



Phosphorus sorption potential of natural adsorbent materials from a Brazil semiarid region to control eutrophication

Potencial de sorção de fósforo de materiais adsorventes naturais da região semiárida do Brasil para controle da eutrofização

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Abstract: Aim: The aim of the present study was to evaluate the potential soluble reactive phosphorus (SRP) sorption of three natural P adsorbents (Luvisol, Planosol, and Scheelite tailing) from Brazil's semiarid region. **Methods:** The adsorption tests were done under pH 8 conditions with the natural adsorbents and Lanthanum-Modified Bentonite (LMB). The effect of humic substances on SRP sorption was also tested. For this, Luvisol and Planosol were incinerated to reduce their humic components, and new adsorption tests were done. The effect of adsorbents on water pH was also evaluated. **Results:** The SRP sorption potential of the natural adsorbents was high at pH 8. Of the natural adsorbents, Luvisol achieved the highest maximum SRP adsorption capacity (Q) of 17.5 mg g⁻¹, followed by Scheelite tailing (8.3 mg g⁻¹) and Planosol (7.7 mg g⁻¹). Scheelite tailing, Planosol and LMB increased the pH of the water. After treatment to reduce humic substances, Planosol showed a Q of 22.3 mg g⁻¹ while Luvisol produced 11.1 mg g⁻¹. Reducing the amount of humic substances potentiated the sorption process in the Planosol. However, the isotherms of untreated Luvisol and treated Planosol have not reached equilibrium and therefore may be overestimated. **Conclusions:** The precipitation process was probably the main sorption mechanism, being more expressive than adsorption. Scheelite tailing was the most promising material for eutrophic environments because it is alkaline, calcium-rich, and this capacity will probably remain high under anoxic conditions. It also has a small amount of organic matter and, consequently, contains less humic substances. The quality of the clay present in natural adsorbents was more important than quantity in the sorption process.

Keywords: adsorption tests; clay minerals; humic substances; Langmuir isotherm; mitigation.

Resumo: Objetivo: O objetivo do presente estudo foi avaliar o potencial de sorção de fósforo reativo solúvel (FRS) de três adsorventes naturais (Luvisol, Planosol e rejeito de Scheelita) da região semiárida do Brasil. **Métodos:** Os testes de adsorção foram realizados sob pH 8, com os adsorventes naturais e com a Bentonita Modificada com Lantânio (BML). O efeito de substâncias húmicas na



sorção de FRS também foi testado. Para isso, o Luvisol e o Planosol foram incinerados para redução das substâncias húmicas e novos testes de adsorção foram realizados. O efeito dos adsorventes no pH da água também foi avaliado. **Resultados:** O potencial de sorção FRS dos adsorventes naturais foi alto em pH 8. Dos adsorventes naturais, Luvisol atingiu a maior capacidade máxima de adsorção FRS (Q) de 17,5 mg g⁻¹, seguido pelo Rejeito de *Scheelita* (8,3 mg g⁻¹) e Planosol (7,7 mg g⁻¹). O Rejeito de *Scheelita*, Planosol e BML aumentaram o pH da água. Após tratamento para redução de substâncias húmicas, Planosol apresentou Q de 22,3 mg g⁻¹ e Luvisol de 11,1 mg g⁻¹. A redução da quantidade de substâncias húmicas potencializou o processo de sorção no Planosol. No entanto, as isotermas do Luvisol não tratado e do planol tratado não atingiram o equilíbrio e, portanto, podem estar superestimadas. **Conclusões:** O processo de precipitação foi provavelmente o principal mecanismo de sorção, sendo mais expressivo que a adsorção. O Rejeito de *Scheelita* foi o material mais promissor para ambientes eutróficos por ser alcalino, rico em cálcio, e essa capacidade provavelmente permanecerá alta em condições anóxicas. Além disso, possui pequena quantidade de matéria orgânica e, conseqüentemente, menos substâncias húmicas. A qualidade da argila presente nos adsorventes naturais foi mais importante do que a sua quantidade no processo de sorção.

Palavras-chave: testes de adsorção; minerais de argila; substâncias húmicas; isotermas de Langmuir; mitigação.

1. Introduction

Eutrophication is a process that occurs naturally in aquatic ecosystems but has been accelerated by anthropogenic activities (Schindler, 2012; Le Moal et al., 2019). Reducing the external supply of nutrients is generally insufficient to mitigate nuisance eutrophication symptoms in a short time, due to the remaining internal P loading process (Hilt et al., 2006; Lürding et al., 2016). The sediment represents the cumulative site and legacy of nutrient loading (Paerl et al., 2020), storing nutrients that can be exchanged rapidly between the bottom and the water column (Le Moal et al., 2019). In this process, phosphorus can be immobilized and inactivated using techniques such as geo-engineering, which allows the biogeochemical cycle of phosphorus to be manipulated and can promote the rapid recovery of aquatic ecosystems (Douglas et al., 2016; Lürding et al., 2016; Wang et al., 2017).

Geo-engineering techniques use P adsorbents to effectively reduce P concentrations in the water column and P release from sediment to the overlying water (Douglas et al., 2016; Lürding et al., 2016). One of the mechanisms used in geo-engineering to remove phosphorus from water bodies is sorption (Rheinheimer et al., 2003). Sorption is the transfer of ions between the solution and solid-phase materials; it corresponds to a broader mechanism that includes the processes of adsorption and precipitation (Fang et al., 2017; Zhang et al., 2018). Adsorption is a colloidal fraction mechanism and occurs through electrostatic or covalent connections, while precipitation consists of binding water-soluble ions (such as Al³⁺, Fe²⁺, Mn²⁺, Ca²⁺ and Mg²⁺) with phosphate. Both precipitation and adsorption are

difficult to distinguish and are not differentiated by mathematical models (Sposito, 1984).

