Assessment of the use of tropical peats as local alternative materials for the adsorption of Pb, Zn and Cd: An equilibrium study

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ABSTRACT

Peat is an organic material that has been widely used as an efficient and low-cost adsorbent. As many studies tend to focus on temperate peats, there is a lack of knowledge about the adsorption mechanism of tropical peats. This paper investigates the use of two Brazilian peats (Cravinhos - C and Luis Antônio - LA) from the Mogi-Guaçu river basin for the adsorption of lead (Pb), zinc (Zn), and cadmium (Cd), in order to contribute to the use of local and easy access materials to remediate contaminated sites. The peats adsorbed a high percentage of cations, especially Pb cations (100.0-46.3%), with commercial peat C showing higher adsorption than peat LA. The removal order was Pb\(^{2+}\) > Cd\(^{2+}\) ≥ Zn\(^{2+}\) for C and Pb\(^{2+}\) > Zn\(^{2+}\) > Cd\(^{2+}\) for LA. The batch data for both peats and for all metals were better fit by the Langmuir isotherm, with adsorption capacities (q\(_m\)) for Pb, Zn, and Cd of 37.3134, 29.0674 and 21.2890 mmol kg\(^{-1}\) in peat C and 21.7391, 14.2550 and 3.6460 mmol kg\(^{-1}\) in LA, respectively, values comparable to those of other peats and biosorbents. The studied peats are considered efficient, alternative and low-cost adsorptive materials for these metals. The proximity of peatlands to areas with high potential for contamination necessitates the use of local materials to reduce remediation costs.

RESUMEN

Evaluación del uso de turbas tropicales como materiales alternativos locales para la adsorción de Pb, Zn y Cd: Un estudio de equilibrio

La turba es un material orgánico que se ha utilizado ampliamente como adsorbente eficiente y de bajo costo. Dado que muchos estudios tienden a centrarse en las turbas templadas, hay una falta de conocimiento sobre el mecanismo de adsorción de las turbas tropicales. Este trabajo investiga el uso de dos turbas brasileñas (Cravinhos - C y Luis Antônio - LA) de la cuenca del río Mogi-Guaçu para la adsorción de plomo (Pb), zinc (Zn) y cadmio (Cd), con el fin de contribuir al uso de materiales locales y de fácil acceso para remediar sitios contaminados. Las turbas adsorbieron un alto porcentaje de cationes, especialmente cationes Pb (100.0-46.3%), mostrando la turba comercial C una mayor adsorción que la turba LA. La orden de eliminación fue Pb\(^{2+}\) > Cd\(^{2+}\) ≥ Zn\(^{2+}\) para C y Pb\(^{2+}\) > Zn\(^{2+}\) > Cd\(^{2+}\) para LA. Los datos de equilibrio por lotes para turbas y para todos los metales se ajustaron mejor a la isoterma de Langmuir, con capacidades de adsorción (q\(_m\)) para Pb, Zn y Cd de 37.3134, 29.0674 y 21.2890 mmol kg\(^{-1}\) en turba C y 21.7391, 14.2550 y 3.6460. mmol kg\(^{-1}\) en LA, respectivamente, valores comparables a los de otras turbas y biosorbentes. Las turbas estudiadas se consideran materiales adsorbentes eficientes, alternativos y de bajo costo para estos metales. La proximidad de las turberas a áreas con alto potencial de contaminación requiere el uso de materiales locales para reducir los costos de remediación.
Introduction

Peat is formed by the decomposition of several plant materials in the waterlogged environments of marshes, bogs and swamps (Spedding, 1988; Zulkiifley et al., 2016) and is present on all continents, from sea level to high altitudes (Joosten and Clarke, 2002). Peatlands cover an estimated area of 400 million hectares. However, peats located in tropical and subtropical regions correspond to a small portion of the total: 35.80 million hectares (Andriesse, 1988; IPS, 2008).

The typical characteristics of a tropical climate (high precipitation, high evapotranspiration and high average annual temperatures) directly affect the type of peat formed in this region. Climate has both direct (for example, via hydrology) and indirect (via the vegetation species; trees, containing woody material, are typically present in tropical regions, whereas sedges and *Sphagnum moss* are found in temperate regions) effects on peatlands. The temperature also influences the rate of oxidation of the material, and since tropical soils frequently have larger sesquioxide contents than soils in temperate regions, their iron and aluminum contents may be higher. The tropical climate region is defined as that located between the Tropics of Cancer and Capricorn. However, the typical characteristics of tropical peat do not necessarily coincide with the geographical limits, especially at high altitudes. Thus, tropical peatlands can be found on the entire African continent and in most of South America (notably Brazil and Uruguay), southern Florida, North Carolina and Southeast Asia (which contains the largest extension, approximately 57%, of tropical peat deposits) (Andriesse, 1988).

Peat is a material with a high organic matter content, consisting of mainly lignin, cellulose and humic substances (which include humic acids, fulvic acids and humin). The presence of functional groups (such as carboxylic acids, phenolic hydroxides and alcohols) associated with these organic compounds imparts a polar character; therefore, peat is a material with high potential for adsorbing metals and polar organic molecules (Couillard, 1994).

Due to its characteristics, peat has been studied over the past decades as a low-cost, efficient and environmentally friendly adsorbent for potentially toxic elements (PTEs) (Babel and Kurniawan, 2003; Bolan et al., 2014; Zehra et al., 2014; Leiviskä et al., 2018; Lima et al., 2018). Contamination by PTEs contributes to environmental degradation. Several anthropogenic sources, such as fertilizers, mines, landfills and industrial sites, may result in potential hotspots of PTEs pollution (Orgiazzi et al., 2016; Mohamed et al., 2017). The presence of PTEs as contaminants can create significant environmental risks over time, as these metals are nondegradable and can become mobile and available to biological receptors. These elements may bioaccumulate and biomagnify to critical levels in the food chain, generating grave effects on human health as well as on flora and fauna (Siegel, 2002; Yong and Mulligan, 2003).

Pb, Zn and Cd are PTEs frequently present in areas contaminated by industrial and mining activities (Kasemodel et al., 2016; Marques et al., 2019). Pb is a toxic element that is nonessential and has the potential to accumulate in humans, affecting fundamental biochemical processes; it has the ability to imitate Ca and consequently inhibit Ca-protein interactions (ATSDR, 2007). Cd is another environmental pollutant. It is toxic to plants and organisms at smaller concentrations than Zn, Pb and copper (Cu) are (Adriano, 1986). Studies have provided evidence that Cd is a carcinogenic element and that acute exposure can lead to death in humans and animals (ATSDR, 2012; Santos et al., 2016). Zn is an essential nutrient for plants and animals and it is important for the biological functions of living tissues. However, when present in high concentrations in the environment, Zn becomes toxic to organisms (Kabata-Pendias, 2011). Chronic ingestion of Zn is also dangerous and may have negative effects on the gastrointestinal and hematological systems (WHO, 2001; ATSDR 2005).

