**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 to 1600 kg m⁻³. The tests were performed using a lab-scale setup with a soil capacity of 675 cm³ 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.

Keywords: Electrokinetic remediation; unsaturated soils; multiphysics simulation; soil flushing; numerical model

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 to 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.

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

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 an electric multimeter (Figure 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 cm³). 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

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

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

$$3 \quad m_w = \phi \cdot Sr \cdot \rho_w \quad (2)$$

4 where ϕ is the porosity of the soil, Sr is the saturation degree of the soil, and ρ_w is the
 5 water density. The mass flux of water, $\mathbf{l}_w$, is the sum of the hydraulic flux, $\mathbf{l}_w^h$, calculated
 6 using Darcy's law and the electroosmotic flux, $\mathbf{l}_w^{\text{eo}}$, estimated using the semiempirical
 7 formula of Helmholtz-Smoluchowski [49], which is widely used in other EKR models
 8 [41, 47, 50, 51]. Thus,

$$9 \quad \mathbf{l}_w = \mathbf{l}_w^h + \mathbf{l}_w^{\text{eo}} = \rho_w \cdot (\mathbf{q}_w^h + \mathbf{q}_w^{\text{eo}}) \quad (3)$$

$$10 \quad \mathbf{q}_w^h = -K_e^h \cdot (\nabla P_L + g \cdot \rho_w \cdot \nabla z) \quad (4)$$

$$11 \quad \mathbf{q}_w^{\text{eo}} = -K_e^{\text{eo}} \cdot \nabla E \quad (5)$$

12 where $\mathbf{q}_w$ is the total volumetric flux, which is the sum of $\mathbf{q}_w^h$ and $\mathbf{q}_w^{\text{eo}}$, the hydraulic and
 13 electroosmotic volumetric fluxes, ∇ is the gradient differential operator, g is the
 14 acceleration due to gravity, z is the vertical coordinate, P_L is the liquid pore pressure, and
 15 E is the electric potential. K_e^h and K_e^{eo} are the effective hydraulic and electroosmotic
 16 permeability of soil, both calculated with the following expressions:

$$17 \quad K_e^h = K_{\text{sat}}^h \cdot k_{\text{rel}}^h = K_{\text{sat}}^h \cdot Sr^3 \quad (6)$$

$$18 \quad K_e^{\text{eo}} = K_{\text{sat}}^{\text{eo}} \cdot k_{\text{rel}}^{\text{eo}} = K_{\text{sat}}^{\text{eo}} \cdot Sr^3 \quad (7)$$

19 where K_{sat}^h and $K_{\text{sat}}^{\text{eo}}$ are the saturated hydraulic and electroosmotic conductivities,
 20 respectively, and k_{rel}^h and $k_{\text{rel}}^{\text{eo}}$ are the corresponding relative conductivity functions,

which are based in both cases on a Brooks and Corey [52] type power function with an exponent of 3.

The experimental system modelled is shown in Figure 1. This configuration was selected to be able to model the experiments using the one-dimensional conceptual model defined in Figure 2. In this manner, the water balance in the electrolyte compartments was formulated using the following expression:

$$\frac{\partial V^*}{\partial t} = \pm \mathbf{q}_w \cdot S \quad (8)$$

where the subscript * is equal to *a* for the anolyte and *c* for the catholyte. The sign of the volumetric flux of water is negative in the anolyte (mass exit term in the balance) and positive in the catholyte (mass input term in the balance). *S* is the surface of the well-soil interface ($S_a = S_c = 45 \text{ cm}^2$).

(A)

(B)

1

2 **Figure 1.** (A) Schematic of the experimental setup. (B) Dimensions.

2.5. Numerical implementation.

The proposed mathematical model was implemented in Comsol Multiphysics [46, 47], a partial differential equation solver based on the application of the finite element method with Lagrange multipliers. We defined the differential and algebraic equations to be solved, the initial conditions to be considered and the boundary conditions to be imposed. At all times, the "Multiphysics" capability was used without using the preprogrammed modules offered by the software.

