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Selective Biosorption of Zirconium and Hafnium from Acidic Aqueous Solutions by Rice Bran, Wheat Bran and Platanus Orientalis Tree Leaves

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Abstract: The Zr(IV) and Hf(IV) biosorption characteristics of rice bran, wheat bran and Platanus orientalis tree leaves were examined as a function of initial pH, contact time, temperature, and initial metal ions concentration. Adsorption equilibriums were achieved in about 1, 5 and 40 min for rice bran, wheat bran, and leaves respectively. The biosorption behavior of leaves was significantly affected by solution pH whereas rice bran and wheat bran adsorption efficiencies were slightly affected by solution pH. The Freundlich and Langmuir adsorption equations, which are commonly used to describe sorption equilibrium for metals removal by biomasses, were use to represent the experimental and equilibrium data fitted well to the Langmuir isotherm model. The negative Gibbs free energy values obtained in this study with rice bran wheat bran and Platanus orientalis tree leaves confirmed the feasibility of the process and the spontaneous nature of sorption. In the optimum conditions, the adsorption efficiencies of other metal ions such as Fe^{3+}, Cu^{2+}, Pb^{2+}, Hg^{2+}, La^{3+}, Ce^{3+} were significantly lower than Zr(IV) and Hf(IV) ions and these biomasses are excellent sorbents for the selective uptake of proposed ions from acidic aqueous solutions.

Keywords: Biosorption, zirconium, hafnium, rice bran, wheat bran, Platanus orientalis tree leaves

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INTRODUCTION

Zirconium and hafnium co-exist in nature, but they have opposite nuclear characteristics. Zirconium is used in the nuclear industry as a fuel rods cladding, in metal alloys, as catalyst in organic reactions, in manufacture of water repellent textiles, in dyes pigment and ceramics. Hafnium is used for alloying with iron, titanium, aluminum and other metals. This metal is used for nuclear control rods and is an efficient "getter" for scavenging oxygen and nitrogen (1, 2).

Physico-chemical methods, such as chemical precipitation, chemical oxidation or reduction, electrochemical treatment, evaporative recovery, filtration, ion exchange and membrane technologies have been widely used to remove heavy metal ions from industrial waste water. These processes may be ineffective or expensive, especially when the heavy metal ions are in solutions containing in the order of 1–100 mg dissolved heavy metal ions L^{-1} (3, 4). Therefore, the need of alternative low-cost sorbents has encouraged the search for new and cheap sorption processes for aqueous effluent treatment, as these materials could reduce significantly the waste water-treatment cost. With the increase in environmental awareness and governmental policies there has also been an emphasis on the development of new environmentally friendly ways to decontaminate waters using low-cost methods and materials. 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 (5).

The bioadsorption of metals to the biomass surface occurs mainly as a result of either physical binding involving London–Vander Waals forces and electrostatic attraction, or by chemical binding such as ionic or covalent binding between the adsorbent and the adsorbate (6–9) Studies have shown that the biosorption mechanisms depend on the type of functional groups on the surface of the biomass, the nature of the metal, and the characteristics of the matrix around the biosorbent species (10–13). However, the exact adsorption mechanism is not well understood yet.

Extensive investigations have been carried out to identify suitable and relatively cheap biosorbents that are capable of removing significant quantities of metal ions. In recent years, agricultural by-products have been widely studied for metal removal from water. These include peat, wood, pine bark, banana pith, soybean and cottonseed hulls, peanut shells, hazelnut shell, rice husk, sawdust, wool, orange peel, and compost and leaves (14).

