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ORIGINAL PAPER

Electro ultrasonic remediation of polycyclic aromatic hydrocarbons from contaminated soil

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Abstract The polycyclic aromatic hydrocarbons (PAHs) with high molecular mass are renown for their high persistence in the soil, hydrophobic and toxicity. Remediation of these pollutants is still an unsolved task and needs more researches to be performed. The coupling of electrokinetics (EK) with ultrasonic energy (US) has advantages on desorbing and migrating PAHs from contaminated soil. US and EK work together to destroy PAHs. The objective of this study was to treat PAHs contaminated soil by using EK and ultrasonication. The contaminated oil contained about 100 mg kg^{-1} chrysene. Experiments with US, EK and combined EK and ultrasound were conducted in reactors and pans with and without iron anodes. Results indicated that the removal was more effective with lower concentrations of chrysene. The average removal was better in experiment with combined EK and ultrasound using iron anode. This might be due to increase in electroconductivity by iron ions.

Keywords Chrysene · Electrokinetics · Electroosmosis · Soil remediation · Ultrasonic energy

1 Introduction

Pollution by chemicals creates serious problems to environment. Among the main soil pollutants, polycyclic aromatic hydrocarbons (PAHs) are of particularly hazardous. PAHs persist in the environment, and bioaccumulated through the food web, causing adverse effects to human health and the environment [1]. Chrysene was taken as the model pollutant, a representative of PAHs and large hydrophobic compounds with four fused aromatic rings. In case of PAHs, the hydrophobic nature increases with increase in weight [2]. It is not produced for commercial purposes but it is released into the environment as a by-product of many industrial processes such as distillation of coal, distillation or pyrolysis of fats and oils [3]. If it is in the air, it adsorbs to soil and dust particles and is dispersed over large areas, contaminating both soil and watersheds [4, 5]. Once entered in the soil they accumulate in horizons rich in organic matter where they are likely to be retained for many years due to their persistence and hydrophobicity [6].

Its half life depends on the matrixes. For examples, 1.25 h in air, 4.4 h in water, years in soil. There are limited studies on microbial degradation of chrysene due to its negligible solubility and high soil–water distribution ratios, which stand against its ready microbial utilization and promote its accumulation in the solid phases of terrestrial environment [7]. Approximately 60% of the chrysene can be removed in the slurry reactor with nutrients and microorganism [8]. A white rot fungus can have the capability to degrade 30 mg PAHs kg^{-1} soil, but operation time was 30 days. It is difficult to distinguish analytically between chrysene disappearance due to microbial degradation and that from adsorption to soil [9]. There is still lack of knowledge in biodegradations and absorption by soil. The rhizospheric microflora is found to be stimulated to degrade chrysene [10]. Masten and Davies [11] used ozone to overcome the limitations imposed by the low aqueous solubility of PAHs on their rate of biodegradation and/or dissolution for in situ chemical oxidation processes. It was found that the degradation decreased with increase

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in molecular mass in PAHs. It was also concluded that after 4 h of exposure to ozone, the chrysene concentration in a contaminated soil was reduced 100–50 mg kg^{-1}). 7.8% of chrysene was removed in 30 min at a KMnO4 concentration of 160 mM from about 65 mg kg^{-1} [12].

There is a great need of fast, low cost, environmental friendly and in situ remediation technologies. Among in situ remediation technologies, electro-osmosis remediation method (EOR) has become a promising, inexpensive, publicly accepted and innovative technique for removing organic contaminants from contaminated soil. This technique is best suited for a low-permeable soil. Most of organic pollutants will not precipitate or bind to soil differently at higher or lower pH values. With electroosmosis (EO), a higher pH actually increases pore water movement. Organic pollutants move along with pore water towards the electrode. Upon their migration to the electrode, the pollutants accumulate by the electrode or are transported into the water, which need secondary treatment such as electroplating, precipitation/co-precipitation, pumping near the electrode or complexion with exchange resins [13, 14].