In recent years, modified clays with cation exchange properties have proven effective when used to manage and measure eutrophic ecosystems (Moharami & Jalali, 2015; El Bouraie & Masoud, 2017; Wang et al., 2017; Elsergany & Shanbleh, 2018). Of these, lanthanum-modified bentonite (LMB) in particular stands out (Douglas, 2002; Lürding & van Oosterhout, 2013; Copetti et al., 2016; Douglas et al., 2016; Mucci et al., 2018). Among the clays used in restoring eutrophic lakes in Brazil, LMB has been extensively tested and its efficiency in phosphate removal has been proven, both in the waters of humid tropical climate systems (Miranda et al., 2017; De-Magalhães et al., 2019) and in semiarid tropical climates (Lucena-Silva et al., 2019). However, it is expensive and thus difficult to use on a realistic scale in developing countries.

To be considered potentially useful and effective P adsorbents, compounds must meet specific criteria: they must have an affinity to adsorb P and be safe, inexpensive, and easy to prepare and use (Lürding et al., 2016). For this reason, natural materials gathered from the watershed area itself have shown promising results in P removal and the sedimentation of cyanobacteria (Douglas et al., 2016; Noyma et al., 2016, 2017; De-Magalhães et al., 2017; Miranda et al., 2017; Mucci et al., 2018).

Reservoirs in tropical semiarid regions are naturally more vulnerable to eutrophication (Barbosa et al., 2012; Nobre et al., 2020) and are subject to potentially toxic cyanobacterial blooms (Panosso et al., 2007; Costa et al., 2009; Medeiros et al., 2015; Braga & Becker, 2020).

This process is aggravated by extreme events such as droughts, because any reduction in the volume of water in a reservoir increases the concentration of nutrients and biomass it contains (Rocha Junior et al., 2018; Figueiredo & Becker, 2018; Braga & Becker, 2020).

Most soils in tropical semiarid regions are poorly developed, with high natural fertility and a sandy texture; some have an accumulation of illuvial clays in their subsurface horizons (Oliveira et al., 2019; Falcão et al., 2019). In these less-weathered soils, primary minerals and 2:1 clay with permanent negative charges predominate, resulting in fewer anion adsorption sites, such as phosphate (Meurer, 2006; Oliveira et al., 2019; Dunne et al., 2020). This is one of the main reasons for attributing a reduced potential for phosphorus adsorption to these soils compared to the oxidic soils found in humid tropical climates.

Some properties of adsorbent materials have a strong effect on the phosphorus sorption process, such as the content of organic matter and clay content, because they directly influence the availability of electrical charges (Wei et al., 2019). The organic matter in soil—predominantly humic substances—can interfere in the phosphorus adsorption process because it forms complexes on clay surfaces with cations, thereby physically preventing phosphorus adsorption (Lurling et al., 2014).

Given the need for more accessible and cost-effective techniques for mitigating eutrophic ecosystems, the aim of the present study was to evaluate the soluble reactive phosphorus (SRP) sorption potential of three natural adsorbents in semiarid regions. The effect of humic substances on SRP sorption was also tested. The hypothesis tested was that the natural adsorbents with the best SRP sorption capacity will be those composed of a higher amount of clay and a lower amount of humic substances.

2. Material and Methods

2.1. P-adsorbents tested

In this study, the natural adsorbent materials used were from semiarid tropical steppe climate (BS'h Köppen climate classification; Alvares et al., 2013), northeastern Brazil: Fine tailings derived from the mining and processing of Scheelite, Haplic Planosol, and Chromic Luvisol, as defined by the Brazilian Soil Classification System (Santos et al., 2018), which correspond to Planosol and Luvisol,

respectively, according to the World Reference Base for Soil Resources (FAO, 2015). Lanthanum-modified bentonite (LMB, Phoslock, SCIRO, Australian) (Douglas, 2002) was also used as a positive control due to its proven efficiency in phosphate sorption (Meis et al., 2013).

The natural adsorbent materials were collected up to a maximum of 20 cm deep, packed in plastic bags, and taken to the laboratory. In the laboratory, the samples were dried in an oven until their weight became constant; they were then removed and passed through 2 mm sieves (Teixeira et al., 2017) for the subsequent analysis of the physical and chemical composition of the material.

2.2. Material composition

The natural adsorbents were physically and chemically characterized according to the methods presented in table 1. The equipments used was BEL W3B pH meter and UV-visible spectrophotometer digital 320-1000nm Global Trade Technology.

The results obtained from the exchange complex revealed the potential cation exchange capacity (CEC) (Teixeira et al., 2017). The point of zero charge was also estimated using to the Equation 1 proposed by Keng & Uehara (1974):

$$PCZ = 2pHKCl - 2pHH_2O \quad (1)$$

The total organic carbon was determined using the modified Walkley-Black method (Silva et al., 1999), through oxidation with potassium dichromate in a sulfuric medium and subsequent titration with ammoniacal ferrous sulfate. The organic matter was estimated by multiplying the product of the organic carbon value by 1.724, considering that humus is

Table 1. Analyzes and methods used for the characterization of adsorbents materials.

