Influence of the type of surfactant on the mobility of flushing fluids for electro-remediation processes

R. López-Vizcaíno^a, C. Sáez^a, P. Cañizares^a, V. Navarro^b, M.A. Rodrigo^{*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*

Abstract

The mobility of four flushing fluids in an electro-remediation process has been studied. A mock-up plant with two rows of three electrodes positioned in semipermeable electrolyte wells was used in this study. Two different cases were considered: (i) an initial state when the soil was wet with water and the addition of surfactant starts and (ii) a second state when the surfactant front had passed through the soil. The results show that the electro-osmotic flux strongly depends on the nature of the flushing fluid and on the voltage gradient applied between electrode rows. The presence of ionic surfactants (both cationic and anionic) led to lower electro-osmotic flow-rates. The concentration of surfactants in the drain tanks increased in the case of the flushing fluid with the non-ionic surfactant because the surfactant transport was more efficient. Conversely, the anionic surfactant accumulated more in the injection well. This finding is related to the effect of migration, which in the reception wells was opposite to the electro-osmotic flux.

Keywords: electro-osmotic, surfactant, electro-remediation, electro-migration

*Corresponding author: manuel.rodrido@uclm.es
Tel.: +34 902204100 ext. 3411; fax: +34 926295256.

1. INTRODUCTION.

Industrial activity can cause pollution problems in soils and groundwater. This type of pollution has a complex impact and any evaluation of this issue must take into account numerous factors including, the physicochemical properties of the pollutants and the geological and chemical characteristics of the soil. In the last few years, a wide variety of remediation technologies have been developed to deal with soil pollution [1-4]. Among these approaches, 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 [5-8]. This technology is particularly recommended for the treatment of low-permeability soils contaminated with ionic pollutants [9-14], although it can also be used to remove non-ionic organic pollutants (aided by the use of surfactant solutions as flushing fluids) [15-19].

In electrokinetic processes the soil essentially becomes part of an electrochemical cell. Soils themselves are not electrically or ionically conductive materials and the moisture is the real electrolyte in these electrochemical processes. For this reason, electrokinetic processes often require the addition of flushing fluids to guarantee hydraulic saturation, to enhance the conductivity of soils and to maintain the ionic circuit in the soil. In addition, the flushing fluid may contain substances that favour the treatment by increasing the mobility of the pollutants. In the case of soils polluted with inorganic compounds (e.g. heavy metals) the flushing fluid is usually an acidic or basic pH buffer solution depending on the properties of the particular pollutant to be removed. On the other hand, if the soils are polluted with hydrophobic organic compounds (HOCs), the flushing fluids usually contain substances that increase the polarity of these pollutants and hence their solubility in water. These substances are typically

1 surfactants and they are able to improve the mass-transfer of HOCs from the soil into the
2 aqueous phase by decreasing the interfacial tension and by accumulating HOCs within
3 surfactant micelles.

4
5 In recent years several reports have focussed on this topic [20-29]. Most of these studies were
6 carried out on the laboratory scale and the soil electro-remediation reactor consisted of a
7 hermetic column or a rectangular cell with a volume of less than 1 dm³. Kaolinite is
8 frequently used as a model for low-permeability soils [30-38]. Generally, flushing fluids
9 consist of aqueous solutions containing surfactants, although cyclodextrins and cosolvents
10 such as ethanol have also been used. The use of these synthetic soils, pollutants and flushing
11 fluids has contributed to our knowledge of the fundamentals of electrokinetic processes.

12
13 At this point, it is important to note that very few applications have been assessed on a large
14 scale and our current knowledge regarding such processes is limited to the results obtained in
15 laboratory scale studies in which the electrodes are situated in independent chambers of an
16 electrokinetic reactor [10,14,15,20,21,25,26]. The extrapolation of such results to a real
17 application without an appropriate scale-up study would be unwise. Many of the
18 technological processes available (especially those running at the full-scale level) are
19 developed within the R&D departments of large companies (e.g. Dupont, Monsanto) or by
20 small companies that are fully devoted to the development of remediation technologies (e.g.
21 Hak Milieutechniek BV). These companies are clearly not concerned with publishing their
22 results (as proprietary technology is their main commercial advantage) but in selling the
23 process for full-scale soil and/or groundwater remediation.

