

Removal of phenanthrene from synthetic kaolin soils by eletrokinetic 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*

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 cm³), bench (28 x10³ cm³) and pilot scale (175x10³ cm³) 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. Electroosmotic 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.

Keywords

Scale up, soil remediation, electrokinetic

**Corresponding author: manuel.rodriigo@uclm.es*

Tel.: +34 902204100 ext. 3411; fax: +34 926295256.

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 sorbed 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 than 1 dm³, 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 sulphate (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 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 (Figure 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 $175 \times 10^3 \text{ cm}^3$, 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 cm³ 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 1x1x10 cm³.

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; 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 literature (0.5 to 2.0 V/cm) for this technology [7,9,10]

The cell current, electroosmotic 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 [36]. It is carried out in Eppendorf tubes (15 ml) and using hexane as solvent (ratio polluted soil/solvent = 0.2 w/w). Both phases was vigorously stirred in a VV3 VWR multi-tube and subsequent phase separation was accelerated by the use of a centrifuge rotor angular CENCOM II P-elite.

The concentration of phenanthrene in liquid phase was determined by UV-visible spectrometry (Shimadzu UV-1603). The characteristic absorbance peaks of phenanthrene in the UV-visible spectrum were at 346, 338 and 330 nm. The absorbance at these three wavelengths was used to quantify the phenanthrene concentration. The standard deviation of this determination was lower than 5 %.

3. Results and discussion

During the electrochemically assisted remediation of a soil, there are very significant changes in many of the operation parameters of the electrochemical process and of the soil characteristics. One of the more significant is the current intensity which results for the electric field applied between the electrode rows. In this work, electro-remediation of the soil is carried out at a constant electric field of 1V/cm, value within the range typically propose in the literature for this technology [7,9,10]. Taking into account the distance between the rows of anodic and cathodic wells, in the experimental pilot mock-up used in this work this means the application of 50 V of cell voltage.

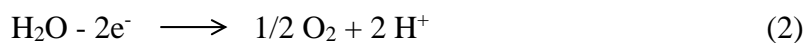
Figure 2 shows the changes obtained in the current during the course of the experiment. As it can be observed, current is not constant during the experiment, but there is a rapid increase during a first stage (200 hours) from a value below 0.2 A to a value higher to 0.8 A and then, there is a soft decrease down to an intensity slightly over the initial value.

As a first approach, current density can be understood as a globalized measurement of the rate of the electrochemical processes (both electrodic and electrokinetic) and accounts for various factors being the most significant the conductivity of soil and the reactions taking place on the electrode surface.

One of the parameters that could influence on the conductivity is soil moisture. Initial content of water in soil contained in the pilot mock-up was around 24%, but during the treatment it increased significantly up to almost the double the initial value, as it can be clearly observed in Figure 3 where the moisture map at the end of the remediation

experiment is shown (6.08 Ah Kg⁻¹ soil). This increase is very important, but it has to be taken into account that it is not sufficient to explain the change in the current, because it could explain a greater current but not the time course of this parameter. Increase in moisture is a direct consequence of the addition of flushing fluids in the anodic wells and in flushing-fluid wells. This flushing fluid contains salts and surfactants, and the increase of the conductivity produced by these species explains the slight increase observed in the current. One important additional observation is the non-uniform distribution of water in the soil with moisture ranging from 37 to 43% and with lower moisture in the nearness of the anodic wells zone.

Another important parameter that may influence on the conductivity of the soil is the pH. This conductivity can be greatly affected by the changes in the pH of the anodic and cathodic wells as a consequence of the electrodic processes, and in particular of the oxidation and reduction of water on the surface of the electrodes (Eqs. 1 and 2).



These changes are very abrupt as it can be clearly observed in Figure 4, in which it is shown the changes pH in the anodic and cathodic wells during the experiment (average value of the three wells contained in each row) and also the pH of the water drained in the system.

Modifications of the cathodic pH follow the same trend than current intensity changes, suggesting that increase in OH⁻ concentration contributes to reduce significantly the resistance of the soil and allows a greater current intensity during the operation of the process at a constant electric field. These changes in the pH reflect in the profile of pH in

the soil due to the diffusion and migration of the ions which produce the acid and basic fronts. This may be related the adsorption of charged species at the kaolinite surface [21]. The map of pH at the end of the experiment is shown in part b of Figure 4 and it can be clearly seen that effect of the acidic front is much more important than that of the basic front. It is important to bear in mind that the acidic and basic front may have significant effects on the precipitation and ion exchange properties of the soil. It is also important to see that water drained by gravity from the system (only got after more than 1000 h of operation) shows a pH not very far from neutrality, indicating that although there is a huge pH profile in the soil, water drained is a mixture of that coming from different zones of the pilot mock-up.

Another parameter which can influence on conductivity is temperature. In this case the profiles are not caused by electrodic processes but to electric heating due to ohmic losses. As it can be observed in Figure 5, temperature profiles also changes in a very important way from an uniform temperature of 18°C before applying an electric field to a well defined profile with an increase of temperature of more than 10°C in some parts of the mock-up due to the electric heating of the soil [8,37]. More intense heating are observed in the cathode zone and at the proximity of the anodic wells although not directly in them. Opposite, less intense changes are observed in the anodic and in the flushing fluids wells maybe because of the cooling effect produced by the addition of the flushing fluid.

