Surfactant flushing remediation of toluene contaminated soil: Optimization with response surface methodology and surfactant recovery by selective oxidation with sulfate radicals

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A B S T R A C T

Surfactants are usually used in remediation of subsoil and aquifers contaminated with hydrophobic organic compounds (HOCs) such as benzene, toluene, ethylbenzene and xylenes (BTEX). Laboratory soil column experiments were conducted, using the anionic surfactant sodium dodecyl sulfate (SDS), to optimize toluene removal efficiency from contaminated soil. The influence of flushing time, SDS concentration and flow velocity on toluene removal efficiency was investigated. In the column tests the maximum toluene removal efficiency of 89.9% was achieved with 2% (wt/vol) SDS solution and 5 mL/min flow velocity for 300 min. Response surface methodology (RSM) based on Box–Behnken statistical experiment design (BBD) was applied to analyze the experimental variables which all showed a positive effect on toluene removal efficiency. The interactions between SDS concentration and flushing time or flow velocity were significant, while the interaction of flushing time with flow velocity was not pronounced. Under optimal conditions, the predicted and observed removal efficiencies were 96.2% and 91.0% respectively. The results confirmed that the proposed models were accurate and reliable for the analysis of the variables of surfactant flushing treatment. Furthermore, the use of the $UV/S_2O_8^{2-}$ selective oxidation process was proposed for surfactant recovery and degradation of contaminant present in the solution collected. It was found that after 270 min of treatment toluene was 90.1% degraded for the second time the surfactant was used and 94.7% for the third time. In addition, a test in which the regenerated solution was employed in the flushing process was carried out in a soil column. The results indicated that the $UV/S_2O_8^{2-}$ oxidation process was potentially effective in selective degradation of toluene with most of the surfactant left for potential reuse in another polluted soil treatment.

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1. Introduction

BTEX (benzene, toluene, ethylbenzene and xylenes) is normally found in petroleum products and the leakage of gasoline from faulty, poorly maintained underground storage tanks or release from large bulk facilities, surface spills and pipeline leaks are the main sources of BTEX contamination. Once released into the environment, BTEX can volatilize, dissolve, attach to soil particles and then pollute air, water and soil, respectively. The United States Environmental Protection Agency [1] has established a Maximum Contaminant Level (MCL) in public drinking water systems because BTEX is toxic (e.g. benzene) or potentially toxic (e.g. toluene, ethylbenzene and xylene) to humans and their release into the environment can cause neurological damage [2]. BTEX is usually described as being a hydrophobic organic contaminant (HOC)

because of its low solubility and high interfacial tension [3]. Since BTEX can "stick" to soil particles, it moves slower than the groundwater and represents a long-term source of soil and aquifer contamination.

Among all remediation technologies for treating hydrophobic organic contaminated soil, flushing is an effective and economical method because it is an in situ process, where a flushing fluid is applied to the surface of the contaminated site or injected into the saturated contaminated zone [4]. However, low hydraulic conductivity and the high interfacial tension of BTEX result in large capillary forces and high displacement entry pressures that resist flushing by water [5]. The extensive research on soil and groundwater remediation has demonstrated that surfactant-based treatment appears to be a viable alternative for improving the efficiency of soil flushing processes [6,7]. Most studies have shown that aqueous surfactant solution significantly enhances the removal of HOCs from soil and groundwater [5,8,9]. In particular, surfactants have been extensively researched for in situ flushing remediation of soil and groundwater [10].

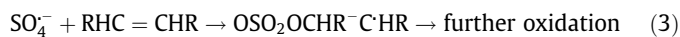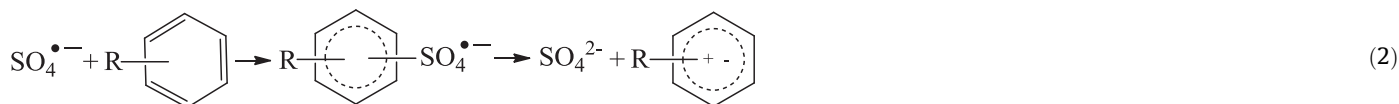* Corresponding author. Tel.: +86 27 68775837; fax: +86 27 68778893.
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Traditional optimization methods normally examine a single factor at a time while fixing all other variables at one level, which are extremely time-consuming and expensive [11–13], especially for surfactant flushing processes [14]. This traditional approach fails to consider interaction effects between the different parameters and cannot determine the practical optimal conditions [15–17]. However, a more effective approach would be to use an experimental design, which utilizes statistical data as an optimization tool [14]. Response surface methodology (RSM) is an approach which can evaluate the relationship existing between controlled experimental factors and measured responses according to one or more selected criteria and then identify the optimum conditions for a multivariable system [18,19]. RSM experimental approaches include three-level factorial design, central composite design (CCD), Box–Behnken design (BBD) and D-optimal design [20,21]. One of most efficient techniques is the Box–Behnken design (BBD) which not only consumes less time or resources and requires fewer experiments than other methods with the same number of factors, but is also more effective than CCD and three-level factorial designs [19,22,23]. In addition, it is a modified central composite experimental design with excellent predictability [20,21]. Therefore, in this paper, a BBD was employed to investigate the surfactant flushing process.

