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Surfactant-enhanced flushing enhances colloid transport and alters macroporosity in diesel-contaminated soil

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ABSTRACT

Soil contamination by diesel has been often reported as a result of accidental spillage, leakage and inappropriate use. Surfactant-enhanced soil flushing is a common remediation technique for soils contaminated by hydrophobic organic chemicals. In this study, soil flushing with linear alkylbenzene sulfonates (LAS, an anionic surfactant) was conducted for intact columns (15 cm in diameter and 12 cm in length) of diesel-contaminated farmland purple soil aged for one year in the field. Dynamics of colloid concentration in column outflow during flushing, diesel removal rate and resulting soil macroporosity change by flushing were analyzed. Removal rate of *n*-alkanes (representing the diesel) varied with the depth of the topsoil in the range of 14%–96% while the *n*-alkanes present at low concentrations in the subsoil were completely removed by LAS-enhanced flushing. Much higher colloid concentrations and larger colloid sizes were observed during LAS flushing in column outflow compared to water flushing. The X-ray micro-computed tomography analysis of flushed and unflushed soil cores showed that the proportion of fine macropores (30–250 μm in diameter) was reduced significantly by LAS flushing treatment. This phenomenon can be attributed to enhanced clogging of fine macropores by colloids which exhibited higher concentration due to better dispersion by LAS. It can be inferred from this study that the application of LAS-enhanced flushing technique in the purple soil region should be cautious regarding the possibility of rapid colloid-associated contaminant transport *via* preferential pathways in the subsurface and the clogging of water-conducting soil pores.

Introduction

Diesel is commonly used for agricultural machinery and transportation vehicles. Soil contamination by diesel, which is known as a typical light non-aqueous phase liquid in soil, may occur as a result of accidental spillage and leakage and inappropriate use (Pasha et al., 2012; Hernández-Espriú et al., 2013). Soil contamination by oil can ruin the balance of the

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ecosystem and cause various environmental and human health damages (Falciglia et al., 2011; Lee et al., 2012). Great efforts have been made to develop environmentally sound and cost-effective techniques for remediating oil-contaminated soils. Among these technologies, surfactant-enhancing soil flushing is a time-efficient and versatile method (Mao et al., 2015), and therefore attracts increasing attention in recent years (Svab et al., 2009; Davezza et al., 2011; Rosas et al., 2011). Surfactants are a group of amphiphilic chemicals, which contain both hydrophilic and hydrophobic groups (Vishnyakov et al., 2013). Surfactants' unique molecular structures allow enhancing the water solubility and mobilization of soil contaminants (Dwarakanath and Pope, 2000), especially for hydrophobic organic compounds (Lee et al., 2013). Soil flushing using surfactants (surfactant-enhanced flushing) has been recognized as a promising *in situ* technique for remediation of soils contaminated by low-solubility organic chemicals (Cowell et al., 2000; Mao et al., 2015; Trellu et al., 2015). The applications of surfactant-enhanced flushing technique for contaminated soils have been extensively investigated (Khalladi et al., 2009; Lee et al., 2013; Park and Bielefeldt, 2005) focusing mostly on the selection of surfactants showing high removal efficiency, low cost and toxicity on soil microorganisms (Hernández-Espriú et al., 2013). Linear alkylbenzene sulfonates (LAS), the most widely used anionic surfactant, have weaker sorption to soil than cationic and nonionic surfactants and thus could be of great interest for soil remediation companies (Ying, 2006; Guan et al., 2008). In addition, LAS biodegrade easily in soil (Larson et al., 1989). For example, their half-lives in sludge-amended soils were found to be 3–33 days (Berna et al., 1989; Cavalli and Valtorta, 1999). Although this technique is generally efficient to clean up soil, the major concern remains because of mixed results of its application in soil matrix (Urum et al., 2006). Surfactant-enhanced soil flushing treatment could lead to changes in soil hydraulic properties and other potential environmental consequences (*e.g.*, decreased soil fertility, inhibited plant growth and changes in microbial community structure) (Renshaw et al., 1997; Elsgaard et al., 2001; Jia et al., 2005; Laha et al., 2009). For example, hydraulic conductivity reduction by up to two and three orders of magnitude was observed in some loamy soils (Allred and Brown, 1994; Gabr et al., 1998); immediate plugging of soil columns followed surfactant injection in a fine silty loam (Roy et al., 1995). Contrastingly, some other researches showed that, extensive soil column tests achieved high oil recoveries without significant problems such as pore clogging and high surfactant retention (*e.g.*, Abdul et al., 1992; Dwarakanath and Pope, 2000). A comparison study (Lee and Cody, 2001) showed that more clogging occurred in a clay loamy soil than a sandy soil for all three anionic surfactants used for flushing, including sodium diphenyl oxide disulfonate, sodium lauryl sulfate and trideceth-19-carboxylic acid. The saturated hydraulic conductivity was strongly affected by surfactant type. The least pore clogging occurred with the double-head hexadecyl disulfonate surfactant sodium diphenyl oxide disulfonate. Notably, it was reported that higher surfactant concentrations might lead to increased colloid mobilization (Gardner and Arias, 2000). Colloids could potentially act as transport vehicles for various strongly-sorbing contaminants such as heavy metals and organic contaminants (Tang et al., 2012; Zhang et al., 2015, 2016). Colloid transport may not only promote the migration of contaminants but also alter soil structure and flow paths in the subsurface (Zhang et al., 2015). The interactions between surfactants and soil matrix may lead to swelling of the clay, release and re-deposition of clay colloids and thus alter soil pore system (Gardner and Arias, 2000).

