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Removal of phenanthrene from synthetic kaolin soils by electrokinetic soil flushing

R. López-Vizcaíno [a], J. Alonso [b], P. Cañizares [a], M.J. León [b], V. Navarro [b], M.A. Rodrigo [a,*], C. Sáez [a]

[a] Department of Chemical Engineering, Facultad de Ciencias Químicas, Universidad de Castilla-La Mancha, Campus Universitario s/n, 13071 Ciudad Real, Spain
[b] Department of Civil Building Engineering, Escuela Técnica Superior de Ingenieros de Caminos, Canales y Puertos, Universidad de Castilla-La Mancha, Campus Universitario s/n, 13071 Ciudad Real, Spain

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ABSTRACT

In this work, the scale up of the flushing-fluid-assisted electrokinetic remediation of kaolin soil polluted with phenanthrene has been studied. Three different scales have been used: lab ($25\ \mathrm{cm}^3$), bench ($28 \times 10^3\ \mathrm{cm}^3$) and pilot scale ($175 \times 10^3\ \mathrm{cm}^3$) plants. Results show that electrokinetic fluxes, removals of PHE and pollutant distribution in soil were very different in the three setups in spite of being the same soil, pollutant and operation conditions. Electro-osmotic fluxes were much bigger in the case of the lab scale setup and very similar in the bench scale plant and in the pilot mock up, just as expected according to the PHE fluxes and to the distribution of PHE removal. Moreover, in the pilot scale plant used, hydraulic flux produced by gravity and evaporation flux by electric heating of the soil should be taken considered. This variety of results suggests a very complex process with many factors influencing on results. In the lab scale plant, the main mechanisms involved in the removal of PHE are dragging with electro-osmotic flow in the cathodic wells and electrophoresis after interaction of surfactant with phenanthrene in the anodic wells. Just on the contrary, desorption of PHE promoted by the electric heating seems to be a very significant removal mechanism in the bench scale plant and in the pilot mock-up.

1. Introduction

Numerous compounds are now known to cause serious pollution problems in soils. Some organics can be degraded in situ by microorganisms but the low solubility of others hinders their accessibility and prevents bio-degradation. Polycyclic aromatic hydrocarbons (PAHs) have become an important group of pollutants because some of these compounds have been identified as carcinogenic, mutagenic and teratogenic [1,2]. PAHs are characterized by their low solubility in water and their apolarity [3]. These characteristics hinder the removal of this type of compound from soils [4].

In the last few years, a great variety of applicable technologies have been developed to deal with PAH soil pollution [5–7]. Among them, it is important to highlight the electrokinetic techniques, which are the result of different processes that occur in a soil when a DC electric potential is applied through a group of electrodes located in the soil [7–13]. This technology is particularly recommended for the treatment of low-permeability soils polluted with ionic and water soluble pollutants [14,15], although it can also be used to remove hydrophobic compounds by the use of special flushing-fluids. These flushing-fluids usually consist of solutions of surfactants, and they are able to improve the mass transfer of HOCs from the soil into the aqueous phase by decreasing the interfacial tension and by breaking up PAH into the hydrophobic cores of surfactant micelles [16–20]. Pure kaolinite is often used as a model material to test the PAH removal enhancement by surfactants, because of its very low fractions of OM and its very high specific surface area. However, surfactant added to enhance PAHs removal can be adsorbed on kaolinite surface. In this point, anionic surfactant seems to be less strongly retained in kaolinite than non-anionic and cationic ones, due to the repulsive negative surface charges they are partially adsorbed on the mineral surface [21–26].

At this point, it is important to note that there are many factors that can influence on the efficiency of the soil flushing electro-remediation process, such as electrode material, electrode location, composition and flux of flushing fluids, electric field and, of course, operation time. Unfortunately, very few applications have been assessed on a large scale and our current knowledge regarding such processes is limited to the results obtained in laboratory scale studies in which the electrodes are situated in independent chambers of electrokinetic reactor [16–28]. Generally, the soil electro-remediation reactor consisted of a small hermetic column of less

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* Corresponding author. Tel.: +34 902204100x3411; fax: +34 926295256.
E-mail address: manuel.rodrigo@uclm.es (M.A. Rodrigo).

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than 1 dm^3, in which kaolin (or other clay or lime but not a real soil) was used as a model of low-permeability soil [16,19,29]. Moreover, it is important to point out that in a real application the electrokinetic reactor is expected to be an open system in which both electrolyte wells as the soil were at atmospheric pressure. This fact can alter the controlled mechanism and thus, the extrapolation of lab scale results to a real application without the appropriate scale-up would be unwise.

This work aims to describe the removal of PHE from soils using electrokinetically assisted soil flushing and to compare the significance of the different mechanisms of removal of pollutant included this technology at different scales, ranging from lab to pilot plant in order to point out the significance of the scaling factors on the results obtained in electrochemically assisted remediation studies.

