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Treatment of petroleum hydrocarbon contaminated soil by combination of electro-Fenton and biosurfactant-assisted bioslurry process

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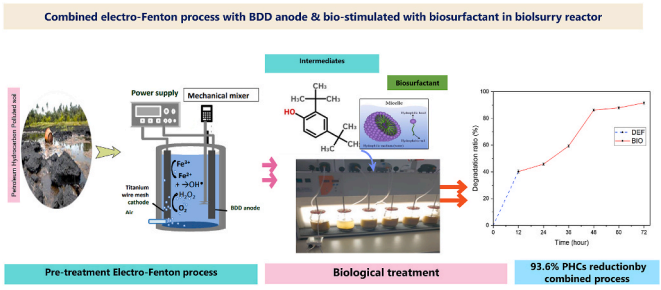
HIGHLIGHTS

- Integration of electro-Fenton & biological processes for PHCs degradation in soil was evaluated.
- The boron-doped diamond (BDD) anode was effective in the electro-Fenton process.
- The biodegradability of PHCs was enhanced after electro-Fenton treatment.
- Long-chain rhamnolipid was used as a stimulant in the biological process.
- A 93.6% reduction rate of PHCs was achieved in the combined process.

GRAPHICAL ABSTRACT



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ABSTRACT

Removing petroleum hydrocarbons (PHCs) from polluted soil is challenging due to their low bioavailability and degradability. In this study, an experiment was carried out to treat soil polluted with petroleum hydrocarbon using a hybrid electro-Fenton (with BDD anode electrode) and biological processes stimulated with long-chain rhamnolipids (biosurfactants). Electro-Fenton treatment was applied as a pretreatment before the biological process to enhance PHC biodegradability, which would benefit the subsequent biological process. The effects of initial pH, hydroxide concentration, soil organic matter composition, PHCs intermediates during the electro-Fenton process, and total numbers of bacteria in the biological process were analyzed to determine the optimum conditions. The results showed that the optimized electrolysis time for the electro-Fenton was 12 h. The

Abbreviations: BDD, Boron-doped diamond; FID, Flame-ionization detection; FA, Fulvic acid; GC-MS, Gas chromatography–mass spectrometry; HA, Humic acid; •OH, Hydroxyl radical; qPCR, Real-time polymerase chain reaction; PHCs, Petroleum hydrocarbons; SHE, Standard hydrogen electrode; SOM, Soil organic matter; US, Ultrasonic; TEO, Total dichloromethane-extractable organics; AOPs, Advanced oxidation processes.

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change induced during pretreatment at a specified time was found suitable for the biological process stage and led to 93.6% PHC degradation in combination with the electro-Fenton-and-biological process after 72 h. The combined system's performance was almost 40% higher than individual electro-Fenton and biological treatments. GC-MS analysis confirms the formation of 9-octadecen-1-ol (Z), 2-heptadecene, 1-nonadecene, 1-heneicosene, and pentacosane as fragmentation during the PHCs degradation process. Thus, the electro-Fenton process as pretreatment combined with a biological process stimulated with rhamnolipids (biosurfactants) could be effectively applied to remediate soil polluted with PHCs. However, the system needs further research and investigation to optimize electrolysis time and biosurfactant dose to advance this approach in the soil remediation process.

1. Introduction

Petroleum hydrocarbons (PHCs) are known organic pollutants; particularly petrogenic products, waste from the coking industry, and other anthropogenic activities are primary sources of PHCs, which pollute soil adversely (; Ambaye et al., 2022, 2022a). Many studies have shown that it has a high octanol-water partition coefficient and hydrophobicity (Saber et al., 2021), and as the benzene number of rings in PHCs increases, they become more difficult to degrade (Vaccari et al., 2020). Therefore, soil contamination by PHC is a major international issue due to its low degradability, high carcinogenicity, teratogenicity, and ecotoxicity. Moreover, PHC rich in toxic and carcinogenic compounds not only pose a threat to intertidal environments and aquatic organisms but also to human health owing to their accumulation in foods (Ambaye et al., 2023). Therefore, the removal of PHC pollutants from soil has become an important research topic.

