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Optimization of pyrene removal from contaminated soil by electrokinetic remediation process

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ABSTRACT

The electrokinetic remediation process has been intensively investigated by many researchers as a novel technique to remove different pollutants from soil. The process utilizes a direct-current electric field to soils to insert some process such as electroosmosis and electrolytic migration. In the present study, the removal of pyrene as a model of polycyclic aromatic hydrocarbons (PAHs) were optimized using response surface methodology (RSM) based on central composite design (CCD). The electrokinetic experiment was performed using an electrokinetic setup that includes an electric power supply, a plexiglass soil box and two square stainless steel electrodes electrodes. In the optimum condition, electrode type, moisture and voltage were determined as stainless steel, 30% and 12 volt, respectively. Pyrene removal efficiency in optimum condition estimated 80.05 %. Analysis of variance (ANOVA) exhibited a reasonable correlation coefficient between the predicted and experimental values (R^2=0.95).These results showed that electrokinetic remediation process could be applied as an efficient technique for pyrene removal.

Key words: Electrokinetic; Pyrene; Soil; Remediation; Optimization

INTRODUCTION

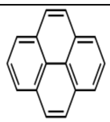
In the last decades, various anthropogenic products including a broad spectrum of hydrocarbon classes were released to the environment where it may affect a variety of biological processes and is a potent cell mutagen and carcinogen [1-3]. PAHs are natural organic compounds that have high retention time and can penetrate the interface in different zone of soils due to their low solubility, high lipophilicity, semi-volatility and low degradation [4]. The main source of PAHs in the environments are industrials and vehicle emissions [5]. Soil contamination PAHs are an environmental problem and the removal of them from soil have become a major concern. The large molecules of PAHs such as pyrene are more lipophilic and they have much attention for over the past decades due to their toxicity, carcinogenic and mutagenic characterizations. The US environmental protection agency created a list of the PAHs most frequently found in environmental samples. Pyrene has known to cause serious health issues in this list [6]. In recent years, researchers have a large number of studies in the developing of innovative technologies for soil remediation. Various soil treatment techniques have been proposed for soil treatment in different parts of the world, especially in regions and places where faster development activities are taking place. Depending on the nature of contamination, a range of remediation technologies has been recommended and are being practiced in the world. The electrokinetic remediation of soils is increasing in many countries of the world [6]. It has been introduced as one of the best technologies in soil remediation. Various studies have demonstrated the effect of an electric field to the soil to improve the removal of organic pollutants and have summarized the state of knowledge on physical, physico-chemical, engineering and remediation aspects [7]. The electrokinetic cleaning of soils is based on processes of electroosmosis and electromigration, which arise in water-saturated soils at imposing a field of a constant electrical current. If a toxic components in the water environment (in the water-saturated soils) dissociate on the anions and cations in a field of a constant electrical current the negatively charged components (anions) will be migrate to a positive pole (cathode), and the positive - to negative (anode). As a result of this electrical migration the division of toxic components in soils can be generated. Various technologies have been applied to remove pollutants such as pyrene from the soil. Nevertheless, these techniques have several drawbacks such as high costs, difficult operation, further treatment and slow process. Hence, there is a need for applying and cost-effective methods for removal of pollutants. A large number of researchers have focused on the removal of pollutants by the electrochemical process because of its efficiency [6]. Electrokinetic remediation is a favorable technology that it was presented to remediate fine-grained soils contaminated with inorganic, organic, and mixed contaminants by 1980s. In recent years, electrokinetics process was suggested as a clean technology for contaminated soil treatment. This process, sometimes named as electrokinetic soil processing, electromigration, electrochemical decontamination or electroreclamation, uses electrical current to remove special pollutants such as organic compounds and heavy metals from soils and sludge [6]. Electrokinetic remediation has a high potential to decontaminate organic pollutants in low permeable soils under different conditions [7]. The application of electrokinetic remediation involves utilization of electrodes into the soil to transfer the pollutants to electrodes. The electric potential induces the moving of contaminants toward the electrode by two primary transport processes, namely electromigration and electro-osmosis [8]. Generally, electromigration is the main transfer approach for metal ionic, and electroosmosis is a fluid moving in the pores of the soil due to the utilization of an electric field and is the main migration mode for organic pollutants. In this study, the electrokinetic remediation process was applied to study the pyrene removal from soil. Therefore, the objective of this study was to optimize the main factors in the electrokinetic remediation process for pyrene removal from soil.

MATERIAL AND METHODS

Materials

Pyrene was purchased from Merck and applied without further treatment. The properties of pyrene were shown in Table 1.

