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Evaluation of biosurfactant obtained from *Lactobacillus pentosus* as foaming agent in froth flotation

X. Vecino [a], R. Devesa-Rey [a,b,*], J.M. Cruz [a], A.B. Moldes [a]

[a] *Chemical Engineering Department, School of Industrial Engineering (EEI), University of Vigo, Campus As Lagoas-Marcosende, 36310 Pontevedra-Vigo, Spain*
[b] *Defense University Center, Naval Academy, University of Vigo, Plaza de España 2, 36920 Marín, Spain*

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This study analyzes the kinetics of sediment sorption on two chemical surfactants (Tween 20 and SDS) and a biotechnologically produced surfactant (obtained from *Lactobacillus pentosus*). Biosurfactants were produced by fermentation of hemicellulosic sugars from vineyard pruning waste supplied as a substrate to *L. pentosus*. Results obtained showed that almost no SDS was adsorbed onto the sediments, whereas Tween 20 and biosurfactants from *L. pentosus* were absorbed after a few minutes. Kinetic models revealed that adsorption of surfactant onto riverbed sediments is governed not only by an intra-particle diffusion model (evaluated by the Weber and Morris model), but also by surface reaction models (evaluated by first, second, third order equations and Elovich equation), showing the best fit when employing the Elovich model. The adsorption properties showed by biosurfactant from *L. pentosus* onto sediments present it as a potential foaming agent in froth flotation.

1. Introduction

Froth flotation is a process for selectively separating hydrophobic from hydrophilic materials and it is based on attachment of the mineral particle to an air bubble. As mineral particles are suspended in water the air bubble has to displace water from the surface of the mineral and make an effective contact, which occurs when the mineral surface is or has been made hydrophobic to an appreciable degree (Rao, 2004). In froth flotation mineral particles are initially stirred with the reagent solution in a mixer, and then transferred into a specifically designed cell for the flotation processes. Then, air is pushed into the cell and dispersed by a rotation impeller. Hydrophobic particles attach to the air bubbles and levitate to the top of the cell, where they are skimmed off and hydrophylic material is collected at the bottom of the cell. Flotation is therefore employed to separate metals and waste, and it is typically employed in mining, wastewater treatment or paper recycling, among others (Altaher et al., 2012; Li et al., 2012; Van Le et al., 2012).

The use of environmental friendly surfactants for froth flotation is an area of great potential. A number of studies include surfactants in the group of Emerging Organic Contaminants (EOCs) (Cantarero et al., 2012; Kuster et al., 2008; Pal et al., 2010), which are biologically active but are not yet regulated or are not commonly regulated. For example, polyfluoroalkyl compounds (PFCs) are known to be persistent and bioaccumulative in the aquatic environment and to have possible adverse effects on humans and wildlife (Ahrens, 2011; Theobald et al., 2012); anionic surfactants derived from naphthenic acids in crude oil are acutely lethal to fishes and other aquatic organisms (Young et al., 2011). Instead, other studies have reported the environmentally safe behaviour of linear alkylbenzene sulfonate (LAS), alkyl ethoxysulfate (AES), and alcohol ethoxylate (AE) for periphyton and macroinvertebrate communities and fish (Belanger et al., 2002; Sanderson et al., 2006). In this sense, the development of new environmental-friendly surfactants for froth flotation processes is a relatively unattended area and with great interest.

This study proposes the use of biosurfactants obtained from lignocellulosic residues after fermentation with *Lactobacillus pentosus*. Biosurfactants are biological compounds that exhibit good surface-active properties, and they are significantly less toxic than synthetic petroleum-based surfactants (Banat et al., 2000). Biosurfactants can be obtained from agricultural waste, such as grape marc or lees (residue from wine-making), so that their production contributes to decreasing the environmental impact of waste disposal. In this study it was tested the adsorption properties onto

* Corresponding author. Defense University Center, Naval Academy, University of Vigo, Plaza de España 2, 36920 Marín, Spain. Tel.: 0034 986812215.
E-mail address: rosa.devesa.rey@uvigo.es (R. Devesa-Rey).

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sediments of a biotechnological biosurfactant produced by *L. pentosus* during fermentation of vine pruning wastes as a substrate. Results were compared with these obtained using chemical surfactants (SDS and Tween 20) and other commercial biotechnological biosurfactant named surfactin. The effect of the adsorption on the surface tension of the solutions containing suspended particles was evaluated. Kinetic processes were also evaluated in order to obtain key parameters that describe the adsorption of surfactants obtained from *L. pentosus* onto sediments. Results obtained will serve as a basis for the development of new environmentally friendly processes for froth flotation.

2. Materials and Methods

2.1. Commercial surfactants

The commercial surfactants used in this study were Tween 20, sodium dodecyl sulphate (SDS) and surfactin. These surface-active compounds were used as reference surfactants for the evaluation of adsorption experiments. Surfactants were added onto sediments at their critical micellar concentration (CMC). CMC is defined as the concentration of surfactants above which they start aggregating into micelles, thus lowering the energy of the interface, expressed as mol L^{-1} or mg L^{-1}.

