Water transport in electrokinetic remediation of unsaturated kaolinite. Experimental and numerical study

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ABSTRACT

This work evaluated water transport that occurs in a partially saturated soil of low hydraulic permeability when undergoing an electrokinetic remediation process. The soil used was a compacted kaolinite. To evaluate a wide range of possible conditions, soil with three different initial water contents (10, 15 and 20%) was used, obtaining a range of dry densities of 1300–1600 kg m^{-3}. The tests were performed using a lab-scale setup with a soil capacity of 675 cm^3 and applying different electrical potential gradients (0.5, 1, 1.5 and 2 V cm^{-1}). The experimental results obtained were used to validate a conceptual model implemented in COMSOL. The validated model was used to conduct a detailed interpretation of the observed water transport processes and to perform a study of the hydraulic behaviour of the soil as a function of the initial conditions of compaction, water saturation and applied electrical potential gradient.

1. Introduction

Soil contamination generates a high environmental and human impact in many industrial, agricultural and urban areas. The different origins of contamination and types of pollutants, together with the heterogeneity of the environment, imply that there is a great diversity of pollution events. For this reason, there is a need to develop and optimize soil remediation technologies adapted to each specific case.

"Pump and treat" (P & T) technology applied to remediation of contaminated soil has aroused great interest in recent years. Thanks to the great operational flexibility that this technology offers [1–3], it is a promising alternative among the wide variety of techniques currently available. As its name indicates, it is based on two stages of action. In the first stage, the "pump" phase, the soil is "washed" using a fluid that allows the contaminants to be transported to a controlled extraction point. There are two application techniques: in situ (soil flushing, SF [4–8]) and ex situ (soil washing, SW [9–11]). In these techniques, the pollutants contained in the soil are transferred to external liquid effluents. This stage can be readily adapted to each contamination event by optimally selecting the washing fluid employed (typically surfactants, cosolvents and complexing agents to improve the removal non-polar aromatic hydrocarbons, others organics compounds and heavy metals, respectively [12–16]). The second stage, "treat", corresponds to the final treatment of the liquid effluent generated by coupling a decontamination process of liquid effluents, such as biological treatments [17,18], photo-Fenton and Fenton oxidation [19,20], chemical and electrochemical coagulation [21–23] and electrochemical oxidation [24,25], among others.

Despite all these advantages, applications of P & T technologies is limited to treatment of soils with high hydraulic permeability, such as gravel and sand. In the case of soils with significant clay fractions, their low hydraulic permeability may compromise the technical viability of the treatment. This drawback can be avoided if the driving force of the fluid transport (pressure gradient) is replaced by one that is feasible with low permeability soils, such as an electric potential gradient. Electrokinetic soil flushing (EKSF) offers this possibility, since this technology includes different transport mechanisms governed directly by the electrical potential gradient generated by applying an electric current through a group of electrodes sited in the soil to be treated [26–29]. During EKSF processes applied to clayey soils, the washing fluid moves through the soil via electroosmosis (electrically neutral compounds as nonionic surfactants), electromigration (ionic compounds as oxidant inorganic salts or ionic surfactants and cosolvents), or a combination of them, if the directions of the fluxes are the same, and, to a lesser extent, via a Darcy flux due to the low hydraulic permeability of this soils. The direction of electroosmotic flux mainly depends on the zeta potential of soil particles. Clayey soils have negative surface charge (zeta potential in the range of 10–100 mV [29]);

therefore, the water layer that is around the surface of soil particles (Debye layer) has a high concentration of positive ions. For this reason, the direction of water mobilized by electroosmosis is from anode to cathode.

Many studies have been performed to evaluate the effectiveness of EKSF in the mobilization of different pollutants. In these studies, when EKSF is applied for remediation of soils contaminated by polycyclic aromatic hydrocarbons (PAHs) [30,31], pesticides [32–34] and metals [35–39], among others, all with a common point, the treated soil is initially saturated or very close to saturation. The results obtained are very valuable, since they provide increased knowledge regarding the technical viability of EKSF. However, natural soils are generally not saturated. In the environment, the saturated area is below the water table, while the surface area of the soil (area most exposed to a pollutant discharge) usually exhibits partial saturation. For this reason, and to complement the currently available knowledge, which is very limited in literature [40–43], it is interesting to evaluate the fluid transport processes that occur in a partially saturated soil with low hydraulic permeability when subjected to an EKSF process.

Such an evaluation is the fundamental objective of this work. In this study, low-salinity water was used as the washing fluid. As a study soil, a kaolinite was selected; because it is a clay, this soil presents low hydraulic permeability, but there are no relevant swelling or shrinkage processes that could have distorted the analysis [44]. To assure the repeatability of the tests, the soil was compacted by applying the compaction energy of the Standard Proctor compaction test [45]. To analyse the sensitivity of the EKSF process to the different unsaturated conditions, soil with three initial water contents, w_o, 10, 15 and 20%, was used, thus obtaining a range of dry densities of 1300–1600 kg m^{-3}. Consequently, a wide range of possible natural conditions was sampled. In addition, the sensitivity of the system to the application of different potential gradients, E_x, was analysed.

