

Preparation of activated charcoal adsorbent from pitombeira seeds (*Talisia esculenta*) and its application for Ca^{2+} ions removal

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ABSTRACT

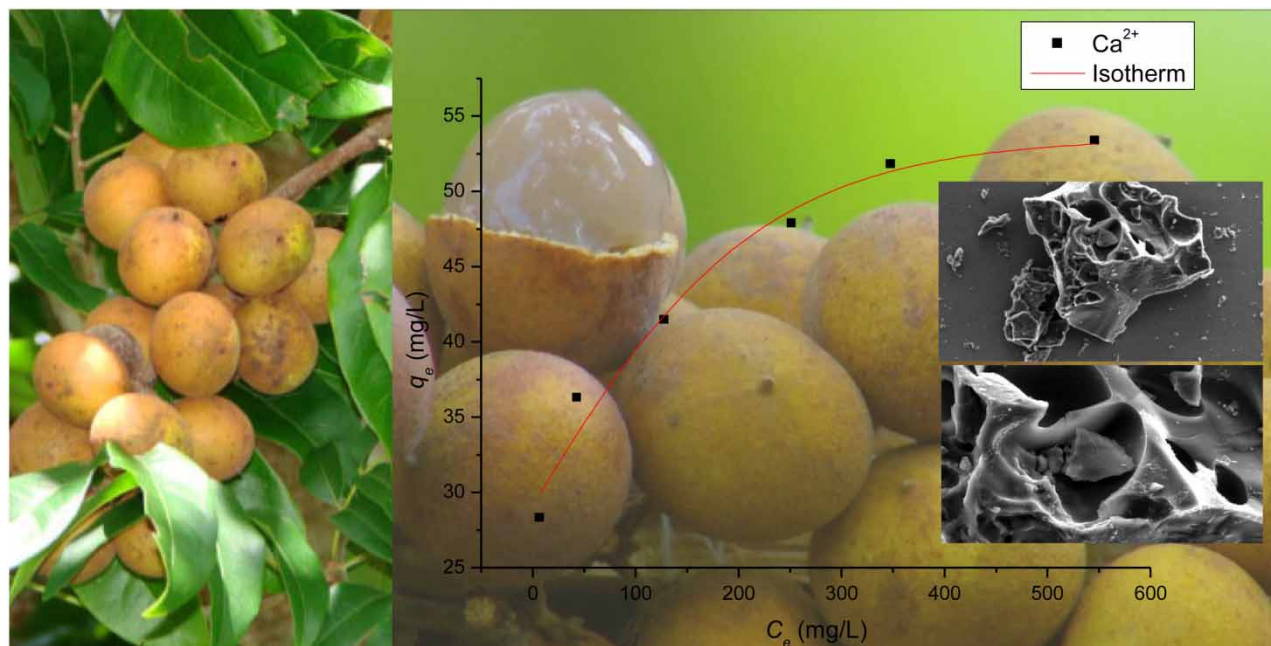
Water quality that the population has access to can undergo a series of changes, contaminations and interferences. Poor water quality may be related to several contamination sources and can pose a health risk for the ecosystem and for people. The calcium ion is a determinant of water hardness, and its excess in the human body can result in a series of complications and diseases such as renal and bladder lithiasis. The seeds of the pitombeira (*Talisia esculenta*) were used to produce phosphoric acid activated carbon (PAC). Adsorption studies were conducted by batch technique, and isothermal and kinetic models were systematically used to evaluate the potential of PAC to remove Ca^{2+} ions from aqueous media. The adsorbent was characterized using BET surface area (141.6 m^2/g), SEM, pH_{PZC} (2.75), Boehm titration, and by content analysis of the moisture and ashes. The time required for the system to equilibrate was only 5 min. According to the kinetics study, the data were best fitted by the pseudo-second-order model, while the equilibrium sorption data fitted well with the Freundlich model, with a maximum adsorption capacity of 19.05 mg/g, with 90% of Ca^{2+} ions removal. Therefore, due to its efficiency and low cost, PAC could be employed as an alternative adsorbent for Ca^{2+} removal.

Key words: activated carbon, adsorption, Ca^{2+} , isotherms, *Talisia esculenta*

HIGHLIGHTS

- Biocarbons are highlighted in fine chemistry and the production of new materials.
- High added value because the demand for chemoselective materials is of economic interest.
- Low production cost and ecological appeal today.
- Biochar seeks to meet the need for high selectivity systems to remove metals from contaminated water.
- Reduction of material discarded in nature, contributing to a more sustainable chemistry.

GRAPHICAL ABSTRACT



INTRODUCTION

Raw water or untreated water for human consumption can cause several types of endemic diseases. The health risks related to water regard two types of agents: biological agents, by direct contact or vectors, and chemical agents (Fu & Wang 2011). In Brazil, about 6.93 million households live without access to water through distribution systems, and a common strategy to overcome the lack of a supply network is using artesian wells. However, in most cases, the water that comes from them presents a high degree of salinization (hard water) and does not undergo any type of treatment before consumption (Brasil, Ministério da Saúde 2006). This situation can pose several problems, both for the population's health and for industrial use. Water with a high concentration of dissolved calcium and magnesium mineral ions is classified as hard water. These ions are derived from underground deposits, such as limestone or dolomite, and an excessive amount of these is added to the water composition in the form of bicarbonates, nitrates, chlorides, and sulfates (Piratoba *et al.* 2017). When water passes through the soil, the carbon dioxide in the water dissolves the limestone, making groundwater harder than surface water (Memon *et al.* 2011).

Regarding water hardness, the Brazilian Ministry of Health establishes for potable water standards the maximum permissible value of 500 mg/L for the sum of calcium and magnesium concentrations. Generally, when water contains less than 50 mg/L of CaCO_3 , it is considered as soft, up to 150 mg/L is classified as semi-hard, with less than 300 mg/L is labeled as hard and when it presents values above 300 mg/L it is classified as very hard (Brasil, Ministério da Saúde 2006; da Silva *et al.* 2016). As a comparison, European countries, such as Portugal, use the 150–500 mg/L range as a reference value for total hardness. The increased concentration of these metals in artesian wells may pose a serious threat to human health (Kozisek 2020). Calcium, although present in the human body as an essential element, both because it performs a series of functions related to cellular metabolism, as well as bone and tooth maintenance, when exceeded can bring a series of complications and diseases such as renal and bladder lithiasis, which are mainly associated with the intake of calcium and magnesium highly concentrated in water, and hypercalcemia, which is when the calcium level in blood is above normal (Kozisek 2020). Other problems related to an excess of calcium in the blood are renal failure, soft tissue calcification, headaches, and interference with the absorption of minerals such as magnesium, phosphorus, iron, and zinc (Whiting *et al.* 1997).