Table.1: properties of pyrene

Name	**Chemical formula**	**Structure**	**Molar mass (g/mol)**	**Density (g/ml)**	**Melting point (Ċ)**	**Boiling point (Ċ)**	**Solubility mg/L**
Pyrene	$C_{16}H_{10}$		202.25	1.271	145-148	404	0.135

The acetone [(C3H6O, Assay99.8%, MW: 58.08gr/mol, B.P:56-57°c, Density: 0.791g/cm^3] and n-hexane [CH_3 $(CH_2)_4CH_3$, MW: 86.17 3gr/mol, B.P:69°c, solubility: 0.1 gr/100gr water)] as a solvent purchased from Mojalali company (Tehran, Iran).

Soil characterization

A CL-ML (Clay with low plasticity- Silt with low plasticity) soil from south of Tehran was utilized for the experiments. The soil has the lower exchange capacity and high uniform mineralogy which leads to a lower buffering capacity. The characterization of the soils was included: specific gravity 2.64 (ASTM method D854), density 1.53 g cm^3, hydraulic conductivity (at porosity 23%) 4.7×10^{-5} (ASTM method D2434), organic content 0. 5% (ASTM method D2974), moisture content 4% (ASTM method 2216), and pH 7.9 - 8.1 (ASTM method D2947).

Soil contamination with pyrene

For the electrokinetic experiments, the soil was artificially contaminated with pyrene solution completely dissolved in a mixture of acetone and hexane from 50 MgL^{-1} (37.76 mg/kg) to 500 mg L^{-1} (377.6 mg kg^{-1}). The CL-ML soil was picked up for each analysis test plus some extra soil for the determination of the initial pyrene concentration. The pyrene completely dissolved in a mixture of n-hexane and acetone. Acetone and n-hexane were applied because of the low solubility of pyrene in water. The dissolved pyrene was mixed with the CL-ML soil, and additional solvents were added so that the mixture could be easily homogenates. The mixtures were blended with a metal spoon, and all mixing activities were conducted within glass beakers. The samples shacked with an orbital shaker, and then placed under a ventilation hood until the solvents completely evaporated. Finally, a sample was picked up to determine the exact initial concentration of pyrene in the soil, since a portion of the pyrene may be volatilized along with the acetone and n-hexane. Water was used to prepare electrical conductivity in the electrokinetic reactor. The contaminated soil was thoroughly mixed with a measured amount of water in a glass beaker, so that the soil water content would be adjusted. The optimum moisture content for the pyrene removal experiments were 30%. The moist contaminated soil was then transferred into the designed reactor.

Electrokinetic set up

The electrokinetic remediation experiments were conducted in a cubic plexiglass reactor, with dimensions 10×10×5 cm, including stainless steel electrodes. As the pre-test, we have examined various electrodes, such as titanium and iron. The area of electrodes and distance between electrodes were 48 cm^2 and 1 cm, respectively. In order to create an electric field between the electrodes, a DC power supply (ATTEN APS model 3005S-3D) was applied to create voltages 10, 11.5, 15, 18.5 and 20 volts. The voltage and intensity were determined using a digital multimeter (MT-1280, Japan). For each experiment, by 500 g of contaminated clay soil was utilized. After soil transfer into the electrokinetic reactor, the electrodes were attached, and a constant voltage of 10-20 volt was utilized. During the experiments, the voltage, electrical current and moisture were measured periodically. The experiments were conducted by the current and moisture. Finally, the soil was picked up from the electrokinetic reactor to analyze the pyrene concentration.

Experimental design

The electrokinetic remediation were optimized using response surface methodology (RSM) based on a central composite design (CCD). RSM is a statistical method that uses quantitative data from appropriate experiments to determine regression model equations and operating conditions. It is an important branch of experimental design and a critical methodology in developing new processes, optimizing their performance and improving the design and formulation of new products [9]. Experimental data were analyzed using Design-Expert 7.1 program software. To evaluate the effect of electrokinetic remediation on the pyrene removal efficiency, three variables regarding electrokinetic remediation including the electrode type, moisture and current density were utilized. The number of required experiments was calculated using the following equation [10]:

$$N = 2^k + 2k + x_0 \quad (1)$$

Where N is the number of required experimental runs (fact), k is the number of variables and x_0 (axial) is the number of central points. Hence, according to the Eq. 1, the total number of required experimental runs is 13 (k =2, x_0 = 5). Design-Expert software was applied for the analyses of the obtained data. The variables X_i were coded as x_i for statistical analysis according to the following equation [10]:

$$x_i = \frac{X_i - X_0}{\delta X} \quad (2)$$

Where X_0 and δX are the values of X_i at the center point and step change, respectively. The experimental ranges of the variables concerning pyrene removal are presented in Table 1. The process can be described by the following second-order model:

$$Y = b_0 + \sum_{i=1}^{n} b_i x_i + \left(\sum_{i=1}^{n} b_{ii} x_i\right)^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} x_i x_j \quad (3)$$

