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Isotherm and thermodynamic studies of the biosorption of lead, cadmium and copper from aqueous solutions by rice bran

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ABSTRACT

The biosorption of lead [Pb(II)], cadmium [Cd(II)] and copper [Cu(II)] onto rice bran, a residue of rice processing industry, in a batch experiment has been studied. Equilibrium isotherms and thermodynamic parameters have been evaluated. Equilibrium data agreed well with Langmuir isotherm model. Gibbs free energy was spontaneous for all interactions, and the biosorption process exhibited exothermic enthalpy values. Although rice bran presented a quite high metals sorption ability for Cd(II) and Cu(II), it seemed to be especially suitable for removal of Pb(II). Rice bran was shown to be a promising biosorbent for Pb(II), Cd(II) and Cu(II) removal from aqueous solutions.

Keywords: Rice bran; Heavy metals; Equilibrium; Biosorption; Thermodynamic; Wastewater treatment

1. Introduction

Industrial wastewater containing heavy metal can cause serious environmental pollution problems. Lead is a nonessential, highly toxic metal, and all known effects of lead on biological systems are deleterious. Acute and classical lead poisoning in human adults is manifested by anemia, renal damage, and sometimes encephalopathy. Cadmium [Cd(II)] enters waterways through industrial discharges and galvanized pipe breakdown. It is all a nonessential metal to living organisms and can become toxic by displacing zinc [1]. Low exposures may result in kidney damage and, in addition, epidemiological studies have revealed that Cd(II) may be a contributing factor in some forms of cancer in humans. Copper [Cu(II)] at excessive concentration is also toxic to a variety of living organisms from humans to bacteria, especially fish. Low exposures can impact respiration and affect cell walls of microorganisms. Therefore their removal from wastewater before they are discharged into surrounding water bodies is of importance.

At present there exist a number of different technologies for treating heavy metals-bearing waste streams. Chemical means of removing heavy metals from water would be expensive, incomplete metal removal, toxic sludge generation and intensive maintenance [2,3]. On the other hand, biological methods, such as biosorption, show potential for ease of construction and maintenance. Biosorption is a process that utilizes inexpensive inactive/dead biological materials as adsorbents to sequester toxic heavy metals and is particularly useful for the removal of contaminants from industrial effluents. Biosorbents are generally available at low cost, non hazardous and abound in nature [4,5]. A variety of

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agricultural waste and by-products of cellulosic origin such as sugar beet pulp [6], grape stalks [7], spent grains [8], pine sawdust [9], and tea fungus [10] have been studied in literature for their capacity to remove heavy metals from aqueous solutions.

Rice bran, generated in the rice processing, is often used as a fertilizer or fuel [11]. Due to its granular structure, chemical stability and local acquirability, rice bran being chosen as a sorbent material for metal ions has been a focus of our research. In this study, the potential of rice bran to be used in the removal of Pb(II), Cd(II) and Cu(II) from synthetic polluted waters was investigated. Batch experiments were carried out to study the factors affecting the sorption of metals, such as pH, contact time, initial concentration. The present manuscript reports on the Pb(II), Cd(II) and Cu(II) biosorption capacity of the rice bran biomass. In addition, adsorption isotherms were used to describe the biosorption equilibrium and to calculate some thermodynamic parameters. The main mechanism that could be controlling the biosorption was also discussed.

2. Materials and methods

2.1. Materials

Metal stock solutions of a concentration of 1000 mg l^{-1} (Pb(II) 3.01 mmol l^{-1}, Cd(II) 4.24 mmol l^{-1} and Cu(II) 5.32 mmol l^{-1}) were prepared by dissolving calculated amount of their salts in double distilled water. Pb(II), Cd(II) and Cu(II) were used as their nitrate salts. All the salts were in their hydrated state. In order to be close to real wastewater, metals-bearing water was prepared by diluting stock solution with tap water rather than distilled water to a given certain concentrations.

Rice bran obtained from locally industry of rice processing, has been directly used as biosorbent without any pre-treatment. The samples were then dried at 75°C for a period of 24 h, and stored dry until use.

