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Wastewater treatment enhancement by applying a lipopeptide biosurfactant to a lignocellulosic biocomposite

M. Perez-Ameneiro, X. Vecino, J.M. Cruz, A.B. Moldes*

Chemical Engineering Department, University of Vigo, School of Industrial Engineering (EEI), Campus As Lagoas, Marcosende, 36310 Vigo – Pontevedra, Spain

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ABSTRACT

In this work, a natural lipopeptide biosurfactant obtained from corn steep liquor was included in the formulation of a lignocellulosic biocomposite used for the treatment of wastewater. The results obtained indicate that the dye sorption capacity of the hydrogel containing hydrolysed vineyard pruning waste can be significantly promoted via surfactant modification using natural detergents. The elimination of dye compounds and the removal of sulphates were increased around 10% and 62%, respectively, when the biocomposite modified with biosurfactant was used. This outcome can be intrinsically related to the rougher, rounder, more compact and better-emulsified sphere achieved after the addition of the lipopeptide biosurfactant. The bioadsorption process followed a pseudo-second order kinetic model and both intraparticle diffusion and liquid film diffusion were involved in the bioadsorption mechanism. Therefore, the utilisation of biosurfactants shows great potential in the formulation of eco-friendly adsorbents for environmental application.

1. Introduction

Recently, the number of studies about the modification of classical and non-classical adsorbents by the incorporation of surfactants in their formulation has increased in order to develop more efficient adsorbents (Kumar, Prasad, & Siddhanta, 2012; Sumanjit, Mahajan, & Gupta, 2015; Yang, Gao, & Luo, 2014; Zhao, Shang, Xiao, Dou, & Han, 2014. However, in most of the cases, these surfactants consist in no eco-friendly detergents obtained by chemical synthesis.

Thus, Sumanjit et al. (2015) have modified the properties of Eichhornia charcoal by incorporating a cationic surfactant in the formulation of the adsorbent; whereas Yang et al. (2014) have investigated the effect of the different spacers of gemini surfactants on 2-naphthol adsorption onto modified clays, observing a stronger hydrophobic interaction between the surfactant and the organic pollutants and, therefore, improving the adsorption capacity of the adsorbent. Other authors (Zhao et al., 2014) have used wheat straw soaked with 1% of cetrimonium bromide (CTAB), a cationic surfactant, for the removal of anionic dyes from water. Additionally, some authors have proposed the combination of inorganic and organic materials to elaborate a new type of functional composites with better thermal and mechanical properties than the classical ones (S. Kumar et al., 2012).

On the other hand, lignocellulosic residues such as vineyard pruning waste or grape marc are also a good source of polymeric hydrocarbons, useful in the formulation of adsorbents for the treatment of industrial wastewater effluents (Perez-Ameneiro, Vecino, Barbosa-Pereira, Cruz, & Moldes, 2014; Perez-Ameneiro, Vecino, Vega, et al., 2014; Vecino, Devesa-Rey, Cruz, & Moldes, 2015; Vecino, Devesa-Rey, Moldes, & Cruz, 2014). Biomass-derived biocomposites are more biodegradable and less toxic than those adsorbents obtained by chemical synthesis.

Regarding to the production of natural detergents, Vecino, Barbosa-Pereira, Devesa-Rey, Cruz, and Moldes (2015) have found a lipopeptide biosurfactant contained in corn steep liquor, a liquid stream from the corn milling industry. This biosurfactant is able to reduce the surface tension (ST) of water from 70.6 ± 0.2 to 40.9 ± 1.7 mN/m, with a critical micelle concentration (CMC) of 399.4 mg/L. Some chemical surfactants used in the formulation of biomaterials have similar CMC values than the biosurfactant extracted from corn steep liquor. For instance, CTAB, a cationic detergent used in the formulation of nanoparticles and in the formulation of bioadsorbents, has a CMC of 9.2×10^{-4} mol/L, corresponding to 335 mg/L of detergent (Grzeiczak, Pérez-Juste, Mulvaney, & Liz-Marzán, 2008; Zhao et al., 2014).

* Corresponding author. Tel.: +34 986812215; fax: +34 986812201.
E-mail addresses: mp.ameneiro@uvigo.es (M. Perez-Ameneiro), xanel.vecino@uvigo.es (X. Vecino), jmcruz@uvigo.es (J.M. Cruz), amoldes@uvigo.es (A.B. Moldes).

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In this work, a biosurfactant obtained from corn steep liquor was incorporated in the formulation of a biocomposite based on activated vineyard pruning waste and encapsulated in calcium alginate beads. The variation in its morphology was compared to that of a regular vineyard pruning waste-based biocomposite. Furthermore, the performance in terms of bioadsorption capacity of this biosurfactant-modified biocomposite was evaluated by means of different kinetic models.

2. Materials and methods

2.1. Activation of lignocellulosic residue

Vineyard pruning waste was collected from a local wine-producer (Galicia, North-West Spain), dried, milled (<1 mm) and homogenised in a single batch. Following, it was subjected to chemical activation during 15 min using 3% sulphuric acid at 130 °C (Bustos, Moldes, Cruz, & Domínguez, 2004). After hydrolysis, the solid fraction composed of cellulose and lignin was dried, sieved up to a particle size of 0.5 mm and stored for the formulation of the biocomposite.

