Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2015.1107503

57 (2016) 19927–19938
September

Taylor & Francis
Taylor & Francis Group

Biosorption of Pb^{2+}, Cr^{3+}, and Cu^{2+} by peach palm sheath modified colonized by *Agaricus Blazei*

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Received 8 April 2014; Accepted 7 October 2015

ABSTRACT

In this study, the behavior of lead (Pb^{2+}), chromium (Cr^{3+}), and copper (Cu^{2+}) ions in several aqueous solutions during biosorption of peach palm sheath colonized with *Agaricus blazei* (PS + *A. blazei*) was evaluated. The modifications of the chemical structure of the biosorbent due to fungal growth were verified by scanning electronic microscopy (SEM) which showed the differences on the material surface. Biosorption of Pb^{2+} and Cr^{3+} was dependent of solution pH. Although *in natura* peach palm sheath and peach palm sheath with *A. blazei* growth have shown different behaviors in pH evaluations for the three metals, it was chosen to use pH 5.0 in all the other experiments due to the high biosorption values for all metal/biosorbent relations when compared to other pH values. The reaction reached equilibrium in 15 min and the pseudo-second-order model presented the best results for all metal/biosorbent interactions. The data for $q_{\max}$ showed that for all metals PS + *A. blazei* was better to retain ions when compared to *in natura* peach palm (PS). Peach palm sheath colonized with *A. blazei* presented the highest biosorption capacity when interacting with Pb^{2+} ion (53 mg g^{-1}). Biosorption isotherms were tested for the mathematical models of Langmuir, Freundlich, Dubinin–Radushkevichs and Temkin, and all of them were adequate for the equilibrium experimental data. The differences of sorption affinity are directly linked to electronegativity difference which also follows this order: $Pb^{2+} > Cu^{2+} > Cr^{3+}$. Through thermodynamic parameters, it was verified that biosorption processes are spontaneous and exothermal.

Keywords: Biosorption; Heavy metals; *Agaricus blazei*; Pewa sheath

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1. Introduction

The activity of some industrial sectors, such as metallurgy, tanneries, chemical industry, battery manufacturing, and fossil fuel industry, are responsible for the generation of effluents that contain heavy metals. These pollutants, when discharged into waterways without any type of treatment, may harm aquatic life and at the same time make these waters inappropriate for human intake [1]. Lead (Pb^{2+}) is among the most dangerous heavy metals commonly found in industrial residues and may cause the death of animals and plants as well as brain damage, anemia, metal deficiency, anorexia, vomiting and sickness in humans [2]. Some essential metals like chromium in its trivalent form (Cr^{3+}) and copper (Cu^{2+}), although they have biological importance, when in high concentrations, may be harmful causing intoxications, allergies, hepatitis, erythematous lesions, brain bleeding, and seizures among other problems [3]. Therefore, the Health Ministry Resolution 2914/2011 establishes that the maximum concentration of these metals in drinking water are of $0.01\ mg\ L^{-1}$ for Pb^{2+}, $0.05\ mg\ L^{-1}$ for Cr^{3+}, and $2.00\ mg\ L^{-1}$ for Cu^{2+}.

Biosorption is a new technology that uses sequestering properties of natural biological materials including microbial biomass to remove pollutants from aquatic environments [4]. It is used for effluent treatment with biological materials that are able to sequester metals from diluted solutions. These techniques are getting more important because they offer good performance associated with low cost [5]. The cell walls of bacteria, algae, and fungi are efficient metallic biosorbent. The use of microbial biomass for the biosorption of metals from wastewater has been proposed as a promising alternative to conventional heavy metal management strategies. The sorption to polysaccharides, proteins, peptides, pigments or other molecules occurring in the outer layer of the cell wall probably plays the most important role. Wood-inhabiting basidiomycetes as *Agaricus blazei* seem to be a promising material for biosorption since they can be easily cultivated in high yields on various substrates [6].

There is tendency to use several agricultural organic residues for the biosorption process [7–10] such as orange peel [11], banana skin [12], rice husk [13], sugarcane bagasse [8] among other cellulosic materials [14]. Brazil has a large agricultural production which implies in a large quantity of several agroindustrial by products and residues. One of them is peach palm sheath (*Bactris gasipaes* Kunth) that is able to retain metallic ions, the adsorption of lead ions followed the kinetic model of pseudo-second-order and the Langmuir isotherm, besides being economically viable due it comes from renewable sources [15]. Thus, the waste generated by mushroom cultivation (*A. blazei*), the peach palm sheath containing mycelium of the fungus, can be an great biosorbent, due as porosity and chemical groups capable of interacting with the metal ions.

A. blazei Murrill ss. Heinemann is a fungus (*Basidiomycota*) native to Brazil that has been reclassified. However, there is no consensus on the right name of the fungus; in this article, we are going to use the name *A. blazei* as suggested by Colauto and Linde [16]. *A. blazei* is able to grow in several lignocellulolitic residues such peach palm sheath. This is possible due to the production of a series of lignocellulolitic enzymes that allow them to degrade lignin and cellulose [17]. The fungal growth in agricultural substrates could be an advantage in the biosorption process due the natural fungal capacity of substrate degradation, increasing the porosity and allowing new chemical groupings that could improve interaction with metals.

Thus, using a residue from mushroom cultivation may provide a material with high adsorption capacity for metal ions. Therefore, the objective of this study was to investigate the biosorption efficiency of peach-palm sheath colonized by *A. blazei* mycelium on synthetic effluents contaminated with Pb^{2+}, Cr^{3+}, and Cu^{2+}.