Figure 6 shows a map with the removal of PHE at the end of the experiment. As it can be observed, removal of PHE is appreciable but not very important in spite of the large current charges applied (6.08 Ah kg⁻¹ soil, 0.304 kWh kg⁻¹ soil). The average removal is 12.8% of the initial PHE and the distribution is not uniform. The most important removals

are obtained in the zone of the cathodic wells where the flushing fluid is collected. It is also the hottest zone in terms of temperature because it corresponds to the zone of more intense electric heating and flushing fluid is removed and not added (not a cooling effect of flushing fluid on the soil is expected as it is obtained in the other wells). There is other higher efficiency zone close to the flushing fluid wells which could be explained by dilution or dragging of the PHE. A last higher efficiency zone close to the anode surface with not a clear explanation at this point because the only remarkable point of this zone is its smaller moisture (Figure 3) which can be correlated with a higher temperature (Figure 5).

For comparison purposes, the PHE distribution map of the two electro-remediation systems of smaller scale studied in this work are shown in Figure 7. As it can be observed, removal of PHE is very different in the three setups in spite of being the same soil, pollutant and operation conditions. In the bench scale plant, removal of PHE is much more significant (33.25%) in spite of being obtained for a smaller electric charge (2.73 Ah kg⁻¹ soil, 0.082 kWh kg⁻¹ soil). In addition PHE distribution is completely different of that obtained in the pilot mock-up and at a first glance no similarities can be found. PHE removal does not seem to follow a simple pattern. Just on the contrary, it can be observed that zones with a great and a low removal are combined.

Likewise distribution of PHE in the lab scale setup is different. In this case, due to the simpler geometry and the smaller size the profile is as expected (uniform change) and it can be stated that cathodic removal is much more important than anodic removal. However, global removal is only 21.35% (for an electric charge of 2.94 Ah kg⁻¹ soil, 0.029 kWh kg⁻¹ soil), value much smaller than that obtained for the bench scale plant but

higher than that obtained for the pilot mock-up. This variety of results suggests a very complex process with many factors influencing the results.

Fluxes of PHE removed in the anodic and cathodic wells are shown in Figure 8. It is important to observe that fluxes to the cathodic wells are much more significant than those coming to the anodic wells. In the first case, these fluxes are motivated by electroosmotic drag. In the second case, they can be explained by electrophoresis of the PHE after the action of the surfactant on the PHE. SDS is an anionic surfactant and it is effectively transported from the feeding point to the anode by electromigration. The interaction of the surfactant contained in the flushing fluid with PHE transforms the non-polar organic pollutant into a charged particle. Significance of fluxes decreases with the size of the setup. This effect is more clearly observed for the electrophoresis of the PHE. This should be related to the resulting operation current in every experimental setup for the applied cell potential. At this point, it is important to bear in mind that experiments are carried out at a constant electric field of 1 V cm^{-1} and this field results in very different intensities in every setup.

Figure 9 shows the current density (current normalized respect to the cross-sectional area of the setups) observed in the three setups assessed. It can be observed that changes in the current density of the bench scale are as described in Figure 2 for the pilot mock-up and values are within the same range. On the contrary, the current density in the lab scale setup is very high and it increases continuously during the whole treatment period, suggesting very different controlling mechanisms in the smallest setup assessed in this work. In particular, it suggests a greater influence of electro-kinetic mechanisms in the lab scale setup as compared to the two greater setups.

Both, PHE fluxes and current densities should be related to the electro-osmotic fluxes. Figure 10 shows the EO fluxes in the three experimental setups shown. As it can be observed they are 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. Another important observation is the appearance of a hydraulic flux produced by gravity. Gravity flux only becomes significant after a very important period after the start up because hydraulic fluxes are not promoted in a clay soil such as the one used in this work. The two smaller setups (lab and bench scale facilities) do not have a system to separate and collect gravity fluxes and this implies that gravity flux is avoided. For this reason this flux is only significant in the pilot mock up. An important observation is that gravity flux did not drag any PHE in the system because the concentration of PHE in that liquid was nil. In addition to this gravity fluxes, there is also an important evaporation flux, which was estimated by mass balance in $0.277 \text{ cm}^3/\text{cm}^2 \text{ d}$.

At this point, an interesting point of discussion is the comparison of the removals of PHE obtained in the three setups. To do this, the amount of PHE removed in the anodic and cathodic wells and the amount of PHE still remaining in the soil at the end of the experiment were determined experimentally and a mass balance was used to account for the PHE removed by other mechanisms, among which desorption is the most probable possibility, because of the volatilization of PHE taking in to account the electric heating of the soil. At this point it is interesting to consider that the main mechanisms involved in the removal of PHE are dragging with electro-osmotic flow in the cathodic wells, electrophoresis after interaction of surfactant with PHE in the anodic wells.

From the Figure it can be stated that dragging by EO flow and electrophoresis are very important in the lab scale plant, being most significant mechanism. The small surface in contact with atmosphere prevents the massive desorption of PHE at this scale. Just on the contrary, desorption of PHE promoted by the electric heating seems to be a very significant removal mechanisms in the bench scale plant and in the pilot mock-up. In fact there is a clear correlation between the moisture of the soil (which can be indicative of the evaporation) and the removal of PHE. Thus, in spite of the complexity of the system, moisture patterns and PHE removal patterns correlates well in the bench scale (Figure 12) and pilot mock-up plants (Figure 3), suggesting that desorption is a very important mechanism to explain the removal of PHE in electrokinetic soil remediation systems. The lower moisture found in the bench scale setup could be explained in terms of the surface to soil weight ratio. Surface related to soil is $43 \text{ cm}^2/\text{kg}$ in the case of the bench scale plant and $25 \text{ cm}^2/\text{kg}$ in the case of the pilot mock-up. This means that evaporation could be more easily produced in the bench scale plant than in the pilot plant. This is agreement with the greater desorption observed for PHE in that system.

