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# Box–Behnken methodology for Cr (VI) and leather dyes removal by an eco-friendly biosorbent: *F. vesiculosus*

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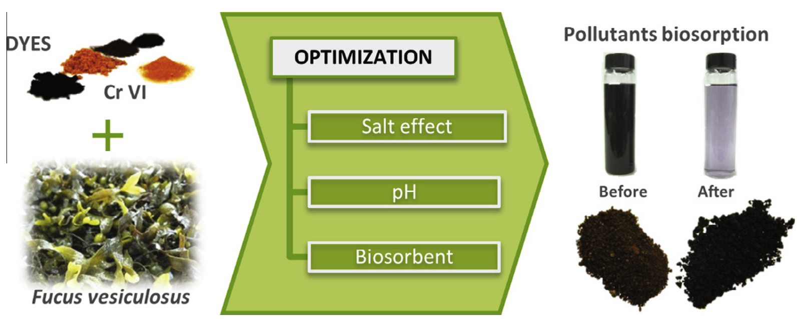
## HIGHLIGHTS

- The use of *F. vesiculosus* for biosorption of leather effluents pollutants was studied.
- The selected key parameters were salt pretreatment, pH and biomass dosage.
- The Box–Behnken design provided that biomass dosage and [$CaCl_2$] were significant.
- *F. vesiculosus* shows to be a low-cost and effective biosorbent for studied pollutants.
- Triple benefit: valorization of algal waste, pollutants removal and enzyme production.

## GRAPHICAL ABSTRACT

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## ABSTRACT

This study focused on leather industrial effluents treatment by biosorption using *Fucus vesiculosus* as low-cost adsorbent. These effluents are yellowish-brown color and high concentration of Cr (VI). Therefore, biosorption process was optimized using response surface methodology based on Box–Behnken design operating with a simulated leather effluent obtained by mixture of Cr (VI) solution and four leather dyes. The key variables selected were initial solution pH, biomass dosage and $CaCl_2$ concentration in the pretreatment stage. The statistical analysis shows that pH has a negligible effect, being the biomass dosage and $CaCl_2$ concentration the most significant variables. At optimal conditions, 98% of Cr (VI) and 88% of dyes removal can be achieved. Freundlich fitted better to the obtained equilibrium data for all studied systems than Temkin, Langmuir or D–R models. In addition, the use of the final biosorbent as support-substrate to grown of enzyme producer fungi, *Pleurotus ostreatus*, was also demonstrated.



## 1. Introduction

The high use of water required in leather industry generates wastewater that it is recognized as a potential hazard for the environment due to their content of pollutants such as heavy metals and organic compounds. These effluents should be treated in order to avoid their released to the environment. The decontamination of these effluents must undergo several treatments prior to their release; however, in some cases, these treatments are not effective, and the pollution of surface and groundwater is generated (Rosales et al., 2012).

The presence of dyes in aqueous media produces color, which prevents the passage of light and oxygen and, therefore, disfavors the development of organisms and thus, the self-depuration or even the performance of biological treatments naturally occurring in the environment (Robinson et al., 2001). The treatment of these dye polluted effluents is often limited to homogenization and deposition processes. However, chemical coagulation and sludge digestion are sometimes performed due to the recalcitrant properties of dyes (stable to light, heat, and oxidizing agents) (Sun and Yang, 2003).

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Furthermore, the existence of metals such as chromium, widely used in leather industry, increases the toxic effect of these wastewaters. During the chrome tanning process, high unused chromium salts are usually discharged in the final effluents, causing a serious threat to the environment. These effluents content both Cr (III) and Cr (VI) (Pakshirajan et al., 2013). Also, when the tanning residual water has Cr (III), the oxidation to Cr (VI) can occur under particular environmental conditions. This is an important fact due to Cr (VI) is the most dangerous form; it causes adverse effects for the human health and generates environmental toxicity. The typical treatments to remove Cr (VI) include chemical precipitation, ion exchange, solvent extraction or adsorption (Low et al., 1999).

Nowadays, the treatments for removing pollutants of the different nature, such as metals and organic compounds, have some disadvantages: inefficiency, high energy and operating requirements, and maintenance costs. For these reasons, the management of these wastewaters is an issue that has taken the attention of researchers worldwide, which leads in several new treatments proposed for solving this environmental problem (Robinson et al., 2001). Adsorption is one of the most attractive processes due to its versatility; it can be used for removing metals and/or organic pollutants. However, the main drawback is the elevated cost of high efficient adsorbent materials, such as activated carbon. The search for new low-cost adsorbent materials is the goal of many studies (Nguyen et al., 2013; Ali et al., 2012). A suitable low-cost adsorbent requires a porous structure, mechanical stability and affinity for the target pollutants; furthermore it should be environmentally friendly. At the present time, the scientific community is searching adsorbents from industrial residues without commercial interest or materials naturally found in the environment (Ali et al., 2012).

