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Research Paper

Sorption and desorption of 17α-ethinylestradiol onto sediments affected by rhamnolipidic biosurfactants

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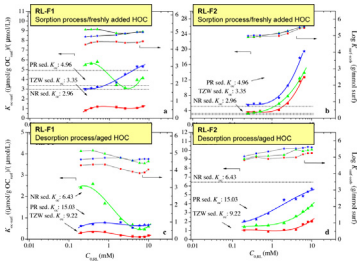
HIGHLIGHTS

- We compared EE2 distribution derived by mono- and di-rhamnolipids.
- Dirhamnolipids facilitated EE2 mobilization within sorption and desorption processes.
- EE2 partitioning to sorbed monorhamnlipids was influenced by sorbate age.
- A conceptual model was used to estimate rhamnolipid-HOC-sediment interactions.
- Rhamnolipid type is an important factor influencing organic distribution.

GRAPHICAL ABSTRACT

This study estimated and compared the influence of mono- and di-rhamnolipids on HOC distribution within different sediment-water sorption and desorption systems.



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ABSTRACT

Many studies have addressed the desorption and mobilization performances of sorbed contaminants affected by different rhamnolipidic biosurfactants. Study results have been mixed and complicated. Rhamnolipids are always microbial produced with variable homologues. In this study, two representative rhamnolipidic fractions (i.e., RL-F1 and RL-F2, which are mono- and di-rhamnolipids, respectively) were investigated and compared to determine their influence on 17α-ethynylestradiol (EE2) distribution within sediment-water sorption and desorption systems. In general, the coexistence of RL-F1 and EE2 enhanced EE2 sorption in a wider monorhamnolipidic dosage range when freshly treated sorbate was used. The sorbed EE2 concentration decreased as the RL-F1 dosage increased in the aged sorbate desorption systems. However, RL-F2 facilitated EE2 mobilization in both sorption and desorption processes. Experimental data were estimated using a conceptual model that considered the sorbed rhamnolipids and aqueous micelles for organic partitioning. The model results indicated that the rhamnolipid type is an important factor influencing organic distribution, in addition to sorbate aging process and sediment characteristics. The use of a rhamnolipidic mixture containing both mono- and di-rhamnosyl components may not achieve the desired effect when the biosurfactant-enhanced mobilization or immobilization approach is selected. These results are significant for selecting and applying rhamnolipids to remediate contaminants.

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1. Introduction

Rhamnolipids are microbial produced surfactants, and have been broadly investigated for their potential to enhance hydrophobic organic compound (HOC) bioremediation and biodegradation. They are beneficial because of their high specificity, surface activity, biodegradability, and biocompatibility compared to chemical surfactants [1–3]. Due to microbial metabolic synthesis, rhamnolipids are typically produced as homologue mixtures that differ in the number of rhamnose moieties and in their fatty acid chain composition, which may or may not be saturated. To date, 60 rhamnolipidic homologues and congeners have been found to be produced by different microorganisms [4].

The sorption and desorption behaviors of HOC when treated by surfactants play an important role in bioremediation. Many studies have addressed the desorption and mobilization performances of sorbed contaminants affected by different rhamnolipidic products; however, the results have been mixed and complicated. For example, Mata-sandoval et al. [5] reported the influence of Triton-100 and a rhamnolipid mixture from *P. aeruginosa* UG2 on the desorption of three pesticides from soils. The rhamnolipids failed to effectively support the desorption of atrazine, and the sorbed rhamnolipids was a better sorbent for pesticides than Triton-100. However, in a different investigation by Chen et al. [6], HOC partitioning into aqueous rhamnolipidic micelles was found to be a major contributor, facilitating contaminant transport and mobilization using a crude rhamnolipidic extract from a *P. aeruginosa* ATCC 9027 strain.

The diversity of rhamnolipids produced by different microbial species may allow specific microbial products to be selected for specific applications. However, despite several studies, the dominance of individual homologues and the relationship between their functional effects and different rhamnolipids are not well understood when applied to HOC remediation. A previous study by Zhang et al. [7] evaluated the solubilization and biodegradation of phenanthrene when exposed to mono- and di-rhamnolipids. Noordman et al. [8] investigated the adsorption of a multicomponent rhamnolipidic surfactant onto soil, finding that individual components of the rhamnolipidic mixture altered adsorption in soil. The resulting composition change of such biosurfactants due to varied adsorption may affect the surfactants' solubilizing or mobilizing properties, which could potentially complicate HOC remediation. This highlights the need for a more in-depth study of the sorption and desorption behaviors associated with HOC remediation for rhamnolipidic homologues.