Analyses	Method
Granulometry	Pipette method
pH in water	(1:2.5)
pH in KCl (1mol L ⁻¹)	(1:2.5)
ΔpH	pH in KCl – pH in water
Phosphorus available	Colorimetry after extraction with Mehlich -1
Potassium and Sodium exchangeable	Flame emission photometry after extraction with Mehlich -1 extractor
Calcium and Magnesium exchangeable	Titration, after extraction in KCl solution 1 mol L ⁻¹

Source: Teixeira et al. (2017).

approximately 58% carbon (Teixeira et al., 2017). The mineralogical analysis of the adsorbent materials was conducted using clay fractions (Teixeira et al., 2017) analyzed in suspension in EDX-720.

2.3. Effect of adsorbents on the pH of the water

To evaluate the effect of the adsorbent materials on pH, a batch experiment was conducted using 100, 200, and 400 mg of each adsorbent added to Falcon tubes containing 50 mL of deionized water. No adsorbent was added for the control treatment. The tubes remained on a shaking table for 1 hour and the pH was measured in the tube before and after the material was added. Each test was performed in triplicate. The pH was measured with a pHmeter (BEL W3B). The Shapiro-test was done to confirm the normality of the data and the Brown-Forsythe test was made to confirm the homogeneity of variance. Posteriorly, the test one-way ANOVA ($p < 0.05$) and a Tukey's test ($p < 0.05$) were performed post-hoc, and the data obtained were used to verify the effect of the amount of adsorbent on the pH of the solution.

2.4. Adsorption experiment

Prior to use, the natural adsorbents were dried and ground using a pestle and mortar, then shaken through a 0.5 mm sieve (De-Magalhães et al.,

2017). The adsorption experiments were conducted according to the methodology described by Mucci et al. (2018) to evaluate the SRP sorption of the three natural adsorbents (Scheelite tailing, Luvisol, and Planosol) and clay-modified LMB.

All treatments were carried out using water with a pH of 8, which is the average pH of the water in the reservoirs of tropical semiarid regions (Barbosa et al., 2012; Medeiros et al., 2015; Brasil et al., 2016; Figueiredo & Becker, 2018). The experiments were conducted according to Figure 1, the procedure was done for each concentration in triplicate and each adsorbent.

The following parameters were measured at the beginning of the experiments and after the incubation period of each sample: pH (using a BEL W3B pH meter), dissolved oxygen (using an Instruterm MO-900 oximeter), and SRP, after filtration through glass-fiber filters (0.45 μm), by colorimetric method, according to the method developed by Murphy & Riley (1962). Humic substances (UV254 nm) were also estimated using the colorimetric method (Leenheer & Croué, 2003).

2.5. The effect of humic substances on sorption

The effect of humic substances on the efficiency of adsorbents was evaluated only for Luvisol and

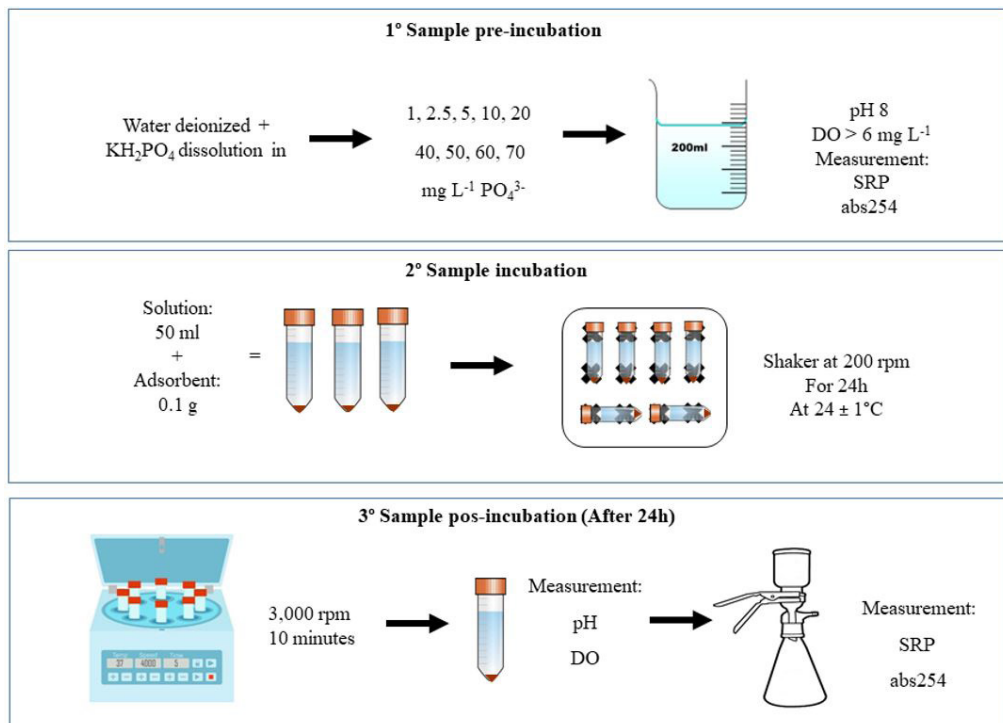


Figure 1. Experimental design of adsorption tests. DO= Dissolved oxygen; SRP= Reactive Soluble Phosphorus.

Planosol, which had the highest of absorbance UV values at 254 nm. After being dried, stripped, and sieved, the adsorbents were separated into 20 g portions and placed in porcelain crucibles, which were placed in a muffle furnace heated to 500 °C for 3 hours to incinerate any organic matter present in the adsorbent. New adsorption tests were then conducted with the treated material according to the previous topic (2.4 adsorption experiment).

