Emerging organic contaminants in soil irrigated with effluent: electrochemical technology as a remediation strategy

Ana Rita Ferreira[1], Paula Guedes[1,2], Eduardo P. Mateus[1], Alexandra B. Ribeiro[1*], Nazaré Couto[1]

[1] CENSE, Center for Environmental and Sustainability Research, NOVA School of Science and Technology, NOVA University Lisbon, 2829-516 Caparica, Portugal

[2] Instituto de Tecnologia Química e Biológica António Xavier, NOVA University Lisbon, Av. da República, 2780-157 Oeiras, Portugal

*corresponding author
E-mail address: abr@fct.unl.pt (Alexandra B. Ribeiro)

Abstract

The effluent reuse for soil irrigation is foreseen as a possible strategy to mitigate the pressure on water resources. However, there is the risk of potential accumulation in soil of emerging organic contaminants (EOCs).

In the present work the electrokinetic remediation (EKR) technology, use of direct current, was applied for the removal of EOCs from a soil irrigated with effluent. For this, a soil collected from a rice field (located in Portugal) was mixed with spiked effluent to simulate flood irrigation in one time-period. The experiments were carried out for 6 days applying a low current intensity of 2.5 mA. Different current strategies were tested: continuous mode, reversed electrode polarization (REP), On/Off time periods, and the combination of the last two. The target EOCs comprises a list of six pharmaceuticals and personal care products widely detected in treated wastewater.

This study showed that once introduced in soil through effluent irrigation, 20-100% of the EOCs were still present in the soil after 6 days. EKR enhanced up to 20% of the EOCs removal when comparing with control (without current). The EOC removals showed to be related to the microcosm location (anode, central or cathode sections) and dependent of EOCs characteristics. Soil characteristics did not change when On/Off system was combined with REP as a current strategy, and a more homogenous removal of the studied EOCs was achieved in the tested conditions. EKR showed to be a promising technology to be applied in EOCs contaminated soils, not only for removal purposes, but also to avoid possible dispersion in the environment.

Keywords: effluent reuse, soil irrigation, electrochemical oxidation, pharmaceuticals and personal care products

1. Introduction

The water resources are increasingly under stress leading to water scarcity and quality deterioration. This fact has encouraged a more active consideration on the use of alternative water sources as a strategic option to supplement water supplies and protect natural resources.

Water reuse and recycling has been identified as one of the five top priorities of the European Innovation Partnership on Water (EIPW, 2012). The European Commission has proposed on May 2018 new rules to stimulate and facilitate water reuse in the EU for agricultural irrigation (European Comission, 2018). Agriculture is the largest sector that consumes the most water at the global level, accounting approximately 40% of total annual water use in Europe. In southern Europe, it can exceed 80% in the summer months (European Environment Agency, 2019). Moreover, agricultural production has been increasing to ensure the food supply of a population that is continuously growing, thus the reuse of treated wastewater is foreseen as a possible strategy to mitigate the pressure on water resources (FAO, 2015).

Pharmaceuticals and personal care products (PPCPs), classified as emerging organic contaminants (EOCs), are not completely removed by conventional processes in wastewater treatment plants (WWTPs) and have been detected in effluent over the years (Archer et al., 2017; De Jesus Gaffney et al., 2017; Verlicchi et al., 2012; Wang & Wang, 2016). In this sense, the reuse of treated wastewater for irrigation can represent a risk to human health as EOCs can be mobile and reach the groundwater due to leaching (Helmecke et al., 2020; Sui et al., 2015), and in agriculture they might be accumulated within crop plants potentially increasing the risk upon consumption (Ben Mordechay et al., 2018; Christou et al., 2017; Pan & Chu, 2017; Paz et al., 2016). Some studies have been assessing the bioaccumulation of PPCPs in soils submitted to effluent irrigation. The work carried out by Malchi et al., 2014)found 14 different PPCPs, such as carbamazepine, caffeine, clofibric acid, diclofenac, ibuprofen, ketoprofen and naproxen in carrots and sweet potatoes irrigated with effluent. The study carried out by Wu et al. (2015) (Wu et al., 2015) also showed caffeine, carbamazepine, naproxen and triclosan in eight vegetables, with a total PPCPs concentration in the range of 0.01-3.87 ng g^{-1} (dry weight). In tomato plants, a cocktail of pharmaceuticals (carbamazepine, valporic acid, phenytoin, diazepam, lamotrigine) induced a stress response in leaf and root tissues (Gorovits et al., 2020). The adverse effects of these contaminants in wastewater irrigated agro-ecosystems and human health are still under study (Carter et al., 2019).

Some studies have been conducted to investigate the environmental risk of PPCPs by comparing the difference between predicted concentration and measured concentration or predicting the adverse effect concentration with regard to specific organisms. Previous research works have suggested that environmental exposure to PPCPs is inducing the formation of antibiotic-resistance in bacteria, which may represent a major human health risk associated with antimicrobial resistance (Piña et al., 2018). Also, chronic impacts on biodiversity including alteration of the metabolism, development, and/or reproduction of fish (Meador et al., 2016).

The research of cost-efficient and non-invasive techniques for soil clean-up is not only of scientific interest, but also in the public interest as it can avoid potential risks after soil irrigation. Electrochemical technologies have attracted attention in the treatment of EOCs since no reagents are required, and no secondary waste/sludge is generated after the treatment. The electrokinetic remediation (EKR) involves the application of a low intensity direct current between suitably located electrodes as the ‘‘cleaning agent”. The electrolysis reactions at the inert electrodes produces protons at the anode and hydroxyl ions at the cathode causing large pH gradients by the transport of protons and hydroxyl ions generated (Acar & Alshawabkeh, 1993).

