

BIOSORPTION KINETICS OF Cd (II), Cr (III) AND Pb (II) IN AQUEOUS SOLUTIONS BY OLIVE STONE

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Abstract - A by-product from olive oil production, olive stone, was investigated for the removal of Cd (II), Cr (III) and Pb (II) from aqueous solutions. The kinetics of biosorption are studied, analyzing the effect of the initial concentration of metal and temperature. Pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion models have been used to represent the kinetics of the process and obtain the main kinetic parameters. The results show that the pseudo-second order model is the one that best describes the biosorption of the three metal ions for all the range of experimental conditions investigated. For the three metal ions, the maximum biosorption capacity and the initial biosorption rate increase when the initial metal concentration rises. However, the kinetic constant decreases when the initial metal concentration increases. The temperature effect on biosorption capacity for Cd (II) and Cr (III) is less significant; however, for Pb (II) the effect of temperature is more important, especially when temperature rises from 25 to 40°C. The biosorption capacity at mmol/g of olive stone changes in the following order: Cr>Cd>Pb. Thus, for an initial concentration of 220 mg/l, a maximum sorption capacity of 0.079 mmol/g for Cr (III), 0.065 mmol/g for Cd (II) and 0.028 mmol/g for Pb (II) has been obtained.

Keywords: Heavy metals; Biosorption; Olive stone; Kinetics; Wastewater.

INTRODUCTION

Several heavy metals, like chromium, manganese, cadmium, cobalt, copper, zinc, molybdenum, vanadium or iron, are involved in catalytic functions relevant to living beings. However, they can be used by the microorganisms at very low concentrations (trace levels) (WHO / FAO / IAEA, 1996), but the necessary balance has been affected by human activity, that has increased significantly the contributions to the natural environment of metal ions. This contribution presents different anthropogenic routes, which include mining and smelting operations (Costa and Leite, 1990; Groenendijk et al., 1998), discharges of urban waste water (Erlinch, 1997), industrial discharges (Kasan and Stegmann, 1987), waste metals handling (Iñarra

et al., 1989) and the use of fertilizers and pesticides (Basiric et al., 1982; Beiger and Jernelöv, 1986).

The contaminated effluent treatment is a process that is sometimes more complicated than any other manufacturing process, because waters can have a very variable composition in terms of organic or inorganic components, extreme acidity or basicity, presence of volatile substances and so on. Therefore, few processes provide clean effluents while fulfilling, at the same time, requirements such as economic costs, flexibility in terms of both the amount of effluent to be treated and the pollutant concentration present, continuity of the system, minimal supervision and maintenance and sufficient selectivity regarding the removal of the metals considered (Vilchez, 2005). In this sense, biosorption has been proposed as one of the most promising

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technologies for the removal of toxic metals from wastewater (Brady et al., 1999; Pagnanelli et al., 2000; Zhou et al., 2005).

The kinetic study of the biosorption process determines the rate at which the contaminants are removed from the aqueous media. In this sense, numerous kinetic models have been proposed that are capable of describing the mechanism through which the biosorption process takes place. This mechanism is, in most cases, complex and can cause chemical reactions between sorbent functional groups and metal ions, ionic interchange reactions and/or formation of complexes; in addition, mass transfer processes such as the transportation of substances in the liquid phase, diffusion from the liquid phase to the surface of the solid and diffusion in the interior of the macropores and micropores must be taken into consideration.

In this paper, the kinetics of biosorption of Cd (II), Cr (III) and Pb (II) using olive stone as solid sorbent are studied, analyzing the effect of the initial concentration of metal and temperature. Pseudo-first-order, pseudo-second-order, Elovich and intraparticle diffusion models have been used to represent the kinetics of the process and obtain the main kinetic parameters.

EXPERIMENTAL

Preparation of Biosorbent

Olive stones were supplied by the orujo oil extraction plant "Cooperativa Nuestra Señora del Castillo" located in Vilches, province of Jaen, Spain.

The olive stones supplied by the plant were milled in the laboratory from an initial size range of 4 mm to a fraction smaller than 1 mm, which is the solid used for the entire test. Previous tests studied the effect of particle size on the biosorption process and determined that the best results were achieved for the fractions between 0.250 and 1.00 mm and that this size range represented over 70% of the total milled stone mass (Blázquez et al., 2005). As a result, it was decided that milled stone would be used straight from the mill with a 1 mm sieve-separator, with no subsequent screening for sorting according to size.