Among various remediation strategies, advanced oxidation processes (AOPs) (Hassani et al., 2021) and various electrode materials-based electrochemical advanced oxidation processes (EAOPs) have recently been widely used and reported to be the most efficient approach to restoring deteriorated natural resources, particularly for PHC removal from soil (Huang et al., 2017; Ahmadi et al., 2021; Hassani et al., 2022). H_2O_2/UV, Fe^{2+}/H_2O_2, hetero- and homogeneous Fenton-like processes, ozonation, and photocatalysis are all examples of AOPs (Huang et al., 2017; Hassani et al., 2021, 2022). By creating hydroxyl radicals ($^{\bullet}OH$), Fenton processes (Fe^{2+}/H_2O_2) can oxidize contaminants (Li et al., 2022). Hydroxyl radical ($^{\bullet}OH$) is the essential reactive intermediate in the oxidation of organics and is recognized as the most important oxidant (Periyasamy et al., 2022).

Electro-Fenton processes have emerged as the most appealing AOPs due to their fast reaction time, high efficiency, and wide range of targeted pollutants degradation (Hassani et al., 2021, 2022; Wei et al., 2022). However, despite its higher removal efficiency, the Fenton process uses H_2O_2 and Fe^{2+} as catalysts, making it expensive in large-scale applications. Furthermore, Fe^{2+} consumption results in secondary contamination and needs further treatment (Wei et al., 2022). In order to address these flaws, electro-Fenton has been thoroughly investigated with the goal of in situ H_2O_2 creation, cathodic Fe^{2+} regeneration, or a combination of the two. The boron-doped-diamond (BDD) electrode is applied as an anodic material in the Fenton process to avoid secondary pollution. It has drawn attention due to its long-term response stability, higher potential for O_2 evolution reactions, strong corrosion resistance, high chemical inertness, low background currents, large potential window, and chemical stability (Muddemann et al., 2021).

The water stability zone (E 2.3 V relative to the standard H_2 electrode (SHE)) and the potential area of water disintegration (E > 2.3 V relative to the SHE) are both the ranges in which BDD oxidation takes place. As a result, free and slightly adsorbed hydroxyl radicals (BDD ($^{\bullet}OH$)) can develop on its surface. These radicals are non-selective in destroying tenacious organic contaminants (Muddemann et al., 2021). However, electro-Fenton PHC reduction using a BDD anode electrode still has some challenges, such as the high cost of electrodes and energy consumption.

On the other hand, the bioslurry process is considered an environmentally friendly method for pollutant treatment, but the reaction conditions must be carefully regulated (Huang et al., 2017; Xiao et al., 2015; Wan et al., 2013).

Moreover, due to the limited resistance of microorganisms to toxicity, bioslurry technologies may not be efficient at high pollution levels (Kundu et al., 2012). Nevertheless, adding a stimulant such as a biosurfactant or integrating bioslurry with other methods is a potential remediation strategy since it increases pollutants' bioavailability to microbes (Ortega-Calvo et al., 2013). Furthermore, considering the disadvantages and advantages of biological treatment and advanced oxidation, combining advanced oxidation and biological treatment is now considered a more feasible and practical option (Aboudalle et al., 2021; Baiju et al., 2018; Xu et al., 2015; Hassani et al., 2021; Hassani et al., 2022). That opens a new horizon for researchers to use the Fenton process in the combination system to improve the biodegradability of PHCs, which is beneficial to bioslurry treatment. While the same bioslurry treatment combination system can stabilize waste and reduce the use of Fenton chemicals (Liu et al., 2020).

In the combined process, chemical oxidation as an initial step would convert the persistent organic pollutants into more biodegradable intermediates, which could be easily removed in a subsequent biological step (Ambaye et al., 2021). For example, Xu et al. (2015) used the direct electro-Fenton process before biotreatment. They found that the removal rate of pyrene increased from 50% (individual electro-Fenton and biotreatment) to 91.0% (combined treatment). The combined treatment has been confirmed as a valuable method for the remediation of contaminated soil. However, its application for soil remediation is at the initial stage and requires further research and investigation to be applied on a large scale. To the best of our knowledge, the use of electro-Fenton degradation of PHCs using a BDD anode electrode and a biological process stimulated with long-chain rhamnolipids in a hybrid system has not been investigated previously.