The overall EKR efficiency in soil is dependent on two direct main mechanisms: (i) mobilization of EOCs by electroosmosis and electromigration or (ii) destruction of the compounds by induced electrochemical reactions due to strong oxidizing intermediates (mainly $OH^{\bullet}$ radicals) (Ferreira et al., 2017; Guedes et al., 2019). However, in the specific case of *in-situ* soil remediation, biodegradation might play an important role (Thelusmond et al., 2018). Thus, it becomes crucial to control the negative effects that may arise from EKR, while promoting a balance between bacteria and contaminants. For example, the high soil pH changes should be mitigated while promoting good electroosmotic and electromigration rates. One option to achieve this, is to use current strategies like electro-polarization as it has been successfully employed to control soil pH (Harbottle et al., 2009) while enhancing mixing of substances *in-situ* by alternating the migration path (Mena et al., 2016). Moreover, these two main mechanisms in EKR are also regulated by the type of electrodes employed. For example, higher values of electroosmosis have been achieved with RuO_2/Ti and Pd/ Ti comparing to Ti electrodes (Yuan et al., 2013). A recent study employed graphite electrodes, which are cheap and commercially available, for the removal of EOCs from a clay soil (Guedes et al., 2019). The tested electrodes were unstable to currents above 10 mA (3.5 mA cm^{-2}) showing significant signs of corrosion (Guedes et al., 2019). Dimensionally stable anodes (DSA) have been gaining interest due to their high catalytic activity, high stability to anodic corrosion, excellent mechanical and chemical resistance and lower energy consumption (Wu et al., 2014). DSA electrodes have been extensively used due to the excellent performance, however up until present, studies on their application on EKR as an *in-situ* technology to remove EOCs from soil irrigated with effluent were not found. Therefore, and even though EKR have showed to be a promising technology to remove

PPCPs from soil *in*- and *ex*-*situ* (Ferreira et al., 2017; Guedes et al., 2014, 2019), there is also lack of information regarding the performance of this technology on EOCs removal from soil after irrigation with real effluent.

The present work is focused on the EOCs removal from soil with a silty clay texture, collected from a rice field, applying *in*-*situ* EKR using DSA electrodes made of metal mixed oxide coated titanium with mesh shape. This research is targeting an effective soil remediation strategy with a minimum maintenance and disturbance after irrigation with effluent. The aim was to assess the fate of EOCs after the soil being (i) flood irrigated with contaminated secondary treated effluent and in parallel and (ii) subjected to different EKR current strategies as periodic electric current and polarity reversal.

For this study, PPCPs selection was based on their frequency in effluent and aquatic bodies focusing in Portugal, Spain and France: a) pharmaceuticals: sulfamethoxazole (SFM; antibiotic), diclofenac and ibuprofen (DCF and IBF, respectively; anti-inflammatories), carbamazepine (CBMP; anticonvulsive), ethinylestradiol (EE2; synthetic estrogen), and b) personal care compound: oxybenzophenone (MBPh; UV-filter). The EOC selected have a different range of physical and chemical characteristics (Table 1): $0.89 < \text{Log } K_{ow} < 4.51$; $4.15 < \text{pKa} < 13.9$ and $2.37 < \text{solubility} < 610$ mg L^{-1}.

PLEASE INSERT TABLE 1

2. Materials and methods

2.1. Standards and chemicals

All solvents, HPLC grade, were from Merck (Darmstadt, Germany) and Sigma–Aldrich (Steinheim, Germany). Deionized water was purified with a Milli-Q plus system from Millipore (Bedford, MA, USA). All standards were purchased from Sigma-Aldrich

(Steinheim, Germany) with high purity grade (>97%). All pharmaceutical standards used were of high purity grade (>90%). Individual stock solutions for calibration purposes were prepared by dissolving each compound in MeOH at a concentration of 4000 mg L^{-1} and stored at -18 ºC.

2.2. Soil sampling and characterization

The soil was sampled at a rice field located at Paul de Magos, Salvaterra de Magos, Portugal, at 0-20 cm depth, corresponds to a Fluvisol (World Reference Base for Soil), and its characteristics are presented in Table 2. The soil has a silty clay texture with high mineral and organic colloid contents, which leads to a high cation exchange capacity (Table SM1).

2.3. Effluent sampling and characterization

Effluent samples were collected after the secondary settler in a WWTP located in Quinta do Conde, Sesimbra, Portugal (38°34'13" N, 9°2'7" W). The WWTP has the capacity to treat 19,300 m^3/day of urban wastewater, corresponding to about 94,000 equivalent inhabitants, and discharges into Tagus river. The WWTP has an aerobic reactor of suspended biomass and the effluent from this reactor goes to the secondary settling tank for phase separation where liquid samples were collected. The initial effluent characterization was performed by the WWTP and the main physicochemical characteristics are presented in Table SM2 in supplementary material. All samples were transported in a cooling box from the WWTP to the laboratory and kept at ±4 ºC in dark conditions until the start of the experiments.

2.4. Experimental set-up and design

The experiments were carried out in a simulated microcosm assembled in a parallelepiped-shaped glass box with round corners (14 x 14 x 5 cm), externally covered with aluminum foil (to prevent light exposure). Two metal mixed oxide electrodes with mesh shape (IrO_2/RuO_2-Ti; 90 x 20 x 1 mm) were placed at microcosms lateral sections, 4.5 cm apart from each other.

For each experiment, the microcosm was filled with 300 g of soil and irrigated mimetizing a flood system using effluent (3:1 m:V) previously spiked with a mixture of the EOCs under study (5 mg/kg d.w. of SFM, CBMP, EE2, DCF, IBF and MBPh). The high concentration was used to guarantee compounds quantification even if high degradation and mobilization ratios were achieved.

The microcosms were left for 3 days at 6 ºC to simulate contamination aging while minimizing biological activity.

The EKR experiments were carried out in duplicate applying a low direct current (DC) intensity of 2.5 mA (power supply, Agilent E3612A) to the soil during 6 days at controlled room temperature (22 ºC). The different current strategies applied are schematically represented in Figure 1 and consisted in:

- **Continuous current** (CC): DC was kept continuous during EKR;
- **Switched current** (On/Off): DC was switched Off during day 3 for 24 h and turned back On at day 4;
- **Reversed electrode polarization** (REP): electrodes polarization was reversed at day 3 for 24h;
- **Combination of On/Off and REP** (On/Off + REP): DC was switched Off during day 3 (24 h) and turned back on with a simultaneous polarization reversion at day 4.

