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Study of electrochemical remediation of clay spiked with C12-C18 alkanes / Proietto, F., Meli, P., Prestigiacomo, C., Galia, A., Scialdone, O.. - In: JOURNAL OF ENVIRONMENTAL CHEMICAL ENGINEERING. - ISSN 2213-3437. - 12:1(2023), pp. 1-9. [10.1016/j.jece.2023.111780]

Availability:

This version is available at: 11583/3015763 since: 2026-09-21T12:09:14Z

Publisher:

Elsevier

Published

DOI:10.1016/j.jece.2023.111780

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Study of electrochemical remediation of clay spiked with C₁₂-C₁₈ alkanes

Federica Proietto^{*}, Paola Meli, Claudia Prestigiacomo, Alessandro Galia, Onofrio Scialdone

Dipartimento di Ingegneria, Università degli Studi di Palermo, Viale delle Scienze, Ed. 6, 90128 Palermo, Italy

ARTICLE INFO

Editor: Giovanni Palmisano

Keywords:

ElectroChemical GeoOxidation
Electrokinetic
Alkanes
Soil remediation
Organic pollutants
Low electric fields

ABSTRACT

To date, the management of polluted soils and sediments is challenging because they can be characterized by heterogeneous conditions, miscellaneous contaminants (organic and inorganic ones), fine grains and low-hydraulic permeability. In these cases, the current treatment methods are poorly effective. ElectroChemical Remediation Technologies (ECRTs) are considered some of the main appealing strategies for the remediation of such complex sites. The ECRTs are based on the application of a relatively low cell potential value, between two or more electrodes, inducing an electric field (E) through the polluted media, which prompts the remediation of the contaminated site. This work was focused on the study of the electrochemical remediation of kaolin artificially spiked with a miscellaneous of five alkanes (C₁₂H₂₆, C₁₃H₂₈, C₁₄H₃₀, C₁₆H₃₄, C₁₈H₃₈), namely C₁₂-C₁₈. Kaolin was selected as a model reproducible, low-buffering, and low-permeability clay and the mixture C₁₂-C₁₈ as a hazardous model of petrol hydrocarbon compounds. The effect of several operative conditions, including the E intensity, type of technology, presence of supporting electrolyte, was investigated. It was found that adopted low E values can simultaneously mobilize and degrade in situ the C₁₂-C₁₈ mixture and that the shorten the chain compound, the easier the remediation efficiency, R . It was shown that the usage of E of approximately 0.50 V cm⁻¹ allows to reach a total C₁₂-C₁₈ removal ($R(C_{12}-C_{18})$) of ~70% after 96 h. Finally, it was demonstrated that the usage of sodium chloride improves the performances of the process: $R(C_{12}-C_{18})$ increased from 61 to 83% when NaCl was added.

1. Introduction

Nowadays, soil remediation polluted by total petroleum hydrocarbons (TPHs) and their derivatives is crucial to preserve agriculture manufacture and environmental healthiness [1]. Persistent organic pollutants, such as TPHs, are difficult to remediate in soil [2–4]. Although specific bacteria present in the soils can biodegrade TPH pollutants, their degradation capacity is reduced by increasing contaminants' concentration and it depends on physicochemical soil properties [4,5]. Restoration of polluted clays is challenging because these sites are characterized by heterogeneous conditions, miscellaneous of contaminants (organic and inorganic ones), fine grains and low-hydraulic permeability [6] thus causing a poor efficacy of current treatment methods (e.g., soil washing). Moreover, the efficacy of treatments strongly depends on several factors, including proprieties, composition, sources, nature of pollution, type of sites, pollutants' distribution, degradation's mechanism, relationships and interaction with microorganisms. To date, several technologies, including chemical, biological, thermal, physico-chemical, electromagnetic, ultrasonic and

electrochemical methods, are under investigation for the treatment of such complex sites [7]. Among these approaches, Direct Current Technologies (DCTs), whereby an electric field (E) is induced through the polluted media thanks to the application of a direct current between two or more electrodes directly inserted or adjacent to the contaminated site [8], are considered among the most practical, sustainable, cost-effective and noninvasive in situ and ex situ options in the case of low permeability clays [7,8]. In these treatments, the induced E promotes *i*) the flow of ions (electromigration), water (electroosmosis), colloids (electrophoresis) and contaminants and *ii*) redox reactions at the electrodes and/or on the soils' particles. Electromigration and electroosmosis are the most involved transport mechanisms [4]. Electromigration is the movement of charged dissolved ions through an aqueous medium towards the electrode with a polarity opposite to the ion charge (i.e. negative ions move to the anode and positive ions towards the cathode side). Electroosmosis is the movement of pore fluid water and dissolved constituent within a porous material in the direction parallel to the applied E . Typically, the E causes fluids to flow from the anode towards the cathode side although the electroosmosis direction can change with

^{*} Corresponding author.

E-mail address: federica.proietto@unipa.it (F. Proietto).

<https://doi.org/10.1016/j.jece.2023.111780>

Received 6 October 2023; Received in revised form 11 November 2023; Accepted 19 December 2023

Available online 21 December 2023

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the variation of the soil surface charge. ElectroChemical Remediation Technologies (ECRTs) and ElectroKinetics (EKs) are two types of DCTs used for environmental remediation, which mainly differ in energy input intensity, operative mechanisms and resulting outcomes. ECRTs consist of two main processes: i) ElectroChemical GeoOxidation (ECGO), which mineralizes organics, and ii) induced complexation, which complexes metal contaminants. ECGO technologies involve less energy (i.e., typical induced E is between 0.0025 and 0.25 V cm^{-1}) than the EK processes (i.e., E higher than or equal to 1 V cm^{-1}) [11].

The involved mechanism of the redox reaction on the soils' particles was not totally explained, although, according to the literature, the application of low E values might enhance the organics' mineralization [8–11]. Indeed, each particle would act as 'microconductor' and wet minerals as a diluted electrochemical solid-bed-reactor. Under an induced E , microconductors are polarized and act as microelectrodes, which might induce reduction-oxidation reactions in the vicinity of the particles of the soil [12,13]. According to the literature, these redox reactions might lead to the generation of various reducing and oxidant agents (such as $\text{H}\bullet$, $\text{OH}\bullet$, $\text{HO}_2\bullet$, etc...) and consequently to the transformation of organic pollutants in safe compounds, such as CO_2 and water, near the particles' surface [9,11,14]. Fan et al. studied the electrochemical remediation of a real soil contaminated by TPHs under a constant E [9]. They demonstrated that, after 80 days, a removal efficiency of approximately 22% was reached under 0.34 V cm^{-1} , highlighting that, under their operative conditions, the observed reduction in the concentration of the pollutants can be explained in part only by the electrochemical oxidation near the electrodes and in part by the presence of electrochemical oxidation reaction on or near the soil's particles [9]. Saini et al. studied the real soil remediation dragged from BHP (BHP Group Limited) in Western Australia via electrochemical remediation under 0.6 V cm^{-1} showing the possibility to reduce the concentration of the light TPHs (C10-C16 fraction) of approximately 37% after a week [4]. This approach might be suitable for several sites and different contaminants' nature. Recently, Proietto et al. reported that the electrochemical remediation under 0.15 V cm^{-1} for 96 h can be a viable way to degrade in situ phenol from the kaolin with a good removal efficiency (~90%) using compact graphite's electrodes and Na_2SO_4 as supporting electrolyte [10].