Equilibrium studies that give the capacity of the adsorbent and the equilibrium relationships between adsorbent and adsorbate are described by adsorption isotherms which are usually the ratio between the quantity adsorbed and the remaining in solution at fixed temperature at equilibrium. Freundlich and Langmuir isotherms are the earliest and simplest known relationships describing the adsorption equation. In our previous works (15, 16) we had reported removal of Cd^{2+}, Hg^{2+}, Cr^{3+}, Pb^{2+}, Ni^{2+}, Cu^{2+}, and Fe^{3+} from water and waste water samples by wheat and rice bran. In this paper, three biosorbents (rice bran, wheat bran and Platanus orientalis tree leaves) were applied to remove Zr(IV) and Hf(IV) ions from aqueous media. It was found that these biomasses are excellent sorbents for the studied ions and have some preferences over other methods.

EXPERIMENTAL

Reagents

All reagents were pro-analysis grade and purchased from Merck Company. Stock solutions of 1000 $\mu g\ mL^{-1}$ zirconium and hafnium were prepared by dissolving the appropriate amounts of $ZrOCl_2 \cdot 8H_2O$ and $HfOCl_2 \cdot 8H_2O$ (Merck) in 1000 mL of 0.1 M hydrochloric acid. The raw rice bran and wheat bran used as biosorbent were taken at local micro industry of rice and wheat processing. The species of rice and wheat were O. sativa and T. aestivum respectively. The rice bran, wheat bran and Platanus orientalis tree leaves were dried in the oven at 100°C for 24 h and then ground and sieved to obtained uniform material (100 μm) for sorption tests.

Apparatus

Absorbance values were measured with a Varian model Liberty 150 AX ICP-AES. A Metrohm model 744 digital pH meter equipped with a combined glass-calomel electrode was used for pH adjustment.

Procedure

Batch experiments were performed at room temperature (25 ± 1°C), using 50 mL capped tubes. Desired pH of 10 mL cation solution containing exactly known concentration was adjusted by sodium hydroxide or hydrochloric acid then a known amount of adsorbent (50 mg) added to it. After known stirring time at 200 rpm, the adsorbent was filtered and washed with distilled water until filtrate reached 20 mL. In the following, the absorbance of this solution was recorded by ICP-AES.

RESULTS AND DISCUSSION

Selection of the optimum conditions

The adsorbed cations in percent as a function of particle size was studied. The obtained results showed that particle size of the studied biosorbents is not effective on the adsorption of cations.

The pH of solution plays an essential role in determination of different species occurring in solution. Cations are found in the form of cationic, hydroxide complexes (cationic or anionic) and hydroxide precipitate based on the pH of the solution. The effect of hydrogen ion concentration on sorption efficiency of zirconium and hafnium was examined from solutions at pH ranging from −0.3 to 4. Higher pH values (>4) were not tested because of the possibility of the precipitation of Zr(IV) and Hf(IV) in the solution. In Fig. 1, percentage adsorbed cotions is plotted as a function of pH rang. As it is observed, rice bran and wheat bran adsorption efficiencies were slightly affected by varying pH rang and these biosorbent are able to adsorb zirconium and hafnium even in the strong acidic solutions. But about Platanus orientalis tree leaves, their adsorption efficiency was decreased with decreasing of pH, because the overall surface charge on the particles becomes positive and binds the approach of positively charged metal cations. The description above agrees with other studies on other similar adsorbents (17). The maximum adsorption Zr(IV) and Hf(IV) by Platanus orientalis tree leaves occurs in the pH 3. Also obtained data indicate that percentage adsorbed of the Zr(IV) and Hf(IV) ions are almost equal due to similar chemical properties of Zr(IV) and Hf(IV).