In parallel, to assess natural attenuation effect on EOCs remediation, an experiment without DC was performed (in duplicate) and named as control.

PLEASE INSERT FIGURE 1

Prior the beginning of the experiments, soil sub-samples were collected and analyzed for EOCs, moisture content, pH and conductivity. The concentration of EOCs detected after these 3 days of incubation was considered as the initial (preliminary effluent analysis did not show the presence of the compounds under study, <LD).

Along the experiments, the parameters current intensity, voltage drop between the electrodes, and soil temperature were continuously monitored, and microcosms were daily irrigated with deionized water (without EOCs) to keep moisture content constant (soil was weighted once a day and deionized water added till initial weight). At the end of the EKR experiments, the soil layer was carefully segmented into three sections (with 4.6 cm each) parallel to the electrodes. and named anode, central, cathode, in reference at its position in respect to the electrodes.

Each soil section was carefully homogenized, weighted and immediately extracted and analyzed for EOCs in duplicates (n=2). Soil moisture, pH and conductivity were also measured (procedure in Section 2.5.1.).

2.5. Analytical procedures

2.5.1. General parameters

The water content of the soil was measured as the weight loss after 24 h at 105 ºC. Soil pH_{H2O} and conductivity were measured using a soil deionized water ratio of 1:2.5 (w:v), followed by 1 hour and 30 min of agitation in a magnetic stirrer (AccuPlate^{TM}, LAbNet, USA), respectively. After 1h contact time, soil pH_{H2O} and conductivity were measured using a pH electrode (Solitrode with Pt1000, Metrohm AG, Switzerland) and a conductivity meter (LAQUAtwin B-711, Horiba Ltd, Japan), respectively.

2.5.2. EOCs extraction

2.5.2.1. Soil

The levels of each EOC in the soil sections were determined using a QuEChERS (quick, easy, cheap, effective, rugged, and safe) method described elsewhere (Guedes et al., 2019). In brief, each 2.5 g of soil were mixed with 1.5 mL of deionized water (vortex: *ca*. 15 s); then with 2.5 mL of acetonitrile (vortex: 1 min); and finally, with 1 g $MgSO_4$ (mixed manually then vortex: 30 s). The supernatant (organic phase) was recovered by centrifugation (5,000 rpm, 5 min) and filtrated through 0.45µm polytetrafluoroethylene (PTFE) Syringe Filters (FILTER-LAB®, Filtros Anoia S.A., Spain), previously passed through acetonitrile and transferred to a vial. The samples were kept at 5ºC until analysis.

2.5.2.2. Effluent

The initial effluent samples were pre-cleaned/concentrated by solid phase extraction (SPE), Oasis HLB 500 mg (Waters; Saint-Quentin En Yvelines Cedex, France), and an SPE manifold connected to a vacuum pump. The cartridges were conditioned by washing with 3×6 mL of MeOH, followed by re-equilibrium with 3×6 mL of Milli-Q water. For organic compounds enrichment, the samples were acidified to pH 2 before extraction, using nitric acid. The aqueous samples (200 mL) were passed through the cartridge at a flowrate of approx. 10 mL/min. After, cartridges were dried for approx. 2 min by vacuum. The extracts were eluted with 2×6 mL of MeOH and concentrated under a gentle stream of nitrogen. Before analysis, each sample was filtrated through 0.45µm PTFE Syringe Filters (FILTER-

LAB®, Filtros Anoia S.A., Spain), previously passed through methanol. The samples were kept at 5 ºC until analysis.

2.5.3. EOCs analysis

The EOCs quantification was performed by high performance liquid chromatography with a diode array and fluorescence detectors (HPLC–DAD-FLD). HPLC analysis was performed on 1260 Infinity II LC Systems (Agilent Technologies, USA) equipped with 1260 Infinity II Quaternary Pump (G7111B), a 1260 vial sampler (G7129A), a diode array detector (G1315B) and a fluorescence detector (G1321A), both from Agilent 1100 Series. The UV wavelength was set to scan from 200 to 500 nm and the fluorescence to 220 nm of excitation and 290 nm of emission.

The separation of the analytes was carried out using a Chromolith High Resolution RP-18 column with 100 mm x 4.6 mm from Merck (Darmstadt, Germany) connected to an Onyx SecurityGuard C18 cartridges (5mm×4.6mm) from Phenomenex (Torrance, USA). The oven was set to 36 °C. The HPLC runs were performed at a constant flow of 0.5 mL/min, in gradient mode. The two eluents used were composed of a given percentage of Mili-Q water/ACN/Formic acid (eluent A: 94.5/5/0.5; eluent B: 5/94.5/0.5). The formic acid was diluted 50% in water. All eluents were filtered before use by Nylon 66 membranes (pore size of 0.45 µm; Bellefonte, PA, USA). The gradient run was set to 3 min 5% B, after 95% B until 20 min, then 97% B from 20-22 min, where it was held constant until 25 min, then to 95% A until 27 min.

All operations and data analysis were processed using the LC OpenLab software. Methods limits of detection and quantification (LD and LQ, respectively) can be found in Supplementary Material.

2.6. Statistical analysis

Statistically significant differences among samples for 5% level of significance (95% confidence interval, $p<0.05$) were evaluated through one-Way ANOVA Tukey’s multiple comparisons test, using GraphPad Prism software (version prism 7).

3. Results and discussion

3.1. General results

- *pH*

The soil pH before and after application of the EKR is represented in Figure 2.

The controls (without electric current) did not show ($p>0.05$) soil pH changes comparing with the initial value (6.48 ± 0.04 *vs.* 6.23 ± 0.02, respectively).

Under a continuous electric field soil pH changes were expected due to the electrolysis of water that generates H^+ and OH^- ions, which makes the pH acidic and alkaline in the anode and cathode, respectively. In soil central compartment, the pH decreased because of the effective ionic mobility of H^+ that is about 1.8 times higher than OH^- and, under an electric field, the acid generated at the anode advances across the soil column, neutralizing the base (Acar & Alshawabkeh, 1993).