In this framework, the electrochemical remediation of kaolin artificially spiked with a miscellaneous of five alkanes ($\text{C}_{12}\text{H}_{26}$, $\text{C}_{13}\text{H}_{28}$, $\text{C}_{14}\text{H}_{30}$, $\text{C}_{16}\text{H}_{34}$, $\text{C}_{18}\text{H}_{38}$), namely C_{12} - C_{18} , was investigated using a simplified cell in which the electrodes are directly inserted into the contaminated kaolin avoiding the usage of expensive processing fluids and the energy consumption for their pumping. Kaolin was used as a model low-buffering, reproducible and low permeability clay mineral, while a C_{12} - C_{18} mixture was chosen as hazardous model for not polar hydrocarbon compounds. The process was investigated under a wide range of E values ($0.05 < E < 2.00 \text{ V cm}^{-1}$) for 96 h. Moreover, for the sake of comparison, the electrochemical remediation was performed under more conventional operative conditions EK reported in the current literature, such as a E of 1.00 V cm^{-1} and in the presence of electrode compartments and processing fluids. Eventually, the effect of the addition of sodium chloride as supporting electrolyte was investigated.

2. Materials and methods

2.1. Reagents

Deionized water (DW) (HPLC grade, Sigma Aldrich) was used to fix the water content of the kaolin and as processing fluid in the EK treatments. Sodium Chloride as supporting electrolyte (NaCl , Sigma Aldrich, purity $\geq 99\%$, 0.5 M) was used. Five higher alkanes congeners, n-Dodecane (C12) ($\text{C}_{12}\text{H}_{26}$, Alfa Aesar, purity $> 99\%$), n-Tridecane (C13) ($\text{C}_{13}\text{H}_{28}$, Alfa Aesar, purity $> 98\%$), n-Tetradecane (C14) ($\text{C}_{14}\text{H}_{30}$, Alfa Aesar, purity $> 99\%$), n-Hexadecane (C16) ($\text{C}_{16}\text{H}_{34}$, Alfa Aesar, purity $> 99\%$), and n-Octadecane (C18) ($\text{C}_{18}\text{H}_{38}$, Alfa Aesar, purity $> 99\%$),

namely C_{12} - C_{18} , were chosen as hazardous organic model to spike the kaolin. Hexane (C_6H_{14} , Carlo Erba, GC-MS analytical grade) was used to extract the C_{12} - C_{18} from the dried kaolin and as solvent to prepare the sample for GC analyses. Methyl Heptadecanoate ($\text{C}_{18}\text{H}_{36}\text{O}_2$, TCI analytical standard, purity $> 98\%$) was adopted as internal standard for GC-FID analyses.

2.2. Spiked kaolin with alkanes

Kaolin ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) (Sigma-Aldrich, CAS N. 1332–58-7) was selected and used for this work as a model low-permeability, reproducible and low-buffering clay mineral. Spiking of clay was carried out as follows: i) 100 g of clean kaolin was dried in an oven at 105°C for 24 h; ii) artificially contaminated by the addition of a certain amount of each i -contaminants (C12, C13, C14, C16, C18) to reach 100 mg/Kg of each compound (i.e., total C_{12} - C_{18} concentration of 500 mg/Kg); iii) 2 h of homogenization in a rotary vapor balloon; iv) water was added to reach the target W of 66%; finally v) the artificially spiked kaolin was equilibrated at 200 rpm using a horizontal shaker for 24 h.

2.3. Electrochemical cells

The electrochemical setups used in this work were previously reported by Proietto et al. [10]. Fig. 1 report the schematic view of the Cell I and II, Figs. 1A and 1B, respectively. In brief, Cell I was a Plexiglass® cell ($V = 60 \text{ mL}$) used to study the electro-remediation of contaminated kaolin (Fig. 1A). The used electrodes were a plate of compact graphite, which were directly placed in contact to the contaminated clay. The inter electrode gap was fixed at 10 cm and the wetted electrode's area was 3 cm^2 . The spiked-kaolin was set down inside the cell layer by layers, pressed and pack down to minimize void space for at least 12 h, as better described in ref. [10]. The evaporation of the water was hindered by covering the cell with a Plexiglass® cover. Cell I was filled with 66 g of moist mineral. In the cell, the kaolin W was 66% with a bulk density of 1.65 g cm^{-3} , porosity of 0.59 and a specific gravity G_s of 2.43 at 20°C (ASTM D 854–02).

At the beginning of each electrolysis, at least two kaolin samples were taken and analyzed to check the initial content of the different contaminants, pH and W , because a little amount of water and contaminants might be volatilized in the course of preparation. An AMEL 2549 potentiostat/galvanostat was used to apply a constant direct E (range: $0.05 - 1.00 \text{ V cm}^{-1}$) and a power supply VOLTcraft PS-302A to apply 2.00 V cm^{-1} .

Electrochemical treatment under E of 1.00 V cm^{-1} with the auxilium of external processing fluids was performed in Cell II (Fig. 1B). This configuration was previously described in ref. [10]. Cell II presents three compartments: two external compartments, where deionized water (DW) (30 mL) was placed, and a middle section in which 100 g of wet kaolin were placed. The electrodes of graphite (working area 3 cm^2) were placed in the external compartments and close to the spiked kaolin. Filter paper was used to separate the compartments. Also, for this configuration, a Plexiglass® cover was used to seal the middle section to avoid evaporation of the water content. AMEL 2549 potentiostat/galvanostat was used.

To guarantee reproducibility, the electrochemical experiments were performed in triplicate for 96 h at ambient temperature. For sake of comparison, a control test (blank tests) without the application of a gradient E were carried out. In this case, approximately 96% of the initial content of the mixture C_{12} - C_{18} was restored (which is coherent with the aim of this study). Volatilization of alkanes and/or their adsorption to the electrochemical apparatus (e.g., sample vials, electrodes, cells) might be the reason why a mass balance difference was observed.