Figure 2 shows the initial and boundary conditions considered in the modelling. A hydraulic pressure constant (P_{Lo}) was defined as the initial hydraulic condition in the whole domain and was estimated as a function of w_o and the void ratio (e) of the soil used in each test. As an initial electrical condition, a null E_x was set. At the points of the domain coincident with the soil-electrolyte compartment interface, Dirichlet boundary conditions were imposed, $P_L = P_{atm} = 100$ kPa. Likewise, at the domain points corresponding to the electrodes, the electric potential was set according to the electric potential gradient selected in the test to be reproduced.

Figure 2. Experimental setup abstraction. Initial and boundary conditions.

2.6. Experimental determination of hydraulic parameters.

In this work, it is very important to perform a hydraulic characterization of the soil used to obtain the correct inputs for the proposed model. In this manner, $K_{\text{sat}}^{\text{h}}$ was estimated using the one-dimensional consolidation method described in ASTM D-2435 [53]. In addition, $K_{\text{sat}}^{\text{eo}}$ was estimated also from an electroosmotic permeability cell [54]. Different kaolinite samples were prepared with different compaction levels and in a complete saturation state. With the results obtained in both processes of parameter identification, two fits were performed to relate the hydraulic (Figure 3A) and electroosmotic (Figure 3B) permeabilities saturated with the void ratio for a range of $0.65 < e < 0.95$. In both cases, an increase of the permeabilities was exhibited as e increases [55, 56]. The resulting expressions for both conductivities are shown below:

$$K_{\text{sat}}^{\text{h}} \left(\text{m s}^{-1} \right) = 3.329 \cdot 10^{-9} e - 2.151 \cdot 10^{-9} \quad (9)$$

$$K_{\text{sat}}^{\text{eo}} \left(\text{m}^2 \text{ s}^{-1} \text{ V}^{-1} \right) = 6.101 \cdot 10^{-9} e - 3.615 \cdot 10^{-9} \quad (10)$$

The retention curve of kaolinite was also determined using a model WP4 psychrometer from Decagon (Washington, USA) based on the chilled-mirror dew-point technique [57]. The experimental data regarding the degree of saturation versus suction (Figure 4) were fit using the model proposed by Van Genuchten [58] using the following expression:

$$Sr = \left(1 + (\alpha \cdot s)^n \right)^{-m} \quad (11)$$

where s is the matric suction, which is defined as the difference between gas pressure and liquid pressure ($P_{\text{G}} - P_{\text{L}}$), assuming P_{G} is constant and equal to atmospheric pressure, P_{atm} (100 kPa). The results of the fitting can be observed in Figure 4.

Figure 3. Hydraulic characterization of the soil: (A) Saturated hydraulic permeability; (B) saturated electroosmotic permeability

Figure 4. Water retention curve. Fitting parameters: $\alpha = 2.39 \times 10^{-3} \text{ kPa}^{-1}$, $n = 1.843$ and $m = 1 - 1/n$.

Finally, the dry density (ρ_d) of the soil in the EKR reactor was analysed in each test to check the applied compaction. Figure 5 shows the results obtained compared with the previously estimated Proctor standard compaction curve [59] following the procedure described in ASTM D698-12e1 [45]. It can be observed how the level of compaction reached is of the same order of magnitude as the estimate in the standard test.

Figure 5. Comparison of the dry densities achieved in the soil compaction of the reactors (marker) and the Proctor Normal compaction curve (solid line).

3. RESULTS AND DISCUSSION.

3.1. Model validation.

First, the capacity of the model to reproduce the tests performed was checked (Table 2). Very satisfactory fits were obtained (see Figure 6), especially at the initial times. The model enabled reproducing the decrease and subsequent rise observed in the volume of catholyte which, as will be observed below, is explained by the influence of the degree of soil saturation on water transport phenomena involved in EKSF processes.

1 **Table 2.** Experimental protocol.

Test	w_0 / %	E_x / V cm ⁻¹
E-01	10	0.5
E-02	10	1.0
E-03	10	1.5
E-04	10	2.0
E-05	15	0.5
E-06	15	1.0
E-07	15	1.5
E-08	15	2.0
E-09	20	0.5
E-10	20	1.0
E-11	20	1.5
E-12	20	2.0

2

3

4 **Figure 6.** Dynamic response of catholyte volume (V_c). Markers, experimental results and lines,
5 model results. w_0 (A) 10%, (B) 15% and (C) 20%.