The means used to control and/or remove metal ion excess in aquatic systems are quite diverse. For instance, there are chemical precipitation (Liu *et al.* 2020) and reverse osmosis (Wang *et al.* 2020), as well as electrochemical methods (Xie *et al.* 2018). Adsorption is also a very versatile technique and, depending on the adsorbent type, is economically feasible. Among the many types of adsorbents available in the market for metal adsorption in aqueous media, the most important

are the activated carbons, which may be of both mineral and vegetable origin (Santoso *et al.* 2020). Activated carbons obtained from carbonaceous materials are characterized by high porosity and surface area, and are able to adsorb ions or molecules, both in the liquid and gas phase. There are several raw materials used for their preparation, such as wood, coconut husks, seeds, peat, sawdust, residues of fertilizers, and rubbers, among others (Nor *et al.* 2013). The use of lignocellulosic biomass for activated carbon production is an important approach as a strategy to take advantage of vegetal waste. The conversion of these wastes to value-added products, such as activated carbon, can solve environmental problems such as waste accumulation and air and water pollution (Tan *et al.* 2017).

The species *Talisia esculenta*, which is popularly known in Brazil as pitombeira and is abundant in northern states of the Brazilian northeast, mainly between January and April, may be an alternative for the production of activated carbon, since the consumption of its fruit, the pitomba, is restricted to its pulp. Excess, such as bark and stone, is discarded into nature as residue because it does not have a specific use (Guarin Neto *et al.* 2003). Therefore, the use of pitomba pits for the production of activated carbon can provide an alternative adsorptive material, of low cost and with a similar efficiency to that of biochars already available in the literature for the removal of different contaminants. The raw material type plays a principal role in the properties of the activated carbon, influencing its quality and overall characteristics (Abechi *et al.* 2013).

Thus, in this work, the adsorptive potential of phosphoric-acid-impregnated activated carbon originated from pitomba pits against calcium ions (Ca^{2+}) in an aqueous medium was investigated. The quantification of adsorbed quantities was carried out using the complexometric titration technique, using standard solutions of the metal cation titrated with ethylenediamine-tetraacetic acid (EDTA) in an aqueous medium. The experimental results were adjusted to isothermal and kinetic models (Sarabadian *et al.* 2019).

METHODS

Materials

The pitombas were purchased at the fairs of São Luis city/MA and their cores were separated from the pulp by hand. The chemical activator used was phosphoric acid (H_3PO_4) (SYNTH), the complexing agent was EDTA (SYNTH), Eriochrome black T indicator and calcium ions were generated from aqueous solutions of its carbonate (CaCO_3) (SYNTH). Deionized water was applied to prepare the solution in all experiments.

Instruments

The pitomba pits were oven-dried and crushed in a cyclone rotor mill (TE-651/2). The studies of thermal behavior and characterization were performed using a thermobalance, model TGA-51 (Shimadzu), in the following experimental conditions: (a) flow rate of 100 mL/min for synthetic air and 50 mL/min for argon; (b) alumina crucibles; (c) heating rate of 10 °C/min; (d) sample mass of 22.00 ± 0.50 mg; (e) temperature range of 25–600 °C. The pyrolysis was carried out in a Microprocessor Based Programmable Muffle Furnace 2000-C.

The moisture and ash content were performed according to the Technical Standards ASTM D 2867-09 (2014) and 2866-94 (2004) respectively. The specific surface area was determined by Quantachrome NovaWin, a surface area and pore size analyzer, using $\text{N}_2(\text{g})$ at a temperature of 77.35 K. The identification of functional groups present on the surface of the activated carbon was done by the Boehm method. Infrared absorption spectroscopy was performed using a Bruker Equinox 55 IR spectrometer. Infrared spectra were recorded at 4 cm^{-1} resolution over a wavenumber region of 400–4,000 cm^{-1} and 100 scans per sample on KBr pellets. The morphology of the materials was studied by scanning electron microscopy (SEM) analysis with 500-fold Phenom Pro X equipment. The surface pH at the point of zero charges of PAC was determined by isoelectric point titration as a function of pH using a HANNA HI-2315 digital pH meter.

Preparation and characterization

The pitomba pits were dried at 100 °C for 24 hours. The ground powder was put together with the activating agent (H_3PO_4) 100 mg/L, in a 1:1 ratio for 24 hours. To identify the best burning temperature of the material for the formation of the coal, a thermogravimetric analysis of the phosphoric-acid-impregnated pit was carried out. Based on the results of the thermogravimetric analysis, the burning temperature was set at 350 °C. After the burning step, the activated coal of the pitomba pits, called PAC, was obtained. PAC was washed with distilled water until the pH of the supernatant reached the pH of the distilled water used (pH = 5.9). After the washing process, the coal was oven-dried for one hour at 100 °C, crushed in a mortar, and set for granulometry ($\leq 150 \mu\text{m}$).

Determination of pH at point of zero charges (pH_{PZC})

The pH at the point of zero charges (pH_{PZC}) was determined using the batch equilibrium method. Amounts of 100 mg of the adsorbent and 10 mL of the 100 mg/L NaCl solution were added with pH values adjusted from 1 to 11 with 100 mg/L NaOH and HCl solutions. The mixtures were shaken at 25 °C for 24 hours at 99 rpm, and after this contact time they were filtered and the pH values (pH_{final}) were recorded.

Batch experiments

All adsorption tests were performed in batch, from a standard solution of CaCO_3 , 400 mg/L. The adsorbed quantities were determined by complexometric titration with EDTA 400 mg/L in aqueous medium using the Eriochrome black T indicator.

Equilibrium time

The kinetics study was conducted in a batch system. To each 100 mg of PAC was added 100 mL of Ca^{2+} ion solution at a concentration of 400 mg/L at pH 7. The system was under constant stirring at time intervals of 5–60 min. For each time interval, aliquots of 25 mL were removed and the Ca^{2+} ion content was quantified by complexometric titration.

Effect of pH

To verify the pH influence on Ca^{2+} adsorption, the studies were conducted in batches at 25 °C, with a coal mass of 0.1 g added in Erlenmeyers, with the same volume of solution (100 mL) and the same standard solution of CaCO_3 , 400 mg/L. The pH influence on the adsorption process was verified for pH ranges 2–3, 7, and 11–12, with 5 min contact and constant stirring. For pH correction, solutions of NaOH and HCl 100 mg/L were used.

