



Electrochemical remediation of synthetic and real marine sediments contaminated by PAHs, Hg and As under low electric field values

Federica Proietto^{a,*}, Fabio D'Agostino^b, Maria Bonsignore^b, Marianna Del Core^b, Mario Sprovieri^c, Alessandro Galia^a, Onofrio Scialdona^a

^a Dipartimento di Ingegneria, Università Degli Studi di Palermo, Viale delle Scienze, Ed. 6, Palermo, 90128, Italy

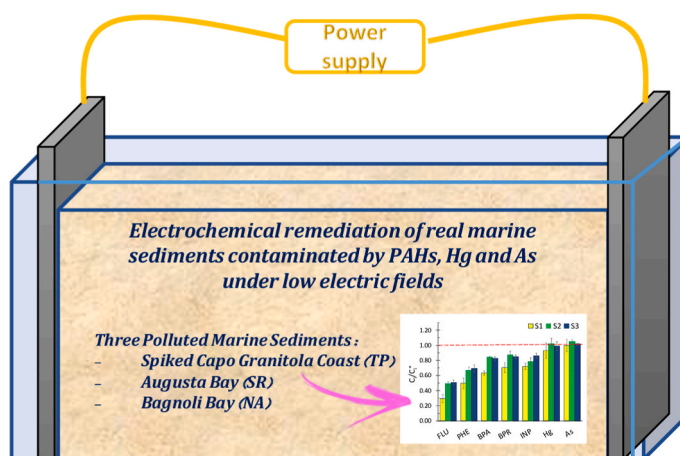
^b Istituto per lo Studio Degli Impatti Antropici e Sostenibilità in Ambiente Marino (IAS-CNR), Via del Mare 3, Torretta Granitola, TP, 91021, Italy

^c Istituto di Scienze Marine (ISMAR - CNR), Venezia Consiglio Nazionale delle ricerche, Venezia (Tesa 104 - Arsenale, Castello 2737/F 30122), Italy

HIGHLIGHTS

- Electrochemical remediation of real polluted marine sediments at low electric fields.
- Low electric fields allowed to simultaneously desorb, mobilize and degrade PAHs.
- Low electric fields are not appropriate for the remediation of Hg and As.

GRAPHICAL ABSTRACT



ARTICLE INFO

Handling Editor: Thamaraiselvi Kaliannan, Ph. D

Keywords:

Electrochemical remediation
Electrokinetic
Electrochemical GeoOxidation
Marine sediments
PAHs
Heavy metals

ABSTRACT

To date, remediation, protection, and restoration of contaminated sites is a global concern. The current technologies to restore sediments characterized by heterogeneous characteristics, several pollutants, fine grains, and low hydraulic permeability are poorly effective; hence their remediation is still challenging. A promising approach for the sediment's remediation could be the electrochemical route since it is a not-expensive, effective and noninvasive in situ technology. Electrochemical remediation (ER) is commonly studied under relatively high electric fields ($E \geq 1 \text{ V cm}^{-1}$) and using costly processing fluids in a three compartments cell aiming to desorb and transport the contaminants into the processing fluids (secondary dangerous effluent). In this work, contaminated marine sediments were electrochemically treated focusing on the insertion of electrodes directly in the sediments and adopting, for the first time for real sediments, low E values ($\leq 0.25 \text{ V cm}^{-1}$) for 4-days period. It was observed that PAHs can be simultaneously transported and degraded in situ preventing the production of a secondary dangerous effluent and reducing the energy consumption. Firstly, clay marine sediments dragged from

* Corresponding author.

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

<https://doi.org/10.1016/j.chemosphere.2023.141009>

Received 29 July 2023; Received in revised form 30 November 2023; Accepted 19 December 2023

Available online 21 December 2023

0045-6535/© 2023 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

Capo Granitola Coast (Trapani, Italy) spiked with five PAHs congeners (5PAHs), Hg and As were used as a simplified model matrix and treated to simulate a real case study. A total PAHs removal efficiency of 57% was reached after 96 h of treatment under 0.05 V cm^{-1} . Then, real polluted marine sediments from Augusta Bay (Syracuse) and Bagnoli-Coroglio Bay (Naples) in the southern Italy were treated as real contaminated sediments to be restored, to validate the proposed approach for real cases. A quite good removal efficiency of PAHs was reached after 96 h of electrochemical treatment coupled with a low energetic consumption due to the rather E values adopted. In addition, it was observed that this approach, under the adopted conditions, is unsuitable for the remediation of Hg and As.

1. Introduction

Over the last decades, the contamination of marine sediments due to human actions has been one of the most pressing environmental problems. Many polluted sites worldwide are present because of improper management and accidental spills of dangerous chemicals (Chen et al., 2018; Gereslassie et al., 2019; Huysegoms and Cappuyns, 2017; Ronchi et al., 2019; Song et al., 2018). Based on the pollutants in the environmental matrices, the Italian government has identified 39 Sites of National Interest (SIN) (MATTM, DM 2013), namely areas requiring immediate restoration due to the high level of dangerous pollutants, including Pb, As, Hg, and recalcitrant hydrocarbons, such as Polycyclic Aromatic Hydrocarbon (PAHs). As an example, marine sediments of the Bagnoli-Coroglio Bay (Naples) and Augusta Bay (Syracuse) were identified as SIN due to the severe state of pollution caused by almost 140 years of industrial exploitation (including production of cement, steel and fertilizers, chlor-alkali plant, crude oil refining) (Armiento et al., 2022; Buccino et al., 2022; Romano et al., 2018, 2021). To date, handling actions for polluted marine sediments include low-efficiency techniques requiring treatments with serious impact on the environment, need a long time, and are expensive. Moreover, currently used technologies are extremely invasive, leading to a low-level of a social and environmental sustainability (Rosestolato et al., 2015). For example, phytoremediation treatments require extremely long remediation time, due to the slow hyperaccumulation process for the removal of contaminants, which is unsuitable for the applicative scale (Han et al., 2012; Muscetta et al., 2023). In bioremediation, there is a low mobility of the microorganisms, and their metabolism can be inhibited by the pollutants' toxicity. In leaching, a huge amount of secondary pollution is generated, which must be disposed and treated properly (Han et al., 2012).

Among the other strategies, a prominent approach to remediate such contaminate sites characterized by low-hydraulic permeability, fine grains, heterogeneous conditions and miscellaneous of pollutants (Sharma and Reddy, 2004) is the electrochemical technology (Reddy and Cameselle, 2009). Electrochemical remediation (ER) presents singular benefits (Acar and Alshawabkeh, 1993; Reddy and Cameselle, 2009; Zanko et al., 2020) including:

- adaptable technology as *ex-situ* or *in-situ* method to transport and/or convert or extract contaminants which are difficult to recovery by other means;
- environmentally friendly methods which avoid the usage of not ecofriendly solvents or enhancing agents;
- manageable design and application in real polluted sites the field;
- simple integration with other process, versatility, noninvasive technology and amenability to automation;
- low-cost for the simple needed equipment and could allow to mineralize organics with lower power costs with respect to conventional methods.

Moreover, empirical evidence reveals that traditional remediation techniques, including chemical oxidation or soil flushing, are poor effective in low permeability soils and sediments because of their low permeability and their high sorption capacity (Ferrarese and

Andreottola, 2010). ER technologies are adaptable and practicable for various pollutants and sediments/soils, mainly for low-hydraulic permeability clays enclosing adsorbed and/or solubilized chemicals (Saini et al., 2021).

A difference of potential between two or more electrodes was used in the ER to induce a gradient electric field (E) in the polluted sites. Under gradient E , electroosmosis, electromigration, electrophoresis (motion of water, ions, and charged particles, respectively) and redox reactions were induced into the sediments (Acar and Alshawabkeh, 1993; Reddy and Cameselle, 2009; Zanko et al., 2020). In the case of electrokinetic (EK) under low values E (namely also electrochemical geo-oxidation (ECGO) or EK at low potentials) ($0.0025 < E < 0.25 \text{ V cm}^{-1}$) other than these four mechanisms involved in the high relatively E ($\geq 1 \text{ V cm}^{-1}$) (Malarbì et al., 2015; Wen et al., 2021), an additional degradation mechanism was observed, via redox reactions at the micro-scale (Reddy and Cameselle, 2009; Zanko et al., 2020). Even if, the mechanism of this last route was not completely clarified, it was demonstrated that under suitable conditions, the use of low E values can increase the mineralization of organics in the soil (Proietto et al., 2023; Zanko et al., 2020). Particles of soil would serve as 'micro-conductors' and moist soil as a 'diluted' electrochemical solid bed reactor, where redox reactions might be promoted on or near the particles of the soil (Rahner et al., 2002; Röhrs et al., 2002), theoretically leading to the conversion of part of organic pollutants to CO_2 and water near the conducting surface of the particles (Sharma and Reddy, 2004; Zanko et al., 2020).

The mobility of PAHs and heavy metals in low-hydraulic permeability sites is typically low, resulting in low-rate processes remediation. Several authors investigated the removal of these contaminants (Alcántara et al., 2008; Ammami et al., 2014; Colacicco et al., 2010; Falciglia et al., 2017; Iannelli et al., 2015; Lofrano et al., 2017; Malarbì et al., 2015; Pazos et al., 2010; Wang et al., 2012) aiming to transport the contaminants from the sediments towards the external compartments under a relatively higher E ($\geq 1 \text{ V cm}^{-1}$). Among these authors, Falciglia et al. (2017) reported relevant results. This work reveals that the simultaneous use of an anolyte based on MGDA and Tween 80, as enhancing agents, under 1.2 V cm^{-1} for 240 h resulted in a removal of both Hg and total PAHs up to approximately 60% using stainless steel as electrodes.