The treatment of PTE-contaminated water and soil includes several processes, including adsorption. To date, knowledge is still limited, and a complete understanding of the mechanisms involved in adsorption has not been achieved. Although several studies have explored adsorption by peat from temperate and boreal climate zones (e.g., Coupal and Lalancette, 1976; Gosset et al., 1986; Chen et al., 1990; Brown et al., 2000, Qin et al., 2006; Kalmykova et al., 2008; Koivula et al., 2009; Bartczak et al., 2018; Egene et al., 2018; Hammi et al., 2019), there are little works using tropical peat deposits (Petroni, 2004; Balasubramanian et al., 2009; Abat et al., 2012; Lima, 2017; Santos et al., 2018; Marques et al., 2020). Nonetheless, interest in PTE adsorption by tropical peat is increasing due to its low cost and high availability. In Brazil alone, there are approximately 24,000 km² of peatlands (WER, 2013), therefore, there are many areas still available as a natural resource. According to Franchi et al. (2006), the use of peat in countries with tropical climate is recent, increasing the interest in these areas.

The Mogi-Guaçu river basin, located in the northeast of the state of São Paulo (Brazil), and drainage area of approximately 15,000 km², is an example of an area with extensive peatland that can be easily exploited (PERH, 2005). The Mogi-Guaçu peat deposits are found in the extensive flood plains associated with the meandering river system (Franchi et al., 2006). These peatlands originate from predominantly the remnants of grasses or, alternatively, woody plants (Franchi, 2004).

Brazil, like many other developing countries, struggles with PTE contaminations (Reis et al., 2019; Trevizani et al., 2019; Fernandes et al., 2020). As regards Mogi-Guaçu river basin, some studies have shown the presence of Pb, Cd, and Zn (among others PTE) in high concentrations in water, sediments, and living organisms; wherein, their concentrations can vary according to the period of floods (Tomazelli and Martinelli, 1999; Tomazelli, 2003; Silva, 2005; La Serra, 2015). In addition, the Mogi-Guaçu river basin Committee (SIGRH, 2020) establishes that the basin is classified as industrial, with emphasis on agribusiness (including sugarcane and orange), pulp and paper industry, slaughterhouses, among others. The agriculture is considered an important source of PTE for soil and water bodies, which can occur through fertilizers, pesticides, and soil amendments (Silva et al., 2016; Shanshan and Yanqing, 2020); however, the effluents of the pulp and paper industry stand out due to the presence of Pb, Cd, Zn and Cu in their composition (Frisso et al., 1996). PERH (2005) confirmed the high demand of organic water for industrial activity in the Mogi-Guaçu river system. These pointed factors could increase the risk of contamination of the region by PTE in a short or long-term.

Some studies have shown good results regarding the adsorption of metals to Brazilian peats from various river basins in the states of Sergipe, Bahia, São Paulo, Rio de Janeiro and Santa Catarina (Santos, 1998; Lamim et al., 2001; Franchi, 2004; Petroni, 2004; Crescêncio Junior, 2008; Batista et al., 2009; Cerqueira et al., 2012; Oliveira et al., 2015; Carvalho, 2015; Marques et al., 2020). However, studies are necessary to evaluate the adsorption capacity of peat from the Mogi-Guaçu river basin, since this is a strategically located area (industrial area with high potential for Pb, Zn and Cd contamination) containing peatlands with easy access, which would facilitate the use of and reduce the acquisition costs associated with this reactive material.

Because of this lack of knowledge, the aim of this study was to comparatively assess the Pb, Zn and Cd adsorption capacities of two Brazilian peats collected in two cities from the Mogi-Guaçu river basin: Cravinhos (already commercialized in the country) and Luis Antônio. This study also intends to verify whether the adsorption results are compatible with those of other peats (including tropical and temperate ones), as well as those of other biosorbents. Studies such as this might encourage the use of locally available adsorptive materials and might also provide a promising direction for the development of low-cost and ecofriendly technologies for soil and water remediation, especially in tropical contaminated areas.

**Materials and methods**

**Field sampling**

Peat samples for this study were sourced from the Mogi-Guaçu river basin (São Paulo State, Brazil) in two different cities: Cravinhos (peat C) and Luis Antônio (peat LA) (Figure 1).

Peat C is exploited for commercial use since its modified form (as liquid humic acid) is widely used as a fertilizer for local crops. The peat C is extracted and placed in piles in the field (Figure 2) to subsequently proceed to air drying (in covered area) and to modification (Marques et al., 2020). Peat C collection and placed in piles in the field (Figure 2) to subsequently proceed to air drying (in covered area) and to modification (Marques et al., 2020). Peat C collection and placed in piles in the field (Figure 2) to subsequently proceed to air drying (in covered area) and to modification (Marques et al., 2020).
Peat C is a commercialized peat, and after receiving it from the company, the samples were sieved through 2 mm mesh, dried at 50°C for 48 h and then homogenized. Peat LA was first dried at room temperature, homogenized in a porcelain mortar, sieved through 2 mm mesh, and subsequently dried at 50°C for 48 h. Both peats were stored at room temperature prior to analysis. Some physicochemical properties of both peats were published by Raimondi et al. (2019) and are summarized in Table 1. Table 1 also shows additional characteristics to those presented by Raimondi, such as specific surface area and pore volume, which are important properties for adsorption studies. According to Raimondi et al. (2019), both peats have similar characteristics, and the results indicate that these materials are favorable for PTE ion retention. Most of the characteristics of the two peats were similar, but peat C had a higher organic matter content, and specific surface area, besides a lower cation exchange capacity (CEC).

### Table 1. Physicochemical properties of peat C and peat LA

| Parameter                  | Peat C          | Peat LA         | Reference          |
|----------------------------|-----------------|-----------------|--------------------|
| Organic matter             | 520.43 ± 2.08 g kg⁻¹ | 510.06 ± 8.26 g kg⁻¹ | Raimondi et al. (2019) |
| Ash content                | 47.9 ± 0.2%     | 48.9 ± 0.8%     |                    |
| Cation exchange capacity   | 91.0 cmol kg⁻¹  | 116.0 cmol kg⁻¹ |                    |
| pH                         | 5.1 ± 0.1       | 5.9 ± 0.1       |                    |
| Specific surface area      | 3.45 m² g⁻¹     | 2.04 m² g⁻¹     | This study         |
| Pore volume                | 0.025 cm³ g⁻¹   | 0.014 cm³ g⁻¹   |                    |

### Metal adsorption experiments

Batch adsorption experiments were carried out to evaluate the adsorption capacities of the peats. These procedures were based on and adapted from the methodology used by Roy et al. (1992), Soares and Casagrande (2000) and ASTM D4646 (2016). One gram of the tropical peat samples was added to a Falcon tube containing 50 mL of a single metal solution. This peat/solution ratio (1/50) was used because it is the most favorable condition according to the preliminary step presented in Lima (2017) and Raimondi et al. (2019), studies that characterized both tropical peats from the Mogi-Guaçu river basin.

