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Chestnut shells to mitigate pesticide contamination

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A B S T R A C T

In the last years, the presence of pesticides in aquatic environments has increased mainly as a result of the intensification of agricultural activities. Among the different techniques that can be used to remove these contaminants, the adsorption process can disclose as an appropriate treatment. In this work, chestnut shells were evaluated as a low-cost biosorbent for the pesticides pirimicarb, imidacloprid, acetamiprid and thiamethoxam, widely used in agricultural activities. Furthermore, economic acid pretreatments were evaluated in order to increase the removal efficiency. The highest removal was obtained when chestnut shells were pretreated with citric acid, increasing a 15% of adsorption capacity in comparison to raw chestnut shells. Scanning electron microscopy images, energy disperse spectroscopy analysis, Fourier transform infrared spectroscopy and Boehm method were performed in order to characterize the biosorbent. The new biosorbent was analysed in deep by kinetic and isotherm studies. The values of the correlation coefficients and standard error of estimate indicated that the Freundlich isotherm and pseudo-second-order model fitted well to the experimental data. In addition, the biosorbent showed a good behaviour working in continuous mode. The reported results open a new alternative for the restoration of polluted aquatic environments through the application of this new low-cost biosorbent developed.

1. Introduction

Pesticides are considered as one of the persistent organic pollutants, and their production and application in agriculture, forestry, and domestic activities have progressively increased worldwide during recent decades [1]. These compounds reach the water resources by leachate runoff when they are used in agricultural activities.

Adsorption process is one of the most attractive techniques for removing contaminants in aquatic environments. This treatment has advantages over the other physical–chemical methods because of simple design; however, its use has been found to be limited because it can involve high investment related to the adsorbent material cost. Many years ago, activated carbon was used as the adsorbent par excellence because it can remove a variety of pollutants [2], but its production process is expensive. Therefore, the scientific community is focusing its attention in the search of new low-cost adsorbent materials [3,4]. In recent times, materials easily available such as wastes from forestry, agricultural or industrial activities are being studied as low-cost adsorbents. Among them, agricultural lignocellulosic materials, commonly used for preparing activated carbon [2,5] appear as promising biosorbents [6,7]. These lignocellulosic materials possess numerous advantages, such as eco-friendly, renewable, cheaper, and easily available, as compared to commercial adsorbents [8]. Lignocellulosic materials have appropriate properties to act as adsorbent, due to their porosity and the presence of carboxylic and phenolic groups in their structure [9]. These materials have a rather polar surface and will prefer polar and ionic adsorbates. Furthermore, simple chemical treatments can improve their affinity to compounds with different structure [4,10–12].

Among the different industrial wastes that can produce valuable adsorbent, in this work chestnut shells were selected. This biomaterial is a waste of different food industries and nowadays it has neither added value nor reuses. This waste was extensively studied to adsorb inorganic pollutants such as heavy metals, but there is not so much bibliography about its capacity of organic pollutants adsorption [13]. For this reason, this study evaluates the pesticides adsorption capacity of chestnut shells. Several pesticides (pirimicarb, imidacloprid, acetamiprid and thiamethoxam), commonly used in agroindustrial activities, were selected to evaluate the adsorption capacity of chestnut shells. Initially, the efficiency of the waste was evaluated as raw material and after chemical treatments. After that, physical and chemical analyses were carried out and kinetics and isotherms studies were performed in order to characterize the biosorbent. Finally, column assays were carried out to validate the efficacy of the new biosorbent for environmental applications.

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2. Material and methods

2.1. Pesticides

Different pesticides were tested to evaluate the adsorption capacity of the chestnut shells. Pirimicarb, imidacloprid, acetamiprid and thiamethoxam were assayed as model pesticides. All of them were provided by Sigma-Aldrich as Pestanal analytical standard.

2.2. Biosorbent

Chestnut shells were collected from Cuevas & Cía, S.A., a food industry placed in Ourense, Spain. In this company, the chestnuts are used to elaborate Marrón Glacé and the shells were removed with steam. The chestnut shells were collected and dried in oven at 60 °C for 48 h. After that, they were crushed in a grinder at a particle size lower than 0.5 mm.

2.3. Acid pretreatments

Three different acid pretreatments were performed to modify the surface of chestnut shells. The concentrations of acid solutions were based on the literature thus; 1.1 M was used for citric acid and oxalic acid pretreatments [15] and 0.1 M was used for nitric acid pretreatment [10]. For each pretreatment, dried chestnut shells were mixed with acid solution in a ratio of 1:20 (g:mL) and the mixture was maintained at 25 °C for 3 h under shaking (120 rpm) in a shaker (Thermo Scientific MaxQ800). After that, the liquid was decanted and chestnut shells were dried in an oven at 60 °C during 24 h and subsequently the temperature of the oven was increased up 120 °C and maintained at this temperature for 90 min. The obtained biosorbents were repeatedly washed with $NaHCO_3$ and with distillate water to remove the acid excess and finally they were dried in oven at 60 °C for 24 h [15].