Up to our knowledge, the ER of marine sediments from recalcitrant organic pollutants (e.g., PAHs) using low values of E (i.e., $< 0.25 \text{ V cm}^{-1}$) was explored mostly assisted by microbial activities (Chen et al., 2021; Huang et al., 2011; Li et al., 2017; Wu et al., 2018). Recently, a successful demonstration of the ECGO with a high removal efficiency was reported by Zanko et al. (2020) for the treatment of polychlorinated biphenyls polluted sediments from the New Bedford Harbor (Massachusetts) for approximately 1900 days. Moreover, EK/EGCO technology was investigated by Hsueh et al. (2022), also, for the treatment of metal-polluted soils (i.e., Cr/Ni) under different operative conditions (such as E gradient, process' electrolyte and electrodes). More recently, Proietto et al. (2023) studied the ER of spiked kaolin with phenol using extremely low gradient E values ($\leq 0.25 \text{ V cm}^{-1}$). According to that work, the proposed approach can desorb, mobilize and, also, in-situ degrade the contaminant with a total removal of up to 90% at 0.15 V cm^{-1} in the presence of Na_2SO_4 into the kaolin and using compact graphite's electrodes.

ER is commonly studied under relatively high electric fields ($E \geq 1 \text{ V cm}^{-1}$) and using costly processing fluids in a three compartments system aiming to desorb and transport the contaminants into the processing fluids, producing a secondary dangerous effluent which must be treated and disposed properly. Here, polluted marine sediments were electrochemically treated focusing on the insertion of electrodes directly in the sediments and adopting low E values (less than 0.25 V cm^{-1}) for 4-days period for the first time for real sediments. This approach allows to avoid the generation of a secondary effluent and minimizes the energetic consumption due to the low involved current. Also, more conventional operative conditions, such as E of 1 V cm^{-1} and the presence of electrode compartments and electrolyte solutions, were used for the sake of comparison. In the first stage, a simplified model matrix to simulate real marine sediments was used. This model matrix consists of marine sediments dragged in the Capo Granitola Bay (Sicily region) spiked with proper synthetic mixtures of five PAH congeners (Fluorene - FLU, Phenanthrene - PHE, Benz(a)pyrene - BAP, Benzo(ghi)perylene - BPR, Indeno(123cd)pyrene - INP), named 5PAHs, and two heavy metals, i.e. Hg and As (CG-spiked). Hence, the effect of the ER under low values of E on the performances of the treatment was explored and analyzed regarding the distribution of each i -pollutant (C_i/C°_i) and its total removal (R) from the sediments. Afterwards, to validate this approach in a real context, two real polluted model sites were electrochemically treated using a very low value of E . Real marine sediments dragged in the Augusta Bay (characterized by relevant organics and Hg) and Bagnoli-Coroglio Bay (characterized by relevant amounts of organics and As) were used.

2. Material and methods

2.1. Chemicals

To set the moisture of the model marine sediments water HPLC grade (Sigma Aldrich) was used. A mix of sixteen PAH congeners (acenaphthylene, naphthalene, fluorene, acenaphthene, phenanthrene, anthracene, pyrene, fluoranthene, chrysene, benzo(a)anthracene, benzo(k)fluoranthene, benzo(a)pyrene, benzo(b)fluoranthene, indeno(123cd)pyrene, benzo(ghi)perylene and dibenz(a,h)anthracene), and a mix of deuterated PAHs (AcenaphthyleneD8, PyreneD10, Benzo(a)pyreneD12) were used to fine-tune the GC/MS. A mix of five PAH congeners was realized *ad-hoc* in acetone, mainly Fluorene (FLU), Phenanthrene (PHE), Benzo(a)Pyrene (BPA), Benzo(ghi)Perylene (BPR), Indeno(123cd)Perylene (INP), named 5PAHs and used to spike the sediment sample and as a hazardous model for organic compounds, and two heavy metals, i.e. Hg (supplied by Carlo Erba) and As (supplied by Fisher Scientific), as model inorganic persistent pollutants.

Acetone (HPLC grade, Sigma Aldrich), and hexane (Pesticides grade, Sigma Aldrich) were used to extract PAHs from the sediment samples. Compact graphite (supplied by Carlo Erba-Reagents) was used as electrode material.

2.2. Marine sediments: sampling and characterization

Clean clay marine sediments from Capo Granitola Coast, CG, (western Sicily, N $37^\circ 33.895'$, E $12^\circ 39.626'$ and N $37^\circ 30.941'$, E $12^\circ 33.263'$), Italy, were used to be artificially contaminated with 5PAHs, Hg and As.

Real polluted marine sediments from Augusta Bay (Syracuse, southern Italy, N $37^\circ 12.244'$, E $15^\circ 11.175'$) and Bagnoli-Coroglio (Naples, southern Italy, N $40^\circ 48.691'$, E $14^\circ 09.755'$) were selected and used for their well-known contamination. After being dragged, real marine sediments were stored in a freezer for six months before their characterization.

2.2.1. Spiking of clean marine sediments

Spiking of real and clean marine sediment was carried out following

the OECD Guidelines (OECD, 2007). About 500 g of clean sediments (CG) were artificially contaminated with 3 mL of 1000 mg/L of Hg(II) (standard for ICP/MS, CAS N. 10,045-94-0, supplied by Carlo Erba) and 45 mL of 1000 mg/L of As(V) (purity 99,9%, supplied by Fisher Scientific) standard solutions, respectively. After 2 h of homogenisation in a rotary vapor balloon, the sediment under vacuum was dried. After that, 3 mL of 5PAHs mixture with a concentration of 1000 mg/L per each component was added. Following the previous procedure, after the homogenisation in a vapor balloon, the sediment was dried under vacuum.

Finally, this aliquot of 500 g of spiked sediment was mixed with another 2.5 Kg of the same sediment and homogenised for 24 h in a 10 L closed rotary tank bottle. These spiked sediments were named "spiked-CG". The artificially dried sediment samples were stored for 6 months at 4°C to maximize the contaminants—sediments interactions. Therefore, the moisture content of the CG-spiked was fixed at approximately 50%, to be close to the real marine sediments.

2.2.2. Grain size method

Horiba Partica LA-950V2 laser particle size analyzer was used to determine the grain size of Capo Granitola and Augusta samples. Data were subsequently processed using the HORIBA LA950 V. 5.20 software for Windows, which calculates statistical parameters and reconstructs the grain size distribution curves.

Bagnoli sediments were analyzed using a mechanical vibrating shaker and an ASTM sieve stack at half-phi intervals $\phi/2$, with apertures ranging from 2 mm (-1ϕ) to $63 \mu\text{m}$ (4ϕ). Data samples were elaborated with the "Fritsch Particle Sizer AUTOSIEB/A20" software.

Geometric Wentworth classification (Wentworth, 1922) was used to categorize all the samples (logarithmic transformation (φ scale) with limits expressed in ϕ ($\phi = -\log 2d$, d is the grain diameter, mm)), according to the scale proposed by Krumbein (1934). Six independent replicate tests were performed for the grain size characterization of the sediments.

2.2.3. Heavy metals determinations

For total Hg measurements an aliquot of $\sim 0.05 \text{ g}$ of dry sediments was loaded in nickel boats and directly transferred into the DMA 80 (Milestone_DMA-80 Tricell, Wesleyan University, Middletown, CT, USA) and analyzed following the US-EPA (7473) method.

As determination in sediment was carried out using ICP/MS. The analyses were performed by previous microwave-assisted digestion of 0.25 g of sediment (dried at 35°C) with an acid mixture of concentrated HNO_3 , HCl and HF and with a solution of HBO_3 (4%), nitric and hydrofluoric acids (EPA 3050b) and then according to EPA 6020 method. DISCOVER SP-D80 microwave oven (CEM Corporation) was used for the digestion of the mixture of acid and sample placed in a Teflon closed vessel (EPA 3052 EPA 3051A). Inductively Coupled Plasma with technologies in the Q Cell (by Thermo Fischer - iCAP-Q) was used for the quantitative determination of total dissolved metals. Quality control on Hg and As determination in sediment samples was carried out by analysing a Marine Sediment Certified Reference Material (PACS-3; NRCC, Canada) every ten samples to assess accuracy and precision (routinely) both for DMA-80 and ICP/MS instruments. Referring to Hg, accuracy and precision were estimated to be between 94 and 109% and less than 7% (RSD% on 5 replicates), respectively. Moreover, samples were analyzed in duplicate to evaluate the reproducibility of sediment samples ($<5\%$). Referring to As concentrations, the accuracy and precision within 94–106 % and less than 7% (RSD%, on 3 replicates), respectively, were estimated. Furthermore, duplicate samples were analyzed to estimate reproducibility (about 94%). To determine the heavy metals' initial concentration level (namely, C°_{Hg} and C°_{As}), ten aliquots of each sediment (CG-spiked, Augusta and Bagnoli) were measured.

2.2.4. PAHs determination

The concentration of PAHs of real marine sediments of Augusta Bay

and Bagnoli Bay was evaluated GC/MS. The concentration of the PAH congeners in surface sediment was performed using: a microwave probe a microwave probe (HD, 2070 SONOPULS get by Bandelin, Germany) at high-frequency sonication treatment with 20 kHz pulse frequency (activity 0.7 s (ON) – inactivity 0.3 s (OFF)) directly immersed in a glass test tube containing 0.5 g of dry sample and 3 mL of a mixture of hexane: acetone (80:20 v/v) for at least 10 min with an 80% of the power. Then a spoon of Na_2SO_4 anhydrous was added in the test tube, agitated with vortex for 1 min, and at the end, a solution was separated by sediment using a centrifuge at 3000 rpm.

The extracted solution was purified (EPA 3630C method) using SPE FLORISIL 200mg/3 mL cartridge, the eluted solution was dried by a multi-vapor (get by BUCHI), and the residual was re-dissolved in 1 mL of n-Hexane with $200 \mu\text{g mL}^{-1}$ of PAH-mix9 (internal standard deuterated). The detection of PAH was performed by GC/MS in SIM Mode, following the EPA 8270D method. GC was equipped with a DB5-MS (30 m \times 0.25 mm \times 0.5 μm) capillary column. The GC/MS was set as follows: injector in split-less mode; T = 280 °C; volume injected: 2 μL ; oven temperature T = 60 °C for 4 min, T = 270 °C at 10 °C min^{-1} (hold for 5 min), T = 340 °C at 20 °C min^{-1} (hold for 5 min).