Adsorption isotherms

The determination of the adsorption isotherms was performed with 100 mg of the adsorbent added to 100 mL of Ca^{2+} standard solution in concentrations ranging from 40 to 600 mg/L at pH 7. The system was kept under stirring at room temperature for 5 min. The adsorbent capacity, q_e (mg of the metal/g adsorbent) was determined based on the difference in concentration of the metal ions, from Equation (1):

$$q_e = \frac{(C_0 - C_e) V}{m} \quad (1)$$

where C_0 is the initial concentration of Ca^{2+} ions (mg/L) and C_e , the concentration of Ca^{2+} at equilibrium (mg/L); V is the volume of the solution (L), and m , the adsorbent mass (g). The experimental results were adjusted to the isotherm models proposed by Langmuir and Freundlich (Cantanhede *et al.* 2005).

In the Langmuir model, each active site on the surface of the coal can accommodate a molecule or ion per adsorptive site in which the energy of the adsorptive sites is the same for all other sites on the surface, thus forming monomolecular adsorption. Equation (2) represents the linear form for the equation proposed by Langmuir (Largitte & Pasquier 2016):

$$\frac{C_e}{q_e} = \frac{1}{q_{\max}} C_e + \frac{1}{K_L q_{\max}} \quad (2)$$

where q_e is the amount of adsorbate retained in the solid at equilibrium (mg/g), q_{\max} is the Langmuir parameter relative to the maximum adsorption capacity (mg/g), K_L is the Langmuir constant relative to the adsorbate/adsorbent (L/mg) adsorption or interaction energy, and C_e is the concentration of the ion in solution at equilibrium (mg/L). The values of q_{\max} and K_L represent the maximum theoretical adsorption capacity at equilibrium and the Langmuir constant, respectively. Another important component of the Langmuir model is the dimensionless constant (R_L), which corresponds to the equilibrium parameter and can be determined by Equation (3):

$$R_L = \frac{1}{1 + K_L C_0} \quad (3)$$

when a separation factor value in the range $0 < R_L < 1$ is obtained, the adsorption is considered favorable, i.e., the adsorbate will prefer the solid phase over the fluid phase. When $R_L > 1$, the adsorption is considered unfavorable and the solute will

prefer the fluid phase. For a value of $R_L = 1$, the obtained isotherm is linear, and when $R_L = 0$, the adsorption process is irreversible (Cazetta *et al.* 2011).

Freundlich's proposed model equation for isotherm calculation can be applied to non-ideal systems, taking into consideration that the adsorption in a solid happens in heterogeneous surfaces and multilayers. Equation (4) presents the linear form of the Freundlich equation (Largitte & Pasquier 2016):

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

where q_e and C_e have the same meaning as the Langmuir equation, K_F (L/g) is a constant related to the adsorption capacity and n is a constant related to the adsorption intensity and the spontaneity of the adsorption when this value is greater than 1 (Rout *et al.* 2015).

Kinetic adsorption models

The kinetics study was performed in a batch system, where 100 mL of Ca^{2+} ion solution at a concentration of 400 mg/L, at pH 7 and 25 °C was added to a series of 250 mL Erlenmeyers, containing 100 mg of PAC each. This system was under constant stirring for time intervals varying from 5 to 60 min. For each time interval, aliquots of 25 mL were withdrawn and the concentration of Ca^{2+} ions was quantified by complexometric titration with EDTA 0.001 mol /L in aqueous medium using the Eriochrome black T indicator. All data were adjusted to kinetic models of pseudo-first-order (Equation (5)) (Mahamadi & Mawere 2013), pseudo-second-order (Equation (6)) (Balouch *et al.* 2013), and intraparticle diffusion (Equation (7)) (Elmorsi *et al.* 2014):

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \quad (6)$$

$$q = k_{id} t^{1/2} + C \quad (7)$$

RESULTS AND DISCUSSION

Thermogravimetric analysis

The behavior of lignocellulosic materials as a function of temperature can be observed by thermal analysis. The selection of the carbonization temperature for the raw material used in this activated carbon production was based on the thermogravimetric analysis (TGA) curves. Figure 1 shows the thermal behavior of each sample of *in natura* pitomba core.

The behavior of the observed curve shows a constant mass in thermal degradations of the sample at 550 °C or higher, indicating that at this temperature all organic matter has already been decomposed. First losses refer to the moisture present and some volatile compounds (0–100 °C). The first loss of significant mass at a temperature range between 100 and 300 °C refers to the degradation of hemicellulose and cellulose that occurs at lower temperatures, and the second one corresponds to degradation of lignin and small amounts of cellulose, with lignin being dominant in high conversions (Bridgeman *et al.* 2008). Lignin is more thermally stable when compared with cellulose and hemicellulose (Branca & Di Blasi 2003). From the results of thermal degradation of the samples against temperature, it is noted that the samples' mass loss at 300 °C or higher is quite similar, so the samples' pyrolysis temperature was set at 350 °C, with 90 minutes heating ramp and plateau, summing three hours of total burning time, which is enough time for the degradation of volatile materials and hemicellulose and cellulose components (dos Santos *et al.* 2011).

Characterization of PAC adsorbent

The determination of the coal's moisture content was carried out to verify the adsorbent's affinity for water molecules. A high moisture content means the adsorbent can have its adsorptive capacity compromised by the incorporation of water molecules on its surface (Yakout *et al.* 2015). On the other hand, the ash content is a parameter used to characterize the coal after the pyrolysis process. Ashes generally consist of iron, aluminum, calcium, magnesium, sodium, and potassium oxides, sulfates or carbonates (Borges *et al.* 2015). Table 1 shows the percentages obtained for yield, moisture content, and ash of PAC and other activated carbons of the same nature.

