

METAL IONS BIOSORPTION BY MACROPHYTE *SALVINIA CUCULLATA*

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ABSTRACT: In this work the non-living macrophyte *Salvinia cucullata* potential on removing Cr^{3+} and Pb^{2+} has been studied. Adsorption equilibrium tests were carried out under batch operation. The experimental data obtained were fitted to models. For the equilibrium experiments the maximum uptake capacities were 0.858 and 0.562 mmol.g^{-1} for Cr^{3+} and Pb^{2+} , respectively. In order to know the biosorption mechanism FT-IR analyses were performed for the biomass before and after biosorption surface and the ability of these groups bind with Cr^{3+} and Pb^{2+} . The thermodynamics data showed the spontaneity of the process.

KEYWORDS: chromium; lead; macrophyte; biosorption.

1. INTRODUCTION

The water contamination with metal ions is a very current problem in the world. Considerable attention has been paid to methods for metal removal from industrial wastewaters because they pose serious environmental problems and are dangerous to human health (Miretzky et al., 2006).

Lead can be traced to industrial discharges from a variety of sources, such as batteries, paints, pigments and ammunition, petrol, cables, alloys and steels, plastics, and glass industry (Yoonaiwong et al., 2011).

The trivalent chromium are released into the environment from different industrial activities such as tannery, chromium plating, iron and steel manufactory, and other anthropogenic sources (Maine et al., 2004).

A number of methods are available to remove toxic metals from water: ion exchange resins, reverse osmosis, precipitation, solvent extraction, membrane technologies, activated carbon, sorption, etc (Mar Areco et al., 2012; Miretzky et al., 2006). Generally, they are expensive or ineffective, especially when the metal concentrations are in the order of 1–100 ppm (Volesky, 2000).

There is a wide variety of biomaterial that have been shown to exhibit some affinity for

metal ions. This indicates that the use of biosorbent could be of advantage in water pollution control. A biosorbent of choice should be inexpensive and readily available locally (Dang et al., 2009).

The aquatic macrophytes have been shown a high affinity by metal ions, which makes feasible their use in biosorption process.

Lima et al (2011) studied Cr^{3+} removal by *Lemna minor* macrophyte. The essays were carried out in batch system with the biomass and the time to achieve equilibrium was about 7h. The authors observed a maximum of 0.237 mmol.g^{-1} removal obtained from Langmuir model.

Saraswat and Rai (2010) evaluated the Zn^{2+} , Cd^{2+} and Cr^{6+} removal using the aquatic macrophyte *Echornia crassipes*. The experiment were conducted in simple and competitive systems. For simple system the maximum uptake for an initial metal concentration of 40 mg.L^{-1} , were 12.4, 9.3 and 5.6 mg.g^{-1} for Cd^{2+} , Zn^{2+} and Cr^{6+} respectively. The uptake increased for Cd^{2+} in competitive system, while that values decreased for Zn^{2+} and Cr^{6+} . The authors concluded that the main mechanism was ion exchange and electrostatic interaction.

The metal ions accumulation in macrophytes species as *Salvinias* are well reported in literature. However, the studied carried out until now are focused, mainly, on the living biomass and few



metal ions (Sen and Bhattacharyya, 1994; Dhir et al., 2008, 2009; Dhir and Srivastava, 2011), which makes difficult choosing the initial concentration of the ions due the toxicity of the metal ions may confer when at high concentrations. Therefore, it is important the study with non-living biomass.

The aim of this work was to study the biosorption process using the aquatic macrophyte *Salvinia cucullata* to remove Cr^{3+} and Pb^{2+} . The biomass was characterized by FT-IR analyses. The biosorption experiments were performed in batch system and models of equilibrium were adjusted to experimental data.

