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Sorption and desorption characteristics of anionic surfactants to soil sediments

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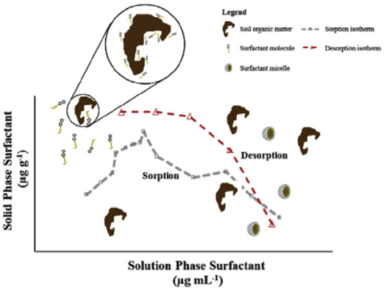
HIGHLIGHTS

- Both SDBS and DPDS surfactants show a sorption maximum near the CMC.
- DPDS micelles compete with sediment organic matter for DPDS sorption.
- Desorption of SDBS and DPDS deviate significantly from the sorption process.
- Surfactant desorption is similar to hydrocarbon irreversible desorption from soil.
- A higher surfactant aqueous concentration reduces surfactant loss due to sorption.

GRAPHICAL ABSTRACT



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ABSTRACT

Surfactants are important environmental chemicals due to their extensive domestic and industrial applications, such as subsurface organic pollution remediation and enhanced oil recovery. However, the interaction of surfactants with subsurface material particularly the desorption behavior of surfactants is less understood. Surfactant desorption is essential to control the fate and transport of surfactants as well as organic pollutants. In this study, the sorption and desorption of linear sodium dodecylbenzene sulfonate (SDBS) and sodium hexadecyl diphenyl oxide disulfonate (DPDS) with two types of soil sediment samples are compared. Sorption of surfactants can be modeled by hydrophobic sorption. Less DPDS sorption is observed at a higher aqueous concentration, which is attributed to the competition between surfactant micelles and sediment organic matter for DPDS sorption. A significant fraction of the sorbed surfactants resists desorption, and this is not a result of surfactant precipitation or desorption kinetics. Surfactant desorption behavior is similar to the irreversible desorption of hydrocarbons from soil with only half of the resistant phase surfactant being readily extracted by heated solvent extraction. The sorption/desorption data are interpreted with a molecular topology and irreversible sorption model. The knowledge of this study can be useful in understanding the environmental fate and transport of these

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Abbreviations: cEOR, chemical enhanced oil recovery; CMC, critical micelle concentration; DBS, Dickinson bayou sediment; DPDS, hexadecyl diphenyl oxide disulfonate; HPLC, high-performance liquid chromatography; HSA, hydrophobic surface area; LSS, Lula surface sediment; OC, organic carbon; OM, organic matter; SER, surfactant enhanced remediation; SDBS, sodium dodecyl benzene sulfonate.

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common anionic surfactants. The methodology developed in this study can be expanded to study the sorptive nature of a wider range of surfactants in the environment.

1. Introduction

Surfactants have extensive domestic and industrial applications, such as in pharmaceutical, agricultural, petroleum, and environmental industries (Rosen, 2012; Tadros, 2014). In the field of environmental remediation of organic pollutants, the use of surfactants to enhance subsurface remediation via surfactant enhanced remediation (SER) has generated considerable interests since the past decade (Pan et al., 2009; Paria, 2008; Pei et al., 2017; Wei et al., 2015). Conventional pump-and-treat approach is proved to be ineffective towards chlorinated organic compounds because of their low aqueous solubility and slow dissolution kinetics. Surfactants can serve as a mobilizer to treat the organics-contaminated soil to remove pollutants due to the enhanced pollutant sorption. Surfactants can profoundly impact the solubilization and mobility of organics in the subsurface (Dollinger et al., 2018; Kang and Jeong, 2015; Schwarzenbach et al., 2016). In oilfield operations, chemical enhanced oil recovery (cEOR) involves the injection of a volume of chemical solutions, such as polymers, surfactants and alkali, into subsurface to recover the otherwise unextractable oil droplets. The injected surfactant molecules are able to reduce the interfacial tension and change the wettability of subsurface materials to increase oil recovery and oil production from the reservoir (Budhathoki et al., 2016). On the other hand, surfactants, as one of the major components of domestic wastewaters, are also environmental pollutants themselves. Thus, the fate of surfactants in the environment have raised considerable concerns, due to their common presence in industrial and household wastes (Kang and Jeong, 2015; Ochoa-Herrera and Sierra-Alvarez, 2008). The presence of surfactants can form foams leading to a reduction of water oxygen level and a deterioration of aquatic ecosystem. Moreover, surfactants can emulsify certain aquatic toxins by increasing the toxicity of these pollutants via secondary contamination (Huang et al., 2012). A number of technologies are available to achieve the removal of surfactants from wastewater including electrochemical oxidation, photocatalytic degradation, membrane technology, precipitation and sorption (Özdemir et al., 2011). Among them, sorption is the most widely used method due to its effectiveness and being environmentally friendly.