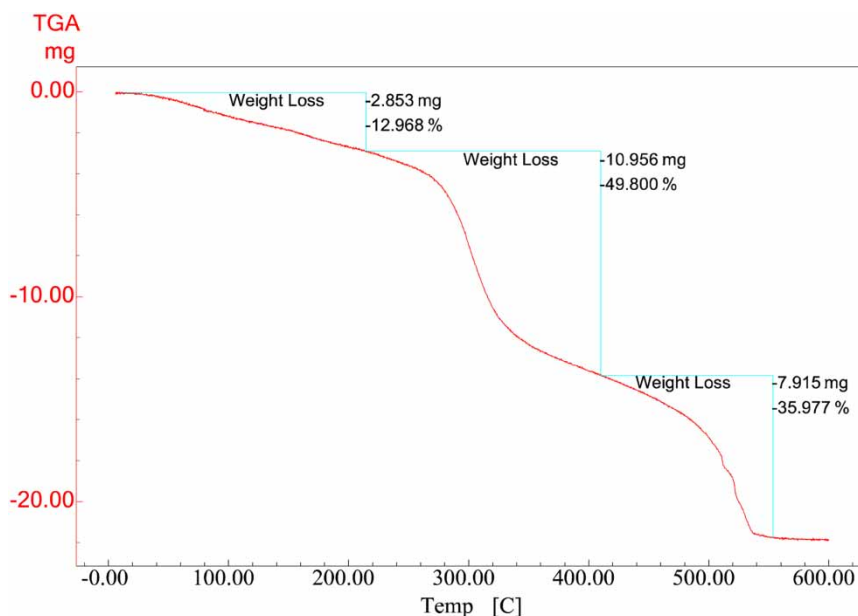


Figure 1 | The thermogravimetric curve of the pitomba core (PC) crushed *in natura*. The heating rate is 3.9 °C/min for 90 min.

Table 1 | Comparison of the characteristics of PAC with other types of coals

Carbon	Moisture content (%)	Ash content (%)	Reference
PAC	8.78	2.9	Present study
Activated charcoal of pumpkin residue	19.05	22.38	Futalan <i>et al.</i> (2011)
Activated carbon from sugarcane bagasse	2.90	22.0	Carrier <i>et al.</i> (2012)
Activated charcoal pineapple residue	1.46	1.57	Mahamad <i>et al.</i> (2015)

The ash content was 2.9%, which is a very satisfactory result, seeing as a low ash content indicates a high amount of organic matter and a low content of inorganic material, favoring the adsorptive potential of the coal. The high content of inorganic matter may lead to changes in the solution pH when coal is present, since mineral matter causes a dielectric effect in the adsorption process, preferentially adsorbing water, due to its hydrophilic character (Momčilović *et al.* 2011).

The surface properties of the PAC were evaluated according to the original classification proposed by BET. The PAC presented a specific surface area of 141.6 m²/g and a mean radius of 1.3 nm, classifying the coal as microporous according to IUPAC (Bayne *et al.* 2013). The Boehm titration used to evaluate the functional groups present on the surface of the PAC showed a predominance of acidic groups, which is justified by the use of the activating agent (H₃PO₄). Phenolic groups (1.7 mEq/g), carboxylic (0.6 mEq/g) and lactonic (0.57 mEq/g) occur in greater quantity.

The FT-IR spectrum indicated the presence of C = O bands at 1,544–1,600 cm⁻¹ (carboxylic, lactones), and there are also many overlapping peaks appear that form an absorption band in the 1,300–1,000 cm⁻¹ region, what can be attributed to carboxylic acid CO, phenolic structures and esters (Anirudhan & Sreekumari 2011). There are no peaks in the range of 3,600–3,200 cm⁻¹ indicating the disappearance of water molecules (Nono *et al.* 2016).

The morphology of the PAC (Figure 2), analyzed from the coal's surface micrographs, shows a porous structure, irregular open pores, and recesses that may be characteristic of the presence of transport pores (Gregg & Sing 1982).

The micrographs show the effects of the activation and pyrolysis steps of the precursor material, since they are meant to infer functional groups on the surface of the adsorbent and to promote the increase of the porosity of the material. PAC presents an irregular porous morphology and the analysis of the surface area indicates that the pore radius is on the order of 1.3 nm, within the range of microporous materials (Dąbrowski 2001).

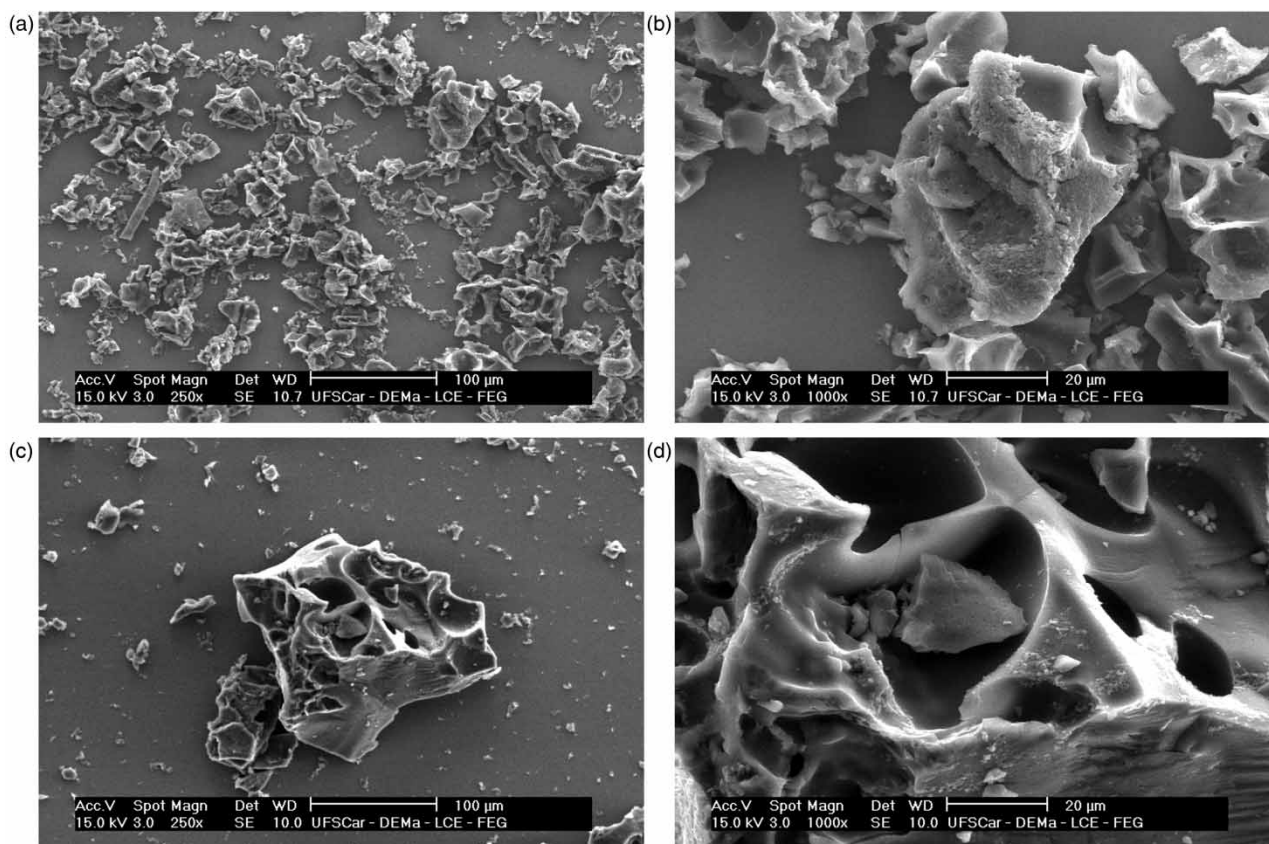


Figure 2 | Micrograph obtained by scanning electron microscopy: pitomba pits crushed *in natura*, magnification level (a) 250x; (b) 1000x. Activated carbon from pitomba pits (c) 250x; (d) 1000x.