For these reasons, one of the novel aspects of the work described here is the scale of the study. Experimental work was carried out in a mock-up plant with a volume of 175 dm³ with the intention of simulating the real electrokinetic treatment of contaminated soil. The electrodes were positioned in semipermeable electrolyte wells with a linear distribution (two rows of three electrodes facing one another). Both the electrolyte wells and the soil were at atmospheric pressure as the electrokinetic reactor was an open system. As mentioned above, electrokinetic techniques can require the use of a polar reagent to increase the solubility of hydrophobic pollutant(s) and, thus, to enhance the transport of these substances through the soil. Moreover, the physicochemical properties of these reagents can have a significant influence on the feasibility of the treatment. In this context, three surfactants (cationic, non-ionic and anionic) were selected and used at a concentration of 10 g/l. The influence of the nature of the surfactant on the electro-osmotic flux and electrical efficiency was studied. The aim was to evaluate how the formulation of a flushing fluid (in terms of type of surfactant) can affect the electro-osmotic fluxes and how the mobility of surfactants in multi-electrolyte well electro-remediation processes is affected under well-controlled conditions. This investigation represents a the first step in a broader study that aims to develop efficient technologies for the removal of organic pollutants from soils using electrokinetic flushing supported by surfactants.

2. MATERIALS AND METHODS.

2.1. Flushing fluids.

Four types of flushing fluid were studied in this work, namely no surfactant (FF-NS), anionic (FF-AN), cationic (FF-CA) and non-ionic (FF-NI), according to the type of surfactant contained in the fluid. In all cases the water used in the formulation of the flushing fluids

1 contained different salts in order to simulate the composition of surface water (Table 1).
2 Sodium dodecyl sulphate (SDS) was used as a model anionic surfactant,
3 alkylbenzyltrimethylammonium chloride (ABDMA) was used as a representative cationic
4 surfactant and polyoxyethylene sorbitan monooleate (Tween 80) was used as a representative
5 non-ionic surfactant. In all cases the surfactant concentration was 10 g/l. These compounds
6 were selected to evaluate the influence of the nature of the flushing fluid in electrokinetic
7 processes. Cationic surfactants are not commonly used in electrokinetic remediation.
8 However, the use of such systems in flushing fluids allowed us to evaluate the adsorption of
9 this type of compound in clay soils. The properties of the surfactants are given in Table 2.

11 **2.2. Experimental setup.**

12 All of the electrokinetic experiments were carried out in a mock-up electro-remediation plant
13 (Figure 1). Kaolinite was selected as the model for clay soil. This soil is characterized by its
14 lack of reactivity, low hydraulic conductivity, lack of organic content and low cation
15 exchange capacity. The properties of the particular synthetic soil used in this study are
16 presented in Table 3. The soil was loaded into an electrochemical reactor ($LWH = 70 \times 50 \times$
17 50 cm) that was constructed from a methacrylate polymer. The model soil consisted of two
18 materials: kaolinite and gravel, the latter of which was used to simulate the unsaturated
19 stratum located beneath the clay (17 dm^3). The soil was compacted for two days with a
20 compacting load of 140 kg m^{-2} . The electrode distribution was two rows of three electrodes
21 separated by 40 cm and positioned face to face. Electrodes with the same polarity were
22 separated by 12 cm; these electrodes were located in semi-permeable electrolyte wells.
23 Porous graphite was selected as the material for the anodes and cathodes, both of which had a
24 height of 10 cm. A constant voltage gradient (ranging from 0.5 to 2.0 VDC cm^{-1}) was applied
25 using a power supply (Delta Elektronika BV, with a maximum output of 400 V and 4 A).

Under these experimental conditions, the current intensity ranged from 0.2 to 0.5 A. The flushing fluid was injected into the anodic wells through electro-valves because it was necessary to compensate for the water transported from anodic wells to cathodic wells by electro-osmosis (the flushing direction in most experiments was from the anodic to the cathodic wells). The electro-valves were controlled by a level controller located within the wells in order to provide a constant level in the anodic wells. The cathodic wells were connected to three drain tanks, each of which had a volume of 0.1 dm³. The objective of these drain tanks was to collect all of the fluid transported through the soil. Prior to starting the experiments, the cathodic wells were filled with water and the anodic wells were filled with the appropriate flushing solution. As discussed later, in some experiments the flushing direction is reversed. In those cases, the electro-valves were placed in the cathodic wells to feed the flushing solution and the drain tanks were located in the anodic wells (not shown in the Figure)

