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Kinetic and morphology study of alginate-vineyard pruning waste biocomposite vs. non modified vineyard pruning waste for dye removal

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ABSTRACT

In this work a comparative bioadsorption study between a biocomposite consisting of hydrolysed vineyard pruning waste entrapped in calcium alginate spheres and non entrapped vineyard residue was carried out. Results have demonstrated that the biocomposite based on lignocellulose-calcium alginate spheres removed 77.3% of dyes, while non entrapped lignocellulose eliminated only removed 27.8% of colour compounds. The experimental data were fitted to several kinetic models (pseudo-first order, pseudo-second order, Chien–Clayton model, intraparticle diffusion model and Bangham model); being pseudo-second order the kinetic model that better described the adsorption of dyes onto both bioadsorbents. In addition, a morphological study (roughness and shape) of alginate-vineyard biocomposite was established under extreme conditions, observing significant differences between hydrated and dehydrated alginate-vineyard biocomposite. The techniques used to carry out this morphological study consisted of scanning electron microscopy (SEM), perfilometry and 3D surface analysis.

Introduction

Nowadays environmental requirements are becoming of great importance, since there is an increased interest in the industrial use of renewable resources such as lignocellulosic residues for the formulation of eco-friendly adsorbents (Kim et al., 2014; Alves et al., 2013; Deng et al., 2011; Perez-Ameneiro et al., 2014a). Thus, significant efforts are now being made in the research and development of polysaccharide derivatives as the basic materials for new applications. In particular, the increasing costs of conventional adsorbents certainly make lignocellulosic-based materials, composed by natural polymers, one of the most attractive bioadsorbents for wastewater treatment (Sharma and Rajesh, 2014; Kumar et al., 2014). Different studies have demonstrated that lignocellulosic-based polymers have exceptional removal capabilities for certain pollutants such as dyes and metal ions as compared to other low-cost adsorbents and commercial activated carbons (Batzias et al., 2009; Rosas-Castor et al., 2014; Sidiras et al., 2013; Velazquez-Jimenez et al., 2013). Thus, cellulose-based biocomposites, has been widely used in wastewater purification due to its good biocompatibility, and excellent handling, which can be easily formulated into spheres, membranes and hollow fibres. Cellulose is composed of β-1,4 linked glucopyranose units, with polymer chains associated by

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hydrogen bonds forming bundles of fibrils, also called microfibrillar aggregates, where highly ordered crystalline regions alternate with disordered amorphous domains. Therefore, peat and grape marc compost, entrapped in calcium alginate hydrogels, have been proposed for their dye-binding capability from wastewater (Vecino et al., 2013; Perez-Ameneiro et al., 2014b). Nevertheless, peat and composted grape marc have other uses like soil amendments that can prevent their use as bioadsorbents in comparison with the lignocellulosic fraction of vineyard pruning waste. Moreover it was observed that the lignocellulosic fraction of vineyard pruning waste, encapsulated in calcium alginate beads, has excellent properties for the removal of micronutrients from wastewater (Vecino et al., 2014); although it would be important to evaluate the capacity of this lignocellulosic residue to remove other contaminants like dyes and study the adsorption mechanism under different kinetic models. In addition it would be interesting to know if the immobilization of this lignocellulosic residue in calcium alginate spheres increases the bioadsorption capacity of vineyard pruning waste in comparison with the raw hydrolysed vineyard pruning waste.

This work deals with a comparative study between the directly utilization of the lignocellulosic fraction of vineyard pruning waste against the utilization of an alginate-vineyard biocomposite spheres, for the removal of dye compounds from an agro-industrial effluent. Different kinetic models (pseudo-first order, pseudo-second order, Chien–Clayton model, intraparticle diffusion model and Bangham model) were used to explain the adsorption of dyes onto the two bioadsorbents. Moreover, 3D surface visualizations and perfilometry analysis of hydrated and dehydrated calcium alginate spheres, containing vineyard pruning waste, were included in this study.