In the batch adsorption assays, eight initial concentrations of the three ions (Pb²⁺, Zn²⁺, and Cd²⁺), which ranged from 0.10 to 2.36 mmol L⁻¹, were used. The most concentrated solutions of each metal (1.05, 2.36 and 1.45 mmol L⁻¹ for Pb²⁺, Zn²⁺ and Cd²⁺, respectively) were prepared by dissolving the corresponding chloride salt (PbCl₂, ZnCl₂, and CdCl₂·H₂O) in deionized water. The remaining concentrations were obtained by diluting the concentration solutions in deionized water. The pH of the initial suspensions was not adjusted, and the pH of the solutions ranged from 4.0 to 6.0 depending on the peat and the PTE analyzed. The suspensions were agitated on a horizontal shaking table (Novatécnicas, NT 155) at an agitation rate of approximately 120 rpm. After being agitated for 24 h (contact time determined according to ASTM D4646 (2016), the samples were centrifuged and filtered through Unifil filter paper (weight of 80 g m⁻² and particle retention of 4-12 μm). The Pb²⁺, Cd²⁺ and Zn²⁺ concentrations in the filtrates were determined by an atomic absorption spectrometer (PerkinElmer PinAAcle 900F). The instrument standard curves had three points at different concentrations (dilution of the respective PerkinElmer standards - ISO 9001 Purity Certification - in deionized water), and correlation coefficients higher than 0.995 were utilized. The solutions were diluted according to the instrument’s quantification limits (0.448 mg L⁻¹ Pb²⁺, 0.006 mg L⁻¹ Zn²⁺, and 0.018 mg L⁻¹ Cd²⁺), and the maximum value indicated by the manufacturer for a linear fit zone of the equipment (10.00 mg L⁻¹ Pb²⁺, 0.75 mg L⁻¹ Zn²⁺, and 1.00 mg L⁻¹ Cd²⁺). Batch equilibrium tests were performed in triplicate at room temperature (approximately 25°C).

The efficiency of metal removal by both peats was calculated as a percentage, as shown in Equation 1:

\[
\text{metal removal}(\%) = \frac{(C_0 - C_e) \times 100}{C_0}
\]  

(1)

The ions adsorbed by a mass of material at equilibrium \((q_e)\) in mmol kg⁻¹ was calculated by Equation 2:

\[
q_e = \frac{(C_0 - C_e) V}{m}
\]

(2)

In Equations 1 and 2, \(C_0\) is the initial concentration of ions in solution (mmol L⁻¹), \(C_e\) is the ion concentration after adsorption equilibrium (mmol L⁻¹), \(V\) is the solution volume (L), and \(m\) is the mass of peat (kg).

The Langmuir (types I and II) and Freundlich (linearized forms) isotherm models were chosen to investigate the mechanism of target adsorption.
metal adsorption. According to Febrianto et al. (2009), both Langmuir and Freundlich isotherms are widely used to describe PTEs adsorption by biosorbents (which include peat).

The Freundlich isotherm has been used to interpret adsorption onto heterogeneous surfaces or surface sites with different affinities (Bulgariu et al. 2011, Freitas et al. 2018). The Freundlich isotherm is expressed in Equation 3:

\[ q_e = K_f C_e^n \]  

(3)

The linearized form of the Freundlich isotherm is expressed in Equation 4:

\[ \log q_e = \log K_f + n \log C_e \]  

(4)

The Langmuir isotherm is based on monolayer adsorption onto homogeneous surfaces and can be used to estimate the maximum adsorption capacity of the surface (Langmuir, 1997). This isotherm is expressed in Equation 5:

\[ q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \]  

(5)

The linearized forms of the Langmuir isotherm are expressed in Equation 6 for Langmuir I and Equation 7 for Langmuir II:

\[ \frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} \]  

(6)

\[ \frac{1}{q_e} = \frac{1}{K_L q_m C_e} + \frac{1}{q_m} \]  

(7)

In Equations 3 to 7, \( K_f \) and \( K_L \) are the Freundlich equilibrium constant (L kg\(^{-1}\)) and Langmuir constant related to the binding energy (L mmol\(^{-1}\)). The separation factor \( R_s \) is a dimensionless constant calculated to predict the feasibility of the Langmuir isotherm (Foo and Hameed, 2010) and is defined in Equation 8:

\[ R_s = \frac{1}{1 + K_L C_0} \]  

(8)

The adsorption process can be described as a function of \( R_s \) as follows:

- \( R_s > 1 \): Unfavorable;
- \( 0 < R_s < 1 \): Favorable;
- \( R_s = 0 \): Irreversible

Additionally, the change in free energy \( (\Delta G) \) was evaluated from the Langmuir constant. Thermodynamic parameters are often used in environmental engineering to determine whether the process will occur spontaneously (Ho, 2006). The \( \Delta G \) calculation is presented in Equation 9.

\[ \Delta G = -RT \ln K_L \]  

(9)

In Equation 9, \( R \) is the universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), and \( T \) is the absolute temperature (K). The temperature in the experiments was 25°C.

**Results and discussion**

In the batch adsorption experiments, the adsorption percentage of both peats was calculated as a function of the initial concentration, and the results are shown in Figure 3. The ion adsorption on peat occurred in single-solution systems. The removal percentage of the three ions was dependent on the initial concentration, and higher removal occurred at lower concentrations, with maximum removal reached at the lowest concentration (for example, 100\% Pb, 81.4\% Zn and 90.8\% Cd for peat C).

Peat C had a higher efficiency than peat LA, and the difference in metal ion removal can be seen in Figure 3. Both peats adsorbed more Pb than Cd and Zn, showing the preference of peat for this cation. In peat C (Figure 3a), the Pb adsorption was above 70\% at all concentrations (from 100.0 to 71.9\%), while in LA (Figure 3b), the Pb removal ranged from 98.6 to 46.3\%. For peat C, the removal order was Pb\(^{2+} > Cd^{2+} > Zn^{2+}\). The removal efficiency was very similar for Zn and Cd (81.4 to 27.8\% Zn and 90.8 to 34.4\% Cd) but was slightly higher for Cd. For peat LA, the removal efficiency followed an order of Pb\(^{2+} > Zn^{2+} > Cd^{2+}\), with Zn removal ranging from 39.6 to 12.5\% and Cd removal from 52.6 to 9.8\%. Figure 3b shows that Cd removal achieved higher percentage (52.6\%) over Zn (39.6\%) at the lowest initial concentration, however, its removal was generally lower. Therefore, following the order of Pb\(^{2+} > Zn^{2+} > Cd^{2+}\).