2. MATERIALS AND METHOD

2.1. Biomass preparation and metal ions solutions

The *Salvinia cucullata* biomass was collected by the collected by the CPAA (Research Center in Environmental Aquaculture) of State University of West of Parana – Brazil. After collecting, the biomass was washed and dried at temperature of 55 ° C for 24 hours. The biomass was crushed and sieved to a diameter of 0.855 mm and then used in biosorption studies. The chromium and lead synthetic solutions were prepared by dissolving the $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Pb}(\text{NO}_3)_2$ salts (trade Vetec) in deionized water, respectively. The metal ions concentration values ranged from 0.025 to 4 $\text{mg} \cdot \text{L}^{-1}$. The pH of the solution was adjusted to 4 using HNO_3 (0.5 M) and NaOH (1 M). The presence of Cr^{3+} and Pb^{2+} Absorption Spectrophotometer - AA 100 - Perkin Elmer, Laboratory of Environmental Engineering – Unicamp

2.2. FT-IR analyses

The FT-IR spectroscopy characterization was applied to identify the functional groups presents onto macrophyte surface before and after biosorption process. The analyses were conducted using a using a Perkin-Elmer Spectrum RX I FT-IR system. The spectra were acquired in the range of 4000 to 400 cm^{-1} .

2.3. Equilibrium essays and thermodynamics

Equilibrium experiments were conducted by mixing 100 mL of solution with different concentrations of Cr^{3+} (0.025 to 4 $\text{mmol} \cdot \text{L}^{-1}$) with

0.2 g of *S. cucullata* at different temperatures (15; 30 and 45 °C) and pH 4. The solution with the biomass was maintained under stirring for a period of 2 h. Then the samples were centrifuged and concentrations of the metal ion were determined by Atomic Absorption Spectrophotometry (AAS). The adsorption capacity was calculated by Eq. 1.

$$q = \frac{(C_0 - C_f)V}{m} \quad (01)$$

where q is the metal ion uptake ($\text{mmol} \cdot \text{g}^{-1}$), C_0 and C_f are the initial and equilibrium concentrations of the metal ions ($\text{mmol} \cdot \text{L}^{-1}$), V is the volume of solution (L), m is the weight of biosorbent (g).

The experimental data were adjusted by Langmuir, Freundlich and Dubinin-Radushkevich (D-R) models, Eq. (2). (3) e (4), respectively.

$$q_e = \frac{q_0 b C_e}{1 + b C_e} \quad (02)$$

where q_0 represents the concentration of ions in the macrophyte for a total coverage of available sites ($\text{mmol} \cdot \text{g}^{-1}$), b represents the Langmuir adsorption parameter ($\text{L} \cdot \text{mmol}^{-1}$) and C_e is the equilibrium concentration of Cr^{3+} in fluid phase ($\text{mmol} \cdot \text{L}^{-1}$).

$$q_e = k_F C_e^{1/n} \quad (03)$$

where k_F is the Freundlich constant and indicates the adsorption capacity of the adsorbent ($\text{mmol} \cdot \text{g}^{-1}$) and 1/n is the heterogeneity factor.

$$\ln q_e = \ln q_m - k_{DR} \varepsilon^2 \quad (04)$$

where k_{DR} is the porosity factor ($\text{mol}^2 \cdot \text{J}^{-2}$), q_m is the monomolecular adsorption capacity of ions biosorption by the biomass surface ($\text{mmol} \cdot \text{g}^{-1}$) and the variable ε can be related to the equilibrium concentration (Eq. 5):

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (05)$$

where ε is the Polanyi potential ($\text{J} \cdot \text{mol}^{-1}$), R is the universal gas constant ($8.314 \times 10^{-3} \text{ kJ} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$) and T is the absolute temperature (K).

A plot of $\ln q_e$ versus ε^2 ($\text{J}^2 \cdot \text{mol}^{-2}$) must be linear with inclination of the straight line (K_{DR}) and intercept the y axis at ($\ln q_m$) providing the values

for K_{DR} which allows the calculation of the mean free energy of adsorption E ($\text{kJ}\cdot\text{mol}^{-1}$) per molecule of the adsorbate when it is transferred from the solution to the biomass surface according to Eq. 6 (Ergene et al., 2009).

$$E = (-2K_{DR})^{-1/2} \quad (06)$$

The thermodynamics were obtained by Xiaofu et al. (2009) method which gives the thermodynamic parameter, ΔG (kJ/mol) represented by Eq. 7.

$$\Delta G/(RT) = (A_0)\ln(1-x/y) + (W_0\cdot\beta)\ln(1-x/\beta) \quad (07)$$

where, A_0 is the initial ion concentration ($\text{mg}\cdot\text{L}^{-1}$), x is the adsorption density of the adsorbent, $\text{mg}\cdot\text{g}^{-1}$, $y = A_0/W_0$ is the ratio of the initial ion concentration (A_0), to the adsorbent concentration, W_0 , $\text{g}\cdot\text{L}^{-1}$, β is the adsorption capacity of the adsorbent (or the maximum adsorption capacity).

