k, m and o). The micropores present have a diameter of 20 nm, and after the addition of cations, they undergo a slight increase.

The results obtained are promising, in spite of the reduced values of adsorption of the ions studied. Biochar can be a viable alternative for getting around environmental and agronomic problems related to losses of nutrients in the system. Deeper studies are needed in relation to the diverse raw materials that can be used, as well as other possible processes of doping that may make optimization of the biochars feasible.
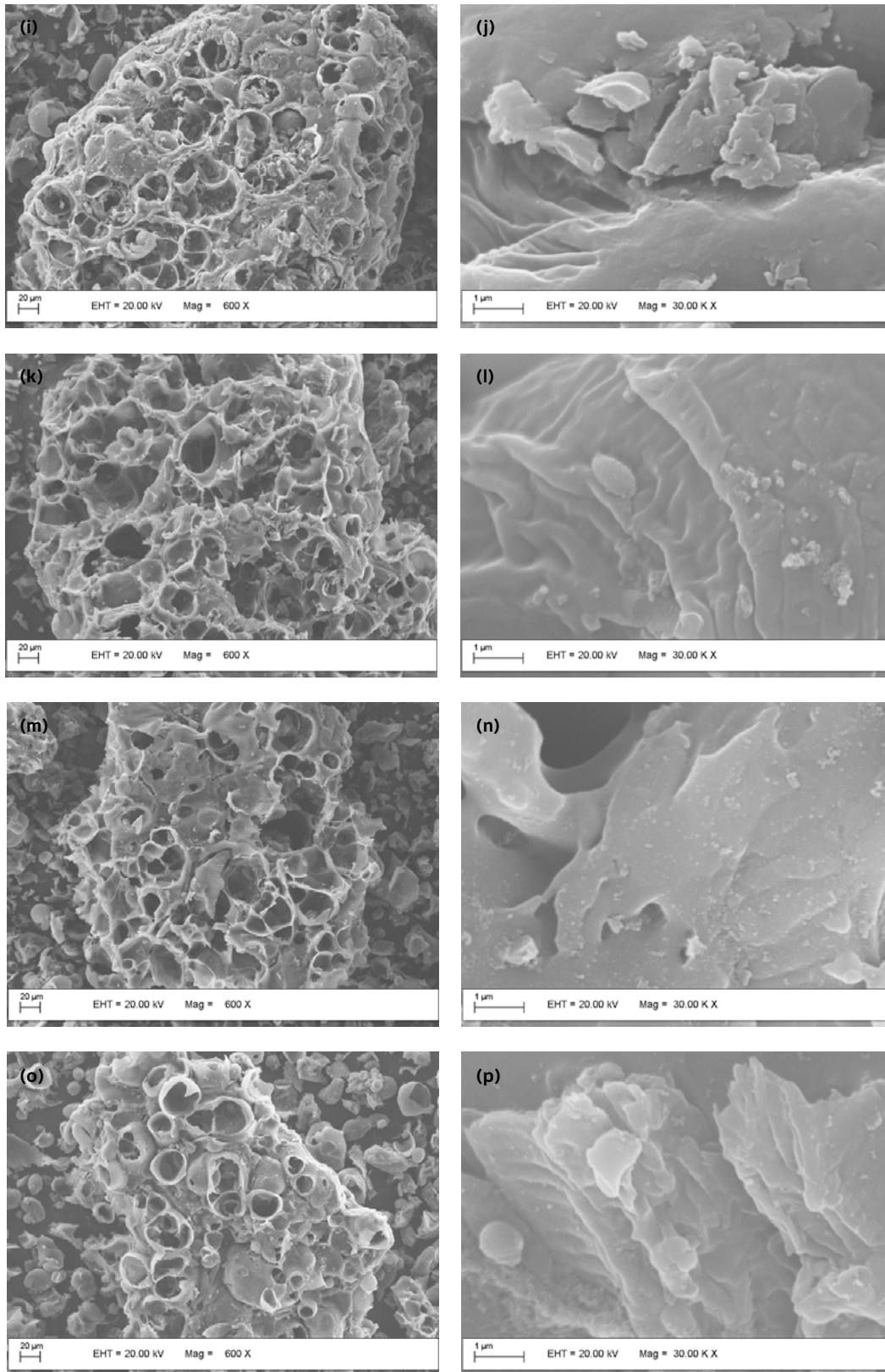
Figure 3. Images obtained by SEM at different magnifications (600 and 30000 ×) for PP (a, b); PB (c, d); PB-P (e, f); PB-Ca (g, h); PB-Mg (i, j); PB-Al (k, l); PB-Al4.5 (m, n); and PB-Al+P (o, p).

Source: Elaborated by the authors.

CONCLUSION

Potato biochar shows preference for adsorption of cations, and doping with Al^{3+} proves to be efficient for increasing adsorption of anions, such as $H_nPO_4^{(3-n)-}$. The probable low concentrations of the elements used for adsorption did not allow good detection of significant differences by the techniques used among the materials obtained.

AUTHORS' CONTRIBUTION

Conceptualization, Gonçalves, F. A. R., Castro, G. F., Tronto, J. and Novais, R. F.; **Methodology,** Gonçalves, F. A. R., Castro, G. F., and Tronto, J.; **Investigation,** Gonçalves, F. A. R., Castro, G. F., Tronto, J. and Novais, R. F.; **Writing – Original Draft,** Gonçalves, F. A. R., Castro, G. F., Tronto, J. and Novais, R. F.; **Writing – Review and Editing,** Gonçalves, F. A. R., Castro, G. F., Tronto, J. and Novais, R. F.; **Funding Acquisition,** Tronto, J. and Novais, R. F.; **Resources,** Tronto, J. and Novais, R. F.; **Supervision,** Castro, G. F., Tronto, J. and Novais, R. F.

DATA AVAILABILITY STATEMENT

All data sets were generated or analyzed in the current study.

FUNDING

ACKNOWLEDGMENTS

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