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Hybrid sequential treatment of aromatic hydrocarbon-polluted effluents using non-ionic surfactants as solubilizers and extractants

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HIGHLIGHTS

- Physico-biological treatment based on ATPS led to very high remediation levels.
- Treatment train was able to remove more than 97% of PAHs.
- The organic salt potassium citrate proved to be an effective salting out agent.
- Concomitant use of non-ionic surfactants as solubilizers and extractants.

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ABSTRACT

A treatment train combining a biological and a physical approach was investigated for the first time in order to remediate polycyclic aromatic hydrocarbons (PAHs)-polluted effluents. Given the hydrophobic nature of these contaminants, the presence of non-ionic surfactants is compulsory to allow their bioavailability. The presence of these surfactants also entails an advantage in order to ease contaminant removal by the formation of aqueous two-phase systems (ATPS). The segregation ability of environmentally benign salts such as potassium tartrate, citrate, and oxalate was discussed for extracting phenanthrene (PHE), pyrene (PYR), and benzo[a]anthracene (BaA). The biological remediation efficiency reached circa 60% for PHE and PYR, and more than 80% for BaA. The coupling of ATPS subsequent stage by using potassium citrate allowed increasing the total PAH remediation yields higher than 97% of PAH removal. The viability of the proposed solution was investigated at industrial scale by using the software tool SuperPro Designer.

1. Introduction

The current life standards and environmental awareness urge petrochemical industry to give its attention to sustainable growth. The rapid industrialisation has resulted in the depletion of natural resources and has caused an adverse impact on ecosystems. Nowadays, there is a growing interest in the effect of hazardous wastes generated from petrochemical processes, since complex mixtures of hydrocarbons are often identified on soil–water environment as common contaminants. Among them, PAHs stand out as highly toxic, mutagenic, genotoxic and carcinogenic compounds (Simarro et al., 2011; Zhong et al., 2011). They are introduced in the environment through different natural and anthropogenic activities, and 16 of them are considered as priority pollutants (Zhao et al., 2009; Bautista et al., 2009) by the US Environmental Protection Agency (USEPA).

Their environmental risks are mostly due to their inherent properties such as persistence, low vapour pressure, high hydrophobicity and thermodynamic stability of the aromatic ring (Cao et al., 2009). The presence of pollutants with a recalcitrant nature in the environment has promoted an intense research effort focused on the development of more effective technologies for the removal of contaminants from industrial locations and polluted effluents. These treatments have been classified in three main categories: physical (volatilisation, photolysis, adsorption, filtration and electro remediation), chemical (oxidation, photocatalysis and coagulation–flocculation) and biological (biosorption or biodegradation) (Kim and Lee, 2007; Janbandhu and Fulekar, 2011).

Usually, the application of one single technique does not allow achieving high remediation levels, and a promising strategy consist in combining biological and physical methods to form efficient treatment trains. The foundation for betting in this approach is

motivated in the fact that persistent hydrophobic compounds possess a limited bioavailability (Kanaly and Harayama, 2000). To overcome this drawback, the addition of surface active compounds appears as one of the acceptable strategies licensing the increase of solubility by decreasing the interfacial surface tension between the hydrophobic contaminant and the soil–water interphase. Among the typical surfactants used, Tween and Triton families have been highlighted in many studies, as a non-toxic and efficient alternative (Bautista et al., 2009; Ulloa et al., 2012a). Therefore, the biological treatment is facing a biphasic medium composed of an organic phase (PAH and surfactant) and an aqueous phase (with salts and organic matter dissolved). This biphasic nature made us to bet in the coupling of a physical method based on a liquid–liquid equilibrium strategy to yield high levels of PAH removal.

The liquid–liquid equilibrium makes up one of the appealing alternatives (García-Chavez et al., 2012; Domanska et al., 2006) and the extraction by means of aqueous two-phase systems (ATPS) has become a viable, sustainable and competitive alternative in the field of separation processes. The reasons behind this attractiveness are the low energy consumption and costs, rapid phase disengagement, and high efficiencies in the separation of different kinds of biomolecules and chemicals (Freire et al., 2012).

The basis of this strategy lies in merging two hydrophilic polymers, or salts, or a polymer and a salt, with water, leading to a biphasic system over a certain concentration (Deive et al., 2011a,b,c). This segregation is the result of a competitive interplay between salts or polymers and the water molecules and multifarious interactions between polymers and salts. One of the novel alternatives of ATPS are based on the use of non-ionic surfactants such as Tween and Triton families (Ulloa et al., 2012b; Álvarez et al., 2012a,b).