The recovered contaminants achieved (>90%) were satisfactory for the aim of this work.

2.2.5. Moisture and organic content, specific gravity and pH

ASTM D2974-14 method was followed for the moisture and organic

matter determination, ASTM D854-92 method for the specific gravity Sediment pH (ratio sediment/water of 1:5) was measured by applying the ISO 10390:2021. Checker® pH Tester (HI98103) HANNA® instrument was used.

Soil buffering capacity measures the capacity of the solid to hold out an alteration in pH. The acid titration method was used to evaluate the acid buffering capacity. In particular, the initial pH of a suspension of sediment/water 1:5 was measured after a mixing by magnetic stirrer for 30 min. Then, the pH was measured after the addition of 1 mL of 0.1 M HCl every 60 min. This operation was iterated until the pH value was stable. Hence, pH values vs the amount of H^+ added per g of sediment ($\mu\text{mol g}^{-1}$) were plotted for four kinds of sediments: CG-spiked, Augusta, Bagnoli and kaolin (see Supporting Materials, Fig. S1). Data were discussed in qualitative form, by the comparison of the sediments with the kaolin (characterized by low acid buffering capacity).

2.3. Electrochemical treatment

Two electrochemical cells were used for the electrochemical treatment, i.e., system I (Fig. 1a) and system II (Fig. 1b), previously described by Proietto et al. (2023). Briefly, system I is a Plexiglass® cell with an empty volume of 60 mL. Graphite electrodes were inserted directly in contact with the sediments at an electrode distance of 10 cm. The working area of the electrodes was 3 cm^2 . To fill the cell, sediments were allocated inside the cell layer by layers, pressed and packed down to

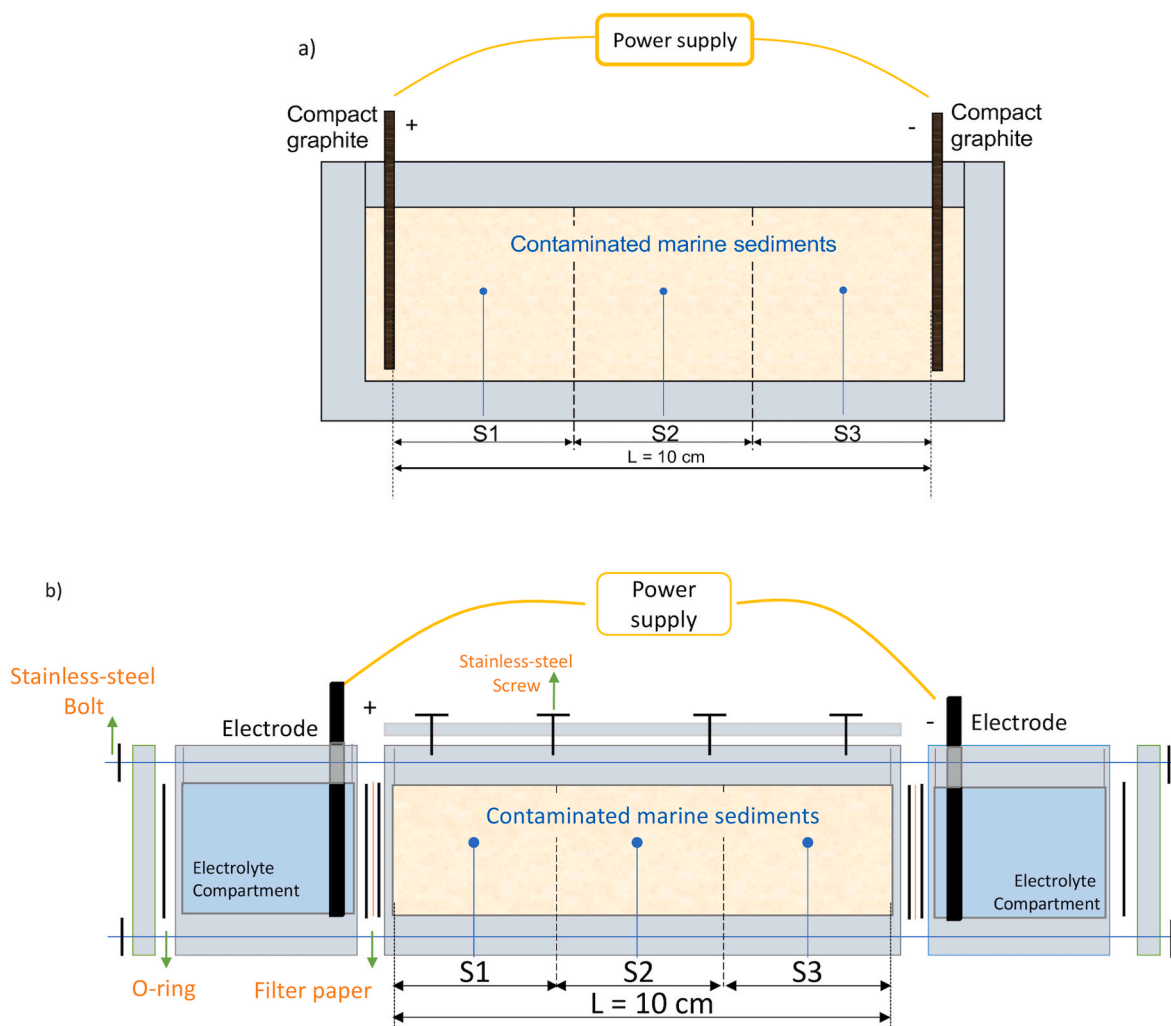


Fig. 1. a) System I: Illustrative ECGO cell for the electrochemical treatment under low E values. b) System II: Illustrative EK cell for the electrochemical treatment under 1 V cm^{-1} .

minimize void space for 12 h, as better described in Proietto et al. (2023). Plexiglass cover was used to prevent evaporation of water. 66 g of sediments was inserted in system I. At time zero, since a small amount of water and contaminants might be volatilized in the course of preparation, at least 3 sediment samples already placed in the cell were analyzed to check the initial contaminants concentration, moisture, and sediment pH. An Amel 2053 potentiostat/galvanostat was used to apply a constant direct E (range: 0.05–0.25 V cm⁻¹).

EK treatment under E of 1 V cm⁻¹ was performed using system II (Fig. 1b), in detail described by Proietto et al. (2023). The main difference with system I is that this configuration presents 3 compartments. Two of these are external compartments, where deionized water (30 mL) and graphite electrodes were placed, while the sediment (CG spiked: 100 g with W of 66%) was placed into the middle compartment. The working area of the electrodes was 4 cm² and placed very close to the sediment. The three compartments were separated by filter paper. To avoid water evaporation the middle compartment was sealed with a Plexiglass cover. AMEL 2549 potentiostats/galvanostat was used.

Electrolyses were performed over a 4-day period at ambient temperature and, at least, in duplicate to assure repeatability of the results. Moreover, blank tests (control) without the application of a gradient E were performed for comparison over a 4-day period. In the control test, approximately 94% of the initial PAHs were recuperated (which is consistent with this work's aim). Volatilization of PAHs and/or their adsorption to the ER apparatus (such as graphite, sample vials, and cells) may be the cause of the mass balance difference.

After 96 h, sediment samples were retained from three different sampling points, shown in Fig. 1 and namely S1 (near to the anode), S2 (in the middle) and S3 (near the cathode). Moisture, sediment pH and residual amount of sediment's contaminants were determinate following the procedure described in Section 2.2. Analyses were carried out three times and data were reported as the average of them.

2.4. Performances

At the end of the treatment, the distribution of the i -contaminant in the sediments along sections S1, S2 and S3 was analyzed considering the ratio between the final i -contaminant content (C_i) and the initial content (C_i^0). For each experiment, the C_i^0 was evaluated to certify the contaminants homogeneity distribution in the sediment by sampling sediment samples from each region S1, S2 and S3, drying and analysing them following the procedure reported in Section 2.2. At the zero time, it was found that the initial value concentration for all the contaminants was approximately to the fixed one $C_i/C_i^0 \sim 1 \pm 0.06$.

PAHs removal efficiency was calculated by eq. (1) (Falciglia et al., 2017).

$$R_{PAHs} = \frac{(C_{PAHs}^0 - C_{PAHs}^t)}{C_{PAHs}^0} * 100 [=] \% \quad (1)$$

In which C_{PAHs}^0 and C_{PAHs}^t are the initial content of PAHs (mg Kg⁻¹) and the residual PAHs after 96 h (mg Kg⁻¹) per all the g of dried treated sediments in the test.

Energetic consumption (EC) was evaluated according to eq. (2):

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

Where I is the intensity current (A), ΔV the applied cell potential (V), t treatment time (s) and w is total amount of dried sediments treated (Kg).

3. Results and discussion

In this work, clay marine sediments dragged from Capo Granitola Coast (Trapani, Italy) spiked with a certain amount of five PAHs congeners, namely 5PAHs, (i.e., FLU, PHE, BPA, BPR, INP), Hg and As were

first used as a simplified model matrix, namely CG-spiked, to simulate a real case study. Real marine sediments dragged from Augusta Bay (Syracuse, Italy) and Bagnoli-Coroglio Bay (Naples, Italy) were also used as models of real contaminated sediments to be restored.

In the first stage of this work, CG-spiked and real marine sediments from Augusta Bay and Bagnoli-Coroglio Bay were chemically and physically characterized. In the second stage, to evaluate the proposed approach (e.g., EK at low-strength electric fields) and find best operative conditions for the remediation of this kind of matrix, CG-spiked with 5PAHs sediments were treated under very low values of E . Finally, real marine sediments dragged from Augusta Bay and Bagnoli-Coroglio Bay were treated as models of real contaminated sediments to be restored, to validate this approach for real cases.

