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Optimization of the use of a biosorbent to remove heavy metals: Regeneration and reuse of exhausted biosorbent

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ABSTRACT

In this paper, the olive tree pruning (OTP) was treated with three chemical agents (H_2SO_4, HNO_3 and NaOH) and the ability of untreated and treated OTP to remove lead ions from aqueous solution was investigated in a packed bed column. The obtained biosorption capacities (q_e) were 39.25, 68.64, 121.39 and 112.01 mg/g for untreated, H_2SO_4, HNO_3 and NaOH treated OTP respectively. Thus, the chemical treatment improved highly the biosorption capacity of OTP. The breakthrough curves and parameters from them were obtained for each biosorbent. It was observed that the biosorption capacity at breakthrough time (q_{eb}) also improved with the treatments, being 5.38, 6.48, 31.56 and 34.42 mg/g for untreated, H_2SO_4, HNO_3 and NaOH treated OTP respectively. This value is the most significant from an operational point of view. In all studied cases the exhausted time was higher than 500 min. Desorption process was studied and HCl 0.3 mol/L was chosen as the optimal eluting agent to regenerate the biosorbent. Then, the treated OTP with better results in the breakthrough curves (NaOH-OTP) was used in several biosorption/desorption cycles. Results indicated that in the first cycle of biosorption an important releasing of Na(I) ions and retaining of Pb(II) ions were occurred (biosorption an ionic change process). However, in other cycles of biosorption this process not appears. Finally, the obtained life factor of the NaOH-OTP (without data of first cycle) was 20 cycles.

1. Introduction

Organic wastes are an important problem nowadays due to the high volumes produced and the requirement to dispose of them safely [1]. Concretely, in Spain, wastes derivate from olive activity are very abundant, as this country is the main olive oil producer in the world, with approximately 13.9 million tons each year produced [2]. Therefore, finding new eco-friendly uses for these organic wastes is specially important. The olive tree pruning is a periodical culture operation by means of which less productive branches are cut off and trees are rejuvenated and this action generates an annual volume of lignocellulosic residues. Therefore, it presents a widely available and renewable resource in the Mediterranean areas for which no industrial applications were yet consistently envisaged. Traditionally, organic waste has been disposed of by incineration or landfill, but recently there has been a tendency to recycle waste and prevent and reduce biogenic waste by adopting a more sustainable waste management program [3,4]. However, the application of untreated agroindustrial wastes as biosorbents can also bring several problems such as low adsorption capacity or high total organic carbon (TOC) release to solution due to liberation of soluble organic compounds contained in these materials. In this sense, different physical methods such as boiling, heating, autoclaving and freeze drying or chemical treatments with strong/weak acids, detergents, alkalis and organic/inorganic chemicals, or a combination of both physical and chemical methods have been employed by various workers [5–9]. In particular, wastes which have been chemically modified before being used as biosorbent to remove heavy metals have significantly improved their properties, mainly their biosorption capacities [10–12].

On the other way, the discharge of large amount of metal-contaminated wastewater from industry is one of the most hazardous problems of the industrial activity. Heavy metals tend to accumulate in the food chain and they have a high solubility in the aquatic environments, therefore living organisms can absorb them. Once they enter the food chain, large concentrations of heavy metals may accumulate in the human body. Inside heavy metal is the lead ions; high levels of this metal can affect brain development in children, resulting in learning disabilities, behavioral problems and language difficulties [13,14]. Additionally, long-term exposure to Pb(II) ions can cause anemia, anorexia, hypertension, convulsions, coma and cancer [15–17]. Therefore, it is necessary to treat metal contaminated wastewater prior to its discharge to the environment [18].

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Nomenclature

C	effluent metal concentration (mg/L)
C_e	equilibrium metal concentration (mg/L)
C_f	desorbed metal concentration (mg/L)
C_i	inlet metal concentration (mg/L)
C_P	peak concentration (mg/L)
C_R	removal metal concentration (mg/L)
CF_P	factor of overall sorption process concentration (mg/L)
k_L	life factor
L	total length of the bed (cm)
LUB	length of bed not used (cm)
n	cycle number
m_{total}	total amount of metal ions sent to the column (mg)
q_e	biosorption capacity (mg/g)
$q_{d,total}$	amount of lead desorbed (mg)
q_{eb}	biosorption capacity at the breakthrough time (mg/g)
q_{ed}	desorption capacity (mg/g)
q_{ex}	biosorption capacity at the exhausted time (mg/g)
q_i	amount of metal remained on biomass after elution step (mg/g)
q_0	initial column uptake (mg/g)
q_{total}	total mass of metal biosorbed (mg)
Q	volumentric flow (mL/min)
t_b	breakthrough time (min)
t_P	time of the peak (min)
t_{total}	total flow time (min)
t^*	stoichiometric time (min)
V_{ef}	volume of effluent (mL)
w	mass of biosorbent (g)