2.4. Biosorbent characterization

Scanning Electron Microscopy and Energy Dispersive Spectrometry (SEM/EDS) were performed on a JEOL JSM-6700F SEM equipped with an EDS Oxford Inca Energy 300 SEM using an accelerating voltage of 20 kV. The biosorbent surface was observed and the elemental analysis was determined. This analysis can be used to obtain information about the physical characteristics and the elemental composition of the biosorbent.

Fourier transform infrared spectroscopy (FTIR) and Boehm method are different techniques to obtain information about the functional groups. FTIR analyses were performed in a JASCO FT/IR-4100 spectrometer to evaluate the changes in the functional groups on the biosorbent surface. Solid samples were dried at 60 °C in an oven overnight, crushed and analysed between 400 and 4000 cm^{-1}.

On the other hand, the Boehm method [16] was used to measure the amount of surface functional groups. 1 g of biosorbent was added to series of 250 mL Erlenmeyer flasks containing 50 mL of 0.1 N: sodium bicarbonate, sodium carbonate, sodium hydroxide and hydrochloric acid. The mixtures were shaken 120 rpm (Thermo Scientific MaxQ800) for 24 h at 25 °C, after which the resulting suspensions were filtered and 10 mL of aliquot were titrated by 0.1 N hydrochloric acid or 0.1 N sodium hydroxide in order to estimate the residual base or acid.

2.5. Flask adsorption studies

The adsorption of the pesticides was studied individually and as mixture. Adsorption assays were carried out in 250 mL Erlenmeyer flasks by mixing 1 g of biosorbent with 50 mL of the pollutant solution. Flasks were shaken in a shaker (Thermo Scientific MaxQ800) at 120 rpm and 25 °C. During kinetics assays, samples were taken along the time to evaluate the kinetic profile and concentration of equilibrium. For the isotherms studies only a final sample was taken when equilibrium was reached.

The samples were centrifuged at 10,000 rpm for 5 min. The supernatant was separated to analyse pH and pollutant removal. The assays were performed twice, and the experimental error was calculated as the standard deviation, which was below 3% in all cases.

2.6. Column adsorption system

A glass column with dimensions of 16 cm height and 2 cm of internal diameter was employed. The fixed-bed column was filled with 7.2 g of biosorbent. As shown in Fig. 1, different polyamide sponge discs (2 cm of diameter and 0.5 cm of thickness) were placed along the column to prevent the biosorbent caking. A continuous flow (0.62 mL min^{-1}) was provided thought a peristaltic pump (Master Flex L/S Model 77202-60). The polluted solution was a mixture of the four pesticides (5 mg L^{-1} each one), and it was kept in an amber bottle to prevent light breakdown. The assays were performed at room temperature. Samples were periodically taken from the outflow, and they were processed as described previously.

Pesticide distribution along the column was obtained using methanol extraction. For this purpose, 1 g of biosorbent was mixed with 50 mL of methanol in 250 mL Erlenmeyer flasks during 48 h/25 °C at 120 rpm (Thermo Scientific MaxQ800) and Teflon screw caps were used to avoid evaporation. After that, samples were taken and processed as it was described previously.

2.7. Pesticides analysis

Pesticides concentration in aqueous samples was determined by HPLC (Agilent 1100) equipped with an XDB-C8 reverse-phase column (150 × 4.6 mm^2 i.d., 5 μm). Prior to injection, the samples were filtered through a 0.45 μm Teflon filter. The injection volume was set at 5 μL, and a gradient of eluent (acetonitrile/water) was pumped at a rate of 1 mL min^{-1} for 16 min. Detection was performed with a diode array detector from 200 to 600 nm, and the column temperature was maintained at 20 °C.

3. Results and discussion

3.1. Acid pretreatments

In this study, several acid pretreatments [10,12] using citric acid, oxalic acid, and nitric acid were tested to modify the surface of the biosorbent for increasing its sorption capacity. It is expected that the surface charge of the chemically-treated chestnut shells, particularly cellulose fraction, will be transform to negative charge.

The adsorption capacity of the raw chestnut shells for the removal of imidacloprid was evaluated and compared with the obtained when chestnut shells were pretreated with the different acids. It was found that the raw material reached a pesticide removal nearby 70%; however, the pretreatment with citric and oxalic acids increased their adsorption capacity at values around 85%. This can be explained by the fact that these organic acids have carboxylic groups in their structure and they can be linked to the surface of the chestnut shells increasing the number of carboxylic groups [17]. These groups are well-known as the main groups in the adsorption processes in lignocellulosic materials to obtain activated carbon [18] or their direct use [19,20].

On the other hand, the pretreatment realized with nitric acid reached the lowest removal of pesticide, around 50%. It was expected that the chemically treated biosorbent showed an enhancement in the pollutant removal due to the protonation of the biomass surface by the acid attack [21]. However, the removal reached was lower than obtained by the raw material. This can be explained by the fact that