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Evaluation of soil flushing of complex contaminated soil: An experimental and modeling simulation study

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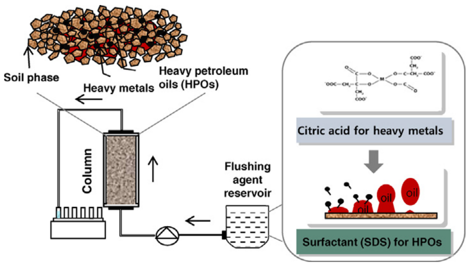
HIGHLIGHTS

- Remediation of complex contaminated soil achieved by sequential soil flushing.
- Removal of Zn, Pb, and heavy petroleum oils using 0.05 M citric acid and 2% SDS.
- Unified desorption distribution coefficients modeled and experimentally determined.
- Nonequilibrium models for the transport behavior of complex contaminants in soils.

GRAPHICAL ABSTRACT



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ABSTRACT

The removal of heavy metals (Zn and Pb) and heavy petroleum oils (HPOs) from a soil with complex contamination was examined by soil flushing. Desorption and transport behaviors of the complex contaminants were assessed by batch and continuous flow reactor experiments and through modeling simulations. Flushing a one-dimensional flow column packed with complex contaminated soil sequentially with citric acid then a surfactant resulted in the removal of 85.6% of Zn, 62% of Pb, and 31.6% of HPO. The desorption distribution coefficients, K_{Ubatch} and K_{Lbatch}, converged to constant values as C_e increased. An equilibrium model (ADR) and nonequilibrium models (TSNE and TRNE) were used to predict the desorption and transport of complex contaminants. The nonequilibrium models demonstrated better fits with the experimental values obtained from the column test than the equilibrium model. The ranges of K_{Ubatch} and K_{Lbatch} were very close to those of K_{Ufit} and K_{Lfit} determined from model simulations. The parameters (R, β, ω, α, and f) determined from model simulations were useful for characterizing the transport of contaminants within the soil matrix. The results of this study provide useful information for the operational parameters of the flushing process for soils with complex contamination.

1. Introduction

In many manufactured gas plant sites, numerous kinds of hazardous materials such as petroleum-based products, toxic organic compounds, and heavy metals are extensively used. The soils are easily contaminated with these substances due to inappropriate management or accidental spills. Therefore, soil contamination with a mixture of substances (i.e., complex contaminants) is more frequent than single substance contamination in manufactured gas plant sites [1]. Military bases and railroad sites have also been receiving increased interest as places with complex soil contamination, where the soils are contaminated with a complex mixture of heavy metals (Zn, Pb, Fe, and Cu) and heavy petroleum oils

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(HPOs; waste oils and used lubricants and greases). These complex contaminants are strongly associated within the soil matrix. Their desorption takes longer period than the initial sorption due to the large activation energy required for desorption [2]. Therefore, it is recommended that the removal of complex contaminants from the soils must be accomplished as quickly as possible for successful remediation [3]. Moreover, the complexity resulting from the heterogeneous relationship between contaminants and soils makes it very difficult to establish an appropriate soil remediation practice, compared with soils contaminated with a single substance [4].

It is known that soil washing and flushing are effective for the remediation of soils contaminated with a wide range of compounds. Soil washing and flushing agents specific to the contaminants are utilized to stimulate desorption of contaminants bound to soils in these processes [5,6]. In a number of studies, the application of various soil flushing agents, in mixed form or in sequence, has been suggested as an in-situ remediation technology for soils with complex contamination [4,7,8]. For instance, Zhang et al. [8] reported that a soil contaminated with total petroleum hydrocarbons (TPHs) and Pb was effectively remediated by simultaneous or sequential flushing with sodium dodecyl sulfate (SDS) and ethylenediaminetetraacetic acid (EDTA). However, they also noted that the chelating effect of EDTA can be reduced when it is used with SDS. This is because Fe and Mn oxides combined with Pb can react with SDS and form ternary surface complex compounds, essentially resulting in the suppression of the EDTA extraction of Pb. Therefore, it is very important to understand the relationship among contaminants, flushing agents, and soils for the optimization of the soil flushing process.