6 **3.2. Numerical interpretation.**

7 The quality of the fit, i.e., the validity of the model, invited us to use the model to obtain
8 more information about the phenomena related to water transport in partially saturated
9 clayey soils under the action of an electric field. As an example, the test E-07 was
10 selected, with a w_0 of 15%, e of 0.78 and an E_x of 1.5 V cm⁻¹, since the same phenomena,
11 but with different magnitudes, occur with other initial and boundary conditions.

Figure 7A shows the dynamic response of the volume of the electrolyte compartments and the incoming or outgoing water flux of both. It can be observed that in the case of the anolyte, there was a progressive decrease in its volume (V_a), which indicates a net transport of water into the soil. The evolution of the volume of catholyte (V_c) was different. In the initial moments of the test, a decrease occurred during a determined time (t_o) in which the saturation of the soil occurred, and then, the cumulative volume exhibited a linear increase. To interpret this evolution, Figure 7B shows the temporal variation of total water flux into the electrolyte compartments. The sign of the flux indicates its direction: the positive values correspond to outfluxes of the anolyte entering the soil (anode-cathode direction), whereas negative values indicate outfluxes of the catholyte entering the soil (cathode-anode direction). With this in mind, it could be verified that there was a flux of water entering the soil from both electrolyte compartments with a maximum value of approximately $1.1 \times 10^{-6} \text{ m s}^{-1}$ at the initial moments of the test. As the experiment progressed, the flux decreased to a steady value of $1.3 \times 10^{-7} \text{ m s}^{-1}$ after 9.5 hours of testing and from anode to cathode.

Figure 7. Dynamic response of (A) volume of electrolyte and (B) flux of incoming/outgoing water into the electrolyte compartments.

From a qualitative point of view, these processes can be explained in terms of degree of saturation and suction of the soil. These parameters were not measured experimentally, since the insertion of a system of tensiometers that would allow an online reading of the soil suction would significantly alter the reduced soil volume used. However, because of the numerical model, it was possible to analyse the hydraulic behaviour of the soil during the test. Figure 8 shows the spatial distribution of the saturation degree and the suction obtained for different times, ranging from the start of the test to after a steady state (10 h).

Figure 8. (A) Degree of saturation and (B) suction of soil at different test times.

Initially, the soil had a degree of saturation of 0.51, presenting significant suction of 1200 kPa. This state explains the rapid transport of water from both electrolyte compartments to the soil. The hydraulic gradient was the predominant driving force at this stage. As the test progressed, the soil saturation increased progressively with a consequent decrease of the suction until near zero values in the whole domain at 10 h. At that moment, the system reached a steady state in which the electrical gradient was the main driving force of water transport.

1 Finally, the spatial distribution of hydraulic and electroosmotic flux contributions in the
2 global water transport was analysed. The results are shown in Figure 9.

3

4 **Figure 9.** Spatial distributions of (A) hydraulic flux, (B) electroosmotic flux and (C) total flux at
5 different test times. Positive values indicate flux from anode to cathode, and negative values
6 indicate flux from cathode to anode.

7 Analysing the hydraulic flux profiles (Figure 9A), it is observed that the highest values
8 were obtained in the first moments of the test in the soil zone between the electrodes and
9 the electrolyte compartments, with a common direction of entry into the soil. This is in
10 agreement with the flux evolution observed in the electrolyte compartments (Figure 7B)
11 and may be explained by the Sr and s trends analysed (Figure 8). These fluxes decreased
12 over time due to the observed decrease in soil suction until reaching a stable value of

4.7×10⁻⁸ m s⁻¹ at 10 h of testing. At this time, the direction of flux was from cathode to anode because in the vicinity of this electrode, the soil had a slightly higher suction, as observed in Figure 8B. On the other hand, Figure 9B shows how the profiles obtained from electroosmotic flux are very different. First, and as expected, the direction of this flux was from anode to cathode in the soil zone between the electrodes, as this zone of soil was subjected to an electric gradient in the evaluated 1D configuration. An increase in the flux over time, with a spatial distribution analogous to the one observed in the analysis of the degree of saturation, was observed. The maximum flux obtained stabilized at approximately 10 h of testing at a value of 1.8 × 10⁻⁷ m s⁻¹, when the soil was in a state of total saturation. This fact indicates that the electroosmotic flux is strongly influenced by the degree of saturation of the soil and that it is favoured in saturated conditions [60-62]. Finally, Figure 9C shows the total flux profiles obtained as the sum of the previous ones. Once the steady state was reached, the total flux reached a positive value (anode to cathode) of 1.3 × 10⁻⁷ m s⁻¹ throughout the domain.