In this work, we propose a feasible treatment train composed of a previous biodegradation process by the use of *Pseudomonas stutzeri*, followed by a non-ionic surfactant-based ATPS. The search for more sustainable process included the analysis of the solubility curves obtained for three potassium organic salts (citrate, oxalate and tartrate) in the presence of aqueous solutions of Triton surfactants. Merchuk, Othmer–Tobias and Bancroft equations served our goal to properly characterise the proposed ATPS. Finally, a commercial software (SuperPro Designer) was used to simulate the treatment of a PAHs-polluted industrial effluent.

2. Methods

2.1. Chemicals

Phenanthrene (PHE), pyrene (PYR) and benzo[a]anthracene (BaA) (purity higher than 99%) used in degradation experiments were purchased from Sigma Aldrich (Germany). PAHs stock solutions were 5 mM in acetone.

Potassium citrate ($K_3C_6H_5O_7·H_2O$), potassium tartrate ($K_2C_4H_4O_6·0.5H_2O$), potassium oxalate ($K_2C_2O_4·H_2O$), and the non-ionic surfactants Triton X-100 and Triton X-102 were supplied by Sigma Aldrich (Germany). All chemicals used were at least, reagent grade or better.

2.2. Microorganism and culture conditions

Bacterium *P. stutzeri* CECT 930 was obtained from the Spanish Type Culture Collection (ATCC 17588). Culture medium was composed of (g/L): $Na_2HPO_4·2H_2O$ 8.5, KH_2PO_4 3.0, NaCl 0.5, NH_4Cl 1.0, $MgSO_4·7H_2O$ 0.5, $CaCl_2$ 14.7×10^{-3}. This medium also contained trace elements as follows (mg/L): $CuSO_4$ 0.4, KI 1.0, $MnSO_4·H_2O$ 4.0, $ZnSO_4·7H_2O$ 4.0, H_3BO_3 5.0, $FeCl_3·6H_2O$ 2.0.

2.3. Biodegradation reaction

Biodegradation cultures were carried out in 250-mL Erlenmeyer flasks with 50 mL of medium containing 1% w/v of the non-ionic surfactant Triton X-100, and 2% v/v of acetone (used as solvent to prepare the contaminant solution, due to its low solubility in aqueous media), following the strategy proposed by Moscoso et al. (2012). The flasks, capped with cellulose stoppers, were inoculated (3%) with previously obtained cell pellets, and incubated in the darkness for 15 days in an orbital shaker (INNOVA 4400 New Brunswick) at 37 °C, initial pH 8.0, and 150 rpm. Samples were withdrawn daily to monitor PAH biodegradation and cell density. All samples were analysed in triplicate, and the biodegradation experiments were repeated to check the reproducibility. The presented data in tables and figures are mean values. All the material used was made of glass in order to avoid contaminants losses due to sorption.

2.4. Aqueous two-phase systems

The phase diagrams of the ATPS were carried out by means of the cloud point titration method (Albertsson, 1986) at 25 °C. A given amount of organic salt, determined by weighing, was added to the different surfactant-based aqueous solutions until the detection of turbidity, and then followed by the drop-wise addition of ultra-pure water until a clear monophasic region was achieved. The system was always operating under constant stirring. The ternary system compositions were determined by the weight quantification of all components within an uncertainty of $\pm 10^{-4}$ g. The temperature was controlled with a F200 ASL digital thermometer with an uncertainty of ±0.01 K.

The tie-lines (TLs) determination started with the addition of a potassium-based organic salt (citrate, oxalate and tartrate) to an aqueous solution of Triton X-100 or Triton X-102, up to achieve a point within the immiscibility region. The mixture was left to settle for 24 h to ensure a complete separation of the layers, after a vigorous stirring at room temperature. The estimated uncertainty in the determination of Triton and salt phase mass compositions is less than 2×10^{-4}. The TLs data were determined by solving a system of four equations: two of them consider the relationship between the upper phase and the overall system mass composition by means of the lever arm rule and the others are based on Merchuk expression for top and bottom phases.

2.5. Analytical methods

2.5.1. Cell growth determination
Biomass concentration was measured by turbidimetry at 600 nm in a Unicam Heλios β spectrophotometer, and the obtained-values were converted to grams of cell dry weight per litre using a calibration curve.

2.5.2. PAH analysis
PHE, PYR and BaA concentrations in the culture media were analysed by reversed-phase high performance liquid chromatography (HPLC) equipped with a reversed phase C8 column (150 × 4.6 mm, 5 μm particle size, Zorbax Eclipse) with its corresponding guard column. The HPLC system was an Agilent 1100 equipped with a quaternary pump and photodiode array UV/Vis detector (252.4 nm). 5 μL of filtered cultivation media (through a 0.45 μm Teflon filter) were injected and then eluted from the column at flow rate of 1 mL min^{-1} using acetonitrile:water (67:33) as mobile phase. The temperature was maintained at 25 °C.