2.2. Biosorption experiment

In batch pH studies, 0.5 g rice bran and 100 ml single metal ion solutions (Pb(II) 0.60 mmol l^{-1}, Cd(II) 0.85 mmol l^{-1} and Cu(II) 1.06 mmol l^{-1}) with a range of pH values from 2.0 to 7.0 were transferred in a conical flask, and shaken on a temperature controlled shaker incubator at 150 rpm for 40 min (the time required for equilibrium to be reached). The pH of the solutions was adjusted with HNO_3 or NaOH solution by using a pH meter.

In the determination of equilibrium adsorption isotherm, 0.5 g rice bran and 100 ml of different concentrations (Pb(II) 0.30 ≈ 3.01 mmol l^{-1}, Cd(II) 0.42 ≈ 4.24 mmol l^{-1} and Cu(II) 0.53 ≈ 5.32 mmol l^{-1}) of single metal ion solutions were shaken for 40 min at the initial optimal pH 5 and different temperatures (293–313 K).

All the mixture after adsorption operation was filtered using filter paper, and the metal ion concentration was determined by an inductively coupled plasma–atomic emission spectrometer (Intrepid II XSP). To ensure the accuracy, reliability, and reproducibility of the collected data, all the batch experiments were carried out in triplicate and the mean values of three data sets are presented.

3. Results and discussion

3.1. Effect of pH on heavy metals biosorption

The pH plays an important role in the biosorption process by affecting the surface charge of biosorbent, the degree of ionization and speciation of the adsorbate. Thus the effect of pH in the solutions on the removal efficiency of single metal ion was studied at different pH ranging from 2.0 to 7.0. Results are shown in Fig. 1.

It was observed that a sharp increase in the Pb(II) removal from 56.4% to 98.2%, from 39.3% to 93.9% for Cd(II) removal, and from 21.9% to 87.2% for Cu(II) removal occurred when the pH values of the solutions changed from 2.0 to 4.0. This can be explained on the basis of a decrease in competition between positively charged H^+, H_3O^+ and single metal ion for the surface sites and also by the decrease in positive surface charge on the biosorbent (The pH_{ZPC} of rice bran is 6.8), which results in a lower electrostatic repulsion between the surface and the metal ions. As shown in Fig. 1, the maximum removal efficiency occurred at pH 5–7. But some precipitation was observed at pH 6. Hence, pH 5.0 was

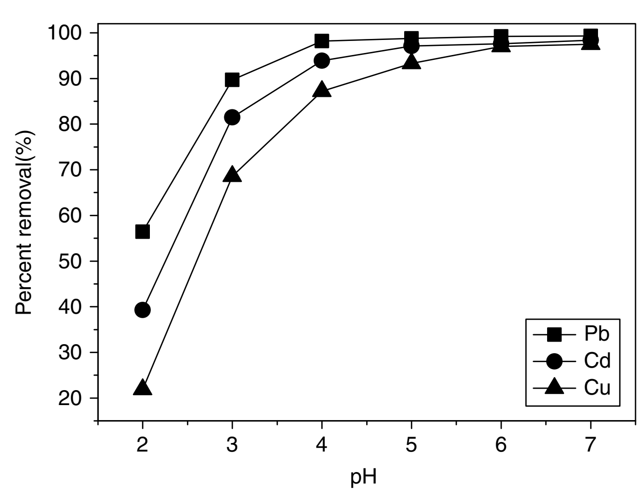

Fig. 1. Effect of the solution pH on the biosorption of single metal ion onto rice bran (C_0 = Pb(II) 0.60 mmol l^{-1}, Cd(II) 0.85 mmol l^{-1} and Cu(II) 1.06 mmol l^{-1}, V = 100 ml, M = 0.5 g, T = 293 K).

selected as optimum pH for metal ion biosorption onto rice bran. At this pH, there are three species of Pb(II) present in the solution, that is, Pb^{2+} and $Pb(OH)^{+}$ (large quantity) and $Pb(OH)_2$ (small quantity). This indicates that Pb^{2+} and $Pb(OH)^{+}$ are predominantly adsorbed on rice bran, which are similar for Cd(II) and Cu(II).