After 96 h of treatment, moist spiked kaolin samples were taken from three different points, (see Fig. 1: S1 near to the anode electrode; S2 in the middle section; and S3 near the cathode electrode). Hence, the

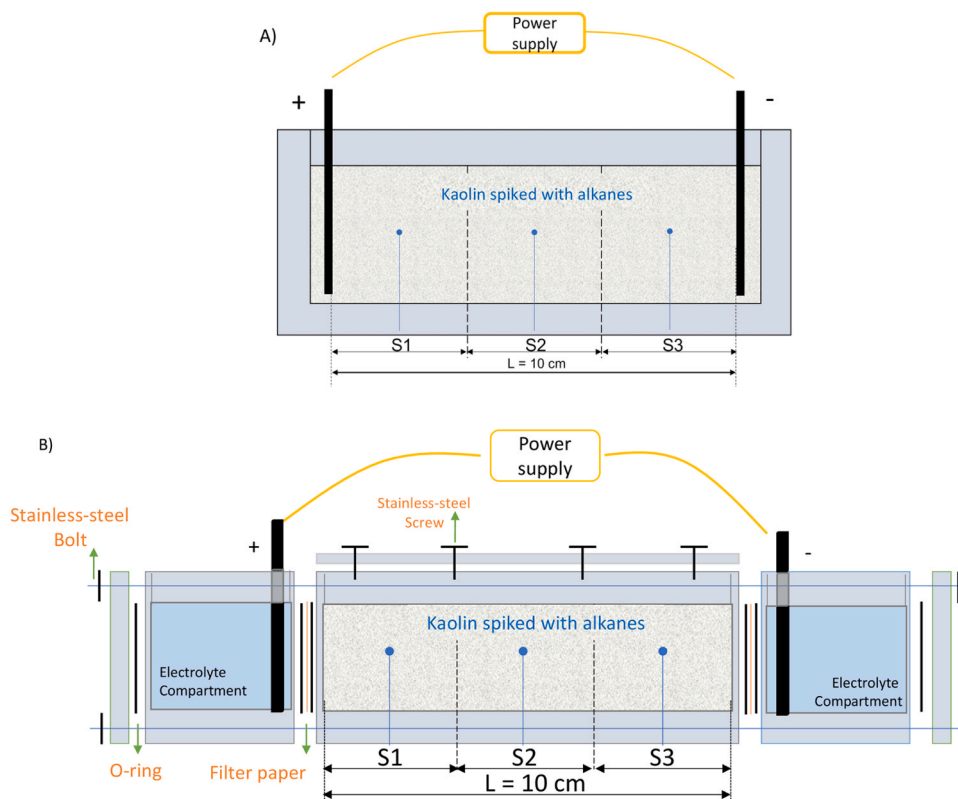


Fig. 1. Electrochemical cells' schematic view used in this work. A) *Cell I*, where the electrodes were directly inserted into the bed spiked-kaolin and B) *Cell II*, which is made by three compartments: two external compartments where the electrodes were placed (Electrolyte compartment) and a middle compartment where the bed kaolin is placed.

residual amount of each contaminant, the W and pH were evaluated following the procedure reported in [Section 2.4](#). The analyses were carried out three times and the data's results were reported as the average of them.

2.4. Analytical methods and performances

Water content, W , was determined following the procedure of the ASTM D2974–14 method, while specific gravity following the ASTM D854–92 method. Kaolin pH was determined following the ISO 10390:2021 fixing a kaolin/water ratio at 1/5. To measure the pH, Checker® pH Tester HANNA® instruments (HI98103) was used.

Alkane C_{12} – C_{18} concentrations were determined by GC-FID analyses (Perkin Elmer, AutoSystem XL, Gas Chromatograph) after solid-liquid extracting procedures. First a certain amount of moist kaolin treated sample was dried, for 24 h, in an oven at 40 °C under atmospheric pressure. Then, 1 g of dry sample and 4 g of hexane were poured in a Pyrex centrifuge tube. To facilitate the solid-liquid extraction of the phases inside the centrifuge tube, mechanical agitation using a vortex (Maxi-Mixer) for a duration of 2 min, followed by sonication using a Falc ultrasonic bath operating at a frequency of 50 KHz for a duration of 1 h, were used. Then, the tube underwent centrifugation at a speed of 6000 rpm for a duration of 20 min, using the BICASA, ALC, 4218 centrifuge. Subsequently, the liquid phase of the supernatant was isolated by means of a Pasteur pipette and carefully collected in a glass vial that had been pre-weighed (SUR1). Methyl heptadecanoate, which was chosen as the internal standard, was dissolved in the extracted solution at a concentration of 1 mg_{Methyl heptadecanoate}/g_{SUR1} for the purpose of executing GC-FID analysis. The detection of alkanes C_{12} – C_{18} was conducted using a Perkin Elmer Autosystem XL gas chromatograph (GC) that was fitted with an HP-5 capillary column of 30 m in length and 0.32 mm in diameter. The flame ionization detector (FID) was heated to

a temperature of 250 °C. The experimental protocol for conducting the analysis included setting the beginning temperature of the oven to 160 °C for a duration of 0 min. Subsequently, a gradual increase in temperature was implemented, with a ramp rate of 10 °C per minute, until reaching a final temperature of 260 °C. Following this, the temperature was maintained at 260 °C for a period of 5 min. The carrier gas used in the analysis was helium (supplied by Rivoira, purity 5.0), which was held at a constant pressure of 15 psig. The temperature of the injector was adjusted to 250 °C. The volume of the injection was 0.2 μ L. The chromatograms were identified and calibrated using different concentration of GC analytical standards in order to construct the calibration lines. A typical chromatogram is shown in [Fig. S1 \(Supplementary Materials\)](#). The retention times of the different compounds were 1.4 for the hexane, 1.65 min for C_{12} , 1.82 min for C_{13} , 2.08 min for C_{14} , 2.85 min for C_{16} , 4.10 min of C_{18} , and 5.88 min for the Standard. To check the potential evaporation of C_{12} – C_{18} during the drying step, a control test was performed analyzing the quantity of contaminants presents in the supernatant of both the dried spiked kaolin before and after the drying step after the spiking stage. It was observed that approximately 95% of the content of the C_{12} – C_{18} mixture was restored, which is consistent for the aim of this work. Volatilization of alkanes and/or their adsorption to the apparatus (e.g., sample vials) might be the reason why a mass balance difference was observed.

Agilent Cary 60 UV spectrophotometer was used to check the presence of hypochlorous acid (HClO) and hypochlorite (ClO^-) at an UV-Vis scan rate value of 600 nm/min. The wavelength λ was 235 and 289 nm for HClO and 294 nm for ClO^- . Sodium hypochlorite pentahydrate (supplied by TCI, $\text{NaClO} \cdot 5 \text{H}_2\text{O}$) was used for the calibration curves. More in detail, 2 mL of DW was added to 2 g of the wet treated kaolin sample in a Pyrex centrifuge tube; then this suspension was homogenized using a Vortex mixer, sonicated for 10 min, centrifugated for 10 min. Hence, the suspension was analyzed at the UV-VIS.

After 96 h, the residual content of each contaminant was determined for each section S1, S2 and S3, and was compared with the initial concentration, in order to analyze the distribution of each contaminant by considering the normalized C_i/C_i^0 concentration. C_i^0 was evaluated to verify the contaminants homogeneity distribution in the clay for each experiment at the time zero. For each alkane at the beginning the ratio C_i/C_i^0 was approximately 1.

i-alkanes removal efficiency was computed by Eq. 1.

$$R(C_i) = (c_i^0 - c_i^t)/c_i^0 * 100 [\%] \quad (1)$$

In which c_i^0 and c_i^t are the initial content of the *i*-alkane and the residual *i*-alkane (mg/Kg), respectively, after the treatment. The total C_{12} - C_{18} removal ($R(C_{12}-C_{18})$) was computed with the Eq. 1 in which c_i^0 and c_i^t are the initial and total amount of $C_{12}-C_{18}$ (mg/Kg) present in the kaolin and total amount of $C_{12}-C_{18}$ ($R(C_{12}-C_{18})$) after 96 h per all the g of dried treated kaolin, respectively.

