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Valorization of tannery wastes: Lipoamino acid surfactant mixtures from the protein fraction of process wastewater

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HIGHLIGHTS

- Valorization of a tannery waste by production of lipoamino acid surfactant mixtures.
- Surfactants obtained show high surface activity and form stable foams and emulsions.
- These lipoamino acid surfactants are readily biodegradable and show low toxicity.
- Potential application of these surfactants as emulsifiers or foaming agents.

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ABSTRACT

The first stages of the transformation process of hides into leather (beamhouse process) generate an important waste in the tanning industry, since a considerable fraction of solubilized proteins ends up in waste water with the corresponding increase in contamination parameters, especially when the process is carried out without hair recovery (hair-pulping process). The objective of this work was the valorisation of this waste (the separated protein fraction) which conveniently hydrolyzed to amino acid level constituted the starting material for the production of biodegradable surfactants. The lipoamino acid surfactants were obtained by acylation of the amino acids from the protein hydrolysate. These surfactants were characterized and their physico-chemical and biological properties evaluated. They exhibit very low cmc values (about 40 mg/L). These surfactants are readily biodegradable and present an aquatic toxicity significantly lower than many common commercial surfactants derived whether from renewable or petrochemical feedstock. The mixtures of surfactants obtained are able to form oil/water emulsions that remain stable for at least 1 year. The results obtained in this work confirmed that it is possible the production of biodegradable and efficient lipoamino acid surfactant mixtures from the protein fraction present in beamhouse process wastewaters. This study constitutes a promising approach for the reduction of the pollution load from industrial tannery wastes and its valorisation as raw material for the production of surfactants with excellent environmental properties and good technical properties.

1. Introduction

Any industrial activity generates wastes to a greater o lesser extent and the growing demands of environmental respect in the production processes force companies to reuse the most of their wastes. Besides the respect for the environment, the reuse of wastes is of great importance and interest also from an economical point of view since the lower the amount of wastes generated, the lower the management cost in specialized plants. Moreover, the reuse of wastes can represent a sustainable solution to the lack of raw material to be used for the production of energy, fuel and chemicals than can be integrated again in the industry. The production of high added value materials as bio-products, nanomaterials and bio-polymers starting from wastes underlines, even more, the interest for their reutilization [1–5].

The leather industry generates a considerable amount of wastes. However, the studies dealing with its potential valorization are scarce [6,7]. According to Sykes and Corning [8], each tonne of raw hide yields 200 kg of finished leather, 50 m^3 of contaminated wastewater and the rest are solid wastes. Therefore, only 20% is transformed into useful material. According to Aloy [9], the main pollution load is produced in the beamhouse operation (stages before tanning process): 83% of BOD_5 (five-day biochemical oxygen demand), 73% of COD (chemical oxygen demand) and 76% of toxicity. In another study, Portavella [10], states that for every 100 kg of

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dry raw sheepskin from Catalonia, 15 kg of solubilized proteins that are more or less structured (keratins, albumins, globulins, glycoproteins, etc) and that contain nearly 18% nitrogen will end up in waste water following beamhouse operations. Portavella [11] found that 70% of COD from the beamhouse operations is due to the skins themselves and that only 30% comes from added chemical products. Although the values of the parameters may vary as a function of the type of raw material treated, there is no doubt that the beamhouse operations produced most contamination, much of which is due to the solubilized components (proteins) of hides or skins. Therefore, separation of the dissolved protein fraction represent not only a way to significantly reduce the contamination of beamhouse wastewaters [12], with the economic savings this entails, but also provides a residue, the separated protein fraction, which conveniently hydrolyzed to amino acid level, could be used as the raw material for the production of surfactants. Protein hydrolysates from different sources have been used with the same aim [13,14]. Other possible applications of the separated protein fraction from the beamhouse tannery process could be the production of liquid leaf fertilizer, solid fertilizer for soils or retanning agents for tannery. However, these possible applications will be the subject of future works.

The use of this liquid waste of the leather industry as starting material for the production of surfactants is of great interest for several reasons: (i) to reduce water pollution load, (ii) to reduce the cost of waste disposal and (iii) to provide an appropriate source of renewable raw materials not derived from petrochemical feedstocks.

Amino acids are a very interesting raw material for the chemical preparation of environmentally friendly surfactants [15]. Twenty different α-amino acids are commonly present in proteins. Amino acid based surfactants are biodegradable and biocompatible compounds that can be prepared using natural compounds as fatty acids and amino acids as starting material [16,17]. Also, several commercial firms offer the possibility of finding amino acid surfactants on the market (series Amilite® from Ajinomoto; series Aminofoam™ from Croda; series Perlastan® from Schill&Seilacher, series Lamepon® from Basf; N^{α}-lauroyl ethyl ester (LAE) from Lamirsa S.A. [18], etc).