2. Materials and methods

2.1. Biosorbents

The peach palm sheath was obtained at Umuarama–PR, Brazil. The *A. blazei*, U2-1 strain, former *A. blazei* ABL 97/11 strain, from the Culture Collection of the Laboratory of Molecular Biology at the Paranaense University were utilized. The residue modification was done by the fungal growth on the substrate according to D'agostini et al. [17]. After the complete colonization of the residue by the fungus, the material was dried in an oven at 55°C for 24 h, ground in a knife grinder until the obtained granulometry was smaller or equal to 0.42 mm. This granulometry was utilized in the subsequent experiments.

2.2. Material characterization

Biosorbent characterization was done by scanning electronic microscopy (SEM), Fourier transform infrared (FTIR) spectroscopy, point zero charge (PZC).

2.2.1. Scanning electronic microscopy

To characterize material by SEM, the samples were placed on a double-side carbon tape and fixed on a tin sample support. Later, the samples were coated with gold until reaching thickness of approximately 30 nm using a Baltec Scutter Coater SCD 050 (Germany). The SEM, FEI Quanta 200 (Netherlands), was operating at 30 kV.

2.2.2. Fourier transform infrared spectra

FTIR spectra were obtained using a BOMEM device (MB-102 model). The samples were macerated with potassium bromide (KBr) crystals in a proportion of 1 mg sample for 100 mg KBr and then placed in a pastillator. The analysis was done in the spectral range of 4,000–400 cm^{-1}.

2.2.3. Point zero charge

The procedure to determine PZC, i.e. the pH in which the solid surface has neuter charge, was done using 0.5 g of biosorbent with 50 mL of 0.1 mol L^{-1} KCl aqueous solution under different pH values (ranging from 2.0 to 8.0), and adjusting them by adding 0.1 mol $\text{L}^{-1}$of NaOH and 0.1 mol L^{-1} of HCl. After 24 h of agitation, the final pH was measured and the obtained values were expressed through a final pH minus initial pH multiplied by initial pH graphics, where PZC corresponds to the value that intercepts the x-axis for each sample ($\text{pH}_\text{f} - \text{pH}_\text{i}$ = zero).

2.3. Biosorption experiments

2.3.1. Biosorption in function of pH

To obtain a better pH value for biosorption, a mixture was prepared with 0.5 g of biosorbent and 50 mL of a solution of Pb^{2+}, Cr^{3+}, and Cu^{2+} (50 mg L^{-1}), homogenized in an orbital agitator for 24 h at ambient temperature (25˚C) and were centrifuged using a rotation of 2,500 rpm for ten minutes. Five solutions of each metal at different pH values ranging from 2.0 to 6.0 were used. The desired pH was obtained through the addition of 0.1 mol L^{-1} NaOH and 0.1 mol L^{-1} HCl. The amount of metal in solution after the biosorption process was measured using a flame atomic absorption spectrophotometer (GBC 932 Plus). Next, the amount of adsorbed metal per gram of residue (q) was calculated using Eq. (1):

$$q = \frac{(C_\text{o} - C_\text{eq})V}{M} \tag{1}$$

where C_o and C_eq correspond to the initial concentrations and solution metal equilibrium concentrations (mg L^{-1}), respectively, V is the solution volume in liter (L) and M is the residue mass in gram (g).

2.3.2. Kinetics, isotherm, temperature, and desorption

After defining the optimal pH for biosorption, Pb^{2+}, Cr^{3+}, and Cu^{2+} biosorbent experiments were done on the adsorbent material in function of contact time with the solution (kinetics), adsorbate concentration (isotherms), temperature and metallic ion desorption according to the procedure done by Santos et al. [8–10]. The ions concentrations were analyzed by flame atomic absorption spectrophotometer, GBC 932plus.

The mean and standard deviation were calculated using the software Biostart 5.0.

2.3.3. Thermodynamic parameters

The thermodynamic parameters, enthalpy (ΔH), entropy (ΔS), and Gibbs' free energy (ΔG) were calculated by biosorption experiments in which temperature varied 0.5 g of sample and 50 mL of Pb^{2+}, Cr^{3+}, and Cu^{2+} (50 mg L^{-1}) was added, separately, agitated constantly in pH 5.0 for 12 h. The biosorption were evaluated at 10, 20, 30, 40, and 60˚C, verified with a thermostat. After the filtration of the mixtures, the quantification of metal solution was carried out using a flame atomic absorption spectrophotometer (GBC 932 Plus). The amount of adsorbed metal was calculated using Eq. (1).

3. Results and discussions

3.1. Biosorbent characterization

3.1.1. Scanning electronic microscopy

SEM analyses were done to visualize changes on the peach palm sheath surface. According to the images (Fig. 1), a harsh structure in several layers was observed *in natura* peach palm sheath (A). After the mycelial growth of *A. blazei* in peach palm sheath (B), the fiber fissures and scales can be better seen. The modification of lignocellulosic chains of peach palm sheath indicates that there was the action of lignocellulosic enzymes produced by this fungus in order to obtain the necessary nutrients for its development by substrate degradation.