Eq. 2 was used to calculate the energetic consumption (EC):

$$EC = \Delta V * I * t / w * 10^{-3} [=] \text{ kWh/g} \quad (2)$$

Where I (A) is the current, t (s) treatment time, ΔV (V) the applied cell potential, and w the total quantity of kaolin treated (g).

The treated kaolin in both technologies (Cell I and II) was characterized by the same amount of mg of contaminant per Kg of dried kaolin and the performances were discussed in terms of the normalized concentration C_i/C_i^0 and the removal efficiency R which refers also to the amount of organics removed respect to the treated dried kaolin that were placed into the cells.

3. Results and discussion

A first series of electrolyses was planned to validate the investigated approach for the remediation of artificially contaminated kaolin with a miscellaneous of alkanes (dodecane - C12, tridecane - C13, tetradecane - C14, hexadecane - C16, octadecane - C18, namely C_{12} - C_{18}), which were chosen as model hazardous not polar hydrocarbons, under a constant gradient E of 0.25 V cm^{-1} . In the second stage, the E strength effect (range $0.05 \div 2 \text{ V cm}^{-1}$) was studied in detail on the performance of remediation, and, for the sake of comparison, electrochemical treatment was performed using two different electrochemical cells at 1 V cm^{-1} . Eventually, the presence of sodium chloride as supporting electrolyte was reported.

3.1. Electrochemical treatment of C_{12} - C_{18} spiked kaolin under direct electric field

To explore the electrochemical treatment of C_{12} - C_{18} spiked kaolin under low values of gradient E , first experiments were performed at 0.25 V cm^{-1} , for 96 h. Graphite electrodes, directly inserted in the kaolin to prevent added electrical resistances, were used. According to the literature, the usage of graphite *i)* does not need complex pretreatment before its implementation (as an example with respect to the usage of the anticorrosion pretreatment mandatory for the stainless-steel electrode), *ii)* limits the cost (e.g., in comparison with platinum or Dimensionally Stable Anode electrodes, which are much more expensive) and *iii)* guarantees the electrical conductivity [10].

Fig. 2 reports the distribution of each contaminant of the C_{12} - C_{18} spiked kaolin in terms of *i)* normalized concentration C_i/C_i^0 in the sections S1, S2 and S3, and *ii)* the total removal efficiency of each *i*-contaminant, $R(C_i)$. At the zero time, the C_i/C_i^0 of each contaminant C_{12} - C_{18} was approximately 1, which means that the contaminants were homogeneously distributed along the clayed-bed (Figure 2, $C_i/C_i^0 \sim 1$, refers the black dashed line – primary y-axis). Following the electrochemical treatment, for each *i*-contaminant a similar distribution in the kaolin was observed. In detail, C_i/C_i^0 increased from the section S1 (anode region) to S2 (middle region) and S3 (cathode area), and it was always lower than 1 in sections S1 and S2 ($C_i/C_i^0 < 1$) and close or slightly higher than 1 in section S3 ($C_i/C_i^0 \geq 1$), except for C12. For example, in the case of C13, the C_{13}/C_{13}^0 was 0.50, 0.22 and 1.10 in sections S1, S2 and S3, respectively. The higher content of contaminants in the region S3 indicates that the organics were transported from the section S1 to S3, where they accumulated. Moreover, under the adopted operative parameters, it was also observed that each C_{12} - C_{18} contaminant was partially removed from the kaolin. In particular, the shorter the carbon chain, the higher the removal efficacy: indeed, the total removal, $R(C_i)$, was estimated to be approximately 78%, 55%, 50%, 47% and 24% in the case of C12, C13, C14, C16 and C18, respectively (Fig. 2, refers to the secondary y-axis). Moreover, under adopted operative conditions, a total C_{12} - C_{18} removal, $R(C_{12}-C_{18})$, of approximately 40% was reached. Similar results were reported by Saini et al. [4] which highlights a decrease of approximately 37% in C_{10} - C_{16} content under 0.60 V cm^{-1} after 7 days.

These results can be rationalized by taking into account the considerations summarized below.

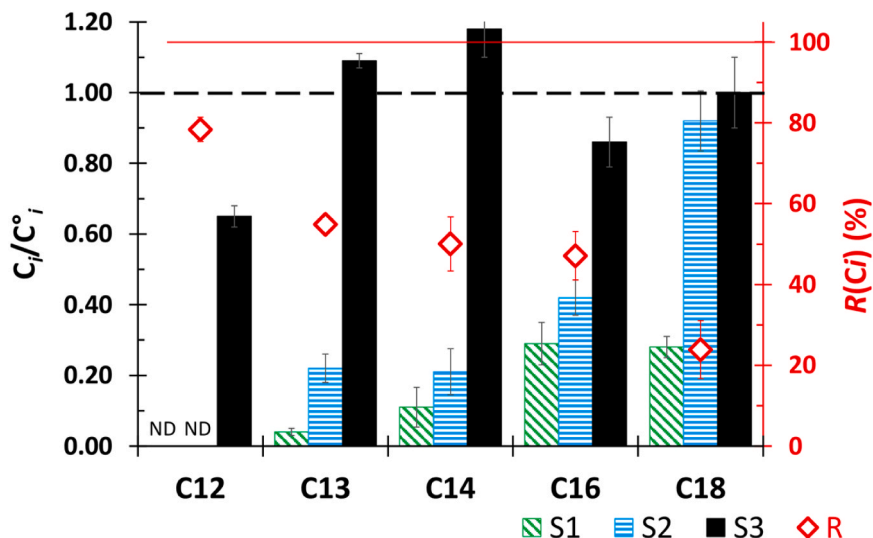


Fig. 2. C_i/C_i^0 of the different contaminants C12, C13, C14, C16, C18 in regions S1, S2 and S3 (primary y-axis) and total R of each contaminant (%) from the kaolin ($R(C_i)$) (secondary y-axis). Black dashed line (— — —) marks C_i/C_i^0 equal to 1. Red solid line marks the 100% of $R(C_i)$. Time: 96 h. $E = 0.25 \text{ V cm}^{-1}$. Compact graphite electrodes. ND: Not detected. Electrochemical cell: I.