Batch Experiments

The experiments were performed by mixing 0.5 g of olive stone in 50 mL of the synthetic metal ion solutions with a predetermined concentration of metal ion. Three heavy metals (Cd^{2+} , Cr^{3+} and Pb^{2+})

were selected as a modelled metal species. Solutions of these heavy metals were prepared in distilled water using the metal salts $(\text{CH}_3\text{COO})_2\text{Cd}\cdot 2\text{H}_2\text{O}$, $\text{Cr}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ and $\text{Pb}(\text{NO}_3)_2$, respectively.

These solutions were placed in a 100 mL jacketed reactor connected to a thermostat-controlled bath, the pH of the solution was adjusted with 0.1M HCl or 0.1M NaOH solutions and the temperature set at the desired value.

Once the operation time had elapsed, the liquid phase was taken out of the reactor and centrifuged for 10 min; then the supernatant solution was filtered and analysed for metal concentrations by a flame atomic absorption (AA) spectrophotometer (Perkin Elmer Model 3100). The amount of metal ions sorbed at equilibrium per unit mass of biosorbent was determined according to the following equation:

$$q_t = \frac{(C_i - C_e)}{m} \cdot V \quad (1)$$

where q_t is the metal uptake at equilibrium, expressed as mg metal/g of the biosorbent, V , the liquid volume, in ℓ , C_i , the initial concentration of metal in the solution, in mg/ ℓ , C_e , the equilibrium concentration of the metal in the solution, in mg/ ℓ , and m the amount of the biosorbent sample on a dry basis, in g.

Each experiment was carried out at least twice to check reproducibility of the results and biomass-free blanks were used as control.

RESULTS AND DISCUSSION

To study the kinetics of biosorption of Cd (II), Cr (III) and Pb (II) by olive stone as a solid sorbent, four of the main models proposed in the literature have been selected for the adjustment of the experimental results obtained and to determine the kinetic parameters.

Pseudo-First Order Model

The pseudo-first order equation (Lagergren, 1898), is generally expressed as follows:

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad (2)$$

where q_e and q_t are the sorption capacity at equilibrium and at any time, t , respectively, in mg/g, and k_1 is the pseudo-first order rate constant, in min^{-1} .

By integrating this expression between the limits $t = 0, q_t = 0$ and $t = t, q_t = q_t$, the following equation is obtained:

$$\log\left(\frac{q_e - q_t}{q_e}\right) = -\frac{k_1}{2.303} t \quad (3)$$

By plotting the value of $\log((q_e - q_t)/q_e)$ versus t , the value of the rate constant k_1 can be obtained from the slope.

Pseudo-Second Order Model

Pseudo-second order kinetics can be expressed through the following equation (Ho and McKay, 2000),

$$\frac{dq_t}{dt} = k_{s2} (q_e - q_t)^2 \quad (4)$$

where k_{s2} is the pseudo-second order rate constant, in g/mg·min.

By integrating this equation between the limits $t = 0, q_t = 0$ y $t = t, q_t = q_t$, the following equation is obtained:

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (5)$$

where $h = k_{s2} \cdot q_e^2$ is the initial sorption rate, in mg/g·min

By plotting t/q_t versus t , the values of q_e and k_{s2} can be obtained from the slope and the intercept, respectively.

Elovich Model

The Elovich equation has been used for describing reactions involving chemisorption of gases on a solid surface, but also for simulating sorption kinetics in a liquid phase. The Elovich equation can be written as (Günay et al., 2007):

$$\frac{dq_t}{dt} = a \exp(-b q_t) \quad (6)$$

where a and b are the model parameters. The parameter a is the initial adsorption rate, in mg/g·min, and the parameter b is related to the occupied surface, in g/mg.

To simplify the Elovich equation, Chien and Clayton (1980) assumed that $a \cdot b \cdot t \gg t$ and, given

that for $t = 0, q_t = 0$ and for $t = t, q_t = q_t$, the final form of the equation is:

$$q_t = \frac{1}{b} \ln(a b) + \frac{1}{b} \ln(t) \quad (7)$$

By plotting q_t versus $\ln(t)$, the values of the parameters can be obtained.

