

REMEDICATION OF DIESEL CONTAMINATED SOIL BY THERMAL DESORPTION AND SOIL WASHING

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Abstract

Desorption of diesel molecules from sand was investigated by thermal desorption. Reaction rate constants were found as $k=0.0723 \text{ min}^{-1}$, $k=0.1969 \text{ min}^{-1}$ and $k=0.8525 \text{ min}^{-1}$ at 100°C, 200°C and 400°C, respectively. Using Arrhenius equation, the activation energy for desorption was found as 17.20 KJmole⁻¹. In this study, dose effect of anionic surfactant sodium dodecyle sulfate surfactant and that of salinity effect were also investigated on soil washing. Removal efficiency increased with increasing surfactant dose. 1%, 3% and 5% of NaCl were used with 4% of surfactant concentration in soil washing. Maximum enhancement was observed at 5% salinity, indicating surfactant-enhanced remediation (SER) efficiency in saline water was higher than that in freshwater. This research can be an implication on designing an integrated type of soil washing and thermal desorption equipment. In addition, calculation of activation energy makes it possible to provide optimal temperature on thermal desorption and the intuition for remediating the soil contaminated with persistent organic pollutants.

Introduction

Soil contamination by hydrophobic components is one of the most common types of pollution in environment. Till now, various remediation techniques have been used in soil remediation process¹. Among them, thermal desorption and soil washing are the most widely used removal technology. The basic principle of soil washing is solubilization of hydrocarbons by lowering the interfacial tension at the soil/organic phase and water/organic phase interfaces². In general, thermal desorption and surfactant-enhanced remediation (SER) are done by detaching organic molecules adsorbed on soil and trapped in the pores, followed by their encapsulation within micelles formed at a concentration greater than the critical micelle concentration (CMC)³.

While SER of contaminated soils has been investigated widely, its application in the remediation of contaminated soils or sediments in saline environments has received little attention^{4,5}. It is very important to examine the effect of SER on soil washing in an estuaries environment because many pollutants enter the environment via direct disposal or surface run-off as well.

The aim of this study is to investigate the temperature effects on the thermal desorption of diesel from sand particles and to examine the effect of anionic surfactant dose and salinity on soil washing.

Materials and Methods

An anionic surfactant SDS (99%, Sigma-Aldrich), dichloromethane (DCM, 99.9%, Merck), sodium sulfate anhydrous (99%, Samchun), diesel (0.815g/cm³) were used in this study. All the chemicals were used without any further treatment. Deionized water was used to prepare the surfactant solution. Sand used in the experiment contains quartz (70.6 weight %), microcline (23.7 weight %), albite (4.8 weight %) and biotite (0.8 weight %).

50µL of diesel diluted by 5mL of dichloromethane was spiked in sand to make adsorb homogeneously. It was dried in the air environment. For thermal desorption process, 7g sand contaminated with diesel was kept in heat proof dish and covered with foil paper. A muffle furnace was used to heat the samples at 100°C, 200 °C and 400 °C. For soil washing, 7g sand contaminated with diesel was equilibrated with 30 ml surfactant solution of different concentrations in 50ml Pyrex tube. The equilibration was achieved by rotary tumbler. Control tests were conducted to ensure there is a washing effect by water itself. All samples were prepared in duplicate.

The residual diesel from sand was extracted with dichloromethane three times by ultrasonication after being centrifuged at 5000rpm. The extracted diesel was filtered through sodium sulfate and concentrated by rotary evaporator. All the samples were diluted to 5ml using DCM and were measured by a Hewlett Packard 5890 gas

chromatograph (GC) equipped with an flame ionization detector (FID) and a SPM-5 column (30 m × 0.25 mm × 0.25 μm). The temperature of injector and detector was 200°C and 220 °C, respectively and oven temperature was programmed from 50°C to 300°C with a rate of 10°C/min. The split ratio was 1:4, and N₂ (1.4 mL/min) was used as carrier gas. The flow rates of H₂ and air were maintained at 25 mL/min and 250 mL/min for the ionization, respectively.

Results and Discussion

1. Desorption of diesel from sand particles at three different temperatures

Figure 1 shows the temperature effect on thermal desorption of diesel at 100°C, 200°C and 400°C. The pseudo-first order kinetic rate constants were summarized in Table 1. From this experiment, it has been proved that at the same treatment time, thermal desorption at higher temperature could degrade larger amount of organic compound from sand than that at lower temperature. Temperature and time were considered to be suitable for kinetic analysis because these two parameters are significant in thermal desorption process. The basic equation in kinetics related to temperature and rate constant is the Arrhenius equation, $k = Ae^{-Ea/RT}$, where k is the kinetic rate constant, A is the pre-exponential factor and Ea is the activation energy. Converting the form of Arrhenius equation to the natural logarithm yields the next equation such as $\ln k = \left(-\frac{Ea}{R}\right)T^{-1} + \ln A$. Activation energy ($Ea=17.20\text{KJmole}^{-1}$) was calculated from the slop of the graph by plotting T^{-1} with respect to natural logarithm values of k. Also, pre-exponential factor ($A=17.50 \text{ min}^{-1}$) was calculated from the graph. At 400°C (673k), the fraction of molecules desorbed from sand particle was proportional to the value of $e^{-(Ea/RT)}$, which was 0.0462. Other fractions of molecules listed in Table 1.