3.2. Biosorption isotherm

The biosorption isotherm indicates how the adsorbate molecules distribute between the liquid phase and the solid phase at equilibrium. Equilibrium studies were carried out to determine the conditions for maximum removal of Pb(II), Cd(II) and Cu(II) over rice bran. It is observed that biosorption capacity reaches an equilibrium value beyond which there is a negligible change in the residual single metal ion concentration (Fig. 2). In this research, biosorption isotherm study was carried out on two well known isotherms, that is, Langmuir isotherm and Freundlich isotherm.

Langmuir equation was applied to quantify biosorption capacity and is given as follows:

$$\left(\frac{C_e}{q_e}\right) = \left(\frac{1}{q_m K_L}\right) + \left(\frac{C_e}{q_m}\right) \quad (1)$$

where C_e is the concentration of the metals solution at equilibrium (mmol l^{-1}), q_e the amount of metals sorbed at equilibrium (mmol g^{-1}), q_m the monolayer adsorption saturation capacity of the metal-rice bran system (mmol g^{-1}) and K_L is constant related to the binding energy of the biosorption system (l $mmol^{-1}$). q_m and K_L were determined from the plot of C_e/q_e versus C_e, and tabulated in Table 1. High R^2 values (Table 1) indicate that the biosorption of metal ion onto rice bran follows the Langmuir model, which indicated the monolayer coverage process of metals onto rice bran. As shown in Table 1, the constants q_m and K_L decreased with increasing temperature, which indicates that, at lower temperatures, the biosorption density was higher and the biosorption energy was lower.

Table 2 summarizes the comparison of metal ions biosorption capacities (q_m) by various living/dead biomass by-products. Compared to other biosorbents in Table 2, rice bran presents higher biosorptive capacity, reflecting a promising future for rice bran utilization in metal ions removal from aqueous solutions.

The Freundlich isotherm is suitable for a highly heterogeneous surface [20] and expressed by the following linearized form [21]:

$$\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \quad (2)$$

where q_e is the amount of metals adsorbed at equilibrium (mmol g^{-1}), C_e the equilibrium concentration of metals in solution (mmol l^{-1}), K_F and $1/n$ the Freundlich constants, which represent the biosorption capacity (mmol g^{-1}) and biosorption intensity of these sorbents, respectively. The constants K_F and $1/n$ are evaluated from the intercept and the slope of the straight lines using a least-square fit program and were listed in Table 1. Although the R^2 values (Table 1) for the Freundlich isotherm models