1. Materials and methods

1.1. Preparation of the lignocellulosic fraction of vineyard pruning waste

Lignocellulosic residue was collected from a local wine-producer (Galicia, North-West Spain). Vineyard pruning waste was dried and milled (<1 mm), homogenized in a single batch and hydrolysed with H_2SO_4 following the methodology proposed by Bustos et al. (2004). After hydrolysis a solid fraction composed by cellulose and lignin was dried and sieved up to a particle size of 0.5 mm and submitted to a quantitative hydrolysis in order to determine the cellulose and lignin concentration in the bioadsorbent (Vecino et al., 2014). Thus the percentage of cellulose in the adsorbent was calculated on the basis of glucose in the liquid phase, which was analysed by high performance liquid chromatography (HPLC) equipped with diode array detection (DAD) and refractive index detection (RID) (Agilent Technologies 1200 Series, Germany). Separation was performed using a Rezex RHM-Monosaccharide H+ (8%) column (Phenomenex, USA) with the column oven kept at 65°C. The mobile phase consisted in Milli-Q water plus 0.005 N of H_2SO_4, the injection volume was 20 μL and the flow rate was 0.4 mL/min.

Otherwise, the solid residue that remains after quantitative hydrolysis, was considered as the Klason lignin.

1.2. Development of the alginate-vineyard biocomposite spheres

Alginate-vineyard biocomposite spheres were prepared by mixing 1.25% of cellulosic residue with 2.2% of sodium alginate, in order to form an emulsion that was introduced drop-wise in a crosslinking solution of calcium chloride 0.475 mol/L (Vecino et al., 2014).

For comparative purposes, during the kinetic adsorption study, hydrolysed vineyard pruning waste was also used without encapsulation.

1.3. Morphology characterization of lignocellulosic powder and alginate-vineyard biocomposite

1.3.1. Scanning electron microscope (SEM) images

Previously to obtain SEM images, the alginate-vineyard biocomposite was washed with sodium cacodylate 0.1 mol/L buffer and fixed with 2.5% of glutaraldehyde in cacodylate 0.1 mol/L buffer during 2–4 hr at 4°C. Following, the alginate-vineyard biocomposite was introduced in 1% OsO_4 in cacodylate 0.1 mol/L buffer during 1 hr at 4°C. Dehydration was carried out with 30% of ethanol during 15 min and then ethanol using a different graded series (50%–2× 15 min; 70%–2× 15 min; 80%–2× 15 min; 90%–2× 15 min and 100%–3× 15 min) and amylacetate:ethanol in an ordered series (1:3–2× 15 min; 2:2–2× 15 min; 3:1–2× 15 min and amylacetate 100%–3× 15 min) in order to replace the ethanol for a liquid miscible with liquid CO_2. The biocomposite was dried at the chamber critical point, cut in liquid N_2, covered with gold and observed using SEM (Jeol JSM-6700F FEG) operating at an acceleration voltage of 5.0 kV for secondary-electron imaging (SEI/LEI).

The lignocellulosic powder undergoes non dehydration process. The powder was covered with gold and observed by SEM.

1.3.2. 3D surface roughness analysis

3D images of alginate-vineyard biocomposite were obtained with an Infinite Focus-SL Alicona GmbH (Graz, Austria) using an objective lense 10×, lateral resolution of 2 μm and vertical resolution of 500 nm. This system allows intuitive and quick measurement of micro structured surfaces, due to the high resolution and high density of number of points measured (4 millions of points); it is possible to calculate the diameter and the surface roughness within the same 3D measurement of the alginate-vineyard biocomposites. Post-processing Measure Suite software provides the tools to filter out the 3D measurement into waviness and roughness components by using a cut-off frequency filter of 80 μm.

In addition, an optical profilometer Zeta-20™ (Zeta Instruments, CA) was used in order to obtain a 3D surface visualization and roughness parameters (Ra, Rq, Rz, Rp, Rv) using Z scan range of μm and controlled by Zeta 3D software.

The roughness and radius of calcium alginate spheres containing the lignocellulosic adsorbent were studied during 22 min of hydration followed by a period of 75 min of dehydration at 19.5°C and 73 min of rehydration.

1.4. Commercial dye

Amaranth is a commercial dye (85%, Acros organics, USA) that was used as standard to obtain the amount of dye compounds