3.3. Sensitivity analysis

The analysis of the experimental tests indicated that both the initial soil conditions, given their initial saturation (Sr_o) and their initial pore index (e_o), in addition to the applied potential gradient, have a significant influence on the hydraulic behaviour of the soil in an EKR process. For this reason, the convenience of developing a sensitivity study that provides additional information and thus improve the knowledge of the process studied was evaluated.

For this, simulations were performed with soil models with different degrees of initial saturation (range of Sr_o : 0.15 to 1) and levels of compaction ($e = 0.68, 0.80$ and 0.92) in which an electric potential gradient between 0.25 and 5 V cm⁻¹ was applied. The variables

1 evaluated were the time required to reach complete soil saturation (t_0) and the volume of
 2 water transported from the catholyte compartment to the soil during the time t_0 expressed
 3 as a percentage of decrease with respect to the initial volume of catholyte. Figure 10
 4 shows the results obtained.

6 **Figure 10.** Sensitivity analysis. Influence of the Sr_0 , E_x and e in the hydraulic behaviour
 7 of the soil under an electrokinetic process.

8 First, it can be observed that the percentage of decrease in the volume of catholyte
 9 exhibited a similar evolution in the three levels of compaction evaluated. The transport
 10 of water from the catholyte to the soil was favoured in soils with a higher pore index and
 11 a lower degree of saturation.

12 On the other hand, analysing the results concerning t_0 in qualitative terms, additional
 13 tendencies were observed independently of the level of compaction of the simulated soil.
 14 It indicated a decreasing evolution of t_0 as both the value of the initial degree of saturation

of the soil in addition the gradient of electric potential applied in each case increase. However, the degree of influence of these variables was different. The acceleration of the saturation process can be explained taking into account, on one hand, the potential dependence (order 3) of the hydraulic and electroosmotic permeabilities with S_r , Equations (6) and (7), and on the other, the definition of electroosmotic flux, which is proportional to the electric potential gradient applied. In quantitative terms, noticeable differences were observed depending on the level of compaction of the soil. In soils with an initial pore index of 0.8 and 0.92 and with a lower S_{r_0} (0.16) and electric potential gradient (0.25 V cm^{-1}), t_0 maxima of approximately 12 and 8 h, respectively, were obtained. However, with these same conditions of initial saturation and electric gradient, in the simulated cases with a more-compacted soil ($e = 0.68$), t_0 could increase up to 42 h, mainly due to the reduction of saturated permeabilities, which are a function of the pore index; see Equations (9) and (10).

For realistic conditions of a clayey natural soil in the intermediate zone ($S_r = 0.8$ and $e = 0.8$) [63], t_0 varied between 2 and 5 h, depending on the applied electric gradient. A priori, these times do not seem very high; however, it is important to remember that these data have been obtained in the simulation of a soil mockup with an electrode separation of 11 cm and that although it is not possible to perform an exact extrapolation of the process, we can obtain an approximation of the contribution of the initial stage of soil saturation within the total duration of an actual EKSF process. In trials performed on a larger scale, where the volume of soil to be treated can range from tens of cubic meters in research prototypes [64-66] to thousands of cubic meters in real cases, the saturation step could reach a duration on the order of months or even years, as long as the water supply to the system occurs only from the electrolyte wells. This time can be reduced if a previous stage is performed in which the soil is wetted to S_r values close to 1, as shown in Figure

10. However, both t_o and the volume of electrolyte needed to reach the saturation state are two essential parameters to be taken into account in the experimental design of the test and in the overall cost analysis of the treatment.