Intraparticle Diffusion Model

The intraparticle diffusion equation can be expressed as (Weber and Morris, 1963),

$$R = K_{id} t^a \quad (8)$$

where R is the percent of metal biosorbed, t is the contact time, in min, a is an dimensionless constant and K_{id} is the intraparticle diffusion rate constant, in min^{-a} .

This expression can be converted into another one that determines the value of the biosorption capacity at any time t (amount of metal ion sorbed at time t), q_t , because the percent of metal removed, R , and q_t can be related by the corresponding expressions for q_t and R . Then, the values of the biosorption capacity at any time t, q_t , are obtained from Equation 1 and the percent of metal removed, R , from the following equation:

$$R = \frac{(C_i - C_f)}{C_i} \cdot 100 \quad (9)$$

C_i and C_f being the initial and final metal concentrations, respectively, in mg/ℓ, V the solution volume, in ℓ, and m the amount of biosorbent, in g.

In this manner, the percent of metal biosorbed, R , can be expressed as a function of the biosorption capacity at any time t, q_t , by the following equation:

$$R = \frac{q_t m 100}{C_i V} \quad (10)$$

Considering this equation, the intraparticle diffusion model can be written as:

$$q_t = \frac{C_i V}{m 100} K_{id} t^a = K'_{id} t^a \quad (11)$$

where q_t is the biosorption capacity at any time t , in mg/g, t is the contact time, in min, a is a

dimensionless constant and K'_{id} is the new intraparticle diffusion rate constant, in $\text{mg/g}\cdot\text{min}^{-a}$

By plotting $\ln(q_t)$ versus $\ln(t)$, the values of a and K'_{id} can be obtained from the slope and the intercept, respectively.

In this work, the influence of initial metal concentration and temperature on the kinetics of cadmium, chromium and lead biosorption using olive stone as sorbent was studied. For this, experimental tests were carried out varying the initial metal concentration from 10 to 220 mg/l (keeping the temperature constant at 25°C) and changing the

temperature from 25 to 60°C (at an initial metal concentration of 10 mg/l). In Figures 1, 2 and 3 the biosorption capacity values, q_t , versus time, t , are shown for cadmium, chromium and lead, respectively.

The results were fitted by linear regression to the four kinetic models chosen: pseudo-first order, pseudo-second order, Elovich and intraparticle diffusion. Tables 1, 2 and 3 report the parameter values obtained from the application of the kinetic models for cadmium, chromium and lead ions, respectively.

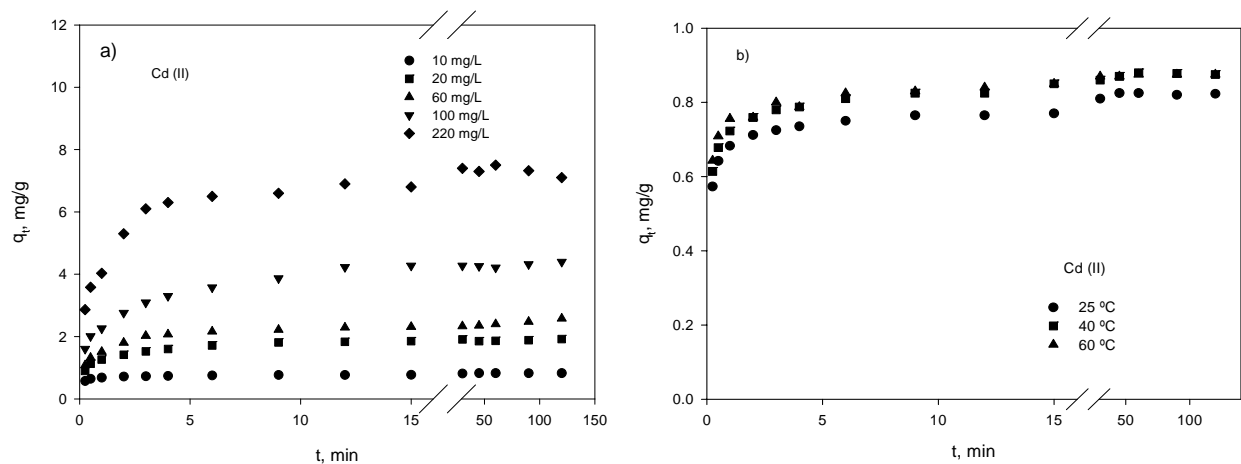


Figure 1: Biosorption capacity of olive stone for Cd (II) versus operation time: a) different initial metal concentrations; b) different temperatures.

