

Removal of metal ions from aqueous solutions by sorption onto rice bran

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Abstract

A new sorbent (raw rice bran) was investigated for heavy metal ions removal from aqueous solutions. Rice bran characterisation was carried out in order to identify the functional groups possibly involved in the metal binding. The binding process was studied in terms of binding capacity and metal affinity. The adsorption equilibrium was well described by the Freundlich isotherm model. The negative Gibbs free energy values obtained in this study with rice bran confirm the feasibility of the process and the spontaneous nature of sorption.

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1. Introduction

The interest in the development of cost-effective methods for the removal and recovery of heavy metals from contaminated waters has greatly increased because of the ecological awareness of the role of metals in the environment. A number of methods for metal ions removal from wastewaters has been used, but most have several disadvantages, such as continuous input of chemicals, high cost, toxic sludge generation or incomplete metal removal [1]. Activated carbon is a very efficient solid sorbent in many different applications. But activated carbon is expensive, and the need of an alternative low-cost sorbent has encouraged the search for new sorption processes. Biosorption is the process of metal ions removal by biological materials and the biomaterials have been considered as potential sorbents for heavy metal removal, representing an important breakthrough [2]. The major attention has been focused on abundant in nature, waste or low-cost materials. Of particular interest are abundant biomass types generated as a waste by-product of large-scale industrial pro-

cesses and vegetable biomass [1,3–7]. However, in order to be accepted, a new metal ion biosorption process must be economically competitive and perform as well as existing technologies.

Brazil produces million tonnes of rice annually. Rice bran is a by-product of the rice milling industry and the amount of rice bran available is far in excess of any local uses, thus frequently causing disposal problems [8].

The possibility of the use of rice bran as a sorbent material for metal ions removal has been a focus of our research. Rice bran was chosen due to its granular structure, insolubility in water, chemical stability and local availability. In this work, the potential of rice bran to be used in the removal of Cd(II), Cu(II), Pb(II) and Zn(II) from aqueous solutions was investigated. Studies have included the identification of functional groups involved in metal ion binding, and the characterization of metal ion binding process in terms of binding capacity, affinity and metal ion sorption mechanisms. The derivation of sorption isotherms has been used for assessing biosorbent capacities and two commonly used equilibrium models (Langmuir and Freundlich isotherm) have been fitted to the experimental data [9].

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2. Materials and methods

The rice bran used as biosorbent was taken at a local micro industry of rice processing. The biomass was dried in an oven at 105 °C for a period of 24 h, and stored in closed amber glass bottles. Raw, dry ungrounded rice bran was used in all sets of experiments. Binding surface groups were investigated using potentiometric titration. A suspension in 0.1 mol L⁻¹ sodium nitrate (100 mg of rice bran/20.0 mL) was first acidified until pH 3.0 with HNO₃ 0.1 mol L⁻¹, deaerated for 1 h and titrated with NaOH 0.1 mol L⁻¹. Infrared spectra were obtained to characterise the principal groups. Physical–chemical characterization was also carried out and ashes, humidity, metals, acidity, lipid and starch contents were determined. The surface structure of rice bran was analysed by scanning electronic microscopy (SEM).

Analytical grade reagents were used in all the experiments. Water purified by means of a Milli-Q system (Millipore) was used throughout. Metal ion working solutions were made freshly by diluting the stock solutions (1000 mg L⁻¹). Acid washing with 1% (v/v) HNO₃ solution, followed by a triple rinse with Milli-Q water was carried out to avoid metal losses and/or contamination. Flame atomic absorption spectrometry was used for metal ions determinations.

2.1. Batch sorption experiments

The sorption studies were carried out at 25 ± 1 °C in a homemade horizontal shaker using 50.0 mL capped tubes, containing 20.0 mL of the test solution, with a known metal ion concentration. Before mixing with the rice bran, the pH of the solution was adjusted with HNO₃ 0.1 mol L⁻¹ or NaOH 0.1 mol L⁻¹. A known amount of rice bran was added and the tubes were thoroughly mixed, allowing sufficient time for adsorption equilibrium (also examined). The mixtures were filtered through filter paper, and the metal ions were determined in the filtrate. Each experiment was repeated three times, and the results are given as averages.