4. CONCLUSIONS

In the present work, it was shown that to correctly reproduce water transport processes in partially saturated low permeability soils subjected to an EKSF process, it is necessary to use numerical models that take into account the influence of the volumetric water content, and therefore the degree of saturation, in the water fluxes generated by hydraulic and/or electric gradients. In addition, it was verified that in an EKSF process applied to a partially saturated soil, there are two well-differentiated stages in terms of the mechanisms of water transport. Initially, there is a stage of soil saturation in which the fundamental driving force of transport is the hydraulic gradient. Subsequently, once the soil reaches a degree of saturation close to 1, the hydraulic flux is significantly reduced, and the electroosmotic flux becomes predominant. In addition, the initial soil state (saturation degree and compaction level) and the applied potential gradient significantly influence the hydraulic behaviour in an EKSF process. In these processes, we seek to optimize the mobilization of process fluid. For this, the most favourable conditions would be to work with soils with a high saturation (greater than 90%). This condition reduces the saturation time to minimum values and increases the volume of water mobilized by electroosmosis.

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REFERENCES

- [1] C. Trellu, E. Mousset, Y. Pechaud, D. Huguenot, E.D. van Hullebusch, G. Esposito, M.A. Oturan, Removal of hydrophobic organic pollutants from soil washing/flushing solutions: A critical review, *J. Hazard. Mater.*, 306 (2016) 149-174.
- [2] X. Mao, R. Jiang, W. Xiao, J. Yu, Use of surfactants for the remediation of contaminated soils: A review, *J. Hazard. Mater.*, 285 (2015) 419-435.
- [3] C.N. Mulligan, R.N. Yong, B.F. Gibbs, Surfactant-enhanced remediation of contaminated soil: a review, *Engineering Geology*, 60 (2001) 371-380.
- [4] O. Atteia, E. Del Campo Estrada, H. Bertin, Soil flushing: A review of the origin of efficiency variability, *Reviews in Environmental Science and Biotechnology*, 12 (2013) 379-389.
- [5] A. Navarro, F. Martinez, The use of soil-flushing to remediate metal contamination in a smelting slag dumping area: Column and pilot-scale experiments, *Engineering Geology*, 115 (2010) 16-27.
- [6] S.K. Park, A.R. Bielefeldt, Non-ionic surfactant flushing of pentachlorophenol from NAPL-contaminated soil, *Water Research*, 39 (2005) 1388-1396.
- [7] M. Svab, M. Kubala, M. Muellerova, R. Raschman, Soil flushing by surfactant solution: Pilot-scale demonstration of complete technology, *J. Hazard. Mater.*, 163 (2009) 410-417.
- [8] W. Zhou, L. Zhu, Enhanced soil flushing of phenanthrene by anionic-nonionic mixed surfactant, *Water Research*, 42 (2008) 101-108.
- [9] C.K. Ahn, Y.M. Kim, S.H. Woo, J.M. Park, Soil washing using various nonionic surfactants and their recovery by selective adsorption with activated carbon, *J. Hazard. Mater.*, 154 (2008) 153-160.
- [10] P. Conte, A. Agretto, R. Spaccini, A. Piccolo, Soil remediation: humic acids as natural surfactants in the washings of highly contaminated soils, *Environmental Pollution*, 135 (2005) 515-522.
- [11] R.E. Saichek, K.R. Reddy, Evaluation of surfactants/cosolvents for desorption/solubilization of phenanthrene in clayey soils, *International Journal of Environmental Studies*, 61 (2004) 587-604.
- [12] A.P. Khodadoust, K.R. Reddy, O. Narla, Cyclodextrin-enhanced electrokinetic remediation of soils contaminated with 2,4-dinitrotoluene, *Journal of Environmental Engineering*, 132 (2006) 1043-1050.