2.6. Data analysis

To calculate the soluble reactive phosphorus (SRP) sorption, the SRP sorption coefficient (mg g^{-1}) was used, calculated according to Equation 2 and other studies that used this same methodology (Moharami & Jalali, 2015; Noyma et al., 2016; Mucci et al., 2018):

$$Q(\text{mg g}^{-1}) = \frac{(C_i - C_e) * V}{W} \quad (2)$$

where Q (mg g^{-1}) is SRP sorption capacity by an adsorbent at time t ; C_i (mg L^{-1}) is initial SRP concentration; C_e (mg L^{-1}) is SRP equilibrium concentration at time t ; V (L) is the volume of the incubated solution; and W (g) is the weight of the SRP adsorbent (g) used.

For data analysis, the Langmuir and Freundlich isotherm models were used to determine the relationship between the amount of SRP adsorbed and its equilibrium concentration. Both were calculated from an interactive non-linear regression using R software (R × 64 3.6.3).

3. Results

3.1. Description of adsorbent materials

In terms of quantity, clay content predominated mainly in Planosol, followed by LMB, Luvisol and Scheelite tailings (Table 2). Regarding quality, the mineralogical analysis of the clay fraction samples showed a predominance of mica, kaolinite, goethite and hematite in Luvisol and Planosol; vermiculite and gibbsite in Scheelite's tailings; and smectite in LMB.

The pH of the P adsorbents ranged from 6.4-7.6, with LMB having the lowest value and Luvisol the highest (Table 2). All materials showed a point of zero charge of ≤ 6 and a negative ΔpH . The CEC ranged from 19.79 to 77.66 $\text{cmol}_c \text{dm}^{-3}$ and, unlike the results for pH, LMB had the highest CEC values and Luvisol the smallest (Table 2). Most CEC values were obtained from the sum of the bases, most of which were Ca^{2+} and Mg^{2+} (Table 2).

Available phosphorus was present only in Planosol and Luvisol, at values of 25.8 and 70.4 mg dm^{-3} , respectively (Table 1). The available iron content followed the same pattern as phosphorus, being present in greater quantity in Planosol and Luvisol but virtually absent in LMB and Scheelite tailing (Table 2). The organic matter content was higher in soils (Planosol 2.5 g kg^{-1} ; Luvisol 0.8 g kg^{-1}) than in Scheelite tailing or the LMB (Table 2).

3.2. Effect of adsorbents in the water pH

The addition of the Scheelite tailing, Planosol, and LMB in distilled water resulted in increased pH (Figure 2). The Scheelite tailing significantly

Table 2. Physical and chemical characterization of the P adsorbent materials following the removal of SRP.

Variable	Luvisol	Scheelite tailing	Planosol	LMB
Sand (g kg^{-1})	518.2	566.1	22.4	357.5
Silt (g kg^{-1})	206.1	382.5	422.9	259.7
Clay (g kg^{-1})	275.7	51.4	554.7	382.8
pH in water	7.6	7.1	6.9	6.4
ΔpH	-1.9	-0.6	-0.9	-0.3
Point of zero charge (PZC)	3.7	6.0	4.9	5.9
Exchangeable Calcium ($\text{cmol}_c \text{dm}^{-3}$)	9.3	43.8	33.0	43.9
Exchangeable Magnesium ($\text{cmol}_c \text{dm}^{-3}$)	7.4	3.1	23.8	20.3
Exchangeable Sodium ($\text{cmol}_c \text{dm}^{-3}$)	2.4	3.3	7.3	12.9
Exchangeable Potassium ($\text{cmol}_c \text{dm}^{-3}$)	0.7	0.4	1.5	0.5
Iron Available (mg dm^{-3})	35.2	0.3	24.6	0.2
Cation exchange capacity ($\text{cmol}_c \text{dm}^{-3}$)	19.7	50.4	69.2	77.6
Phosphorus Available (mg dm^{-3})	70.4	0.0	25.8	0.0
Organic matter (g kg^{-1})	0.8	0.1	2.5	0.3

LMB = Lanthanum Modified Bentonite; SRP = Soluble Reactive Phosphorus.

changed the pH of the solution from 6.1 to 8.9 ± 0.28 ($p < 0.001$), and LMB increased the initial pH of the water ($p < 0.010$) from 5.9 to 6.4 ± 0.16 . The addition of Planosol changed the pH of the water from 5.9 to 6.3 ± 0.18 ($p < 0.05$), whereas Luvisol did not (5.9 ± 0.23) ($p = 0.179$).

3.3. SRP sorption

All of the adsorbent materials tested showed a capacity to adsorb SRP; the maximum removal observed was in the concentrations up to 20 mg L^{-1} (Figure. 3). Luvisol removal was around 40%, and decreased as the equilibrium concentration increased. Similar results were obtained with the addition of Scheelite tailing and Planosol. At concentrations of up to 20 mg L^{-1} ,

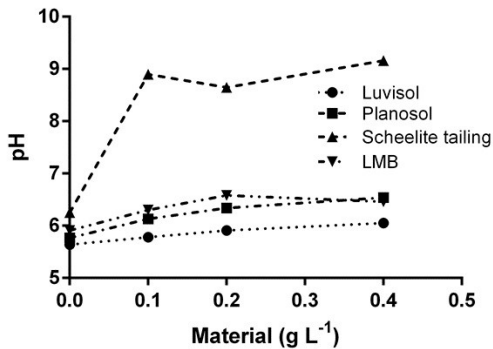


Figure 2. Influence of the addition of 0, 0.1, 0.2 and 0.4 g L^{-1} of adsorbent materials to distilled water on the pH of the solution. LMB=Lanthanum Modified Bentonite.