2.3. Experimental procedure.

The soil was saturated with flushing solution prior to starting the experiments. The initial target moisture level for the kaolinite was 30–34% approximately. Two different cases were studied: (i) an initial state when the soil is merely saturated with water and addition of the surfactant to the anodic wells starts and (ii) a second state when the surfactant front has passed through all of the soil. In order to simulate the latter case and to reduce the test time, the soil was washed with the corresponding flushing fluid before being placed in the mock-up in order to achieve a constant concentration of the surfactant in the flushing fluid solution. All of the electrokinetic experiments were carried out under a constant voltage gradient (ranging from 0.5 to 2 VDC/cm). In each experiment the system was allowed to reach a steady state, which was assumed to be achieved when the electric current was stable. The cell current,

volume accumulated in the cathodic drain tanks, electrolyte pH and conductivity in the anodic and cathodic compartments were measured periodically during the experiments. Conductivity and pH measurement allowed the determination of the variable profiles from the anode to the cathode side.

2.4. Electrical efficiency.

The current density was used to determine the electric consumption (EC) in electro-remediation experiments and this was calculated using Eq. (1), where E (V) is the potential applied, I (A) is the electric current and Q_{eo} is the electro-osmotic flow (in $\text{dm}^3 \text{ h}^{-1}$). EC determines the power necessary to transport 1 dm^3 by the electro-osmosis process.

$$EC \left(\frac{kWh}{dm^3} \right) = \frac{E \cdot I}{Q_{eo}} \quad (1)$$

2.5. Analyses.

The surfactant concentration was evaluated by monitoring the chemical oxygen demand using a HACH DR2000 analyzer [39].

3. RESULTS AND DISCUSSION.

The time-course of the electro-osmotic fluxes between the anode and the cathode rows, measured at two different electric voltage gradients with different flushing fluids, is represented in Figure 2a. The changes in the current intensity during the operation of the electrokinetic soil remediation process are represented in Figure 2b.

From the dynamics point of view, it can be observed that electro-osmotic fluxes achieve a steady state response from the very beginning of the process but that this response is obtained around four hours later in the case of the current intensity. In this context, it must be borne in mind that electro-osmotic flux is believed to depend mainly on the electric voltage gradient,

1 which was kept constant in all tests, while the current density depends on the anodic and
2 cathodic reactions that take place on the surface of the electrodes in the wells. In this respect,
3 water electrolyses produce large quantities of protons in the anodic wells and hydroxyl anions
4 in the cathodic ones – these species are associated with the oxygen and hydrogen evolution
5 processes, respectively. This increase in the ion concentration leads to an increase in the
6 resulting conductivity and this may explain the increase in the electric current, as voltages
7 were kept constant during all experiments. With respect to the small time-constant of the
8 electro-osmotic flux, it must be borne in mind that the almost constant flow-rate values
9 correspond to a pseudo steady-state response, *not* to a real steady-state response, because
10 saturation of the soil with the flushing fluid from the initial soil with a surfactant content of
11 zero would require a very long time (weeks and even months). The shorter time-scale used in
12 this work is negligible with respect to the time necessary to study these slower processes.

13
14 As far as the composition of the flushing fluid is concerned, it can be observed that the
15 presence of ionic surfactants (both cationic and anionic) leads to lower electro-osmotic flow-
16 rates, a trend observed for the two electric voltage gradients tested. However, the
17 corresponding flow-rate values are significantly influenced by the voltage gradient and the
18 differences between flushing fluids also seem to increase with higher voltage gradients. The
19 flushing fluid that contained the cationic surfactant gave the smallest electro-osmotic fluxes,
20 and the difference with respect to the other flushing fluids appears to be more marked at low
21 voltage gradients. On the other hand, for high voltage gradients, the non-ionic flushing fluids
22 and those without surfactant show the same behaviour, and at lower values the presence of
23 the non-ionic surfactant seems to have a detrimental effect on the electro-osmotic flux
24 [7,40,41].

1 It seems clear from the results that the electric voltage gradient has a significant effect on the
2 electro-osmotic fluxes. The influence of the voltage gradient on the values of the pseudo
3 steady-state electro-osmotic flow-rates is represented in Figures 3 and 4. At this point, and
4 according to the above statement concerning the dynamics of the electrokinetic processes, it
5 is important to mention that two different cases exist when an aqueous surfactant solution is
6 used as a flushing fluid: (i) an initial state when the soil is wet with water and the surfactant
7 addition starts and (ii) a second state when the surfactant front has passed through all of the
8 soil. Taking into account that the electro-osmotic flow is 0.7 dm day^{-1} , the required time to
9 saturate the soil is approximately three months. Thus, in order to simulate the latter case and
10 to reduce the test time, the soil can be washed with the corresponding flushing fluid before
11 being placed in the mock-up in order to achieve a constant surfactant concentration in the
12 flushing fluid solution.