When applying On/Off and REP current strategies, the pH also changed ($p<0.05$) in the bulk soil comparing with the initial pH, except in the central section for the On/Off system due to the break of generation and transportation of ions though the section. The soil under study presented a low carbonate content, which according with the literature is related with a low buffer capacity, not being able to effectively counteract the H^+ ions generated at the anode (Reddy et al., 1997). Other studies have reported no pH changes when using REP reporting the importance of the reversal frequencies choice (e.g.: Barba et al., 2017). Thus, the results presented in this study suggest that longer periods of switching the current Off and REP should have been applied in order to avoid pH changes due to generation and transportation of ions. In alternative, combining the two current strategies On/Off + REP allowed to mitigate, to some extent, the pH shifts in the three studied sections (anode, central and cathode), comparing to the initial pH ($p>0.05$). This might be attributed to the break period of ions productions in the electrodes that was combined with an inversion on the transport of the ions, thus allowing soil pH equilibration. Soil pH is a crucial parameter to uniformly control electroosmotic flow, which might influence on EOCs removal and it will be discussed in Section *3.2. EOCs remediation.*

PLEASE INSERT FIGURE 2

- *Conductivity*

The soil conductivity before and after EKR is presented in Figure 3.

The conductivity in control (without current application) decreased from 0.28 ± 0.00 mS cm^{-1} to 0.19 ± 0.02 mS cm^{-1} with significant differences (p<0.05) comparing to the initial value.

Under a continuous electric field, the results showed significant differences (p<0.05) among the different microcosms sections (anode, central and cathode) comparing with the initial value, but with few exceptions. Overall, in the central soil section of the treated soil, the conductivity decreased (p<0.05) approximately ten times due to ions migration imposed by the electric field from the central section towards the electrodes (anode and cathode).

In the anode, the conductivity had the tendency to increase due to H^+ ions generation, with significant differences (p<0.05) when applying continuous or even when switching Off the current for 24 h. In cathode, changes in conductivity were also registered when the current was switched Off, due to the break of OH^- production and H^+ migration with subsequent conductivity drop. The REP was the only current strategy system that did not cause conductivity changes in the anode and cathode sides due to balance of ions production by the electro-polarization reversion. This result was not achieved when combining REP with

On/Off because of the break on ions production for 24 h, which in line with pH results, different periods of time should be tested in order to avoid changes in soil characteristics.

PLEASE INSERT FIGURE 3

- *Voltage*

The voltage between the two electrodes ranged from 3.3 ± 0.6 to 27.6 ± 0.7 V (not shown). The voltage values had some fluctuations/peaks along the time, in which the high levels of voltage were registered (e.g. 60 V). These changes are a consequence of an electrical resistance increase, mainly attributed to the water evaporation. Soils with very low water content are not able to conduct enough electrical current.

The water evaporation during EKR can be a consequence of evaporation caused by room temperature (22 ºC) as the soil surface was exposed to the air. During EKR the ohmic heating caused by the soil acting as an electrical resistor when a current is passed through it also influence the water evaporation. Even though the soil temperature did not significantly increase (p>0.05) and the moisture was tried to be kept constant (20 mL of deionized water was added daily) along the time, there was a moisture content decrease between daily irrigations. This small variation indicates water evaporation which in turns increases electrical resistance and, consequently, the increased voltage drop until water was added to replenish losses (Page and Page, 2002).

3.2. EOCs remediation

The percentage of EOCs detected in soil after EKR in relation to the initial amount determined in the soil after simulated aging (spiking followed by 3 days at 5ºC) was considered as not remediated. Calculations were performed according to Eq. (1). Table 4 shows the amount of EOCs that remained in the soil after the experiments (not remediated).

$$Presence\ (\%) = \left(\frac{EOC\ (mg\ kg^{-1})\ in\ soil\ after\ EKR}{Initial\ EOC\ (mg\ kg^{-1})\ in\ soil}\right) \times 100 \qquad \text{Eq. (1)}$$

- *Natural attenuation*

Comparing with the initial EOCs concentration in soil, the controls (without electric current) show that all compounds suffered natural attenuation during the 6 days. The highest remediation was obtained for the antibiotic SFM (57%) followed by the anti-inflammatory category DCF ≈ IBF (36%), and finally EE2 ≈ MBPH ≈ CBMP (23-29%).

EOCs volatilization from soil is not expected to be an important fate process based upon an estimated low Henry's Law constant (Table 1). The photodegradation is not considered as the experiments were carried out indoor and the microcosms were laterally covered in order to simulate the substrate.

Thus, the data support the hypothesis that bioremediation played a significant role on EOCs removal in the controls (without current). The biodegradation of EOCs in soils by microbial activity has been reported for several authors (Foolad et al., 2016; Lin & Gan, 2011; Thelusmond et al., 2018). Xu et al., 2009)showed that a sterilized soil prolongs the EOCs presence comparing with non- sterilized, indicating that microbial activity played an important role in the degradation of these compounds also in accordance with the present results. The indigenous microbiota capacity to perform the bioremediation of these EOCs may have been enhanced from by the nutrients (e.g. P_{total} =1.67 mg L^{-1}), added by the irrigation with effluent (biostimulation). Another factor that cannot be disregarded is the presence of dissolved organic matter, considered one of the most critical carbon sources, that may also enhance the microbial degradation of organic contaminants in soils (Annamalai et al., 2014; Yu et al., 2014).

- *EKR*

The influence of the current on EOCs removal was extrapolated through the comparison between the percentage of the EOCs detected in soil with and without current application (controls). The total removals when applying the different current strategies are reported in Figure 4. The results showed that EKR enhanced up to 20% the total EOCs removal (total removed from all soil sections), with SFM showing the higher removal rate (75%-83%) among the EOCs in study.

PLEASE INSERT FIGURE 4

Although, in general, EOCs removal in specific soil section increased up to 30% by the use of EKR, the removals were inhomogeneous among the soil's sections (anode, central, cathode sides). A tendency for higher EOCs removal near the electrodes (>20%) was observed, with EOCs being concentrated in the microcosms central section. Thus, it is hypothesized that EOCs removal was mostly due to the induced electrochemical reactions near the electrodes, direct and indirect oxidation. Nonetheless, is has been reported that the generated electric field, under mild conditions, has a positive effect of the bioremediation, including on the electrodes region (e.g. Li et al., 2016).