3. RESULTS AND DISCUSSION

3.1. FT-IR analyses

Figure 1(a-c) shows the FT-IR spectrum obtained for raw *S. cucullata* and after biosorption of Cr^{3+} and Pb^{2+} . The analysis allows to identify the functional groups involved in the process and the links between these groups and the metallic ions present in the samples. The band at $2922\text{-}2849\text{ cm}^{-1}$ vibration of methylene ($\text{C}=\text{H}_2$), respectively, 1736 cm^{-1} is asymmetric and symmetric peak is stretching vibration of $\text{C}=\text{O}$. This peak was observed only in saturated biomass (Fig. 1-b). 1254 cm^{-1} is the stretching $\text{C}-\text{O}$ of carboxylic acids, 908 cm^{-1} of alkenes present only "raw" biomass. $900\text{ - }690\text{ cm}^{-1}$ compounds. It is evident that some functional groups changed with biosorption. The FT-IR results showed that functional groups as carboxyl and alkenes take part of the biosorption process for both metal ions.

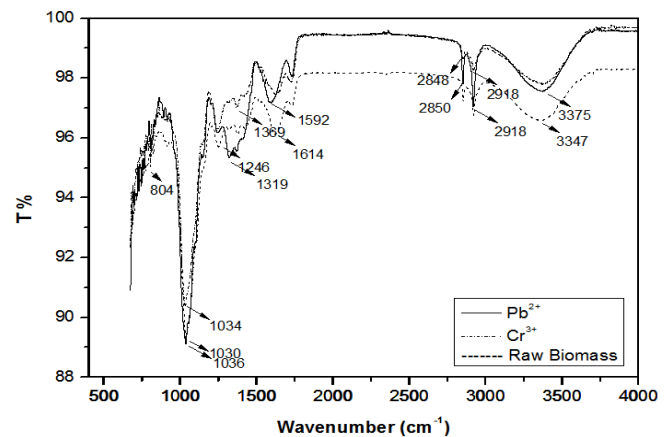


Figure 1. Infrared spectrum of raw *Salvinia cucullata*, saturated with Cr^{3+} and Pb^{2+} .

3.2. Equilibrium essays and thermodynamics

Figures 2 and 3 show the isotherm of biosorption of Cr^{3+} and Pb^{2+} by *S. cucullata* for different temperatures, respectively. The models parameters are shown in Tables 1 and 2. The experimental data showed that the values of maximum uptake given by Langmuir model (q_0) increased with the increase of temperature for Cr^{3+} , and decreased with the increase of temperature for Pb^{2+} indicating the endothermic and exothermic behaviour for Cr^{3+} and Pb^{2+} , respectively. The results showed that the both models, Langmuir and Freundlich, adjusted satisfactorily to the experimental data. The Freundlich model fitted slightly higher with R^2 of 0.984 at $45\text{ }^\circ\text{C}$ for chromium ion. The opposite occurred with lead ion, Langmuir model fitted better with a maximum uptake of $0.562\text{ mmol}\cdot\text{g}^{-1}$ at $15\text{ }^\circ\text{C}$. In the Langmuir model the parameter b represents the affinity between the metal ions and the biomass. High values of b are reflected by the steep initial slope of a sorption isotherm and indicate a high affinity for the adsorbate (Davis et al., 2003). In this work, the high values of b , especially for temperatures of $30\text{ }^\circ\text{C}$ for both metal ions showed the high affinity between the macrophyte and the metal ion and the influence of the temperature on the biosorption process. Furthermore, for the Freundlich model the exponent n when greater than unity represents that the process is favourable for all temperatures.