13
14 With respect to the influence of the voltage gradient on the electro-osmotic fluxes obtained in
15 the initial state (the soil was initially saturated with water only), the maximum values were
16 obtained when the voltage gradient was 2.0 VDC cm^{-1} . The use of water gave rise to the
17 highest flux ($1.83 \text{ dm}^3\text{dm}^{-2}\text{day}^{-1}$) achieved. An electro-osmotic flux of around $1.72 \text{ dm}^3\text{dm}^{-2}\text{day}^{-1}$
18 was obtained on using the non-ionic surfactant, whereas cationic and anionic
19 surfactants gave the worst results (1.22 and $1.27 \text{ dm}^3\text{dm}^{-2}\text{day}^{-1}$, respectively) because an
20 increase in the ionic concentration in the soil led to a decrease in electro-osmotic flux
21 regardless of whether the ions were anions or cations. This finding explains why, when the
22 soil is saturated with either anionic or cationic surfactant solutions, the electro-osmotic flux
23 was similar and lower than that in other experiments with non-ionic flushing fluid. Likewise,
24 the flow obtained is higher than that reported by Reddy and Saichek [24,25], although it is
25 important to mention that in those studies the surfactant concentration was three times higher

(30 g l⁻¹) and this can lead to a decrease in the electro-osmotic transport rate. Furthermore, Sanromán et al. [42] obtained a value of 0.5 dm³dm²day⁻¹ using Brij 35 (10 g l⁻¹) in conjunction with 3 VDC cm⁻¹ and Lu et al. [43] obtained a value of 0.125 dm³dm²day⁻¹ using Tween 80 (10 g l⁻¹) and applying 1 VDC cm⁻¹. It should be noted that these are not direct comparisons and can only be considered as a guide because numerous factors can affect the specific value obtained in a given soil, including soil type, grain size distribution, hydraulic conductivity, cation exchange capacity and surfactant type, concentration and location.

Moreover, it can be observed that ionic flushing fluids have a negative influence on electro-osmotic flux, because these surfactants can cause a reduction in the size of the electrical double layer and, therefore, the volume of fluid transported into the soil is smaller and the electro-osmotic flux decreases. Tests with water and Tween 80 (non-ionic flushing solutions) showed enhanced electro-osmotic flux with respect to samples containing ionic surfactants in the flushing fluid [44,45].

In the second case considered here (soil saturated with the surfactant solution), the soil was saturated with the flushing solution used in each test by washing it with the appropriate surfactant solution. After this step the same experimental procedure was used as described above. As can be observed, the best results were obtained on using water because in this case there are no differences between the soils (i.e. no surfactant is added). The experiments on non-ionic and anionic surfactants gave slightly lower electro-osmotic flux values than the experiments carried out with a soil saturated with water. The experiment carried out on the cationic surfactant showed a decrease in the electro-osmotic flux of approximately 50% in comparison to the experiment in which the soil was saturated with water. Moreover, it is important to note that when the soil was saturated with cationic surfactant, the flushing

solution was transported from the cathode to the anode and, consequently, the electro-osmotic flux had negative values. This finding is due to the fact that the superficial charge of the soil is positive due to the higher concentration of cations absorbed on the surface of kaolinite particles.

Linear trends were observed in all tests when the soil had a surfactant concentration of zero, in accordance with the theoretical model of Helmholtz–Smoluchowski (Eq. 1), where J_{eo} is the electro-osmotic flux, D is the dielectric constant, ϵ_0 is permittivity of a vacuum, ζ stands for zeta potential, μ denotes viscosity and E_z is the electrical gradient. K_{eo} is the electro-osmotic conductivity and this is a grouping of previously defined parameters.

$$J_{eo} = -\frac{D\epsilon_0\zeta}{\mu}E_z = K_{eo}E_z \quad (2)$$

However, in the case of soils saturated with surfactants the linear trend seems to become exponential, a finding that provides an insight into the complexity of the soil system upon the addition of surfactants.