In industrial waste water treatment, one of the most important parameters to increase the sorption process rate of synthetic adsorbents is using chemicals treatments that increase environmental pollution and the disposal costs. As a consequence it has caused researchers to study new low cost adsorbents to substitute these cheap adsorbents instead of high cost sorbents. Recently studies have been done on biosorbents and have received relatively good results because these natural materials can be used either directly or after a simple cheap activation treatment (18–20). In comparison with synthetic ion exchanger, some biomasses have good sorption efficiency and quickly remove heavy metals from aqueous solutions (15). As seen in Fig. 2, adsorption rates are relatively fast and distribution equilibriums between the aqueous solution and biosorbents are established in less than 1 and 5 min for rice and wheat bran respectively, except Platanus orientalis tree leaves (40 min). Therefore, in further studies, to be sure from establishing equilibrium

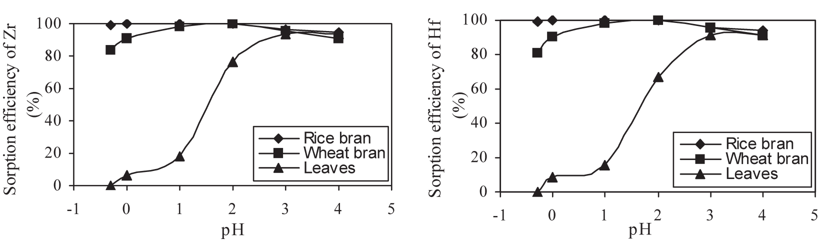

Figure 1. Effect of pH on the zirconium and hafnium sorption onto adsorbents. Contact time, 60 min; *m* (adsorbent), 50 mg; C (metal ions), 50 mg L^{-1}.

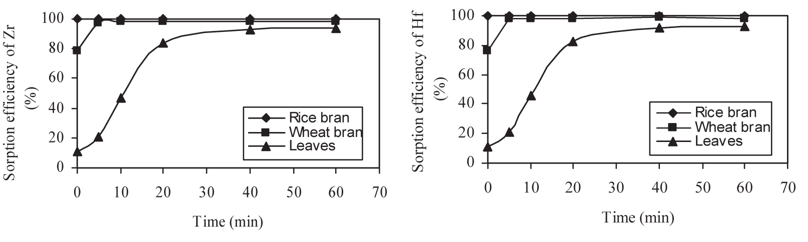

Figure 2. Time dependence of zirconium and hafnium sorption onto adsorbent. pH 1.0 for rice and wheat bran; pH 3.0 for leaf; m(adsorbent), 50 mg; C(metal ions), 50 mg L^{-1}.

between solution and sorbents, the contact time was selected to be 5 min for rice and wheat brans and maintained at 40 min for leaves.

The effect of temperature on the biosorption of zirconium and hafnium onto the rice bran, wheat bran and Platanus orientalis tree leaves was studied between 15 and 45°C (Table 1). It was observed that temperature changes between 15 and 45°C have slight influence on the rate of biosorption.

Sorption Isotherms

The Langmuir and the Freundlich isotherms have been extensively used to investigate the sorption equilibrium between the metal solution and the

Table 1. Effect of temperature on the zirconium and hafnium sorption onto adsorbents

	Percentage adsorbed					
	Rice bran[a]		Wheat bran[b]		Platanus orientalis tree leaves[c]	
Temperature (°C)	Zr	Hf	Zr	Hf	Zr	Hf
15	95.6	94.8	92.6	92.3	82.6	81.8
20	98.9	98.6	95.8	95.4	87.6	86.8
25	99.3	99.4	98.5	99.0	92.0	91.9
30	98.9	99.8	99.5	99.2	93.6	92.1
35	99.1	99.4	99.5	99.6	92.6	91.8
40	99.6	99.6	99.5	99.1	91.6	92.6
45	99.3	99.6	98.9	98.6	92.6	91.5

[a]pH, 1.0; contact time, 5 min; *m* (rice bran), 50 mg; C(metal ions), 50 mg L^{-1}.
[b]pH, 1.0; contact time, 5 min; *m* (wheat bran), 50 mg; C(metal ions), 50 mg L^{-1}.
[c]pH, 3.0; contact time, 40 min; *m* (Platanus orientalis tree leaves), 50 mg; C (metal ions), 50 mg L^{-1}.