2.2. Extraction of lipopeptide biosurfactant from corn steep liquor

The lipopeptide biosurfactant was obtained by liquid–liquid extraction from corn steep liquor (CSL), using a ratio chloroform/CSL of 2 (v/v), at a temperature of 56 °C, during 30 min and an agitation speed of 150 rpm. After extraction, the biosurfactant was separated from the chloroform by rotary evaporation (Buchi R-210, Switzerland) at a pressure of 474 mbar and 60 °C, following the methodology proposed by Vecino, Barbosa-Pereira, et al. (2015).

2.3. Formulation of biocomposite

The biocomposite was prepared conforming to the procedure described by Vecino, Devesa-Rey, et al. (2015), by mixing the activated vineyard pruning waste (1.25%) with sodium alginate (2.2%) and the lipopeptide biosurfactant at the CMC (399.4 mg/L). Following, the previous emulsion was added drop-wise to a crosslinking solution of calcium chloride (0.475 mol/L) in order to obtain calcium alginate beads containing the vineyard pruning waste. In addition, this biocomposite was also formulated without incorporating the biosurfactant with the purpose of using this bioadsorbent as a control.

2.4. Morphological characterisation of vineyard pruning waste biocomposites

2.4.1. Scanning electron microscope (SEM) images

In order to prepare samples to be observed with the scanning electron microscope (SEM), the alginate-vineyard biocomposite was washed with sodium cacodylate 0.1 mol/L buffer and fixed with 2.5% glutaraldehyde in cacodylate 0.1 mol/L buffer, during 2–4 h at 4 °C. Following, the alginate-vineyard biocomposite was introduced in 1% OsO_4 in cacodylate 0.1 mol/L buffer during 1 h at 4 °C. After that, dehydration of the samples with ethanol was carried out. First, samples were immersed in a 30% ethanol solution during 15 min and, then, in different graded series of ethanol solutions (2 × 15 min in 50% ethanol; 2 × 15 min in 70% ethanol; 2 × 15 min in 80% ethanol; 2 × 15 min in 90% ethanol, and 3 × 15 min in 100% ethanol). Next, in order to replace the ethanol for a liquid miscible with liquid CO_2, samples were treated with ordered series of an amylacetate:ethanol solution (2 × 15 min in a solution with a ratio of 1:3; 2 × 15 min in a solution with a ratio 2:2; 2 × 15 min in a solution with a ratio 3:1, and 3 × 15 min in a 100% amylacetate solution). Finally, 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).

2.4.2. Dimensional analysis

A stereoscopic Microscope SMZ 1500 (Nikon) was used to obtain high-resolution optical images of the vineyard pruning waste-based biocomposites, with objective lens HR Plan Apo 1× with eyepiece C-W 10× (F.N. 22), zoom range position 1×, 12 V/100 W halogen illuminator and controlled by Image tool 3.00 software. Measurements of both vineyard pruning waste biocomposites, formulated with and without biosurfactant, were performed in quintuplicate and data on area, perimeter, major and minor axis, elongation, roundness, Feret diameter and compactness were collected.

Thus, elongation can be defined as the ratio of major to minor axis length and was calculated following Eq. (1). Roundness, on the other hand, represents the sharpness of a particle's corners and can be calculated according to Eq. (2).

$$Elongation = \frac{Major\ axis\ length}{Minor\ axis\ length} \quad (1)$$

$$Roundness = \frac{4 \cdot Area}{\pi \cdot (Major\ axis\ length)^2} \quad (2)$$

Moreover, compactness provides a measurement of the object's circleness and was obtained applying Eq. (3). Additionally, Feret diameter was also included in the study. It can be defined as the distance between the two parallel planes restricting the object perpendicular to that direction and is directly calculated following Eq. (4).

$$Compactness = \frac{Feret\ diameter}{Major\ axis\ length} \quad (3)$$

$$Feret\ diameter = \sqrt{\frac{4 \cdot Area}{\pi}} \quad (4)$$

2.4.3. Topographical analysis (3D surface roughness analysis)

The Leica Digital Microscope DVM 2500 was used to obtain 3D images from vineyard pruning waste biocomposites, with a VZ75 C optics at 40× magnification – in a range of 20–160× – with a vertical resolution of the VZ75 C optics at 160× of 125 mm, a resolution of the motorised focusing drive of 500 nm, LED light source and controlled by Leica map 7.0, LAS V4.5 software.

The 3D optical microscopy allowed the characterisation of the studied biocomposites in the three dimensions (x, y, z), gathering information about their height and surface roughness. All measurements were carried out following the protocol specified by the ISO 25178 standard (2012). A fifth grade polynomial correction was applied to the 3D images so that only the texture and microtexture were considered to calculate the following amplitude parameters.

Thus, the parameter S_a is the Mean Roughness, whereas S_q is referred to the Root Mean Square (RMS) Roughness. Both of them are evaluated over the complete 3D surface and can be calculated following Eqs. (5) and (6), respectively.

$$S_a = \iint_a |Z(x,y)| dxdy \quad (5)$$

$$S_a = \sqrt{\iint_a |Z(x,y)| dxdy} \quad (6)$$

On the other hand, S_{sk} is the Skewness parameter and S_{ku} is referred to the Kurtosis of the 3D surface texture. These parameters represent a histogram of the heights from an ideal Normal