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Biosurfactant microfoam: Application in the removal of pollutants from soil

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ABSTRACT

Surfactant solutions are frequently used in environmental decontamination. More recently, the use of microfoams (MF) has been investigated as an alternative to the use of surfactant solutions, since MF have the advantage of improving the contact with the contaminated environment due to their surface properties. The aim of this study was to remove petroleum and diesel oil from soil using microfoams of biological and chemical surfactants and to compare their efficiencies in removing the contaminants. For this purpose, a sandy soil contaminated with 5% (w/w) of petroleum and 5% (w/w) of diesel oil was used. After 72 h, the soil samples were washed with solution or microfoam of two chemical surfactants (sodium dodecyl sulfate – SDS and cetyltrimethylammonium bromide – CTAB) and one biosurfactant (rhamnolipid – RML). At the end of the remediation process using SDS or RML microfoams, petroleum removal efficiencies of 44.26 ± 0.54% and 42.12 ± 0.61% were obtained, respectively; for the soil contaminated with diesel oil, the removal efficiency using MF of SDS and RML was 62.90 ± 0.68% and 44.75 ± 1.22%, respectively. For both contaminants, either CTAB solution or MF had low removal efficiency. Probable mechanisms involved in the remediation process were solubilization for petroleum and mobilization for diesel oil.

Introduction

The pollution of different environmental compartments (water, soil and air) is a consequence of industrialization and human activities [1]. Soil is frequently contaminated by crude oil and its derivatives, which is difficult to treat because oil has a low solubility in water, and these compounds tend to adsorb onto the porous matrix. For this reason, such pollutants can be treated with surfactants, which are amphiphilic compounds having both hydrophilic and hydrophobic groups. Surfactants tend to spread out at the interface between fluid phases with different degrees of polarity (oil/water and water/oil), forming an ordered molecular film at the interface, which reduces the interfacial tension of immiscible phases [2,3].

Researchers are particularly interested in microbial surfactants, called biosurfactants, due to their advantages over synthetic products, such as low toxicity, environmental compatibility, biodegradability and production from renewable sources.

Biosurfactants are divided into different classes, the most studied of which are the glycolipids, carbohydrates combined with long chains of aliphatic acids or hydroxy aliphatic acids. The most important of the glycolipids are the rhamnolipids, produced from fermentation processes in the presence of the bacterium *Pseudomonas aeruginosa*.

Rhamnolipids have been considered for soil remediation in the biotechnological processes of decontamination [4–6]. However, they may also be employed in physical processes to remove contaminants such as petroleum and/or its derivatives [7,8], or heavy metals [9,10]. Rhamnolipid and other surfactants or biosurfactants are generally used in the form of an aqueous solution for the remediation of affected areas [7,8,11]. However, microfoam (or colloidal gas aphrons) is a promising alternative for this, because it contains multiple layers of surfactants and liquids surrounding the gas bubble; the fact that they have a small size enables them to penetrate the soil interstices to carry away the contaminant [12,13].

Given this context, the aim of this study was to remove petroleum and diesel oil from a contaminated soil by using chemical or biological surfactants in solution or in microfoam form, comparing their efficiencies in the removal of pollutants and

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elucidating the possible mechanisms involved in the remediation process.

Materials and methods

Soil

Soil samples were kindly donated by the Research Center Leopoldo Américo Miguez de Mello (CENPES/PETROBRAS) and the Center for Mineral Technology (CETEM). Due to its percentage of sand (82%), clay (10%) and silt (8%), the soil was classified as sandy.

Contaminants

The contaminants used in this study were petroleum and diesel oil. Petroleum was kindly provided by CENPES/PETROBRAS and diesel by the Center for Research and Characterization of Petroleum and Fuel (COPPEComb). Both pollutants were used in the proportion of 5% (w/w) relative to the soil. Considering the types of hydrocarbons present in the petroleum, it was classified as paraffinic oil.

Surfactants

Chemical surfactants (SDS and CTAB) were supplied by VETEC. Rhamnolipid, used without purification, was donated by the Microbial Biotechnology Laboratory (LaBim) of the Federal University of Rio de Janeiro, produced by *P. aeruginosa* PA1 in medium containing the following composition: 1.0 g L^{-1} of $NaNO_3$, 3.0 g L^{-1} of KH_2PO_4, 7.0 g L^{-1} of K_2HPO_4, 0.2 g L^{-1} of $MgSO_4 \cdot 7H_2O$, 5% yeast extract, 5% peptone and 3% glycerol. In order to characterize the surfactants, their surface and interfacial tension were measured as well as the adsorption onto porous medium and the stability of their microfoams.