Several studies have investigated the use of rhamnolipid biosurfactants in mobilizing and bioremediating alkanes, PAHs, and halogenoalkanes, which are all extremely hydrophobic organic compounds [2,3,7,9,10]. Few studies have focused on the ability of rhamnolipids to mobilize polar hydrophobic pesticides [5] and antimicrobial agents [11,12]. These polar hydrophobic contaminant molecules are differentiated from hydrocarbons, as they have nonuniform molecular structures and hydrophilic groups in their molecules and/or complex structures. These characteristics lead hydrophobic but polar contaminants to produce varied and complex behaviors within surfactant-soil systems.

In this study, the emerging contaminant synthetic estrogen 17α-ethynylestradiol (EE2) was used as a model polar hydrophobic substance due to growing concern about its environmental risks. EE2 posed significant potential hazards when transferred from water into a matrix such as sediment through sorption and bioaccumulation due to its relatively high hydrophobicity [13]. Field studies have indicated that sediment served as a storage sink for estrogen contaminants, and the presence and behavior of estrogens in solid environmental matrices were of potential hazards [14]. It was reported that the presence of a dodecylbenzesulfonic surfactant significantly reduced the partition coefficients for estrogen sorption onto estuarine sediment [15]. Our previous study also demonstrated that the incorporation and combination of EE2 molecules with aqueous micelles of mono- and di-rhamnolipids differed, based on their respective micellar morphologies, which are the most commonly isolated rhamnolipids derived from *Pseudomonas* spp. [16].

Therefore, this study compared the performances of both mono- and di-rhamnolipids in EE2 sorption and desorption within sediment-water systems. The study also investigated the effect of sediment characteristics and estrogen aging process on rhamnolipidic performance. A conceptual model that considered the sorbed rhamnolipids and aqueous micelles for HOC partitioning was developed and estimated using the experimental data. The insights provided by the study enables a better understanding of the impact of rhamnolipids on distribution of hydrophobic but polar contaminants in sediment and water.

2. Materials and methods

2.1. Chemicals

RL-F1 and RL-F2 consisting of primarily mono- and di-rhamnolipids were separated and purified from a crude product obtained from *P. aeruginosa* mutant strain MIG-N146, using a previously reported protocol [16,17]. Table 1 lists selected physicochemical properties of RL-F1 and RL-F2. The substance 17α-ethynylestradiol (EE2) with a purity exceeding 98% was purchased from the Sigma Chemical Company (St. Louis, MO, USA). The structure and properties of EE2 are shown in the Supplemental material, Table S1. The water solubility of EE2 was reported to be approximately 3–5 mg/L [14,16,18]. Organic solvents, including methanol and acetonitrile, were chromatographically pure (Sigma, USA). Deionized water (<18.0 MΩ cm) was prepared using a Milli-Q water purification system.

A background electrolyte solution was used for all sorption and desorption experiments. This solution consisted of 100 mg/L NaN_3 to suppress microbial activity, 10 mM NaCl to maintain a constant ionic strength, and 5 mg/L $NaHCO_3$ to buffer the aqueous solutions at a neutral pH.

2.2. Sediment sampling

Three sediments were collected 1.5–2 y ago from different river sites in the Pearl River Delta in southern China. Sediment obtained from the North River was labeled "NR"; the sampling site was located 0.5 km upstream from a surface water intake source for the Guicheng waterworks. Sediment sampled from the Tanzhou Watercourse was labeled "TZW"; it was collected 2 km downstream of the Great Nanhai Wetland. Sediment obtained from the Pearl River, labeled "PR", was collected at an alluvial estuarine site near the north shore of the Yingzhou ecological park. The samples were collected from remote locations, as far away as possible from areas disturbed by human activities. Air-dried sediments were passed through a < 2 mm sieve and stored in sealed brown glass jars at room temperature prior to use. Table 2 lists the physicochemical properties of the sediments.

2.3. Equilibrium sorption of EE2 and rhamnolipids

The effect of RL-F1 and RL-F2 on the EE2 equilibrium sorption isotherms were conducted in duplicate or triplicate using a batch technique in individual 15 mL glass tubes sealed with Teflon-lined screw caps. For each test, a precisely measured volume of the EE2 stock solution was dissolved in methanol and added to the bottom of the pre-weighed tube. The methanol was then allowed to