Conclusions

From this work the following conclusions can be drawn:

- Removal of PHE by electrochemically assisted soil remediation processes is not a very efficient process. Very high current charges are required to obtain an appreciable removal of PHE
- The three main mechanisms to explain the removal of PHE are dragging by electro-osmotic flow in cathodic wells, electrophoresis to anodic wells and desorption produced by electric heating of the soil

- The experimental setup influences strongly on the results obtained. The larger the system, the less promoted are the electrokinetic processes. Volatilization of PHE by the increase of temperature caused by electric heating is the primary mechanism in large scale processes.

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Table 1. Properties of soil.

<i>Mineralogy</i>		<i>Particle size distribution (%)</i>	
Kaolinite	100.00%	Gravel	0
Fe ₂ O ₃	0.58%	Sand	4
TiO ₂	0.27%	Silt	18
CaO	0.10%	Clay	78
K ₂ O	0.75%	Specific gravity	2.6
SiO ₂	52.35%	Hydraulic conductivity (cm/s)	1 x 10 ⁻⁸
Al ₂ O ₃	34.50%	Organic content (%)	0
Others	11.42%	pH	4.9

Table 2. Properties of surfactant.

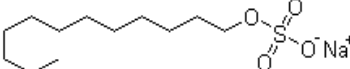
Surfactant	Sodium dodecyl sulphate
Type	Anionic
Formula	C ₁₂ H ₂₅ NaO ₄ S
MW	288.38
CMC/ g l⁻¹	2.3
Molecular structure	
	

Table 3. Water composition.

Parameters	
Conductivity / mS cm⁻¹	0.391
pH	7.64
Salts concentration / mg dm⁻³	

Ca	35.23
Cl⁻	57.26
Fe	0.15
F	0.702
Mg	0.011
Mn	0.048
Na	12.09
K	11.72
NO₃⁻	6.22
SO₄⁻²	44.41

Figure captions

Figure 1. Experimental setups of electroremediation processes: lab scale (25 cm³), bench scale (28 x10³ cm³) and pilot scale (175 x10³ cm³).

Figure 2. Time-course of electric current in the electroremediation of a clay soil polluted with phenanthrene. Operation condition: $E_z = 1$ VDC/cm, initial pollution: 500 mg PHE kg⁻¹ of soil, anolyte: water, catholyte: water, flushing solution: 10 g anionic surfactant dm⁻³.

Figure 3. 2-D Maps of soil moisture after the electroremediation of a clay soil polluted with phenanthrene. Operation condition: $E_z = 1$ VDC/cm, initial pollution: 500 mg PHE kg⁻¹ of soil, anolyte: water, catholyte: water, flushing solution: 10 g anionic surfactant dm⁻³.

Figure 4. a) Time-course of pH of the outfluxes in the electroremediation of a clay soil polluted with phenanthrene. b) 2-D Maps of soil pH after the electroremediation of a clay soil polluted with phenanthrene. Operation condition: $E_z = 1$ VDC/cm, initial pollution: 500 mg PHE kg⁻¹ of soil, anolyte: water, catholyte: water, flushing solution: 10 g anionic surfactant dm⁻³. (◆) Anolyte, (■) Catholyte and (▲) gravity-fluid.

Figure 5. 2-D Maps of soil temperature after the electroremediation of a clay soil polluted with phenanthrene. Operation condition: $E_z = 1$ VDC/cm, initial pollution: 500 mg PHE kg⁻¹ of soil, anolyte: water, catholyte: water, flushing solution: 10 g anionic surfactant dm⁻³.

Figure 6. 2-D Maps of PHE concentration in the soil after the electroremediation of a clay soil polluted with phenanthrene. Operation condition: $E_z = 1$ VDC/cm, initial pollution: 500 mg PHE kg⁻¹ of soil, anolyte: water, catholyte: water, flushing solution: 10 g anionic surfactant dm⁻³.

Figure 7. 2-D Maps of PHE concentration in the soil after the electroremediation of a clay soil polluted with phenanthrene in lab and bench scales setups. Operation condition: $E_z = 1$ VDC/cm, initial pollution: 500 mg PHE kg^{-1} of soil, anolyte: water, catholyte: water.

Figure 8. Variation of PHE flux in anodic (a) and cathodic (b) wells during the electroremediation of a clay soil polluted with phenanthrene in lab (■), bench (□) and pilot (▲) scale setups. Operation condition: $E_z = 1$ VDC/cm, initial pollution: 500 mg PHE kg^{-1} of soil.

Figure 9. Variation of current density during the electroremediation of a clay soil polluted with phenanthrene in lab (■), bench (□) and pilot (▲) scale setups. Operation condition: $E_z = 1$ VDC/cm, initial pollution: 500 mg PHE kg^{-1} of soil.

Figure 10. Variation of electroosmotic flux (a) and gravity flux (b) during the electroremediation of a clay soil polluted with phenanthrene in lab (■), bench (□) and pilot (▲) scale mock-up. Operation condition: $E_z = 1$ VDC/cm, initial pollution: 500 mg PHE kg^{-1} of soil.

Figure 11. PHE balance in the electroremediation of a clay soil polluted with phenanthrene in lab (■), bench (□) and pilot (▲) scale mock-up. Operation condition: $E_z = 1$ VDC/cm, initial pollution: 500 mg PHE kg^{-1} of soil.