3. Results and discussion

3.1. Rice bran characterization

Table 1 shows rice bran characterization. A high fibre and starch content was found, compared with other similar biomasses. This is a very interesting characteristic for metal binding. Silica, calcium and iron are also present in high levels.

The determination of the total ligands concentration is not easy owing to the heterogeneity of the rice bran surface groups. In fact, the determination of the number of sites of heterogeneous ligands is always difficult owing to the large variety of groups and the fact that they respond in different ways to different metal ions. Therefore, the total ligands concentration was determined by using potentiometric

Table 1
Rice bran characterization

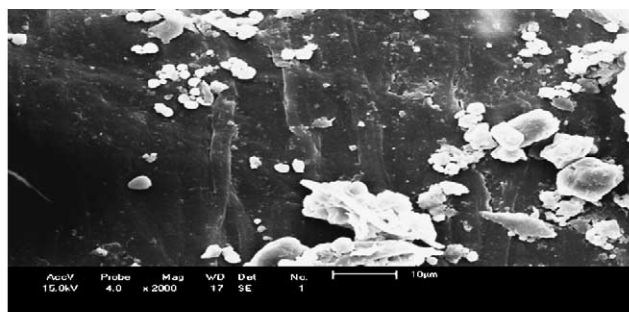
Ash (%)	10.88
Humidity (%)	10.68
Total proton binding ligands (μmol g ⁻¹)	17.00
Fibre (%)	11.58
Starch (%)	17.60
Protein (%)	12.70
Metals (mg kg ⁻¹)	
Iron	73.10
Magnesium	30.22
Calcium	697
Copper	7.13
SiO ₂ (%)	3.34
Acidity (mmol L ⁻¹)	6.23
Particle size (average diameter, μm)	320
Surface area (m ² g ⁻¹)	0.46

titrations. Acidimetric titrations were used to characterise rice bran proton binding capacity, which reflects the number of functional groups available. Only one clear inflection point was observed and an ionisation constant value (pK_a) close to 7.6 was determined, probably due to polysaccharides. The total concentration of complexing groups, 17 μmol g⁻¹, was determined as the concentration of deprotonated groups at the inflection point, more representative of the material.

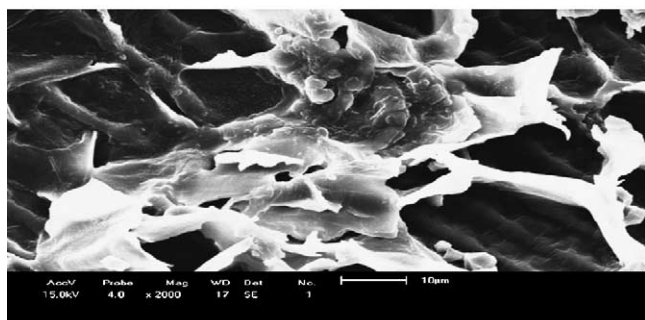
Rice bran IR-spectrum showed four intense bands, around 3400, 2930, 1700 and 1030 cm⁻¹. The broad band around 3400 cm⁻¹ was attributed to the surface hydroxyl groups and chemisorbed water. The bands at 2926 and 1700–1650 cm⁻¹ were assigned to C–H stretches of methylene groups on the surface and to ketonic and aldehydic C=O stretching frequencies, and to amino groups, respectively. Small peaks observed at 1465–1400 cm⁻¹ are attributed to carboxylate groups. At around 1030 cm⁻¹ the band can be assigned to phosphate and silicate groups. Therefore, rice bran IR-spectrum indicated the presence of ionisable functional groups able to bind with heavy metal ions, and showed the influence of pH on the deprotonation of functional groups.

The specific surface area (BET method) of rice bran particles was 0.46 m² g⁻¹; a comparable value was previously determined [10]. This surface area is much smaller than that of activated carbon, a sorbent commonly used for the removal of volatile organic compounds and metal ions in aqueous samples, which presents a very large surface area (>700 m² g⁻¹) [11]. Particle diameters in the rice bran samples were estimated to be in the range of 150–425 μm, with an average particle diameter of 320 μm.

