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Electrokinetic and Ultrasonic Treatment of Kaolin Contaminated by POPs

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Abstract: Three tests were conducted using ultrasound alone, ultrasound as an enhancement for electrokinetic test and electrokinetic test alone to compare the removal performance of the three persistent organic pollutants, hexachlorobenzene, phenanthrene, and fluoranthene from low permeability kaolin. Results show that the removal efficiency in ultrasonically enhanced electrokinetic test was the highest among experiments, though the removal rates improved were small only. The assistance of ultrasound in electrokinetic remediation can help reduce these hydrophobic organic compounds by increasing their mobility, desorption for electroosmotic migration, and also by degrading them through free radical oxidation forming during cavitation process.

Keywords: Clayey soil remediation, electrokinetic process, persistent organic compounds, ultrasonication

INTRODUCTION

As a key component of environmental chemical cycles, soil contamination often contributes to water and air pollution (1). Any hazardous substance

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present in a soil matrix represents a threat to public health and ground water. Among these pollutants, persistent organic compounds are of particular concern because of their long life span and toxicity. Therefore, decontamination of soils through the removal of these organic contaminants becomes a more and more urgent problem in the present world. Site conditions, contaminant types, contaminant source, and the potential impact of the possible remedial measure determine the choice of a remediation strategy and technology. No single technology is appropriate for all contaminant types and various site-specific conditions (2).

For organic contamination particularly, a variety of site remediation technologies are available, which can be categorized as ex-situ and in-situ treatments. Since ex-situ treatments involve soil excavation, they can be costly. On the other hand, in-situ treatments are attractive because of potential low cost and avoiding or lessening hazardous waste spreading, since it allows the soil to be treated without being excavated and transported (3). However, the conventional in-situ treatments such as bioremediation, soil washing etc., are usually very site-specific and often work best on homogenous, permeable soils but are difficult to apply on low permeable soils (4). Fortunately, electrokinetics has emerged as an innovative in-situ technology that can deal with this problem. The electrokinetic process can extract heavy metals, radionuclides, and organic contaminants from saturated or unsaturated soils, sludges, and sediments (5–7). Because of the applicability to a broad range of organic and inorganic contaminants, and especially the ability to work in low permeable soils, there has been considerable interest in electrokinetic processes in recent years (8).

The electrokinetic remediation technique is based on the application of low-level direct current, which is used to mobilize and separate contaminants via electromigration, electroosmotic, and electrophoretic phenomena. Unlike metal or charged ions which are removed electrokinetically from soil mainly by electromigration, non-polar contaminants like most organic compounds are transported primarily by electroosmosis, and the process would not be effective unless the contaminants are soluble in pore fluid. Therefore, enhancement is needed to improve mobility of hydrophobic compounds, which tend to adsorb strongly to the soil, particularly the low permeability one.

On the other hand, ultrasonic irradiation applied into contaminated soils can increase desorption, mobilization of contaminants, as well as porosity and permeability of soil through developing of cavitation (9). Moreover, ultrasonic waves can promotes the formation of free strong oxidative radicals that involve the oxidation of contaminants (10,11), and the high local temperature and pressure forming during ultrasonic cavitation can destroy the contaminants through pyrolysis processes (12). The use of ultrasound offers several advantages such as lack of dangerous breakdown products, and the low energy demand and technology can be made quite compact, transportable, allowing on-site treatment (13).

In this study, ultrasound was used as a treatment method alone and as an enhancement for the electrokinetic test to improve the removal performance of the three persistent organic pollutants (POPs), hexachlorobenzene (HCB), phenanthrene (PHE), and fluoranthene (FLU) from low permeability kaolin.