3.1.2. FTIR spectra

To identify the functional groups present in biosorbents, absorbent spectra in the infrared region were

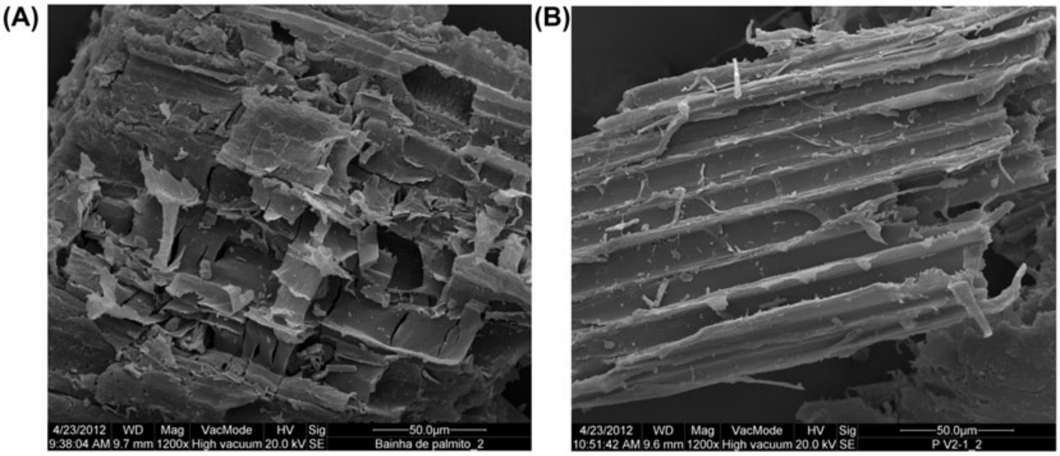

Fig. 1. Micrographs of biosorbents: *in natura* peach palm sheath (A) and peach palm sheath colonized by *A. blazei* (B). These images have been magnified 1,200×.

obtained. Biosorbents are natural polymers mainly consisting of cellulose, hemicellulose and lignin in varied proportions [18]. Through the biosorption spectra shown in Fig. 2, the presence of several characteristic functional groupings of the polymeric structure was verified for both studied biosorbents.

The strong broad peak at 3,429 cm^{-1} is attributed to the vibrational elongation of O–H link with alcohol and phenol. The peak at 2,923 cm^{-1} refers to the vibrational elongation of C–H link of alkanes from carbohydrates (cellulose and hemicellulose), alcohol, and aromatic ring of lignin. The peak at 1,730 cm^{-1} is due to the vibrational elongation of C=O link of nonconjugated ketones, lignin ester, C=O carbonyl. The peak at 1,250 cm^{-1} corresponds to the stretching of C=O lignin. The strong bands at 1,054 cm^{-1} confirmed the presence of polysaccharide [19]. Therefore, it is evident that the carbonyl, hydroxyl grouping, and carboxylic groups are the main responsible for the interaction with metallic ions.

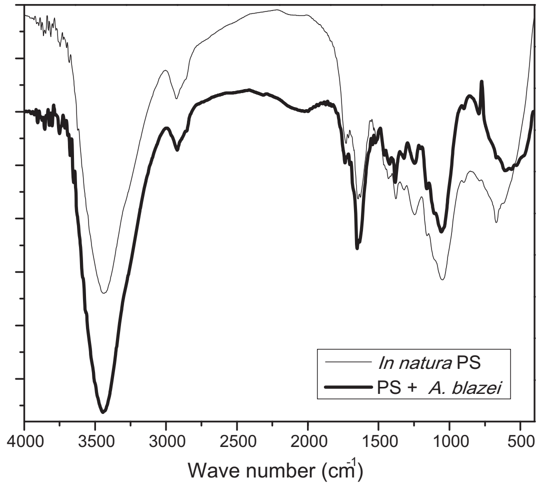

Fig. 2. Infrared spectra for *in natura* PS adsorbent (*in natura* peach palm sheath) and PS + *A. blazei* (peach palm sheath colonized by *A. blazei*).

Although a significant chemical modification was not observed, small alterations of the peaks in the region between 1,517 and 400 cm^{-1} were verified; this region is characterized by peaks referring to chemical groupings present in lignin, indicating that the presence of the fungus was responsible for the disappearance and at the same time, the appearance of chemical groupings in the peach palm sheath.

3.1.3. Point zero charge

The values of pH_{PZC}, 4.2 and 5.7, characterized the buffer effect on the surface of the *in natura* peach palm sheath and peach palm sheath modified by *A. blazei* growth, respectively, is showed in Fig. 3. The differences in the values of pH_{PZC} are probably due to the appearance of new chemical groupings promoted by fungal growth inside of the agricultural by product and also the external fungal presence on the agricultural byproduct.

In contact with solutions that present pH higher than the PZC, the samples will show predominance of negative charge while with solutions with pH are lower than PZC, the predominant superficial charge will be positive [20]. Biosorption of metal ions of Pb^{2+}, Cr^{3+}, and Cu^{2+} (cations) will be favored in pH in which the negative species are predominant on the biosorbent surface since the adsorbate and adosorbent charges have to be opposite so that electrostatic attraction between both exist [21].

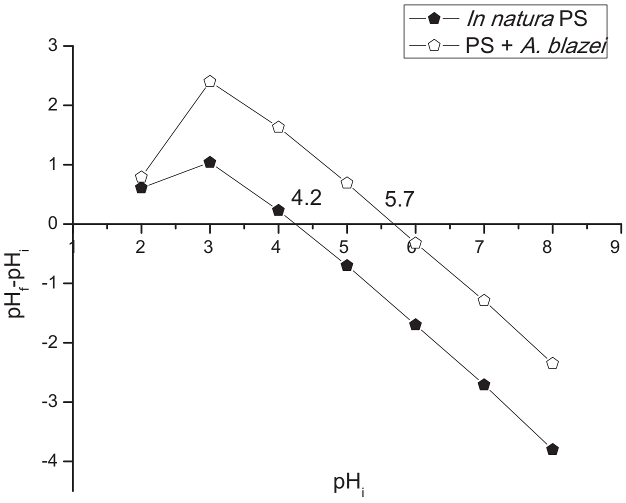

Fig. 3. Values of initial pH and initial pH minus final pH final obtained in the experiment to measure pH_{pzc} in concentration of 0.1 mol L^{-1} of potassium chloride (KCl). *In natura* PS (*in natura* peach palm sheath) and PS + *A. blazei* (peach palm sheath colonized by *A. blazei*). Temperature of 25℃.