The surface structure of rice bran was analysed by scanning electronic microscopy (SEM) before and after Pb(II) sorption (Fig. 1). The micrographs reveal clearly the presence of cylindrical structures, with different diameters, after metal ion sorption; these structures were absent on the rice bran before the sorption process. The presence of pellets on the rice bran particles and inside the cylindrical structures can also be observed after metal ion sorption.



(a) rice bran particle before sorption process



(b) rice bran particle with Pb(II) sorbed

Fig. 1. Typical SEM micrograph of rice bran (magnification: 2000 \times) (a) before metal ion sorption (b) with Pb(II) sorbed.

3.2. Sorption conditions

Batch experiments carried out in different electrolytes solutions – NaCl 0.1 mol L⁻¹, NaNO₃ 0.1 mol L⁻¹ and NaNO₃ 1.0 mol L⁻¹. Maximum efficiency for Cd(II), Cu(II), Pb(II) and Zn(II) removal was observed in chloride medium and NaCl 0.1 mol L⁻¹ has been used throughout the work.

The pH effect on metal ions sorption by rice bran was studied in NaCl 0.1 mol L⁻¹, in the pH range of 2.0–7.0; HNO₃ or NaOH 0.1 mol L⁻¹ were used to adjust to the desired initial pH value. Maximum removal was achieved at pH values around 5–6 for all the metal ions investigated (Fig. 2). The pH

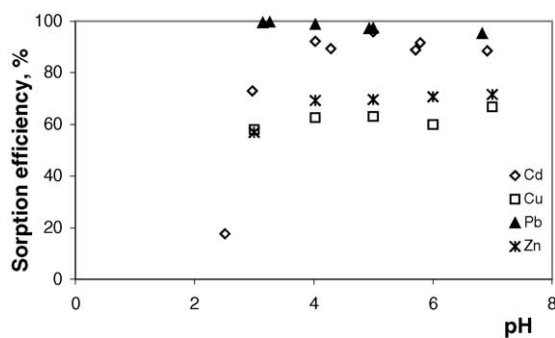


Fig. 2. Kinetic experiment for the metal ion sorption onto rice bran (NaCl 0.1 mol L⁻¹; pH = 5.0; m (rice bran): 200 mg; $T = 25 \pm 1$ °C) (a) Cd(II); (b) Cu(II); (c) Pb(II); (d) Zn(II).

binding profiles can be attributed to the nature of the chemical interactions of each metal ion with the biomass. As the pH is lowered, the overall surface charge on the particles becomes positive, and hinders the approach of positively charged metal cations. At higher pH values, the number of negatively charged groups on the adsorbent matrix probably increases, and enhances the removal of cationic species. pH affects not only site dissociation, but also the metal speciation, and hydrolysis products of metal cations can be produced. The data presented in this study suggest that metal cations are the predominant species, under the experimental conditions used. Metal cations at around pH 5.0 would be expected to interact with the negatively charged binding sites in the rice bran. An increase in the pH from its initial value took place in all solutions after stirring, and this effect was greater for low initial pH values. This mechanism agrees with other studies on other similar adsorbents [12]. This small effect was also observed when rice bran was stirred with pure deionised water, adjusting or not the initial pH. Probably, the increase in pH with stirring time can be attributed to the hydrolysis of rice bran in water.

A fast kinetics is one of the most important aspects for removal processes. Therefore, time dependence experiments for metal ions removal were carried out (pH = 5.0; $T = 25 \pm 1$ °C) up to 180 min of contact time. Pb(II) removal was found to be immediate, and the equilibrium was reached just after 1 min of stirring time. The data obtained showed that a contact time of 10 min was sufficient to achieve equilibrium for all the metal ions. Besides, the metal binding was fast and the sorption did not change at least for 1 h. Therefore, it was chosen 10 min as the contact time for simultaneous Cd(II), Cu(II), Pb(II) and Zn(II) removal by rice bran, considering analytical speed and removal efficiency.

The increasing of rice bran concentration from 1 to 20 g L⁻¹ resulted in a decreasing removal of the metal ions studied per unit weight of biosorbent. This fact may be attributed to some kind of hindrance, as aggregation/agglomeration of sorbent particles at higher concentrations. Besides, the adsorption sites remain unsaturated during the sorption process due to a lower adsorptive capacity utilization of the sorbent. Therefore, a more economical removal of a given amount of metal ions can be carried out using small batches of sorbent rather than in a single batch.

