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Study of kinetics in the biosorption of lead onto native and chemically treated olive stone

G. Blázquez *, M. Calero [1], A. Ronda [1], G. Tenorio [1], M.A. Martín-Lara [2]

Department of Chemical Engineering, University of Granada, 18071 Granada, Spain

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ABSTRACT

In this research, olive stone was used as precursor for the development of new biosorbents for lead ions. Chemical treatments were analyzed in terms of their effects on physical–chemical properties and kinetics of lead removal. A kinetic study of the biosorption of lead ions by olive stone was analyzed according to six different kinetic models (pseudo first, pseudo second, pseudo *n*-order, Elovich, solid diffusion and double exponential models). The biosorption kinetic data were successfully described with pseudo-*n*th order and double exponential models for all biosorbents. The double exponential model allowed estimating the values of external and internal mass transfer coefficients. The values of external mass transfer coefficient (k_e) ranged from 42.62×10^{-6} to 508.3×10^{-6} m min^{-1} and the internal mass transfer coefficient (k_i) from 3.76×10^{-6} to 73.4×10^{-6} m min^{-1}. On the other hand, the analysis of experimental data showed that chemical treatments of the biomass led to increase biosorption capacity of the native biomass.

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1. Introduction

Reclamation of metal-contaminated waters requires tertiary refinement treatments by activated carbons and synthetic resins in order to fulfill ongoing strict regulations. Both these materials can ensure the complete removal of pollutants, but with huge costs. In particular, activated carbon preparation is a highly energy consuming process, in which carbon-containing materials (wood, nut shells, fruit stones, peat, charcoal, brown coal, lignite, bituminous coal, mineral oil products, and other waste materials) are generally pyrolyzed (400–800 °C), and then activated (by gasification in oxidizing atmosphere at 800–1000 °C) to increase specific surface area and porosity [1]. In this scenario, researchers have suggested that biosorption is an emerging, competitive, effective and inexpensive technology which reduces the concentration of heavy metal ions to acceptable levels, especially for the treatment of low-concentration effluents [2,3]. The biosorption process involves a solid phase (sorbent or biosorbent; biological material) and a liquid phase (solvent, normally water) containing a dissolved species to be sorbed (sorbate, heavy metals). For this purpose, many kinds of vegetable wastes have been investigated. Table 1 shows the biosorption efficiency of these new biosorbents and activated carbon.

In particular, olive stone may constitute promising low-cost biosorbent among biomaterials, since this material is produced in great quantities in the Mediterranean area, and is of no market value. The stone has very good properties as a fuel for heating, even for domestic installations. In addition to the use as fuel, stones are also used as abrasive material for cleaning walls, for example, in the manufacturing of furfural, and for the manufacturing of active carbon for the treatment of gases, water or other special applications. But also, olive stone was investigated both as biosorbent [14,24–30] and as raw material for activated carbon production [31–35].

Although these research activities have shown that olive stone is an effective biosorbent for the removal of Cd, Cr, Cu and Pb ions in aqueous solutions, a pretreatment with acids or alkali could improve its natural sorption capacity. Strong acids like H_2SO_4 or HNO_3 can protonate unavailable functional groups contained in the structure of biosorbents. Furthermore, these acids can also transform functional groups mostly to carboxylic groups by oxidation. On the other hand, formation of carboxylate moieties from esters is carried out by NaOH treatment [36,37].

The scope of this work is to study the potential of untreated and chemically modified olive stone as biosorbents of Pb(II). New, low cost and ecofriendly biosorbents from olive stone have been developed and the kinetics of lead ions biosorption onto them has been elucidated.

* Corresponding author. Tel.: +34 958 240770; fax: +34 958 248992.
E-mail addresses: gblazque@ugr.es (G. Blázquez), mcaleroh@ugr.es (M. Calero), alirg@correo.ugr.es (A. Ronda), gtenorio@feugr.ugr.es (G. Tenorio), marianml@ugr.es (M.A. Martín-Lara).
[1] Tel.: +34 958 243311; fax: +34 958 248992.
[2] Tel.: +34 958 240445; fax: +34 958 248992.

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Table 1
Biosorption efficiency of new biosorbents and activated carbon.