solid biomass phase (6–13). The Langmuir model is a non-linear model that suggests a monolayer uptake of the metal on a homogeneous surface, having uniform energies of adsorption for all the binding sites without any interaction between the adsorbed molecules(21, 22). Traditionally, the Langmuir model is represented as:

$$q_e = Q_m K_L C_e/(1 + K_L C_e), \tag{1}$$

where C_e is the equilibrium aqueous metal ions concentration (mg L^{-1}), q_e the amount of metal ions adsorbed per gram of adsorbent at equilibrium (mg g^{-1}), Q_m and K_L are constants related to the maximum adsorption capacity (mg g^{-1}) and the energy of adsorption (L mg^{-1}), respectively. Q_m represents the practical limiting adsorption capacity when the surface is fully covered with sorbed species. The Langmuir constants Q_m and K_L can be determined from the linearized form of Equation (1); the plot of C_e/q_e versus C_e results in a straight line of slope $(Q_m)^{-1}$ and an intercept of $(K_L Q_m)^{-1}$.

$$C_e/q_e = C_e/Q_m + 1/K_L Q_m \tag{2}$$

The Freundlich isotherm is also a non-linear model that assumes a heterogeneous energetic distribution of the active binding sites on the biomass as well as interactions between the adsorbed molecules (21). The Freundlich model considers different affinities for the binding sites on the biomass surface with interactions between the adsorbed molecules. This model also considers that the sites with stronger affinity are occupied first (6). The Freundlich isotherm is expressed using Eq. (3), and this formula is linearized as shown in Eq. (4) as follows:

$$q_e = K_F C_e^{1/n} \tag{3}$$

$$\log q_e = \log K_F + 1/n \log C_e, \tag{4}$$

where K_F indicates the adsorption capacity and $1/n$ is an arbitrary constant related to the adsorption intensity. K_F and n can be determined from the linear plot of log q_e versus log C_e.

The parameters resulted from the Langmuir and Freundlich plots for Zr(VI) and Hf(VI) (Figs. 3, 4, and 5) are presented in Tables 2 and 3. As shown in Tables 2 and 3, for wheat bran, the experimental data well fitted with excellent correlation coefficients to both equations Langmuir and Freundlich. But for rice bran and leaf the correlation coefficients for the Langmuir isotherms ($R^2 > 0.99$) were much better than the Freundlich isotherms $R^2 < 0.94$ and $R^2 < 0.85$ respectively, which suggests that the data fit better to the Langmuir model.

Rice bran showed the greatest adsorption capacity and intensity for zirconium and hafnium among proposed adsorbents (Table 2). The fact that the biosorption data for these metals fit better the Langmuir isotherms suggests that the binding of the two cations occurs as a monolayer on the surface of the biomass.

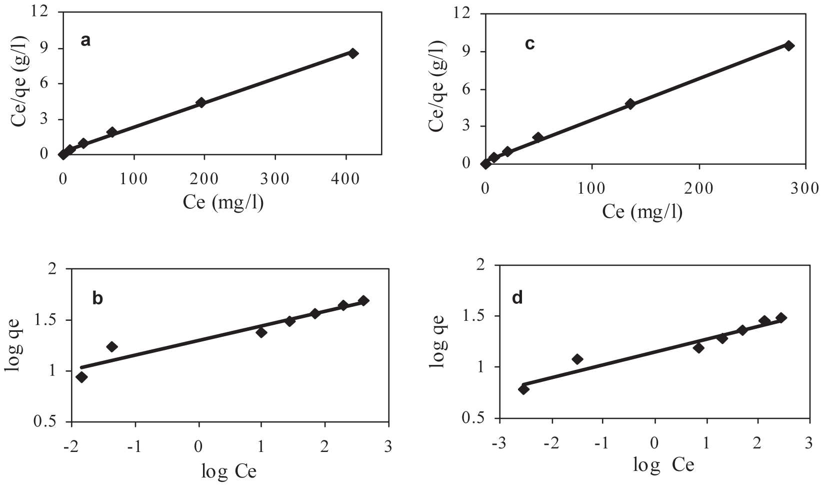

Figure 3. The linearized Langmuir and Freundlich adsorption isotherms of Zr(IV) and Hf(IV) using rice bran. pH, 1.0; contact time, 5 min; *m* (rice bran), 50 mg. (a) Langmuir Zr(IV); (b) Freundlich Zr(IV); (c) Langmuir Hf(IV); (d) Freundlich Hf(IV).