40-60% of the phosphate was adsorbed, stabilizing between 20-35%. The LMB removed 99% of the SRP until saturation; after 40 mg L^{-1} the amount removed decreased until it reached approximately 40% (Figure 3).

The natural adsorbents (Luvisol, Planosol, and Scheelite tailing) showed SRP adsorption isotherms that fit to the Langmuir and Freundlich models, as reflected in the r values of both isotherms (Table 3), as well as the visual analysis of the isotherms (Figure 4). The maximum SRP adsorption capacity (Q) was statistically significant for all adsorbent materials tested (Table 3). Luvisol produced the highest values of SRP adsorption capacity (17.5 mg g^{-1}), followed by LMB (16.0 mg g^{-1}), Scheelite tailing (8.3 mg g^{-1}), and Planosol (7.7 mg g^{-1}).

3.4. SRP adsorption after the reduction of humic substances

At the end of the experiment, high values of humic substances was present in the water to which the natural adsorbents Luvisol (0.105 nm to a maximum of 0.322 nm) and Planosol (0.119 nm to a maximum of 0.488 nm) were released. A smaller volume of humic substances remained present in the water used for the Scheelite tailing (0.013-0.058 nm), so this adsorbent was not used in this step. The treatment was effective in reducing the release of humic substances in water to between 0.011-0.026 nm (Luvisol) and 0.013-0.037 nm (Planosol). Both Planosol and Luvisol adsorbed around 40% or 20 mg L^{-1} ; at this concentration the efficacy of the adsorbents decreased, and Planosol performed better than Luvisol (Figure 3).

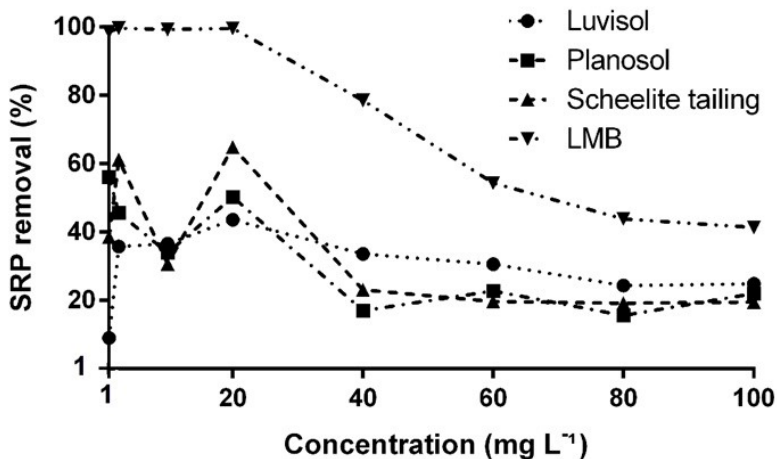


Figure 3. Soluble reactive phosphorus (SRP) removal capabilities of the natural and treated adsorbent materials. LMB=Lanthanum Modified Bentonite; SRP=Soluble Reactive Phosphorus.

Table 3. Maximum SRP sorption capacity of natural and treated adsorbents using Langmuir and Freundlich isotherms.

Adsorbent	Langmuir			Freundlich		
	SRP sorption capacity (mg g ⁻¹)	r	p-value	1/n	r	p-value
Luvisol	17.5	0.91	< 0.001**	1.35	0.93	< 0.001**
Scheelite tailing	8.3	0.90	< 0.001**	1.69	0.92	< 0.001**
Planosol	7.7	1.17	< 0.001**	1.81	1.16	< 0.001**
LMB	16.0	2.14	< 0.001**	3.33	1.70	< 0.001**
Luvisol treated	11.1		0.0178*	-	-	-
Planosol treated	22.3		< 0.001**	-	-	-

LMB = Lanthanum Modified Bentonite; SRP = Soluble Reactive Phosphorus. **p-values less than 0.001; r = model adequacy coefficient; 1/n = indicate whether or not the isotherm is favorable.

