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Removal of metal and organic pollutants from wastewater by a sequential selective technique

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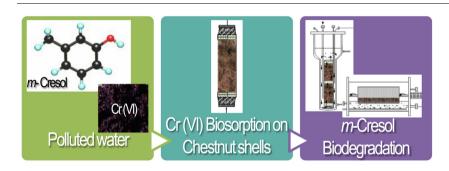
HIGHLIGHTS

- Sequential selective strategy is proposed to removal of metal and organic pollutants.
- Chestnut shell has a dual benefit as an adsorbent and enzymatic inductor.
- Complete Cr(VI) biosorption followed pseudo-second order kinetic and Langmuir isotherm.
- High laccase production and *m*-cresol biodegradation rate in Rotating drum bioreactor.
- Sequential system proposed has been modelled operating in continuous mode.

GRAPHICAL ABSTRACT

ABSTRACT

In this study the application of a sequential selective system that combined biosorption with biodegradation was evaluated as a feasible process for the removal of Cr(VI) and *m*-cresol from effluents. Cr(VI) biosorption on pretreated chestnut shells showed 100% metal removal and modelling efforts demonstrated that the pseudo-second order kinetic model and Langmuir isotherm fit well the process behaviour. Thus, the treated stream was an appropriate environment for the biodegradation of *m*-cresol using a laccase-producer fungus, *Phlebia radiata*. Two bioreactor configurations, rotating drum and modified-airlift, were studied using the fungus grown on chestnut shells, which act as support-substrate as well as oxidative enzyme inductor increasing the laccase activity up to 1000 U L^{-1}. The best bioreactor, rotating drum, reached 100% removal in 7 days. Finally, the best configuration for the sequential selective system was modelled operating in continuous mode by the breakthrough curves generated using FASTv2.0 and the design bioreactor flow model.

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1. Introduction

The discharge of different pollutants to the environment is severely damaging the aquatic ecosystem (Saeed et al., 2016). These pollutants can be both inorganic and organic compounds, with both simultaneously appearing in effluents or in the environment (Quintelas et al., 2006; Talalaj, 2015). In this context, different technologies have been studied to improve or recover water quality. In recent years, the use of biological processes for the restoration of aquatic environments has gained the attention of the scientific community (Kües, 2015). Therefore, biodegradation appears to be a good alternative for the removal of organic pollutants, specially emerging pollutants that could be transformed into other less toxic products or may even be completely mineralised.

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Recently, Gupta et al. (2016) reported the degradation of different pesticides on less-toxic molecules by an isolated strain of *Pseudomonas* sp. and Janicki et al. (2016) showed an effective biotransformation of endocrine disruptors by the fungus *Umbelopsis isabellina*, which was accompanied by a decrease in the toxicity of the culture medium. Furthermore, several microorganisms have been used to reduce the toxicity of heavy metals through the bioreduction of Cr(VI) to Cr(III) (Lin et al., 2011) or to adsorb/immobilise the inorganic pollutants in the biomass (Quintelas et al., 2006). However, in most of cases, an inhibitory effect has been found that is due to the presence of metallic species with a direct and negative influence on the biodegradation of organic pollutants. There are several examples described in the literature where this fact has been reported. For example, Aksu et al. (2007) detected that Remazol Black B removal by *Trametes versicolor* decreased approximately 27% in the presence of 15 mg L^{-1} of Cr(VI). Similar behaviour was also observed by Sumathi and Manju (2000) who reported that the removal of Drimarene Red dye by *Aspergillus foetidus* was reduced from 86.9% to 28.9% in the presence of 5 mg L^{-1} Cr(VI). Recently, Thavamani et al. (2015) showed that the biodegradation of phenanthrene by a bacterial consortium consisting of different strains of *Alcaligenes* sp., *Pseudomonas* sp., *Paenibacillus* sp. and *Pandoraea* sp. can be inhibited by the presence of Cd at concentration higher than 10 mg L^{-1}. This is in accordance with the study of Shi et al. (2013) who reported that a concentration of Cd higher than 5 mg L^{-1} inhibited degradation of polybrominated diphenyl ethers, which was mainly due to the impact of toxic heavy metal on the growth and metabolism of *Pseudomonas aeruginosa*. In order to overcome this problem, it is necessary to combine biodegradation with other technique that eliminates or reduces this inhibitory effect. Bearing in mind the abovementioned, the integration of adsorption process seems to be the most appropriated option.