3.2. *Biosorption in function of pH*

In biosorption of heavy metals, pH is one of the most important parameters. Fig. 4 shows its effect on heavy metal biosorption. The variations of pH values used in this experiment range from 2.0 to 6.0. It was observed that the biosorption capacity of the biomass was pH-dependent for the Pb^{2+} and Cr^{3+} solutions at the same time that the biosorption of Cu^{2+} showed to be independent for this factor, obtaining values between 1.84 and 2.08 mg g^{-1} Cu for *in natura* peach palm sheath, and 2.15 and 2.36 mg g^{-1} Cu for *in natura* PS + *A. blazei*. Biosorption of Pb^{2+} was lower in pH 2.0, whereas the subsequent pH values were practically constant. It was also noticed a higher interaction capacity of Cr^{3+} with biomass in higher pH values, and the best was pH 5.0. Although *in natura* peach palm sheath and peach palm sheath with *A. blazei* growth have shown different behaviors in pH evaluations for the three metals, it was chosen to use pH 5.0 in all the other experiments due to the high biosorption values for all metal/biosorbent relations when compared to other pH values. Moreover, according to CONAMA, the allowed pH range for industrial effluent is from 5.0 to 9.0.

Speciation of solution metals is pH-dependent. At the same time, the chemically active state of the sites that are present on the surface of the adsorbent is also altered by the solution pH [22]. The change of the biosorption capacity with pH variation can be explained by the competition for protons in biosorption reactions. In lower pH values, there is protonation of active sites that are needed for the biosorption process. However, for higher pH values, the presence of negative-charge groups on the biosorbent surface is prevalent, favoring the approach of metallic cations [13].

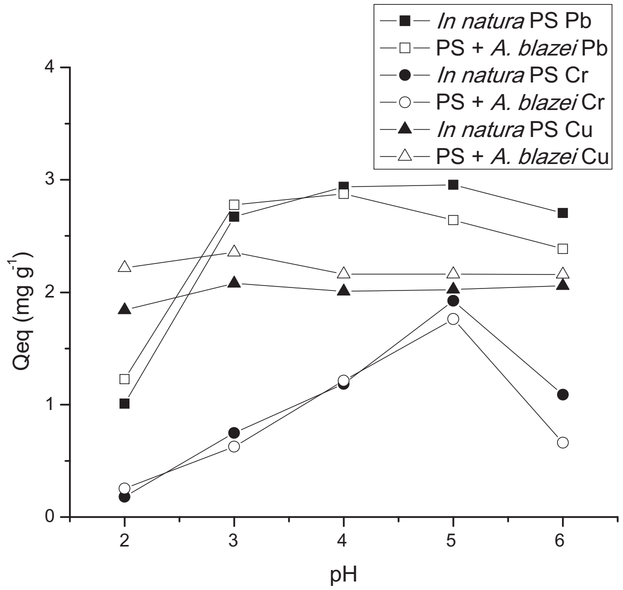

Fig. 4. Effect of pH in the biosorption of Pb^{2+}, Cr^{3+}, and Cu^{2+} *in natura* PS (*in natura* peach palm sheath) and PS + *A. blazei* (peach palm sheath colonized with *A. blazei*). Experimental conditions: metallic ion concentration of 50 mg L^{-1}, agitation time of 24 h, temperature 25℃.

Nevertheless, the increase in pH does not obligatorily correspond to the simultaneous increase of biosorption capacity due to the several existing mechanisms involved in metal biosorption by the surface. The type of interaction that will be predominant depends, besides pH, on several factors like links which are able to form organic–mineral complexes, complexes of electric conductivity and redox potential of the substrate. That is probably the reason that distinct values of pH_{PZC} and optimal biosorption pH were also found.

3.3. *Biosorption kinetics*

The quantification of necessary time for the biosorption reaction to reach equilibrium is very relevant to an industrial process because it is one of the most significant variables that allow determining if the technique can be applied for the depollution of heavy-metal contaminated water.

The obtained results were presented in Fig. 5. It was found that within 15 min already present biosorption constant for all studied samples, not revealing

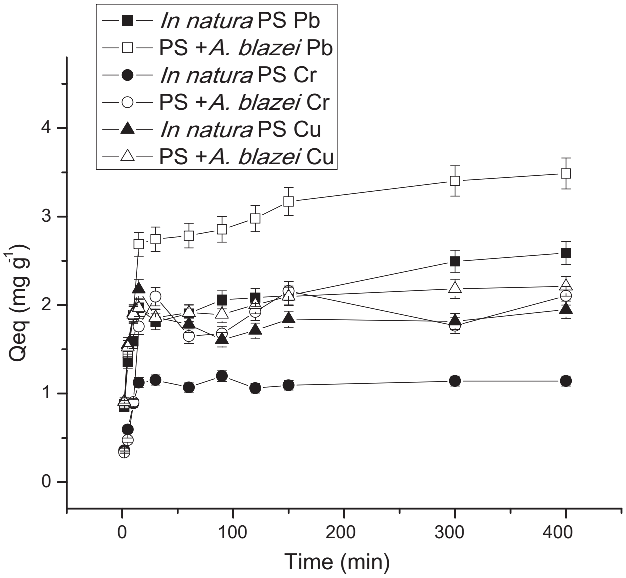

Fig. 5. Amounts of adsorbed Pb^{2+}, Cr^{3+}, and Cu^{2+} per gram of residue (q_{eq}) in function of time (min). *In natura* PS (*in natura* peach palm sheath) and PS + *A. blazei* (peach palm sheath colonized with *A. blazei*). Experimental conditions: 50 mg L^{-1} concentrations of metallic ions, pH 5.0, temperature of 25°C.

great variations in the values of q_{eq} for subsequent times, and being considered efficient and satisfactory to reach equilibrium in a short contact time of solutions and biomasses.