Figure 12. 2-D Maps of soil moisture in the bench scale plant after the electroremediation of a clay soil polluted with phenanthrene. Operation condition: $E_z = 1$ VDC/cm, initial pollution: 500 mg PHE kg^{-1} of soil, anolyte: water, catholyte: water, flushing solution: 10 g anionic surfactant dm^{-3} .

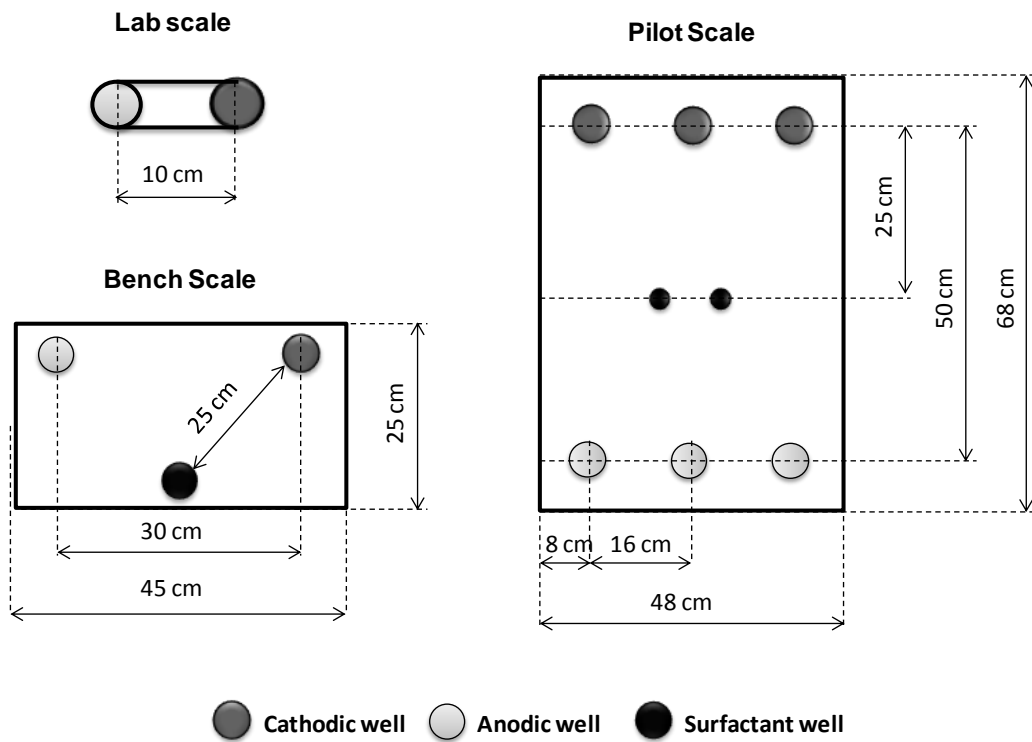


Figure 1.

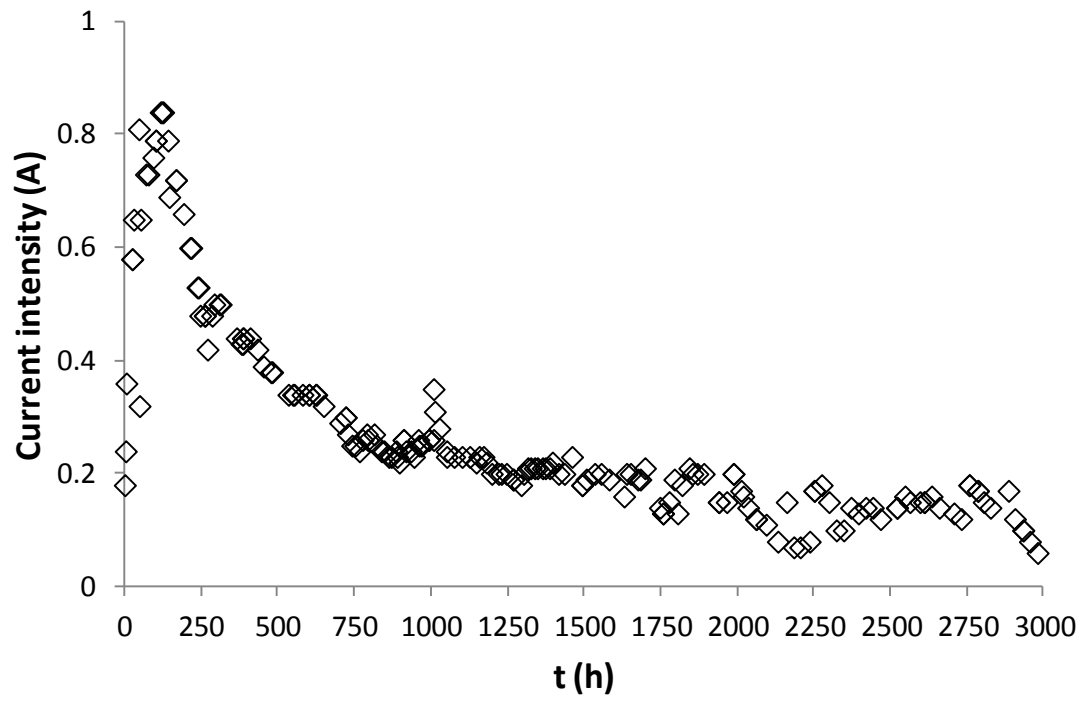


Figure 2.