Additionally, effluent from surfactant flushing is a pollutant in its own right and the collected wastes must be adequately disposed or treated by applying suitable physical, biological or chemical processes before discharge or reuse [24]. Thus it is necessary to develop recovery and reuse technologies for the surfactant flushing process. Many researchers have applied different effective treatments such as ultrafiltration/nanofiltration, pervaporation, precipitation, foam fractionation, solvent extraction, activated carbon adsorption, co-current vacuum stripping, electrochemical and photochemical treatment. Among these technologies, the electrochemical and photochemical treatments are destructive techniques which can degrade the contaminants [25,26], while the other non-destructive technologies just separate contaminants from the flushing solution [27–34]. However, it is imperative that environmentally friendly pretreatment should be applied for selective oxidation target pollutants to reuse most of the surfactant. Persulfate is an emerging and promising oxidant for in situ soil and groundwater treatments due to its high redox potential ($E^0 = 2.01$ V), long-term stability, high-water solubility, easy transport and wide operative pH range [35,36]. The sulfate radical ($SO_4^{\cdot-}$), a strong oxidant ($E^0 = 2.60$ V), has been successfully used for environmental applications in the remediation of aqueous and sediment systems containing BTEX [37–40]. In addition to some of the traditional activation methods such as heat or transition metal ions that can catalyze persulfate yielding $SO_4^{\cdot-}$ [41–44], it can also be produced by photolysis of persulfate with a high quantum yield [45–47], especially activated by ultraviolet (UV) light [48–50].

$$S_2O_8^{2-} + h\nu \rightarrow 2SO_4^{\cdot-} \tag{1}$$
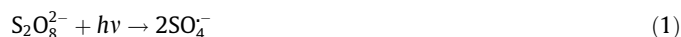
The sulfate radicals react as a strong oxidant with organic compounds in aqueous systems via three different mechanisms (electron transfer, addition or hydrogen abstraction) [36] as outlined in:

$$SO_4^{\cdot-} + RHC = CHR \rightarrow OSO_2OCHR^-C^{\cdot}HR \rightarrow \text{further oxidation} \tag{3}$$

$$SO_4^{\cdot-} + RH \rightarrow HSO_4^- + R^{\cdot} \rightarrow \text{further oxidation} \tag{4}$$

Furthermore, a recent review by Tsitonaki et al. [36] indicates that $SO_4^{\cdot-}$ preferentially removes electrons from an organic molecule to produce an organic radical cation (Eq. (2)), whereas hydroxyl radicals (OH$^{\cdot}$) add to C=C bonds or abstract hydrogen from the C—H bond. They also proposed that $SO_4^{\cdot-}$ is an electrophilic reagent, and when electron donating groups are present on an aromatic molecule, the rate of the reaction with $SO_4^{\cdot-}$ will increase [36]. This means that $SO_4^{\cdot-}$ may oxidize BTEX with a faster reaction rate than straight chain hydrocarbon surfactants which do not contain a benzene ring [47], and compares favorably with degradation of surfactants by ozonation or other advanced oxidation processes (AOPs) in surfactant wastewater [51–53]. Therefore, the surfactant can be reused from the flushing fluid eluate by using the UV/$S_2O_8^{2-}$ treatment.

The objective of this study was to investigate the application of surfactant flushing in the treatment of toluene (as a model BTEX compound) contaminated soil. A Box–Behnken experimental design (BBD) using RSM optimization was employed to evaluate the effects of variables such as flushing time, surfactant concentration and flow velocity on toluene removal efficiency. Moreover, in order to achieve the goal of surfactant recovery, the UV/$S_2O_8^{2-}$ oxidation process is proposed for selective degradation of toluene with most of the surfactant remaining in solution being collected and reused. In addition, the regenerated solution was employed in the flushing process. Furthermore, a direct aqueous injection-gas chromatography/flame ionization (DAI-GC/FID) procedure was applied to investigate the concentration of BTEX present in the aqueous surfactant flushing solution [54,55].

2. Materials and methods

2.1. Soil

The soil was sampled from the campus of Wuhan University and then air dried for several days at room temperature. In order to avoid inconsistency and any other problems at the soil column flushing stage, the soil particles were passed through 2-mm sieve to make them consistent and to remove large stones, plant and other undesirable material. The soil had a pH of 8.2 (measured by a combination electrode at a 1:2.5 soil/water ratio) and contained 2.67% organic carbon (determined by the dichromate oxidation method). The particle size distribution was 42.6% sand (>63 μm), 28.9% coarse silt (21–62 μm), 27.3% fine and medium silt (2–20 μm) and 1.2% clay (<2 μm) measured by MASTER-SIZER3500 apparatus (Micro Instruments, USA).

2.2. Surfactant, oxidant and pollutant

Anionic surfactants are usually chosen for soil contaminant flushing treatment because of their lower degree of adsorption on soil compared to cationic and nonionic surfactants [56]. Moreover, sodium dodecyl sulfate (SDS, $CH_3(CH_2)_{11}SO_4Na$), an anionic surfactant with critical micelle concentration (CMC) of 8 mM, was food grade and was easily biodegradable by soil and/or aquatic

$$SO_4^{\cdot-} + R\text{—}\bigcirc \rightarrow R\text{—}\bigcirc\text{—}SO_4^{\cdot-} \rightarrow SO_4^{2-} + R\text{—}\bigcirc^{+\cdot} \tag{2}$$