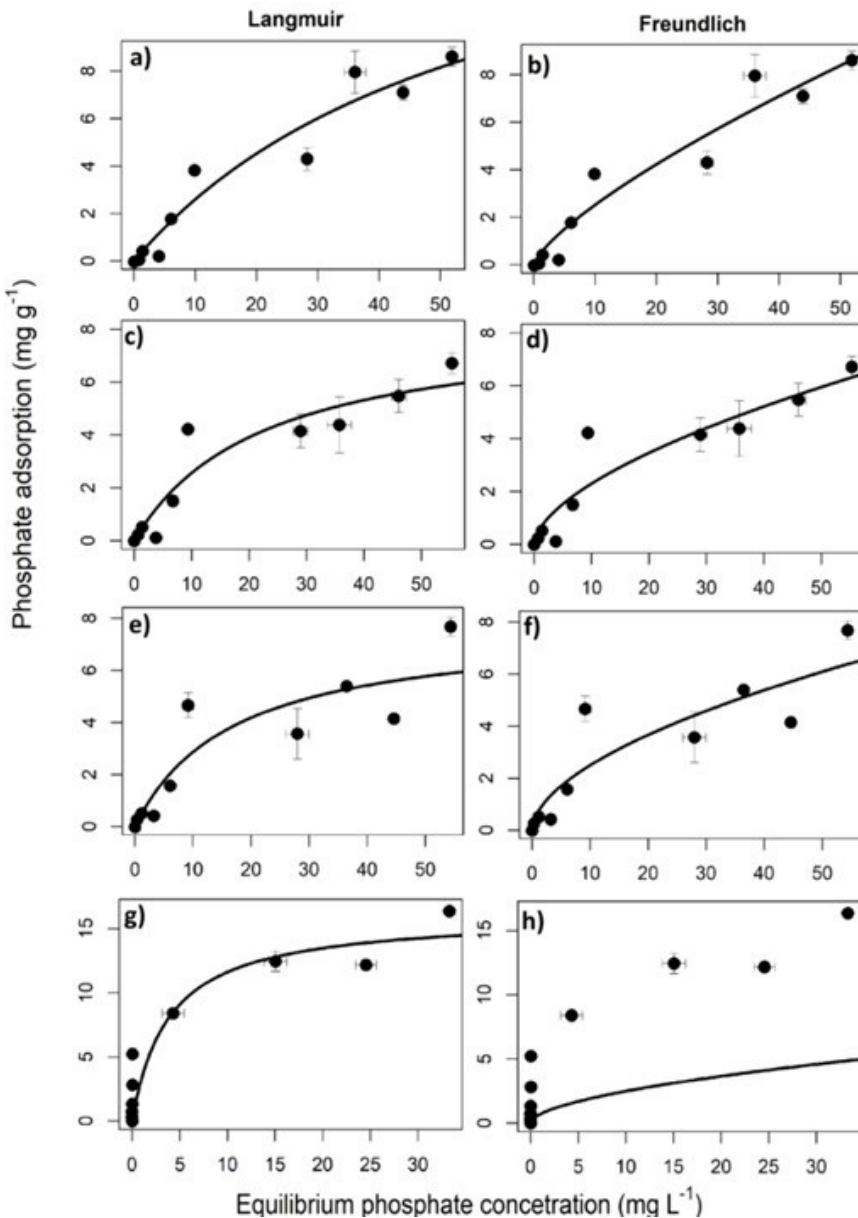


Figure 4. Langmuir (left) and Freundlich (right) adsorption isotherms for the adsorbent materials: (a) and (b) Luvisol; (c) and (d) Scheelite tailing; (e) and (f) Planosol; and (g) and (h) LMB. LMB= Lanthanum Modified Bentonite; SRP=Soluble Reactive Phosphorus.

Planosol was potentiated to SRP adsorption after the treatment, increasing its adsorption capacity from 7.7 to 22.3 mg g⁻¹. In the case of Luvisol, SRP adsorption decreased from 17.5 to 11.1 mg g⁻¹ (Table 3; Figure 5).

4. Discussion

All of the natural adsorbents tested showed high SRP sorption potential. The hypothesis that the best natural adsorbents would be those composed predominantly of clay was refuted; the chemical and mineralogical composition of the materials was found to be more important. However, the hypothesis that materials containing less humic substances would be more adsorbent was confirmed for Planosol and refuted for Luvisol.

The application of Scheelite tailing, Planosol, and LMB increased the pH of the water, which can be explained by high saturation with exchangeable bases of the adsorbent materials. The tailing has a higher alkalization potential due to its chemical composition. Among the tested adsorbents, Luvisol had lower content of exchangeable bases and therefore did not change the pH of the water. In our results, LMB increased the pH of water, unlike the

results reported in most other studies (Lürling & van Oosterhout, 2013; Kasprzyk & Gajewska, 2019). This effect may be reduced in natural water because eutrophic waters are for the most part alkaline in semiarid regions (Barbosa et al., 2012; Brasil et al., 2016) and have greater buffering power, which may prevent the pH change.

The adsorption data of all materials were well adapted to the Langmuir isotherm, and only LMB was not adapted to the Freundlich isotherm. However, the higher values of adsorption capacity and intensity found for the Freundlich isotherm ($1/n > 1$) indicates that this type of isotherm is not favorable (McKay, 1996). This model predicts that for the data to fit well, adsorption must occur through multiple layers and that the adsorbents must be heterogeneous. The Langmuir isotherm predicts exactly the opposite, that adsorption occurs through a single layer (Febrianto et al., 2009). The results suggest that the tested SRP adsorbent materials follow the principle of monolayer adsorption—that is, in the surface areas of the adsorbent materials. The Langmuir isotherm also predicts that adsorption will continue to occur until equilibrium is reached once the binding sites are occupied, and the maximum adsorption capacity for each material can then be found (Febrianto et al., 2009).

Applying the isothermal models revealed that the Scheelita and Planosol tailings reached equilibrium; however, Luvisol did not do it, the results are still in the linear phase of the isotherm, increasing the Q values, so its maximum adsorption capacity may be overestimated. Furthermore, the adjustment of the results using the Langmuir equation did not provide any information on the type of mechanism involved in phosphorus retention (Sposito, 1984).

Although it had a lower content of clay fraction, Scheelite tailing had a high SRP sorption capacity. The presence of gibbsite in this fraction may contribute to the high efficiency of the tailings in SRP sorption. Gibbsite strongly retains phosphate (Rolim-Neto et al., 2004; Eriksson et al., 2016), so knowledge of the mineralogy of clay fraction is essential to understand the potential for SRP sorption by the natural adsorbent materials, even more than quantity. In semiarid regions, gibbsite plays a greater role in the maximum phosphorus sorption capacity of soils than iron oxides (Agbenin & Tiessen, 1994).