It is often very difficult to treat chrysene contaminated clayey soil especially with low permeability only by electrokinetic method as the hydrophobic and non-polar nature help chrysene to adsorb strongly in the soil texture. Therefore, the enhancement is necessary to improve the mobility of it. Several techniques can be used with electrokinetics (EK) to improve the performance such as surfactant [15–18], design and operation enhancement [19–21]. Compared to conventional methods, ultrasonication can bring several benefits like environmental friendly (no production of toxic chemicals) and low cost [22]. Ultrasonic energy (US) applied into contaminated soils can increase desorption and mobilization of contaminants and porosity and permeability of soil through developing of cavitation [23]. Moreover, organic contaminants can be destroyed through pyrolysis or oxidation by strongly oxidative free radicals that generated during ultrasonication [24].

The research-work was focused on the development of in situ electro ultrasound remediation process that has a potential for removal of chrysene, a hydrophobic PAH from contaminated soil without using any surfactants and any other chemicals.

2 Materials and methods

Chrysene was purchased from Acrös organics and hexane from Merck. All chemicals were of analytical grade. The ultrasonic processor used in these experiments was UP100H with operating frequency of 30 kHz, power of 100 W and 10 mm horn diameter from Hielscher—Ultrasound Technology Company. The power of these ultrasonic processors could be controlled in the amplitude range of 20–100%. Graphite electrodes of 10 cm long and 10 mm diameter were connected to the direct current dual power supply. Two plexiglass cylinders were used for EK and combined electrokinetic-ultrasonic (EKUS) tests. Each plexiglass cylinder consists of a central chamber (Φ 10 cm × 20 cm) and two electrolyte chambers (Φ 10 cm × 4 cm) for anode and cathode parts (Fig. 1). In the middle of the central chamber, there is a rectangular hole of approximately 14 cm × 7 cm for acoustic horn position and easily handling with the soil input. The electrolyte chamber has two small holes for electrode position, gas ventilation and pH checking by pipette. Soil in central chamber is separated with electrolyte chambers by polypropylene filter cloths (Sigma-Aldrich Co., Germany). Kaolin (VWR) was used as a model low permeability clayey soil. The physical and chemical properties of kaolin were determined based on the methods prescribed by Soil Science: Methods and Applications [25] and are shown in Table 1.

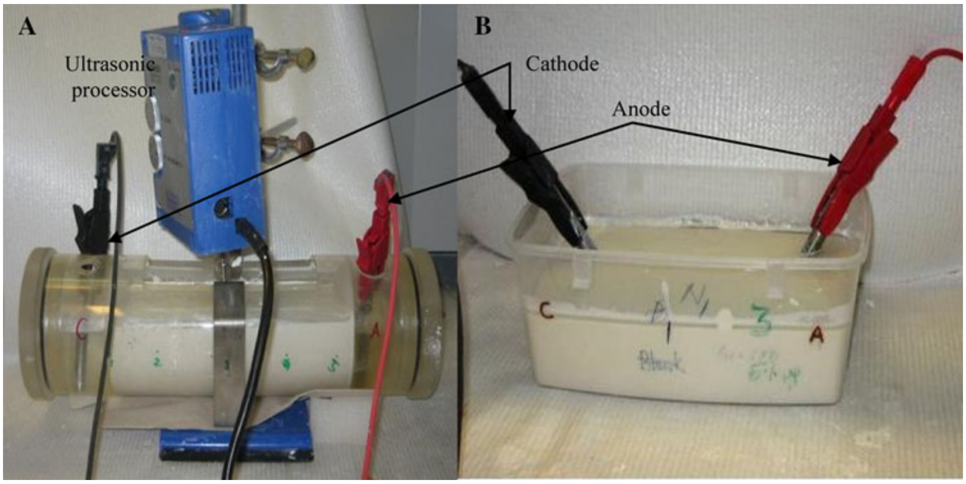


Fig. 1 **a** Treatment in a reactor. **b** Treatment in a pan

Table 1 Characteristics of kaolin

Properties	Values
Kaolin	100%
Colour	White
pH	5.0
Specific density	0.51
Moisture	1.11%
Carbonate content	5.5%
Electrical conductivity	189 μS
Cation exchange capacity	3 mmol 100 g^{-1}
Particle size distribution	
Sand	3.9%
Silt	20.2%
Clay	75.9%