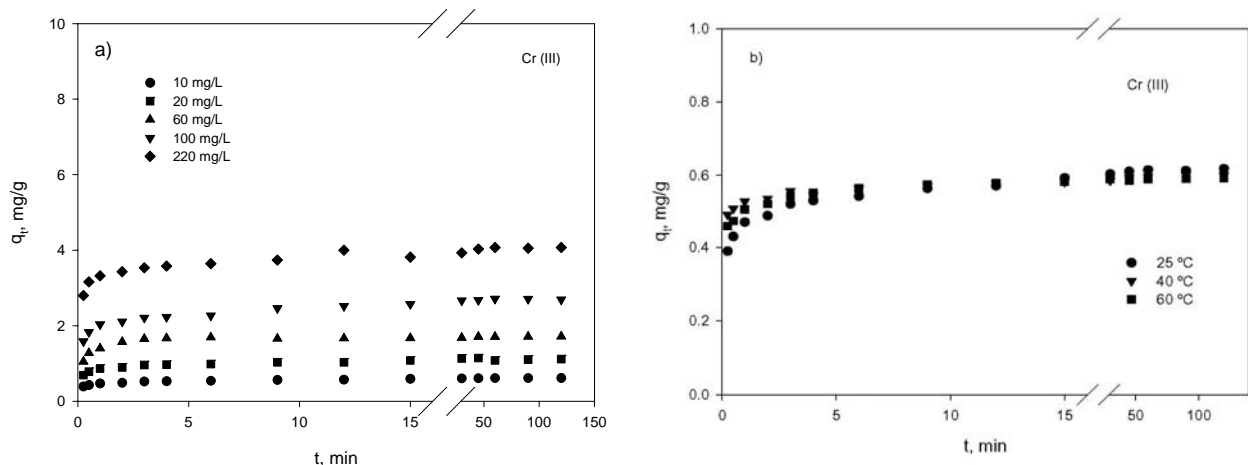


Figure 2: Biosorption capacity of olive stone for Cr (III) versus operation time: a) different initial metal concentrations; b) different temperatures.

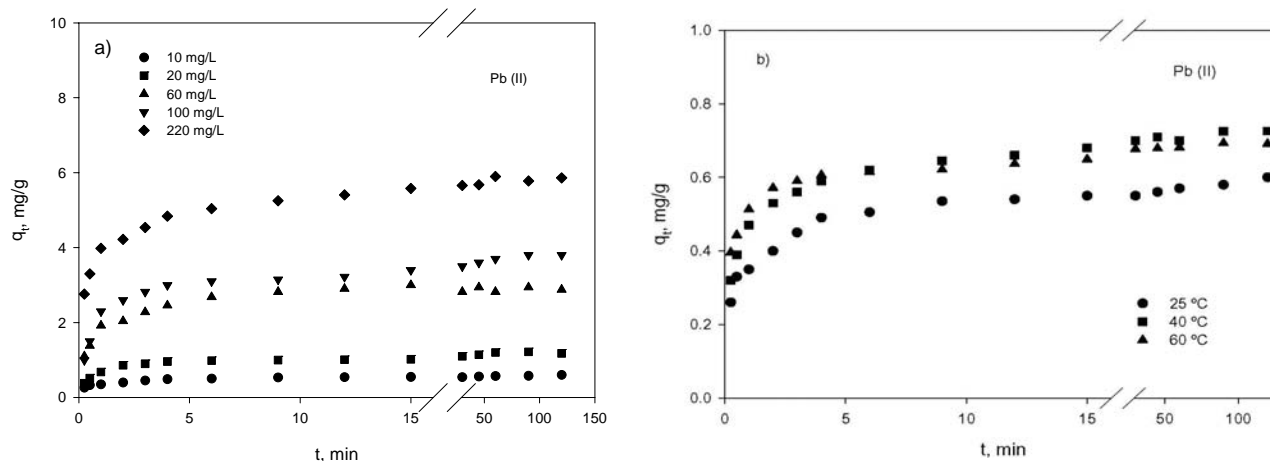


Figure 3: Biosorption capacity of olive stone for Pb (II) versus operation time: a) different initial metal concentrations; b) different temperatures.