Biosorbent	Metal	Biosorption capacity ($mg\,g^{-1}$)	Reference
Agave bagasse	Pb	35.10	Velazquez-Jimenez et al. [4]
Appel residues	Pb	8.30	Chong et al. [5]
Banana peels	Cu	8.24	Liu et al. [6]
Coffe wastes	Pb	19.50	Boonamnuayvitaya et al. [7]
Grape stalks	Cu	10.12	Villaescusa et al. [8]
	Ni	10.67	
Marine algae	Ni	56.58	Yalçin and Sezer [9]
	Cd	114.38	
	Pb	228.6	
Neem sawdust	Cr(VI)	25.51	Vinodhini and Das [10]
Olive stone	Cr(VI)	3.20	Martín-Lara et al. [11]
	Cr(III)	5.19	Blázquez et al. [12]
	Cu	1.97	Blazquez et al. [13]
	Pb	17.7	Martín-Lara et al. [14]
Orange peel	Cd	41.58	Pérez Marín et al. [15]
	Zn	32.04	
	Cr(III)	40.55	
Copolymerization orange peel	Pb	476.1	Feng et al. [16]
	Cd	293.3	
	Ni	162.6	
Preteated orange peel with formaldehyde	Cr(III)	7.59	Lugo-Lugo et al. [17]
	Fe	17.36	
Paper mill waste	Ni	13.7	Suryan and Ahluwalia [18]
	Cu	13.9	
	Pb	14.1	
	Cd	14.8	
Rice bran	Cd	1.10	Montanher et al. [19]
	Cu	0.52	
	Pb	4.55	
	Zn	0.13	
Walnut shell	Cr(VI)	8.01	Almasi et al. [20]
Peanut shell carbon	Pb	195.38	Wilson et al. [21]
Commercial carbon (NORIT GRAN)		139.03	
Commercial carbon (MINOTAUR)		248.69	
Activated carbon (DARACO 20–40)	Pb	13.33	Sulaymon et al. [22]
	Cu	5.85	
	Cr(III)	2.79	
Activated carbon from olive cake	Cd	21	Aljundi and Jarrah [23]

2. Materials and methods

2.1. Biosorbent material

Olive stone (OS) was provided by an oil extraction plant "Cooperativa Nuestra Señora del Castillo" located in Vilches, province of Jaen (Spain). The stones were obtained from the separation process of the olive cake with an industrial pitting machine. Once in the laboratory, air-dried at room temperature to equilibrium moisture content, milled using a laboratory hammer mill (IKA MF-10) to a particle size smaller than 1 mm, homogenized and stored until used.

2.2. Pretreatment of OS

OS was chemically treated in order to transform this biomass into new forms by soaking and shaking it in a 2 M H_2SO_4, HNO_3 or NaOH (Merck p.a.) solutions in a rotary shaker for 24 h, at 50 °C and at a biomass concentration of 10 g L^{-1}. Afterwards, the material was rinsed thoroughly with deionised water until neutral pH was attained. Following filtration, treated biomass was dried in an oven at 40 °C during 24 h.

2.3. Preparation of lead solutions

A stock solution of Pb(II) was prepared by dissolving an accurately weighed amount of lead nitrate ($Pb(NO_3)_2$) in distilled water. This reagent was analytical grade and was purchased from Panreac (Barcelona, Spain). All required initial Pb(II) concentrations were obtained by successive dilutions of stock solution with distilled water.

2.4. Biosorption experiments

The experiments were performed using a batch system to determine the biosorption properties of the different biosorbents. First, in order to characterize the optimum biosorption conditions, experiments were performed varying the following experimental parameters: biosorbent dosage (1–10 g L^{-1}), initial Pb(II) concentration (50–250 mg L^{-1}) and pH range (2–5) (data here not reported). From these previous studies, the operation conditions were fixed (biosorbent dosage of 10 g L^{-1}, initial Pb(II) concentration of 150 mg L^{-1} and pH of 5). Then, kinetic tests of Pb^{2+} sorption were performed by mixing 0.5 g of native or modified OS in 50 mL of the synthetic lead ion solutions (150 mg L^{-1}) in a batch reactor furnished with a thermostated jacket to control the temperature and stirred in a shaker for various contact times (0.5, 1, 2, 3, 4, 5, 10, 15, 20, 30, 40, 50, 60, 70, 80, 90 100, 110 and 120 min). The solution pH was adjusted to 5 using 0.1 M HCl or 0.1 M NaOH.

Once the operation time had elapsed, the liquid phase was taken out of the reactor, centrifuged for 10 min, then the supernatant solution was filtered and analyzed for determined lead ion concentrations.

The concentrations of lead ions were determined by a flame atomic absorption (AA) spectrophotometer (Perkin Elmer Model 3100). The biosorption capacity of the biosorbents (q_t, mg g^{-1}) was calculated as follows:

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

where V is the total solution volume (L), C_i and C_f are the initial and final lead concentration, respectively (mg L^{-1}), and m is the amount of OS on a dry basis (g).

2.5. Mathematical models

In order to determine the biosorption kinetics of lead by native and chemically treated OS, six kinetic models were applied to fit experimental data: the pseudo-first-order rate equation (PFORE, also called Lagergren's equation), the pseudo-second-order rate equation (PSORE), the pseudo-nth-order rate equation (PNORE), the Elovich equation (EE), the resistance to intraparticle diffusion equation (RIDE) and the double exponential equation (DEE). Table 2 shows the kinetic models used in this work.

3. Results and discussion

3.1. Characterization of OS

Characterization of a biosorbent is an important analysis for understanding the behavior or the mechanism of lead removal on the surface of biosorbent. Table 3 shows the results obtained in the

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