EFFECT OF SOIL LOADING AND pH DURING BATCH SOLVENT EXTRACTION OF FLUORENE FROM SOIL USING A LIPOPETIDE BIOSURFACTANT AQUEOUS SOLUTION

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ABSTRACT
In this work a lipopeptide biosurfactant, obtained from an agro industrial residue, was used as washing agent to remove fluorene from soil. Soil extraction carried out with biosurfactants is more environmental friendly than those extraction based on volatile solvents or chemical surfactants. Thus, in order to find the best operational conditions, the effect of soil loading and pH during batch solvent extractions were studied by using different solid/liquid ratios and pH. We found that generally a decreasing soil:solution ratio resulted in a higher extraction efficiency. Thus when the solid/liquid ratio was fixed at 1/50, 100 % of fluorene was extracted from soil at pH 6.

Keywords: biosurfactants, lipopeptide, soil, PAHs, bioremediation

1. INTRODUCTION
Polycyclic aromatic hydrocarbons (PAHs) compounds are considered as carcinogenic, mutagenic, and teratogenic compounds [1,2]. Thus, in 2008, 28 PAHs have been identified as priority pollutants by the National Waste Minimization Programme, in a project funded by US Environment Protection Agency [3].

In previous works [4], a biosurfactant obtained from L. pentosus was used to improve the spontaneous biodegradation of octane in soil; observing that after 15 days of starting the bioremediation experiment, biosurfactants from L. pentosus reduced the concentration of octane in the soil to 58.6 % or 62.8 %, for soil charged with 700 and 70,000 mg/kg of hydrocarbon respectively. It can be speculated that the removal of octane from soil should be easier than the elimination of fluorene because octane is linear hydrocarbon with a low molecular weight, whereas fluorene is a polycyclic aromatic hydrocarbon.

The aim of this research was to evaluate the feasibility of biosurfactants contained in an agricultural residue for the removal and biodegradation of polycyclic aromatic hydrocarbons (PAHs) from contaminated soil. Batch extraction experiments were carried using different soil loadings and pH.

2. MATERIALS AND METHODS
Contamination of soil
Farming soil, collected from a 0-20 cm deep layer in Carballo-Coruña (Spain) was contaminated with 500 mg/L of fluorene. Before contamination, soil was sieved at a particle size lower than 1mm. Following, soil samples, 2.5 g, were contaminated with 1 mL of a solution containing 1.25 mg of fluorene/mL of acetone. Fluorene was dissolved in acetone in order to produce an homogeneous distribution of fluorene in soil. Following, the contaminated soil, at a final concentration of 500 mg/L of fluorene, was stirred vigorously for 30 min to promote homogeneous distribution of fluorene. Soil samples were left to rest for 48 h at 28 °C to eliminate acetone in a shaker at 150 rpm.
**Elemental analysis of soil**

Soil was analyzed using a Fisons-EA-1108 CHNS-O (Thermo Scientific). Previously to analysis soil was submitted to thermo catalytic decomposition. Analyses were carried out by triplicate.

**Desorption of fluorene from soil within a water-soil-biosurfactant system**

Soil samples (0.5 to 2.5 g) were saturated with 25 mL of an aqueous solution, containing a lipopeptide, within pH 3-6.

Following, the water-soil-biosurfactant system was kept under agitation at 150 rpm for 24 h. The soil sample was removed from the solution by centrifugation at 1350 x g for 30 min. To determine the amount of fluorene removed from the samples, the concentration of fluorene in the supernatant was analyzed by spectrophotometry at 254 nm. The wavelength was chosen based on the maxima absorbance values of fluorene. The percentage of fluorene eliminated was calculated based on the content of initial fluorene applied to the soil and the final fluorene concentration in the aqueous phase. Soil samples, also were washed with 25 mL of water in absence of biosurfactant and the percentage of fluorene extracted, was used as control.

Because fluorene has low solubility in water the calibration curve was obtained by dissolving fluorene in acetonitrile: water (1:1). Thus, the aqueous supernatants from samples also were dissolved in acetonitrile: water (1:1) before measuring it in the spectrophotometer at 254 nm.

**3. RESULTS AND DISCUSSION**

The maxima concentration of PAHs that can be achieved in the solvent solution is 10 mg/L; 30 mg/L and 50 mg/L corresponding to the assays containing 0.5 g, 1.5 g and 2.5 g of soil respectively. Table 1 shows the solid/liquid ratio used in the different assays as well as the maxima concentration of fluorene that can be achieved in the aqueous phase.

<table>
<thead>
<tr>
<th>Amount of soil (g)</th>
<th>Solid/liquid ratio (g/mL)</th>
<th>Maxima concentration of fluorene in the aqueous phase (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>1/50</td>
<td>10</td>
</tr>
<tr>
<td>1.5</td>
<td>1/16.6</td>
<td>30</td>
</tr>
<tr>
<td>2.5</td>
<td>1/10</td>
<td>50</td>
</tr>
</tbody>
</table>

Results obtained in this work, showed the ability of biosurfactant to increase the apparent solubility of fluorene in the aqueous phase, and significantly enhanced its biodegradation within 24 hours at the lower solid/liquid ratio (1/50).

The extraction of fluorene to the aqueous phase, containing the biosurfactant, was found to be rapid (within 1 h). Figure 1 shows the percentage of fluorene extracted after one hour at the lower, intermediate and higher soil loading, at different pH: 3, 4, 5, and 6. It can be observed that 1/50 solid/liquid ratio rendered the maximum percentage of extraction (100%) in comparison with higher solid liquid ratios, where the maximum percentage of extraction was about 46 % and 27 % using 1/16.6 at pH 6 and 1/10 solid/liquid ratio at pH 6 respectively. It is important to point out that the maximum percentages of extraction were achieved at pH 6 in all the experiments. These results are in concordance with those reported by other authors. Thus, Pannu et al. [5] found that a pH within the range of 4–8 highest oil recovery from soil was achieved (more than 90%); whereas the highest PAH extraction efficiency occurred at pH of 6–7.

In addition Figure 2 shows the concentration of fluorene in the aqueous phase containing the lipopeptide biosurfactant after 24 hours of starting the extraction process. It was observed that lower solid/liquid ratios not only improved the extraction of fluorene from soil, but also increased the biodegradation or elimination of PAH from the aqueous phase after longer bioremediation times.

In this work, percentages of fluorene extraction were similar to those obtained by other authors using synthetic surfactants like Triton X-100, Tween 80 and Brij 30 [6-8].
4. CONCLUSIONS

The results from this study indicate that aqueous solution containing biosurfactants obtained from an agricultural residue is appropriate as washing agent as well as biodegradation enhancer for the detoxification of PAHs contaminated soil. The extraction and biodegradation of PHAs from soil was increased using low solid/liquid ratios around: 1/50 (g of soil/ mL of biosurfactant aqueous solution).

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5. REFERENCES