Table 1: Parameters values of the kinetic models for the biosorption of Cd (II) by olive stone

		[Cd] _{initial} , mg/l					Temperature, °C		
		10	20	60	100	220	25	40	60
Pseudo-first order	k_1 , min ⁻¹	0.0797	0.158	0.109	0.117	0.116	0.0797	0.0656	0.0853
	r^2	0.901	0.954	0.836	0.831	0.908	0.901	0.872	0.894
Pseudo-second order	k_{s2} , g/mg·min	2.604	0.833	0.474	0.219	0.130	2.604	2.854	3.549
	q_e , mg/g (SD)	0.826 (0.002)	1.910 (0.007)	2.52 (0.03)	4.40 (0.02)	7.33 (0.06)	0.826 (0.002)	0.880 (0.002)	0.878 (0.001)
	q_e , mmol/g	0.0074	0.017	0.022	0.039	0.065	0.0074	0.0078	0.0078
	h , mg/g·min	1.778	3.041	3.020	4.240	6.991	1.778	2.208	2.734
	r^2	0.999	0.999	0.998	0.999	0.999	0.999	0.999	0.999
	Elovich	a , mg/g·min	$19.8 \cdot 10^3$	564.7	284.2	93.19	403.3	$19.8 \cdot 10^3$	$20.4 \cdot 10^3$
b , g/mg		26.51	6.277	4.467	2.097	1.371	26.51	24.71	28.59
r^2		0.941	0.878	0.910	0.906	0.860	0.941	0.929	0.911
Intraparticle diffusion	K'_{id} , mg/g·min ^{-a}	0.668	1.270	1.555	2.416	4.403	0.668	0.715	0.737
	a	0.0526	0.110	0.124	0.159	0.141	0.0526	0.0529	0.0449
	r^2	0.914	0.835	0.853	0.870	0.807	0.914	0.903	0.888

Table 2: Parameters values of the kinetic models for the biosorption of Cr (III) by olive stone

		[Cr] _{initial} , mg/l				Temperature, °C			
		10	20	60	100	220	25	40	60
Pseudo-first order	k_1 , min ⁻¹	0.0870	0.114	0.0709	0.0766	0.0649	0.0870	0.0650	0.710
	r^2	0.946	0.969	0.855	0.916	0.850	0.946	0.847	0.754
Pseudo-second order	k_{s2} , g/mg·min	2.724	2.010	1.077	0.760	0.481	2.724	4.787	6.529
	q_e , mg/g (SD)	0.619 (0.001)	1.116 (0.006)	1.722 (0.002)	2.712 (0.007)	4.08 (0.01)	0.619 (0.001)	0.601 (0.001)	0.5930 (0.0006)
	q_e , mmol/g	0.012	0.022	0.033	0.052	0.079	0.012	0.012	0.011
	h , mg/g·min	1.044	2.504	3.195	5.589	8.020	1.044	1.730	2.296
	r^2	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999
	Elovich	a , mg/g·min	$11.2 \cdot 10^3$	$19.9 \cdot 10^3$	$11.4 \cdot 10^3$	$10.1 \cdot 10^3$	$41.9 \cdot 10^3$	$11.2 \cdot 10^3$	$15.7 \cdot 10^{10}$
b , g/mg		26.97	14.77	11.63	5.520	5.151	26.97	56.65	45.75
r^2		0.950	0.909	0.695	0.949	0.933	0.950	0.960	0.893
Intraparticle diffusion	K'_{id} , mg/g·min ^{-a}	0.465	0.846	1.390	1.965	3.267	0.465	0.526	0.507
	a	0.0720	0.0727	0.0604	0.0819	0.0550	0.0720	0.0320	0.0410
	r^2	0.927	0.885	0.662	0.923	0.912	0.927	0.951	0.879

Table 3: Parameters values of the kinetic models for the biosorption of Pb (II) by olive stone