Scheelite tailing also contains vermiculite, a 2:1 clay with a permanent negative charge density that is high on the face of the mineral and variable

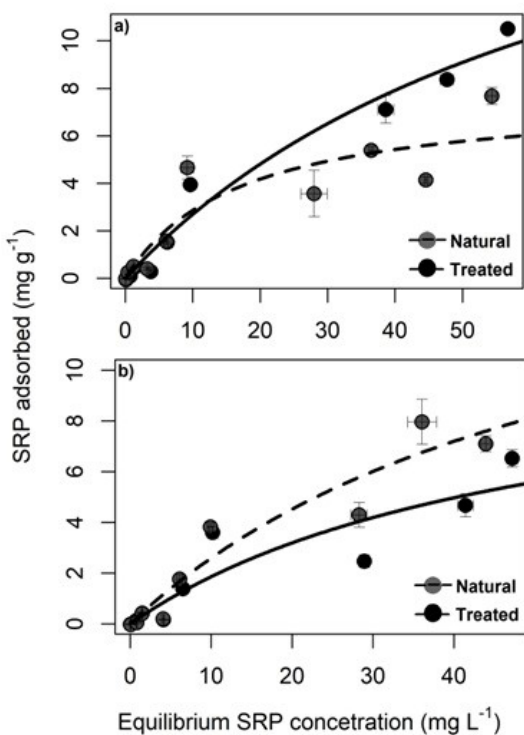


Figure 5. Langmuir adsorption isotherms for the natural adsorbents: (a) Planosol; (b) Luvisol, after the reduction of humic substances. SRP=Soluble Reactive Phosphorus.

at the edges (Tombácz & Szekeres, 2006). This indicates that in the alkaline pH found in soils in tropical semiarid regions, variable loads are predominantly negative with reduced potential for phosphorus sorption. Thus, unlike what happens with gibbsite, the presence of vermiculite indicates that the contribution of specific adsorption to SRP removal is low. However, the high exchangeable Ca^{2+} levels found in these tailings may indicate the considerable participation of precipitation in the P sorption verified for this adsorbent. In semiarid regions, the highest maximum sorption capacities are found in alkaline soils with high levels of Ca^{2+} (Farias et al., 2009; Vieira, 2017).

As the mineralogy of the clay fractions of Luvisol and Planosol did not vary, the differences observed in the SRP sorption potential for these adsorbent materials were due to variations in the contents of exchangeable bases and the organic matter in the soil. Luvisol was found to have the highest Q value in this study. Although this value may have been overestimated, precipitation of the SRP with the available iron, which was present in large amounts in its composition and has a high affinity to bind to phosphate, justified the performance of this adsorbent (Lake et al., 2007).

The idea that the clay fraction content is not the determinant factor of SRP sorption in semiarid regions as it is in humid tropical regions was corroborated by Planosol. This adsorbent was found to have the lowest Q value, although the tested adsorbents indicated that it had a higher clay fraction.

Kaolinite, present in Luvisol and Planosol, is a 1:1 non-expandable clay with a variable charge—that is, it is susceptible to protonation and deprotonation when the pH of the medium changes (Tombácz & Szekeres, 2006). The alkaline pH range of the soils in semiarid regions deprotonates the Al-OH, Si-OH, and Fe-OH binding sites present in the variable charge of the clay minerals and in Fe and Al oxides such as hematite, Goethite, and gibbsite (Fang et al., 2017), resulting in lower SRP sorption capacity (Dunne et al., 2020). In fact, negative ΔpH values, together with PCZ values lower than the pH of the water, indicate a predominance of negative charges in the tested adsorbent materials (Tombácz & Szekeres, 2004, 2006). Negative charges disfavor the anion adsorption process, suggesting the precipitation of insoluble phosphates as the predominant mechanism in the SRP sorption verified in this study. In tropical semiarid soils, such as those found in northeastern Brazil, the

precipitation process is very important and common (Farias et al., 2009).

The release of humic substances in water in the adsorption experiments with Planosol and Luvisol was justified by the higher levels of organic matter found in these soils (Meurer, 2006) compared to the Scheelite tailing. In Planosol, the isotherm equilibrium was not achieved and therefore the Q value (22.3 mg g^{-1}) may have been overestimated. Humic substances can occupy the SRP binding site, competing with it in the sorption process (Dithmer et al., 2016; Lurling et al., 2014). It may also be associated with cations such as Fe^{2+} , Al^{3+} , and Ca^{2+} (Hadgu, 2014), thus blocking adsorption and precipitation.

In the Scheelite tailing, the low content of humic substances released in the water was a factor that favored the high sorption potential of this adsorbent material. In the case of Luvisol, the opposite occurred: the Q values were lower after the reduction of humic substances in the samples. However, after the treatment, the curve was closer to equilibrium, indicating that the previous Q value had probably been overestimated. After the removal of the humic substances, Luvisol reached a maximum sorption capacity greater than that of Scheelite tailing, even though its Q value was less than that of Luvisol prior to incineration.

Previous studies have shown LMB's high potential for SRP sorption (Zamparas et al., 2012; Lüriling & van Oosterhout, 2013; Noyma et al., 2016; Mucci et al., 2018), which was confirmed by the results of this study. LBM is composed of smectites, which are expansive clays such as bentonites (Coelho et al., 2007). However, these bentonites must be modified in order to acquire a greater maximum sorption capacity, making this product more efficient but also more expensive (Haghseresht et al., 2009), thus rendering its use unfeasible for large applications in developing countries, or for repeated interventions (Mucci et al., 2018).

All of the natural adsorbents tested performed well in SRP sorption. The removal percentages of natural materials, even lower than that of LMB, were sufficient to remove SRP, as they are above the phosphorus values in water bodies. The removal percentages of natural materials in tropical semiarid eutrophic waters were found to be average for total phosphorus (TP) above $100 \mu\text{g L}^{-1}$, which is considered a high concentration (Brasil et al., 2016; Cavalcante et al., 2018; Leite & Becker, 2019).