3.1. Characterization of the spiked and real marine sediments

Table 1 reports the chemical and physical characteristics of the selected three marine sediments. From the results of grain size examination, CG-spiked and Augusta sediments are mainly composed of silt and clay compounds (approximately 99.2 and 93.4%, respectively), while marine sediments from Bagnoli Bay are primarily consisting of sands (approximately 97.4%) (Table 1).

The Hg, As and PAHs quantification on sediment samples was carried out on ten replicates and was reported in Table 1. In the artificially contaminated CG sediments, the Hg concentration detected was consistent with the quantity added to the clean CG (about 1.17 mg kg⁻¹); conversely, the As level was greater than that added one (36.7 mg kg⁻¹) since it was already detected in the clean sediments before the contamination (Table 1). Hg concentration in real sediments of Augusta Bay was estimated to be approximately 9.00 mg kg⁻¹, which is over the content in the CG-spiked sediments. This relevant Hg level in Augusta sediments is related to chloro-alkali industrial activities. In the case of Bagnoli samples, a very high level of As was detected of approximately 95 mg_{As} Kg⁻¹, which was higher than that found in Augusta (17.4 mg_{Hg} Kg⁻¹) (Table 1). According to the international Sediments' Quality Standards (SQSS) (MacDonald et al., 2000), which can be used for both sea and freshwater (Muschetta et al., 2023), Hg in the case of Augusta and As in the case of Bagnoli exceeded all the threshold concentration (i.e., Threshold Effect Concentrations (TEC) and Probable Effect Concentration (PEC), see Table 1).

The amounts of PAH congeners added on CG-spiked were about 112, 353, 748, 1036, and 1036 µg kg⁻¹, respectively, for FLU, PHE, BAP, INP, and BPR. It was noted that the concentration of FLU and PHE were less than the expected value (1000 µg kg⁻¹). This low concentration was tentatively attributed to their more volatility than BAP, BPR and INP, and probably evaporated during the vacuum process with rotavapor used to dry sediments. The PAHs concentration level on Augusta sediment is lower than the TEC and PEC value (Table 1), while Bagnoli sediment shows concentration of different orders of magnitude more than the TEC and anyway value greater than PEC, showing the probable effect on live organisms, mainly due to PYR, FLE, ANT, CHR, BAA, BAP pair to 9100, 12761, 1065, 3947, 4603, 5911 µg kg⁻¹ (Table 1).

3.2. Electrochemical remediation of PAHs spiked marine sediments of Capo Granitola (TP)

3.2.1. EK under direct low-strength E

To study the efficacy of the EK approach under very low gradient E values for the remediation of 5PAHs and heavy metal contaminants from CG-spiked sediments, experiments was carried out under a low direct value of gradient E of 0.25 V cm⁻¹ for 4-days. To prevent extra electrical resistance due to the presence of some physical separator, graphite electrodes were inserted directly in contact with the sediments. Compact graphite was selected as electrodes because they are appealing for the applicative scale as regards other kinds of electrodes (e.g., Dimensionally Stable Anode-DSA and platinum, which are expensive materials, or

Table 1
Characterization of synthetic and real marine sediments and contaminants TEC and PEC values.

Physical properties	Marine sediments			SQSs (MacDonald et al., 2000)	
	Spiked Capo Granitola Coast	Augusta Bay	Bagnoli-Coroglio Bay	TEC ^a	PEC ^a
Specific gravity (at 20 °C)	2.53	2.52	2.58		
pH	7.30	7.10	7.20		
Moisture content (%)	50 ± 3.0	53 ± 3.5	49 ± 2.6		
Organic matter (%)	10 ± 0.19	9.46 ± 0.17	6.23 ± 0.02		
Particle size distribution (%)					
Clay	56.9 ± 0.9	36.0 ± 0.7	2.7 ± 0.2		
Silt	42.3 ± 0.9	57.4 ± 0.7			
Sand	0.86 ± 0.2	6.6 ± 0.4	97.4 ± 0.2		
Heavy metals ^b (mg kg ⁻¹)					
Hg	1.17 (0.044)	9.00	0.14	0.18	1.06
As	36.5 (20.4)	17.4	95.1	9.79	33.0
PAHs ^b (µg kg ⁻¹)					
Naphtalene	NAP	4	–	176	561
Acenaphthylene	ACN	12	–	–	–
Acenaphthene	ACA	5	–	–	–
Fluorene	FLU	112	–	77.4	536
Pyrene	PYR	–	46	9100	195
Fluoranthene	FLE	–	61	12761	423
Phenanthrene	PHE	353	58	–	204
Anthracene	ANT	–	14	1065	52.7
Chrysene	CHR	–	26	3947	166
Benzo(b+k)	BBF	–	39	6477	–
Fluorantene					
Benzo(j)	BJF	–	–	1917	–
Fluorantene					
Benzo(a)	BAA	–	24	4603	108
Anthracene					
Benzo(a)	BAP	748	24	5911	150
Pyrene					
Benzo(ghi)	BPR	1036	30	4092	–
Perylene					
Indeno(123cd)	INP	1036	25	5190	–
Pyrene					
Dibenz(a,h)	DAN	–	10	831	33
Anthracene					

^a The Probable Effect Concentration (PEC) represents pollutant's level below which adverse effects on marine organisms are infrequently anticipated; Threshold Effect Concentration (TEC) represents the pollutant level above which negative biological impacts are often found.

^b All these concentration values are the average of 10 replicated with a deviation standard close to 10 %.

stainless steel, that requires anti-corrosion treatment), due to their good electrical conductivity, low-cost, and because their usage does not need complicated treatments (Proietto et al., 2023). The performances of the process were analyzed in terms of *i*) *i*-contaminant distribution (C_i/C_i^0 where *i*- is the selected contaminants: FLU, PHE, BPA, BPR, INP, Hg or As) in the treated sediment, to directly evaluate the relative change of its concentration, and *ii*) the total 5PAHs removal, *R*. The C_i/C_i^0 of the different contaminants after the treatment of CG-spiked sediments is reported in Fig. 2.

At the beginning of the treatment, each *i*-contaminant in CG-spiked sediments was homogeneously distributed ($C_i/C_i^0 \sim 1$). After 96 h, it was observed that, for each of the 5PAHs, the C_i/C_i^0 is lower than 1 and the main distribution into the sediments of each contaminant is characterized by the same trend: the *i*-contaminant concentration is lower in

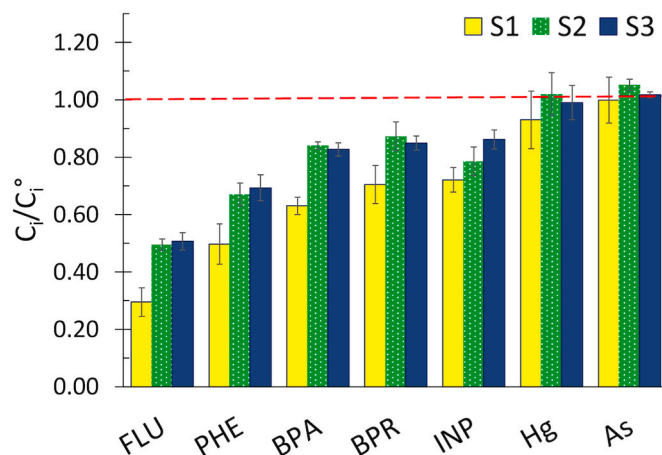


Fig. 2. Plot of C_i/C_i^0 for the different contaminants: FLU, PHE, BAP, BPR, INP, Hg and As at the different position S1, S2 and S3. Red dashed line (— —) marks C_i/C_i^0 equal to 1 (time zero of treatment). $E = 0.25 \text{ V cm}^{-1}$ $t = 96 \text{ h}$. Sediment: CG-spiked. System I.

the region S1 (anode area), and higher in S2 (middle area) and S3 (cathode area). In the ER treatment of contaminated sediments, movement of ions, water and colloids through fine-grained sediment can be mainly due to electromigration and electroosmosis transports which causes the migration of contaminants from the region close to one electrode towards the opposite one (Reddy and Cameselle, 2009). In our case, it is plausible to assume that the migration of the 5PAHs due to the electromigration process can be neglected due to their non-polar characteristics; hence only electroosmotic flow, which moves towards the cathode, could explain why the higher concentration of 5PAHs was observed close to the cathode side (S2 and S3). Although it should be noted that, in this case, also the electroosmotic transport is slow and difficult, due to the PAHs hydrophobic nature and low solubility. Moreover, under the adopted conditions (E of 0.25 V cm^{-1} after 96 h), it was observed a *R* value of approximately 32% (Table 2, entry 1). In particular, the higher the number of the aromatic rings of the 5PAHs (high molecular weight), the lower its removal: $\text{INP} < \text{BPR} < \text{BPA} < \text{PHE} < \text{FLU}$ (Fig. 2). This suggests that, in addition to the electroosmosis movement of the 5PAHs, other mechanisms for the transformation of 5PAHs into other chemicals were involved:

- According to the literature, under an induced E , several chemical radicals are expected to be generated in situ on the sediment particles and they can take part on the degradation process (Reddy and Cameselle, 2009); although, to date, the real associated mechanisms are not totally clear. PAHs can easily react with H or OH radicals to give other organic compounds (Bai et al., 2022; Cordeiro and Corio, 2009; Nayebyzadeh and Vahedpour, 2017).
- Under the adopted conditions, organics could be directly oxidized at the anodic surface. According to the literature, at the anode, the oxidation via electrochemical routes might be started with the direct electron transfer from adsorbed PAHs to the anode, which produces PAHs radicals that undergo successive reactions (Ajab et al., 2020; Cordeiro and Corio, 2009) or by oxidation by electro-generated OH radicals. As an example, Alcántara et al. (2008) demonstrated a total degradation of PHE, BAP and ANT in aqueous solution using graphite electrodes over 3 days, highlighting that currently the involved mechanisms are complicated and not entirely clear.