- [13] C. Liang, C.L. Hsieh, Evaluation of surfactant flushing for remediating EDC-tar contamination, *J. Contam. Hydrol.*, 177-178 (2015) 158-166.
- [14] K.R. Reddy, S. Danda, R.E. Saichek, Complicating factors of using ethylenediamine tetraacetic acid to enhance electrokinetic remediation of multiple heavy metals in clayey soils, *Journal of Environmental Engineering*, 130 (2004) 1357-1366.
- [15] K.R. Reddy, R.E. Saichek, Electrokinetic removal of phenanthrene from kaolin using different surfactants and cosolvents, in: *Evaluation and Remediation of Low Permeability and Dual Porosity Environments*, ASTM International, Reno, NV, 2002, pp. 138-161.
- [16] X. Wang, J. Chen, C. Lv, Evaluation of foam surfactant for foam-flushing technique in remediation of DDT-contaminated soil using data envelopment analysis method, *Environ. Sci. Pollut. Res.*, 22 (2015) 2994-3003.
- [17] E. Hallmann, R. Tomczak-Wandzel, K. Medrzycka, Combined chemical-biological treatment of effluents from soil remediation processes by surfactants solutions flushing, *Ecological Chemistry and Engineering S*, 19 (2012) 9-18.
- [18] P. Haapea, T. Tuhkanen, Integrated treatment of PAH contaminated soil by soil washing, ozonation and biological treatment, *J. Hazard. Mater.*, 136 (2006) 244-250.
- [19] E. Bocos, C. Fernandez-Costas, M. Pazos, M.T. Sanroman, Removal of PAHs and pesticides from polluted soils by enhanced electrokinetic-Fenton treatment, *Chemosphere*, 125 (2015) 168-174.
- [20] R.D. Villa, A.G. Trovo, R.F. Pupo Nogueira, Soil remediation using a coupled process: soil washing with surfactant followed by photo-Fenton oxidation, *J. Hazard. Mater.*, 174 (2010) 770-775.
- [21] T. Chatterjee, S. Chatterjee, D.S. Lee, M.W. Lee, S.H. Woo, Coagulation of soil suspensions containing nonionic or anionic surfactants using chitosan, polyacrylamide, and polyaluminium chloride, *Chemosphere*, 75 (2009) 1307-1314.
- [22] R. López-Vizcaíno, C. Sáez, P. Cañizares, M.A. Rodrigo, The use of a combined process of surfactant-aided soil washing and coagulation for PAH-contaminated soils treatment, *Separation and Purification Technology*, 88 (2012) 46-51.
- [23] R. Lopez-Vizcaíno, C. Sáez, P. Cañizares, M.A. Rodrigo, Electrocoagulation of the effluents from surfactant-aided soil-remediation processes, *Separation and Purification Technology*, 98 (2012) 88-93.

- [24] E.V. dos Santos, C. Sáez, C.A. Martínez-Huitle, P. Cañizares, M.A. Rodrigo, Combined soil washing and CDEO for the removal of atrazine from soils, *J. Hazard. Mater.*, 300 (2015) 129-134.
- [25] C. Saez, R. Lopez-Vizcaino, P. Canizares, M.A. Rodrigo, Conductive-Diamond Electrochemical Oxidation of Surfactant-Aided Soil-Washing Effluents, *Industrial & Engineering Chemistry Research*, 49 (2010) 9631-9635.
- [26] Y.B. Acar, R.J. Gale, A.N. Alshawabkeh, R.E. Marks, S. Puppala, M. Bricka, R. Parker, ELECTROKINETIC REMEDIATION - BASICS AND TECHNOLOGY STATUS, *J. Hazard. Mater.*, 40 (1995) 117-137.
- [27] A.N. Alshawabkeh, Electrokinetic Soil Remediation: Challenges and Opportunities, *Separation Science and Technology*, 44 (2009) 2171-2187.
- [28] M.M. Page, C.L. Page, Electroremediation of contaminated soils, *Journal of Environmental Engineering-Asce*, 128 (2002) 208-219.
- [29] J. Virkutyte, M. Sillanpaa, P. Latostenmaa, Electrokinetic soil remediation - critical overview, *Sci. Total Environ.*, 289 (2002) 97-121.
- [30] R. Lopez-Vizcaino, J. Alonso, P. Canizares, M.J. Leon, V. Navarro, M.A. Rodrigo, C. Saez, Removal of phenanthrene from synthetic kaolin soils by electrokinetic soil flushing, *Separation and Purification Technology*, 132 (2014) 33-40.
- [31] M. Pazos, E. Rosales, T. Alcántara, J. Gómez, M.A. Sanromán, Decontamination of soils containing PAHs by electroremediation: A review, *J. Hazard. Mater.*, 177 (2010) 1-11.
- [32] C. Risco, S. Rodrigo, R. López-Vizcaíno, A. Yustres, C. Sáez, P. Cañizares, V. Navarro, M.A. Rodrigo, Electrochemically assisted fences for the electroremediation of soils polluted with 2,4-D: A case study in a pilot plant, *Separation and Purification Technology*, 156, Part 2 (2015) 234-241.
- [33] C. Risco, H. Rubí-Juárez, S. Rodrigo, R. López Vizcaíno, C. Saez, P. Cañizares, C. Barrera-Díaz, V. Navarro, M.A. Rodrigo, Removal of oxyfluorfen from spiked soils using electrokinetic fences, *Separation and Purification Technology*, 167 (2016) 55-62.
- [34] A.B. Ribeiro, E.P. Mateus, J.M. Rodríguez-Maroto, Removal of organic contaminants from soils by an electrokinetic process: The case of molinate and bentazone. Experimental and modeling, *Separation and Purification Technology*, 79 (2011) 193-203.
- [35] Interfaces and Interphases in Battery Systems, in: *Interfaces and Interphases in Battery Systems - PRiME 2012*, Honolulu, HI, 2012.