pH at the point of zero charges (pH_{PZC})

The importance of this variable in the adsorption process is that the adsorbate and adsorbent charges must be opposing so that there is the greater electrostatic interaction between both, because, if the charges are equal, the adsorption process will be impaired, and electrostatic repulsion will happen (Bautista-Toledo *et al.* 2005). The adsorbent may present negative charges when the pH of the medium is higher than pH_{PZC} and positive ones when the pH value is below pH_{PZC} (Ding *et al.* 2014). A graph of ΔpH vs pH was plotted and the point of intersection of the two graphs represents the pH_{PZC} of the PAC (Figure 3).

The pH at the point of zero charge for the PAC matrix was 2.75. In this way, PAC tends to present negative charges in solutions with a pH greater than 2.75. Therefore, higher adsorption of calcium ions is expected to occur at pH values greater than 2.75. Nono *et al.* (2016) produced phosphoric acid activated carbons of coffee husk and corncob, obtaining pH_{PZC} values of 3.27 and 3.00, respectively.

Contact time effect

Several factors, such as adsorbent type, pore shape, and the surface area beyond the type of metal involved, may influence the contact time required for equilibrium between the phases (AL-Othman *et al.* 2012). Figure 4 shows the effect of the adsorbed amount as a function of contact time.

The curve behavior indicates a maximum adsorption peak at 10 min. During the adsorption process, a decrease in the amount adsorbed by PAC can be observed, characterizing a desorption process of Ca^{2+} ions. The adsorption peak presented may occur due to the higher availability of vacant active sites on the surface of the adsorbent at the initial stage. At the moment that the sites are being occupied, availability decreases and the adsorption process becomes slower due to repulsive forces between adsorbed molecules and free molecules in the solution. Similar results were observed for other metal adsorptions, such as Pb^{2+} and Cd^{2+} on activated carbon derived from bamboo, obtaining equilibrium time after 30 minutes (Stevens *et al.* 2014).

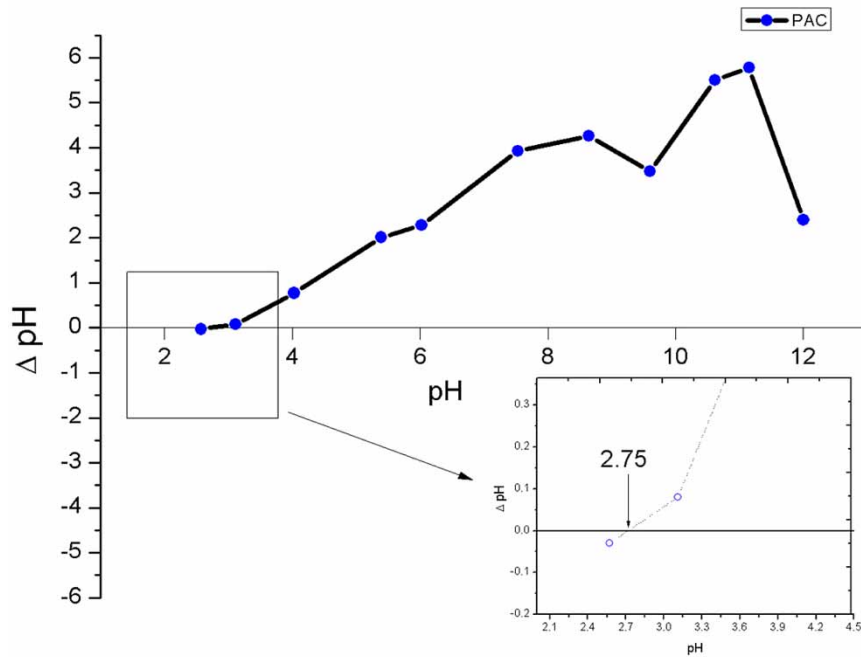


Figure 3 | Curve for determination of the pH in point of zero charges (pH_{PZC}) of the PAC.

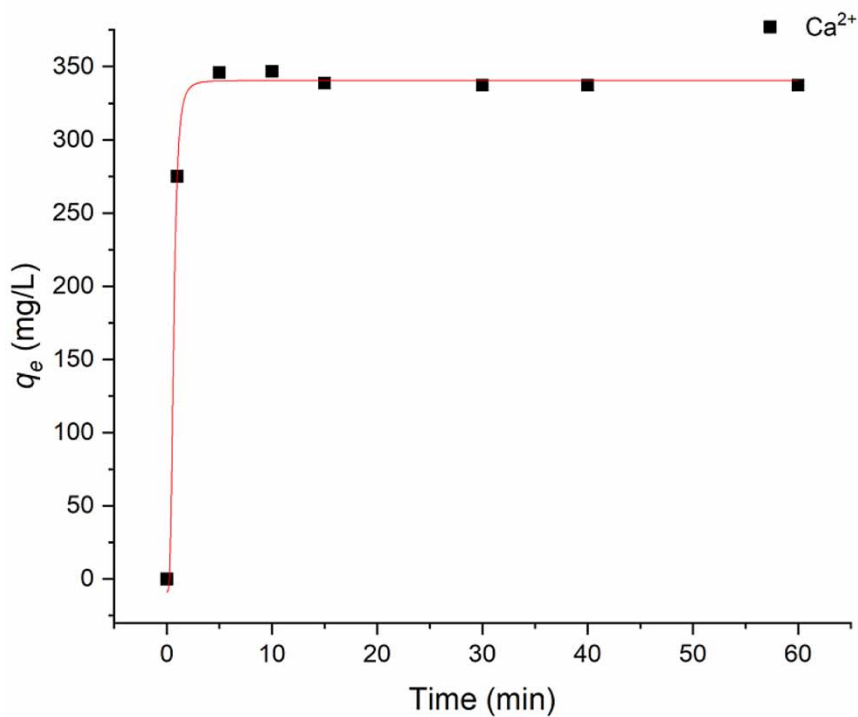


Figure 4 | Effect of contact time on adsorption of the Ca^{2+} ions in PAC (adsorbent mass = 0.1 g, $[\text{Ca}^{2+}] = 400 \text{ mg/L}$, $T = 25.0 \pm 0.1^\circ\text{C}$ and $\text{pH} = 7$).