To investigate the mechanism that controls the biosorption process, four mathematical models were tested: pseudo-first-order, pseudo-second-order, Elovich and intraparticule diffusion. A good correlation of kinetic data indicates the biosorption mechanism to which it applies.

A simple analysis of the biosorption kinetic can be done with a Langergren pseudo-first-order equation [23]. This model proposes that the adsorbate removal speed, in time, is directly proportional to the difference in the saturation, concentration and the number of active sites of the solid [24]. It is represented by the following Eq. (2):

$$\log(q_{eq} - q_t) = \log q_{eq} - \frac{k_1 \cdot t}{2.303} \tag{2}$$

where q_{eq} and q_t are the amounts of adsorbed metallic ions (mg g^{-1}) in equilibrium (eq) and in time (t); k_1 is the biosorption speed constant (min^{-1}). Through the linear and angular coefficient of the graphic of log ($q_{eq} - q_t$) vs. t, the values of de q_{eq} and k_1 can be calculated, respectively.

The pseudo-second-order model developed by Ho et al. [24] assumes that the reaction speed depends on the amount of adsorbed solute on the adsorbent surface and the adsorbed amount in equilibrium.

The model equation is (Eq. (3)):

$$\frac{t}{q_t} = \frac{1}{k_2 q_{eq}^2} + \frac{t}{q_{eq}} \tag{3}$$

where q_t is the adsorbed amount of metallic ions (mg g^{-1}); k_2 is the speed constant of second-order biosorption (mg g^{-1} min^{-1}) obtained by the inclination of the straight line in the graphic of t/q_t vs. t; q_{eq} is the adsorbed amount in the solid phase of the equilibrium that can be calculated through the linear coefficient (mg g^{-1}).

Elovich model is applied in chemical sorption processes assuming that active sites of the biosorbent are heterogeneous and, therefore, exhibit different energy for activation [25].

The equation of Elovich model is expressed in the following way (Eq. (4)):

$$q_t = A + B \ln t \tag{4}$$

where q_t is the amount of removed metal in a determined time (mg g^{-1}), A and B are Elovich constant and t is the contact time in minutes.

Finally, the biosorption mechanism can still be used by the intraparticle diffusion model. It is utilized to identify the phases in which the biosorption phenomenon occurs, assuming that several phases happen. The first phase is the instant biosorption or biosorption of the external surface. The second stage is the gradual biosorption stage where the diffusion inside the particle is the limiting phase. The third phase is the final equilibrium one where the diffusion inside the particle starts to decrease due to the extremely low concentrations of solution sorbate [26]. In this case, the equation is represented below (Eq. (5)):

$$q_t = k_{id} t^{1/2} + C_i \tag{5}$$

where q_t is the amount of removed adsorbate in a determined time (mg g^{-1}); k_{id} (mg g^{-1} $min^{-1/2}$) is the intraparticle diffusion constant index; C_i (mg g^{-1}) is the constant that shows the limit layer thickness, the greater C_i value, the greater is the limit layer effect.

The kinetic parameters for the four presented models are available in Table 1.

Table 1
Kinetic parameters obtained through the linearization of pseudo-first-order model and pseudo-second-order model. Elovich model and intraparticle diffusion model for Pb^{2+}, Cr^{3+}, and Cu^{2+} using the biosorbents: *in natura* PS (*in natura* peach palm sheath) and PS + *A. blazei* (peach palm sheath colonized with *A. blazei*)

		In natura PS Pb	PS + *A. blazei* Pb	*In natura* PS Cr	PS + *A. blazei* Cr	*In natura* PS Cu	PS + *A. blazei* Cu
	$q_{eq,exp}$ (mg g^{-1})	2.58	3.48	1.14	1.68	1.91	2.18
Pseudo-first-order	k_1 (min^{-1})	4.6×10^{-3}	6.7×10^{-3}	-5.9×10^{-4}	-5.9×10^{-3}	-2.5×10^{-3}	-9.7×10^{-3}
	q_{eq} (mg g^{-1})	1.12	1.04	1.98	1.69	1.45	1.73
	R^2	0.997	0.992	0.845	0.895	0.968	0.952
Pseudo-second-order	k_2 (g mg^{-1} min^{-1})	9.9×10^{-2}	1.7×10^{-2}	3.8×10^{-1}	-7.3×10^{-2}	7.2×10^{-2}	4.6×10^{-2}
	q_{eq} (mg g^{-1})	2.16	3.62	1.14	1.68	1.92	2.25
	R^2	0.997	0.998	0.998	0.994	0.995	0.999
Elovich	A (mg g^{-1} h^{-1})	3.6×10^{-1}	1.32	8.61×10^{-1}	6.33×10^{-1}	8.38×10^{-1}	1.34
	B (g mg^{-1})	3.8×10^{-1}	3.6×10^{-1}	4.7×10^{-2}	2.5×10^{-1}	1.8×10^{-1}	1.4×10^{-1}
	R^2	0.993	0.992	0.772	0.832	0.714	0.961
Intraparticle diffusion	k_{id1} (mg g^{-1} $min^{-1/2}$)	4.6×10^{-2}	4.1×10^{-2}	6.2×10^{-4}	8.5×10^{-4}	-5.4×10^{-3}	2.5×10^{-2}
	C_{i1} (mg g^{-1})	1.56	2.52	1.12	1.86	1.90	1.73
	R_1^2	0.980	0.997	–0.160	–0.142	–0.130	0.946
	k_{id2} (mg g^{-1} $min^{-1/2}$)	4.8×10^{-2}	2.9×10^{-2}	–	–	–	–
	C_{i2} (mg g^{-1})	1.65	2.88	–	–	–	–
	R_2^2	0.942	0.996	–	–	–	–