The solubility of a metal is an essential property to enable the metal ion to penetrate into the porous structure of sorbent. Zirconium and hafnium form many hydrolyzed species such as $MO(OH)^-$, $M(OH)_2^{2-}$, $M(OH)_3^-$ and also polymerized species with general form $[M(OH)_x^{4-x}]_n$ in the studied pH

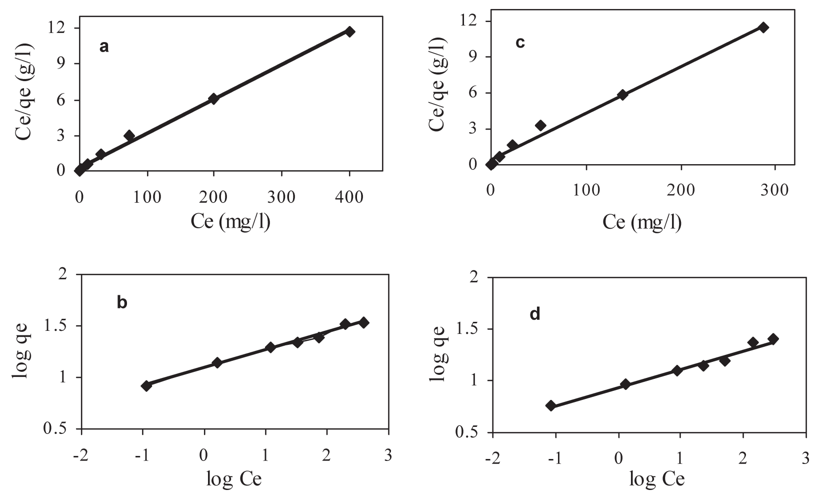

Figure 4. The linearized Langmuir and Freundlich adsorption isotherms of Zr(IV) and Hf(IV) using wheat bran. pH, 1.0; contact time, 5 min; *m* (wheat bran), 50 mg. (a) Langmuir Zr(IV); (b) Freundlich Zr(IV); (c) Langmuir Hf(IV); (d) Freundlich Hf(IV).

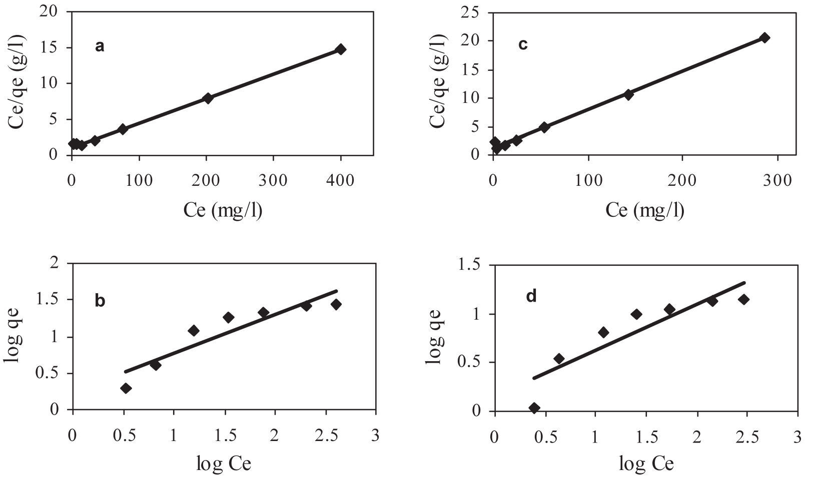

Figure 5. The linearized Langmuir and Freundlich adsorption isotherms of Zr(IV) and Hf(IV) using Platanus orientalis tree leaves. pH, 3.0; contact time, 40 min; *m* (Platanus orientalis tree leaves), 50 mg. (a) Langmuir Zr(IV); (b) Freundlich Zr(IV); (c) Langmuir Hf(IV); (d) Freundlich Hf(IV).