Volatilization might be also one of the causes of the removal of 5PAHs from sediments. At 0.25 V cm^{-1} , a current density of $0.300 \pm 0.025 \text{ mA cm}^{-2}$ was recorded; according to the literature, under the adopted conditions, it can be neglected the fluctuation of the sediment temperature (Falciglia et al., 2017; Garcia-Blas et al., 2020; Proietto

Table 2
Effect of the electrochemical treatments on the performances of the process ^a.

Entry	Sediments	Technology/Electrolyte	E/V cm ⁻¹	pH			R of PAHs/%	EC/10 ⁻³ kWh/kg
				S1	S2	S3		
1	CG-spiked	System I/—	0.25	6.65	6.60	7.66	32.0	9.100
2	CG-spiked	System I/—	0.15	6.76	6.50	7.68	34.8	1.680
3	CG-spiked	System I/—	0.10	6.80	6.65	7.70	40.0	0.540
4	CG-spiked	System I/—	0.05	6.70	6.50	7.70	57.1	0.057
5	CG-spiked	System II/DW	1.00	8.50	11.3	12.1	45.3	1610
6	Augusta Bay	System I/—	0.05	7.50	7.75	8.10	57.7	0.067
7	Bagnoli Bay	System I/—	0.05	7.25	7.05	7.50	49.5	0.048

^a Overall removal efficiency of Hg or As was approximately zero. DW: Deionized Water. 66 or 100 g of CG-spiked sediments were treated in system I or II respectively.

et al., 2023). In addition, a control test in the absence of E was performed, and minimal variation in the 5PAHs level was assessed within 4 days. Reasonably, in our approach, the reduction of 5PAHs from the sediments due to the volatilization could be neglected. Hence, it is plausible to suppose that, in our case, the reduction of 5PAHs concentration at the end of the treatment can be due to both their direct oxidation at the anode surface and its chemical conversion, through these free radical ions, into other organics and/or, optimistically, to their mineralization.

In the case of heavy metals, after 96 h of electrochemical treatment no change in concentration values of both Hg and As was observed (Fig. 2); thus, showing that heavy metals cannot be moved in the sediments under in-situ EK under low strength E , at least under adopted operative conditions. This compartment could be attributed to the nonionic nature of the complexes formed in the CG sediments after the contaminations, which were not transported under the E or attracted towards the electrodes. Moreover, according to the literature, the electrochemical processes could affect the binding strengths between the sediments and metals. Hsueh et al. (2022) demonstrated that the ECGO process contributed to shifting the more stable bindings between metals and soils to the less stable bindings, favoring metals removal from soil, working under relatively high potential gradient E of 0.6–1 V cm⁻¹ and for 26–34 days. Our experiments were carried out under significant lower E values and, in particular, for shorter treatment time of 96 h (4 day), which cannot be suitable for appreciating the binding strengths and the consequent mobility of the metals. Thus, suggesting that this approach under the adopted operative conditions is not effective for the remediation of heavy metals.

Overall, the achieved results show that ER, performed at a low gradient E value (of 0.25 V cm⁻¹), of marine sediments artificially contaminated by persistent organic pollutants and heavy metals might be a proper strategy for concomitantly desorbing, mobilizing and degrading PAHs from marine sediments, even if this approach seems not appropriate heavy metals removal.

3.2.2. Effect of the electric field strength

The gradient E strength could significantly affect the process, hence, to improve the performances, electrolyses were planned with the aim to study the effect of E values on the remediation of CG-piked. Compact graphite was used as electrode material. Fig. 3 reports the C_i/C_i^0 of FLU (Fig. 3a), PHE (Fig. 3b), BPA (Fig. 3c), BPR (Fig. 3d), INP (Fig. 3e), Hg (Fig. 3f) and As (Fig. 3g) in section S1, S2 and S3 of the treated sediments over 96 h at different E values (range: 0.05 ÷ 0.25 V cm⁻¹). In the case of FLU, at 0.15 V cm⁻¹, the C_{FLU}/C_{FLU}^0 is also lower than 1 (close to 0.30) (Fig. 3a). Moreover, by reducing the induced E value, a further decrease in the FLU final concentration was observed reaching approximately 0.20 at 0.05 V cm⁻¹ (Fig. 3a). Similar trends as a function of the E value were observed also for the other contaminants, although an absolute higher final value of concentrations was recorded. As an example, in the case of BPR, by decreasing the applied E progressively from 0.15 to 0.10 and 0.05 V cm⁻¹, C_{BPR}/C_{BPR}^0 was reduced from approximately 0.85 to 0.80 and 0.57, respectively (Fig. 3d). Overall, an enhancement of the

efficacy of the treatment of the sediments on the PAHs removal was observed by decreasing the applied gradient E (Table 2). An increase of R from 32 to 35 and 40% was achieved by changing from 0.25 to 0.15 and 0.10 V cm⁻¹ (Table 2, entries 1–3), respectively. A further reduction of E at 0.05 V cm⁻¹ allowed to increase the R of 5PAHs up to 57% (Table 2, entry 4). Hence, the lower the E value, the higher the R ; which is in line with the literature. Indeed, this behavior was previously reported for the remediation of artificially phenol-polluted kaolin (Proietto et al., 2023). The beneficial results might be tentatively imputed to the fact that using 0.25 V cm⁻¹ the current is expected to be transported partly by the sediment particles (thus allowing them to serve as microelectrodes and to activate reduction-oxidation reactions at the interface of the diffuse-double layer (DDL)) and in part in the fluid of the pore (Rahner et al., 2002). By lowering the value of the applied E , the amount of current transported by particles is likely to be higher than the ionic one in the pore's fluid; this should increase the impact of redox reactions involved at the DDL interface (Zanko et al., 2020), and consequently improve the generation of free radicals on the particle of the sediment, which become the main actors in the in situ PAHs chemical oxidation).

Under the applied E , no significant changes in the pH of the marine sediments were observed (Table 2, entries 1–4), thus suggesting that the selected sediments are characterized by a high buffer capacity. To clarify this point, a series of chemical tests was performed by the addition of a certain amount of acid to the sediments and waiting for the equilibrium. It was found that the pH of the CG-spiked slightly changes with the addition of H⁺ (see Supporting Materials, Fig. S1), thus confirming the high buffer capacity of the used marine sediments. Hence, it is plausible to assume that the movement of H⁺ towards the cathode (acid front) might be hindered as a consequence of the high acid sediment buffering capacity.

The distribution of Hg (Fig. 3f) and As (Fig. 3g) did not significantly change by varying the E value after the treatment of the sediments, thus, confirming that this approach is not suitable for the remediation of heavy metals.

To compare the ER under low E values with the electrokinetic (EK) process, electrochemical remediation of CG-spiked sediments was performed under 1 V cm⁻¹ (values in accordance with the usual operative conditions adopted for EK in literature) using system II. EK processes use higher values of E and two external electrode/electrolyte compartments (see Section 2.3, Fig. 1b). Moreover, to avoid additional costs due to the usage of enhancing agents, water was utilized as the processing fluid. During the process, the electrolyte solution was replaced with fresh deionized water every 24 h. Approximately 100 g of CG-spiked with a water content of 50% was used. Fig. 4 reports the C_i/C_i^0 of the 5PAHs in the regions S1, S2 and S3 after the treatment. Also in this case, the concentration of each 5PAHs is lower than the initial concentration value (Fig. 4) with a similar distribution of the experiments performed under very low E (Fig. 2). Furthermore, in this case, the R reached approximately 45% (Table 2, entry 5). Under EK treatment, the removal of PAHs from the sediments can be attributed to the migration process towards the electrolyte's compartments and their electrochemical degradation at the electrode's compartments, which is in line with the