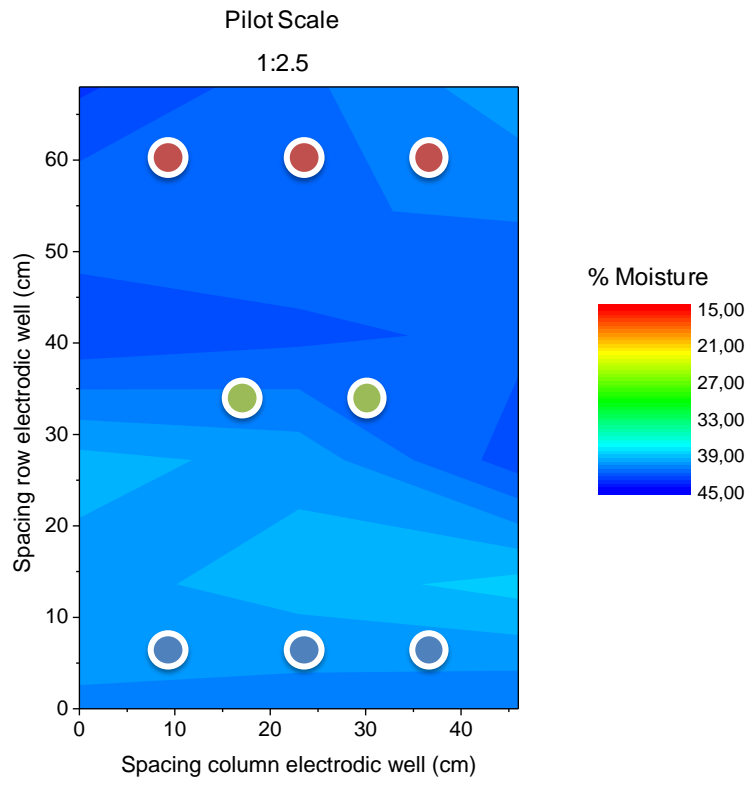


Figure 3.

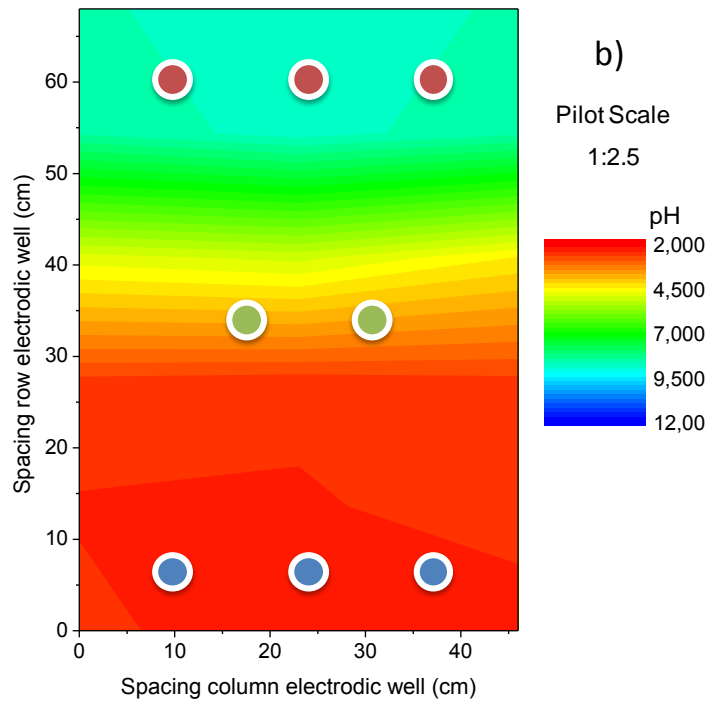
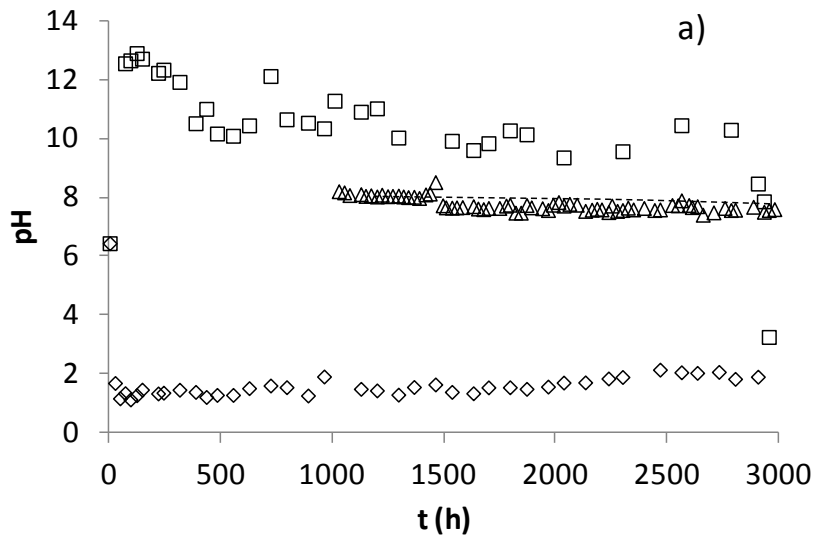


Figure 4.