EXPERIMENTAL

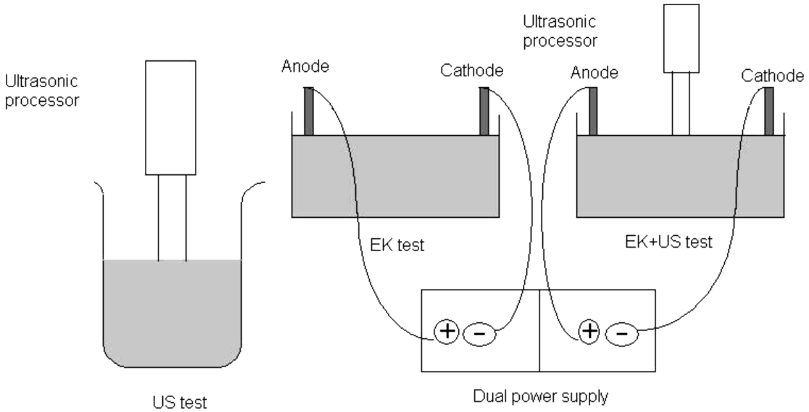
The representative persistent organic compounds chosen in these experiments were HCB (99%), a typical polychlorinated hydrocarbon and two PAHs, PHE (97%), and FLU (98%). Hexachlorobenzene and fluoranthene were purchased from Sigma-Aldrich (Germany). Phenanthrene and hexane were purchased from Merck (Germany). All chemicals were of analytical grade. Model clayey soil used in the experiments was white kaolin purchased from VWR International (Finland). Kaolin was often used as the model clay due to its high content of clay, negligible content of organic matter, low cation exchange capacity and inertia (14). Some of the main characteristics of kaolin are summarized in Table 1.

The ultrasonic processor used in the experiments was UP200H from Hielscher – Ultrasound Technology (Germany), with an operating frequency of 24 kHz and a maximum power of 100 W. The power of this ultrasonic processor can be controlled in the amplitude range of 20–100%.

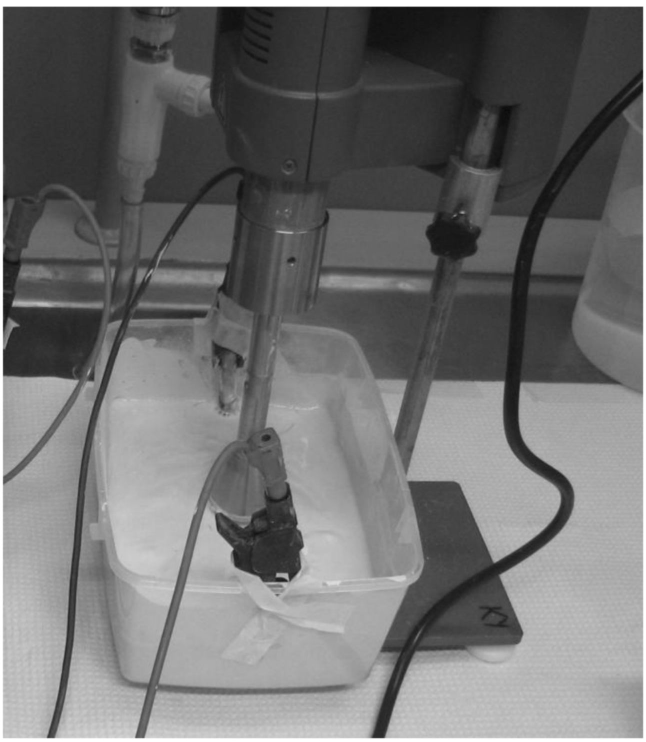
Kaolin was artificially contaminated with these three POPs at target concentrations of 100 mg kg^{-1}. The amount of kaolin used for each test was about 500 g. Because of the low solubility of these organics in water,

Table 1. Main characteristics of kaolin

pH	4.68
Dry bulk density (g cm^{-3})	0.508
Moisture (%)	1.03
Electric conductivity (μ S cm^{-1})	448
Cation exchange capacity (c mol kg^{-1})	3.1
Organic content (%)	0
Particle size distribution:	
% sand (>0.05 mm)	3.9
% silt (0.05–0.002 mm)	20.2
clay (<0.002 mm)	75.9



(a)



(b)

Figure 1. Sketch for experiment set-up: Ultrasonic (US) test, Electrokinetics (EK) test, Ultrasonically enhanced Electrokinetics (EK + US) test.

hexane was used as a solvent to dissolve them completely for the target concentration (15). Kaolin was soaked with this solution at the ratio of approximately 500 ml per 1 kg kaolin. It was stirred well to make kaolin spiked homogenously. Then, it was kept in fumehood nearly a week for the solvent to evaporate entirely and the kaolin could be ready for experiments. Samples were taken to check the actual initial concentrations of POPs in kaolin, because some portion of contaminants may be lost along the process.