According to Qin et al. (2006), adsorption affinity is frequently correlated with electronegativity and softness. The preference of peat for Pb\(^{2+}\) can be explained, for example, by the theory of hard and soft acids and bases (HSAB) (Pearson, 1968). According to this theory, “C class cations”, such as Pb\(^{2+}\), form stronger complexes with fulvic and humic acids in peat than “B class ions” (Zn\(^{2+}\) and Cd\(^{2+}\)) (Kalmykova et al., 2008). When considering electronegativity, the more electronegative the element is, the more strongly it is attached to the surface (McKay and Porter, 1997). Pb has the maximum adsorption capacity and the greatest electronegativity (2.33) (Table 2). Nonetheless, the order of Cd (1.69) and Zn (1.65) held true for only peat C. However, it is important that the electronegativity of Cd and Zn are similar, as are the removal efficiency results for both metals in the peats. Regarding the order Zn\(^{2+} > Cd^{2+}\) for peat LA, Liu et al. (2009) reported that the larger ionic radius of Cd may interfere with its access to the adsorbent pores, even though it has a higher affinity for binding sites. In fact, the larger pore volume of peat C (0.025 cm\(^3\) g\(^{-1}\)) could allow greater access to Cd ions than the LA peat pore volume (0.014 cm\(^3\) g\(^{-1}\)) could allow.

**Figure 3** Percentage of metal ion removal versus the initial concentration of Pb\(^{2+}\), Cd\(^{2+}\) and Zn\(^{2+}\) for two natural Brazilian peats: (a) Peat C, (b) Peat LA

**Table 2. Properties of the metal ions**

| Metal ions | Electronegativity\(^1\) | Pearson’s HSAB\(^2\) |
|------------|----------------------|------------------|
| Pb\(^{2+}\) | 2.33 | Between hard and soft |
| Zn\(^{2+}\) | 1.65 | Soft |
| Cd\(^{2+}\) | 1.69 | Soft |

\(^1\) Alleoni et al. (2009)
\(^2\) HSAB = hard and soft acids and bases (Pearson, 1968)

The superior efficiency and higher maximum adsorption capacity of peat C in the removal of all three tested ions from solution could be explained by its specific surface area (3.45 m\(^2\) g\(^{-1}\) for C and 2.04 m\(^2\) g\(^{-1}\) for LA – Table 1) as well as its higher organic matter content (520.4 g kg\(^{-1}\) for peat C and 510.06 g kg\(^{-1}\) for peat LA – Table 1). These characteristics may favor the performance of specific adsorption mechanisms. The higher efficiency of C may also be associated with the functional groups present on the surface of this peat.

The pH variation during the batch equilibrium test was also verified (Figure 4). In Figure 4, the “solution pH” was considered the pH of the metallic ion solution (pH at each initial concentration), “initial pH” was the pH after contact between the peat and metallic ion solution, and “final pH” was the pH after 24 h of the experiment. Batch equilibrium tests were performed without buffering the pH because the resulting initial pH of all samples (between 4 and
The adsorption behavior of the Pb\(^{2+}\), Cd\(^{2+}\), and Zn\(^{2+}\) ions onto two tropical peats (C – Cravinhos; LA – Luis Antonio) was within the range considered ideal for the adsorption of metal ions onto peat and soils, between approximately 4 and 8 (Couillard, 1994; Petroni et al., 2000; Qin et al., 2006; Lim and Lee, 2015). Peats generally have a pH of approximately 4.0 due to the humic acids present, and their structures degrade at pH values higher than 9.0 and below 3.0, decreasing their chelation capacity. In addition, at low pH values, the high concentration of H\(^+\) in solution competes with metallic ions in ion exchange reactions, and at high pH values, the formation of metal oxide precipitates is the main active retention mechanism (Couillard, 1994).

As shown in Figure 4, in general, the “initial pH” tended to decrease in relation to the “solution pH”. The “initial pH” resulted from an equilibrium between the “solution pH” and the pH of the material. This decrease compared to the “solution pH” is mainly due to the acidic properties of the carboxylic and phenolic functional groups present in peat (Bloom and Mcbride, 1979; Sharma et al., 2011). The “initial pH” of peat C was lower than the “initial pH” of LA (comparing the same metal – Figure 4). As an example, the “initial pH” of Pb for C ranged from 4.4 to 3.9 as the initial concentration increased, while in LA, this variation was from 4.7 to 4.5. This slight difference in the “initial pH” of the peats may have resulted from the pH of each peat, because the pH of pH\(_{sox}\) (measured in water) for C was 5.1 and that for LA was 5.9 (according to Raimondi et al., 2019). The difference in “initial pH” may have contributed to the higher efficiency of peat C. pH is one of the main parameters that influences adsorption processes, and at lower pH values, Pb, Zn and Cd tend to be ionized and, therefore, more soluble and available for adsorption. Therefore, the higher efficiency of peat C than of LA may be a result of their properties (such as the specific surface area, organic matter content and surface functional groups, as previously mentioned) and the lower pH values under the initial test conditions.

For both peats and for the three metals analyzed, the “final pH” of the samples (pH after 24 h of the experiment) was between 4 and 6. Koivula et al. (2000) emphasized that the final pH resulted from an equilibrium between the “solution pH” and the pH of the material. This decrease compared to the “solution pH” is mainly due to the acidic properties of the carboxylic and phenolic functional groups present in peat (Bloom and Mcbride, 1979; Sharma et al., 2011). The “initial pH” of peat C was lower than the “initial pH” of LA (comparing the same metal – Figure 4). As an example, the “initial pH” of Pb for C ranged from 4.4 to 3.9 as the initial concentration increased, while in LA, this variation was from 4.7 to 4.5. This slight difference in the “initial pH” of the peats may have resulted from the pH of each peat, because the pH of pH\(_{sox}\) (measured in water) for C was 5.1 and that for LA was 5.9 (according to Raimondi et al., 2019). The difference in “initial pH” may have contributed to the higher efficiency of peat C. pH is one of the main parameters that influences adsorption processes, and at lower pH values, Pb, Zn and Cd tend to be ionized and, therefore, more soluble and available for adsorption. Therefore, the higher efficiency of peat C than of LA may be a result of their properties (such as the specific surface area, organic matter content and surface functional groups, as previously mentioned) and the lower pH values under the initial test conditions.