Table 1. Kinetic rate constant and Fraction of molecules at different temperatures

| T (°C) | Fraction of molecules | Rate Constant (min^{-1}) |
|--------|-----------------------|-------------------------------------|
| 100 | 0.0039 | 0.0723 |
| 200 | 0.0126 | 0.1969 |
| 400 | 0.0462 | 0.8526 |

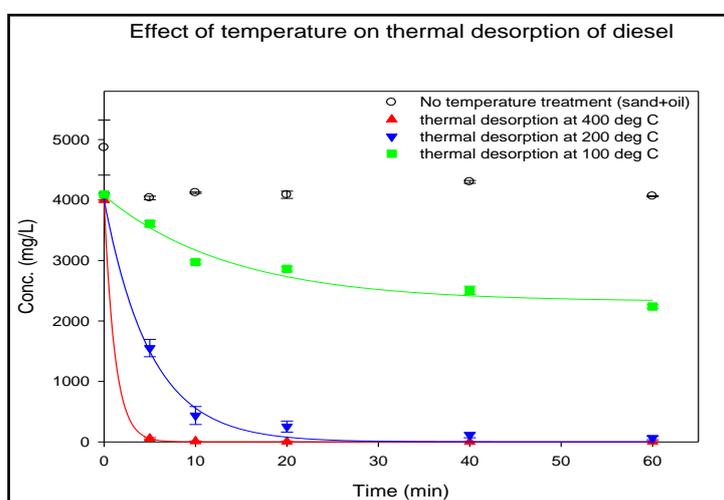


Figure 1. Thermal desorption of diesel from sand at 100°C, 200°C and 400°C.

2. Effect of surfactant dose on soil washing

Figure 2 shows removal efficiency of diesel with respect to time at two different surfactant doses. Higher removal efficiency was shown at the 15 times CMC concentration of SDS. Soil washing with only water also showed high removal efficiency. It might be mainly due to the lower organics in the sand, which make contaminant such as diesel difficult to be adsorbed.

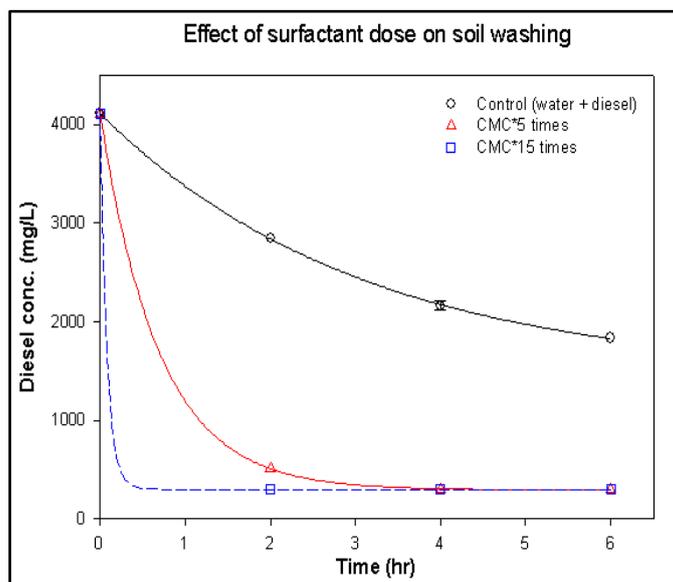


Figure 2. Effect of surfactant (SDS) dose on soil washing

3. The influence of salinity in SER on the soil washing process

Figure 3 shows the enhanced diesel removal pattern in saline water environment. Increasing the concentration of NaCl increased the removal efficiency of diesel from sand at constant surfactant dose. It could be explained in terms of aggregation number and micellar size of surfactant. Increasing salinity could increase these two values, which could provide more favorable environment for diesel molecules to be encapsulated within micelles⁶. This result indicates that saline environment itself can give higher removal efficiency of diesel.

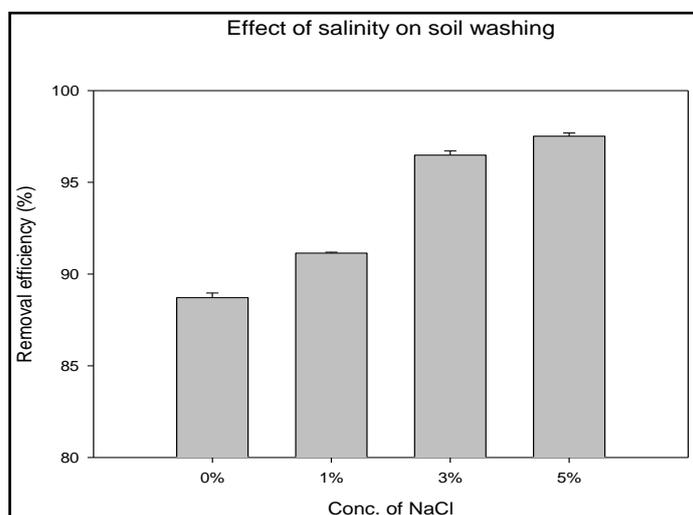


Figure 3. Effect of salinity on soil washing at 1%, 3% and 5% of NaCl with 4% of surfactant concentration.

Acknowledgements

This research was supported by the grants from HRHR Project (KAIST).

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