range. All these species can be viewed as potential sorbates in the uptake of zirconium and hafnium from aqueous solution. The data presented in this study suggest that, under considered experimental conditions, the species responsible for the sorption of zirconium and hafnium are the predominant from these complex species that due to difficult penetration into biomass their adsorption occurs on the sorbent surface.

Thermodynamic Parameters

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

$$\Delta G^\circ = -RT \ln K \tag{5}$$

Table 2. Langmuir constants for metal ions removal by biosorbents

	Zr			Hf		
	Q_m	K_L	r^2	Q_m	K_L	r^2
Rice bran	48.30	0.102	0.9967	30.30	0.140	0.9963
Wheat bran	34.72	0.090	0.9955	25.64	0.082	0.9894
Platanus orientalis tree leaves	29.49	0.0302	0.9963	14.74	0.057	0.9966

Table 3. Freundlich constants for metal ions removal by biosorbents

	Zr			Hf		
	K_F	n	r^2	K_F	n	r^2
Rice bran	19.89	6.993	0.9236	14.17	8.077	0.9388
Wheat bran	12.48	5.824	0.9923	8.677	5.600	0.9776
Platanus orientalis tree leaves	1.71	1.891	0.8493	1.436	2.136	0.8029

where G° 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:

$$K_C = C(\text{biosorbent})_{eq}/C(\text{solution})_{eq} \tag{6}$$

where $C(\text{biosorbent})_{eq}$ and $C(\text{solution})_{eq}$ 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) and the Gibbs free energy of the biosorption process (23, 24). The free energy changes for Zr(IV) and Hf(IV) sorption onto rice bran, wheat bran, and Platanus orientalis tree leaves were determined at $25 \pm 1°C$ and are shown in Table 4. The negative values of ΔG° validate the feasibility of the sorption process, and the spontaneity of sorption.

Adsorption Efficiency of Other Metal Ions in Comparison with Zirconium and Hafnium

Adsorption efficiencies of zirconium and hafnium with other metal ions were studied under the optimum conditions by rice bran, wheat bran, and Platanus orientalis tree leaves in concentrations of 2, 20, and 100 mg L^{-1}. The results obtained are summarized in Table 5 and showed that adsorption efficiency of

Table 4. Thermodynamic parameters for metal ions removal by biosorbents

	Zr			Hf		
	K_c	ΔG° ($kJ\ mol^{-1}$)	r^2	K_c	ΔG° ($kJ\ mol^{-1}$)	r^2
Rice bran	9.32	−5.41	0.9957	8.22	−5.10	0.9909
Wheat bran	5.62	−4.18	0.9970	4.71	−3.75	0.9925
Platanus orientalis tree leaves	1.77	−1.38	0.9272	1.71	−1.30	0.9344

Table 5. Comparison of adsorption efficiency of studied cations by the rice bran, wheat bran and Platanus orientalis tree leaves with other metal ions