The equilibrium capacity for metal ions sorption onto rice bran increased on increasing the initial metal ion concentration up to certain concentration, and then did not change with additional increase of initial metal concentration. This is due to the increase in the concentration gradient (driving force). However, the sorption efficiency is reduced with increasing metal ion concentrations in the solution, thus indicating saturation. These results may be explained considering that, at low metal ion concentrations, the ratio of surface active sites to total metal is high, and hence all metal may interact with the biosorbent and be removed from the solution.

3.3. Adsorption equilibrium modelling

The sorption isotherm represents the relationship between the amount adsorbed by a unit weight of solid sorbent and the amount of solute remaining in the solution at equilibrium. Both Langmuir and Freundlich isotherm models have been shown to be suitable for describing short-term and monocomponent adsorption of metal ions by different materials [5,13]. So, in order to investigate the sorption capacity of rice bran, these equilibrium models were fitted to the experimental data.

Langmuir model assumes the presence of a finite number of binding sites, homogeneously distributed over the sorbent surface, presenting the same affinity for sorption of a single layer, and with no interaction between sorbed species. The well-known Langmuir expression [9] is represented as follows:

$$q_{\text{eq}} = \frac{Q^0 b C_{\text{eq}}}{1 + b C_{\text{eq}}} \quad (1)$$

where q_{eq} is the amount of metal bound per gram of biomass at equilibrium, C_{eq} the residual metal concentration in solution after binding, Q^0 the maximum amount of metal ion per unit weight of biomass to form a complete monolayer on the surface bound at high C_{eq} , and b a constant related to the affinity of the binding sites. Q^0 and b can be determined from the linear form ($C_{\text{eq}}/q_{\text{eq}}$ versus C_{eq} plot) [13].

The Freundlich expression is an equation based on heterogeneous surfaces suggesting that binding sites are not equivalent and/or independent. The Freundlich equation is given by [13,14]

$$q_{\text{eq}} = K_F C_{\text{eq}}^{1/n} \quad (2)$$

Table 2
Freundlich constants for metal ion removal by rice bran

	K_F	n	r^2
Cd(II)	0.61	0.90	0.9734
Cu(II)	0.21	0.61	0.9808
Pb(II)	2.62	0.68	0.9421
Zn(II)	1.34	0.42	0.9147

where K_F and n are the Freundlich constants characteristic of the system. K_F indicates the adsorption capacity and n is associated to the adsorption intensity. The equation is commonly used in the linear form (logarithmic form), and K_F and n constants can be determined.

The adsorption isotherms for Cd(II), Cu(II), Pb(II) and Zn(II) removal were studied at $25 \pm 1^\circ\text{C}$. The data obtained were not well fitted to the Langmuir adsorption model, but were found to obey Freundlich isotherm, and this can be attributed to the rice bran structure. Diffusion and binding steps control the adsorption process [7]. Rice bran is a cellulose fibre material and shrinks in acid solutions, causing an increasing compactness; as a consequence, diffusion steps become relatively slow, and should be the rate-determining steps in the metal binding process. If the diffusion steps are slow, they become the rate-determining step in the binding to the active sites. The adsorption, in this case, is at random due to the existence of active sites with different energies. Freundlich constants were calculated from the linear logarithmic expression and are given in Table 2. The data showed that rice bran has a higher adsorptive capacity for Pb(II) and Zn(II) removal, under our experimental conditions. Rice bran adsorption intensity was weaker for Zn(II). The n values indicate the presence of a heterogeneous surface and binding sites with different adsorption energies.