Table 1 presents the three surfactants investigated in this work, their chemical nature and evaluated concentrations. Aqueous solutions of all surfactants were employed at the critical micelle concentration (CMC). For RML, a concentration 10 times greater than its CMC was also employed, in order to evaluate its performance in the remediation process.

Table 1
Characteristics of the surfactants used in this study.

Surfactant	Concentration (g L^{-1})	Chemical nature
Sodium dodecyl sulfate (SDS)	2.30	Anionic chemical surfactant
Cetyltrimethylammonium bromide (CTAB)	0.34	Cationic chemical surfactant
Rhamnolipid (RML)	0.10 1.00	Anionic biological surfactant

Measurement of surface and interfacial tension

The measuring of surface (ST) and interfacial (IT) tension of the surfactant solution samples was carried out with a tensiometer (KSV Sigma 70 Tensiometer) using the Du Noüy method. To measure the interfacial tension, *n*-hexadecane was added as the organic phase.

Adsorption of the surfactant onto the soil

To evaluate the adsorption of surfactants onto the soil, surfactant solutions were used at concentrations 20% below the CMC, to assure the presence of monomeric species only. Thus, 0.08 g L^{-1} of RML, 1.84 g L^{-1} of SDS and 0.288 g L^{-1} of CTAB solutions were used; all solutions were adjusted to pH 6.5.

The tests were carried out in 15 mL flasks under stirring (50 rpm). Different amounts of soil for the same volume of surfactant solution (10 mL) were employed. After 10 min (time required for equilibrium to be achieved) the flasks were centrifuged, and the supernatant was used to measure the surface tension. In this experiment, the method used to measure the surface tension was the pendant drop (OCA Goniometer Data-Physics 15 EC), since it requires a much lower volume of sample when compared to the Du Noüy method. Upon surfactant adsorption, the surface tension of the aqueous solution increases; the difference between the surface tension of the initial solution and after equilibrium is proportional to the amount of surfactant adsorbed at the soil.

Stability of microfoams (MF)

MF stability was evaluated by determining its half-life (time for draining half of the microfoam liquid content). The process of obtaining the MF was based on the study by Couto et al. [13]. Therefore, a high-speed homogenizer (Ultra Turrax T25) was employed at 15,000 rpm for 3 min. The effect of the pH on microfoam stability was also investigated (at pH 5.0, 6.5 and 8.0).

Soil remediation

First, soil was contaminated by hand-stirring of the soil with 5% (w/w) of diesel oil or petrol, for 72 h. After that time, the remediation column method was employed (Fig. 1), which consisted of filling an acrylic column with impacted soil and percolating it with MF at a flow rate of 100 mL min^{-1} in a descending flux with the aid of a peristaltic pump. MF was produced in line with the column, using the homogenizer at

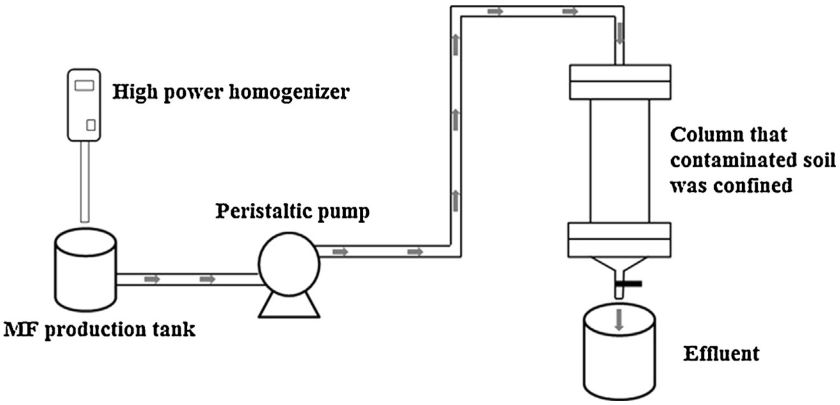

Fig. 1. Schematic diagram of the remediation system.