Tween 20 is a polysorbate surfactant whose stability and relative non-toxicity allows it to be used as a detergent and emulsifier in a number of domestic, scientific, and pharmacological applications. It is a polyoxyethylene derivative of sorbitan monolaurate, and it is distinguished from the other members in the polysorbate range by the length of the polyoxyethylene chain and the fatty acid ester moiety. Tween 20 is a non-ionic surfactant and its CMC in pure water is 1.2×10^{-5} mol/L at 21 °C (Kunchala, 2008).

Sodium dodecyl sulfate (SDS) is an anionic surfactant used in many cleaning and hygiene products. SDS is a highly effective surfactant and is used in any task requiring the removal of oily stains and residues. It is not carcinogenic when applied directly to skin or consumed (CIR, 1983). However, it has been shown to irritate facial skin after prolonged and constant exposure (more than an hour) in young adults (Marrakchi and Maibach, 2006). The CMC of SDS is about 0.0082 mol/L in pure water at 25 °C (Kunchala, 2008).

Surfactin, a surfactant obtained from *Bacillus subtilis*, consists of a peptide loop of seven amino acids and a hydrophobic fatty acid tail and exhibits affinity for monovalent and divalent cations. Surfactin is a powerful biosurfactant, reducing surface tension to 27 mN/m, and its CMC in pure water at 25 °C is 7.5×10^{-6} mol L^{-1}, as determined in the present study (Heerklotz and Seelig, 2001).

2.2. Biotechnologically-produced biosurfactants

Biosurfactant extracted after fermentation of hemicellulosic sugars present in vine pruning, using *L. pentosus*, was obtained following the protocol described in previous works (Bustos et al., 2007; Devesa-Rey et al., 2011c; Moldes et al., 2007; Portilla-Rivera et al., 2009, 2008; Vecino et al., 2012). It can be speculated that biosurfactant produced by *L. pentosus* is not toxic to animal or plants because lactic acid bacteria are considered generally regarded as safe microorganisms. Protocol and methods used to produce this biosurfactant is described in the supplementary material (available online).

The surface activity of biosurfactants produced by the *L. pentosus* was determined by measuring the surface tension of the samples by the ring method (Kim et al., 2000; Vecino et al., 2012) using a KRUSS K6 Tensiometer equipped with a 1.9 cm Du Noüy platinum ring. Measurements were made on triplicate samples to increase the accuracy.

The biosurfactant concentration was determined from a calibration curve including concentrations ranging between 0.29 and 1.35 mg L^{-1} as equivalents of surfactine. The resulting surface tension of the solutions was obtained from the following equation: CMC = (Surface Tension (mN/m)-72.6)/(-8.64). The calibration curve was calculated for a commercial biosurfactant produced by *Bacilli* (surfactin) with different concentrations of biosurfactant solutions, below the critical micelle concentration of known surface tension (Rodrigues et al., 2006). In this range of concentration of biosurfactant, the decrease in surface tension is linear and it is possible to establish a relationship between the biosurfactant concentration and the surface tension (Kim et al., 2000).

2.3. Chemical characterization of sediments

The organic matter content (%) in sediments was determined by oxidation with a mixture of $K_2Cr_2O_7$ and H_2SO_4 and titration with Mohr Salt, following the method proposed by Sauerlandt and modified by Guitián and Carballas (1976). Grain size distribution was measured by the pipette method according to Guitián and Carballas (1976). N was determined by wet digestion with H_2SO_4, by the Kjeldhal method, as described by Guitián and Carballas (1976). Total phosphorus in sediments was determined by acid digestion (HF, H_2SO_4, HCl, 10:1:10) followed by colorimetric determination with molybdenum blue, as described by Murphy and Riley (1962). pH was measured with a portable device (HANNA instruments, HI 9025 microcomputer).

2.4. Surfactant sorption onto sediments

Ten grams of sediments were added to different solutions of surfactants (Tween 20, SDS, surfactin and biosurfactant from *L. pentosus*) at different solid/liquid ratios (1:5; 1:10; 1:20), and the surface tension of the water, once filtered by 0.45 μm, was measured with a KRUSS K6 Tensiometer equipped with a 1.9 cm Du Noüy platinum ring. Surface tension was measured for up to 200 min. Triplicate samples were analyzed and the average values were calculated. The concentration of surfactants used in the sorption experiments was two times higher than the respective CMC.

2.5. Fourier-transform infrared (FTIR) spectroscopy

The sediments used in the surfactant adsorption experiments were analyzed by FTIR to identify the functional groups in the sediment surfaces before and after adsorption. Two mg of the samples were mixed with 100 mg of spectroscopy grade KBr, dried by irradiation with an FTIR lamp, and pressed into pellets. The FTIR spectra were recorded on a Thermo Nicolet 6700 instrument in the absorption mode with a resolution of 4 cm^{-1}, in the range of 4000–400 cm^{-1}. Baseline correction and height normalization were applied to all spectra.

2.6. Evaluation of kinetic parameters

The kinetics of the surfactant adsorption onto riverbed sediments was studied by applying four surface reaction models (i.e. first order, second order, third order, and Elovich) and an intraparticle diffusion model (Weber and Morris) (Table 1).

2.7. Statistical analysis

In order to determine if adsorption results of surfactants employed significantly differ from each other, the student's *t*