Adsorption isotherms describe the distribution of metal ions between the phases of the solid peat and the aqueous solution and are important elements for obtaining valuable information about the mechanism and nature of the adsorption process (Sposito, 2004; Balan et al., 2008).

The isotherm models fitted to the experimental data were Freundlich and Langmuir (linearized form I and II), and Table 3 provides the parameters of the adsorption models for the three metal ions and their correlation coefficients (R\(^2\)). The equilibrium adsorption isotherm and fitting of the models to the experimental data are shown in Figures 6, 7 and 8 for Pb\(^{2+}\), Zn\(^{2+}\), and Cd\(^{2+}\), respectively.

The highest values of the correlation coefficient R\(^2\) (above 0.9000) are highlighted in gray in Table 3. As seen from the R\(^2\) data, the Langmuir I model fits the data on Pb and Cd for peat C (values of 0.9940 and 0.9366, respectively) and Pb, Zn and Cd for peat LA (0.9369, 0.9772 and 0.9264, respectively), and Langmuir II was a good fit of the data on Cd for peptide C (0.9607) and Zn for peptide LA (0.9938). The Freundlich isotherm model also fit the data for most metallic ions, except for Zn on peptide C (0.6378) and Cd on peptide LA (0.6574).

The correlation coefficient of the Freundlich model was 0.9891 for Pb and 0.9387 for Cd with peptide C and 0.9357 for Pb and 0.9674 for Zn with peptide LA.

The R\(^2\) results from Table 3 suggest that the Langmuir isotherm model is a better fit for Pb, Cd and Zn adsorption on both tropical peats, which is in agreement with other studies of peats, including those from tropical and temperate areas (Bencheikh-Lehocine, 1989; McKay and Porter, 1997; Franchi, 2004; Qin et al., 2006; Batista et al., 2009; Sõukand et al., 2010; Carvalho et al., 2017). Brown et al. (2000) found that Langmuir isotherms were frequently effective in studies modeling the binding of a metal to peat.

For the case of peat C and Zn, the good fit was not obtained for any of the models (Freundlich or Langmuir) (R\(^2\) < 0.7000). As can be seen in Figures 3a and 7, the adsorbed Zn increased rapidly with increasing Zn equilibrium concentrations in the isotherm initial stage and then increased slowly, tending to reach saturation condition. According to the system of isotherm classification (Giles et al., 1974), this behavior suggests that data experimental fit in the “L”-type curve (i.e., Langmuir). This finding is similar to the other metals studied. However, the batch equilibrium results for peat C and Zn revealed two points of adsorption capacity associated with the highest initial concentrations that appear to be above this saturation plateau. This may indicate a change in the adsorbate retention mode evidenced by the completion of the first adsorption monolayer and the start of a second adsorption layer. This may have been the cause of the lack of adjustment to the adsorption models.

The Langmuir isotherm model is assumed to represent monolayer surface coverage without interaction between the adsorbed ions, and the existence of a
In general, for both peats, the parameter $R^2$ (Table 3) ranged between -28.2588 and -19.8527 which are considered from the best fit of the Langmuir model (Langmuir I or II). These two values represent values closer to zero indicate more favorable adsorption. On the basis of the $R^2$ parameter, peat C was very favorable for Pb and Cd adsorption but less favorable for Zn adsorption. In contrast, peat LA was more favorable for Pb and Zn adsorption than for Cd adsorption, following the order of preference obtained from the Langmuir model (Pb$^{2+}>$Zn$^{2+}>$Cd$^{2+}$). Overall, peat C is more favorable than peat LA for the adsorption of metallic ions, except for Zn.

The negative values for the change in free energy ($\Delta G$) (Table 3) ranged between -28.2588 and -19.8527 (kJ mol$^{-1}$) and indicate that metal ion adsorption is spontaneous and feasible at 25°C, while the absolute magnitudes indicate a physisorption process, in accordance with the results determined from the pH data that suggested an ion exchange process. Adsorption with $\Delta G$ between -20 and 0 kJ mol$^{-1}$ implies a physical process, while values from -80 to -400 kJ mol$^{-1}$ correspond to chemisorption (Fernandes et al., 2010). In comparison, Ho (2006) obtained a value of -11.1 kJ mol$^{-1}$ for the adsorption of Pb, while Balan et al. (2008) obtained a value of -26.054 kJ mol$^{-1}$ for Cd adsorption. Both experiments were carried out in Sphagnum moss peat with temperatures close to 30°C, and the parameters were obtained from a Langmuir I linearization. These two values are close to those obtained for the peats in this study and show that the process of metallic ion adsorption in peat is generally achievable and spontaneous and is characterized by physical processes.

![Figure 5](image308x74 to 562x244)

**Figure 5.** Plot of $R_o$ versus the initial concentrations ($C_o$) of Pb$^{2+}$, Cd$^{2+}$ and Zn$^{2+}$ for the two Brazilian peats.
Table 4. Comparison of adsorption capacities ($q_e$) for Pb$^{2+}$, Zn$^{2+}$ and Cd$^{2+}$ of some adsorbents

| Metal adsorbed | Adsorbent | $q_e$ (mmol kg$^{-1}$) | Reference |
|----------------|-----------|------------------------|-----------|
| Pb$^{2+}$      | Peat (Brazil) | 752.86 | Lattuada et al. (2014) |
|                | Peat (Denmark) | 730.00 | Qin et al. (2006) |
|                | Peat (Romania), alkaline treated | 660.30 | Bulgariu et al. (2011) |
|                | Peat (Estonia) | 571.00 | Sõukand et al. (2010) |
|                | Peat (Romania) | 562.40 | Bulgariu et al. (2011) |
|                | Peat (China) | 428.00 | Qin et al. (2006) |
|                | Peat (Poland) | 397.23 | Bartczak et al. (2018) |
|                | Peat (Brazil) treated with HCl | 155.69 | Franchi (2004) |
|                | Peat (Brazil) | 150.36 | Franchi (2004) |
|                | Sugar cane bagasse | 419.67 | Abdelhafez and Li (2016) |
|                | Sugar beet pulp | 356.00 | Reddad et al. (2002) |
|                | Orange peel | 134.45 | Abdelhafez and Li (2016) |
|                | Sugar cane bagasse | 61.78 | Mahmood-ul-Hassan et al. (2015) |
|                 | Peat C (Brazil) | 37.31 | This study |
|                 | Peat L.A (Brazil) | 21.74 | This study |
| Zn$^{2+}$      | Peat (Brazil) treated with HCl | 247.78 | Franchi (2004) |
|                | Peat (Brazil) | 183.54 | Lattuada et al. (2014) |
|                | Peat | 179.00 | McKay and Porter (1997) |
|                | Peat (Brazil) | 102.78 | Franchi (2004) |
|                | Sugar beet pulp | 272.00 | Reddad et al. (2002) |
|                | Commercial activated carbon | 160.60 | Lattuada et al. (2014) |
|                | Rice husk | 35.64 | Lattuada et al. (2014) |
|                | Peat C (Brazil) | 29.07 | This study |
|                | Peat L.A (Brazil) | 14.25 | This study |
| Cd$^{2+}$      | Peat (Denmark) | 447.40 | Qin et al. (2006) |
|                | Peat (Estonia) | 374.00 | Sõukand et al. (2010) |
|                | Peat (China) | 285.00 | Qin et al. (2006) |
|                | Peat | 188.00 | McKay and Porter (1997) |
|                | Peat (Brazil) treated with HCl | 149.76 | Franchi (2004) |
|                | Peat (Romania) | 92.27 | Balan et al. (2008) |
|                | Peat (Brazil) | 59.36 | Franchi (2004) |
|                | Sugar beet pulp | 217.00 | Reddad et al. (2002) |
|                | Compost of organic waste | 14.28 | Simantiraki and Gidarokos (2015) |
|                | Sugar cane bagasse | 6.98 | Mahmood-ul-Hassan et al. (2015) |
|                | Peat C (Brazil) | 21.29 | This study |
|                | Peat L.A (Brazil) | 3.65 | This study |