- Clay minerals have a well-defined layered clay structure constituted by micro-meter size particles with a large surface area and dominated by mesopores, denoting that both the surface and the pore structure of kaolin might control the absorption and desorption compartment of organics dispersed in clay [15,16]. According to the literature, the interaction between C₁₂-C₁₈ alkanes and kaolin are van Der Waals interaction due to their non-polarity [17] and they mostly exist in the mesopores of kaolin [15]. The adsorption of C₁₂-C₁₈ alkanes is not expected to change the interlayer distance of the clay minerals after spiking thus showing that the molecules would not be adsorbed on the interlayer surfaces of the clay [16]. Hence, the induced *E* is expected to affect these interactions and promote the desorption.
- In the electrochemical remediation of pollutes sites, the induced gradient *E* causes the transport of water, ions and colloids due mainly to electroosmosis and electromigration through low hydraulic permeability clay which might help the transport of the pollutants [6]. Among the various transport mechanisms involved in this approach, the movement of C₁₂-C₁₈ in the kaolin cannot be attributed to the electromigration due to their neutral charged-properties. Hence, the transport of C₁₂-C₁₈ through the kaolin during the electrokinetic treatment might be attributed to the electroosmotic flow, which moves from the anode towards the cathode side, explaining the higher concentration of these organics nearly the cathode section (S3). However, it is worth to highlight that the electroosmotic transport is tricky and slow, due to the hydrophobicity of alkanes and their very low solubility in water [18].
- In addition to the transport caused by the electroosmosis, a value of *R* higher than zero ($R(C_{12}-C_{18}) > 0\%$) suggests that the conversion of the C₁₂-C₁₈ into other kind of chemicals took place in the spiked kaolin. According to the literature, the organics might be oxidized at both the anode surface and near the particles surface, due to the in-situ redox reaction; although, to date, the real associated mechanisms are not totally clear. According to the literature, it is expected that numerous chemical radicals (such as hydroxyl radicals (•OH)), generated on the clay particles and on the anode surface, might be involved on the degradation process [6]. Ideally, under oxidative conditions, the transformation of linear alkanes might first form carbonyl groups and some oxidized by-products, such as carboxylic acids, and then obtain CO₂ and water from the degradation of the latter, which are easier to oxidize [19].

Moreover, it was noted that the kaolin pH changed with respect to the initial values (pH° = 6) after the treatment. After 96 h, the pH was approximately 4.9, 6.0 and 7.7 in sections S1, S2 and S3, respectively (Table 1, entry 3). This behaviour is full in line with the literature and might be imputed to the electrolysis of water because the used cell potential (2.5 V) is appropriate to initiate this reaction. Under a constant *E* imposed to a moist low-hydraulic permeability kaolin, water electrolysis

is expected to be the main reaction at the electrodes, producing protons at the anode and hydroxylic ions at the cathode [20]. This results in a change of the mineral pH and might affect the sorption, dissociation and conversion of organics presents in the mineral. According to Ossai et al. [7], several chemical transformations involved in degradation of petroleum hydrocarbons allows to reduce the pollutants content by converting them into other chemicals by hydrolysis (which is catalysed by the in-situ generated protons or hydroxylic ions) and redox reaction.

The lower content of C₁₂-C₁₈ at the end of the electrochemical treatment might be caused by volatilization. For the sake of comparison, a control test without the application of the gradient *E* through the kaolin was carried out and a negligible change of the C₁₂-C₁₈ content was recorded after 96 h, thus highlighting that volatilization can be ignored. Moreover, under the adopted operative condition of 0.25 V cm⁻¹, a current of 0.180 ± 0.015 mA was recorded and, in line with the literature, the variation of the clay-bed temperature can be neglected [10,21,22].

These outcomes confirm that the electrochemical remediation under low *E* value (0.25 V cm⁻¹) might be a suitable way to, at the same time, mobilize and degrade alkanes from the kaolin. According to these results, various experiments were performed with the purpose to enhance the removal efficiency of alkanes from the kaolin.

3.2. Effect of electric field values

A set of electrochemical treatments was planned with the aim to study the effect of the intensity of the *E* value on the process performances. Electrolyses were carried out applying a constant gradient of *E* both in the typical range of the ECGO process (approximately 0.05 - 0.25 V cm⁻¹) and higher values up to 2.00 V cm⁻¹, which are commonly used for the EK treatment, for 96 h using Cell I. Fig. 3A-E report the effect of the *E* strength on the concentration of each C₁₂-C₁₈ contaminant. In the case of C12 (Fig. 3A), it was observed that the usage of *E* values lower than 0.25 V cm⁻¹ resulted in higher residual amounts of C12 in the different sections of treated kaolin coupled with a lower total C12 removal, *R*(C12). More in detail, under both 0.05 and 0.15 V cm⁻¹, an accumulation of C12 in the region S2 was observed and the reduction of *E* from 0.25 to 0.15 and 0.05 V cm⁻¹ decreased the *R* (C12) from 78 to 58% and 34%, respectively. Conversely, when *E* was increased at value higher than or equal to 0.375 V cm⁻¹, no C12 was detected in almost all the cases. A similar effect of *E* on *R*(C_{*i*}) was found for the other organics. Indeed, the higher the induced *E*, the higher the *R* for all investigated alkanes even if a plateau value is reached in most of cases. Although, for long chain alkanes, a lower abatement was achieved for the same value of *E*. As an example, for C13, a *R*(C13) efficiency higher than 90% was achieved at *E* equal to or higher than 0.375 V cm⁻¹ (Fig. 3B), while for C18 removals higher than 60% were obtained for *E* ≥ 0.50 V cm⁻¹ (Fig. 3E).

Fig. 3F reports the total *R* of the mixture C₁₂-C₁₈: *R*(C₁₂-C₁₈)

Table 1
Effect of the *E* strength on the pH, electric current (*I*) and the energetic consumption (EC)^a.

Entry	Technology	Processing fluids	Supporting electrolyte	<i>E</i> (V cm ⁻¹)	pH			<i>I</i> (mA)	EC (kWh g ⁻¹)	EC (kWh/C ₁₂ -C ₁₈ removed) ^b
					S1	S2	S3			
1	Cell I	-	-	0.050	5.25	5.95	6.15	0.004	4.8 × 10 ⁻³	1.9 × 10 ⁻³
2	Cell I	-	-	0.150	5.00	5.90	6.50	0.054	0.19	0.04
3	Cell I	-	-	0.250	4.90	6.00	7.70	0.18	1.08	0.22
4	Cell I	-	-	0.375	3.60	4.90	7.75	0.37	3.33	0.43
5	Cell I	-	-	0.50	3.20	5.50	9.50	0.54	6.48	0.74
6	Cell I	-	-	0.75	2.70	6.45	8.60	0.98	17.6	1.96
7	Cell I	-	-	1.00	2.50	5.40	7.60	1.73	41.5	4.45
8	Cell I	-	-	2.00	2.45	4.80	6.70	3.50	168	18.5
9	Cell II	DW	-	1.00	1.90	6.50	11.4	1.30	20.8	4.63
10	Cell I	-	NaCl	0.375	1.90	9.90	12.2	4.90	44.1	4.25

[a] Electrochemical treatments were performed by using compact graphite electrodes for 96 h. DW: Deionized Water.

[b] C₁₂-C₁₈ removed is the mass of C₁₂-C₁₈ removed per kg of treated kaolin (mg Kg⁻¹).