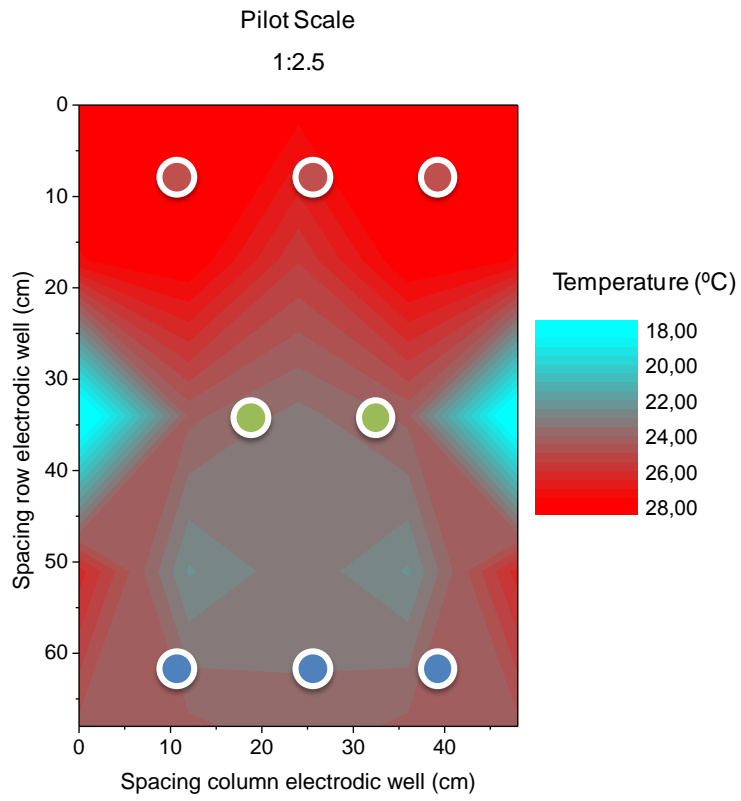


Figure 5.

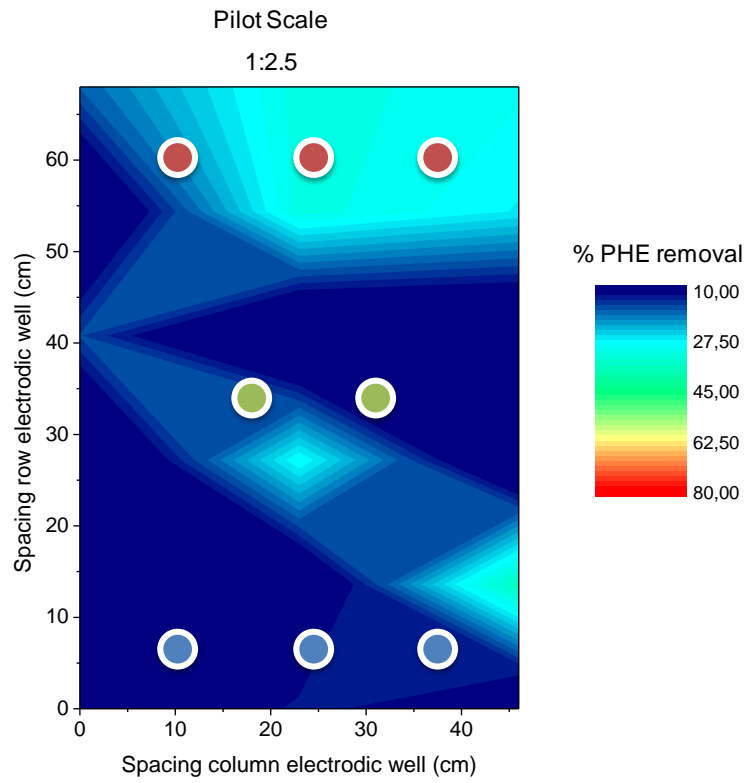


Figure 6.

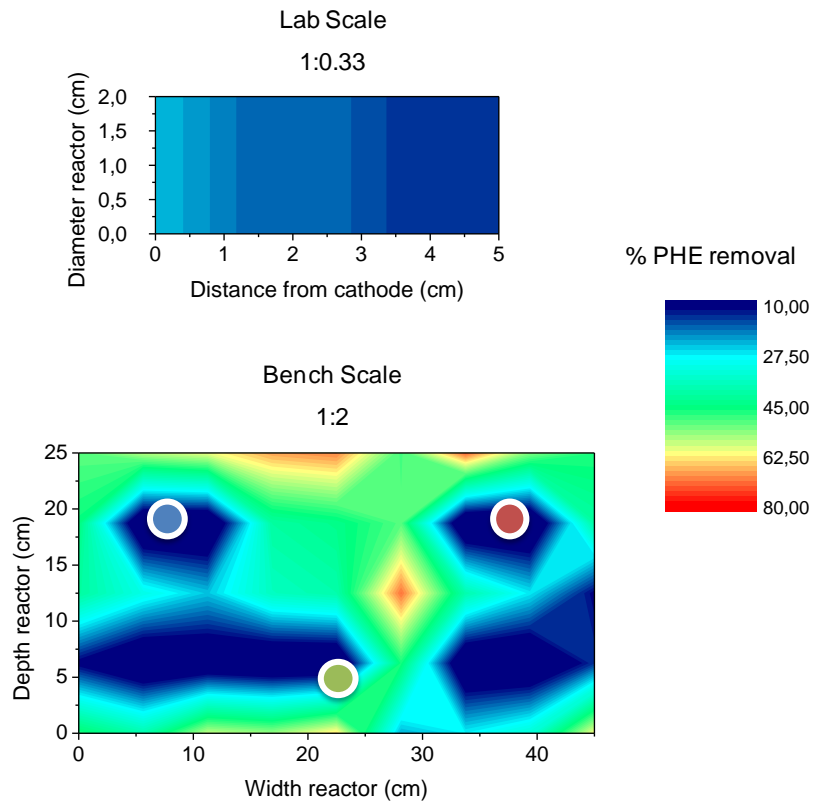


Figure 7.