Where Y is the dependent variable (pyrene removal efficiency %), b_0 is a coefficient constant, b_i are linear coefficients, b_{ij} are interaction coefficients and b_{ii} are quadratic coefficients. Moreover, x_i and x_j are the coded values for the experimental variables. Experimental range and levels of independent variables in five levels is shown in Table 2. The experimental ranges of the variables concerning pyrene removal are summarized in Table 3.

Analysis

Sample preparation for analyses of pyrene concentrations were conducted as follows: 2 g of sample was mixed with 6 mL of n-hexane and acetone mixture (1:1) in a glass beaker. The samples were shaking for the complete mixing of contaminated soil and they transferred into the ultrasonic bath (Starsonic18-35, Italy) for 40 min to collect the organic compounds extracted from the soil texture into hexane-acetone solvent. The glass tubes were centrifuged at 4000 rpm for 10 min. Soil extracts from the experiment were analyzed for determination of pyrene concentration using a gas chromatography (GC) equipped with a flame ionization detector and a column HP-5 with dimensions 30 m×0. 32 mm×0. 25 µm film thickness.

Table 2: Experimental range and levels of independent variables

Variables	Type	Low axial (-α)	Low factorial (-1)	Center (0)	High axial (1)	High factorial (+α)
A: distance between electrodes (cm)	Numeric	1	1.3	2	2.7	3
B: Voltage (v)	Numeric	10	11.5	15	18.5	20

Table 3: Response surface methodology (RSM) design for two variables with coded values for pyrene removal percent

Run	Factor1 A: distance between Electrodes (cm)	Factor2 B: Voltage(Volt)	Pyrene removal percent (%)
1	0(2)	0(15)	76±3.9
2	0(2)	+α (20)	80±4
3	0(2)	0(15)	75±3.75
4	0(2)	0(15)	77±3.85
5	+α(3)	0(15)	73±3.65
6	+1(2.7)	-1(11.5)	62±3.1
7	+1(2.7)	+1(18.5)	77±3.85
8	-1(1.3)	+1(18.5)	80±4
9	0(2)	0(15)	77±3.85
10	0(2)	0(15)	78±3.9
11	0(2)	-α (10)	65±3.25
12	-1(1.3)	-1(11.5)	73±3.65
13	-α(1)	0(15)	79±3.95

Nitrogen as a carrier gas was used to make-up flow at a constant pressure of 25 ml min-1. The oven temperature was held at 50°C for 3 min, and then increased at 3 °C per minute to a final temperature of 100°C. Pyrene was used as an external standard for calibration, and the standards for the GC analyses were prepared in different concentration ranges. The linearity of the calibration curve was checked. The average regression coefficient (R^2) was 0.996. Also, sample blanks, without contamination, were injected regularly to ensure that the system remained uncontaminated. Duplicate standard samples were commonly injected to certify a uniform response, and to ensure that the calibration curve and the baseline remained stable. The syringe was rinsed with solvent several times between sample injections to remove every contamination. Water contents were determined using ASTM method D 2216. The soil pH measurements were determined using a soil to water ratio of 1:1 as described in ASTM method D 4972. All the equipment’s for experiments, such as the multimeter, GC instrument, and pH meters, were in good condition and were calibrated.