Electro-osmotic conductivity (K_{eo}) can be calculated by fitting data to eq. 2 for each test. The electro-osmotic conductivity values calculated in each test are given in Table 4. In the case of water the K_{eo} value is the same in both states. In the non-ionic test, K_{eo} decreased slightly in comparison to the test in water due to the greater viscosity of the surfactant system. However, when the flushing solution was an anionic surfactant, K_{eo} increased significantly because this surfactant accentuated the negative charge of the clay soil and the layer of solution present at the surface of the soil had a high positive charge; therefore this fluid is strongly attracted by

1 the cathodes. In the test with the cationic flushing fluid the opposite occurs because the
2 cationic micelles are strongly retained in the soil matrix due to the negative charge of the soil
3 surface [40].

4
5 The changes in the surfactant concentration in the anionic and cationic wells during the
6 progress of the electrokinetic assays are shown in Figures 5 and 6. These experiments were
7 carried out on the soil saturated with the corresponding flushing fluid. It is worth bearing in
8 mind that, under these conditions, the flushing fluid flows from the anodic to the cathodic
9 wells for the NS, NI and AN flushing fluids, and from the cathodic to the anodic wells in the
10 case of the CA flushing fluid (i.e. the flushing direction is reversed). In order to provide
11 flushing fluid in the appropriate wells, in experiments with the CA the flushing fluid was fed
12 into the cathodic wells and collected in the anodic ones, while in the other cases the flushing
13 fluid was added to the anodic wells and collected in the cathodic ones.

14
15 It can be observed that in all cases the surfactant concentration increased in the drain tanks,
16 with the surfactant transport greater in the case of the NI surfactant and of similar importance
17 in the cases of the AN and CA surfactants. This observation can be easily explained in terms
18 of electro-osmotic flow, which drags surfactant molecules towards the cathodic well where it
19 is periodically collected and removed from the mock-up. The lower concentration obtained
20 with the ionic surfactants can be explained by the effect of migration, which in the reception
21 wells opposes the electro-osmotic flux.

22
23 In the case of the injection wells, there is also an increase in the surfactant concentration
24 inside the well. The anionic surfactant was once again the one that accumulated most in the
25 injection well and this can be easily explained in terms of the contribution of migration,

1 which prevents a decrease in the concentration of charged molecules in the injection well – in
2 the case of the AN flushing fluid these are the anodic wells and in the case of the CA flushing
3 fluid the cathodic wells. This phenomenon also explains the almost constant value for the NI
4 flushing fluid, because in this case there is no electric charge on the functional groups in the
5 surfactant molecules.

6
7 The accumulation of surfactant in both types of wells, regardless of the type of surfactant,
8 indicates that these compounds should not be dosed directly into the electrolyte wells (to
9 which only water should be added). Indeed, these results suggest that the surfactant should be
10 added to non-electrolytic wells positioned inside the zone enclosed by the two electrode rows
11 so that it can be dragged by the electro-osmotic flux and also by migration (in the case of
12 charged surfactants). In addition, this approach ensures the total disappearance of this
13 compound from the treated soil once it has been used to mobilize the organic pollutants.

14
15 The specific energy requirements for the mobility of the flushing fluid as a function of the
16 type of surfactant and of the conditions of the soil (saturated with flushing fluid or with a
17 surfactant concentration of zero) are represented in Figure 7. It can be clearly observed that
18 the energy required increases with the amount of surfactant contained in the soil and the
19 negative effect of the addition of surfactant on the mobility of the flushing fluid is also
20 evident.

4. CONCLUSIONS.

The following conclusions can be drawn from this work:

- The electro-osmotic flux seems to depend strongly on the nature of the flushing fluid and on the voltage gradient. The presence of ionic surfactants (both cationic and anionic) leads to lower electro-osmotic flow-rates. The differences between flushing fluids also seem to increase at higher voltage gradients.
- Ionic flushing fluids have a negative influence on electro-osmotic flux as they lead to an increase in the ionic force of the soil and, therefore, the volume of fluid transported into the soil is smaller and the electro-osmotic flux decreases.
- Electro-osmotic flow drags surfactant molecules towards the cathodic well and, consequently, the surfactant concentration increases in the drain tanks. Surfactant transport is greater in the case of the NI surfactant but is less important for the AN and CA surfactants in which electro-migration to the electro-osmotic flux are opposed. Similar results were obtained for the injection wells.
- In surfactant-saturated soil the fluid flows from the anodic to the cathodic wells for the NS, NI and AN flushing fluids, and from the cathodic to the anodic wells in the case of the CA flushing fluid. This fact is related to the surface charge of soil.
- The energy required for the process increases with the amount of surfactant contained in the soil and the addition of surfactant has a negative effect on the mobility of the flushing fluid.