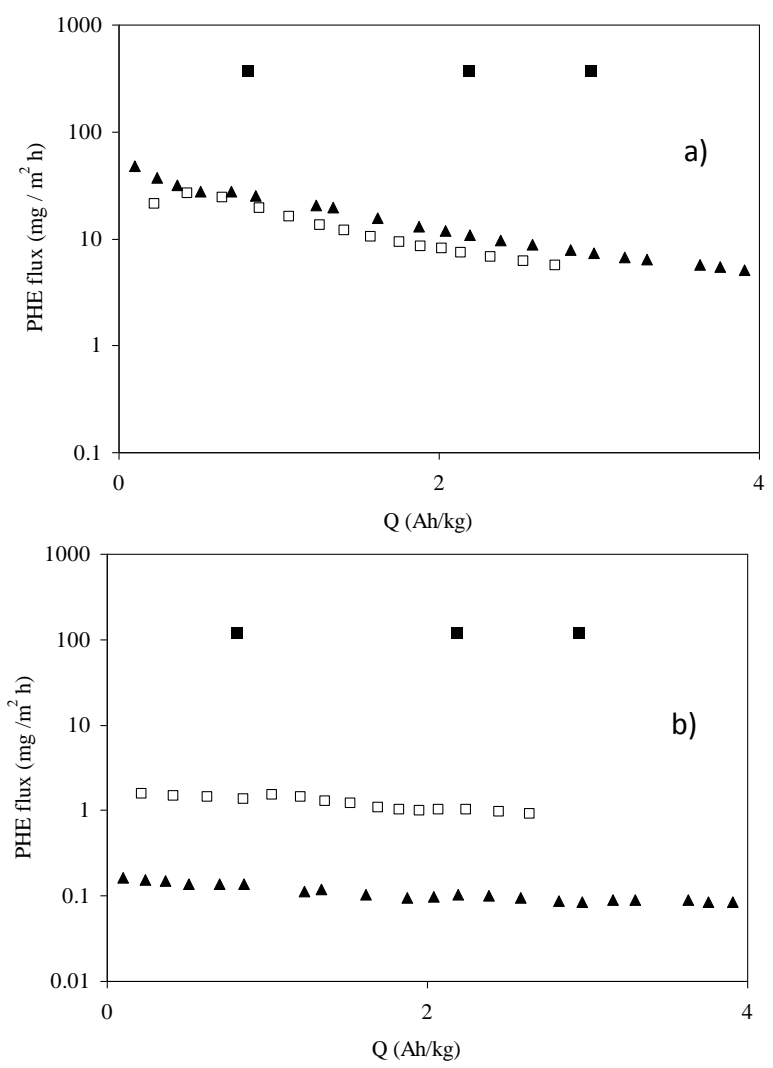


Figure 8.

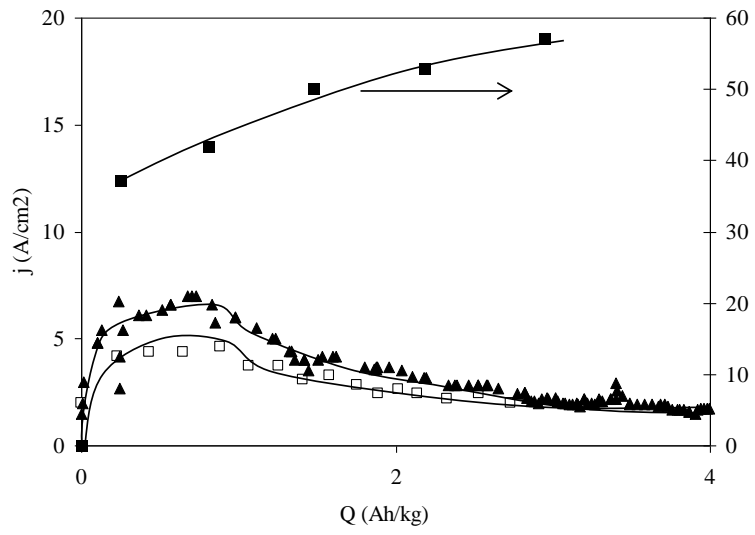


Figure 9.