In this sense, it is postulated that the application of a sequential selective system, which combines adsorption with biodegradation, will allow for the removal of the metal and organic compounds from aquatic environments. In this study, Cr(VI) and *m*-cresol were selected as model metal and persistent organic pollutant, respectively. Both may be found in water resources by direct or indirect sources such as leachate runoff or from industrial effluents such as tanneries. Cr(VI) has been designated as one of the top-priority toxic pollutants by the EPA because it is a carcinogen (U.S. EPA, 1998). On the other hand, cresols are widely used in a variety of different industries (pesticides manufacturing, pharmaceutical, resin manufacturing, etc.). Their release to the environment generates serious ecological problems due to their inherent toxicity; therefore, cresols are also considered as a priority pollutant by the EPA (U.S. EPA, 1999).

The application of a new treatment system should be a cost-effective process. This fact requires the reduction of the adsorbent cost and also the increased degradation ability of the microorganism used. To achieve this goal, chestnut shells were selected due to their dual benefit as an adsorbent and enzymatic inducer. Chestnut shells are food industrial waste with low commercial value, and it is a well-known adsorbent of different pollutants as a result of its porosity and presence of carboxylic groups in its structure (Ertas and Öztürk, 2013; Cobas et al., 2015). In addition, the potential of lignocellulosic wastes, which have a considerable proportion of cellulose in their composition, for induction of oxidative enzymes production, such as laccase by white-rot fungi, has been reported in previous studies (Dong et al., 2014; Selvaraj et al., 2015). Laccase is an enzyme of considerable biotechnological interest, since it can be employed in numerous environmental applications due to its ability to degrade a widely range of organic pollutants, such as phenols, endocrine-disrupting compounds, dyes, polycyclic aromatic hydrocarbons, and pesticides (Kües, 2015; Garcia-Morales et al., 2015; Yadav and Yadav, 2015;

Nguyen et al., 2014). Thus, the potential of this lignocellulosic material as a support-substrate and as an economical way of improving laccase production by the white-rot fungus *Phlebia radiata* have been evaluated.

Finally, the sequential selective system was modelled operating in a continuous flow system by the breakthrough curves generated using FAST Fixed-bed Adsorption Simulation Tool v 2.0 and the application of the bioreactor flow model.

2. Methods

2.1. Pollutants

The *m*-cresol was purchased from Sigma Aldrich, Spain. Cr(VI) was supplied by Riedel de Haën as $K_2Cr_2O_7$.

2.2. Biosorption assays

2.2.1. Preparation of biosorbent

Chestnut shells were collected from Cuevas & Cía, S.A., a food industry located in Ourense, Spain. The provided chestnut shells were dried in an oven at 60 °C for 48 h. According to Cobas et al. (2015) dried chestnut shells were mixed with 1.1 M of citric 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 an orbital shaker (Thermo scientific MaxQ8000). 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. After drying, the shells were ground using a grinder and afterwards were sieved (1.5 mm) (Retsch SM 100) and kept at room temperature in hermetic plastic bags until use.

The biosorbent point zero charge (pH_{PZC}) were calculated according with Fiol and Villaescusa (2009), using the immersion technique. Suspensions of 7% (w/v) of chestnut shells were out into contact with 0.1 M $NaNO_3$ solution adjusted, with HNO_3 or NaOH, at different pH values (3–10). The suspensions were agitated for 24 h in an orbital shaker (Thermo scientific MaxQ8000) at 150 rpm until an equilibrium pH value was reached. The change of pH (ΔpH) during equilibration was calculated and the pH_{PZC} was identified as the initial pH with minimum ΔpH.

2.2.2. Kinetic studies and isotherms

The adsorption behaviour of the biosorbent was extensively studied through kinetic and isotherms assays. Adsorption assays were carried out in 250 mL Erlenmeyer flasks by mixing 0.5 g of biosorbent with 50 mL of the pollutant solution in an orbital shaker at 120 rpm and 25 °C (Thermo scientific MaxQ8000). To perform the kinetic studies, a solution of 250 mg L^{-1} of Cr(VI) and 10 mg L^{-1} of *m*-cresol was used at natural pH. Samples were periodically taken through time (0, 0.5, 5, 15, 30, 45, 75, 120, 180 and 360 min) to evaluate the solution pH, Cr(VI) concentration and the time necessary to reach the equilibrium concentration. In the isotherm studies, different pollutant concentrations (100–750 mg L^{-1} of Cr(VI)) were tested and only a final sample was taken when equilibrium was reached.

The samples were centrifuged in plastic tubes at 10,000 rpm for 5 min. The supernatant was separated to analyse the pollutant biosorption. All assays were performed in duplicate. The experimental error was calculated as the standard deviation, which was below 5% in all cases and the reported results are the average values.