Biosorption is an alternative for both problems (this technology uses an organic waste and removes the heavy metals from wastewater). It is an effective technology widely studied over recent years, because of its wide range of target pollutants, high sorption capacity, excellent performance, ecofriendly nature and low operating cost [19–21]. In recent years, the characterization and application of different agricultural waste from olive cultivar have been studied to use them as biosorbent. Results have showed that these materials present good properties as biosorbent and they are efficient to remove heavy metal ions from aqueous solutions, including Pb(II) [22–26]. On the other hand, some physical and chemical pretreatments have been proposed for improving their properties and for increasing their biosorption capacity [27,28]. Thus, in a previous work [22], different pretreatments were applied to investigate their effect on physic-chemical properties of the OTP. These changes are very important in the behavior of the biosorbent to remove heavy metals, being a relevant aspect to optimize their use as biosorbent.

Finally, the regeneration of these materials to an improved use of this is important to take into account. So, the regeneration of the biosorbent with a minimum amount of residual heavy metal and consequently reusing of biomass are important for cost-effective implementation of the process [29].

The purpose of this research was to optimize the use of OTP as biosorbent of lead from aqueous solutions by successive biosorption–desorption cycles in a fixed-bed column and to compare the behavior between the untreated biosorbent and the treated one. First, various desorption agents were evaluated according to their effectiveness of desorbing Pb(II) from the biomass in batch studies. Then, the breakthrough curves to removal of Pb(II) with untreated and treated OTP were studied and finally, the regeneration of the exhausted biosorbent which presented the best biosorption capacity in continuous mode was evaluated in several sorption–desorption cycles by using an optimal desorption solution.

2. Materials and methods

2.1. Biomass

Olive tree pruning (OTP) was obtained from the olive tree pruning process in Jaen (Spain). The olive cultivar was located in Vilchez, with a total area of 25,000 m^2. The pruning process was performed during months from February to March. After, in the laboratory, biomass was milled with an analytical mill (IKA MF-10) and $<10^{-3}$ m fraction was chosen for the lead biosorption tests. Finally, this fraction was treated with different chemical solutions to increase its biosorption capacity.

The chemical modification of OTP was performed using three chemical solutions: nitric acid (HNO_3), sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) at 1 mol/L (this concentration was chosen by a previous study of experimental design [26]). One liter of these solutions and 10 g of biomass were mixed in a flask at constant temperature (50 °C) for 24 h. Then, the biomass was repeatedly washed with distilled water until the pH of rising water remained constant. Finally, the treated OTP was dried in an oven at 40 °C for 24 h and it was stored in a hermetic container for later use.

2.2. Experimental procedure

2.2.1. Column experiments

The column experiments were performed in a packed bed column (internal diameter = 1.5×10^{-2} m and length = 2.3×10^{-1} m). Glass beads of 5×10^{-3} m diameter were place inside the column to enable uniform inlet flow into the column. The amount of waste inside the column was 5 g. The feed solution and the packed bed column temperature were maintained at 25 °C with a thermostatic bath. The lead solution was prepared from a stock solution of 2 g/L Pb(II) that was prepared by dissolving desired amount of $Pb(NO_3)_2$ in 0.5 L of distilled water. After that, the lead solution at a known concentration was pumped through the column using a peristaltic pump (Dinko model D21 V) at a flow rate of 10^{-4} L/s. Samples from the column effluent were collected at regular intervals and analyzed by atomic absorption spectrometry at $\lambda = 217$ nm using a Perkin-Elmer model 3100 spectrophotometer (sensitivity of 0.19 mg/L and detection limit of 0.04 mg/L). Fig. 1 shows a schematic illustration about the packed bed column with the biosorbent.

First, to analyze the effect of chemical treatments of the OTP in the biosorption of lead, experiments in a packed bed column were performed in continuous system with untreated and treated OTP with H_2SO_4, HNO_3 and NaOH at 1 mol/L. Then, breakthrough curves were obtained and the behavior of them was compared. The operational conditions were the following: flow rate = 10^{-4} L/s; initial lead concentration = 0.15 g/L; pH 4; biosorbent mass = 5 g; temperature = 25 °C (operational conditions were chosen according to a previous study [26]). The operational times were different in each experiment, to ensure that the exhausted of the column was reached.

2.2.2. Regeneration of biosorbent

The regeneration of the biosorbent and its reuse in several biosorption–desorption cycles is an important aspect from a point of view of its real implementation [30]. However, the interest of the regeneration of the biosorbent depends on a lot of aspects as cost of the process, disponibility of the biosorbent, value of recovery metal, *etc.*

The regeneration is usually carried out by using various eluting agents (acids or base) by different desorption mechanisms to release the adsorbed heavy metal ions into the solution [31–36]. In this study, the OTP treated by NaOH 1 mol/L (the optimal biosorbent) was chosen to its reuse in several cycles.