Sorption, a general term used to encompass the processes of adsorption, precipitation, partition, ion exchange, etc., is the primary cause of surfactant retention by subsurface materials. Sorption of surfactants by soil/sediment can substantially influence the transport and distribution of surfactants in the subsurface (Chen et al., 2016; Kang and Jeong, 2015; Schwarzenbach et al., 2016). The most characteristic property of surfactants is their strong amphipolarity caused by the primary structure of the molecules: a polar head group linked to an apolar hydrocarbon body. The spatial separation between the head group and the apolar body and the chemical difference between both parts of the molecule give surfactants their specific properties (Rosen, 2012). The mechanism responsible for surfactant sorption includes ion exchange, hydrophobic bonding and π-electron polarization (Yang et al., 2010). It is generally believed that soil organic matter contributes significantly to surfactant sorption and soil minerals provide the sorption sites (Schwarzenbach et al., 2016). In many industrial applications, sorption of surfactant to soil/sediment is regarded as undesirable. For instance of subsurface remediation or SER, surfactant loss to the subsurface material due to sorption has been considered both economically and environmentally unfavorable (Paria, 2008.). Similarly, efforts have been made to minimize the sorption of surfactant molecules to subsurface materials during the cEOR process. The sorbed surfactants cannot lower the interfacial tension and thus are no longer available to mobilize oil (Gogoi, 2011). In light of its industrial and environmental significance, extensive research has been conducted to evaluate the sorption characteristics of surfactants to various sorbent materials. Higgins and Luthy suggested that sediment total organic carbon plays a major role in determining anionic perfluorochemical surfactants sorption while hydrophobic interaction is the underlying mechanism of sorption (Higgins and Luthy, 2006). In another study, anionic surfactant petroleum sulfonate was removed by adsorption to freshly generated magnesium hydroxide. The removal mechanism was determined to be a coagulation-adsorption based process involving flocculation and charge neutralization (Huang et al., 2012).

Although many scholars have extensively studied the sorption process of surfactants to soil/sediment, the majority of these studies focus on the sorption or uptake process and limited research has been carried out to study the desorption process where the sorbed surfactants were released from the surface (Ishiguro and Koopal, 2016; Kang and Jeong, 2015). The knowledge of surfactant desorption from soil/sediment is essential to evaluate the fate of surfactants in the environment and to prevent the loss of surfactant during SER or cEOR (Kang and Jeong, 2015; Paria and Yuet, 2006). A key question related to surfactant desorption is desorption reversibility as of whether the desorption is simply the reversible process of the sorption or desorption can deviate from the sorption process, i.e., desorption hysteresis. Pan et al. argued that surfactant sorption reversibility can be more influential than sorption itself in controlling the fate and transport of surfactants as well as organic pollutants (Pan et al., 2009). The sorption reversibility is affected by many factors including type and properties of soil/sediment and concentration and characteristics of surfactants. You et al. reported the sorption and desorption behaviors of perfluorooctane sulfonate at sediment-water interface (You et al., 2010). It shows that desorption hysteresis occurred over the range of the salinity conditions evaluated and that irreversibility index increased as a result of increasing concentration of $CaCl_2$. These authors elucidate the underlying mechanisms as the salting-out and calcium-bridging effects.

Anionic surfactants are widely used in industry and thus they are commonly present in domestic and industrial wastewaters (Ma et al., 2012). Sodium dodecyl benzene sulfonate (SDBS) is a well-known anionic surfactant extensively used in various industries. In addition, SDBS has a recalcitrant molecular structure with a low biodegradability and can retain in the environment for a long time (García et al., 2009). Another sulfonate-based surfactant hexadecyl diphenyl oxide disulfonate (DPDS) is a “twin-head” surfactant and commonly used during SER operations. It was found that sorption of DPDS was significantly lower than most of other anionic and nonionic surfactants, making this type of surfactant a promising candidate for groundwater clean-up (Rosen, 2012; Rouse et al., 1993). In this study, the sorption and particularly desorption behaviors of SDBS and DPDS surfactants were extensively investigated. Multi-step desorption and cyclic sorption/desorption approaches were adopted to evaluate the desorption hysteresis of