2. Materials and methods

2.1. Materials

Kaolinite was selected as model of low-permeability soil. This soil is characterized by its inertness, low hydraulic conductivity, lack of organic content and low cation exchange capacity. The properties of the particular synthetic soil used in this study are given in Table 1. Phenanthrene (PHE) (97%) was selected as model of PAHs and sodium dodecyl sulfate (SDS) as model of anionic surfactant. Its properties are shown in Table 2.

2.2. Preparation of polluted soil

The soil was spiked with a solution of phenanthrene/acetone. The soil–acetone–PHE mixture was stirred and blended homogeneously. After that, the mixture was aerated for a day to promote evaporation of the acetone as described in the literature [29–32].

2.3. Experimental setup

All of the electrokinetic experiments were carried out in three electrokinetic remediation plants with different scale: lab, bench and pilot scale (Fig. 1).

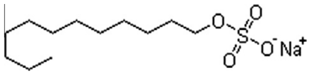
The lab scale plant consists of an electrochemical setup and a power source. The setup is divided into three cylindrical sections: two wells electrolyte with a volume of 235 cm^3 (where the electrodes are immersed in the electrolyte and the compartment accommodating the soil with a volume of 25 cm^3. Electrodes are graphite rods which were introduced without any physical separation in electrolytes. Electrical current was supplied by a DC power supply FA-376 Power Supply PROMAX. The working range of the source is from 0–30 V to the potential and 0–5 A for intensity. The electric current is monitored using a high precision digital multimeter Digital Multimeter KEITHLEY 2000 (Ohio, USA).

The electrokinetic setup used in a bench and pilot scale plants was a methacrylate prism with a soil capacity of 28×10^3 and 175×10^3 cm^3, respectively. The electrodes were positioned in semipermeable electrolyte wells, in order to facilitate removal of effluents generated in the process as described elsewhere [33,34]. The level of these electrolyte wells were controlled by a level control system connected to the feed tank to adjust the volume added of water or fluids to the soil. Cathode wells were connected to sewers of 100 cm^3 to accumulate the fluid transported through the soil and facilitate sampling [33,34]. Voltage gradient was supplied by a power source 400 SM-8-AR ELEKTRONIKA DELTA BV. The electrode material used in both anode and cathode were graphite rods dimensions $1 \times 1 \times 10$ cm^3.

Table 1
Properties of soil.

Mineralogy		Particle size distribution (%)	
Kaolinite	100.00%	Gravel	0
Fe_2O_3	0.58%	Sand	4
TiO_2	0.27%	Silt	18
CaO	0.10%	Clay	78
K_2O	0.75%	Specific gravity	2.6
SiO_2	52.35%	Hydraulic conductivity (cm/s)	1×10^{-8}
Al_2O_3	34.50%	Organic content (%)	0
Others	11.42%	pH	4.9

Table 2
Properties of surfactant.

Surfactant	Sodium dodecyl sulfate
Type	Anionic
Formula	$C_{12}H_{25}NaO_4S$
MW	288.38
CMC (g l^{-1})	2.3
Molecular structure 	

2.4. Experimental procedure

The synthetic polluted soil was moistened with water (with the composition shown in Table 3) before locate inside the setup. The initial target moisture level for the kaolin was 30% in lab and bench scale experiments and 24% in pilot scale. Preparation of the soil in order to make it close to an actual soil not only from the chemical point of view but also from the geomechanical is very important and it was taken into account in the case of the pilot mockup. This preparation consists of five sequential stages: (1) positioning of three layers of gravel with different granulometry as mechanical and drain soil support; (2) pollution of the soil with a phenanthrene/acetone solution and the aeration of the spiked soil to promote evaporation of the acetone; (3) moisten of the soil up to 20% (value fixed by Proctor compaction study); (4) compacting of the soil in the electrokinetic setup by compacting layers of fixed height (5 cm) until achieving a typical density of real soil; and (5) placing a capillary barrier consisting of a layer of sand on the top of the soil that helps to assure the saturated conditions in the upper boundary of the setup. This layer helps to maintained moisture of soil and to minimize the effect of the air on the surface. The composition of electrolyte depends on scale used, since, in lab scale tests, the surfactant was added to catholyte, and the anolyte was composed on water. Therefore, in bench and pilot scale test, the catholyte and anolyte were composed on water and the surfactant was injected in an intermediate wells. All of the electrokinetic experiments were carried out under a constant voltage gradient, 1 VDC cm^{-1}. This value is clearly inside the range proposed in the literature (0.5–2.0 V/cm) for this technology [7,9,10].

The cell current, electro-osmotic flux, phenanthrene flux, electrolyte pH in the anodic and cathodic compartments were measured periodically during the experiments. Phenanthrene concentration, humidity temperature and pH measurements in the soil allowed the determination of the variable profiles from the anode to cathode side.

2.5. Analyses

The surfactant concentration was evaluated by monitoring the chemical oxygen demand (COD) using a HACH DR2000 analyzer [35]. To quantify the amount of phenanthrene present in the soil, it is used a liquid–solid extraction procedure described elsewhere