The scheme of these experimental setups was described in Fig. 1. Experiments were conducted in three tests for 15 days. In each test, 500 g kaolin was mixed with 600 ml distilled water to make slurry. The ultrasonic (US) test was carried out in a plastic beaker. The electrokinetic (EK) test and ultrasonically enhanced electrokinetic (EK + US) test were conducted in two rectangular plastic pans with $20 \times 14 \times 8$ cm dimensions. Titanium electrodes of 10 cm long and 1 cm diameter were connected to the direct current dual power supply. The constant voltage applied in both EK and EK + US tests was 30 V, with the initial direct current of 0.03 A. The kaolin slurry in US alone and EK + US tests were subjected to 100 W ultrasonic waves at 24 kHz for 1 hour per day, during 15 days. Water was added manually on the anode side of EK and EK + US tests, about 50 ml per day, to compensate the lost amount due to evaporation over a long time of experiment and maintain certain moisture for treatment.

At the end of the experiments, the dual power supply was switched off. Samples were dried in an oven at 80°C overnight. The dried kaolin was then pulverized for pH measurement and POPs analysis. Samples were analyzed in duplicates for quality assurance. One gram of sample were mixed with 5 ml hexane in a glass tube and was put into ultrasonication bath for 30 minutes to get the organic compounds extracted from the soil into hexane solvent. The glass tubes were centrifuged at 5000 rpm for 10 minutes (14). The supernatants were then taken into 2 ml glass vials for GC-MS (Agilent 5975) analysis to determine the residual POPs concentration.

RESULTS AND DISCUSSION

Current Progress

Figure 2 shows the changes in electrical current of EK and EK + US tests during experimental period, when the voltage was kept constant at 30 V. As seen in this figure, most of the time, the current in the EK test fluctuated around 0.03 A. On the other hand, the current in EK + US test had been rising up to 0.05 A within first 3–4 days, then declined and remained

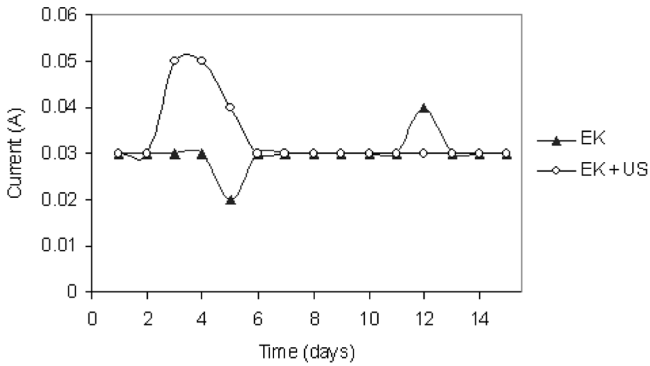


Figure 2. Current change during experimental period in EK and EK + US tests.

around 0.03 A till the end of the experiment. It could be considered that the higher current in EK + US test at the beginning of the experiment is attributed to ultrasonication effects, which made the slurry more porous and permeable. It was observed that the slurry's moisture tended to decrease along the time (especially in anode parts) because of electroosmosis towards the cathode as well as because of evaporation, and this can affect the current of the tests since the current primarily results from electromigration of ions through the pore fluid (16). Therefore, after 5 days of operation, when the current started to fall, water was added regularly into the test pans, to maintain certain moisture and current.

pH Distribution

At the end of the experiments, samples were taken from nine positions, numbered as distributed in pan matrix (Fig. 3). Figure 3 shows that the pH distribution among pan matrix follows quite the same pattern in both tests as there is no big difference of pH between EK and EK + US tests. Our previous studies on ultrasonication of kaolin slurry also demonstrated that ultrasound did not affect pH of kaolin slurry. Sample 2 (near anode) had the lowest pH of 1.97 (EK test) and 2.11 (EK + US test) while sample 8 (near cathode) had the highest pH of 10.28 (EK test) and 9.91 (EK + US test). It is explained by the acid front generated at the anode and the base front generated at the cathode. As a result of electroosmosis and electromigration, low pH (high H^+ concentration) solution generated at the anode was transported in the soil and moved towards the cathode (17). The low pH solution migrated faster because the electromigration of H^+ is concurrent with the electroosmotic flow and the mobility of H^+ is