2.1 Ultrasonic treatment

Kaolin was artificially contaminated with chrysene at initial concentrations of 25, 50, 75 and 100 mg kg^{-1}. Because of the low solubility of POPs in water, hexane was used as solvent to dissolve completely the POPs required to yield the target concentrations [26]. To contaminate the kaolin, chrysene–hexane solution was slowly added to dry kaolin. The mixture were stirred with stainless steel spoons within glass beakers and then placed in fume hood for nearly a week until the hexane completely evaporated. Samples were taken to determine the actual initial concentrations of POPs in kaolin, because some portion of contaminants may be lost along the process. The dry kaolin was then mixed with deionised water to simulate field moisture conditions for ultrasound process.

A series of laboratory batch ultrasound experiments was conducted on chrysene-contaminated kaolin with different concentration of chrysene (0, 25, 50, 75 and 100 mg kg^{-1}) to know maximum removal efficiency of ultrasound at 100 W for 24 h. Samples were taken every 2 h.

2.2 EK treatment

The cell designed, shown in Fig. 1 consists of a polyethylene body which has negligible capacity of adsorption of chrysene. The amount of dry kaolin packed in the cell was approximately 500 g. There were two compartments for electrodes filled with tap water. The graphite electrode was always taken as cathode. The separation distance between the two compartments was 20 cm. The filter cloth membrane was placed between cell and compartment in each site to allow the exchange of electrolytes into and out of the compartment. Two types of experiments were conducted in simple electrokinetic treatment with graphic anode and iron anode (iron might show similar effects as Fenton). The duration of experimental period was 10 days.

2.3 EKUS treatment

The kaolin–water mixed slurry in EKUS tests was subjected to ultrasonic waves at the same condition of 5 h on the first day and 1 h per day for the rest of experimental period (10 days). In both EK and EKUS tests, catholyte solution was tap water. During experimental period, the voltages were kept constant at 30 V (the voltage gradient was 1.5 V cm^{-1}), and the change of currents was recorded daily.

Similar experiments for EK and EKUS were carried out in an open pan without separation chambers for electrodes. The dimensions of pan were 20 cm × 14 cm × 8 cm and pan was made of HDPE (Fig. 1). Approximately 500 g of contaminated kaolin was put into it. Electrodes were inserted into soil at end of the pan. These experiments were designed in considering of implementation of the process in the field.

In all experiments, the ratio of water and soil was maintained about 2:1. The sonochemistry based on the fact that a liquid is exposed to sufficiently large acoustic field [27]. The convenient of hydraulic transport of soil in slurries is typically by 40% by weight [28].

2.4 Extraction and chemical analysis

At the end of experiments, the dual power supply was switched off. The final soil mass was divided into five sections in case of reactor and nine sections in case of open pan experiments, from anode to cathode. These samples were dried in an oven at 80 °C over 24 h. The dried kaolin was then pulverized for analysis. Samples were analyzed in duplicates for quality assurance. One gram of sample were mixed with 5 mL hexane in glass tube and was put into ultrasonication bath for 30 min to get the organic compounds extracted from the soil mediums into hexane solvent. The glass tubes were centrifuged at 4000 rpm for 20 min [18]. The supernatants were then put into 2 mL glass tubes. TA Finnigan Trace 2000 GC equipped with a Finnigan Polaris Q mass spectrometer was used for determining the remained concentrations of chrysene in the extracts. pH values of the soil samples were also measured in time series and all sections of final soil mass at the end of the experiments.

3 Results and discussion

3.1 Ultrasonic treatment

Figure 2 gives the idea about the efficiency of removal of chrysene from the soil. It shows that the efficiency of