- [36] E.-K. Jeon, J.-M. Jung, W.-S. Kim, S.-H. Ko, K. Baek, In situ electrokinetic remediation of As-, Cu-, and Pb-contaminated paddy soil using hexagonal electrode configuration: a full scale study, *Environ. Sci. Pollut. Res.*, 22 (2015) 711-720.
- [37] E.D. Mattson, E.R. Lindgren, Electrokinetics: an innovative technology for in-situ remediation of heavy metals, (1994) 235-245.
- [38] M. Pazos, S. Gouveia, M.A. Sanromán, C. Cameselle, Electromigration of Mn, Fe, Cu and Zn with citric acid in contaminated clay, *Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering*, 43 (2008) 823-831.
- [39] J.M. Rodríguez-Maroto, C. Vereda-Alonso, Electrokinetic modeling of heavy metals, *Electrochemical Remediation Technologies for Polluted Soils*, (2009).
- [40] Q. Luo, X. Zhang, H. Wang, Y. Qian, Mobilization of phenol and dichlorophenol in unsaturated soils by non-uniform electrokinetics, *Chemosphere*, 59 (2005) 1289-1298.
- [41] E.D. Mattson, R.S. Bowman, E.R. Lindgren, Electrokinetic ion transport through unsaturated soil: 1. Theory, model development, and testing, *J. Contam. Hydrol.*, 54 (2002) 99-120.
- [42] E.D. Mattson, R.S. Bowman, E.R. Lindgren, Electrokinetic ion transport through unsaturated soil: 2. Application to a heterogeneous field site, *J. Contam. Hydrol.*, 54 (2002) 121-140.
- [43] S. Wieczorek, H. Weigand, M. Schmid, C. Marb, Electrokinetic remediation of an electroplating site: design and scale-up for an in-situ application in the unsaturated zone, *Engineering Geology*, 77 (2005) 203-215.
- [44] I. Aksu, E. Bazilevskaya, Z.T. Karpyn, Swelling of clay minerals in unconsolidated porous media and its impact on permeability, *GeoResJ*, 7 (2015) 1-13.
- [45] S.A. International, ASTM D698-12e1, Standard Test Methods for Laboratory Compaction Characteristics of Soil Using Standard Effort (12 400 ft-lbf/ft³ (600 kN-m/m³)), in, West Conshohocken, 2012.
- [46] C. AB, COMSOL Multiphysics Reference Manual Version: COMSOL 5.1., (2015).
- [47] R. López-Vizcaíno, A. Yustres, M.J. León, C. Saez, P. Cañizares, M.A. Rodrigo, V. Navarro, Multiphysics Implementation of Electrokinetic Remediation Models for Natural Soils and Porewaters, *Electrochimica Acta*, 225 (2017) 93-104.
- [48] S.A. International, ASTM D2487. Classification of Soils for Engineering Purposes (Unified Soil Classification System), in, West Conshohocken, Pensilvania, USA., 2006.