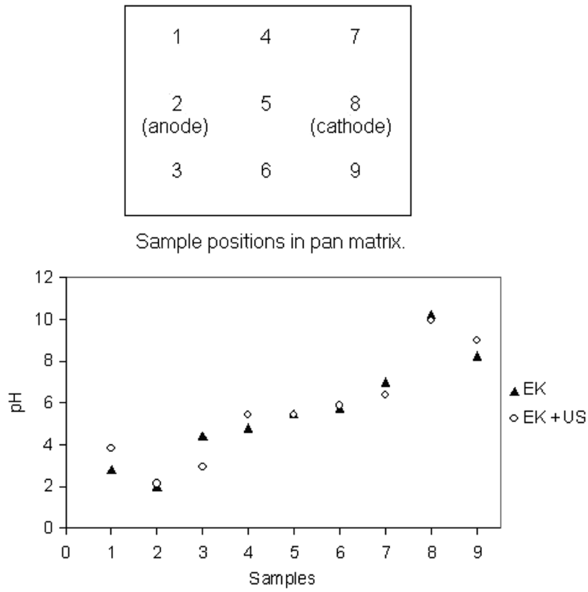


Figure 3. pH distribution among pan matrix.

about 1.76 times higher than that of OH^- (6). Moreover, the initial pH of kaolin is 4.68. Therefore, pH of most of samples were lower than 7, except those samples near the cathode. Samples at the center of the pans (numbered 4, 5, 6) had a pH of around 5–6.

POPs Removal

The study investigated the effectiveness of combining ultrasound and electrokinetic treatment in POPs removal from a contaminated clayey medium. As described previously, electrokinetic remediation is particularly helpful for clayey soil treatment while this type of low permeable soil is often a problem for other techniques. However, electrokinetic remediation is more effective with metal or charged ion removal through electromigration than non-polar contaminants or organics removal through electroosmosis. In contrast, ultrasonic irradiation, is specifically used for organics removal through enhancing the desorption and mobilization of these contaminants, as well as their destruction by oxidation and pyrolysis. Thus, ultrasonication can help as a complement or enhancement for electrokinetic remediation. The combination of these two methods was expected to have coupling effects that take advantage of the strong points from both techniques. The remediation mechanisms involve complex ultrasonic and electrokinetic processes. Ultrasound increases kaolin porosity and permeability as well as increases desorption of the low-soluble POPs (9), therefore, electroosmotic migration of these contaminants was enhanced. The electroosmotic flow was not checked but the electroosmotic phenomenon was observed obviously through the accumulation of water into the cathode side. Moreover, ultrasonication can induce high fluid–solid shear stresses (18), thermal decomposition, and hydroxyl radical oxidation (12) that involves sonolysis of organic compounds in the slurries. The POPs concentrations in kaolin samples of EK and EK + US tests after experiments are described in Fig. 4 as average residual percentages of samples from anode, central and cathode parts. Figure 4 shows that in both EK and EK + US tests, all three POPs concentrations had been reduced to certain levels, in which, residual percentages of the two PAHs, PHE (16–26%) and FLU (20–34%), are considerably lower than that of HCB (47–67%). This could be explained by the very stable chemical structure of HCB that makes it difficult to treat. Residues of POPs tended to concentrate mostly highest at the central part and decrease at the two electrode ends. Oxygen produced at the anode can be attributed to organic oxidation in this part. During experiments, kaolin accumulated in the anode side due to electrophoresis (since kaolin particle's surface charge is negative) while water accumulated in the cathode side of the pan. Thus, the slurry in the cathode part was more dilute and contaminants there were more easily desorbed and removed from the kaolin. On the other hand, in both tests, the two PAHs had been removed more in anode side while HCB had been removed more in the cathode side. It could be explained that the two PAHs are more easily destroyed by oxidation than HCB, while HCB