RESULTS AND DISCUSSIONS

In order to obtain the pyrene removal from soil, the polluted soil must be treated by the application process. For the reason, electrokinetic process was proposed as a feasible treatment. In the electrokinetic treatment, the electric current induces redox reactions upon the surface of the electrodes and generates the destruction of the organic compound [11]. The electrokinetic treatment of soils is based on processes of electroosmosis and electromigration [12, 13]. Generally, most soils are negatively charged due to isomorphous compounds. Therefore, cations could be adsorbed on the soils with negative charges. When water is inserted into the soil, these adsorbed cations dissolve in water and have an affinity to diffuse away from soil to homogenize the cation concentration of the pore fluid. The diffusion is induced by the electrostatic force exerted on the ions by the negatively charged soil. In this case, a diffuse double layer has formed. The diffuse double layer prepare a mobile layer of cations in the matrix of the soil. When a direct current electric field is utilized in the soil, the mobile cations are transferred toward the cathode. If the soil pore is idealized as a capillary, the mobile cations form a concentric shell within the capillary. When this mobile shell is moved toward the cathode, it drags the pore fluid within the shell along resulting in electroosmosis, i.e., a hydraulic flow induced by an electric field [14]. The second mechanism induced by the voltage is electromigration, which is the movement of ions in the pore solution under the influence of an electric field. Positive ions transfer to the cathode while negative ions are immigrated to the anode. Because of electromigration, ions tend to concentrate near the opposite charged electrode [15]. During an electrokinetic remediation, the applied direct current electric field could prepare an effective electroosmotic. In order to obtain efficient results, electrokinetic process of soil should carry out under constant conditions. It is obvious that during the remediation process, other reactions, occur and affect the remediation process. In this study, after the preliminary study and evaluation of the factors affecting the process, optimization design was performed using RSM based on the central composite design CCD. The most extensive applications of RSM are in industrial research, particularly in situations where several input variables influence the process performance measure. This process performance measure is called the response and the input variables are called independent variables [16, 17]. Also the behavior of the system is explained by the following quadratic equation:

$$y = \beta_0 + \sum_{i=1}^{k} \beta_1 x_1 + \sum_{i=1}^{k} \beta_{ii} x_i{}^2 + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} x_i x_j + \epsilon$$

Using the CCD model, an empirical mutual relationship between the response (Pyrene removal efficiency %) and independent variables based on the coded factors were established according to the following equation:

$$.Y = 86.74 + 5.92\ x1 - 0.68\ x2 - 2.37\ x1x2 - 4.12\ - 1.83 \qquad (4)$$

Where Y is the pyrene removal efficiency.(%)

In order to investigate the effect of main operating factors in the electrokinetic remediation process, experiments were performed for the parameters using statistically designed experiments. The voltage ranges were between 10 and 20 volt. The moisture values were varied between 0 and 30 percent and initial pyrene concentration between 50 and 500 mg L-1. According to the statistical data for the quadratic models presented in Table 4, The Model F - value of 40.39 implies the model is significant. There is only a 0.01 % chance that a "Model F-value" this large could occur due to noise. Values of " Prob >F less than 0.0500 indicate model terms are significant. In this case A, B, AB and B2are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The results also show that the amount of P value of the model is less than 0.0001, thus the model is significant, and for A, B, AB and B2, the P value is ≤0. 05. But, P-value of A2 is greater than 0.05 thus that is non-significant .

Table 4: Optimum process conditions for different objectives according to numerical optimization

Source	Sum of Square	df	Mean square	F-value	P- value	
Model	352.10	5	70.42	40.39	< 0.0001	Significant
A- distance between electrode(cm)	63.20	1	63.20	36.25	0.0005	
B- Voltage	233.42	1	233.42	133.89	<0.0001	
AB	16.00	1	16.00	9.18	0.0191	
A^2	2.61	1	2.61	1.50	0.2607	
B^2	38.83	1	38.83	22.27	0.0022	
Residual	12.20	7	1.74	-	-	
Lack of Fit	7.00	3	2.33	1.80	0.2873	not Significant
Pure Error	5.20	4	1.30	-	-	
Cor Total	364.31	12	-	-	-	

Std. Dev.	**1.32**	**R-Squared**	**0.9665**
Mean	**74.77**	**Adj. - R- squared**	**0.9426**
C.V.	**1.77**	**Pred.- R- squared**	**0.8410**
PRESS	**57.93**	**Adeq. -Pression**	**18.310**

The 'prob > F' values for the models which were less than 0.05 (<0.0001) indicated that the models were statistically significant with a confidence interval of 99.99%. According to the results of Table4, the values of R2is evaluated as 0.9658 while that of R2 adj was 0.9665 for the model R1. The R2 and R2 adj coefficients in this study ensured a satisfactory adjustment of the quadratic model to the experimental data. The coefficient of variance (CV) for the pyrene removal has been found to be (%): 1.77. The CV as the ratio of the standard deviation of the mean-value of the observed response (as a percentage) is a measure of reproducibility of the model and as a general rule a model can be considered reasonably reproducible. The "Pred R - Square" of 0.8410 is reasonable agreement with the "Adj R- Square" of 0.9426. "Adequate Precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. Our ratio of 18.310 indicates an adequate signal. This model can be used to navigate the design space. Response surface and corresponding contour plot were applied to interaction of any two parameters. The effects of voltage transmission from electrodes and distance on pyrene removal in the electrokinetic remediation process are shown in Fig. 1.