1 **Acknowledgements**

2 This work was supported by the MCT (Ministerio de Ciencia y Tecnología, Spain) and by the
3 EU (European Union) through projects CTM2007-60472/TECNO and CTM2010-
4 18833/TECNO.

5

6

7

8

References.

1. Mulligan, C.N.; Yong, R.N.; Gibbs, B.F. (2001) Remediation technologies for metal-contaminated soils and groundwater: an evaluation. *Eng. Geol.*, 60: 193.
2. Reddy, K.R. (2010) Technical challenges to in-situ remediation of polluted sites. *Geotech. Geol. Eng.*, 28: 211.
3. Gan, S.; Lau, E.V.; Ng, H.K. (2009) Remediation of soils contaminated with polycyclic aromatic hydrocarbons (PAHs). *J. Hazard. Mater.*, 172: 532.
4. Fenyvesi, É.; Molnár, M.; Leitgib, L.; Gruiz, K. (2009) Cyclodextrin-enhanced soil-remediation technologies. *Land Contam. Reclam.*, 17: 585.
5. Page, M.M.; Page, C.L. (2002) A review of electroremediation of contaminated soils. *J. Environ. Eng.*, 128: 208.
6. Saichek, R.E.; Reddy, K.R. (2005) Enhanced Remediation of Hydrophobic Organic Compounds in Soils: A Review. *Environ. Sci. Technol.*, 35: 115.
7. Virkutyte, J.; Sillanpää, M.; Latostenmaa, P. (2002) Eletrokinetic soil remediation – critical overview. *Sci. Total Environ.*, 289: 97.
8. Alshawabkeh, A.N. (2009) Electrokinetic soil remediation: Challenges and opportunities. *Sep. Sci. Technol.*, 44: 2171.
9. Rutigliano, L.; Fino, D.; Saracco, G.; Specchia, V.; Spinelli, P. (2008) Electrokinetic remediation of soils contaminated with heavy metals. *J. Appl. Electrochem.*, 38: 1035.
10. Garcia-Gutierrez, M.D.; Gomez-Lahoz, C.; Rodriguez-Maroto, J.M.; Vereda-Alonso, C.; Garcia-Herruzo, F. (2007) Electrokinetic remediation of a soil contaminated by the pyritic sludge spill of Aznalcollar (SW, Spain). *Electrochim. Acta.*, 52: 3372.
11. Shi, W.-X.; Cui, C.-W.; Yu, S.-L.; Feng, W.-M. (2007) Study on electrokinetic remediation of cadmium contaminated soils. *J. Harbin Inst. Technol.*, 14: 385.

12. Dragut, L.; Bogatu, C.; Verbitchi, V.; Ionescu, D.; Harjan, I.; Masu, S. (2009) In situ remediation of soils polluted with heavy metals. Part II. Using of electrokinetic treatment. *J. Environ. Prot. Ecol.*, 10: 49.
13. Reddy, K.R.; Maturi, K.; Cameselle, C. (2009) Sequential electrokinetic remediation of mixed contaminants in low permeability soils. *J. Environ. Eng.*, 135: 989.
14. Colacicco, A.; De Gioannis, G.; Muntoni, A.; Pettinao, E.; Polettini, A.; Pomi, R. (2010) Enhanced electrokinetic treatment of marine sediments contaminated by heavy metals and PAHs. *Chemosphere*, 81: 46.
15. Alcántara, M.T.; Gómez, J.; Pazos, M.; Sanromán, M.A. (2010) Electrokinetic remediation of PAH mixtures from kaolin. *J. Hazard. Mater.*, 179: 1156.
16. Maturi, K.; Reddy, K.R.; Cameselle, C. (2009) Surfactant-enhanced electrokinetic remediation of mixed contamination in low permeability soil. *Sep. Sci. Technol.*, 44: 2385.
17. Alcántara, T.; Pazos, M.; Cameselle, C.; Sanromán, M.A. (2008) Electrochemical remediation of phenanthrene from contaminated kaolinite. *Environ. Geochem. Health*, 30: 89.
18. Conte, P.; Agretto, A.; Spaccini, R.; Piccolo, A. (2005) Soil remediation: humic acids as natural surfactants in the washings of highly contaminated soils. *Environ. Pollut.*, 135: 515.
19. Mulligan, C.N.; Yong, R.N.; Gibbs, B.F. (2001) Surfactant-enhanced remediation of contaminated soil: a review. *Eng. Geol.*, 60: 371.
20. Chang, J-H.; Qiang, Z.; Huang, Ch-P.; Ellis, A.V. (2009) Phenanthrene removal in unsaturated soils treated by electrokinetics with different surfactants—Triton X-100 and rhamnolipid. *Colloids Surf. A.*, 348: 157.