Soil pore structure governs various important physical and biological processes in soil–plant-microbial systems, such as nutrient cycling, diffusion, mass flow, nutrient uptake by roots and the distribution and structure of microbial community (Young and Crawford, 2004; Martinez et al., 2010; Garbout et al., 2013). For soils showing weak aggregate stability, in addition to the contaminant removal efficiency of surfactant-enhanced flushing technology, due attention should be paid to the colloid-associated contaminant export with the flushing outflow as well as resulting changes in soil pore characteristics. Evidence from field applications of this technique indicate that soil flushing with surfactants can cause decreased percolation rates and restricted flow (*e.g.*, Nash, 1988; Sorel et al., 1998). These observations were attributed to poor clogging/blockage due to the enhanced dispersion of clay particles (Tumeo, 1997), the extremely high concentrations of oil and grease (Nash, 1988), mineral precipitation under changed pH by flushing (Yan et al., 2015), the formation of viscous emulsions (Crawford et al., 1997), surfactant micelles (Gabr et al., 1998; Chu and Kwan, 2003) and flocs (Rosen, 1989). However, these understandings are mainly based on perceived changes in hydraulic conductivity during soil flushing and are thus more speculative than conclusive (Henry and Smith, 2003). To the best of our knowledge, no previous studies have been conducted with intact columns of soils contaminated by hydrophobic pollutants in the field to quantitatively identify how pore structure and colloid transport are affected by surfactant flushing.

In the vast hilly region (160,000 km^2) of Sichuan in the upper Yangtze River, the poorly structured, aggregated purple soil (an entisol according to USDA soil taxonomy) is dominant. Macropore flow prevails in the soil and thus the potential of colloid transport in the subsurface upon rainfall is high (Zhao et al., 2013; Zhang et al., 2015). Field aging of contaminated soils under natural wetting-drying cycles can lead to not only decomposition and migration of hydrophobic pollutants but also enhanced soil macroporosity and decreased pore heterogeneity (Leij et al., 2002; Bodner et al., 2013). Therefore, the feasibility of applying surfactant-enhanced flushing technology in this region for soil remediation needs to be evaluated with respect to colloid transport and soil porosity, particularly macropores, which were reported to be the main contributing pores to flow (Wang et al., 2015). It should be noted that, in the few previous studies with packed soil columns to evaluate the effects of surfactant flushing on hydraulic conductivity (Renshaw et al., 1997; Lee and Cody, 2001), macropores developed in soils under field condition were neither simulated properly nor characterized quantitatively.

Macropores allow quick movement of water, solutes, colloids and air through soil (DeNovio et al., 2004). They provide habitat for soil organisms (biota) including microbes and plant roots can grow through them. The visualization and quantification of macropores are essential for a better understanding of soil structure and functioning. In recent years, X-ray micro-computed tomography (micro-CT) has been employed to study

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