The Freundlich isotherm of sorption is also one of the most commonly used mathematical descriptions due to its wide adjustment range for experimental concentrations (Mobasherpour et al. 2012). The isotherm theory assumes that the adsorption energy decreases logarithmically as the surface becomes covered by the adsorbate. The Freundlich isotherm is better adjusted to heterogeneous surfaces (Soares and Casagrande, 2000). As occurred for the Langmuir model, most metallic ions were well adjusted to the Freundlich model, with the exception of Cd on peat LA ($R^2$ of 0.6574) and Zn on peat C (0.6378) (Table 3). For the adjustment of Cd on peat C and Pb on peat LA, the correlation coefficients of the Freundlich isotherm (0.9387 and 0.9357, respectively) were practically the same as those of Langmuir I ($0.9366$ for Cd and $0.9369$ for Pb). Lattuada et al. (2014) and Koivula et al. (2009) also found Freundlich to be the most suitable isotherm for Pb adsorption to tropical peat (from Brazil) and temperate peat (from Finland); Lattuada et al. (2014) and Kalmykova et al. (2008) found the same for Zn, and Qin et al. (2006), Balan et al. (2008) and Kalmykova et al. (2008) found the same for Cd.

The Freundlich constant $n$ for all ions was less than 1 and ranged from 0.1586 to 0.3993 (Table 3), indicating favorable adsorption, strong interaction and surface heterogeneity. The closer the value $n$ is to zero, the more heterogeneous the surface is (Soares and Casagrande, 2000; Bulgariu et al., 2011). Zhang et al. (2010) described $n$ values of humic acid from sediment ranging from 0.735-0.902 and suggested unevenly distributed sorption sites on this material. $K_f$ is considered a Freundlich parameter related to the adsorption capacity (Oliveira et al, 2015), and the determined values indicate the great ability of peat C and peat LA to retain Pb ($K_f$ of 45.9934 and 24.3276 L kg$^{-1}$, respectively). For Zn, the parameters were 20.9218 L kg$^{-1}$ for peat C and 10.1438 L kg$^{-1}$ for peat LA, while for Cd, the values were 29.9778 and 3.3527 L kg$^{-1}$, respectively. The $K_f$ values from this study are in agreement with values obtained for adsorption in soils, such as Zn and Cd adsorption in 11 soils (Spodosols and other types); the $K_f$ ranged from 2.1 to 776.3 L kg$^{-1}$ and 5.4 to 755.09 L kg$^{-1}$, respectively (Buchter et al., 1989).

In addition to the adsorption efficiency of the material, the cost is also an important parameter and is even considered essential in the selection of any treatment process. As this study classifies tropical peat as a low-cost adsorbent, price analysis was also conducted.

In the Brazilian market, local peats have been sold on a large scale in 2019 for an average of US$0.05 per kilo (approximately R$0.22 in national currency). On the other hand, in the same market, activated carbon is traded at between US$1.20 and US$2.10 per kilo (approximately R$5.00 – R$9.00), average prices that are 33 times higher than the price estimated for peats. Activated carbon is the most common and efficient adsorbent but has disadvantages due to its cost (especially in developing countries) (Silva et al., 2020). The financial advantage of peat as an alternative and low-cost adsorbent material confirms the importance of the study of local and efficient materials.

In general, both tested tropical peats are efficient adsorptive materials, especially for the removal of Pb. The peat deposits are located near industrial regions and are already close to areas with great potential for contamination. Both peats are therefore easily accessible materials for the remediation of these contaminated areas and can be used in adsorption technologies. These materials can maintain high efficiencies for contaminant removal but reduce the associated treatment costs. Thus, these findings provide direction for the use of local materials in a tropical area for soil and water treatment. According to Crini (2006) and Sharma et al. (2011), an adsorption process can be an attractive technology if the low-cost adsorbent is easy to acquire and ready for use.

**Conclusion**

The batch adsorption experiments showed a high percentage of Pb, Zn and Cd removal by both tropical peats, with the removal efficiency being a function of the initial concentration of the cation. The removal order was Pb$^{2+}$ > Cd$^{2+}$ > Zn$^{2+}$ for peat C and Pb$^{2+}$ > Zn$^{2+}$ > Cd$^{2+}$ for peat LA, showing the higher affinity of both peats for Pb. Pb removal by both materials ranged from approximately 46.0 to 100.0%. Regarding Zn and Cd, the efficiency of removal by peat C remained between 90.8 and 27.8%, while that by peat LA was between 52.6 and 9.8%.
Peat C was slightly more efficient than peat LA, which may have been due to the characteristics of peat C that were more favorable to adsorption than those of peat LA, such as the higher surface area, higher organic matter content, and lower pH of peat C, which resulted in a lower pH in the initial test condition ("initial pH"). Peat C is already commercialized in Brazil, which would further facilitate its use as an adsorptive material.

During the batch assays, the increase in solution pH after adsorption as the initial concentration increased suggested an ion exchange mechanism. This finding is in accordance with the parameter $\Delta G$, which implied a physisorption process. According to the parameters $\Delta G$ and $R_L$, adsorption occurred in favorable, spontaneous and feasible conditions.