The current study aims to investigate the efficient degradation of petroleum hydrocarbons (PHCs) from polluted soil by combining electro-Fenton and biological processes. In addition, the effects of other parameters that affect the optimum conditions for the combination process were determined.

2. Materials and methods

2.1. Materials and analytical chemicals

Soil contaminated with crude oil used in the experiment was collected from a polluted site in northern Italy. The contaminated soil samples were taken 5–10 cm below ground level, sealed, and transported to the lab. In all the experimental analysis, AR-grades chemicals, *i.e.,* potassium dihydrogen phosphate (KH_2PO_4), potassium nitrate (KNO_3), salicylic acid ($C_7H_6O_3$), sodium sulfate (Na_2SO_4), sulfuric acid (H_2SO_4), alkane mix (C6–C35) and hexane (C_6H_{14}) were purchased from USA-Sigma-Aldrich, Inc. (St. Louis, Missouri) and used to perform samples analysis. A titanium net/mesh electrode was provided by Politecnico di Milano (Italy), and a BDD electrode came from De Nora (Milan, Italy). A boron-doped diamond (BDD) was selected due to its high O_2 overpotential, which enhances the removal rates by promoting

the additional formation of hydroxyl radicals on its surface. Oxygen (O_2) was provided externally from a compressed air facility. In all experiments, chemical solutions and other reagents were prepared using ultra-millipore pure water with simplicity >18.2 MΩ cm. A real-time power supply system (MX100QP, AIM-TTI instruments) was used to manage current and voltage during experiments.

2.2. Soil preparation and physicochemical analysis

After being partially air-dried, the soil samples were processed to make powdered form and sieved to a diameter of less than 2 mm. The main properties of initial soil samples were analyzed for various physicochemical parameters using the standard method of ALPHA 5310 (Napoli et al., 2017). The initial polycyclic aromatic hydrocarbons (TPH) were 4500 mg/kg before being added to the reactor. Polluted soil samples were characterized as sandy-loam soil containing 80% sand, 11% silt, and 9% clay. Soil physicochemical properties were as follows: pH 7.6; organic matter content, 12 g/kg; carbon to nitrogen ratio (C/N) 48 g/kg; cationic exchange capacity, 113.2 μS/Cm. The broths containing long chain rhamnolipids used in the bioslurry reactor were previously produced by a safe bacterium *B. thailandensis* E264 at a large-scale fermenter (10 L) using winey residues, a sole carbon, and energy source. It has yielded 1070 mg/L after extraction, reduced the surface tension of water from 71 mN/m to 34.5 mN/m, and had a CMC value of 500 mg/L and three congeners with the predominance of Rha-Rha-C14-C14 (MS[M − H = 761]) has been described to have two identical genes containing copies of RL synthesis genes (rhlA, rhlB, rhlC) present at different sites in its genome (Chebbi et al., 2021).

2.3. Experimental design

In this experimental design, seven tests were performed following a standard protocol to evaluate the efficient degradation of petroleum hydrocarbons (PHCs) from polluted soil by combining electro-Fenton and biological processes. Details of the experimental setup are given in Supplementary Table S1. Bioslurry and electro-Fenton processes were individually evaluated for degrading PHCs in treatments 1 and 2, respectively. Treatment 3 was performed to measure $^{\bullet}OH$ concentrations during the electro-Fenton process. Treatments 4, 5,6, and 7 were initially kept in electro-Fenton reactors and then transferred to bioslurry reactors after different incubation times to investigate the remediation efficiency of combined electro-Fenton and biological processes. The electrolysis time in the electro-Fenton stage in treatments 4, 5,6, and 7 was 12, 24, 36, and 48 h, respectively. A graphical representation of the designed experiment is shown in Fig. 1.

