Application of Laser Based Spectroscopic Monitoring into Soil Remediation Process of PAH-Contaminated Soil

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ABSTRACT: The application of Laser-Induced Fluorescence (LIF) into soil remediation process is not popular due to the difficulties of the interpretation of remediation process. The monitoring for the lab-scale surfactant enhanced electrokinetic remediation process using the LIF was performed. The variation of the fluorescence intensity and the change of the fluorescence spectral signature reflecting the nature of the surrounding environment were investigated. The diffuse reflectance correction method for the soil matrix properties on fluorescence, and the time resolution for isolation of surfactant which can be overlapped with PAHs spectra of interest were considered to provide the information of contaminants taking place during the remediation process. Electrokinetic (EK) remediation process as control experiment was also performed and this result was compared with the surfactant-enhanced EK process especially in terms of the spectral signature of PAHs. The LIF monitoring for soil remediation process showed that the relative quantities and the state of contaminant in soil media which can be an important key to assess the feasibility of remediation process.

Key words: LIF, PAH-contaminated soils, Electrokinetic remediation process, Soil matrix properties

INTRODUCTION

The increasing awareness of the environmental pollution has resulted in the development of a wide range of techniques to assess the contamination level and monitor contaminated sites. Especially it is highly desirable that the development of a fast, selective, and sensitive in-situ monitoring technique which can overcome the limitations of traditional monitoring methods (Kotzick and Niessner, 1996; Rudnick and Chen, 1998).

Polycyclic Aromatic Hydrocarbons (PAHs) have attracted public attentions because many of these compounds are carcinogens and mutagens. PAH contamination in soil is widespread as gasoline or fuel oil spills are common; in fact it is estimated that 90-95% of all leaking underground storage tanks contain petroleum products (Lewitzka et al., 1999). Because of their known mutagenic and/or carcinogenic properties, the qualitative and quantitative analysis of PAHs is of fundamental importance for implementing a correct clean-up of contaminated areas.

Conventional laboratory techniques have been used for the selective analysis of PAHs. However, due to the limitation such as the high cost, long time period and the losses in concentration of these compounds during sampling or transport, field techniques are surely preferable (Niessner et al., 1991). For on-line and in-situ measurement of PAHs, a Laser Induced Fluorescence (LIF) can be used. Fluorescence organic compounds such as PAHs can be electronically excited in the ultraviolet and visible range spectra and exhibit high fluorescence quantum yield. Therefore, their emission can be usefully employed as a tool for their determination and monitoring in environment system.

In recent years, several research groups developed fiber optic LIF sensors for on-line and in-situ monitoring of soils and aromatic hydrocarbons in water, soil and air. These systems have several interesting applications such as field screening of oil contamination in water and soil after environmental accidents, and localization of subsurface oil plumes at contaminated waste sites (Aldstadt et al., 2002; Apitz et al., 1992; Baumann et al., 2000; Bublitz et al., 1995; Bujewski and Rutherford, 1997a; Bujewski and Rutherford, 1997b; Ferrer et al., 1998; Patra, 2003). In contrast to LIF applications for monitoring pollutants in water, the heterogeneity and the opacity of soil matrices is still a considerable experimental challenge for the qualitative.
and quantitative interpretations of LIF data (Löhmanssröben and Schober, 1999). Up to now, in the field of environment monitoring, the researches related to the matrix effects on the fluorescence have just been interpreted in terms of the fluorescence intensity of contaminants of interest. In this study, the interpretation of the remediation process was performed taking into account the changes of the fluorescence spectral signature depending on the soil matrix effects.

LIF results are influenced by a variety of parameters such as wavelength, time, and intensity (WTI profile). For selected wavelength range showing characteristic fluorescence spectral signature of target contaminant, integrated intensity is easily considered as an indicator of the concentration of contaminant. Using this concept, initial in-situ monitoring technique such as SCAPS-LIF and ROST-LIF just detected the presence of contaminants as a screening purpose (Bujewski and Rutherford, 1997a; Bujewski and Rutherford, 1997b). However, for the accurate interpretation of LIF results in terms of quantitative and qualitative analysis, various photophysical properties of analytes which are present in soil of interest as well as matrices which strongly affect the fluorescence signal should be investigated.

For practical application of LIF to in-situ monitoring of the soil remediation process, lab-scale surfactant-enhanced electrokinetic remediation process was applied, and its result was interpreted in terms of the LIF spectra structures and intensities. The correction method using diffuse reflectance was also considered to enhance the relationship between PAHs concentration and its fluorescence intensity by minimizing matrix effects such as water content and grain size which are also proportional to the reflectance. The change of the spectral signature reflecting the nature of the surrounding environment (i.e., the binding or interaction between soil media and contaminants) was investigated to estimate the state of PAHs in soil media comparing the fluorescence spectra of PAH adsorbed on surface and dissolved in surfactant.