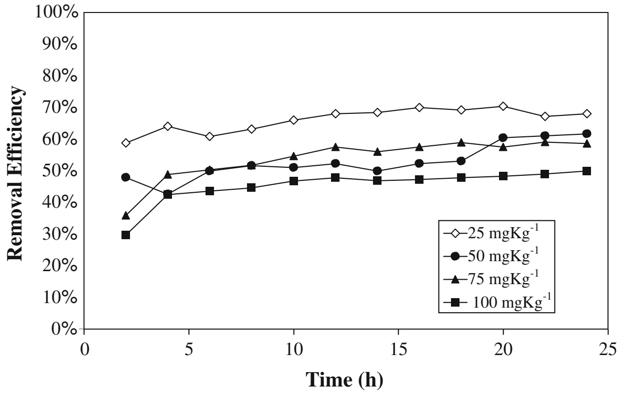


Fig. 2 Chrysene removal from kaolin on treatment of ultrasound alone

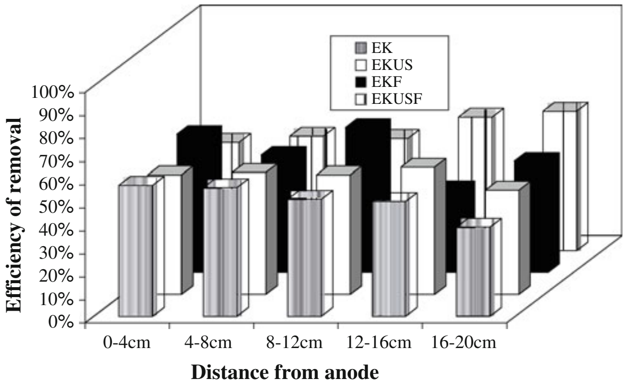


Fig. 3 Removal of chrysene in the reactor

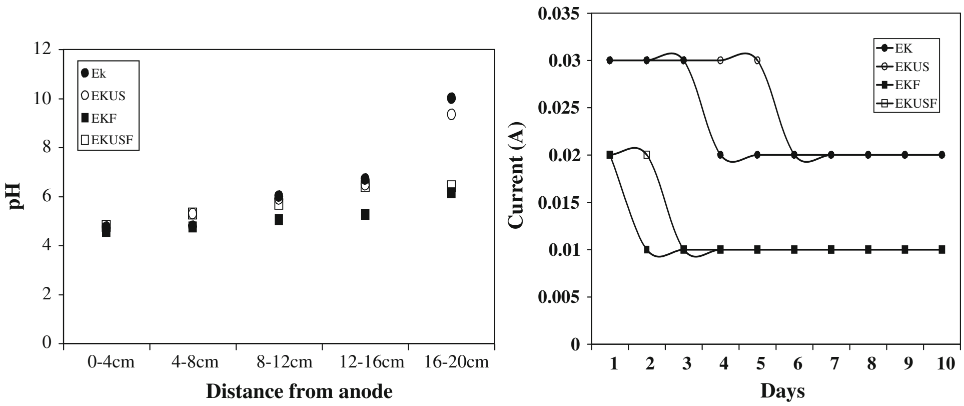
removal depends on the concentration of pollutants in soil. After 24 h ultrasonication, the removal percentages were about 70, 62, 59 and 50 from 25, 50, 75 and 100 mg kg^{-1}. It was found that the oxidation of organic compounds by sonocation highly depends on the concentration [29, 30]. That means the expose with ultrasound covers more in low concentration. At constant moisture content, frequency and power of the ultrasound processor, the remediation decreased with increase in concentration of pollutants. The average removal percentage in case of 100 mg kg^{-1} was about 45.

3.2 Treatment in the reactors

The electrolytes in both cathode and anode compartments consisted of negligible amount of chrysene. The removal percentage of chrysene was observed in EK and EKUS with and without iron anode (Fig. 3). Chrysene removal was higher in anode side in both EK with and without iron anode. In case of EK with iron anode, the removal percentage slightly increased by 1%. It may be due to function of dissolved iron that helped to increase the electroconductivity in the kaolin. It is clearly shown that removal increased 5% more in the anode side in which iron anode was used. In case of ultrasonication, the removal was uniform through out the soil but the removal percentage was increased by 1 in EK. This is different than the lower molecular PAHs. It was found that the removal percentage of PAHs having lower molecular mass and less numbers of aromatic rings than chrysene was 10% more than that of EK [31]. This shows that the rate of remediation depends upon molecular mass and numbers of aromatic rings in PAHs. The removal was high at the anode side in the experiment with EK only. It might be due to migration of chrysene with water (EO) towards cathode and also by oxidation reaction of chrysene by oxygen formed there. In case of experiment with EKUS, remediation was high at cathode because water content was relatively higher there. Amount of water content helped in production of OH-radicals [23].