Among the isotherm models used to describe the metal adsorption, Langmuir had the best correlation, which included the best fit for both the Langmuir I and Langmuir II models. These best fits assume a monolayer sorption capacity ($q_m$), decreasing in the order of 37.3134, 29.0697 and 21.2890 mmol kg$^{-1}$ for peat C and 21.7391, 14.2550 and 3.6460 mmol kg$^{-1}$ for peat LA for Pb, Zn, and Cd, respectively. Such adsorption capacities are comparable to the values for other peats (including temperate and tropical
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peats), as well as for other biosorbents, proving the potential use of the tested peats.

In some cases, the Freundlich model also achieved a high adjustment, comparable to that of the Langmuir model. The removal of Pb and Cd by peat C ($R^2$ of 0.9891 and 0.9387, respectively) and Pb and Zn on peat LA ($R^2$ of 0.9357 and 0.9674, respectively) indicated favorable adsorption, strong interaction and surface heterogeneity.

Regarding costs, the price of peat in the Brazilian market was found to be 33 times lower than that of activated carbon (an efficient adsorbent with regular use).

In general, both tropical peats are efficient, alternative and low-cost adsorption materials, especially with respect to the removal of Pb. Sources of both peats are located near large industrial areas in Brazil, and the presented findings contribute to the use of local materials to remediate contaminated sites, thus lowering costs and maintaining efficiency.

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References

Abat, M., Mclaughlin, M. J., Jirby, J. K. & Stacey, S. P. (2012). Adsorption and desorption of copper and zinc in tropical peat soils of Sarawak, Malaysia. Geoderma, 175, 58-63. DOI: https://doi.org/10.1016/j.geoderma.2012.01.024

Abdelhafez, A. A & Li, J. (2016). Removal of Pb(II) from aqueous solution by using biochars derived from sugar cane bagasse and orange peel. Journal of the Taiwan Institute of Chemical Engineers, 61, 367-375. DOI: https://doi.org/10.1016/j.jtice.2016.01.005

Adriano, D. C. (1986). Trace elements in terrestrial environments. Springer-Verlag, New York, 867 pp.

Agency for Toxic Substances and Diseases Registry – ATSDR. (2005). Toxicological profile for zinc. U.S. Department of Health and Human Services, Public Health Service, Atlanta, GA. http://www.atsdr.cdc.gov/toxprofiles/tp60.pdf (last accessed March 2019).

Agency for Toxic Substances and Diseases Registry – ATSDR. (2007). Toxicological profile for lead. U.S. Department of Health and Human Services, Public Health Service, Atlanta, GA. http://www.atsdr.cdc.gov/toxprofiles/tp13.pdf (last accessed March 2019).

Agency for Toxic Substances and Diseases Registry – ATSDR. (2012). Toxicological profile for cadmium. U.S Department of Health and Human Services, Public Health Service, Atlanta, GA. http://www.atsdr.cdc.gov/toxprofiles/tp5.pdf (last accessed March 2019).

Alleoni, L. R., Mello, J. W. V. & Rocha, W. S. D. (2009). Eletróquímica, ad sorção e troca iônica no solo. In: Mello, J. W. & Alleoni, L. R. (Editors) Química e Mineralogia do solo. Viçosa / MG, Sociedade Brasileira de Ciência do Solo, 69-130.

American Society for Testing and Materials – ASTM. (2016). D4646-16, Standard Test Method for 24-h Batch –Type Measurement of Contaminant Sorption by Soils and Sediments. ASTM International, West Conshohocken, PA.

Andriesse, J. P. (1988). Nature and management of tropical peat soils. Soil resources, management and conservation service. FAO Land and Water Development Division. http://www.fao.org/3/x5872e/x5872e00.htm (last accessed March 2019).

Babel, S. & Kurniawan, T. A. (2003). Low-cost adsorbents for heavy metals uptake from contaminated water: A review. Journal of Hazardous Materials, B97, 219–243. https://doi.org/10.1016/S0304-3894(02)00263-7

Balan, C., Bilbă, D. & Macoveanu, M. (2008). Removal of cadmium (II) from aqueous solutions by sphagnum moss peat: equilibirum study. Environmental Engineering and Management Journal, 7(1), 17-23. DOI: https://doi.org/10.30638/emj.2008.004

Balasubramanian, R., Perumal, S. V. & Vijayaraghavan, K. (2009). Equilibrium isotherm studies for the multicomponent adsorption of lead, zinc, and cadmium onto Indonesian peat. Industrial and Engineering Chemistry Research, 48(4), 2093-2099. DOI: https://doi.org/10.1021/ie801022p
Kabata-Pendias, A. (2011). Trace elements in soils and plants. CRC Press, Boca Raton, United States of America, 505 pp.

Kalmykova, Y., Strömwall, A. M. & Steenari, B. M. (2008). Adsorption of Cd, Cu, Ni, Pb and Zn on Sphagnum peat from solutions with low metal concentrations. Journal of Hazardous Materials, 152, 885-891. DOI: https://doi.org/10.1016/j.jhazmat.2007.07.062

Kasemodel, M. C., Lima, J. Z., Sakamoto, I. K., Varesche, M. B. A., Trofino, J. C. & Rodrigues, V. G. S. (2016). Soil contamination assessment for Pb, Zn and Cd in a slag disposal area using the integration of geochemical and microbiological data. Environmental Monitoring and Assessment, 188(12), 698. DOI: https://doi.org/10.1007/s10661-016-5708-2

Koivula, M., Kujala, K., Rönkkönen, H. & Mäkelä, M. (2009). Sorption of Pb(II), Cr(III), Cu(II), As(III) to peat, and utilization of the sorption properties in industrial waste landfill hydraulic barrier layers. Journal of Hazardous Materials, 164(1), 345-352. DOI: https://doi.org/10.1016/j.jhazmat.2008.08.008

La Serra, L. (2015). Relation between the concentration of heavy metals in water samples from the basins of the rivers Pardo, Mogi Guacu, Sapucai / Mirim and Guarani aquifer with the etiopathogenesis of pemphigus. Graduate Thesis, Ribeirão Preto Medical School, University of São Paulo, Ribeirão Preto, Brazil.

Lamini, A. P. B., Jordão, C. P., Pereira, J. L. & Bellato, C. R. (2001). Chemical and physical characterization of coastal peat and evaluation of competitive adsorption of copper and zinc. Química Nova, 24(1), 18-23. DOI: http://dx.doi.org/10.1590/S0100-4042200001000005

Langmuir, D. (1997). Aquous environmental geochemistry. Prentice Hall, Nova Jersey, United States of America, 600 pp.