- [49] J.K. Mitchell, K. Soga, Fundamentals of soil behavior, John Wiley & Sons, Inc, Hoboken, New Jersey, USA, 2005.
- [50] J.M. Paz-Garcia, K. Baek, I.D. Alshawabkeh, A.N. Alshawabkeh, A generalized model for transport of contaminants in soil by electric fields, Journal of Environmental Science and Health - Part A Toxic/Hazardous Substances and Environmental Engineering, 47 (2012) 308-318.
- [51] J.M. Paz-García, B. Johannesson, L.M. Ottosen, A.B. Ribeiro, J.M. Rodríguez-Maroto, Modeling of electrokinetic processes by finite element integration of the Nernst-Planck-Poisson system of equations, Separation and Purification Technology, 79 (2011) 183-192.
- [52] R.M. Brooks, A.T. Corey, Hydraulic properties of porous media, in: Hydrology Paper no. 3, Colorado State University, Fort Collins, 1964.
- [53] S.A. International, ASTM D2435. Standard Test Methods for One-Dimensional Consolidation Properties of Soils Using Incremental Loading, in, West Conshohocken, Pennsylvania, USA., 2011.
- [54] J. Nogueira Santos, Study on the use of electrical techniques for accelerating the consolidation of clayey soils (in Portuguese), in: Instituto Superior Técnico, Universidade Técnica de Lisboa, Lisbon, 2012.
- [55] X. Ren, Y. Zhao, Q. Deng, J. Kang, D. Li, D. Wang, A relation of hydraulic conductivity — void ratio for soils based on Kozeny-Carman equation, Engineering Geology, 213 (2016) 89-97.
- [56] W.D. Carrier Iii, Goodbye, Hazen; hello, Kozeny-Carman, J. Geotech. Geoenviron. Eng., 129 (2003) 1054-1056.
- [57] E.C. Leong, S. Tripathy, H. Rahardjo, Total suction measurement of unsaturated soils with a device using the chilled-mirror dew-point technique, Geotechnique, 53 (2003) 173-182.
- [58] M.T. van Genuchten, CLOSED-FORM EQUATION FOR PREDICTING THE HYDRAULIC CONDUCTIVITY OF UNSATURATED SOILS, Soil Science Society of America Journal, 44 (1980) 892-898.
- [59] R. López-Vizcaíno López, Remediación electrocinética de suelos de baja permeabilidad contaminados con compuestos orgánicos hidrofobos, in: Departamento de Ingeniería Química, Universidad de Castilla-La Mancha, 2013.
- [60] J. Yuan, M.A. Hicks, Numerical modelling of electro-osmosis consolidation of unsaturated clay at large strain, in: 8th European Conference on Numerical Methods in

Geotechnical Engineering, NUMGE 2014, Taylor and Francis - Balkema, Delft, 2014, pp. 1061-1066.

[61] J. Yuan, M.A. Hicks, C. Jommi, Large strain consolidation of clays: Numerical comparison between evaporation and electro-osmosis dewatering, in: 14th International Conference of International Association for Computer Methods and Recent Advances in Geomechanics, IACMAG 2014, Taylor and Francis - Balkema, Kyoto, 2015, pp. 1655-1660.

[62] M. Manassero, A. Dominijanni, G. Musso, Modeling Applied To Environmental Geotechnics, in: Y. Chen, L. Zhan, X. Tang (Eds.) Advances in Environmental Geotechnics: Proceedings of the International Symposium on Geoenvironmental Engineering in Hangzhou, China, September 8–10, 2009, Springer Berlin Heidelberg, Berlin, Heidelberg, 2010, pp. 57-89.

[63] G.L. Guymon, Unsaturated Zone Hydrology, Prentice Hall, 1994.

[64] R. López-Vizcaíno, C. Risco, J. Isidro, S. Rodrigo, C. Saez, P. Cañizares, V. Navarro, M.A. Rodrigo, Scale-up of the electrokinetic fence technology for the removal of pesticides. Part I: Some notes about the transport of inorganic species, *Chemosphere*, 166 (2017) 540-548.

[65] R. López-Vizcaíno, C. Risco, J. Isidro, S. Rodrigo, C. Saez, P. Cañizares, V. Navarro, M.A. Rodrigo, Scale-up of the electrokinetic fence technology for the removal of pesticides. Part II: Does size matter for removal of herbicides?, *Chemosphere*, 166 (2017) 549-555.

[66] R. López-Vizcaíno, V. Navarro, M.J. León, C. Risco, M.A. Rodrigo, C. Sáez, P. Cañizares, Scale-up on electrokinetic remediation: Engineering and technological parameters, *J. Hazard. Mater.*, 315 (2016) 135-143.