EDTA (a chelating agent) and HCl and HNO_3 (strong acids) are known to be the most effective soil washing and flushing agents for the removal of heavy metals from contaminated soils [9,10]. However, the field application of these compounds is limited because EDTA exhibits low biodegradability and high toxicity to aquatic ecosystems. HCl and HNO_3 can facilitate additional leaching of other inorganic substances from soils [10,11]. Recently, citric acid has received increased attention owing to its eco-friendly and economic characteristics [12]. Meanwhile, surfactants are generally used to desorb and remove non-aqueous phase liquids from soil by increasing their solubility. However, surfactants can be easily adsorbed onto soils and this can result in a considerable reduction in their solubilizing and desorption capabilities. Among the various surfactants available, SDS, which has been employed in a number of previous studies as a representative biodegradable anionic surfactant, has a relatively low tendency to adsorb. Therefore, it has been used extensively in soil flushing practices [13,14].

The desorbed contaminants move through soil pores for long periods of time at steady and/or unsteady states via advection, dispersion, diffusion, retardation, and attenuation. It is very difficult to describe the transport of contaminants within the soil matrix due to the extremely heterogeneous interactions of contaminants with the numerous kinds of soil components such as soil organic matter, minerals, microorganisms, etc. To date, a large number of models have been developed to describe the complex transport of contaminants within the soil matrix. The advection–dispersion equation (ADE) model is a typical equilibrium model, which assumes sufficient contact time between soils and contaminants, i.e., the sorption equilibrium is reached [15]. However, the ADE model shows limitations in the prediction of skewed contaminant transport and breakthrough behavior [16]. Nonequilibrium models, such as the two-site and two-region non-equilibrium (TSNE and TRNE) models, have been developed as alternatives. These models are employed under the assumption that the time for soil-contaminant contact is not sufficient to reach the sorption equilibrium [17]. Variables for these models can be predicted from various input values such as soil properties, relationships between soils and contaminants, and environmental factors; in particular, the transport of reactive solutes involving various interactions with soils, such as redox and sorption reactions, is subject to retardation effects. According to the findings of Mao and Ren [18], the retardation factor exhibits the highest sensitivity among the input variables and therefore, they suggested that the retardation factor should be estimated using hydraulic variables and distribution coefficients obtained from batch tests. However, the distribution coefficient cannot be determined as a fixed variable because the associated behavior of the contaminants with the soils is typically given in a nonlinear fashion across a wide range of solute concentrations [19]. This indicates that the retardation factor should accommodate the effect of nonlinear sorption isotherms for reasonable modeling results.

In this study, a soil with complex contamination involving HPOs (bunker C and lubricant oils) and heavy metals (Zn and Pb) was remediated using a soil flushing process. In order to simulate the desorption and transport of complex contaminants, a one-dimensional (1-D) column was employed. It was packed with complex contaminated soils, and then sequentially flushed with citric acid and SDS. The removal efficiencies of the complex contaminants were evaluated, and the Freundlich and Langmuir distribution coefficients, which describe nonlinear desorption isotherms, were obtained to predict the retardation factor. In addition, the equilibrium and nonequilibrium models were utilized for the simulation of contaminant transport in the column, and the correlation among process operation parameters was assessed.

2. Materials and methods

2.1. Determination of distribution coefficients using desorption isotherm

A sandy loam soil was collected at a depth of 30–50 cm from a forest region in Seoul, Korea, for which no prior contamination history has been reported (Table 1). The procedure of soil contamination is provided in the Supplementary data. The desorption distribution coefficients were determined from desorption isotherm experiments using flushing agents. The complex contaminated soils (S_1) were mixed with 0.05 M citric acid or 2% SDS in a rotary shaker operated at 120 strokes/min and 25 °C for 24 h, and then centrifuged. It was confirmed by additional experiments that 24 h was sufficient to reach the desorption equilibrium (data not present). The contaminant concentrations in the aqueous phase (C_e) and the soil phase (q_e) were determined. The Freundlich (Eq. (1)) and Langmuir (Eq. (2)) models were employed to characterize

Table 1
Properties of the soil used in this study and level of artificial complex contamination.

Soil texture (%)	Sand	76.84
	Silt	15.08
	Clay	8.08
pH	7.59	
Cation exchange capacity (meq 100/g)	7.72	
Organic matter (%, w/w)	3.33	
Particle density, ρ_p (g/cm^3)	2.32	
Bulk density, ρ_b (g/cm^3)	1.41	
Contaminant concentration in the soil phase (mg/kg)	S_1 [a]	S_2 [b]
HPOs	2397 ± 66 [c]	4988 ± 200
Zn	2927 ± 212	2653 ± 49
Pb	972 ± 69	798 ± 7

[a] Soil used in batch desorption test.

[b] Soil used in column test.

[c] Mean ± SD (n = 10).