Under an electric field, bacteria (usually carry a negative charge) move towards the anode and, in addition, the dissolved oxygen produced near the electrode also provides more oxygen for the aerobic microorganisms increasing their population. However, in the present study no differences were found between anode and cathode in terms of EOCs degradation, including when applying 24 hours of REP. These results suggest that microorganisms' role on EOCs degradation in EKR might have been limited and their higher degradation in both electrodes area was due to anodic oxidation and/or cathodic reduction promoted by the electric current, which generate radicals responsible for the removal of these compounds.

The lower removals in central section show that EOCs suffered mobilization during EKR by electro -osmosis and -migration, but the soil changes, such as pH changes and soil moisture content, might have influenced the mechanisms. The distribution between aqueous and solid phase of all EOCs in study is also dependent on sorption mechanisms that also influence the mobilization and/or degradation of each contaminant, which can explain the results achieved in the present study.

There have been many attempts to correlate the sorption and EOCs remediation with the K_d (solid liquid partition coefficient) and Log K_{ow} (octanol water partition coefficient) of the compounds (e.g. Verlicchi and Zambello, 2015). The EOCs under study (excluding SFM; Log $K_{ow} = 0.89$) have $2.45 < \text{Log } K_{ow} < 4.5$, which make them easily adsorbed onto the soil particles. The soil had a high percentage (53.4%) of clay, which may diminish effectiveness of the technology by fostering EOCs sorption onto the clay minerals, with sorption onto soil organic matter also playing a significant role. The soil texture will also play an important role on electroosmotic flow intensity, being expected that soils with high clay content present high electroosmotic flow (Acar et al., 1995), thus having an important role on EOCs mobilization and, consequently, degradation.

The higher Log K_{ow} imply a higher K_d, which makes the degradation of these EOCs more challenging. In the cathode side, IBF ($pKa = 4.91$) and DCF ($pKa = 4.15$) suffer deprotonation ($pH > pKa$), and being as an anion form, they migrate to the anode side. However, when applying a continuous electric field, pH changes over the soil profile and when approaching to the central compartment, the pH changes to acidic (Figure 2) and the mobilization of IBF and DCF is hindered ($pH < pKa$). On the other hand, CBMP, EE2 and MBPh have a higher pKa than the soil pH, which make them less mobile and able to migrate.

Through the application of REP and On/Off, different distribution of EOCs in soil was observed. The removal of DCF and IBF was enhanced ($p<0.05$) in the central compartment by switching Off the current for 24 h. This result can be corroborated with the pH stabilization in this soil section, due to the break of H^+ production at anode, electrode that did not change the pH in the central compartment. In addition to pH control, current switch On/Off showed to positively enhance IBF and DCF removal. Cameselle and Reddy (2013) reported that the Off period during a continuous electric field gives time for the transfer from soil particles to soil moisture being then pulsed with switching On the electric current. In fact, comparing the three soil sections in the On/Off system, the anode section presented lower concentrations for CBMP, EE2 and MBPH, whereas the cathode had lower values of SFM, DCF, IBF (with statistical significant differences $p<0.05$ between anode and cathode for CBMP and IBF).

When applying REP, an homogenous mobilization of EOCs was expected for both directions as favors the homogenization of the system with electro- osmotic flow regeneration, which put in contact pollutants, microorganisms and nutrients, avoiding possible soil heating and extreme pH variation (Mena et al., 2016). This interaction would increase EOCs bioavailability and facilitate their remediation. However, in the present study limitation on EOCs mobilization was observed and might be attributed to (i) the short period between polarity reversal (24 h) not giving enough time for system regeneration and (ii) the unavoidable soil moisture changes during the day that limit the EOCs mobilization and degradation.

PLEASE INSERT TABLE 2

It is reported that current effect may be masked if substantial changes occur in parameters such as pH or moisture content (Harbottle et al., 2009). When not combined, the two current strategies REP and On/Off changed the soil pH and this fact might have affected EOCs remediation (mobilization and degradation). However, even though the combination of both On/Off and REP strategies did not change soil pH, which is reported to be one of the key factors that decreases and hinders the electro-osmotic flow (Cameselle and Reddy, 2012), no significant differences were registered in terms of EOCs remediation when comparing with each individual strategies. This result shows that soil moisture seems to have had an influence on EOCs mobilization and/or degradation during EKR due to water evaporation that affects the electroosmotic flow (Harbottle et al., 2009). It should be pointed out that temperature was kept constant during the EKR and that large number of variables may affect the electroosmotic flow and spatial and temporal variations under applied electric potential, which make it highly variable and very difficult to predict (Cameselle and Reddy, 2012).

Moreover, soil moisture level is also considered relevant for the proper functioning of the biological process as it may influence e.g. oxygen level. Although an effort was made to keep the water content in soil somewhat constant during the 6 days, a daily water loss (20%) due to evaporation was observed in all EKR experiments. This result shows that water replenishment is necessary to maintain the current intensity in order to avoid possible negative effects during the EKR, also possibly influencing the bio- and chemical reactions. Carr et al. (2011) showed that soil under saturated conditions in general exhibited better conditions for occurring biodegradative processes than those soils that remained non-saturated. The evaluation of soil microorganisms for the biodegradation of EOCs was carried out by (Carr et al., 2011), and they found that estradiol derivatives were relatively easy to remove whereas other compounds like IBF were just slightly removed. In the present study the same tendency was found. The current, if suitably applied, may enhance contaminant biodegradation in unsaturated soils (Gill et al., 2014; Harbottle et al., 2009; Li et al., 2012).

In the present study, a period of 24 hours without current or with REP showed to be short to reestablish and regenerate the system, respectively. Thus, further studies should optimize the

REP strategy testing different periods of time in order to take advantage of the reversed polarization mechanism in case by case.