The Q_s of the natural adsorbents tested in this study were high compared to the results for other natural soils reported in the literature (Table 4). Red soil originating in Brazil produced the highest Q found in the literature. This type of soil is more developed and thus more acidic and oxidic, having high levels of H^+ , Al^{3+} , and Fe^{2+} . In these cases, P sorption is attributed to the high levels of iron oxides (Pinto et al., 2013). P sorption by the natural adsorbent materials reviewed in this study was attributed to the precipitation of phosphates, which are extremely stable in the tested environmental conditions. This is characterized as an advantage for Scheelite tailing and Planosol, as the P bound to iron and aluminum are released under anoxic conditions (Kozerski & Kleeberg, 1998; Lake et al., 2007) such as those frequently found in eutrophic reservoirs due to stratification. Another important factor is that P bound to calcium is released only when the pH of the environment is acidic (Kim et al., 2003), whereas in reservoirs in semiarid regions the pH is generally alkaline (approximately 8.0) (Barbosa et al., 2012; Figueiredo & Becker 2018), making calcium phosphate an insoluble compound.

The precipitation of SRP by Luvisol, Planosol, and Scheelite tailing refuted the hypothesis that the greatest SRP adsorption would be that of the natural adsorbent material with a higher clay content, indicating that the mineralogy of this clay fraction in addition to the content of exchangeable bases in the soil is more important than clay fraction

content, as was reported by other studies (Rolim-Neto et al., 2004; Corrêa et al., 2011).

The potential for Luvisol (treated) and Planosol (natural) to reach equilibrium was high; however, in the case of Luvisol, these bonds with phosphorus were probably made with iron, which would be difficult in an anoxic environment. Regarding natural Planosol, this potential was no greater than that of Scheelite tailing, making Scheelite tailing the most promising material for eutrophic environments due to its high sorption capacity. This capacity will probably remain high under anoxic conditions, because Scheelite tailing is a calcium-rich alkaline material. It also has a small amount of organic matter and, consequently, contains less humic substances.

Despite this, the tailings have high concentrations of some heavy metals: Cd, Cr, Cu, Ni, Pb and Zn (Nascimento et al., 2021). Therefore, release and fractionation tests for heavy metals are suggested, as cyanobacteria can absorb heavy metals and biomagnify these elements in the food chain (Rybak et al., 2013), causing effects to aquatic biota and, later on, humans can be exposed to effects carcinogens (He & Chen, 2014). The heavy metals present in the tailings will probably only be released under specific water conditions, such as acidic pH, which is not the case of semiarid waters, nor the pH of the adsorbent material, making these metal fractions not readily bioavailable (Sobral et al., 2011).

Table 4. Data gathered from the literature and the results of this study regarding the maximum SRP adsorption capacity of natural soils in deionized and natural water under different pH conditions.

Material	Water type	pH	SRP sorption capacity(mg g ⁻¹)	Bibliography
Luvisoil	Deionized	8	17.5	This study
Luvisoil treated	Deionized	8	11.1	This study
Planosoil	Deionized	8	7.7	This study
Planosoil treated	Deionized	8	22.3	This study
Scheelite tailing	Deionized	8	8.3	This study
Red Soil	Reservoir	6.5	3.0	Noyma et al. (2016)
Red Soil	Deionized	6	4.5	Mucci et al. (2018)
Red Soil	Deionized	8	1.6	Mucci et al. (2018)
Bauxite	Deionized	6	1.44	Mucci et al. (2018)
Bauxite	Deionized	8	1.78	Mucci et al. (2018)
Bentonite	Deionized	6-7	0.408 (mg m ²)	El Bouraie & Masoud (2017)
Bentonite	Deionized	5.45	0.28	Moharami & Jalali (2015)
Kaolinite	Deionized	5.45	0.32	Moharami & Jalali (2015)
Calcite	Deionized	5.45	1.82	Moharami & Jalali (2015)

SRP = Soluble Reactive Phosphorus.

The high pH caused for the Scheelite tailing in water can trigger the release of phosphate from aerobic sediments on metal oxide-hydroxide surfaces (Andersen, 1975; Eckert et al., 1997). Due to the high buffering capacity of sediments, the effect of pH is believed to be restricted to the oxidized surface layer of the sediment (Drake & Heaney, 1987). Furthermore raising the pH can increase the inorganic N supply of the sediments, making available for absorption by organisms. Thus, pH-induced release of ammonium from sediments can therefore be an important N source of primary productivity during blooms (Gao et al., 2012). Therefore, it is essential that conducting further tests with reservoir water for all of the adsorbent materials tested in this study to observe the sorption potential and the increase of pH. Finally, characterizing this SRP adsorbent material (using granulometry, mineralogy, pH, Δ pH, PCZ, exchangeable cations, and organic matter) was essential to reveal the sorption processes and the possible applications of these materials.

5. Conclusions

The SRP sorption potential of all three semiarid natural adsorbents tested (Scheelite tailing, Planosol, and Luvisol) was high, and the precipitation process was probably the main sorption mechanism, being more expressive than that of adsorption. The mineralogy of the clay present in natural adsorbents was more important than quantity in the sorption process. Of the adsorbents tested, Scheelite tailing was the most promising SRP adsorbent material for eutrophic environments due to its high sorption capacity and low organic matter content (and thus lower humic substance content), however, tests for release and fractionation of heavy metals are needed. For Planosol, reducing its humic substances content was found to increase the SRP sorption process.

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