2.3.1. Analytical methods

In order to perform sample analysis, each reactor's slurry was collected with a 50 mL specialized syringe. Samples were centrifuged at 8000 rpm for 15 min, and precipitates and supernatants were extracted using the solid and aqueous phases, respectively. To determine the PHCs degradation rate in a solid phase, the precipitate was air-dried, crushed into a fine powder, and homogenized. 2 g of precipitate was added to 20 mL of hexane in 100 mL Teflon tubes. After 10 min of vigorous agitation, ultrasonic extraction was performed at 35 °C on each solid-phase sample for 30 min. Next, the tubes were centrifuged at 5000 rpm to clean the extract for 10 min. Finally, PHCs in the aqueous phase were analyzed using liquid-liquid extraction with 20 mL of hexane on 1.10 mL of supernatant. Triple extractions were performed in both the solid and liquid phases. Solid-phase and aqueous-phase extract samples were mixed. Samples (20 ml) were evaporated to dryness with a gentle stream of nitrogen, resuspended in 400 μL of n-hexane, and stored at 4 °C until analysis.

The extent of degradation of petroleum hydrocarbons (PHCs) was determined using Gas chromatography (GC) with flame-ionization detection (FID). DB-5 MASS capillary column (with a film thickness of 30 m, 0.32 mm ID, and 0.25 μm df) was used at a flow rate of 1 mL/min, and N_2 gas (99.99% purity) was used as a carrier gas. The injector temperature was adjusted to 50 °C for 2 min, then gradually increased to 200 °C at 10 °C per minute. It was then elevated linearly to 250 °C at a rate of 5 °C/min for 5 min after being kept at 200 °C for 4 min. There was no split in the sample. PHCs were identified using retention time, and their amount was quantified using an external reference method using the peak area approach.

The quantitative determination of hydroxylated derivatives of SA, 2,3-dihydroxybenzoic acid, and 2,5-dihydroxybenzoic acid was performed by HPLC to determine the concentration of $^{\bullet}OH$. The generation and trapping of $^{\bullet}OH$ radicals were achieved by introducing 1 mL of 10 mM salicylate aqueous solution (SA, 2,3-DHBA, or 2,5-DHBA), 1.0 mL of 10 mM ascorbic acid, 1.0 mL of 2.4 mM Na_2EDTA, and 1.0 mL of 2.0 mM Fe $(NH_4)_2(SO_4)_2$ solution, in the order of listing. Samples were then taken for HPLC analysis various times throughout the reaction process. A C18 reversed-phase column (250 mm × 4.6 mm, 5 mm) was used in this case. This method's detection limit was 0.1 mol L^{-1}. Separation was performed with a mobile phase of 30 mmol L^{-1} acetate (pH 4.9), a flow rate of 1 mL/min, and a column temperature of 25 °C (Kuzma et al.,

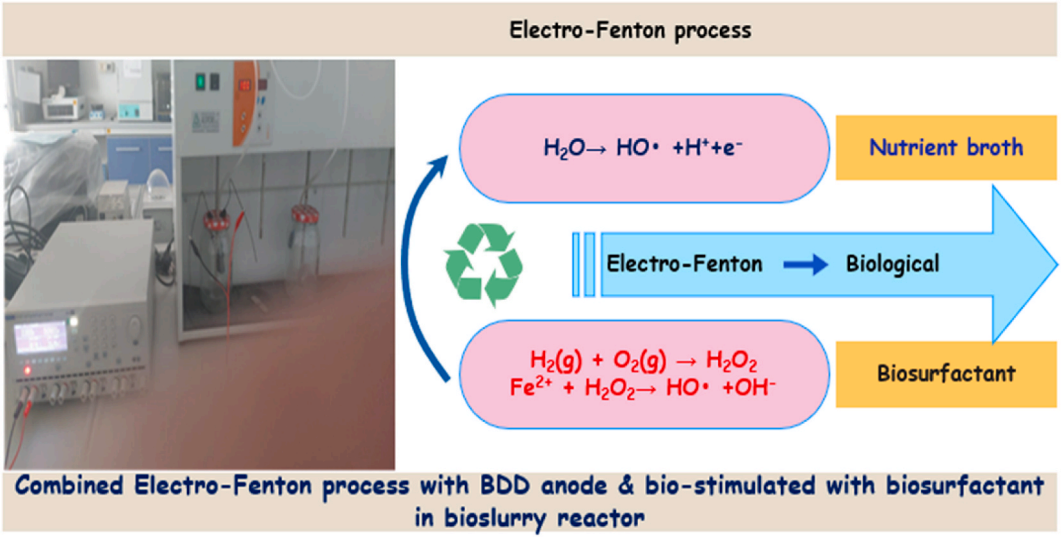


Fig. 1. Graphical representation of the combined process for degradation of PHCs.