Although the linear correlation values for pseudo-first-order kinetic are close to one for *in natura* peach palm sheath and in the peach palm sheath colonized with *A. blazei* regarding Pb^{2+} and Cu^{2+}, calculated q_{eq} does not coincide with the experimental ($q_{eq,exp}$), indicating that these materials do not follow this model. However, optimal adjustments of experimental data were observed for all studied materials and metallic ions in relation to the pseudo-second-order equation, indicating that the kinetic mechanism follows this equation, suggesting a strong interaction between ions and adsorbent. Besides, it was also verified that *in natura* PS Pb, PS + *A. blazei* Pb and PS + *A. blazei* Cu presented good linear correlation values for Elovich and intraparticle models showing that the kinetic of these materials can b explained by these mechanisms, but the values of r^2 are greater for the pseudo-second-order.

3.4. Biosorption isotherms

The biosorption isotherm represents the amount of adsorbed metal in function of the equilibrium concentration. In Fig. 6, the biosorption isotherms of Pb^{2+}, Cr^{3+}, and Cu^{2+} *in natura* peach palm sheath and peach palm sheath colonized with *A. blazei* are shown.

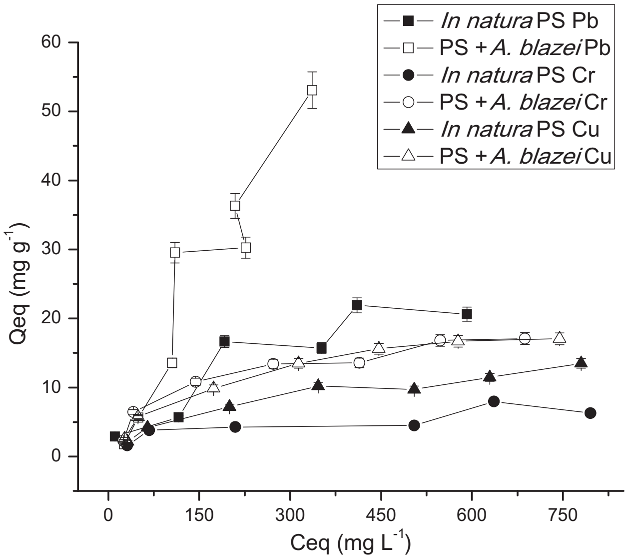

Fig. 6. Biosorption isotherms of Pb^{2+}, Cr^{3+}, and Cu^{2+} *in natura* PS (*in natura* peach palm sheath) and PS + *A. blazei* (peach palm sheath colonized with *A. blazei*). Experimental conditions: agitation time of 24 h, pH 5.0, temperature of 25°C.

It was possible to verify an increase in the biosorption capacity of the three metals in the fungus colonized adsorbent in relation to the one *in natura*. This probably occurred due to changes in the chemical–physical structure of peach palm sheath caused by the fungal growth in the agricultural by product, and the high efficiency of the fungus to sequester metals in aqueous solutions due to the chemical groupings present in the cell structure positively contributes to the biosorption process.

The mathematical models of Langmuir, Freundlich, Dubinin–Radushkevich (DER) and Temkin were applied to obtain important information that influences the biosorption phenomenon.

Langmuir model considers that molecules are adsorbed in a fixed well-defined number of sites. Moreover, each site can only have one molecule and all sites are energetically equivalent and there is no interaction between an adsorbed molecule and the neighbor ones [27]. The expression of this isotherm is represented by Eq. (6):

$$\frac{C_{\mathrm{eq}}}{q_{\mathrm{eq}}} = \frac{1}{q_{\max} b} + \frac{C_{\mathrm{eq}}}{q_{\max}} \tag{6}$$

where $q_{\max}$ is Langmuir parameter related to the biosorption capacity (mg g^{-1}); b is Langmuir constant related to biosorption energy (L mg^{-1}).

Freundlich proposed an empiric model that applies to nonideal systems in heterogeneous surfaces and in multilayer sorption [28]. The mathematical expression of Freundlich isotherm is (Eq. (7)):

$$\log q_{\mathrm{eq}} = \log k_{\mathrm{f}} + \left(\frac{1}{n}\right) \log C_{\mathrm{eq}} \tag{7}$$

where k_{f} is Freundlich constant related to the biosorption capacity; n is the parameter related to biosorption intensity.

With Dubinin–Radushkevich (DER) model, it is possible to estimate the characteristic porosity of the adsorbent and the biosorption free energy [29]. DER admits that the surface is heterogeneous and the adsorption sites have different energies [30]. DER isotherm is represented according to Eq. (8):

$$\ln q_{\mathrm{eq}} = \ln q_{\mathrm{d}} - B_{\mathrm{d}} \varepsilon^2 \tag{8}$$

where $B_{\mathrm{d},}$ is an energy constant (mol^2 J^{-2}); q_{d} is the theoretical saturation capacity; ε is Polanyi potential, calculated by Eq. (9):

$$\varepsilon = RT \ln\left(1 + \left(\frac{1}{C_{\mathrm{e}}}\right)\right) \tag{9}$$

where R is the constant value of ideal gases (8.314 J K^{-1} mol^{-1}); T correspond to temperature in kelvin (K).