Lattuada, R. M., Perbaila, M. C. R., Dos Santos, J. H. Z. & Fisch, A. G. (2014). Peat, rice husk and rice husk carbon as low-cost adsorbents for metals from acidic aqueous solutions. Separation Science and Technology, 49, 101-111. DOI: https://doi.org/10.1080/01496395.2013.815476

Leiviskä, T., Khalid, M. K., Gogoi, H. & Tanskanen, J. (2018). Enhancing peat metal sorption and settling characteristics. Ecotoxicology and Environmental Safety, 148, 346-351. DOI: https://doi.org/10.1016/j.ecoenv.2017.10.053

Lim, S. & Lee, A. Y. W. (2015). Kinetic study on removal of heavy metal ions from aqueous solution by using soil. Environmental Science and Pollution Research, 22, 10144–10158. DOI: https://doi.org/10.1007/s11356-015-4203-6

Lima, J. Z. (2017). Geological-geochemical characterization and adsorption study of Pb, Zn and Cd by peat and organic compounds. Graduate Thesis, University of São Paulo, São Paulo, Brazil.

Lima, J. Z., Raimondi, I. M., Schalch, V. & Rodrigues, V. G. S. (2018). Assessment of the use of organic composts derived from municipal solid waste for the adsorption of Pb, Zn and Cd. Journal of Environmental Management, 226, 386-399. DOI: https://doi.org/10.1016/j.jenvman.2018.08.047

Liu, C. C., Wang, M. K., Chiuo, C. S., Li, Y. S., Yang, C. Y. & Lin, Y. A. (2009). Biosorption of chromium, copper and zinc by wine-processing waste sludge: Single and multi-component system study. Journal of Hazardous Materials, 171, 386-392. DOI: https://doi.org/10.1016/j.jhazmat.2009.06.012

Mahmood-ul-Hassan, M., Suthar, V., Ramique, E. Ahmad, R. & Yasin, M. (2015). Kinetics of cadmium, chromium, and lead sorption onto chemically modified sugarcane bagasse and wheat straw. Environmental Monitoring and Assessment, 187, 470. DOI: https://doi.org/10.1007/s10661-015-4692-2

Marques, J. P., Ferreira da Silva, E. A., Patinha, C., Kasemodel, M. C. & Rodrigues, V. G. S. (2019). Adsorption of lead (Pb) in weathered tropical soil (Ribeira Valley region - Brazil). Earth Sciences Research Journal, 23(2), 385-395. DOI: https://doi.org/10.15446/esrj.v23n4.77869

Marques, J. P., Rodrigues, V. G. S., Raimondi, I. M. & Lima, J. Z. (2020). Increase in Pb and Cd adsorption by the application of peat in a tropical soil. Water, Air, & Soil Pollution, 231, 136. DOI: https://doi.org/10.1007/s11270-020-04507-z

Mckay, G. & Porter, J. F. (1997). Equilibrium parameters for the sorption of copper, cadmium and zinc onto peat. Journal of Chemical Technology and Biotechnology, 69(3), 309-320.

Mobasherpour, I., Salahi, E. & Ebirahimi, M. (2012). Removal of divalent nickel cations from aqueous solution by multi-walled carbon nano tubes: equilibrium and kinetic processes. Research on Chemical Intermediates, 38, 2205. DOI: https://doi.org/10.1007/s11164-012-0537-6

Mohamed, A. M. O, Paleologos, E. K., Rodrigues, V. G. S. & Singh, D. N. (2017). Fundamentals of Geoenvironmental Engineering: Understanding Soil, Water, and Pollutant Interaction and Transport. Elsevier, Butterworth-Heinemann, 688 pp.

Oliveira, L. K., Melo, C. A., Goveia, D., Lobato, F., A., Hernández, M. A. A., Fraceto, L. F. & Rosa, A. H. (2015). Adsorption/desorption of arsenic by tropical peat: influence of organic matter, iron and aluminium. Environmental Technology, 36(2), 149-159. DOI: https://doi.org/10.1016/j.earthpol.2005.12.036

Orgiazzi, A., Bardgett, R. D. & Barrios, E. (2016). Global soil biodiversity atlas. European Commission, Luxembourg.

Pearson, R. G. (1969). Hard and Soft Acids and Bases, HSAB, Part I: Fundamental principles. Journal of Chemical Education, 45(9), 581-587.

Petroni, S. L. G, Pires, M. A. F. & Munita C. S. (2000). Adsorption of zinc and cadmium on peat columns. Química Nova, 23(4), 477-481. DOI: http://dx.doi.org/10.1590/S0100-40422000010000009

Petroni, S. L. G. (2004). Kinetic and equilibrium evaluation of the adsorption process of cadmium, copper and nickel metal ions in peat. Graduate Thesis, IPEN – Nuclear and Energy Research Institute - associated to the University of São Paulo, Brazil.

Plano Estadual de Recursos Hídricos 2004-2007 - PERH (2005). Relatório síntese do plano. Secretaria de Energia, Recursos Hídricos e Saneamento, http://www.sighr.sp.gov.br/arquivos/perh/CRH/1063/ cap_01a03_05a12.pdf (last accessed July 2020).

Poots, V. J. P., McKay, G., & Healy, J. J. (1978) Removal of basic dye from effluent using wood as an adsorbent. Journal (Water Pollution Control Federation), 50(5), 926-935. DOI: https://doi.org/10.1590/S0100-4042200001000005

Qin, F., Wen, B., Shan, X. Q., Xie, Y. N., Liu, T., Zhang, S. Z. & Khan, S. U. (2006). Mechanisms of competitive adsorption of Pb, Cu, and Cd on peat. Environmental Pollution, 144(2), 669-680. DOI: https://doi.org/10.1016/j.envpol.2005.12.036

Raimondi, I. M., Lima, J. Z. & Rodrigues, V. G. S. (2019). The characterization of tropical peats for potentially toxic metals adsorption purposes in an abandoned mine area. In: Shakoor A., & Cato K. (Editors) IAEG/ AEG Annual Meeting Proceedings, San Francisco, California, 2018 - volume 2, Springer, Chamin, 129-134. DOI: https://doi.org/10.1007/978-3-319-93127-2_19

Reddad, Z., Gerente, C., Andres, Y. & Le Cloirec, P. (2002). Adsorption of several metal ions onto a low-cost biosorbent: Kinetic and equilibrium studies. Environmental Science and Technology, 36(9), 2067-2073. DOI: https://doi.org/10.1021/es0102989

Reis, M. M., Tuñi Santos, L. D., da Silva, A. J., de Pinho G. P. & Montes, W. G. (2019). Metal contamination of water and sediments of the Viera River, Montes Claros, Brazil. Archives of Environmental Contamination and Toxicology, 77, 527-536. DOI: https://doi.org/10.1007/s00244-019-00666-1

Roy, W. R., Krapac, I. G., Chou, S. F. J. & Griffin, R. A. (1992). Batch type procedures for estimating soil adsorption of chemicals. Technical resource document. EPA/530-SW-87-006-F, Cincinnati, EUA.