Effect of the pH of the medium

The pH of the medium in which the adsorption occurs determines the degree of distribution of the chemical species. The pH at the point of zero charge (pH_{PZC}) is the pH below which the surface of the adsorbent is positive, being negative above this

value (Islam *et al.* 2015). The adsorption of Ca^{2+} ions in an aqueous medium with different pH values is shown in Figure 5. The importance of this variable in the adsorption is that the adsorbate and adsorbent charges must be opposite to have greater electrostatic interaction between them, because if the charges are equal the adsorption process will be impaired, since there will be electrostatic repulsion (Bautista-Toledo *et al.* 2005).

The adsorption underwent interference at acidic pH (pH value = 2). At this pH value, the availability of negatively charged groups on the PAC surface is required for the adsorption of the Ca^{2+} cation. The adsorption at pH 2 is lower since the carbon's surface is potentially altered due to the predominance of H^+ and H_3O^+ ions. In this system, the H^+ ions compete with the metal cation, resulting in protonation of the active sites preventing the removal of the Ca^{2+} ion that binds itself to the surface of the adsorbent. This means that, at higher H^+ concentration, the surface of the PAC becomes more positively charged, thus reducing the attraction between the Ca^{2+} metal cations. In contrast, as the pH increases, a portion of the biochar surface becomes more negatively charged, increasing the availability of adsorption sites and electrostatic interaction between the surface of the PAC and the positively charged Ca^{2+} cations, thus favoring greater adsorption of the cations. Therefore, the metal ion adsorption tends to increase significantly by increasing the pH (Rao & Khan 2009).

Adsorption isotherm

The determination of the adsorptive capacity of an adsorbent in a constant temperature analysis represents an important parameter for understanding the efficiency and characteristics of the adsorbent. The isothermal models proposed by Langmuir and Freundlich are often used as parameters to characterize some adsorptive properties of porous materials. Normally, the Langmuir isotherm model suggests monolayer adsorption and a surface containing a finite number of adsorption sites. In contrast, the Freundlich isotherm model assumes that the adsorption process is related to a heterogeneous surface (Zhou *et al.* 2017). Figure 6 shows the adsorption isotherm obtained in adsorptive assays from solutions with different concentrations of Ca^{2+} ions.

The adsorption equilibrium was obtained graphically from the experimental amount of adsorbed Ca^{2+} ions, q_e (mg/g), as a function of the metal cation concentration, C_e (mg/L), under equilibrium conditions. The adsorption equilibrium was later evaluated using two isothermal models, namely Langmuir and Freundlich. The isotherm obtained experimentally corresponds to an isotherm that is characteristic of microporous solids (Muttakin *et al.* 2018). Figure 7 shows the adjustments of the experimental data to the Langmuir and Freundlich isotherm models.

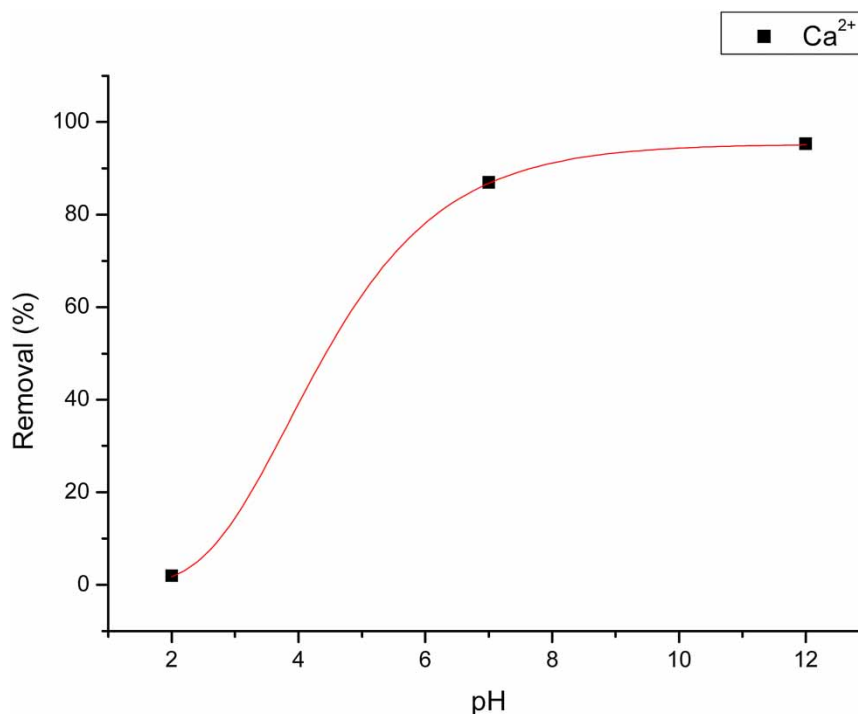


Figure 5 | Effect of pH on the adsorption of the Ca^{2+} ions in PAC (Ca^{2+}] = 400 mg/L, $T = 25.0 \pm 0.1$ °C and 5 min of contact time).