One interesting strategy to reduce the tannery industrial pollution load as well as to obtain environmentally friendly compounds is to synthesize surfactants using the amino acids obtained by acid hydrolysis of the protein fraction recovered from the wastewater of soaking, unhairing-liming and conditioning operations of a hair-pulping (with hair destruction) beamhouse process. In the present work lipoamino acid surfactant mixtures using as raw material the protein fraction were obtained and their physico-chemical and biological properties were investigated. This study constitutes a promising approach to the reduction of the pollution load of industrial wastes and its possible reutilisation as starting material for surfactant production.

2. Experimental

2.1. Materials

Dodecanoyl chloride, decanoyl chloride, dodecanoic acid, decanoic acid, pyreno, and squalane were purchase from Fluka. L-lysine, L-serine, L-proline, L-glutamic acid, glycine, L-leucine, L-arginine and sodium dodecyl sulfate were purchase from Sigma. Acetonitrile was purchase from Fisher Chemical. Acetone, n-hexane and ethanol absolute were purchase from Panreac. Trifluoroacetic acid, n-decane and hydrochloric acid were purchase from Merck. Sodium hydroxide was purchase from Carlo Erba.

2.2. Methods

2.2.1. Preparation of the amino acid mixture from the protein fraction

The protein fraction used in this work as starting material was obtained by acid precipitation (adding 2 M sulfuric acid solution up to the isoelectric point) [19] of the effluents of the unhairing-liming process and subsequent washings in a hair-pulping beamhouse process of hides. This protein fraction was subjected to a degreasing process with dichloromethane during 5 h and subsequently hydrolyzed with 6 N HCl during 24 h. The amino acid mixture was quantitatively determined in accordance with the AccQ-Tag Waters method [20] with previous derivatization with 6-AQC. A Waters 600 model with a 2487 UV detector was used for HPLC analyses.

2.2.2. Synthesis of surfactants from the amino acid mixture

Surfactants were obtained by the introduction of a fatty acid residue, as an acid chloride, to the amino acids obtained from the protein hydrolysate in a strong alkaline aqueous medium. The mixture of amino acids obtained was dissolved in acetone/water (34/66) and NaOH was added until a pH of 10. This solution was filtered to remove the insoluble residue present in the medium. The residue was analyzed by thin-layer chromatography in order to check the absence of amino acids. Next, dodecanoyl chloride or decanoyl chloride were added dropwise maintaining the pH at 10 with NaOH. After adding the acid chloride, the reaction mixture was kept at −10 °C for 3 h. The progress of the reaction was checked by HPLC. Solvent was eliminated using a rotary evaporator and the sample was freeze-dried. Acylation reactions were carried out for different amino acid/acid chloride molar ratios. In some cases, salt formed in the reaction was removed with dry ethanol and subsequent filtration. In other cases, this purification process was not carried out (see Table 2).

2.2.3. Synthesis of pure N^{α}-acyl amino acid surfactants

A series of standard N^{α}-acyl amino acid surfactants was prepared for the characterization of the surfactants synthesized in this work. The standard surfactants were prepared with those amino acids that were present at the highest percentage in the starting protein fraction (glycine, leucine, proline, arginine, glutamic acid, lysine and serine). Dodecanoyl chloride was selected as the acylating agent. The reaction was carried out under the above mentioned conditions. 0.5 g of pure amino acid were taken and the reaction was carried out at the 1:1 ratio. Once obtained, the surfactants were purified by repetitive washings with n-hexane. For identification purposes, the purified standard surfactants prepared for each amino acid were added one by one to the final product of the acylation reaction. HPLC calibration curves were prepared for every pure N^{α}-acyl amino acid surfactant and then, the concentration of the major components in the mixture was calculated.

2.2.4. High performance liquid chromatography (HPLC)

To check the progress of the acylation reaction and for identification purposes, HPLC analyses were performed on a VWR-Hitachi ELITE LaChrom system which consisted of an injection valve fitted with a 20 μl loop, and pump L-2200 and a UV–Vis detector L-2400 at 215 nm wavelength. A Lichrocart 250-4, lichrospher 100 CN (5 μm) column was used at room temperature. The flow-rate through the HPLC column was 1.0 ml/min. Elution was performed in a gradient system of water/acetonitrile. Eluent A was 0.1% (v/v) trifluoroacetic (TFA) in water, and eluent B was 0.085% TFA in water/acetonitrile 1:4. The initial composition A/B of the gradient was 75/25 (v/v), changing over 24 min to a final composition of 5/95.