21. Park, J-Y.; Lee, H-H.; Kim, S-J.; Lee, Y-J.; Yang, J-W. (2007) Surfactant-enhanced electrokinetic removal of phenanthrene from kaolinite. *J. Hazard. Mater.*, 140: 230.
22. Zhou, W.; Zhu, L. (2008) Enhanced soil flushing of phenanthrene by anionic–nonionic mixed surfactant. *Water Res.*, 42: 101.
23. Reddy, K.R.; Ala, P.R.; Sharma, S.; Kumar, S.N. (2006) Enhanced electrokinetic remediation of contaminated manufactured gas plant soil. *Eng. Geol.*, 85: 132.
24. Reddy, K.R.; Asce, M.; Saichek, R.E. (2003) Effect of soil type on electrokinetic removal of phenanthrene using surfactants and cosolvents. *J. Environ. Eng.*, 129: 336.
25. Saichek, R.E.; Reddy, K.R. (2003) Effect of pH control at the anode for the electrokinetic removal of phenanthrene from kaolin soil. *Chemosphere*, 51: 273.
26. Khalladi, R.; Benhabiles, O.; Bentahar, F.; Moulai-Mostefa, N. (2009) Surfactant remediation of diesel fuel polluted soil. *J. Hazard. Mater.*, 164: 1179.
27. Couto, H.; Massarani, G.; Biscaia Jr. E.; Sant’Anna Jr. G.L. (2009) Remediation of sandy soils using surfactant solutions and foams. *J. Hazard. Mater.*, 164: 1325.
28. Laha, S.; Tansel, B.; Ussawarujikulchai, A. (2009) Surfactant–soil interactions during surfactant-amended remediation of contaminated soils by hydrophobic organic compounds: A review. *J. Environ. Manage.*, 90: 95.
29. Paria, S. (2008) Surfactant-enhanced remediation of organic contaminated soil and water. *Adv. Colloid Interface Sci.*, 138: 24.
30. Oonnittan, A.; Shrestha, R.A.; Sillanpää, M. (2009) Removal of hexachlorobenzene from soil by electrokinetically enhanced chemical oxidation. *J. Hazard. Mater.*, 162: 989.
31. Maturi, K.; Reddy, K.R.; Cameselle, C. (2009) Surfactant-enhanced electrokinetic remediation of mixed contamination in low permeability soil. *Sep. Sci. Technol.*, 44: 2385.

32. Lee, Y-J.; Han, H.; Kim, S-H.; Yang, J-W. (2009) Combination of electrokinetic separation and electrochemical oxidation for acid dye removal from soil. *Sep. Sci. Technol.*, 44: 2455.
33. Alcántara, T.; Pazos, M.; Gouveia, S.; Cameselle, C.; Sanromán, M.A. (2008) Remediation of phenanthrene from contaminated kaolinite by electroremediation-Fenton technology. *J. Environ. Sci. Health. Part A Toxic/Hazard. Subst. Environ. Eng.*, 43: 901.
34. Pazos, M.; Cameselle, C.; Sanromán, M.A. (2008) Remediation of dye-polluted kaolinite by combination of electrokinetic remediation and electrochemical treatment. *Environ. Eng. Sci.*, 25: 419.
35. Alcántara, T.; Pazos, M.; Cameselle, C.; Sanromán, M.A. (2008) Electrochemical remediation of phenanthrene from contaminated kaolinite. *Environ. Geochem. Health*, 30: 89.
36. Maturi, K.; Reddy, K.R. (2008) Cosolvent-enhanced desorption and transport of heavy metals and organic contaminants in soils during electrokinetic remediation. *Water Air Soil Pollut.*, 189: 199.
37. Al-Hamdan, A.Z.; Reddy, K.R. (2008) Electrokinetic remediation modeling incorporating geochemical effects. *J. Geotech. Geoenviron. Eng.*, 134: 91.
38. Wang, J-Y.; Huang, X-J.; Kao, J.C.M.; Stabnikova, O. (2007) Simultaneous removal of organic contaminants and heavy metals from kaolin using an upward electrokinetic soil remediation process. *J. Hazard. Mater.*, 144: 292.
39. Clesceri, L.S.; Greenberg, A.E.; Eaton, A.D.; Franson, M.A.H. (1989) *APHA, AWWA, WPCF. Standard Methods for the Examination of Water and Wastewater*, 20th ed.; Eds.; American Public Health Association: Washington, DC.