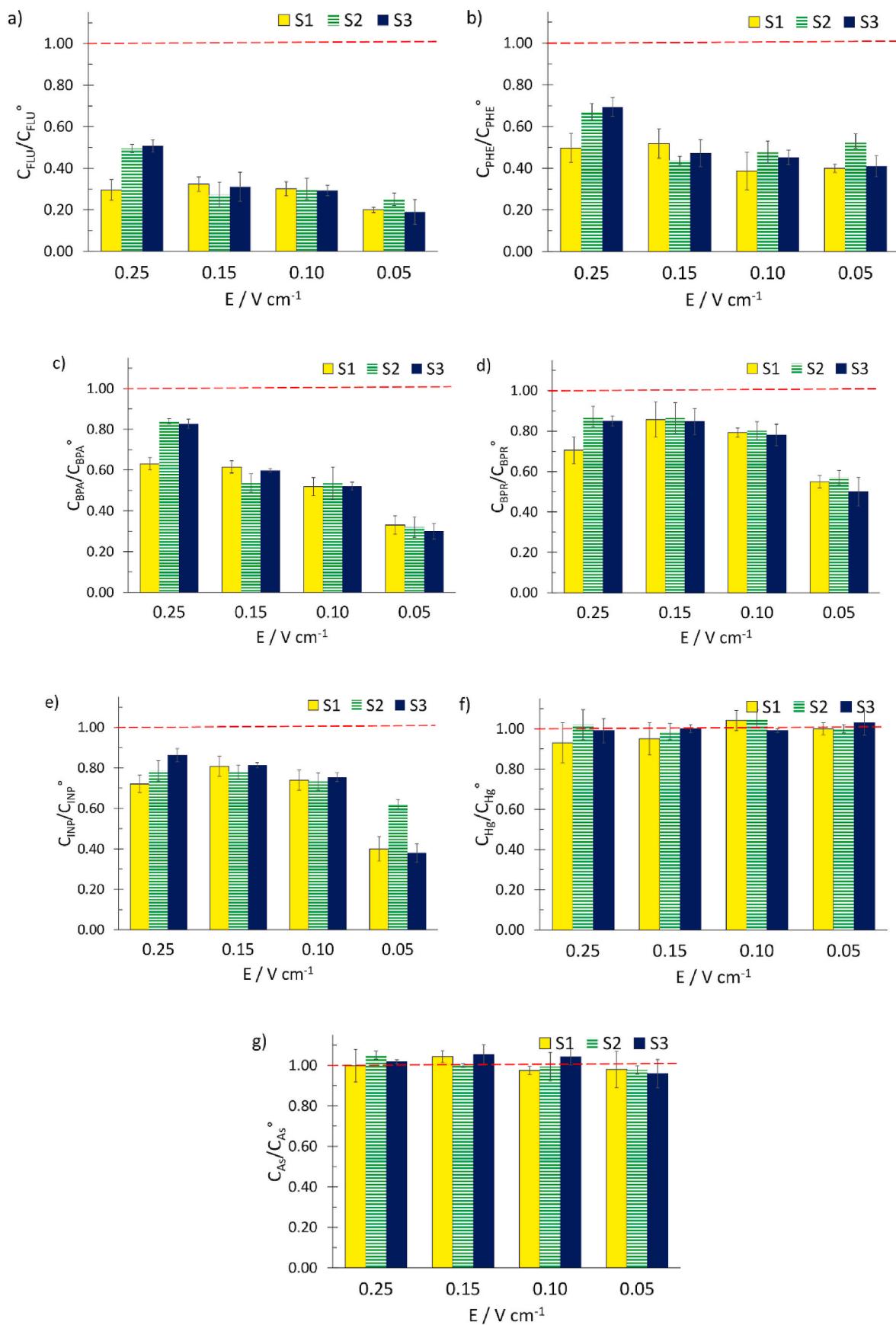


Fig. 3. Plot of the C_i/C_i^0 for a) FLU, b) PHE, c) BPA, d) BPR, e) INP, f) Hg or g) As in the region S1, S2 and S3 under 0.25, 0.15, 0.10, 0.05 $V\ cm^{-1}$. Red dashed line (— —) marks C_i/C_i^0 equal to 1 (time zero of treatment). $E = 0.25\ V\ cm^{-1}$ $t = 96\ h$. Sediment: CG-spiked. System I.

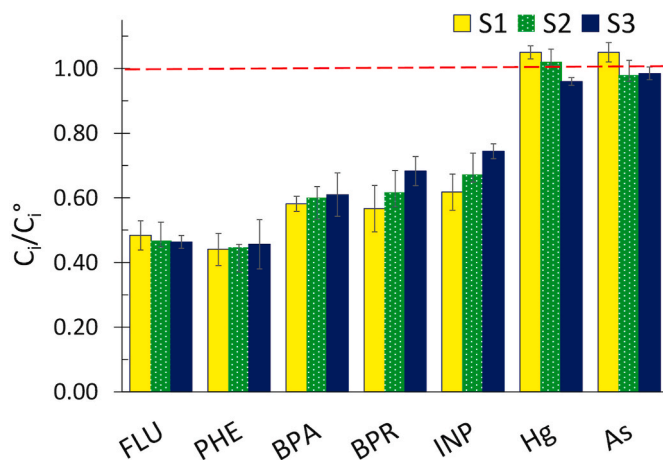


Fig. 4. Electrokinetic treatment of CG-spiked under 1 V cm^{-1} after 4 days using distillate water as electrolyte. Plot of the C_i/C_i^0 vs. S1, S2 and S3. Red dashed line (— — —) marks C_i/C_i^0 equal to 1 (time zero of treatment). $t = 96 \text{ h}$. Sediment: CG-spiked. System II.

literature (Ammami et al., 2015).

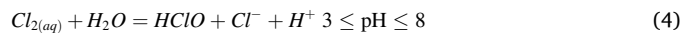
Although quite high removal of R from the sediment can be achieved at 1 V cm^{-1} , higher energetic consumption per kg of dried treated sediments (EC) was observed in the EK approach with respect to the ECGO experiments (compare Table 2, entry 5 with Table 2, entries 3 and 4). In addition, EK process suffers from the production of a dangerous secondary effluent (due to the movement of contaminants in the electrolyte compartments), increasing the post-treatment expense. Sediment pH in this case is higher than the initial value. This can be attributed to the basic front from the cathode showing the low base buffering capacity of the sediments. Hence, it is possible to conclude that, to reach similar values of R , the EC of the treatment can be reduced working at low E value.

In this case, it was observed a slight change in the distribution of Hg and As along the treated sediments. A slightly higher concentration of both metals was observed in region S1, which is near the anode area. This might be tentatively attributed to an electromigration transport of metal ions under the high E values, which can be possible only if Hg and As forms present a negative charge.

3.3. Electrochemical remediation of real marine sediments

To validate the ECGO for the remediation of real case studies, marine sediments dragged from Augusta Bay (Syracuse, Italy) and Bagnoli-Coroglio Bay (Naples, Italy) were treated under low E value of 0.05 V cm^{-1} for 96 h. The sediments dragged from Augusta Bay were treated as clay model matrices containing both PAHs and Hg; while contaminated sediments dragged from Bagnoli-Coroglio were used as sandy model matrices containing high-level PAHs and As. Fig. 5 reports the distribution C_i/C_i^0 of the sixteen PAHs identified in the sediments with respect sections S1, S2 and S3 after the electrochemical treatment of Augusta Bay (Fig. 5a) and of Bagnoli-Coroglio Bay (Fig. 5b). In both cases, it was observed a similar contaminant position in the sediments. In the case of the marine sediments of Augusta Bay, it was observed a C_i/C_i^0 lower than 1 for most of the contaminants except for ACN (Fig. 5a). More in detail, the lower concentrations were observed for contaminants with high molecular weight (i.e. BBF, BPA, INP, BRP, DAN). This results in a total R of PAHs close to 58 %. In the case of real marine sediments, the presence of a quite high concentration of chloride ions is expected (which was confirmed by ionic chromatography analysis of the water content of the Augusta sediments). According to literature, under oxidative conditions, active chlorines might be generated at the anode (adsorbed chloro and/or oxychloro radicals) and at the surface of the particles as a result of the following reaction mechanism (eqs. (3)–(5))

(Scialdone et al., 2021) promoting the abatement of PAHs. The presence of Cl_2 , HClO or/and ClO^- is determined by pH values (Scialdone et al., 2021).



In the case of Augusta, final pH was higher than 7.5 in S1, S2 and S3 (Table 2, entry 6). Hence, this suggests that the concentration of PAHs can be reduced for this real case also due to the synergetic contribution of the presence of various oxidants (including adsorbed chloro and oxychloro radical at the anode surface and active chlorine at both the anode surface and particles surface), of a miscellaneous of other reactive oxygen species, including $\bullet\text{O}_2$, H_2O_2 and $\text{HO}\bullet$ generated by water oxidation and the stimulation of microbial activities. Furthermore, the concentration of Hg did not significantly change after the treatment, resulting in its removal efficiency close to zero.

Also, in the case of Bagnoli marine sediments, the adoption of low E values of 0.05 V cm^{-1} allowed to remove of a significant part of PAHs (Table 2, entry 7), reaching a R of PAHs of approximately 49% after 96 h. A trend of the distribution of the contaminants in the sediments like that observed for Augusta was detected, although, for Bagnoli the highest concentration of the contaminants was recorded in the middle side of the cell (region S2) (Fig. 5b). This behavior was in line with previous works (Falciglia et al., 2017). Also, in this case, the distribution of As did not change.

Moreover, in both cases of Augusta and Bagnoli, a control test without the application of a gradient E was performed and C_i/C_i^0 for each contaminant was approximately 1, hence showing that, without the application of E , no volatilization was observed.

The results achieved for the treatment of the real polluted marine case studies present some differences with respect to that achieved for the treatment of the CG-spiked matrix. More in detail, in the case of the treatment of the real marine case, the removal of low molecular weight compounds was more challenging than in the case of the artificially spiked CG sediments (i.e., the normalized concentration of FLU reached 0.7 in the case of Augusta and 0.25 in the case of spiked-CG after 96 h of treatment under 0.05 V cm^{-1}). This can be tentatively attributed to the different nature of the sediments, the interaction of the different contaminants with the particles of the sediment, the heterogeneous conditions, and the presence of more stable complexes in the real matrices.

4. Conclusions

In the present work, the electrochemical remediation of three type of contaminate marine sediments inserting the electrodes directly in the sediments without the use of electrode compartments/electrolyte solutions was studied under very low gradient E values ($E \leq 0.25 \text{ V cm}^{-1}$). Clay marine sediments dragged from Capo Granitola Coast (Trapani, Italy) artificially spiked with five PAHs congeners (5PAHs), Hg and As were treated as a simplified model matrix (CG-spiked) to simulate a real case study; real polluted marine sediments from Augusta Bay (Syracuse) and Bagnoli-Coroglio Bay (Naples) in the southern of Italy, classified as SIN, were treated as models of real contaminated sediments to be restored, in order to validate this approach for real cases.

The key outcome of this study is that the utilization of very low E values for the remediation of PAHs from the sediments might allow to desorb, mobilize and degrade in situ organic pollutants minimizing the energetic consumption of the process and avoiding the production of a secondary waste effluent.