From B_{d} it is possible to obtain the average biosorption energy, E, in kJ mol^{-1}. This parameter indicates if the adsorbent/adsorbate interaction is a possible physical or chemical biosorption and it is calculated using Eq. (10):

$$E = \frac{1}{\sqrt{2B_{\mathrm{d}}}} \tag{10}$$

Temkin isotherm considers that the effects of biosorption heat linearly decrease with the interaction covering between adsorbate and adsorbent, and biosorption is characterized by a uniform distribution of linking energy [31]. It is represented in Eq. (11) as follows:

$$q_{\mathrm{eq}} = B_1 \ln K + B_1 \ln_C \tag{11}$$

where B is Temkin parameter related to the biosorption heat (kJ mg^{-1}); k is the equilibrium constant of the linking corresponding to the maximum linking energy (L mg^{-1}).

As related by Baldrian [6], the biosorption of heavy metals to the mycelia of white-rot fungi fits the Langmuir biosorption isotherm. From the kinetic viewpoint, it is a two-stage process with a rapid surface biosorption (30 min^{-1} h) and a slow intracellular diffusion (2–3 h). Analyzing the obtained parameters of this work for each isotherm (Table 2), it was verified that all applied models were adequate for *in natura* PS and PS + *A. blazei* regarding the biosorption of the three metallic elements (Pb^{2+}, Cr^{3+}, and Cu^{2+}) for presenting coefficient values of linear determination (r^2) close to 1.

When the obtained information was explored, the maximum biosorption capacity ($q_{\max}$) was analyzed according to Langmuir model, the adsorbed intensity (n) by Freundlich, and the average biosorption energy (E) according to Dubinin–Radushkevich model.

The presented data for $q_{\max}$ showed that for all metals PS + *A. blazei* was better to retain ions when compared to *in natura* PS. The highest maximum capacity value, in mg g^{-1}, corresponds to Pb^{2+} biosorption by PS + *A. blazei*, which is four times greater than the one presented by *in natura* peach palm sheath for the same metal. The second best result of $q_{\max}$ was verified in Cu^{2+} biosorption by peach palm sheath that contained mycelial mass. Finally, from the found values of $q_{\max}$, the biosorption capacity of Cr^{3+} was approximately three times superior when *A. blazei* was used compared to *in natura* PS.

Table 2
Comparison of isotherms of Langmuir, Freundlich, Dubinin-Radushkevich (DER), and Temkin models for the biosorption of Pb^{2+}, Cr^{3+}, and Cu^{2+} using *in natura* PS (*in natura* peach palm sheath) and PS + *A. blazei* (peach palm sheath colonized with *A. blazei*)

		In natura PS Pb	PS + *A. blazei* Pb	*In natura* PS Cr	PS + *A. blazei* Cr	*In natura* PS Cu	PS + *A. blazei* Cu
Langmuir	q_{max} (mg g^{-1})	12.970	52.910	7.023	19.417	17.665	22.143
	b (L mg^{-1})	0.013	0.0019	0.0116	0.0089	0.0040	0.0049
	r^2	0.999	0.999	0.979	0.974	0.975	0.996
Freundlich	k_f (L mg^{-1})	0.425	5.600	0.378	1.866	2.606	1.074
	N	1.543	1.09	2.100	2.916	1.839	2.305
	r^2	0.996	0.961	0.869	0.970	0.972	0.995
Dubinin–Radushkevich	q_d (mg g^{-1})	24.188	50.497	4.542	11.440	12.928	17.412
	B_d	$-3.11\ 10^{-3}$	$-2.44\ 10^{-3}$	$-1.694\ 10^{-4}$	$-1.661\ 10^{-4}$	$-3.92\ 10^{-3}$	$-2.82\ 10^{-3}$
	E (kJ mol^{-1})	12.679	14.315	54.330	54.869	11.294	13.316
	r^2	0.958	0.905	0.991	0.999	0.918	0.995
Temkin	k_t (L mg^{-1})	0.195	0.027	0.0778	0.0880	0.0537	0.0608
	B_1	2.374	16.306	1.910	4.156	3.402	4.726
	r^2	0.993	0.999	0.898	0.969	0.976	0.982

Among several factors that affect the biosorption process as an adsorbent, the physical-chemical properties of metallic species are responsible for the interaction between metallic ions and the biomaterial. Thus, it has been reported that the biosorption of metallic ion increases the ionic radius which follows this order: $Pb^{2+} > Cu^{2+} > Cr^{3+}$. Moreover, the differences of sorption affinity are directly linked to electronegativity difference which also follows this order: $Pb^{2+} > Cu^{2+} > Cr^{3+}$. Thus, the higher the electronegativity and ionic radius are, the greater the ion biosorption by the biosorbent will be, explaining the greater biosorption of Pb^{2+} ion in relation to Cu^{2+} and followed by Cr^{3+} (Bueno et al.).

Regarding parameter n, the values of $1 < n < 10$ range indicate favorable biosorption [32]. Therefore, when verifying the obtained numbers in Table 2, it can be concluded that all processes happened favorably. As to average biosorption energy (E—Dubine model), the values of E ranged from 8 to 25 kJ mol^{-1} for the physical biosorption, and from 42 to 837 kJ mol^{-1} for the chemical biosorption [33]. Cr^{3+} biosorption by *in natura* PS and PS + *A.blazei* exhibited higher values than 54 kJ mol^{-1} for this parameter, indicating that the biosorption involves specific links (covalent) that are characterized by high energy and, therefore, chemical one. The other interactions presented E between 12 and 14, suggesting physical biosorption. However, the presented constants are not enough to define the chemical/physical origin of the interactions, so the values obtained for enthalpy (ΔH) and desorption should be considered.