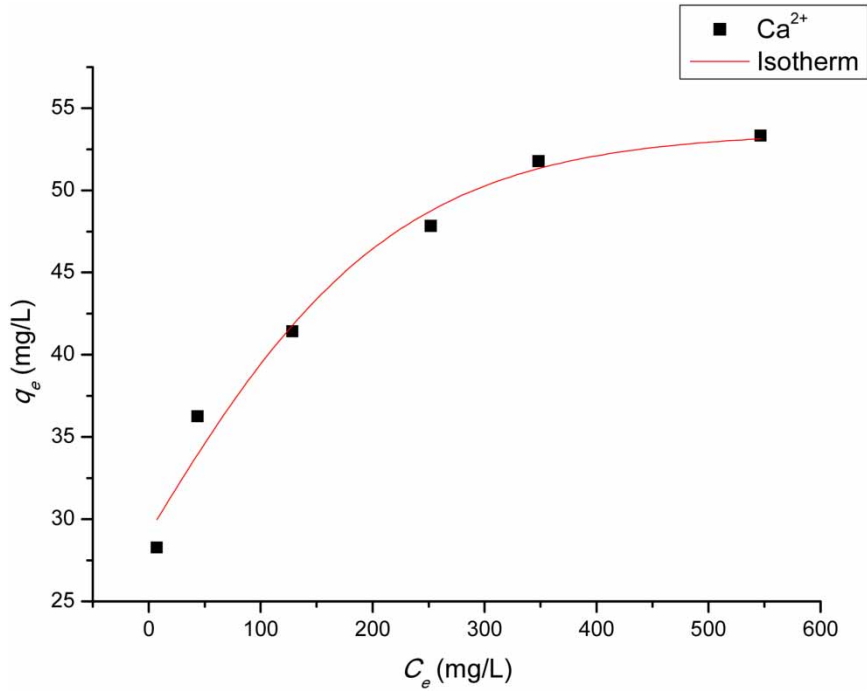


Figure 6 | Ca^{2+} ion adsorption isotherm in PAC ($[\text{Ca}^{2+}] = 0.004 \text{ mg/L}$, $T = 25.0 \pm 0.1 \text{ }^\circ\text{C}$, adsorbent mass 0.1 g, 5 min of contact time, and $\text{pH} = 7$).

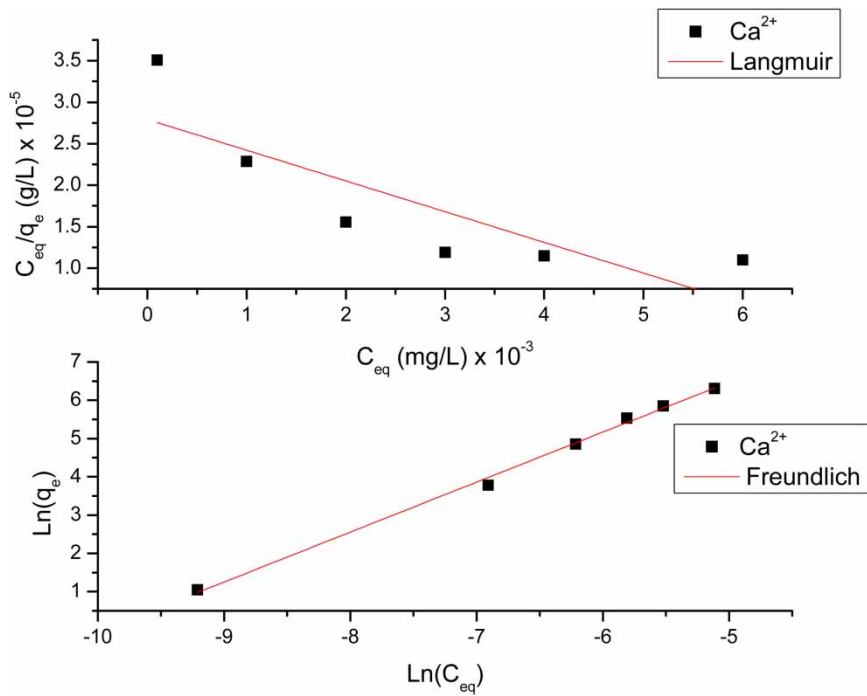


Figure 7 | Langmuir and Freundlich models for PAC ($[\text{Ca}^{2+}] = 0.004 \text{ mg/L}$, $T = 25.0 \pm 0.1 \text{ }^\circ\text{C}$, adsorbent mass 0.1 g, 5 min of contact time and $\text{pH} = 7$).

The parameters of the Langmuir and Freundlich isotherms obtained from their models' equations applied to the Ca^{2+} adsorption data for the PAC sample at 25 °C are shown in Table 2.

The results show that the adsorption process is better adjusted to the Freundlich model ($R = 0.98$). Even though the K_F parameter of the Freundlich model is related to the adsorption capacity, it does not provide the maximum removal capacity, since the Freundlich model does not predict adsorbent saturation (Khan *et al.* 2016). The value of the Freundlich constant obtained was 19.05, and the value of n (6.6) indicates that the adsorption is favorable. Similar results were obtained for the removal of Pb^{2+} , Hg^{2+} and Cu^{2+} metal ions adsorbed by activated carbon from coconut residues, presenting K_F values of 23.81 for Pb^{2+} , 14.96 for Hg^{2+} and 11.32 for Cu^{2+} . The best fit of the experimental data to the Freundlich isotherm model may be due to the heterogeneous distribution of active sites on the adsorbent surface (Anirudhan & Sreekumari 2011). Thus, the activated carbon obtained from pitomba seed proved to be a potential adsorbent for the adsorption of Ca^{2+} ions in aqueous solution, removing about 92% of the ions in solution. Kurniasari *et al.* (2020) used activated charcoal obtained from sugarcane bagasse (*Saccharum officinarum* L.) to remove Ca^{2+} ions from well water, with a removal efficiency of 14.4%.

Adsorption kinetics

The adsorption kinetics can be defined as the rate of removal of the adsorbate, present in the fluid phase, over time. It therefore involves the mass transfer of one or more dissolved components to the adsorbent particle, migrating through the macropores to the innermost regions of the adsorbent particles (Karthikeyan *et al.* 2005). The adsorption kinetics of Ca^{2+} ions in PAC was investigated by applying three kinetic models to the experimental data of the present study. These models included the pseudo-first-order and pseudo-second-order kinetic models. The adsorption mechanism was also investigated by applying the intraparticle diffusion model. Figure 8 presents the adequacy of the experimental data in the kinetic models for PAC.

The kinetic study data for the pseudo-first-order model were further away from linearity when compared with the pseudo-second-order model and intraparticle diffusion. Table 3 presents the values of speed constants, correlation coefficients for the pseudo-first-order kinetic and pseudo-second-order kinetic models, and the intraparticle diffusion model.

The adjustment of the experimental data is in agreement with the kinetic model of pseudo-second order (0.996) and is also favorable for the intraparticle diffusion model (0.998), but the intercept does not cross the origin, implying that intraparticle diffusion is not the main diffusion mechanism (Dural *et al.* 2011). The first step may be related to surface adsorption where the adsorption rate is maximum at five minutes and the adsorption occurs on the outer surface of the adsorbent, whereas the second stage must correspond to adsorption on the internal surfaces of the pores of the coal. After 30 minutes we have the equilibrium process, and it is then suggested that the calcium ion adsorption involved more than one process (Juang *et al.* 2002). Da Silva *et al.* (2016) studied the adsorption of Ca^{2+} ions in lignocellulosic material, and the results of the kinetic study showed that the pseudo-second-order model was a better fit to the experimental data.