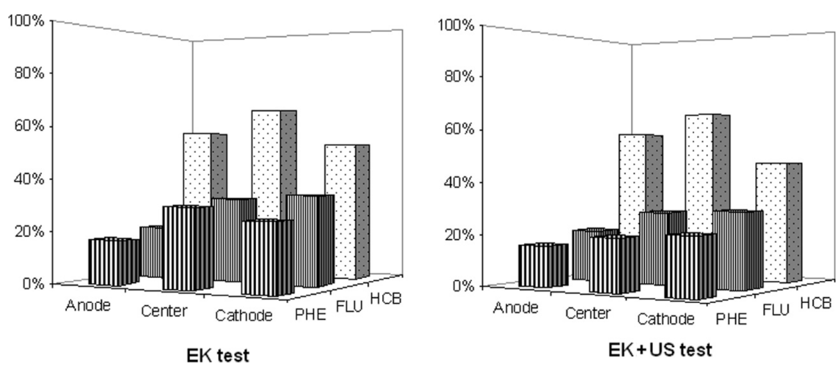


Figure 4. Residual concentration distributed along the soil profile in EK and EK + US tests.

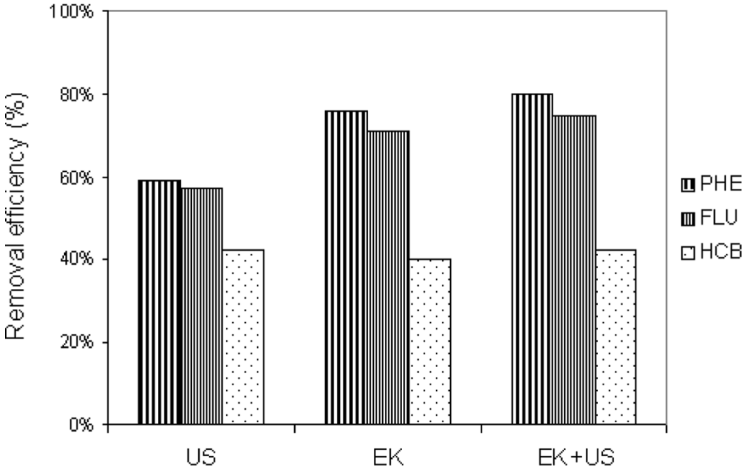


Figure 5. Removal efficiency (%) from different treatment methods.

can be desorbed, mobilized and removed from the dilute slurry. In general, residual concentrations of POPs from EK + US test are lower than that of EK alone test. In addition, the POPs residues distributed along the soil profile in EK + US test were also more homogeneous, compared to EK test alone, because of the physical mixing effect of ultrasound.

The contaminant removal efficiency is calculated by inversing average residual percentage. Figure 5 shows the POPs removal efficiency from different treatment methods. Generally, more than 40% HCB and significant amounts of PAHs (up to 80%) were removed by all methods. Removal efficiencies of POPs in EK + US test were the highest and that in US test alone were the lowest among the three tests (Fig. 5). There is no big difference among the three treatments for HCB removal. However, PAHs removal can be improved by electrokinetic remediation and ultrasonically enhanced electrokinetic remediation.

CONCLUSIONS

Results from experiments show that combined electrokinetic and ultrasonic treatment did prove positive coupling effect in PAHs removal than each single process alone, though the level of enhancement is not much. However, among the three POPs, HCB is the most difficult to treat because of its high stability and the removal of HCB from all three tests did not perform big difference. The assistance of ultrasound in electrokinetic remediation can help reduce POPs from clayey soil by improving the mobility of hydrophobic organic compounds and degrading these contaminants through pyrolysis and oxidation.

Although ultrasound has shown up as quite effective in many studies on organic removals from water, the combination of ultrasound and electrokinetics for soil remediation is still just a recent idea realized in laboratory scale. More future works should be conducted in considering some technical limitations in scale-up, transducer design, physical effects such as noise, medium heating etc., and many other practical aspects.

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