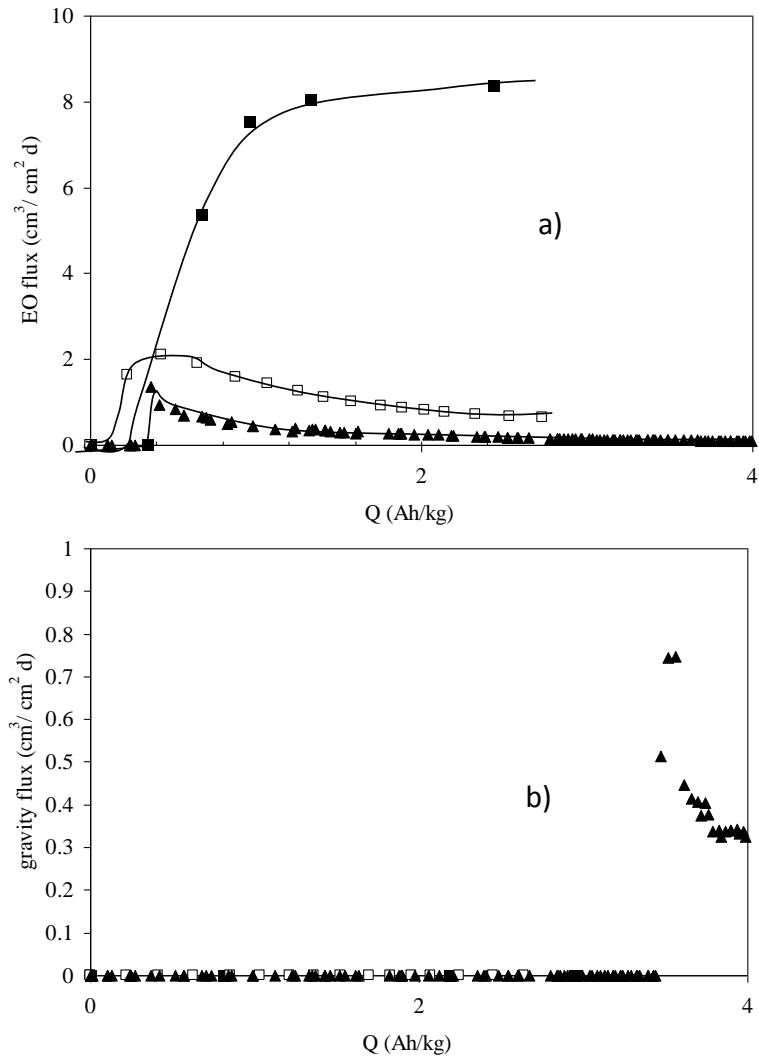


Figure 10

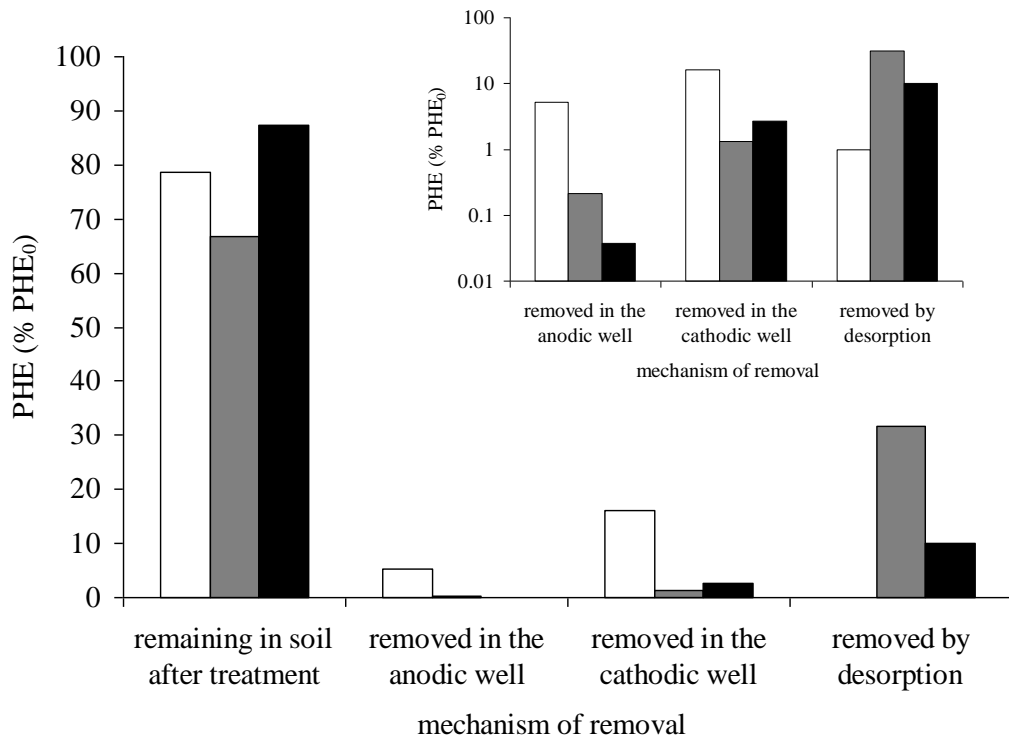


Figure 11

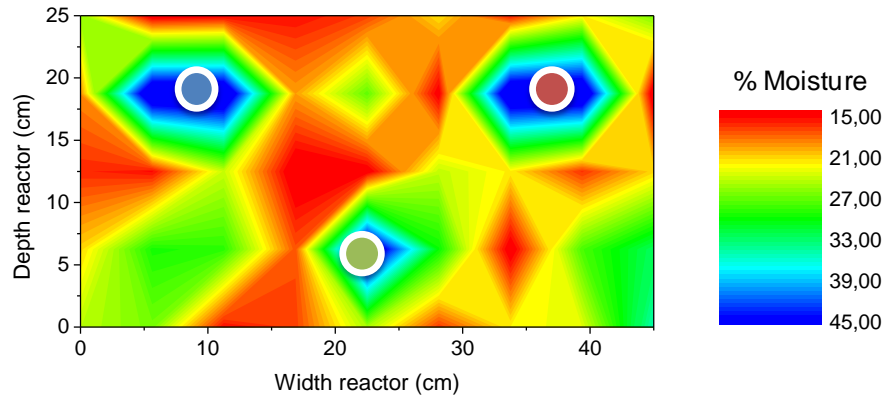


Figure 12