In the case of the CG-spiked sediments, a removal efficiency of approximately 57% was reached by lowering the gradient E and the remediation was easier for low molecular weight 5PAHs. Moreover,

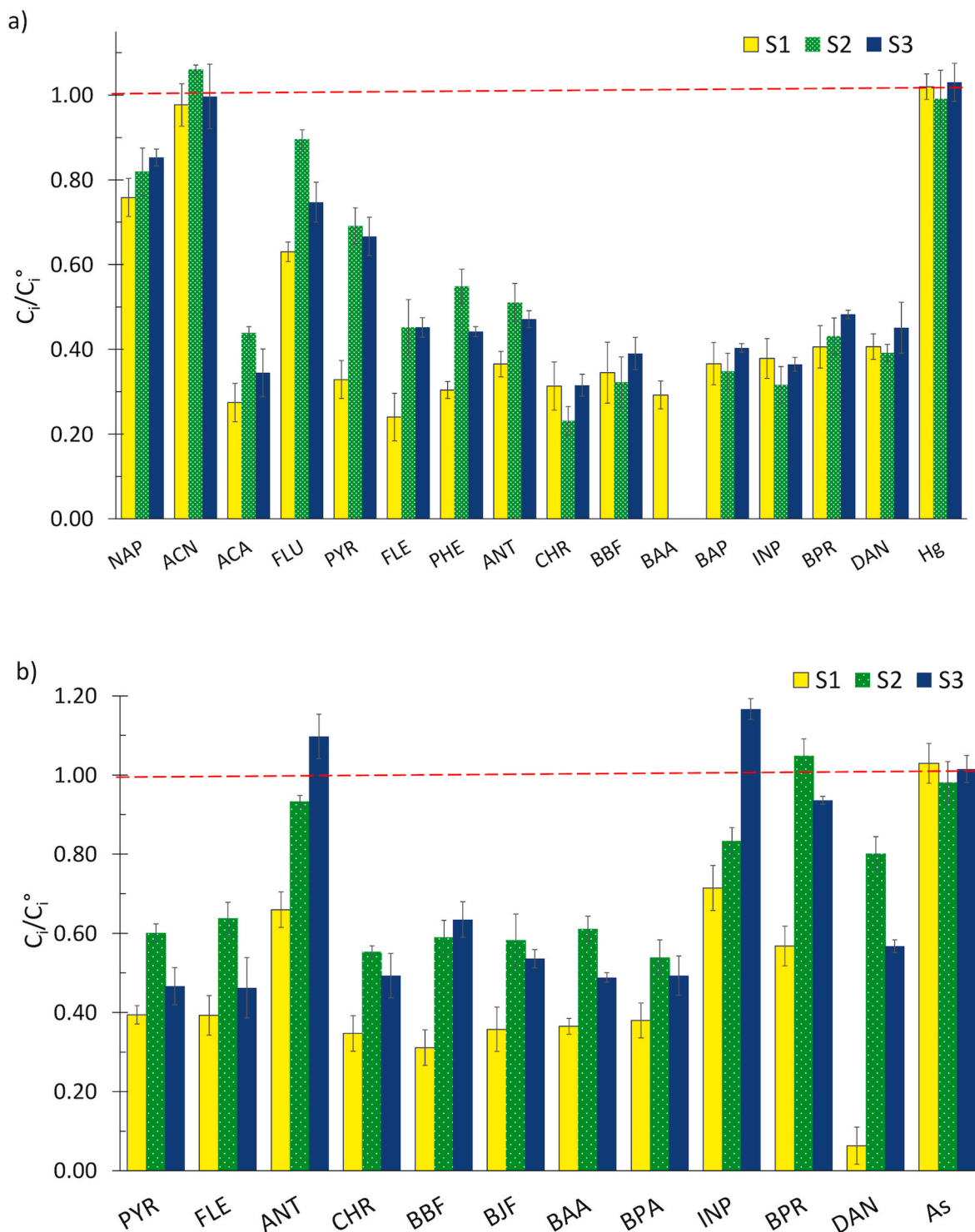


Fig. 5. Effect of the electrochemical remediation of real marine sediment from a) Augusta Bay and b) Bagnoli over 4-day period. Plot of the C_i/C_i^0 vs. S1, S2 and S3. Red dashed line (— — —) marks C_i/C_i^0 equal to 1 (time zero of treatment). $E = 0.05 \text{ V cm}^{-1}$ $t = 96 \text{ h}$. System I.

promising results were observed by the treatment of the two real case studies for the remediation of PAHs under low values E by reaching a removal higher or equal to approximately 50%. However, the used approach is not efficacy for the remediation of heavy metals (Hg and As). To prompt the development of this technology for the restoration of polluted sites, further studies will be focused on investigating in-depth the involved mechanism reaction by the identification of by-products and of the main oxidant agents and on studying the electrochemical remediation process on a larger scale (bench, pilot, prototype).

CRediT authorship contribution statement

Federica Proietto: Conceptualization, Data curation, Investigation, Methodology, Visualization, Writing - original draft, Writing - review & editing. **Fabio D'Agostino:** Data curation, Formal analysis. **Maria Bonsignore:** Data curation, Formal analysis. **Marianna Del Core:** Data curation, Formal analysis. **Mario Sprovieri:** Funding acquisition. **Alessandro Galia:** Funding acquisition, Writing - review & editing. **Onofrio Scialdone:** Funding acquisition, Supervision, Writing - review

& editing.

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.

Acknowledgements

The Marine Hazard project (PON03PE_00203_1) and the University of Palermo “FFR- 2023 Proietto” are gratefully acknowledged for the financial support.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2023.141009>.