3.3. Technology feasibility and further investigations

Overall, the EKR offers an on-site soil remediation strategy avoiding emissions due to transport as well as soil disturbances, e.g. soil characteristics. In the present study, EKR efficiency is site (anode, central, cathode) and contaminant specific dependent, which offers the possibility to concentrate the contamination in one specific area taking advantage of EOCs mobilization towards the electrodes. In this sense, EKR could be optimized with a mobile cathode, which would increase process efficiency. The costs associated with this technology would be mainly material and energetic (calculated based on equation 1), and in this sense, the On/Off approach should be explored as the energy demand might be lower (almost 20% in the present study), depending on the Off period extension, than comparing with a continuous electric field, also including the reversed polarization of the electrodes (0.0045 kWh *vs.* 0.0055 kWh, switching and continuous electric field respectively). It should be also pointed out that under the low current intensity applied electrode material here tested did not show any signs of corrosion, and the material by itself shows to be a cheap option (6 €/meter) from the up-scaling point of view.

$$\boldsymbol{Energy\ consumption}\ (\boldsymbol{kWh}) = \frac{\boldsymbol{V \times A \times h}}{\boldsymbol{1000}} \qquad \text{Eq. (2)}$$

V = cell voltage average, Volts
A = applied current, Amps
h = time of treatment, hours

Based on the present results further research on hybrid technologies should be pursued in order to optimize the effect of the current application on soil microorganisms' and combined EOCs removal. Further studies should also take effluent variability into account. Effluent greatly vary in biological-physical-chemical properties, a systematic understanding of the interactions between water matrix components and EOCs is necessary with simultaneous cycles of effluent irrigation. Concerning samples variability, it is important to take in mind that some samples had higher standard deviations (SD), which influence the statistical analysis and therefore the comparison between current strategies and EOCs removals. The high SD obtained may be associated with EOCs compounds distribution along the two experimental duplicates, as the microcosm were manually prepared. The soil (300 g) was manually irrigated with spiked effluent simulating flooding irrigation and then pressed to even the soil height along the microcosms. These factors may influence soil compaction and consequent water distribution within the two different microcosms (n=2), which in turn may have influenced the EOCs mobilizations/distribution in the soil by electro- migration and -osmosis. Also, no physical separation was used between soil sections, which may have led to a misdistribution when dividing the soil sections in the duplicate microcosms and influencing the SD.

4. Conclusions

This study shows that once introduced in soil through effluent irrigation, 20% - 100% of the studied EOCs remain in the soil after 6 days of EKR treatment, posing a potential risk to the environment and human health. The EKR improved the EOCs removal up to 30% when comparing the different soil sections with natural attenuation (without current application), avoiding their dispersion in soil. Among the EOCs in study, SFM showed the higher remediation rate (75-83%) when EKR was applied, with 57% estimated to be from natural attenuation (bioremediation is believed to be the main degradation mechanism for this compound in the tested conditions). IBF and DCF removal were highly dependent on currents directionality, as their migration towards the anode resulted in their accumulation on the central compartment. These results correspond to a good removal in the cathode side, but, on the other hand, the removal of both IBF and DCF is hindered in the central and anode side. In this study, the combination of On/Off with REP showed to be the most suitable strategy as it did not change the soil characteristics in terms of pH and a more homogenous removal of the studied EOCs in the soil was achieved for the tested conditions.

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Table 1 - Information of the EOCs in study.

Emerging Organic Contaminant	**MW (g/mol)**	**Log K_{ow}**	**pKa**	**Solubility (mg/L)**	***H* (atm-m^3 /mole)**	**Category**
Sulfamethoxazole (SFM)	253.279	0.89	5.7	610 [f]	6.4×10^{-13}	Antibiotic
Carbamazepine (CBMP)	236.274	2.45	13.9	18 [d]	1.1×10^{-10}	Anticonvulsive
17α-ethinylestradiol (EE2)	296.40	3.67	10.3	11.3 [e]	7.94×10^{-12}	Estrogen
Diclofenac (DCF)	296.147	4.51	4.15	2.37 [d]	4.73×10^{-12}	Anti-inflammatory
Oxybenzone (MBPh)	228.25	3.82	7.56	69 [d]	1.5×10^{-8}	UV filter
Ibuprofen (IBF)	206.19	3.97	4.91	21 [d]	1.5×10^{-7}	Anti-inflammatory

References: http://pubchem.ncbi.nlm.nih.gov

Legend: MW: molecular weight; pKa: dissociation constant; Log K_{ow}: octanol water partition coefficient; *H*: Henry’s law constant.

Table 2

Table 2 - Presence (%) of EOCs in soil after EKR (n=2).

		Emerging Organic Contaminants (EOCs)											
		SFM		**CBMP**		**EE2**		**DCF**		**IBF**		**MBPh**	
Electric current strategy	**Soil section**	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Continuous	Anode	22 ^{B}	14	69 ^{b}	11	67 ^{b}	11	**77** $^{a, b}$	17	**89** $^{a, b}$	16	**70** ^{b}	8
	Central	37 ^{B}	10	**82** ^{b}	2	**87** ^{b}	5	**110** $^{A, b}$	7	**127** $^{A, b}$	35	**86** ^{b}	5
	Cathode	16 ^{B}	7	77 ^{b}	5	71 ^{b}	4	58 ^{a}	5	45 ^{a}	9	60	2
	Total	25	9	76	6	75	7	82	9	87	20	72	5
On/Off	Anode	17 ^{B}	7	57 ^{b}	15	61 ^{b}	11	64 ^{a}	12	**94** $^{A, b}$	16	59	10
	Central	22 ^{B}	19	**84** ^{b}	23	**76** ^{b}	12	**84** $^{a, b}$	52	**73** $^{A, a, b}$	47	**72**	17
	Cathode	12 ^{B}	4	**84** ^{b}	3	**79** ^{b}	7	36 $^{a, B}$	9	44 ^{a}	12	**77** ^{b}	6
	Total	17	2	75	14	72	6	62	10	70	7	69	7
REP	Anode / (Cathode)	12 ^{B}	5	51 ^{b}	4	58 ^{b}	0	62 ^{a}	3	**81** $^{a. b}$	7	54	2
	Central	29 ^{B}	2	70	2	**73**	5	**101** $^{A, b}$	6	**114** $^{A, b}$	21	**75**	1
	Cathode / (anode)	10 ^{B}	7	65 ^{b}	5	65 ^{b}	4	44 ^{a}	5	36 ^{a}	9	59	2
	Total	17	4	62	10	65	6	69	13	77	15	63	2
On/Off + REP	Anode/ (cathode)	16 ^{B}	17	69 ^{b}	4	63 ^{b}	8	48 ^{a}	26	48 ^{a}	18	61	3
	Central	37 ^{B}	19	**96** ^{b}	6	**80**	9	**98** $^{A, b}$	6	60 ^{a}	26	**83**	1
	Cathode / (anode)	18	5	60	23	60	26	47 ^{a}	8	64 ^{a}	25	56	29
	Total	24	9	77	23	70	18	67	11	60	11	68	10
Control	-	43	8	77	6	71	4	64 ^{a}	4	64 ^{a}	2	71	1