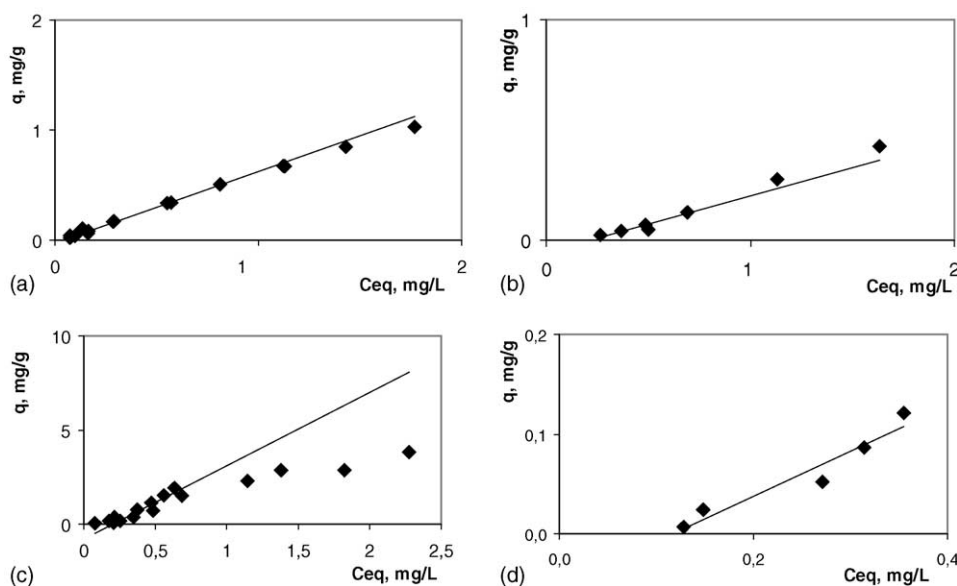


Fig. 3. Experimental and calculated data (Freundlich equation) for metal ion sorption onto rice bran ($\text{NaCl } 0.1 \text{ mol L}^{-1}$; $\text{pH} = 5.0$; contact time: 10 min; $m(\text{rice bran}) = 200 \text{ mg}$; $T = 25 \pm 1^\circ\text{C}$) (a) Cd(II); (b) Cu(II); (c) Pb(II); (d) Zn(II).

Table 3
Thermodynamic parameters for metal ions adsorption onto rice bran

	K^0	$-\Delta G^\circ$ (kJ mol ⁻¹)	r^2
Cd(II)	3.038	2.75	0.9688
Cu(II)	1.326	0.70	0.9018
Pb(II)	4.293	3.61	0.9767
Zn(II)	1.089	0.21	0.9973

Fig. 3 presents plots comparing the Freundlich isotherm with experimental data. An excellent fit was observed for Cd(II), Cu(II) and Zn(II) for all the concentration range studied. For Pb(II), experimental data fitted well Freundlich equation only for low concentrations (up to 1 mg L⁻¹).

3.4. Thermodynamic parameters

The free energy change of the sorption reaction is given by:

$$\Delta G^\circ = -RT \ln K$$

where ΔG° is standard free energy change, R the universal gas constant (8.314 J mol⁻¹ K⁻¹), T the absolute temperature and K the equilibrium constant. The apparent equilibrium constant of the biosorption, K'_C , is obtained from:

$$K'_C = \frac{C(\text{biosorbent})_{\text{eq}}}{C(\text{solution})_{\text{eq}}}$$

where $C(\text{biosorbent})_{\text{eq}}$ and $C(\text{solution})_{\text{eq}}$ are the metal ion concentrations on the biosorbent and in the solution, at equilibrium. K'_C values calculated at different initial concentrations of metal ion and extrapolated to zero allow to determine the thermodynamic equilibrium constant (K_C^0) and the Gibbs free energy of the biosorption process. The free energy changes for Cd(II), Cu(II), Pb(II) and Zn(II) sorption onto rice bran were determined at 25 ± 1 °C, in NaCl 0.1 mol L⁻¹ and pH 5.0, and are shown in Table 3. The negative values of ΔG° validate the feasibility of the sorption process, and the spontaneity of sorption.

4. Conclusions

Rice bran in natura was evaluated for its potential use as a biosorbent for Cd(II), Cu(II), Pb(II) and Zn(II). This new biosorbent is able to successfully sorb the metal ions from aqueous solutions. Metal–rice bran sorption process were analysed according to Langmuir and Freundlich models. The experimental data were well fitted to the Freundlich equation, with good correlation coefficients. The metal ion binding capacity was dependent on the metal ion. The negative Gibbs free energy values obtained in this study with rice bran con-

firm the feasibility of the process and the spontaneous nature of sorption. This work showed that rice bran in natura can be used as an efficient sorbent for the metal ions evaluated, representing an effective and environmentally clean utilization of waste matter. Studies are been developed to confirm the applicability of this new sorbent under real conditions, such as in the industrial effluent treatment.

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