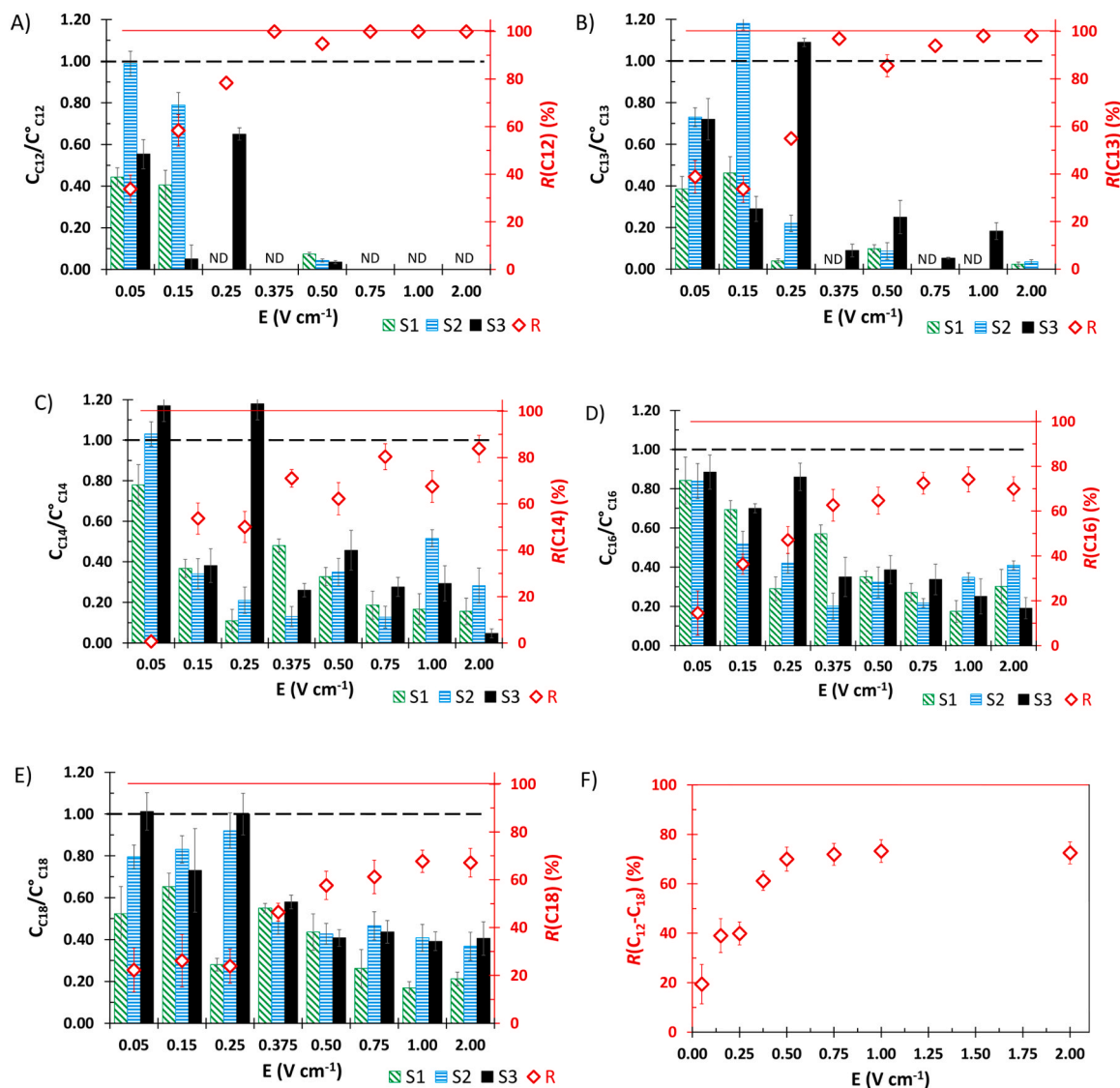


Fig. 3. Effect of E strength on the C_i/C° in the regions S1, S2 and S3 (primary y-axis) and total removal, $R(C_i)$, from the kaolin (secondary y-axis) of each contaminant (A) C12, (B) C13, (C) C14, (D) C16, (E) C18. (F) Effect of E strength on the removal of the mixture C_{12-C18} from the kaolin $R(C_{12-C18})$. Black dashed line (— — —) marks C_i/C° equal to 1 (at the time zero of treatment) (primary y-axis). Red solid line marks the 100% of R (secondary y-axis). Compact graphite electrodes. Time: 96 h. ND: Not detected. Electrochemical cell: I.

increases almost proportionally from $19 \pm 7.0\%$ to $70 \pm 4.8\%$ enhancing the induced E value from 0.05 to 0.50 V cm^{-1} , respectively; while a further increase of E at values higher than 0.50 V cm^{-1} does not improve the removal efficiency (i.e., $R(C_{12-C18})$ reaches a constant values of approximately 72% in the range $0.75 - 2.00 \text{ V cm}^{-1}$). Hence, in line with these results, it should be economically convenient operate at values lower than or equal to 0.50 V cm^{-1} , since higher E values allow to reach almost the same R efficiency coupled with higher energetic consumption (EC) due to the high applied cell potential (EC: 6.5 vs. 168 kWh g^{-1} at 0.75 vs. 2.00 V cm^{-1} , respectively, Table 1). The observed effect at low E values can be rationalized by considering that the higher the induced E values in the range $0.05 - 0.50 \text{ V cm}^{-1}$, the higher the electric current (Table 1, entries 1–5), the higher the driving force of the involved electrochemical reactions, which might lead to a faster production of chemical radicals and/or oxidant and as a consequence a faster removal of the C_{12-C18} alkanes. However, at E values higher than 0.5 V cm^{-1} , the electric current increases almost proportionally with the induced E (Table 1, entries 7–9), while the removal of alkanes reaches a plateau value (Fig. 3F) which is also coupled to higher EC.

It might not be excluded that this trend may be related also to the

effect of E on the kaolin pH change. The electrodes polarization generates hydrogen and hydroxylic ions near the anode and cathode side, respectively [23]. It was observed that, in the range between 0.05 and 0.50 V cm^{-1} , the pH value decreased progressively from 5.35 to 3.20 in the section S1 and increased from 6.15 to 9.50 in the section S3 by enhancing the induced E value from 0.05 to 0.50 V cm^{-1} , respectively, (Table 1, entries 1–5). At 0.5 V cm^{-1} , the most significant difference of pH in the sections S1, S2 and S3 (pH: 3.20 , 5.50 and 9.50 , respectively - Table 1, entry 5) was observed. Under values of E higher than 0.5 V cm^{-1} , the pH near to the anode continues to decrease with the E value (i.e., in the section S1, pH of 2.70 , 2.50 and 2.45 at 0.75 , 1.00 and 2.00 V cm^{-1}); while near to the cathode the measured pH slightly decreases (i.e., in the section S3, pH of 8.60 , 7.60 and 6.70 at 0.75 , 1.00 and 2.00 V cm^{-1}) (Table 1, entries 6–8). In the middle section S2, the pH did not relevantly change (Table 1). According to the literature, the acid front produced at the anode is moved to the cathode side via electroosmosis and electromigration [24]; conversely, the hydroxylic ions produced at the cathode moved to the anode side via electromigration, in opposition to the electroosmosis flow. Moreover, the mobility of the protons through the clayed bed is higher than the hydroxyl ions [24].

Hence, it is plausible to suppose that in the range $0.05 - 0.50 \text{ V cm}^{-1}$, at higher E , the higher electrical current accelerates the electromigration of the ions through the sediments, thus determining a lower pH in section S1 and a higher pH in section S3; while under relatively high value of E higher than or equal to 0.75 V cm^{-1} , the higher mobility of the protons coupled with the very high electromigration transport allows the protons to mitigate the pH value also in the section S3 (indeed, the pH values decrease always with the E (Table 1, column pH S1, entries 1–8)).