- 1 40. Pazos, M.; Rosales, E.; Alcántara, T.; Gómez, J.; Sanromán, M.A. (2010)
2 Decontamination of soils containing PAHs by electroremediation: A review. *J. Hazard.*
3 *Mater.*, 177: 1.
- 4 41. Saichek, R.E.; Reddy, K.R. (2005) Electrokinetically Enhanced Remediation of
5 Hydrophobic Organic Compounds in Soils: A Review. *Crit. Rev. Env. Sci. Technol.*,
6 35: 115.
- 7 42. Gómez, J.; Alcántara, M.T.; Pazos, M.; Sanromán M.A. (2009) A two-stage process
8 using electrokinetic remediation and electrochemical degradation for treating
9 benzo[a]pyrene spiked kaolin. *Chemosphere*, 74: 1516.
- 10 43. Yuan, S.; Tian, M.; Lu, X. (2006) Electrokinetic movement of hexachlorobenzene in
11 clayed soils enhanced by Tween 80 and β -cyclodextrin. *J. Hazard. Mater.*, 137: 1218.
- 12 44. Cañizares, P.; Sáez, C.; Romero-Girón, E.; García-Gómez, J.; Lobato, J.; Rodrigo,
13 M.A. (2007) Electroremediation of soil by electrochemical processes. Part 1.
14 Fundamentals. *Afinidad*, 64: 663.
- 15 45. Cañizares, P.; Sáez, C.; Romero-Girón, E.; García-Gómez, J.; Lobato, J.; Rodrigo,
16 M.A. (2007) Electroremediation of soil by electrochemical processes. Part 2.
17 Technology. *Afinidad*, 64: 671.

18

Table Captions

Table 1. Water composition.

Table 2. Properties of Surfactants.

Table 3. Properties of soil.

Table 4. Electro-osmotic conductivity ($\text{m}^2\text{s}^{-1}\text{V}^{-1}$)

Figure captions

Fig. 1. Diagram (a) and photograph (b) of the mock-up electro-remediation plant.

Fig. 2. Influence of the type of flushing fluid on the time-course of the electro-osmotic fluxes (a) and of the current intensity (b) during soil flushing operation. Voltage gradient 0.5 VDC cm^{-1} ($\diamond$ FF-NS, $\circ$ FF-NI, Δ FF-AN, $\square$ FF-CA); Voltage gradient 1.0 VDC cm^{-1} ($\blacklozenge$ FF-NS, $\bullet$ FF-NI, $\blacktriangle$ FF-AN, $\blacksquare$ FF-CA).

Fig. 3. Influence of voltage gradient on the electro-osmotic fluxes for non-ionic flushing fluids. (a) FF-NS, (b) FF-NI. $\square$ Soil with a surfactant concentration of zero, $\blacksquare$ Soil saturated with flushing fluid.

Fig. 4. Influence of voltage gradient on the electro-osmotic fluxes for ionic flushing fluids. (a) FF-AN, (b) FF-CA. $\square$ Soil with a surfactant concentration of zero, $\blacksquare$ Soil saturated with flushing fluid.

Fig. 5. Accumulation of surfactants in the drain tanks during operation of the electrokinetic process. $\diamond$ FF-AN, Δ FF-CA, $\square$ FF-NI. Voltage gradient: 1 VDC cm^{-1} .

Fig. 6. Accumulation of surfactants in the injection wells during operation of the electrokinetic process. $\diamond$ FF-AN, Δ FF-CA, $\square$ FF-NI. Voltage gradient: 1 VDC cm^{-1} .

Fig. 7. Electrical efficiency in the mobility of the flushing fluids. Operation conditions: $E_z = 1 \text{ VDC cm}^{-1}$. $\square$ Soil with an initial surfactant concentration of zero, $\blacksquare$ Soil saturated with flushing fluids.

1 Figure 1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

17

18

1 Figure 2

2
3
4
5

1 Figure 3

2

3

4

5

6

7

1 Figure 4

2
3
4
5
6
7

1 Figure 5

2

3

4

5

6

7

8

9

10

11

12

1 Figure 6

2
3
4
5
6
7
8
9
10
11
12
13

1 Figure 7

2