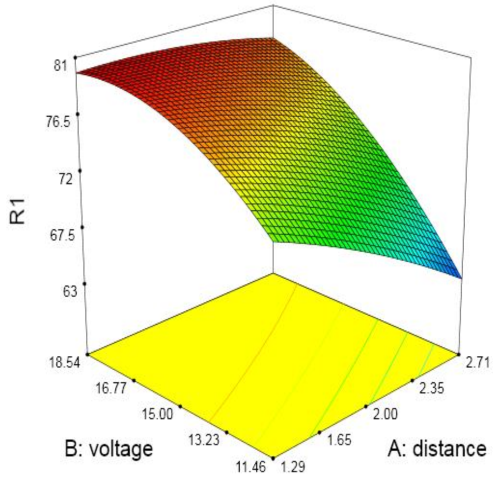


Fig. 1: The interaction between voltage transmission from electrodes and distance between electrodes in the pyrene removal percent

The plot visualizes how high and low values of voltage and electrode distance effect on the pyrene removal. The current density and electric voltage applied in most studies are in the order of a few tens of milli amperes per square centimeter of electrodes and volt, respectively. Generally, a high current intensity could promote the rate of pollutant transportation. An electric current density in the range of 1–10 A/m2 has been demonstrated to be the most efficient in the process [19]. Appropriate selection of electric current density and voltage depends on the characterization of the soil to be treated. The higher the electric conductivity of the soil is, the higher the required electric current density will need to maintain the voltage required. A voltage of 50 V/m can be used as an initial estimate for the process. An optimum electric current density or voltage should be evaluated according to the soil characterization, electrode spacing, and time requirements of the process. Acar and Alshawabkeh [19] discuss different enhancement techniques for the electrokinetic process. The voltage and current density are two parameters for enhancing the process under a constant electrical current. In general, proceeding with exploration and optimization of a fitted response surface may produce poor or misleading results unless the model exhibits an adequate fit [17]. This makes the checking of model adequacy essential. A plot of experimental and theoretical values indicated an excellent fit for pyrene removal (Fig. 2). A high proportion of the variance was explained by the RSM models for pyrene removal as indicated by R2 with all surfactant fractions .

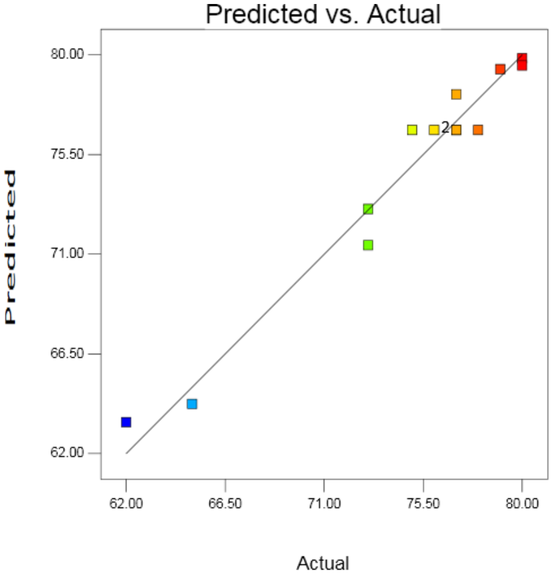


Fig. 2: Predicted vs. actual plot for pyrene removal percent(%)

The initial moisture content significantly affected the current; as the initial moisture content increased, the current increased. Increasing the moisture content could have benefited because the resulting soil might have been more disperse, and this should make it easier for the ionic species to migrate through the soil matrix. The additional water molecule could facilitate a greater amount of charged species hydration and ionic dissolution. The dilution of the ionic strength of the higher moisture content could also lead to an increased diffuse double layer thickness. In this experiment, we utilized 30% moisture as optimum moisture [20.[

The experimental results can be applied to evaluate and predict the pyrene removal from contaminated soils using the electrokinetic remediation process. The advantage of the process is its potential for cost effective in situ and/or ex situ use .

CONCLUSIONS

The present study demonstrated the electrokinetic remediation process using the stainless steel is an applicable technique for pyrene removal from soil. According to the obtained results, optimum condition was gained in 30% moisture, stainless steel electrode with voltage of 12 volt. The results of this study showed that RSM is one of the mathematical methods to optimize the best operating conditions to maximize the pyrene removal. P-value with amounts of < 0.005 for the response model was significant. Removal pyrene efficiency in optimum condition was 73.13.

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