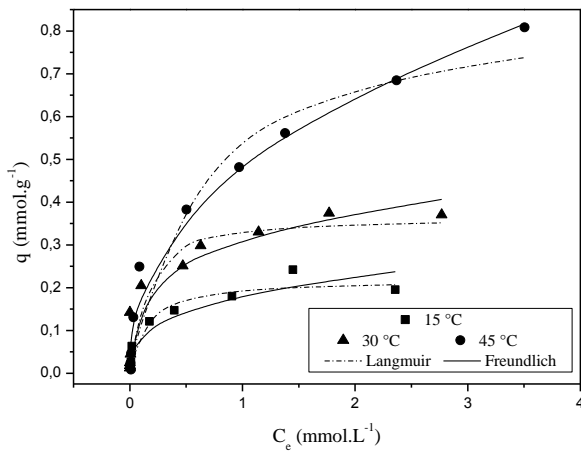


Figure 2. Langmuir and Freundlich isotherms fits for the adsorption at different temperatures for Cr^{3+} .

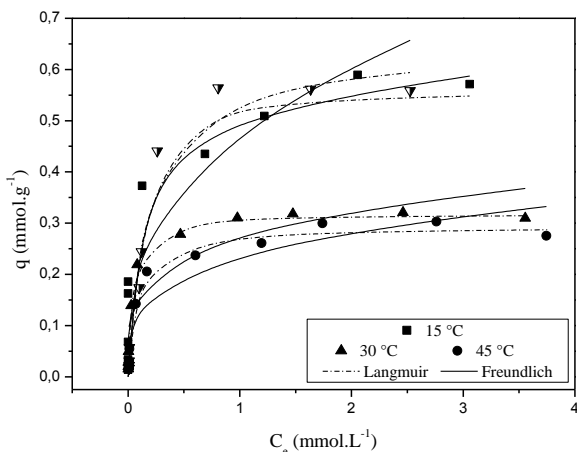


Figure 3. Langmuir and Freundlich isotherms fits for the adsorption at different temperatures for Pb^{2+} .

Table 1. Langmuir, Freundlich and D-R isotherms models parameters for Cr^{3+} .

T (°C)	Langmuir			Freundlich		
	q_0 (mmol.g ⁻¹)	b (L.mmol ⁻¹)	R^2	k_F	n	R^2
15	0.217	8.594	0.936	0.181	3.171	0.908
30	0.365	9.927	0.877	0.310	3.779	0.878
45	0.858	1.755	0.955	0.486	2.415	0.984
T (°C)	Dubinin-Radushkevich					
	q_m (mmol.g ⁻¹ .min ^{-1/2})	k_{DR}^* (10 ⁻⁵ .mol ² .J ⁻²)	E (kJ.mol ⁻¹)			
15	0.981	1.260	0.630			
30	0.990	1.261	0.630			
45	0.977	0.558	0.947			

Table 2. Langmuir, Freundlich and D-R isotherms models parameters for Pb^{2+} .

T (°C)	Langmuir			Freundlich		
	q_0 (mmol.g ⁻¹)	b (L.mmol ⁻¹)	R^2	k_F	n	R^2
15	0.562	13.015	0.857	0.495	6.490	0.868
30	0.318	27.291	0.997	0.273	4.261	0.881
45	0.293	12.317	0.983	0.233	3.730	0.880
T (°C)	Dubinin-Radushkevich					
	q_m (mmol.g ⁻¹)	k_{DR}^* (10 ⁻⁵ .mol ² .J ⁻²)	E (kJ.mol ⁻¹)			
15	1.016	0.614	0.902			
30	0.984	1.090	0.677			
45	1.022	1.221	0.640			

The Dubinin-Radushkevich isotherm model provides information as the character physical or chemical of biosorption process. When E values are between 8 and 16 kJ.mol⁻¹ the adsorption process takes place by chemical ion exchange while $E < 8$ kJ.mol⁻¹ means that the adsorption process is physical (Argun et al., 2007). The E value obtained for the experiments data was less than 8 kJ.mol⁻¹ for all temperatures reflecting the physical process of the biosorption by *S. cucullata* for both metal ions.

Table 3 and 4 summarizes the estimated values of the adsorption density (x) and Gibbs energy thermodynamic property $\Delta G/(RT)$ for different values of initial metal ion concentration (A_0) and temperature (T), and the adsorption density (x) according Xiaofu et al. (2009). Each value of the adsorption capacity parameter β used to the calculations was estimated via plot analysis of the experimental data as 12.574 mg.g⁻¹ (15 °C), 19.3648 mg.g⁻¹ (30 °C) and 38.818 mg.g⁻¹ (45 °C) for chromium and 115.33 mg.g⁻¹ (15 °C), 65.21 mg.g⁻¹ (30 °C) and 60.67 mg.g⁻¹ (45 °C) for lead. All negative values of $\Delta G/(RT)$ are in accordance with the thermodynamic principles which confirms the spontaneous nature of the tested ion adsorption reactions (Xiaofu et al., 2009).