3.5. Desorption

Aiming to possibly recycle the adsorbent and reutilizing the metallic ion, reversibility studies of the biosorption reaction, called desorption, were carried out. Adsorbent materials that present high percentage of desorption indicate that they can be reutilized in a new biosorption process. The experimentally obtained results are shown in Table 3.

Ions of Pb^{2+} and Cu^{2+} showed greater desorption values when compared to Cr^{3+}, for *in natura* residues as well as for the one colonized by *A. blazei*. This suggests that both metals are bivalents and are not strongly linked to the matrix when compared to trivalent ion. Therefore, ion charges can explain this phenomenon which is corroborated by the values presented by parameters b (Langmuir isotherm), n (Freundlich isotherm) and E (Dubini), indicating a stronger interaction between Cr^{3+} and biosorbents. Thus, *in natura* PS and PS + *A. blazei* can be reutilized in new biosorption processes for water contaminated only by Pb^{2+} and Cu^{2+}.

Table 3
Adosrption and desorption values of Pb^{2+}, Cr^{3+}, and Cu^{2+}in initial concentration of 50 mg $L^{-1}$for the biosorbents: *in natura* PS (*in natura* peach palm sheath) and PS + *A. blazei* (peach palm sheath colonized with *A. blazei*). Experimental conditions: agitation time of 24 h, pH 5.0, temperature 25°C

Adsorbent material	Adsorbed concentration (ppm)	Desorbed concentration (ppm)	Desorbed (%)
In natura PS Pb	30.92	28.25	91.35
PS + *A. blazei* Pb	33.35	26.43	79.25
In natura PS Cr	22.87	2.37	10.37
PS + *A. blazei* Cr	18.64	1.31	7.02
In natura PS Cu	21.55	19.48	90.37
PS + *A. blazei* Cu	25.99	21.83	83.96

Table 4
Thermodynamic parameters for the biosorption of Pb^{2+}, Cr^{3+}, and Cu^{2+} using biosorbents: *in natura* PS (*in natura* peach palm sheat) and PS + *A. blazei* (peach palm sheath colonized with *A. blazei*)

Adsorbent material	ΔH (kJ mol^{-1})	ΔS (Jk^{-1} mol^{-1})	ΔG (kJ mol^{-1})
In natura PS Pb	–3.714	27.123	–12.445
PS + *A. blazei* Pb	–1.962	32.023	–12.353
In natura PS Cr	–14.061	–12.739	–10.539
PS + *A. blazei* Cr	–3.741	21.424	–10.363
In natura PS Cu	–9.765	1.875	–10.365
PS + *A. blazei* Cu	–7.881	10.078	–10.932

3.6. Thermodynamic parameters

To verify the effect of temperature on the biosorption, the thermodynamic parameters enthalpy (ΔH), entropy (ΔS), and Gibbs free energy (ΔG) were obtained from the thermodynamic Eqs. (12) and (13):

$$\Delta G = -RT \ln k_d \tag{12}$$

$$\ln(k_d) = -\frac{\Delta G}{RT} = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{13}$$

where k_d = adsorbate distribution coefficient (L g^{-1}); T is the temperature in kelvin (K); R corresponds to the universal gas constant (8.314 J K^{-1} mol^{-1}).

The ΔH are calculated from the slopes of the linear variation of $\ln k_d$ vs. $1/T$ graphic, and ΔS can be determined by the intercept of linear plots. The obtained thermodynamic parameters are found in Table 4.

The fundamental criterion of process spontaneity is the variation of Gibbs free energy (ΔG). A given process occurs spontaneously at a given temperature if $\Delta G < 0$ [34]. Analyzing Table 4, it is concluded that the negative values of ΔG confirmed the viability of adsorption process for all the metal/biosorbent relations and indicate that the interactions occurred spontaneously.

Entropy is associated with the order–disorder variations of a system. Positive values for this parameter signal a disorder increase. Except for *in natura* PS Cr, all the other interactions exhibited entropy as a contributing factor to the spontaneity in biosorption of Pb^{2+}, Cr^{3+}, and Cu^{2+}.

For enthalpy, when $\Delta H > 0$, there is an endothermal reaction, while $\Delta H < 0$ indicates that the reaction is exothermal. Moreover, typical values of enthalpy of physical biosorption are around 20 kJ mol $^{-1}$, whereas in the chemical biosorption this value is approximately 200 kJ mol^{-1} [10]. Thus, it was observed that the studied processes are exothermal physical reactions (physisorption) with weak Van der Waals links between ions and biosorbent.

4. Conclusions

It was concluded that peach palm sheath with mycelium grown (*A. blazei*) has high biosorption of the metallic ions Pb^{2+}, Cr^{3+}, and Cu^{2+}, mainly of Pb^{2+} which reaches a biosorption capacity of approximately fourfold, compared to material without modification.

Biosorption of Pb^{2+} and Cr^{3+} depend of solution pH. The residues follow a pseudo-second-order kinetic in all studied metal/biosorbent interactions. The experimental data of isotherms adjust to Langmuir, Freundlich, Dubinin–Radushkevich and Temkin models. The desorption values ranged from 80 to 90% in the processes that involve Pb^{2+} and Cu^{2+}; however, Cr^{3+} the values were below 10%. The biosorption process of residues for the three metals is spontaneous and exothermal.

Acknowledgements

The authors thank CAPES or the fellowship (PROSUP), CNPq for the fellowship (PEBIC) and Universidade Paranaense for the financial support.

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