Metal ion	Percentage absorbed: Rice bran[a]			Wheat bran[b]			Platanus orientalis tree leaves[c]		
Concentration (mg L^{-1})	2	20	100	2	20	100	2	20	100
Zr^{4+}	99.8	100	100	98.3	98.6	98.4	91.6	93.5	93.3
Hf^{4+}	99.9	99.7	99.9	98.1	97.9	98.4	92.1	90.2	91.4
Pb^{2+}	31.6	29.8	30.4	24.3	22.9	23.6	49.8	51.1	52.3
Hg^{2+}	21.1	25.3	24.8	37.8	36.1	37.3	44.3	47.1	46.4
Fe^{3+}	19.9	20.3	20.5	12.8	14.5	15.1	13.9	15.4	16.8
Ni^{2+}	11.5	10.7	11.7	8.3	9.7	9.6	7.6	10.5	9.8
Zn^{2+}	12.7	14.1	14.6	12.4	11.4	11.8	9.9	12.6	13.4
Cd^{2+}	16.5	19.8	19.2	13.2	15.1	14.6	39.3	37.5	38.1
Cr^{3+}	13.6	14.9	15.4	15.3	17.4	17.2	26.7	30.3	30.6
Cu^{2+}	20.1	19.4	18.3	9.1	11.6	10.9	18.6	16.1	17.8
La^{3+}	23.8	24.4	25.6	18.9	21.5	21.3	22.7	25.7	25.2
Ce^{3+}	28.3	27.5	27.9	19.7	18.6	19.4	19.2	25.1	24.9
MoO_4^{2-}	37.3	35.6	35.7	24.5	26.3	27.4	31.3	29.4	30.6

[a]pH, 1.0; contact time, 5 min; *m*(rice bran), 100 mg.
[b]pH, 1.0; contact time, 5 min; *m*(wheat bran), 100 mg.
[c]pH, 3.0; contact time, 40 min; *m*(Platanus orientalis tree leaves), 100 mg.

other metal ions rather than zirconium and hafnium were relatively low, that clearly show the high affinity of these biomasses to the studied cations in comparison with other metal ions. Therefore these biomasses can be used for selective uptake of zirconium and hafnium from aqueous solutions, in presence of other metal ions.

Comparison of the Rice Bran, Wheat Bran, and Platanus Orientalis Tree Leaves Efficiencies in Removal of Cations in Batch and Continuous Cases

In the continuous case, 1.0 g biomass was filled into glass tube (10 cm long and 1 cm i.d.) consists of filter and stop cock. 50 mL analytes solution was passed through it at a flow rate of 0.5 mL min^{-1}. In the batch case, the experiment was carried out as mentioned previously. Table 6 shows the obtained results. Zr(IV) and Hf(IV) absorption by the rice bran and wheat bran is nearly equal in the continuous and batch cases, but in the case of Platanus orientalis tree leaves, adsorption efficiency of the continuous system is

Table 6. Comparison of adsorption efficiency of studied cations by the rice bran, wheat bran and Platanus orientalis tree leaves in batch and continues cases

	Percentage adsorbed					
	Rice bran		Wheat bran		Leaves	
Cations	Batch	Continuous	Batch	Continuous	Batch	Continuous
Zr(VI)	99.8	99.9	99.7	99.9	91.9	78.6
Hf(VI)	99.7	99.7	99.6	99.8	91.4	75.3

lower than the batch system, probably due to lower adsorption rate of leaves rather than rice bran and wheat bran.

CONCLUSION

The potential use of rice bran, wheat bran, and Platanus orientalis tree leaves as sorbents for zirconium and hafnium was studied. The obtained results present that these materials were excellent reagents to adsorption and remove the zirconium and hafnium ions from acidic aqueous solutions especially rice bran. Adsorption rates are very fast and preference over classical ion exchanger. The adsorption capacity for the proposed cations is relatively high and can be applied for their removal in the range of milligram per liter or higher. Metal sorption process was analyzed according to Langmuir and Freundlich models. The experimental data for rice and wheat bran were well fitted to both the Langmuir and the Freundlich equations, with good correlation coefficients (especially wheat bran), but for leaves, the correlation coefficients for fitting the Langmuir equation were significantly better than the coefficients for Freundlich isotherm. These results suggest a monolayer adsorption of these two metals on the outer surface of the biomass. As a result, this technique showed that using of biosorbents to uptake of ions from aqueous media is suitable and can be used efficiently instead of current techniques, also representing an effective and environmentally clean utilization of waste matter.

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