CONCLUSIONS

Pitomba pits have proven to be a good precursor material for activated carbon production, presenting a low content of ashes and moisture, significant adsorption potential for adsorption of Ca^{2+} ions in aqueous solution, with a removal of about 92% of the ions in solution with suitable pH. The activating agent was able to produce active sites on the surface of the coal, which was evident by the results of the Boehm tests, which showed the predominance of acidic groups on the surface of the PAC, with emphasis on phenolic groups. The pH_{PZC} showed that coal has favorable adsorption for Ca^{2+} ions at pH above 3.

In the adsorption studies, it was observed that equilibrium occurs after about 5 min of the reaction and the most effective pH for the adsorption of calcium ions in the solution is the basic one. The adsorption isotherms were more adequate for the Freundlich model, with a correlation coefficient of 0.98 and maximum adsorption of $500 \text{ mg}\cdot\text{g}^{-1}$. The analysis of kinetic

Table 2 | Results of the adjustment of the isotherms to the Freundlich and Langmuir models for adsorption of Ca^{2+} in PAC

PAC	Langmuir isotherm				Freundlich isotherm		
	$q_{\text{max}} (\text{mg}\cdot\text{g}^{-1})$	$K_{\text{ads}} (\text{L}\cdot\text{g}^{-1})$	R^2	R_L	$K_F (\text{mg}\cdot\text{g}^{-1})$	n	R^2
500	2.22×10^{-2}	0.60	0.47	19.05	6.6	0.98	

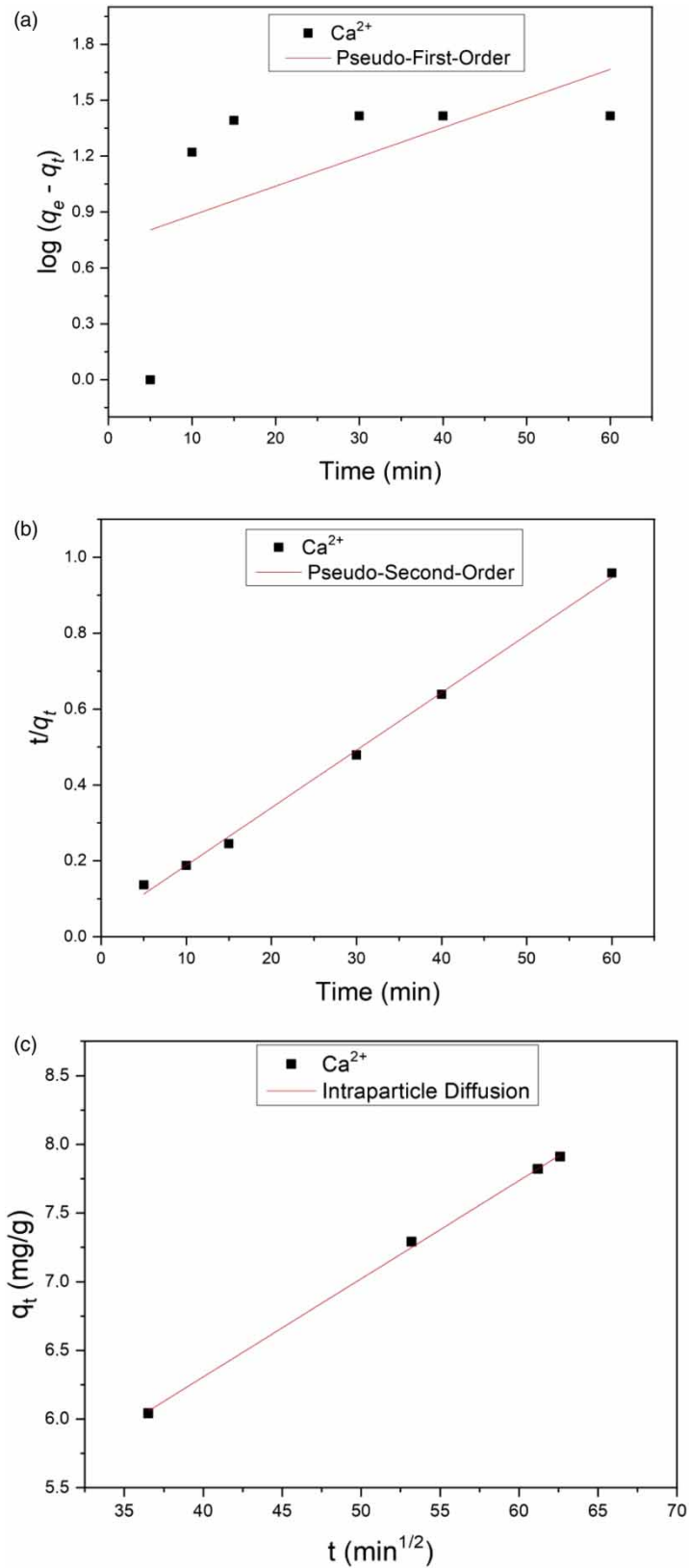


Figure 8 | Adjustment to kinetic models applied to PAC: (a) pseudo-first-order, (b) pseudo-second-order, and (c) and intraparticle diffusion.

Table 3 | Linear regression parameters using the kinetic models of pseudo-first-order and pseudo-second-order and intraparticle diffusion model for the PAC

Pseudo-first-order				Pseudo-second-order			Intraparticle diffusion	
q_e , exp (mg/g)	q_e cal (mg/g)	K_1 (min^{-1})	R^2	q_e cal (mg/g)	K_2 (g/mg min^{-1})	R^2	K_{id} ($\text{g/mg min}^{-1/2}$)	R^2
51.36	53.21	0.036	0.169	65.91	6.25×10^{-3}	0.996	0.071	0.998

models showed that the adsorption kinetics of the activated carbon of the pitomba core was more adequate for the kinetic model of pseudo-second order, with the predominance of chemisorption.

The results showed that the carbon produced can be a potential adsorbent for cations in aqueous solution. The results presented in this work were favorable for the use of activated carbon produced from pitomba pits as an adsorbent in the removal of Ca^{2+} ions in an aqueous medium, which can significantly contribute to the reduction of environmental impacts.

ACKNOWLEDGEMENTS

The authors are grateful to the Chemistry Graduate Program of the Federal Institute of Education, Science and Technology of Maranhão – IFMA, and to FAPEMA, for financial assistance, and to IFMA/Campus Codó.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

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First received 31 March 2021; accepted in revised form 30 July 2021. Available online 16 August 2021