2018).

In order to investigate and verify oxidation and biodegradation by-products qualitatively, the GC-MS Model 6890 N (Agilent Technologies, CA, USA) equipped with the Elite-5MS (5% phenyl methyl polysiloxane) capillary column (30 m * 0.32 mm internal diameters, and film 0.32 μm thick was used. The helium gas was used as a carrier at a flow rate of 1 mL/min. From each sample, 1 μL aliquots were injected in split mode (30:1). The oven temperature was kept at 60 °C for 5 min, then increased to 290 °C at 5 °C/min. The ion source temperature was kept at 250 °C, and the transfer line was at 300 °C, acquisition range of 40–500 amu in electron impact (EI) with an ionization voltage of 70 eV.

2.3.2. Fragmentation identification in GC-MS

GCMS was used for fragmentation identification, component retention indices (RI), and mass spectra that were compared with a NIST database library and literature data [Stein, S.E. NIST/EPA/NIH Mass Spectra Database, V2.1; PerkinElmer, Hong Kong, China, 2000]. Retention indices were calculated by Elite-5MS capillary columns using an n-alkane series (C6–C35) under the same GC conditions as for the samples. Each component's relative amount obtained from GC/MS was expressed as a percentage of the total peak area. The analyses were performed in triplicate.

2.4. Microbial analysis

Real-time polymerase chain reaction (PCR) analysis of the 16S rRNA gene was used to determine bacterial abundance in each soil sample, as guided by Ahn et al. (2009). Furthermore, the total number of bacteria was calculated as the number of copies per mL of slurry.

2.5. Soil organic matter (SOM) analysis

SOM quality was evaluated using uncontaminated soil. The potassium dichromate-external-heating technique was used to estimate the SOM percentage in soil samples. Sodium pyrophosphate ($Na_2H_2P_2O_7$) extraction and the potassium dichromate ($K_2Cr_2O_7$) outside heating method were used, as described by Jarukas et al., 2021, to determine SOM composition (humin, humic and fulvic acid).

2.6. Statistical analysis

Origin Lab Corporation, Northampton, MA, USA software (version 8.0773) was used to assess the statistical difference between current pollutant production and degradation. P values ($P < 0.05$) were used to measure all significance of treatment effects.

3. Results and discussion

3.1. Degradation of PHCs by electro-fenton process

An electro-Fenton process using a boron-doped diamond (BDD) anode was used to improve the degradation of soil polluted with PHCs for about 72 h. PHCs' degradation efficiencies were measured in terms of their reduction rate. The results indicated that 70.6% PHCs removal was achieved at optimal conditions: pH 3 (T2), as shown in Fig. 2. This study also indicated that the degradation of PHCs was probably attributed to the BDD electrode's ability to produce a high quantity of *OH. That was accountable for the high oxidative degradation of micro-pollutants due to weak adsorption on their surface as soon as power was supplied (Periyasamy et al., 2022). However, compared to biological processes, the reduction rate of the electro-Fenton process decreased in the second phase, as shown in Fig. 2. It shows that changes in the oxidation environment, such as H_2O_2 and pH, in the electro-Fenton process (T2) were counteractive to •OH generation reduction during the second half of the electro-Fenton process. This data demonstrated that the degradation rate of PHCs was high in the initial period, which is highly related to the generation of •OH species, as shown in Fig. 3 (Xu et al., 2015; Liu et al., 2020).