Table 3. Equilibrium adsorption density, x (mg/g), and calculated values of $\Delta G/(RT)$ for Cr^{3+} ion adsorption onto *Salvinia cucullata* at different values of A_0 (mg/L) and T ($^{\circ}\text{C}$).

		A ₀ Value										
T($^{\circ}\text{C}$)		1.96	2.36	3.34	7.55	21.67	35.85	65.89	100.53	143	255	--
15	y	0.98	1.18	1.67	3.78	10.83	17.93	32.95	50.27	71.45	127.42	--
	x	0.76	0.94	1.38	3.30	6.31	7.67	9.38	12.63	10.17	26.34	--
		A ₀ Value										
T($^{\circ}\text{C}$)		1.33	1.88	2.63	5.02	14.83	26.57	50.63	63.75	93.81	130.92	182.46
30	y	0.66	0.94	1.32	2.51	7.41	13.28	25.32	31.87	46.90	65.46	91.23
	x	0.66	0.94	1.29	2.34	7.41	10.67	13.06	15.51	17.18	19.46	19.26
		A ₀ Value										
T($^{\circ}\text{C}$)		1.42	2.20	2.80	5.47	15.27	30.33	65.89	100.53	130	194.39	266.32
45	y	0.71	1.10	1.40	2.73	7.64	15.17	32.94	50.27	65.04	97.20	133.16
	x	0.45	0.97	1.22	2.41	6.80	12.95	19.88	25.03	20.19	35.60	42.04
Equation 7		$\Delta G/(RT)=[(A_0) \cdot \ln(1 - x/y) + (W_0 \cdot \beta^a) \cdot \ln(1 - x/\beta)]/52^b$										
15 $^{\circ}\text{C}$	x/y	0.77	0.80	0.83	0.87	0.58	0.43	0.28	0.25	0.14	0.21	--
	x/ β	0.06	0.07	0.11	0.26	0.50	0.61	0.75	1.00	0.81	2.10	--
- $\Delta G/(RT)$		0.09	0.11	0.17	0.45	0.70	0.84	1.09	--	1.22	--	--
30 $^{\circ}\text{C}$	x/y	1.00	0.99	0.98	0.93	1.00	0.80	0.52	0.49	0.37	0.30	0.21
	x/ β	0.03	0.05	0.07	0.12	0.38	0.55	0.67	0.80	0.89	1.00	0.99
- $\Delta G/(RT)$		--	0.22	0.25	0.36	--	1.43	1.54	2.02	2.45	--	4.73
45 $^{\circ}\text{C}$	x/y	0.64	0.88	0.87	0.88	0.89	0.85	0.60	0.50	0.45	0.37	0.32
	x/ β	0.01	0.02	0.03	0.06	0.18	0.33	0.51	0.64	0.75	0.92	1.08
- $\Delta G/(RT)$		0.05	0.13	0.16	0.32	0.94	1.73	2.24	2.88	3.57	5.42	--

^a β = Estimated adsorption capacity parameter for each temperature; gas constant $R = 8.314 \text{ J}/(\text{mol K})$. ^bThe value of 52 was used for the atomic weight of chromium to obtain the molar concentration for calculating $\Delta G/(RT)$.