		[Pb] _{initial} , mg/l				Temperature, °C			
		10	20	60	100	220	25	40	60
Pseudo-first order	k_1 , min ⁻¹	0.126	0.220	0.242	0.214	0.139	0.126	0.054	0.087
	r^2	0.895	0.864	0.892	0.850	0.894	0.895	0.885	0.910
Pseudo-second order	k_{s2} , g/mg-min	1.217	0.611	0.176	0.149	0.120	1.217	1.476	2.176
	q_e , mg/g	0.596	1.21	2.97	3.89	5.93	0.596	0.728	0.694
	(SD)	(0.005)	(0.01)	(0.02)	(0.03)	(0.02)	(0.005)	(0.003)	(0.002)
	q_e , mmol/g	0.0029	0.0058	0.014	0.019	0.028	0.0029	0.0035	0.0035
	h , mg/g-min	0.432	0.888	1.551	2.257	4.214	0.432	0.783	1.048
	r^2	0.999	0.999	0.999	0.999	0.999	0.999	0.999	0.999
Elovich	a , mg/g-min	69.6	29.9	190.7	62.5	1272.3	69.6	97.2	3181.3
	b , g/mg	19.11	7.984	3.469	2.380	2.013	19.11	15.59	21.87
	r^2	0.915	0.921	0.819	0.916	0.926	0.915	0.927	0.913
Intraparticle diffusion	K'_{id} , mg/g-min ^{-a}	0.367	0.652	1.779	2.193	3.818	0.367	0.458	0.504
	a	0.122	0.159	0.141	0.134	0.113	0.122	0.120	0.0823
	r^2	0.870	0.830	0.771	0.828	0.878	0.870	0.871	0.868

As can be observed, the pseudo-second order model is the one that best describes the biosorption of the three metal ions for all the range of experimental conditions investigated. For Cd (II) (Table 1), as the initial metal concentration rises, the maximum biosorption capacity, q_e , and the initial biosorption rate, h , increase, changing from 0.826 to 7.33 mg/g and from 1.778 to 6.991 mg/g-min, respectively. However, the kinetic constant decreases when the initial cadmium concentration is increased. This indicates that, although biosorption increases rapidly with an increase in the initial concentration, the process subsequently proceeds more slowly until equilibrium is reached, as observed in Figure 1. The temperature effect on biosorption capacity is less significant, as can be seen in Figure 1 and in the parameter values of the pseudo-second order model (Table 1), although an increase in the initial sorption rate is produced as temperature rises.

For Cr (III) (Table 2), the results are similar to those obtained for Cd (II), that is, the maximum sorption capacity and the initial sorption rate increase with the initial metal concentration, although the kinetic constant decreases; this indicates a similar behaviour of olive stone in the biosorption of these two metal ions. Likewise, the temperature effect on the biosorption kinetics of chromium is not very important, but an increase of the kinetic constant and the initial sorption rate is produced, especially when the temperature is increased from 25 to 40°C.

For Pb (II) (Table 3), the effect of the initial metal concentration on biosorption kinetics is similar to that obtained for the other two metal ions, that is, an increase is produced in the maximum sorption capacity and the initial sorption rate and a decrease

in the kinetic constant for the range of process variables investigated. However, the effect of temperature is more important, especially when temperature increases from 25 to 40°C, where an increase of the maximum biosorption capacity from 0.596 to 0.728 mg/g is produced. The initial sorption rate and kinetic constant are also increased when temperature is increased.

Table 4 shows the biosorption capacities obtained by other authors using the pseudo-second order kinetic model for the experimental conditions specified in the table, in order to compare the results obtained with olive stone to those of other biosorbents for the three metals studied.

On other hand, if the results obtained for the three metal ions are compared among themselves, it is observed that the biosorption capacity of olive stones (on a molar basis) changes in the following order: Cr>Cd>Pb. In this way, for an initial metal concentration of 220 mg/l, a maximum biosorption capacity of 0.079 mmol/g is obtained when the metal ion is Cr (III), 0.065 mmol/g when it is Cd (II) and 0.028 mmol/g for Pb (II). According to various authors, the amount of metal sorbed should depend on the ionic size, stability of metal ion-biosorbent bonding, nature of the metal ion-biosorbent interaction and the distribution of the reactive groups on the biosorbent. In this sense, molecules having a smaller ionic radius could be more quickly sorbed onto a fixed area of biosorbent. In this work, the smaller ionic radius of Cr (III) (0.69 Å) than Cd (II) (0.97 Å) and Pb (II) (1.20 Å) may be responsible for its higher biosorption by olive stone. These results agree with the finding of others researchers (Tobin et al., 1984; Chong and Volesky, 1996; Pradhan and Rai, 2001; Ansari and Malik 2007).