References

- Acar, Y.B., Alshawabkeh, A.N., 1993. Principles of electrokinetic remediation. *Environ. Sci. Technol.* 27, 2638–2647. <https://doi.org/10.1021/es00049a002>.
- Ajab, H., Isa, M.H., Yaqub, A., 2020. Electrochemical oxidation using Ti/RuO₂ anode for COD and PAHs removal from aqueous solution. *Sustain. Mater. Technol.* 26, e00225 <https://doi.org/10.1016/j.susmat.2020.e00225>.
- Alcántara, M.T., Gómez, J., Pazos, M., Sanromán, M.A., 2008. Combined treatment of PAHs contaminated soils using the sequence extraction with surfactant–electrochemical degradation. *Chemosphere* 70, 1438–1444. <https://doi.org/10.1016/j.chemosphere.2007.08.070>.
- Ammami, M.T., Benamar, A., Wang, H., Bailleul, C., Legras, M., Le Derf, F., Portet-Koltalo, F., 2014. Simultaneous electrokinetic removal of polycyclic aromatic hydrocarbons and metals from a sediment using mixed enhancing agents. *Int. J. Environ. Sci. Technol.* 11, 1801–1816. <https://doi.org/10.1007/s13762-013-0395-9>.
- Ammami, M.T., Portet-Koltalo, F., Benamar, A., Duclairoir-Poc, C., Wang, H., Le Derf, F., 2015. Application of biosurfactants and periodic voltage gradient for enhanced electrokinetic remediation of metals and PAHs in dredged marine sediments. *Chemosphere* 125, 1–8. <https://doi.org/10.1016/j.chemosphere.2014.12.087>.
- Armiento, G., Barsanti, M., Caprioli, R., Chiavarini, S., Conte, F., Crovato, C., De Cassan, M., Delbono, I., Montereali, M.R., Nardi, E., Parrella, L., Pezza, M., Proposito, M., Rimaudo, J., Schirone, A., Spaziani, F., 2022. Heavy metal background levels and pollution temporal trend assessment within the marine sediments facing a brownfield area (Gulf of Pozzuoli, Southern Italy). *Environ. Monit. Assess.* 194, 814. <https://doi.org/10.1007/s10661-022-10480-3>.
- Bai, X., Sun, H., Sun, J., Zhu, Z., 2022. Efficient removal of sixteen priority polycyclic aromatic hydrocarbons from textile dyeing sludge using electro-chemical Fe²⁺-activated peroxymonosulfate oxidation-A green pretreatment strategy for textile dyeing sludge toxicity reduction. *J. Hazard Mater.* 435, 129087 <https://doi.org/10.1016/j.jhazmat.2022.129087>.
- Buccino, M., Daliri, M., Buttarazzi, M.N., Del Giudice, G., Calabrese, M., Somma, R., 2022. A numerical study of arsenic contamination at the Bagnoli bay seabed by a semi-anthropogenic source. Analysis of current regime. *Chemosphere* 303, 134955. <https://doi.org/10.1016/j.scitotenv.2021.146811>.
- Chen, W., Xie, T., Li, W., Wang, R., 2018. Thinking of construction of soil pollution prevention and control technology system in China. *Acta Pedol. Sin.* 55, 557–568. <https://doi.org/10.11766/trxb201711300488>.
- Chen, X., Li, X., Li, Y., Zhao, L., Sun, Y., Rushimisha, I.E., Han, T., Weng, L., Lin, X., Li, Y., 2021. Bioelectric field drives ion migration with the electricity generation and pollutant removal. *Environ. Technol. Innov.* 24, 101901 <https://doi.org/10.1016/j.eti.2021.101901>.
- Colacicco, A., De Giovanni, G., Muntoni, A., Pettinao, E., Poletti, A., Pomi, R., 2010. Enhanced electrokinetic treatment of marine sediments contaminated by heavy metals and PAHs. *Chemosphere* 81, 46–56. <https://doi.org/10.1016/j.chemosphere.2010.07.004>, 2010.
- Cordeiro, D.S., Corio, P., 2009. Electro-chemical and photocatalytic reactions of polycyclic aromatic hydrocarbons. *J. Braz. Chem. Soc.* 20 (1) <https://doi.org/10.1590/S0103-50532009000100014>.
- Falciglia, P.P., Malarbi, D., Greco, V., Vagliasindi, F.G.A., 2017. Surfactant and MGDA enhanced – electrokinetic treatment for the simultaneous removal of mercury and PAHs from marine sediments. *Sep. Purif. Technol.* 175, 330–339. <https://doi.org/10.1016/j.seppur.2016.11.046>.
- Ferrarese, E., Andreottola, G., 2010. Application of electrochemical technique for the remediation of soils contaminated with organic pollutants. *Proc. Ann. Int. Conf. Soils Sediments Water Energy* 13, 26. In: <https://scholarworks.umass.edu/soilsproceedings/vol13/iss1/26>.
- García-Blas, N., Jimenez-Relinque, E., Nevshupa, R., Castellote, M., 2020. Electrokinetic approach to assess the behaviour of a contaminated marine sediment. *J. Soils Sediments* 20, 2673–2684. <https://doi.org/10.1007/s11368-020-02615-1>.
- Gereslassie, T., Workineh, A., Atieno, O.J., Wang, J., 2019. Determination of occurrences, distribution, health impacts of organochlorine pesticides in soils of central China. *Int. J. Environ. Res. Publ. Health* 16, 146. <https://doi.org/10.3390/ijerph16010146>.
- Han, D., Wu, X., Li, R., Tang, X., Xiao, S., Scholz, M., 2012. Critical review of electrokinetic remediation of contaminated soils and sediments: mechanisms, performances and technologies. *Water Air Soil Pollut.* 232, 335. <https://doi.org/10.1007/s11270-021-05182-4>.
- Hsueh, Y.-S., Chen, X., Dai, Y.-D., Yuan, C., 2022. Comparison of Cr/Ni removal by electrokinetic (EK) and electro-chemical geooxidation (ECGO) processes: remediation performance and economic analysis in an in-situ system. *J. Environ. Chem. Eng.* 10, 107018 <https://doi.org/10.1016/j.jece.2021.107018>.
- Huang, D.-Y., Zhou, S.-G., Chen, Q., Zhao, B., Yuan, Y., Zhuang, L., 2011. Enhanced anaerobic degradation of organic pollutants in a soil microbial fuel cell. *Chem. Eng. J.* 172, 647–653. <https://doi.org/10.1016/j.cej.2011.06.024>.
- Huysegoms, L., Cappuyns, V., 2017. Critical review of decision support tools for sustainability assessment of site remediation options. *J. Environ. Manag.* 196, 278–296. <https://doi.org/10.1016/j.jenvman.2017.03.002>.
- Iannelli, R., Masi, M., Ceccarini, A., Ostuni, M.B., Lageman, R., Muntoni, A., Spiga, D., Poletti, A., Marini, A., Pomi, R., 2015. Electrokinetic remediation of metal-polluted marine sediments: experimental investigation for plant design. *Electrochim. Acta* 181, 146–159. <https://doi.org/10.1016/j.electacta.2015.04.093>.
- Krumbein, W.C., 1934. Size Frequency distributions of sediments. *J. Sediment. Petrol.* 4, 65–77. <https://doi.org/10.1306/D4268EB9-2B26-11D7-8648000102C1865D>.
- Li, X., Wang, X., Weng, L., Zhou, Q., Li, Y., 2017. Microbial fuel cell for organic contaminated soil remedial application: a review. *Energy Technol.* 5, 1156–1164. <https://doi.org/10.1002/ente.201600674>.
- Lofrano, G., Libralato, G., Minetto, D., De Gisi, S., Todaro, F., Conte, B., Calabrò, D., Quatraro, L., Notarnicola, M., 2017. In situ remediation of contaminated marine sediment: an overview. *Environ. Sci. Pollut. Res.* 24, 5189–5206. <https://doi.org/10.1007/s11356-016-8281-x>.
- MacDonald, D.D., Ingersoll, C.G., Berger, T.A., 2000. Development and evaluation of consensus-based sediment quality Guidelines for freshwater ecosystems. *Arch. Environ. Contam. Toxicol.* 39, 20–31. <https://doi.org/10.1007/s002440010075>.
- Malarbi, D., Falciglia, P.P., Vagliasindi, F.G.A., 2015. Removal of Hg from real polluted sediments using enhanced-EK decontamination: verification of experimental methods and batch-test preliminary results. *J. Chem.* 2015, 270451 <https://doi.org/10.1155/2015/270451>.
- MATTM - Ministero dell'ambiente e della Tutela del Territorio e del Mare, DM 11/01/2013. (<https://www.gazzettaufficiale.it/eli/gu/2013/03/12/60/sg/pdf>, available on 26/06/2023).
- Muscetta, M., Bianco, F., Trancone, G., Race, M., Siciliano, A., D'Agostino, F., Sprovieri, M., Clarizia, L., 2023. Washing bottom sediment for the removal of arsenic from contaminated Italian Coast. *Processes* 11, 902. <https://doi.org/10.3390/pr11030902>.
- Nayebzadeh, M., Vahedpour, M., 2017. A review on reactions of polycyclic aromatic hydrocarbons with the most abundant atmospheric chemical fragments: theoretical and experimental data. *Prog. React. Kinet. Mech.* 42, 201–220. <https://doi.org/10.3184/146867817X148215275492>.
- OECD, 2007. Test No. 225: Sediment-Water Lumbriculus Toxicity Test Using Spiked Sediment, OECD Guidelines for the Testing of Chemicals, Section 2. OECD Publishing, Paris.
- Pazos, M., Rosales, E., Alcántara, T., Gómez, J., Sanromán, M.A., 2010. Decontamination of soils containing PAHs by electroremediation: a review. *J. Hazard Mater.* 177, 1–11. <https://doi.org/10.1016/j.jhazmat.2009.11.055>.
- Proietto, F., Khalil, A., Maouch, W., Galia, A., Scialdone, O., 2023. Electrochemical remediation of phenol contaminated kaolin under low-strength electric fields. *Environ. Technol. Innov.* 32, 103286 <https://doi.org/10.1016/j.eti.2023.103286>.
- Rahner, D., Ludwig, G., Röhrs, J., 2002. Electrochemically induced reactions in soils – a new approach to the in-situ remediation of contaminated soils Part 1: the microconductor principle. *Electrochim. Acta* 47 (9), 1395–1403. [https://doi.org/10.1016/S0013-4686\(01\)00854-4](https://doi.org/10.1016/S0013-4686(01)00854-4).
- Reddy, K.R., Cameselle, C., 2009. *Electro-chemical Remediation Technologies for Polluted Soils, Sediments and Groundwater*. John Wiley & Sons, Hoboken, New Jersey.
- Röhrs, J., Ludwig, G., Rahner, D., 2002. Electrochemically induced reactions in soils. A new approach to the in-situ remediation of contaminated soils. Part 2: remediation experiments with a natural soil containing highly chlorinated hydrocarbons. *Electrochim. Acta* 47 (9), 1405–1414. [https://doi.org/10.1016/S0013-4686\(01\)00855-6](https://doi.org/10.1016/S0013-4686(01)00855-6).
- Romano, E., Bergamin, L., Celia Magno, M., Pierfranceschi, G., Ausili, A., 2018. Temporal changes of metal and trace element contamination in marine sediments due to a steel plant: the case study of Bagnoli (Naples, Italy). *Appl. Geochem.* 88, 85–94. <https://doi.org/10.1016/j.apgeochem.2017.05.012>.
- Romano, E., Bergamin, L., Croudace, I.W., Pierfranceschi, G., Sesta, G., 2021. Measuring anthropogenic impacts on an industrialised coastal marine area using chemical and textural signatures in sediments: a case study of Augusta Harbour (Sicily, Italy). *Sci. Total Environ.* 755, 142683 <https://doi.org/10.1016/j.scitotenv.2020.142683>.
- Ronchi, S., Salata, S., Arcidiacono, A., Piroli, E., Montanarella, L., 2019. Policy instruments for soil protection among the EU member states: a comparative analysis. *Land Use Pol.* 82, 763–780. <https://doi.org/10.1016/j.landusepol.2019.01.017>.

- Rosestolato, D., Bagatin, R., Ferro, S., 2015. Electrokinetic remediation of soils polluted by heavy metals (mercury in particular). *J. Chem. Eng.* 264, 16–23. <https://doi.org/10.1016/j.ccej.2014.11.074>.
- Saini, A., Bekele, D.N., Chadalavada, S., Fang, C., Naidu, R., 2021. Electrokinetic remediation of petroleum hydrocarbon contaminated soil (I). *Environ. Technol. Innov.* 23, 101585 <https://doi.org/10.1016/j.eti.2021.101585>.
- Scialdone, O., Proietto, F., Galia, A., 2021. Electrochemical production and use of chlorinated oxidants for the treatment of wastewater contaminated by organic pollutants and disinfection. *Curr. Opin. Electrochem.* 27, 100682 <https://doi.org/10.1016/j.coelec.2020.100682>.
- Sharma, H.D., Reddy, K.R., 2004. *Geoenvironmental Engineering: Site Remediation, Waste Containment, and Emerging Waste Management Technologies*, first ed. John Wiley & Sons, Hoboken, New Jersey.
- Song, Y., Hou, D., Zhang, J., O'Connor, D., Li, G., Gu, Q., Li, S., Liu, P., 2018. Environmental and socio-economic sustainability appraisal of contaminated land remediation strategies: a case study at a mega-site in China. *Sci. Total Environ.* 610, 391–401. <https://doi.org/10.1016/j.scitotenv.2017.08.016>.
- Wang, J., Feng, X., Anderson, C.W.N., Xing, Y., Shang, L., 2012. Remediation of mercury contaminated sites – a review. *J. Hazard Mater.* 221 (222), 1–18. <https://doi.org/10.1016/j.jhazmat.2012.04.035>.
- Wen, D., Fu, R., Li, Q., 2021. Removal of inorganic contaminants in soil by electrokinetic remediation technologies: a review. *J. Hazard Mater.* 401, 123345 <https://doi.org/10.1016/j.jhazmat.2020.123345>.
- Wentworth, C.K., 1922. A scale of grade and class terms for clastic sediments. *J. Geol.* 30, 377–392. <https://doi.org/10.1086/622910>.
- Wu, Y., Jing, W., Gao, C., Huang, Q., Cai, P., 2018. Recent advances in microbial electrochemical system for soil bioremediation. *Chemosphere* 211, 156–163. <https://doi.org/10.1016/j.chemosphere.2018.07.089>.
- Zanko, L.M., Wittle, J.K., Pamukcu, S., 2020. Case study: electro-chemical geo-oxidation (ECGO) treatment of Massachusetts new bedford harbor sediment PCBs. *Electrochim. Acta* 354, 136690. <https://doi.org/10.1016/j.electacta.2020.136690>.