3.3. Comparison of two different electrochemical technologies

The current literature reports the usage of several technologies for the contaminated soil and sediments electrochemical remediation. Although a large number of apparatuses are reported, it is possible to identify two common systems: *i)* one in which the E is induced by one or more pairs of electrodes placed directly inside the soil (here namely *Cell I*) and *ii)* the other where the electrodes are placed inside a pair of external electrolyte compartments (in which a processing fluid is used) (namely *Cell II*). Hence, with the aim to compare these technologies, a series of experiments was performed under 1 V cm^{-1} for 96 h using *Cell I* and *Cell II*. The coupling of the induced E value of 1 V cm^{-1} and the usage of the configuration of *Cell II* represents the conventional operative conditions for EK treatments of polluted sites. Fig. 4 reports the C_i/C_i° of each contaminant in the sections S1, S2 and S3 and the total $R(C_{12}-C_{18})$ efficiency. After 96 h, as previously described, in the case of *Cell I*, the C_i/C_i° of C12 and C13 were approximately zero ($R(C_i) \sim 100\%$); while a residual amount of C14, C16 and C18 was detected in all the sections S1, S2 and S3. This was coupled with a total $R(C_{12}-C_{18})$ of approximately $73 \pm 3.7\%$. When the electrochemical treatment was performed by using *Cell II*, two external electrolyte compartments, containing the electrodes and deionized water as processing fluid, were placed and sealed adjacent the middle one where the spiked mineral was inserted. Using this configuration, a higher residual amount of all the compounds was observed with respect to the usage of *Cell I* (Fig. 4A). As an example, an appreciable amount of C12 and C13 were detected (i.e., C_i/C_i° was 0.36, 0.75 and 0.57 in the case of C12, and 0.64, 0.58 and 0.56 in the case of C13, in sections S1, S2 and S3, respectively, Fig. 4A). Hence, a lower $R(C_{12}-C_{18})$ ($54 \pm 5.0\%$) was observed with respect to *Cell I* (Fig. 4B).

Moreover, the use of *Cell I* gave a higher current of approximately 1.7 mA with respect to that recorded in the *Cell II* (1.3 mA) (Table 1, entries 7 and 9), which, according to the literature, can be attributed to the high electrical resistance of *Cell II* due to the presence of the physical barriers [25]. It was also observed a different change in pH kaolin. In the case of *Cell II*, a higher difference of pH among the three sections was recorded with respect to the usage of *Cell I* (Table 1, entries 7 and 9).

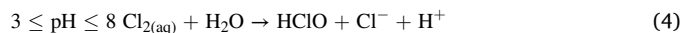
This effect might be attributed also to the lower electric current recorded in the case of *Cell II*, which reduces the driving force for the protons' migration to towards the cathode side.

The usage of *Cell I* at applicative scale could allow to prevent the production of a secondary dangerous effluent, generated from the extraction of organics in the external compartment of *Cell II*, and the additional costs for their disposal and treatment.

3.4. Effect of the presence of sodium chloride

According to the literature, electrochemical remediation's performances can be influenced by the usage of selected solutes, including Na_2SO_4 , KH_2PO_4 , NaCl, NaOH, acetic acid, citric acid [10,26–29].

Recently, it was demonstrated that the usage of NaCl for the treatment of kaolin polluted by phenol allowed to improve the efficiency of the process of 1.5 times respecting the usage of distillate water [10]. Here, electrochemical remediation of kaolin spiked with the mixture of $\text{C}_{12}-\text{C}_{18}$ was carried out in presence of NaCl (0.5 M) at 0.375 V cm^{-1} for 96 h in *Cell I*. Fig. 5 reports the comparison of the treatment performed without and with of NaCl. For each $\text{C}_{12}-\text{C}_{18}$ components, it was observed that, when NaCl was used, their residual amount in the kaolin was lower with respect to the treatment performed in absence of NaCl (Fig. 5 A), thus resulting in an increase of $R(\text{C}_{12}-\text{C}_{18})$ from 61 to 83% in absence and in presence of NaCl, respectively, (Fig. 5B). In particular, the presence of NaCl reduces the concentrations of the long chain compounds (e.g., C16, C18) that were more difficult to remove in the absence of the electrolyte. According to the literature, when an aqueous solution of NaCl is used under oxidative condition, at the electrode surface and on the kaolin particles the generation of active chlorines can be promoted following the reactions (3)–(5) [10,30], as a function of the pH media, and they might assist the conversion of $\text{C}_{12}-\text{C}_{18}$ mixture to other chemicals or lead to the total mineralization.



From the comparison of the distribution of each contaminant along the different sections S1, S2 and S3 in absence and in presence of NaCl (Fig. 5 A), it was observed that, except in the cases of C12 and C13, the residual concentration of the pollutants was highest in the section S1 and gradually decrease in section S2 and S3 (e.g. in the case of C18, C_i/C_i° was 0.55, 0.48 and 0.58 in S1, S2 and S3, respectively, using only water, and 0.44, 0.34 and 0.18 in S1, S2 and S3, respectively, using NaCl). To rationalize these results, it is highly to note the change in pH in presence of NaCl. The sections S2 and S3 were characterized by a very basic

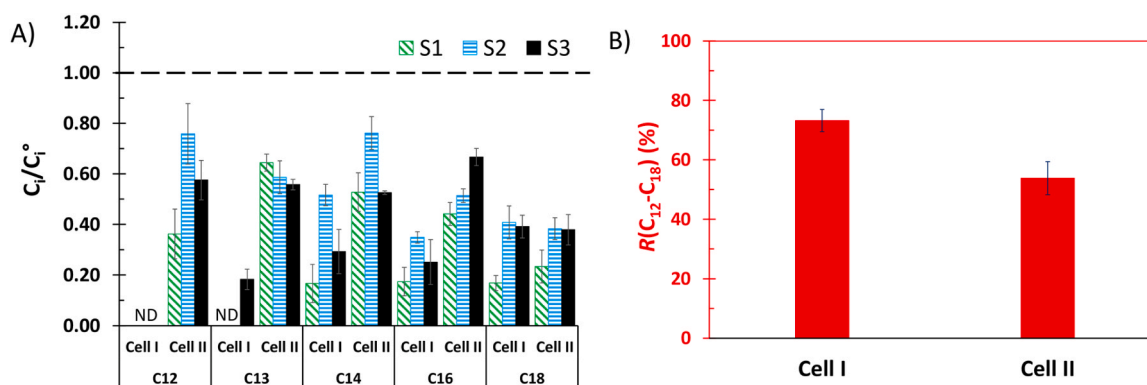


Fig. 4. Comparison of two technologies on the (A) C_i/C_i° of each contaminant C12, C13, C14, C16, C18 in the regions S1, S2 and S3 and (B) total removal of the mixture $\text{C}_{12}-\text{C}_{18}$ from the kaolin, $R(\text{C}_{12}-\text{C}_{18})$. Black dashed line (— — —) marks C_i/C_i° equal to 1. Red solid line marks the 100% of R . Electrochemical treatment was carried out at 1 V cm^{-1} using graphite electrodes for 96 h. ND: Not detected. Electrochemical cells: *Cell I* where the electrodes were directly inserted inside the spiked-kaolin, and *Cell II* where the electrodes were placed into the two external processing compartments adjacent to the middle kaolin compartment.