Legend: Bold values mean the higher value among soil section (anode, central and cathode); The values in bold highlight the values above the values found in control.
The capital letter 'A' means statistical differences (p<0.05) for each EOCs in the different soil sections (anode, central and cathode);
The capital letter 'B' means statistical differences (p<0.05) comparing the contaminants presence for each EKR strategy and each soil section (anode, central, cathode);
Note: for SFM, CBMP, EE2 and MBPh statistical significantly differences were not found for each compound among the EKR strategies.

Figure 1

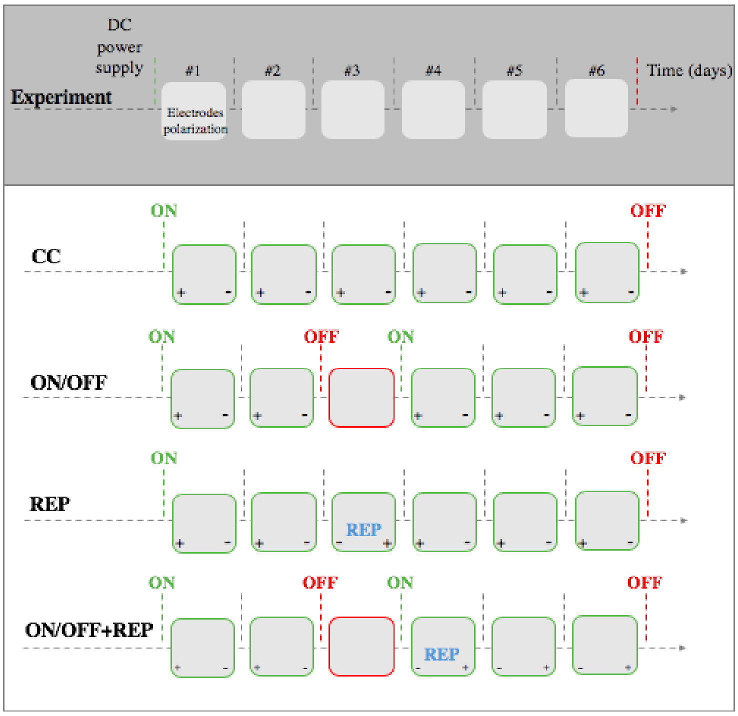
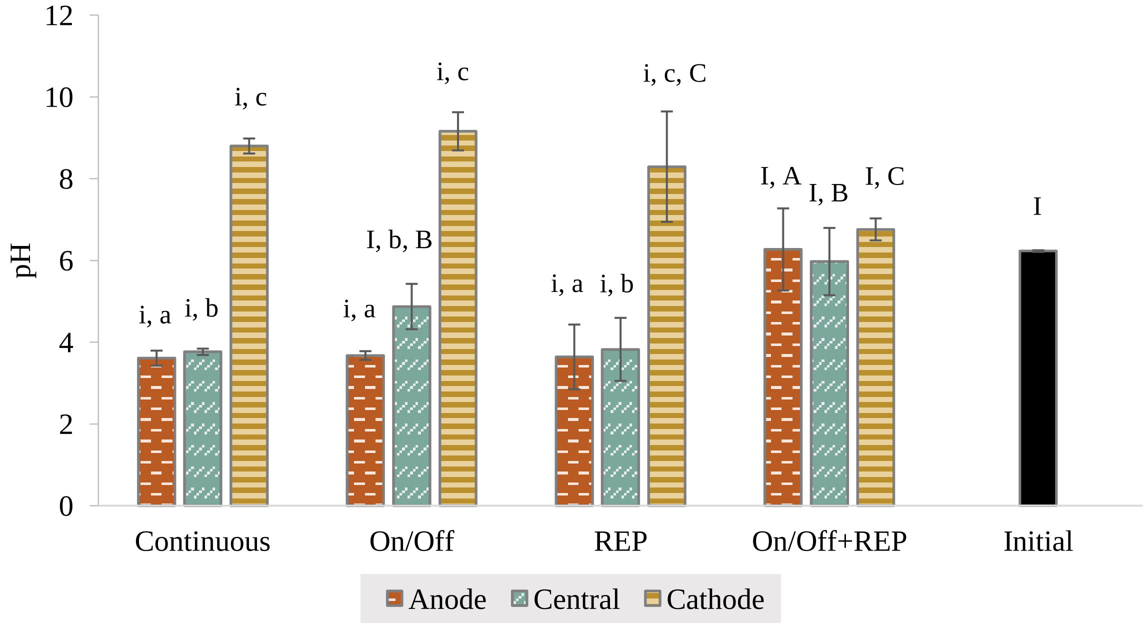


Figure 1 - Schematic representation of the current strategies adopted for the electrokinetic soil remediation experiments. (CC: continuous current; On/Off: current switched On and Off; REP: reversed electrode polarization).



Statistical analysis: capital letters and letter with upper comma means statically differences ($p<0.05$).