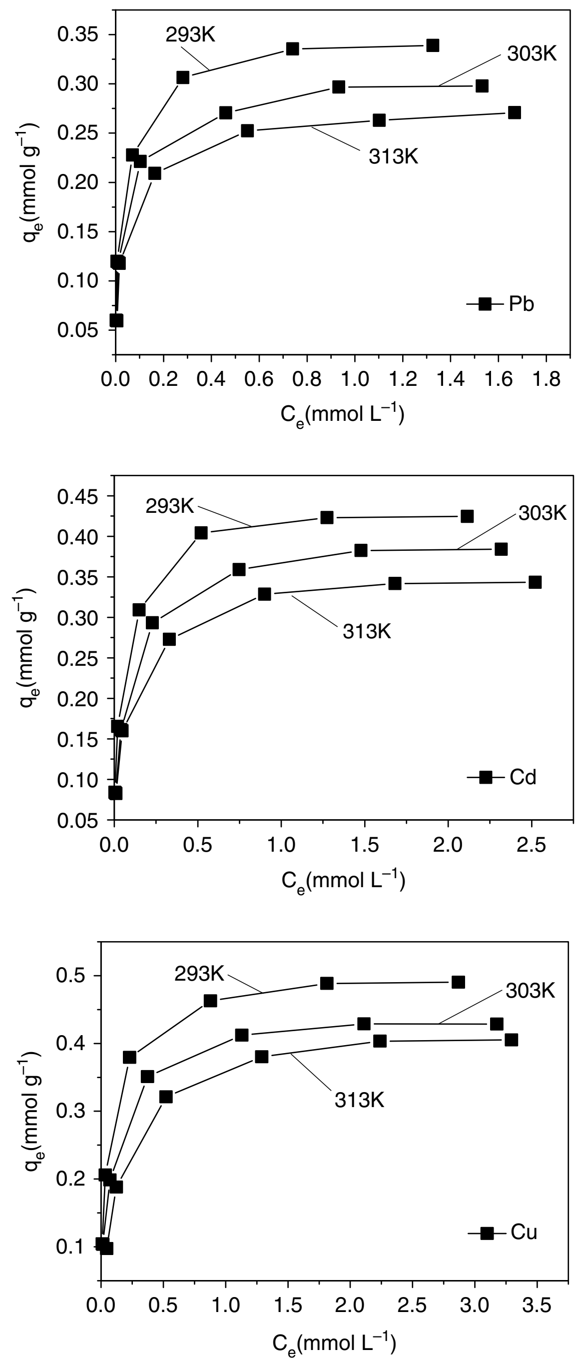

Fig. 2. Effect of initial metal ion concentration on the biosorption of single metal ion onto rice bran (V = 100 ml, M = 0.5 g, pH = 5).

Table 1
Isotherm parameters for metal ion biosorption onto rice bran at different temperatures

Metal ion	Temperature (K)	Langmuir			Freundlich		
		q_m (mmol g^{-1})	K_L (l mmol^{-1})	R^2	K_F	$1/n$	R^2
Pb(II)	293	0.344	49.319	0.998	0.090	0.246	0.969
	303	0.303	36.410	0.999	0.074	0.248	0.961
	313	0.274	29.128	0.998	0.065	0.248	0.958
Cd(II)	293	0.432	28.792	0.999	0.102	0.260	0.972
	303	0.393	17.936	0.999	0.082	0.271	0.974
	313	0.352	16.520	0.999	0.076	0.259	0.972
Cu(II)	293	0.500	18.424	0.999	0.111	0. 264	0.959
	303	0.440	13.724	0.998	0.093	0.264	0.969
	313	0.427	6.392	0.999	0.059	0.324	0.959

Table 2
Heavy metals biosorption by living/dead biomass from the literature

No.	q_m (mmol g^{-1})			Biosorbents	References
	Pb^{2+}	Cd^{2+}	Cu^{2+}		
1	0.41		0.18	*Phanerochaete chrysosporium*	[12]
2		0.73	0.31	Aerobic granules	[13]
3	0.15	0.12		Grape stalk waste	[14]
4	0.21		0.11	Filamentous fungus	[15]
5	0.22		0.33	*Rhizopus arrhizus*	[16]
6	0.23		0.18	Bacterial cells	[17]
7		0.12		*Fontinalis antipyretica*	[18]
8	0.11	0.07		Spent grains	[19]
9	0.34	0.43	0.50	Rice bran	This study

were relatively high, it is lower than that of Langmuir isotherm models. These facts imply that Freundlich isotherm is inappropriate to characterize the metal ions biodsorption onto rice bran.

3.3. Biosorption thermodynamics

The Gibbs free energy change of the adsorption process is related to the equilibrium constant by the classic Van't Hoff equation:

$$\Delta G^\circ = -R\,T \ln K \tag{3}$$

where ΔG° is the standard free energy change (J mol^{-1}), T the absolute temperature (K) and R gas constant (J mol^{-1} K^{-1}) ΔG° was determined by using the equilibrium constants obtained from the Langmuir fitted model at 293, 303 and 313 K.

According to thermodynamics, the Gibbs free energy change is also related to the entropy change and heat of adsorption at constant temperature by the following equation:

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ \tag{4}$$

where ΔH° is enthalpy change (J mol^{-1}), ΔS° entropy change (J mol^{-1} K^{-1}). ΔH° and ΔS° can be calculated from the plot of ΔG° versus T (not shown). The calculated thermodynamic parameters for the biosorption of metals by rice bran are given in Table 3. The negative value of ΔG° indicates the feasibility of the process and indicates the spontaneous nature of the biosorption. ΔG° value is more negative with decreasing temperature, which suggests that lower temperature makes the biosorption easier. The negative value of ΔH° implies that the biosorption phenomenon is exothermic.

Table 3
Thermodynamic parameters for the biosorption of metal ions onto rice bran

Metal ion	Temperature (K)	$\Delta G°$ (kJ mol^{-1})	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (J mol^{-1} K^{-1})	R^2
Pb(II)	293	−17.266			
	303	−17.168	−20.126	−9.761	0.998
	313	−17.071			
Cd(II)	293	−18.142			
	303	−18.038	−21.335	−10.898	0.933
	313	−17.924			
Cu(II)	293	−34.914			
	303	−34.735	−40.146	−17.857	0.964
	313	−34.557			

The negative value of $\Delta S°$ suggests the process is enthalpy driven.