All experimental results were used to validate a conceptual model implemented in COMSOL [46,47], a multiphysical programming environment. The validated model was used to conduct a detailed interpretation of the observed water transport processes and to perform a study of the hydraulic behaviour of the soil as a function of the initial conditions of compaction, water saturation and applied electrical potential gradient.

2. Materials and methods

2.1. Materials

Kaolinite was selected as a model for clayey soil. This soil is characterized by its inertness, low hydraulic conductivity, lack of organic content and low cation exchange capacity. The mineralogical composition, particle size distribution and classification parameters [48] are summarized in Table 1.

2.2. Experimental setup

All of the electrokinetic experiments were performed in a lab-scale EKR setup comprising an electrochemical reactor, a power supply and

Table 1
Properties of soil.

Mineralogy/%		Particle size/%	
Fe$_2$O$_3$	0.58	Sand	4
TiO$_2$	0.27	Silt	18
CaO	0.10	Clay	78
K$_2$O	0.75	**Classification parameters**	
SiO$_2$	52.35	Liquid limit	41
Al$_2$O$_3$	34.50	Plasticity index	13
Others	11.42	USCS	ML/OL

an electric multimeter (Fig. 1A). The electrochemical reactor was constructed from a methacrylate polymer, and it consisted of two electrolyte compartments in which the anolyte and catholyte were located and a central compartment in which the soil was loaded (675 cm^3). Cylinders (with a height of 15 cm and diameter of 1 cm) of graphite were selected as the material for the anodes and cathodes. The electrodes were separated by 11 cm and positioned directly in the soil. Low-salinity water (pH = 7.79 and 0.37 mS cm^{-1}) was used as the flushing fluid, catholyte and anolyte. A constant electric potential gradient (0.5, 1, 1.5 and 2 V cm^{-1}) was applied using a power supply (FA-376 PROMAX, Barcelona, Spain). The electric current fluxing through the cell was measured with a Keithley 2000 digital multimeter (Ohio, USA).

2.3. Experimental procedure

The preparation of the soil was the pre-test stage. First, the soil was moistened with water until the desired value of w_o (10, 15 and 20%) was reached. The wet soil was kept in airtight containers to prevent water loss through evaporation. Subsequently, the soil was placed in the central compartment of the electrokinetic reactor in 5 layers of 3 cm in height. The compaction process of the layers was performed using a USACE manual compaction hammer, applying the compaction energy of 600 kJ m^{-3} used in the Standard Proctor test [45]. The electrodes were then inserted into the soil. Finally, the compartments intended to house the electrolyte were completely filled. The volume of electrolyte in the compartments was kept constant during the tests via addition or extraction of water. The tests began with the power supply connection in potentiostatic mode, setting the electric potential to a value corresponding to the gradient (E_x) recorded in each test. The duration of the tests was determined by the time required to obtain an approximately constant rate of water accumulation in the catholyte compartment. The experimental protocol is presented in Table 2. During the execution of the tests, the evolution of the volume of water withdrawn from the catholyte (V_c) was monitored.

2.4. Conceptual and mathematical model

In the adopted conceptual model, isothermal conditions are assumed, 298.15 K (major changes in the soil temperature have not been observed in previous works [32,33]), and the soil deformability is assumed to be negligible. The balance of the water mass is obtained using

$$\frac{\partial m_w}{\partial t} + \nabla \cdot \mathbf{l}_w = 0 \tag{1}$$

where $\mathbf{l}_w$ is the mass flux of water (kg m^{-2} s^{-1}), ∇ is the divergence operator, and m_w is the mass of water per unit of total volume (kg m^{-3}), which is defined as

$$m_w = \phi \cdot Sr \cdot \rho_w \tag{2}$$

where ϕ is the porosity of the soil, Sr is the saturation degree of the soil, and ρ_w is the water density. The mass flux of water, $\mathbf{l}_w$, is the sum of the hydraulic flux, $\mathbf{l}_w^h$, calculated using Darcy's law and the electroosmotic flux, $\mathbf{l}_w^{eo}$, estimated using the semiempirical formula of Helmholtz-Smoluchowski [49], which is widely used in other EKR models [41,47,50,51]. Thus,

$$\mathbf{l}_w = \mathbf{l}_w^h + \mathbf{l}_w^{eo} = \rho_w \cdot (\mathbf{q}_w^h + \mathbf{q}_w^{eo}) \tag{3}$$

$$\mathbf{q}_w^h = -K_e^h \cdot (\nabla P_L + g \cdot \rho_w \cdot \nabla z) \tag{4}$$

$$\mathbf{q}_w^{eo} = -K_e^{eo} \cdot \nabla E \tag{5}$$

where $\mathbf{q}_w$ is the total volumetric flux, which is the sum of $\mathbf{q}_w^h$ and $\mathbf{q}_w^{eo}$, the hydraulic and electroosmotic volumetric fluxes, ∇ is the gradient differential operator, g is the acceleration due to gravity, z is the vertical coordinate, P_L is the liquid pore pressure, and E is the electric potential.