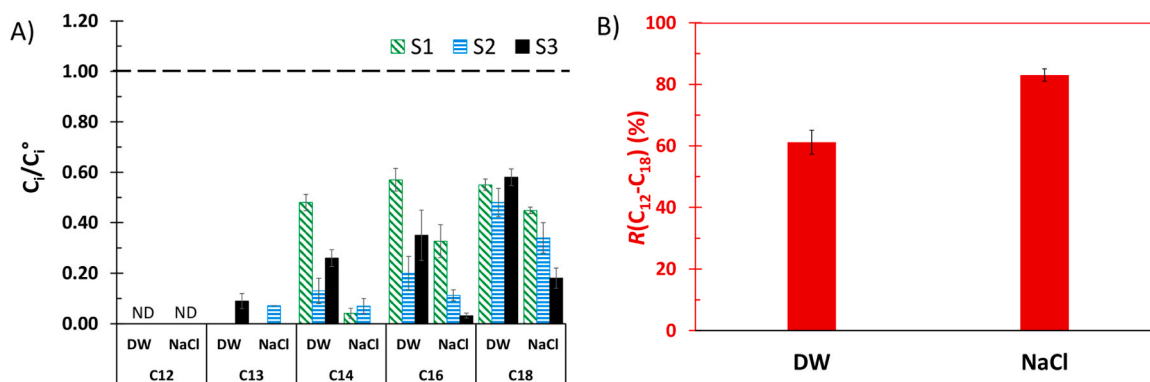


Fig. 5. (A) Plot of C_i/C_i^0 for the different contaminants C12, C13, C14, C16 and C18 in the regions S1, S2 and S3 and (B) total removal of the mixture $C_{12}-C_{18}$, $R(C_{12}-C_{18})$, from the kaolin in the absence (DW) and in presence (NaCl) of sodium chloride. In Fig. A the black dashed line (— — —) marks C_i/C_i^0 equal to 1 (at the time zero of treatment). 0.5 M NaCl. Compact graphite electrodes. Time: 96 h. ND: Not detected. Electrochemical cell: I.

environments (Table 1, entry 10), hence, according to reaction (5), a very relevant amount of active chlorine is expected in these areas of the treated kaolin, which might take part in the electrochemical remediation of the spiked $C_{12}-C_{18}$ kaolin. This hypothesis was confirmed by the presence of ClO^- in section S2 and S3 (qualitative analysis by UV–vis spectroscopy) and the absence of active chlorine in section S1 (very low pH, only Cl_2 is expected). The presence of active chlorine in the kaolin samples after the treatment can be attributed to the oxidation of chloride. Overall, in presence of NaCl, $C_{12}-C_{18}$ alkanes can be oxidized by several oxidants, including oxychloro and adsorbed chloro radicals at the anode surface and active chlorine and/or various reactive oxygen species generated by water oxidation at both the surface of the anode and the particles.

Moreover, when NaCl is added, the conductivity of the clayed medium is expected to be higher than the use of only water due to the presence of free ions; this allows to significantly enhance the current intensity (from 0.370 to 4.90 mA in the absence and presence of NaCl, respectively) and, therefore, speed up the remediation process. Although, a relevant increase of the EC was observed (compare entries 4 and 10 in Table 1).

4. Conclusions

Electrochemical remediation of kaolin artificially contaminated by a mixture of five alkanes ($C_{12}H_{26}$, $C_{13}H_{28}$, $C_{14}H_{30}$, $C_{16}H_{34}$, $C_{18}H_{38}$), namely $C_{12}-C_{18}$, was investigated. The effect of several operative conditions, including the induced E value, the type of technology and the presence of a supporting electrolyte, was explored. The performances of the process were discussed in terms of the normalized residual concentration of each $C_{12}-C_{18}$ contaminant (C/C^0) and the total $C_{12}-C_{18}$ removal efficiency, $R(C_{12}-C_{18})$, from the treated kaolin after 96 h. Compact graphite was used for electrode materials.

It was observed that the total $R(C_{12}-C_{18})$ efficiency is significantly affected by the induced E value. In the range of E between 0.05 and 0.50 $V\ cm^{-1}$, the higher the induced E , the higher the $R(C_{12}-C_{18})$ (i.e., $R(C_{12}-C_{18})$ increases from 19 to 70% by enhancing the E from 0.05 to 0.50 $V\ cm^{-1}$). A further increase of the induced E to higher value than 0.5 $V\ cm^{-1}$ does not give relevant changes on the $R(C_{12}-C_{18})$, which reach a plateau value. Moreover, at a constant value of E , the shorter the carbon chain compounds, the higher the removal efficacy: $C_{12} > C_{13} > C_{14} > C_{16} > C_{18}$. As an example, a $R(C_i)$ efficiency of approximately 78%, 55%, 50%, 47% and 24% in the case of C12, C13, C14, C16 and C18, respectively, was reached under 0.25 $V\ cm^{-1}$.

The addition of chloride ions into the kaolin allows to relevantly improve the performances of the process. In the presence of NaCl, the residual amount of each $C_{12}-C_{18}$ in the kaolin was lower with respect to that recorded in the absence of NaCl, thus resulting in an increase of R

($C_{12}-C_{18}$) from 61 to 83%. Moreover, in this case, also a high reduction of the concentrations of the long chain compounds (e.g., C16 and C18) was observed. This might be attributed to the synergetic effect of the anodic oxidation at the anode and the indirect oxidation due to the production in situ of reactive oxygen species and active chloride.

In addition, two electrochemical configuration cells (*Cell I*, in which the electrodes were directly inserted into the kaolin, and *Cell II*, where the electrodes were placed adjacent to the kaolin inside two external electrolytic chamber), were compared for the remediation of the artificially spiked $C_{12}-C_{18}$ kaolin under 1 $V\ cm^{-1}$ for 96 h using compact graphite as electrodes. The results shown that when the electrodes where inserted in contact with the kaolin higher removal of organics were reached. Moreover, the configuration in which the electrodes are directly inserted into the kaolin (*Cell I*) allows to avoid the production of a secondary effluent, saving money from its safe disposal and treatment as dangerous waste.

CRediT authorship contribution statement

Federica Proietto: Methodology, Visualization, Conceptualization, Investigation, Data curation, Writing – original draft – review & editing; **Paola Meli:** Data curation, Investigation; **Claudia Prestigiacomo:** Data curation, Formal analysis; **Alessandro Galia:** Funding acquisition, Writing – review & editing. **Onofrio Scialdone:** Supervision, Writing – review & editing, Funding acquisition.

Declaration of Competing Interest

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.

Data Availability

Data will be made available on request.

Acknowledgments

FFR- 2023 University of Palermo and Marine Hazard project 416 (PON03PE_00203_1) are acknowledged for the financial support.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jece.2023.111780](https://doi.org/10.1016/j.jece.2023.111780).

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