In this study, the LIF monitoring technique was applied to lab-scale remediation process and assessed the feasibility of the LIF capable of providing the information of any contaminants changes taking place during the remediation process.

**MATERIALS AND METHODS**

**Preparation of contaminated soils**

The soils used in this study were composed of quartz sand and kaolinite to represent sand and silt/clay fraction, and sand content was artificially controlled to 80 %. Phenanthrene and pyrene were selected as target contaminants. The soils were spiked with spiking solution where PAHs were dissolved in dichloromethane at the same time. This procedure made contaminated soils having the concentration of 200 mg-PAH kg⁻¹ dry soil per each contaminant. Artificially contaminated soil was used to monitor the variation of the relative quantities, reduction trends of target contaminants through the fluorescence intensity, and the variation of the spectral signature. Initial moisture content was adjusted to 20 %. The contaminated soils were aged for one week to evaporate the solvent and were used in the electrokinetic (EK) remediation process.

**Experimental apparatus and conditions**

As a remediation process, surfactant-enhanced EK process was evaluated. The main mechanism in EK process for removing the organic contaminant is electroosmosis, which is defined as the flow of an ionic liquid under the action of an applied electric field relative to a charged surface. As shown in Fig. 1, for negatively charged saturated soils, the movement of positively charged counter ions in the diffuse double layer, toward the cathode, creates an electroosmotic flow (EOF) of pore water during the EK process (Kim, 2001). The surfactant-enhanced EK remediation process has the potential to overcome many of the obstacles facing hydrophobic organic contaminants (HOC) removal from fine-grain soils by integrating the beneficial effects of enhanced HOC solubilization by surfactant or other appropriate facilitating agents with the accelerated transports resulting from EK process, thereby accelerating the overall HOC mass transport and subsequent rate of HOC cleanup (Ko et al., 2004).

In the EK process, an array of electrodes (cathodes and anodes) was inserted into both column ends through DC power supply system and electric current was applied into both electrodes. Applied electric current may induce EOF carrying contaminants from anode to cathode. The electrode solution reservoirs are located at both sides of soil specimen (Kim et al., 2002).

In this study, the optimal operation conditions, the concentration and exchange period of both electrode solutions, the applied current and operation duration, were determined by preliminary experiment. The influences of the variation on each condition and the addition of surfactants were considered to understand the significance of each parameter on the EK process. From the basic batch experiment results, various optimal operation conditions were determined and the batch scale experiment was carried out in order to consider the feasibility of LIF monitoring.
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for the remediation process.

The experiment consists of two parts: unenhanced (control test) and surfactant-enhanced scheme by the addition of biosurfactant. Na₂CO₃ was used as anode solution to neutralize the hydrogen ion generated in the anode resulting in the prevention of the decrease of zeta potential and EOF from pH decrease, referred as conventional enhanced scheme. For the similar reason, CH₃COOH was used as cathode solution. Ionic strength was controlled by the addition of Na₂CO₃ and CH₃COOH remaining solution pH above 4-5 and constant ionic strength during entire operation time. The concentration of these solutions was calculated so as to buffer the hydrogen and hydroxyl ions generated in the respective electrode for a 24-hour period, with the solutions being refreshed every 24 hour, which was the exchange period of the electrode solutions. The experiment was performed for 72 hours, as the direction of the EOF reverses after this time, which results from the reversal of the soil surface charge as pH decreases. This reverse electroosmosis changes the transport direction of contaminants and finally makes them, which already migrated towards cathode, move into the soil again. Before the operation, pH and the voltage were measured and pH and EOF at anode and cathode were measured during the operation time. Details on the experimental apparatus and conditions were described previously (Ko, 2002).

LIF measurement with respect to locations in soil specimens where they are divided into five sections was also conducted. The fiber-optic probe was dipped into soil samples without any pretreatment such as extraction. LIF intensity was measured on the soil surface using the optical fiber. Total 16 measurements per each sample were carried out to consider the heterogeneity of soils and the recorded spectra were averaged by wavelength. After each measurement, fiber-optic probe was rinsed with HPLC-grade ethanol and distilled water, and cleansed with a fine laboratory wiping tissue.

Data analysis

Surfactant–enhanced EK process for the remediation of PAH-contaminated soils was evaluated by the LIF. In the EK process cell, the PAHs concentration was expressed as the total fluorescence intensity, which is obtained in two ways. First, for unenhanced EK process (control test), the raw data consisted of wavelength, time and intensity (WTI) profile. The WTI were the integrated intensity for the characteristic wavelength domain showing the presence of PAHs of concern and total time domain. The characteristic wavelength range for the phenanthrene and pyrene was already confirmed from the fluorescence of each PAHs on soil media used in this study. For the second case, surfactant-enhanced EK process, considering the presence of surfactant and the time resolution, was conducted. From previous study, it was observed that the fluorescence of surfactant and PAHs were overlapped. To solve this problem, the decay time of each compound was obtained. Therefore, after complete decay of surfactant (~ 8.27 ns), the fluorescence spectra were integrated for the time range and same wavelength coverage. Total fluorescence intensity was also corrected by the diffuse reflectance to minimize the effect of soil matrix properties. The variation of spectral signature for each location was compared with each other as well as that of initial soil.