In the present study, the brown alga, *Fucus vesiculosus*, was assessed as a low-cost biosorbent for the treatment of a model leather industry effluent. This alga was selected because of its prevalence in Galician coast, and every year, tons of this alga, have to be removed from the beaches and coastal rocks. In addition, the biosorption capacity of the brown algae is well-known to adsorb various pollutants including cadmium, chromium, uranium and dyes (Kousha et al., 2012b; Yalçin et al., 2012; Brinza et al., 2009). Their complex cell wall, with some mucilaginous polysaccharides such as alginate and presence of carboxyl groups, can explain their high metal uptakes compared to other biomasses (Mata et al., 2009). In this work, the efficiency of the alga using different physical and chemical pretreatments will be assessed. Box–Behnken design and response surface methodology (RSM) (Liu et al., 2012; Rosales et al., 2012; Xu et al., 2013) will be applied to design the experiments and optimize the biosorption process for Cr (VI) and dyes using the brown alga, *F. vesiculosus*. This statistical experimental design was performed for obtaining the maximum information in minimum time and resources requirements. Subsequently, in order to perform a deep study of the developed biosorbent, kinetics and equilibrium isotherms were carried out. Finally, solid state fermentations of fungus, *Pleurotus ostreatus*, were carried out to evaluate the feasibility of exhausted biomass being used as a solid-substrate for production of oxidative enzymes with commercial interest.

## 2. Methods

### 2.1. Pollutants

Four different leather dyes (Sella Solid Blue, Special Violet, Burdeuox, and Sella Solid Orange) were provided by Padronesa Industrial de Curtidos S.A. (Spain). Cr (VI) was supplied by Riedel de Haën as $K_2Cr_2O_7$. Leather dyes and Cr (VI) were mixed to simulate a real textile effluent (35 mg $L^{-1}$ Cr (VI) and 50 mg $L^{-1}$ of each dye) (Chowdhury et al., 2013).

### 2.2. Algal biomass and pretreatments

*F. vesiculosus* was collected from Ensenada A Portela, Redondela (Spain) (42°17′18.74″N–8°37′23.22″O) in winter 2013. Algal biomass was cleaned by repeated washes with distilled water for the removal of sand, stones, shellfish and salts. Then the algal biomass was dried in an oven at 60 °C for 48 h. After drying, *F. vesiculosus* was crushed (particle size ⩽2 mm) and stored in glass bottles at 4 °C.

The chemical pretreatment was carried out in 250 mL Erlenmeyer flasks with dry algal biomass and a salt solution in a ratio 2.5:50 (g:mL). Several solutions were prepared at different concentrations of salt solution the studied salt were $CaCl_2$, KCl, and $MgCl_2$ (all of them supplied by Sigma Aldrich). Flasks were maintained in a thermostatic shaker (Thermo scientific MaxQ800) at 25 °C and 120 rpm for 12 h. After that, they were washed with distilled water to eliminate the excess of salts. Then, the algal biomass was dried in an oven at 60 °C for 48 h.

### 2.3. Adsorption assays

All adsorption experiments were carried out in 250 mL Erlenmeyer flasks by mixing biosorbent with 50 mL of the pollutant solution at the desired operating conditions. When pH adjustment was necessary solutions of 1 M NaOH or 1 M HCl were used. Flasks were shaken in an incubator (Thermo scientific MaxQ800) at 120 rpm at 25 °C. All assays were performed in duplicate, and the reported results are the average values.

### 2.4. Experimental design

The statistical method of RSM is used for optimizing several engineering processes. In this study, a three-factorial Box–Behnken was used for the optimization of the biosorption process of a mixture of four leather dyes and Cr (VI) by *F. vesiculosus* biomass. The design was composed by three levels (low (−1), medium (0) and high (+1)) and the number of experiments was calculated as follows:

$$N = k^2 + k + cp \tag{1}$$

where $k$ is the factor number and $cp$ is the replicate number of the central points (Kousha et al., 2012b). In this study, a total of 17 runs were carried out in duplicate to optimize the level of the chosen variables: initial pH ($x_1$), biomass dosage in 50 mL ($x_2$) and $CaCl_2$ concentration in the pretreatment ($x_3$). These variables have been considered as factors that may potentially affect the response functions: dyes biosorption and Cr (VI) biosorption. Table 1 shows the experimental Box–Behnken design matrix, with the real and codified values of each factor.

### 2.5. Statistical analysis and validation of the experimental model

The statistical analysis of this model was performed in order to assess the analysis of variance (ANOVA) using Design Expert® 8.0.0 software (Stat-Ease Inc., Minneapolis, USA). In the RSM, a second-order polynomial equation is usually applied to correlate the dependent and independent variables:

$$Y_i = \beta_0 + \sum \beta_i x_i + \sum \beta_{ii} x_i^2 + \sum \beta_{ij} x_i x_j + \varepsilon \tag{2}$$

where $Y_i$ is the response, $\beta_0$ is the constant, $\beta_i$ is the slope or linear effect of the input factor, $\beta_{ii}$ is the quadratic effect, $\beta_{ij}$ is the two-way linear by linear interaction effect, $x_i$ and $x_j$ are the independent parameters and $\varepsilon$ is the random error (Simsek et al., 2013). Eq. (2) expresses the relationship between the predicted response and the independent variables in coded values.