3.4. *Influence of coexisting cations upon the sorption*

Fig. 3 showed the influence of the addition of coexisting cations (Pb(II) or Cd(II)) on the biosorption capacity of Cu(II). The initial concentration of Cu(II) ion in solution was 1.06 mmol l^{-1} and the initial molar ratios (IMR) of Pb(II) or Cd(II) ions to Cu(II) ion varied from zero (no coexisting cations) to 20.

The influence of coexisting cations on the biosorption capacities of Cu(II) ion in the binary metal system was in the order: Pb(II) > Cd(II). In the mixed metal system, the presence of other cations reduced the biosorption of Cu(II), indicating the existence of competitive binding with rice bran surfaces between coexisting cations and Cu(II). The observed reduction in the biosorption of Cu(II) ion with the coexisting Pb(II) ions was more pronounced compared to the coexisting Cd(II).

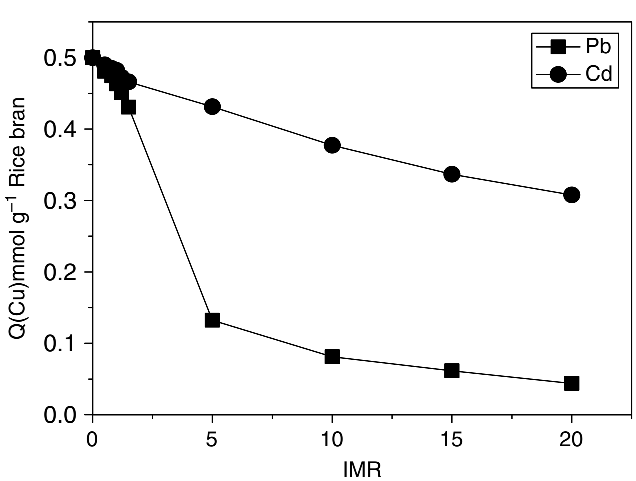

Fig. 3. Cu(II) biosorption capacity Q(Cu) at different initial molar ratios (IMR) of coexisting cations to Cu(II) by rice bran ($C_{0(Cu)}$ = 1.06 mmol l^{-1}, V = 100 ml, M = 0.5 g, pH = 5).

In the binary metal system, the biosorption capacity of rice bran for each metal ion was lower than in the single Cu(II) system, indicating that complex interactions of several factors such as ionic charge, and electrode potential affect the biosorption of metal ions on rice bran. Although many of the functional groups present on rice bran cell wall, much different cations compete for the limited binding sites.

Furthermore, the ion selectivity observed for Pb(II) being higher than those of Cd(II) and Cu(II) might be attributed to the physical aspects of the sorption process. While it has been reported that metal biosorption increased with increasing the ionic radii of metal cations which influenced the ion exchange and sorption process [22]. The strength of ionic bonds that is, electrostatic attraction increases with the charge density of the hydrated ion, z^2/r_{hyd}. It so happens that Pb, which has the largest ionic crystal radius, also has the lowest hydrated radius and therefore the highest strength of electrostatic attraction. Thus a stronger physical affinity for Pb(II) is expected at the sorption sites on the surface of the sorbent [23].

It was observed that of 97% of single Cu(II) ion was removed from the solutions within 40 min of biosorption. This finding maybe owe to the coexist of physical sorption and complexation/covalent bonds during this initial phase of biosorption process.

4. Conclusions

The ability of rice bran biosorbent to remove Pb(II), Cd(II) and Cu(II) from aqueous solution was investigated in equilibrium and thermodynamics. Equilibrium data agreed well with Langmuir isotherm model. The negative values of $\Delta H°$ and $\Delta G°$ revealed the exothermic nature and the feasibility of biosorption. Rice bran presented a quite high sorption ability for metal ions, and seemed to be especially for Pb(II). The investigation shows that rice bran is a promising biosorbent for the removal of Pb(II), Cd(II) and Cu(II) from aqueous solutions.

Acknowledgements

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