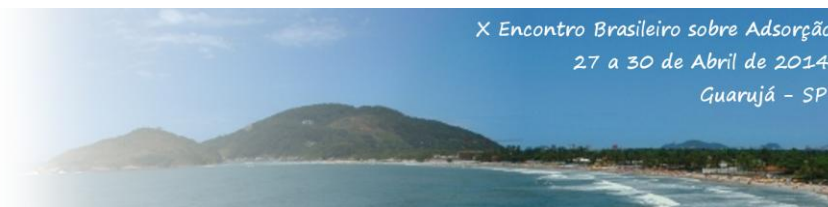
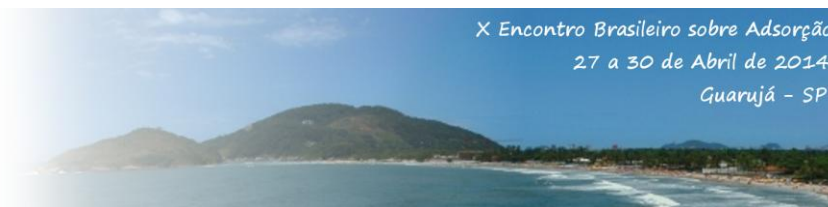


Table 4. Equilibrium adsorption density, x (mg/g), and calculated values of $\Delta G/(RT)$ for Pb^{2+} ion adsorption onto *Salvinia cucullata* at different values of A_0 (mg/L) and T ($^{\circ}C$).

		A ₀ Value										
T($^{\circ}C$)		9.15	11.28	15.19	26	93	126.17	236.7	327.71	401.42	572	755
15	y	4.57	5.64	7.59	13	46.54	63.10	118	163.85	201	286	378
	x	3.48	4.54	6.43	11.82	36.23	50.61	91.30	119.25	117	116.68	116
		A ₀ Value										
T($^{\circ}C$)		6.92	8.95	12.43	21.70	63.56	108	212	332	438	643	865
30	y	3.46	4.48	6.21	10.85	31.78	53.95	106	166	219	322	433
	x	3.15	4.15	5.85	10.30	28.95	45.39	57.60	64.37	65.98	66.66	64.27
		A ₀ Value										
T($^{\circ}C$)		8.85	11	15	25	73.40	120	223	356	485	698	890
45	y	4.42	5.50	7.32	12.50	36.68	60.05	112	178	242.44	349	445
	x	3.33	4.44	6.24	11.3	29.48	42.53	49.12	54	62	63	57
Equation 7		$\Delta G/(RT)=[(A_0) \cdot \ln(1 - x/y) + (W_0 \cdot \beta^a) \cdot \ln(1 - x/\beta)]/207.2^b$										
15 $^{\circ}C$	x/y	0.76	0.81	0.85	0.91	0.78	0.80	0.77	0.73	0.58	0.41	0.31
	x/ β	0.03	0.04	0.06	0.10	0.31	0.44	0.79	1.03	1.01	1.01	1.01
- $\Delta G/(RT)$		0.39	0.53	0.80	1.68	4.37	6.50	13.68	--	--	--	--
30 $^{\circ}C$	x/y	0.91	0.93	0.94	0.95	0.91	0.84	0.54	0.39	0.30	0.21	0.15
	x/ β	0.05	0.06	0.09	0.16	0.44	0.70	0.88	0.99	1.01	1.02	0.99
- $\Delta G/(RT)$		0.45	0.62	0.91	1.68	4.43	6.81	8.58	14.05	--	--	13.33
45 $^{\circ}C$	x/y	0.75	0.81	0.85	0.90	0.80	0.71	0.44	0.30	0.26	0.18	0.13
	x/ β	0.05	0.07	0.10	0.19	0.49	0.70	0.81	0.89	1.02	1.04	0.94
- $\Delta G/(RT)$		0.37	0.53	0.79	1.60	3.85	5.66	6.36	7.66	--	--	8.90

^a β = Estimated adsorption capacity parameter for each temperature; gas constant $R = 8.314$ J/(mol K). ^bThe value of 207.2 was used for the atomic weight of chromium to obtain the molar concentration for calculating $\Delta G/(RT)$.



4. CONCLUSIONS

This work shows that the biosorption process achieved better results under low temperature conditions for lead and high temperature for chromium. The Langmuir model fitted better to Pb^{2+} experimental data and the maximum uptake exhibited was $0.562 \text{ mmol.g}^{-1}$ at 15°C . While Freundlich model fitted better to Cr^{3+} data with R^2 of 0.984. The D-R model showed that the process is physical for both metals. The FT-IR characterization showed that some functional groups as carboxyl and alkenes are essential in the biosorption process. The thermodynamics data showed that the process for the two metal ions are spontaneous. The study results indicated that *Salvinia cucullata* biomass is a promising low-cost biosorbent for the removal of chromium and lead ions.

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