Figure 4 shows the change in current during experiments and pH after experiments. The pH values in the anolyte and catholyte were about 2.0 and 11 during EK and EKUS without iron anode experiments whereas with iron anode, pH of anolyte was about 6.0 and that of catholytes, 11.0. After completing of experiments, the soil samples were divided into five sections in 4 cm difference from

Fig. 4 pH and current change in the reactor



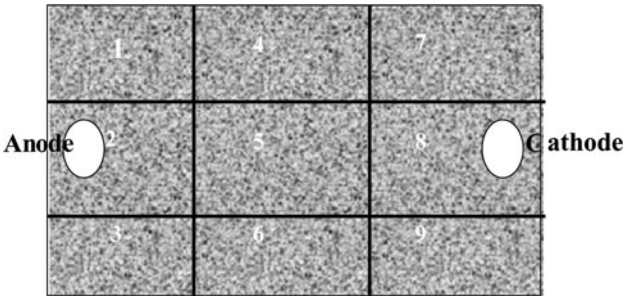


Fig. 5 Sample labeled in the pan matrix (for EK and EKUS tests)

anode and then pH of them were measured. 0–4 cm section nearby anode had lowest pH values around 4.8 and highest pH values around ~10.2 are nearby cathode for experiments without iron anode and pH values around ~6.4 for experiments with iron anode. It happened because of acid front generated at anode and base front at cathode. Due to EO and electromigration, H+ ions moves towards the cathode and OH− ions moves towards anode. As the small H+ ions, they can move twice times faster than OH− ions [32, 33]. In case of experiments with iron anode, pH values were almost same through the sample soil. It may be because iron ions migrated from the anode maintained the pH. There was no significant difference in pH of EK and EKUS. It was already proved in our previous studies on ultrasonication of contaminated kaolin slurry. Figure 5 shows the change in electrical current during the experiments. It has been seen that the current of EK and EKUS tests fluctuated in quite similar pattern that tended to decrease along time and then became constant.

3.3 Treatment in the pans

The percentage of chrysene removal was measured from each of nine sections after 10 days long of each experiment in the pans. The sections were divided as shown in Fig. 5.

The results of measurement are shown in Fig. 6. The removal percentage was somewhat better than that in reactor treatment. The average removal in EKUS was nearly 2% more than in EK without iron anode whereas it was 3% more in EKUSF than in EKF with iron anode in pan. The removal in both EK is higher at anode side. It was always observed in the pan that the kaolin moved to the middle due to migration of water towards the cathode from anode.

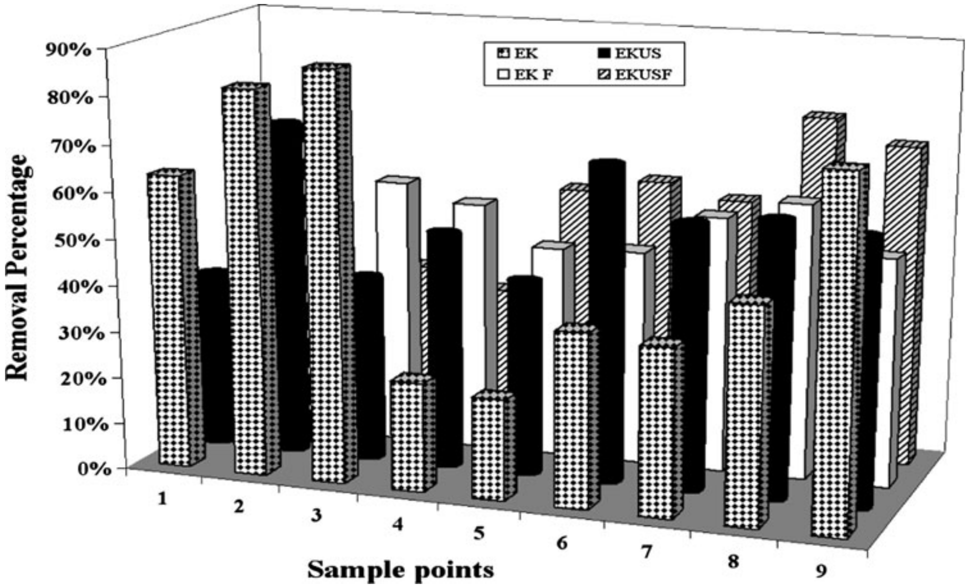
Figure 7 shows the pH profile of soil after completing the experiments and the change in current during the experiments. The trend of current was similar as in reactor, but the pH in experiments with and without iron anode had similar result as in pan. The iron ions could not move fast in this case. The pH values were lower at anode side and higher at cathode side. It might be due to same reasons as in reactors.