RESULTS AND DISCUSSION

The contaminated soil specimens were tested using EK process. The fluorescence spectra for each location in the EK cell were recorded and total fluorescence intensity for the total time range from 0 to 50 ns and characteristic wavelength range at 350-460 nm for phenanthrene and 380-530 nm for pyrene was obtained. Due to the broad fluorescence spectra of pyrene, the spectral structure was examined by focusing on the characteristic peak wavelength. Characteristic peak wavelength for phenanthrene was observed at 375, 385, 405, and 430 nm, while pyren at 530 nm. The total intensity was also corrected by diffuse reflectance.
Therefore, the data was expressed by the relative intensity. Fig. 2 (a) shows three-dimensional fluorescence spectra of initially contaminated soil with 200 mg/kg phenanthrene and pyrene, and (b) a contour map showing the diffuse reflectance at 385, 405, and 430 nm showing phenanthrene and broad peak at 530 nm showing pyrene. The relationship between the normalized fluorescence intensity by diffuse reflectance \((I_F/I_{DR})\) of initially contaminated soils (white circle) and after the EK remediation process (black rectangle), and normalized distance from the anode (0.0) to the cathode (1.0).

As the remediation process proceeds, the contaminants move toward the cathode. Therefore, relatively low quantities of PAHs were observed near the anode, while high accumulation of PAHs at the cathode. As shown in Fig. 4, the fluorescence of cathode was sharper and showed more peak wavelength at the edge revealing the more mobile states or fraction of PAHs due to electro kinetic mobility of PAHs. In addition, the
increased variation of intensity was shown in Fig. 5. During the process, the change of the soil properties was reflected.

The focus of this work was to analyze the fluorescence spectra and relate them to the reactions taking place in the soil. In surfactant-enhanced scheme, same procedure was conducted for data analysis except the integration for the specific time range. In the case of surfactant/PAHs/soil system, it was difficult to interpret and distinguish the fluorescence because of the overlapping of spectral signature. Therefore, the time resolution was used. The time information is valuable to interpret LIF results. After getting decay time of each, time slices above decay time of the surfactant were used to get the fluorescence spectra of pyrene. Based on the results about the decay time of the surfactants, the total fluorescence intensity was obtained by integrating time after 9 ns. The quantum yield of the surfactant is relatively small compared to that of PAHs, after removing surfactant from the total fluorescence, more characteristic spectra are shown. In terms of the normalized fluorescence intensity by the diffuse reflectance, raw data and time resolved data were compared as shown in Fig. 6(b). The peak wavelength was almost identical and the time-resolved data showed little sharper and more peak wavelength.

The fluorescence at normalized location 0 from the anode was compared with that of the initially contaminated soil (Fig. 7). At the location 0, relatively reduced fluorescence was observed due to the loss of pyrene fraction and the spectra showed that it still adsorbed phase of contaminants after moving the more mobile fraction of PAHs by EK process.

In terms of normalized location from the anode in the EK cell, the variation of spectral signature and fluorescence intensity by the remediation process were depicted in Fig. 8(a). From the anode, the PAHs moved by EOF also showed the change of spectral signature. As toward the cathode, sharper peak wavelength, especially around 385 nm, was observed, implying more mobile fraction. On the other hand, near the anode,
remaining adsorbed phase of PAHs revealed pressed bending mode around 385 nm. The comparison of the peak wavelength $I_{385}/I_{405}$ also can be a tool for assessing the state of contaminants on soil media. Also broad peak around 450 nm representing adsorbed pyrene was decreased, implying the change of the state of the pyrene.

As surfactant-enhanced EK remediation advanced, EOF including contaminants moved continuously toward the cathode, resulting in inducing different moisture and silt/clay or sand distribution through soil media. It may influence the LIF intensity of the remediated soils resulting in high variation of intensity (Fig. 8(b)).

CONCLUSION

The capability of LIF monitoring using lab-scale surfactant-enhanced EK remediation process was evaluated to provide real-time information of contaminants. The changes in the soil in terms of semi-quantities and phase of contaminants can be monitored by analysis of the fluorescence spectra of PAHs during the remediation process. Estimation of the state of contaminants in soil media is an important key to assess the feasibility of remediation process. The primary finding in this experiment was the change of fluorescence spectral intensity with increasing distance from anode to cathode. The experimental results clearly showed that it is possible to estimate the state of contaminant changing by adding the surfactant or water on soil media from the obtained fluorescence spectra. If surfactant-enhanced EK process as a remediation process is applied, it will be possible to define a fluorescence probe molecule, which allows optimizing the conditions for remediation process, for example, finding the conditions for highest contaminant mobility. In the future study, the application of the fluorescence probe for specific contaminated sites will be performed.

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