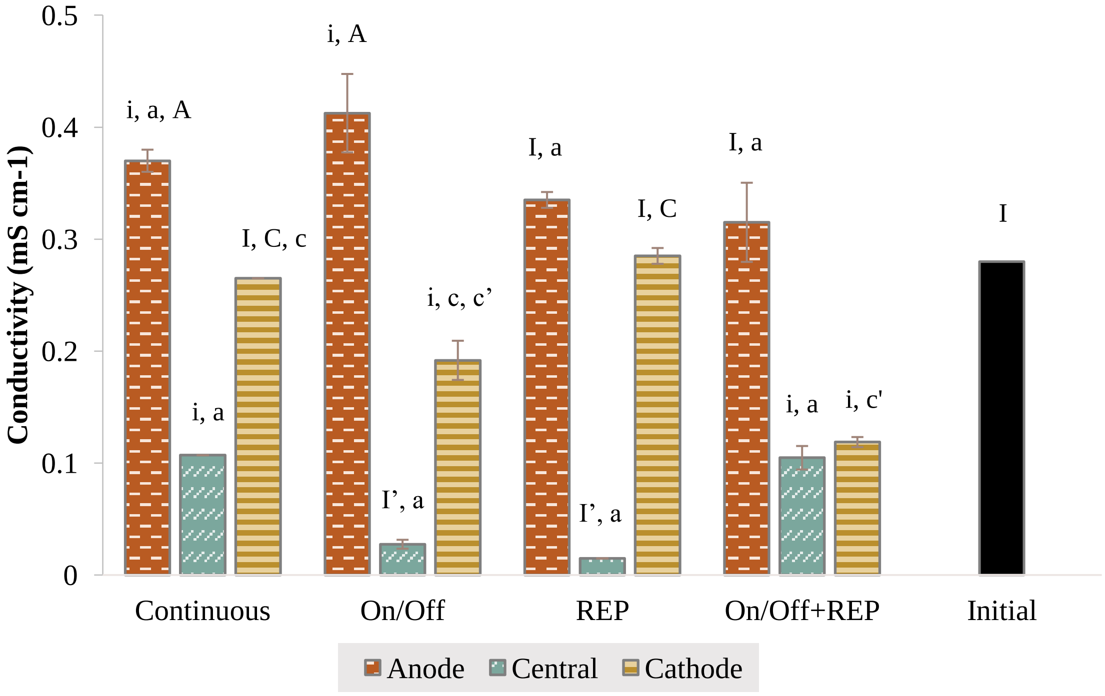
I: significant statistical differences between initial soil pH and the different compartments for all the experiments

A: significant statistical differences for anode compartment between experiments

B: significant statistical differences for central compartment between experiments

C: significant statistical differences for cathode compartment between experiments

Figure 2 – Soil pH values after EKR and the initial one.



Statistical analysis: capital letters and letter with upper comma means statically differences ($p<0.05$).

I: significant statistical differences between initial conductivity and the different compartments for all the experiments.

A: significant statistical differences for anode compartment between experiments.

B: significant statistical differences for central compartment between experiments.

C: significant statistical differences for cathode compartment between experiments.

Figure 3 - Soil conductivity after EKR and the initial value.

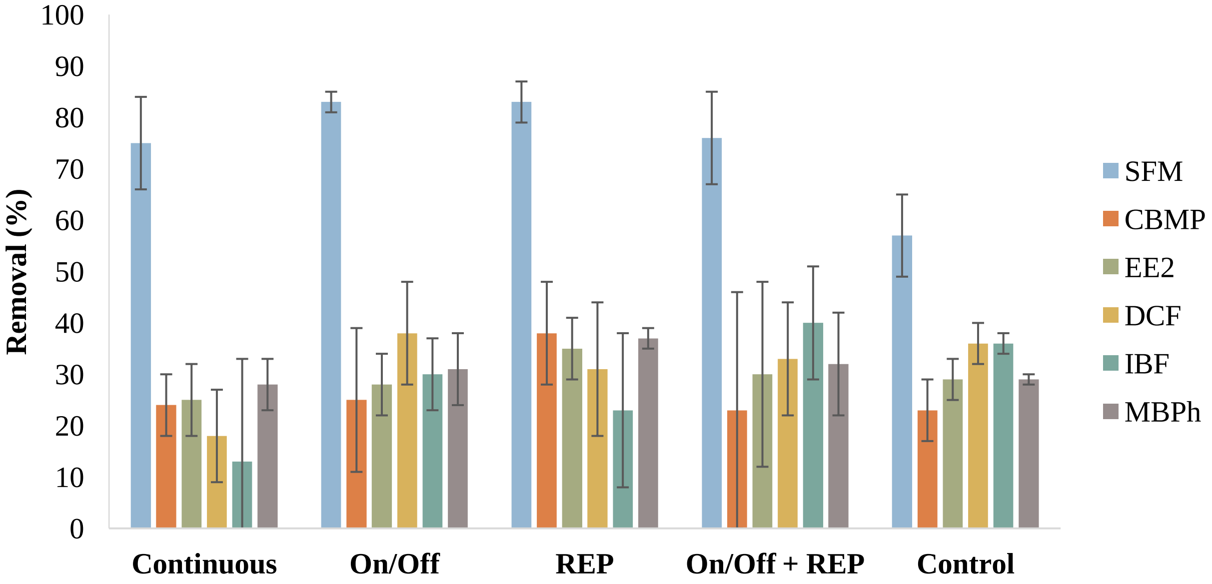


Figure 4 – Total removal (%) of each EOCs (SFM, CBMP, EE2, DCF, IBF, MBPh) applying EKR with different current strategies (continuous, switching On/Off, REP and combination of On/Off and REP):

***conflict of Interest Statement**

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

CRediT author statement

Ana Rita Ferreira: Conceptualization, Investigation, Writing- Original draft preparation.

Paula Guedes: Methodology, Writing- Reviewing and Editing.

Eduardo P. Mateus: Resources, Writing- Reviewing and Editing.

Alexandra B. Ribeiro: Supervision, Resources, Writing- Reviewing and Editing.

Nazaré Couto: Supervision, Funding acquisition, Writing- Reviewing and Editing.