Table 4: Comparison of biosorption capacity of olive stone with that of different biomasses (pseudo-second order kinetic model)

Metal	Initial concentration, mg/L	Biosorbent	q _e mg/g	T, °C	Reference
Cadmium	25	<i>Ulmus carpinifolia</i>	2.32	25	Sangi et al. (2008)
	100	<i>Oedogonium</i> sp.	63.29	25	Gupta and Rastogi (2008)
	500	<i>Spirulina platensis</i>	51.14	25	Seker et al. (2008)
	141	Protonated lemon peels	62.49	50	Schiewer and Patil (2008)
	220	Olive stone	5.08	25	In this work
Chromium	25	<i>Parmelina tiliaceae</i>	0.98	20	Uluzozlu et al. (2008)
			0.96	30	
			0.95	40	
	-	Sawdust	3.34	25	Li et al. (2007)
	-	Modified peanut husk	3.02	25	
	25	Mangrove leaves	1.15	30	Elangovan et al. (2008)
	25	Reed mat	1.57	30	
	100	Gelidium	11.9	20	Vilar et al. (2007)
	97	Agar extraction algal waste	8.3	20	
220	Olive stone	4.08	25	In this work	
Lead	50	<i>Ulmus carpinifolia</i>	4.83	25	Sangi et al. (2008)
	500	<i>Spirulina platensis</i>	98.62	25	Seker et al. (2008)
	-	Sawdust	98.62	50	
	-	Modified peanut husk	4.59	25	Li et al. (2007)
	-	<i>Syzygium comini</i> L.	4.66	25	
			5.32	30	King et al. (2007)
			0.24	20	
	20	Lichen (<i>Cladonia furcata</i>)	0.12	30	Sari et al. (2007)
			0.06	40	
			1.02	20	Uluzozlu et al. (2008)
	25	<i>Parmelina tiliaceae</i>	0.99	30	
		0.95	40		
	220	Olive stone	5.88	25	In this work

The activation energy for metal ion biosorption was calculated from the pseudo-second order constants by the Arrhenius equation. Its linear form is:

$$\ln k = \ln A_0 - \frac{E_a}{RT} \quad (12)$$

where A_0 is the temperature independent Arrhenius constant, E_a is the activation energy, in kJ/mol, R is the gas constant, $8.314 \cdot 10^{-3}$ kJ/mol·K and T is the temperature, in K. The activation energy values calculated for Cd (II), Cr (III) and Pb (II) were 7.37, 20.38 and 13.80 kJ/mol, respectively, and the correlation coefficients were good, higher than 0.95. The low activation energy values suggest that the strength involved in the metal ion and solid surface interaction is physical. These results are similar to those found by other researchers; thus, Han et al. (2006) reported an $E_a = 2.10$ kJ/mol for the biosorption of Pb (II) by manganese oxide coated sand; Vilar et al. (2005) studied the biosorption of Pb (II) by *Gelidium* and found an $E_a = 41.6$ kJ/mol; Lee et al. (1995), studying Cr (III) sorption using moss,

obtained an E_a value of 27.28 kJ/mol; Krishnan and Anirudhan (2003), by studying the removal of Cd (II) from aqueous solutions by steam-activated sulfurised carbon prepared from sugar-cane bagasse pith, obtained an $E_a = 18.28$ kJ/mol.

CONCLUSIONS

The biosorption kinetics of Cd (II), Cr (III) and Pb (II) using olive stone as sorbent is well represented by the pseudo-second order model under all operating conditions tested. For the three metals, the maximum sorption capacity and the initial sorption rate rise as the initial metal concentration increases, while the kinetic constant of the process decreases, indicating that the biosorption occurs faster in its initial phase if the initial metal concentration is increased and then, in a second phase, the biosorption takes place slower until equilibrium is reached.

The effect of temperature on the sorption capacity of cadmium and chromium by olive stone is not very

significant, while for lead an increase in the sorption capacity from 0.596 to 0.728 mg/g is produced when the temperature rises from 25 to 40°C. The kinetic constant and the initial sorption rate increase as the temperature rises for the three metal ions.

The biosorption capacity of olive stone changes in the following order: Cr>Cd>Pb. Thus, for an initial concentration of 220 mg/l, a maximum sorption capacity of 0.079 mmol/g for Cr (III), 0.065 mmol/g for Cd (II) and 0.028 mmol/g for Pb (II) has been obtained.

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