4 Conclusion

It could be concluded that

- It is possible to treat higher ringed aromatic hydrocarbons contaminated soil by ultrasonication within a few hours.
- Removal efficiency of chrysene in EKUS is higher than in EK alone.

Fig. 6 Removal of chrysene in pan



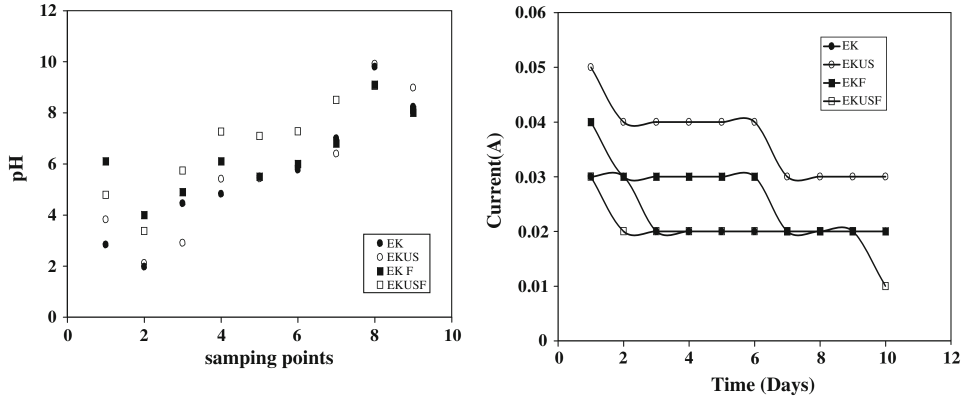


Fig. 7 Trend of pH after experiments and current during experiments

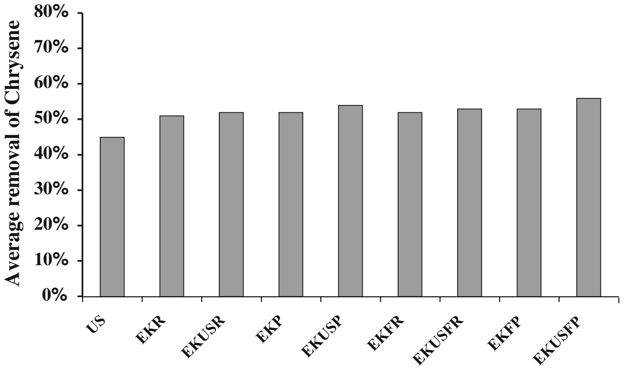


Fig. 8 Average removal percentage of chrysene (*US* ultrasounication, *EKR* electrokinetic in a reactor, *EKUSR* electrokinetic and ultrasonication in a reactor, *EKP* electrokinetic in a pan, *EKUSP* electrokinetic and ultrasonication in a pan, *EKFR* electrokinetic in a reactor with iron anode, *EKUSFR* electrokinetic and ultrasonication in a reactor with iron anode, *EKFP* electrokinetic in a pan with iron anode, *EKUSFP* electrokinetic and ultrasonication in a pan with iron anode)

- Removal efficiency decreases with increase in initial concentrations.
- Soil pH can be maintained by using iron anode in the reactor.
- Efficiency increased in EK-pan experiments but removal was not in uniform across the soil.
- Nearly uniform removal had taken place in the experiments in which both ultrasonication and EK processes were used.
- The highest average removal is in the experiment with EKUS in pan with iron anode (shown in Fig. 8).

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