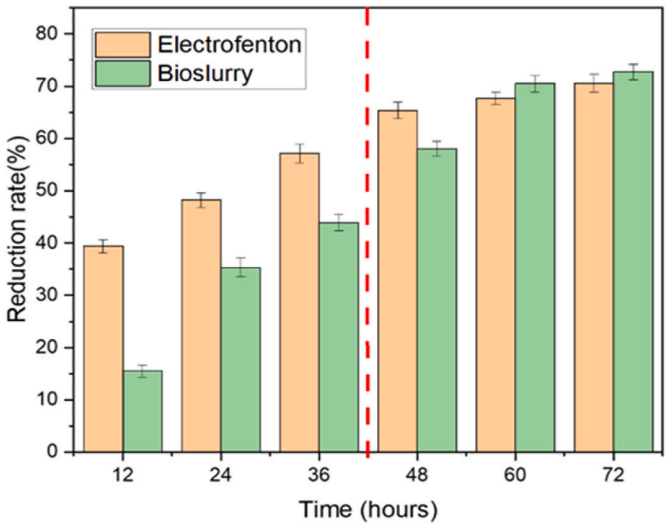


Fig. 2. TPH degradation by electro-Fenton and bioslurry process: data are means of duplicates, and error bars show standard deviation.

3.2. Effect of bioslurry process on the degradation of PHCs

A bioslurry process experiment to degrade PHCs from polluted soil was done in the aerated bottle containing 500 mL of rhamnolipid biosurfactant and nutrients of 1.5 g KNO_3 and 0.1 g NH_42HPO_4 for about 72 h (T1). As indicated in Fig. 2, a PHCs removal rate of almost 72.8% was observed. It demonstrated that heterotrophic bacteria in biosurfactants are anticipated to emulsify hydrophobic pollutants and increase bioavailability by lowering interfacial tension in soil and the aqueous phase (Ambaye et al., 2021). Compared to the electro-Fenton process, the reduction process increased inefficiency in the second phase, as shown in Fig. 2, demonstrating that heterotrophic bacteria in a slurry reactor required an adaptation period before they could proliferate logarithmically during bioslurry treatment (Xu et al., 2015; Liu et al., 2020). Results also showed that the bioslurry degraded PHCs slowly but quickly as the population of heterotrophic bacteria in biosurfactants increased. This increase in bacterial population was positively related to PHCs degradation, as shown in Fig. 3.

The result also showed that electro-Fenton treatment is characterized

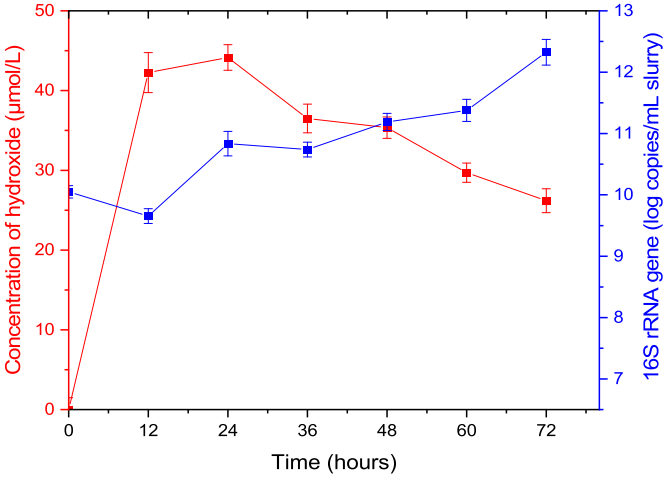


Fig. 3. *OH, concentrations during EF process (T2) and microbial 16S rRNA gene copy number during bioslurry Process (T1).

by strong oxidizing ability (and thus high degradation rates). In contrast, bioslurry treatment necessitated a lengthy adaptation period before achieving similar results. Maximizing the first half of the electro-Fenton process and minimizing the bioslurry process's adaptation phase was the key to integrating the two processes. Additionally, $^{\bullet}OH$ is a powerful oxidant that can transform organic pollutants into useable substrates for living organisms. Therefore, the combined method of Fenton and bio-treatment in contaminated soil remediation shows better treatment efficiency than the sole method. However, pH and electrolysis time optimization would need to improve the degradation of PHC-polluted soil (Periyasamy et al., 2022).

3.3. Effect of pH on the electro-Fenton degradation process

Electro-Fenton process efficiency depends on pH, temperature, and the generation of free radicals that degrade the pollutant. In addition, the speciation of chemical compounds and the reactions involved in many advanced oxidation processes are influenced by acidity or alkalinity. For the electro-Fenton process, pH (2–4) has been widely observed to play a vital role (Nadais et al., 2018).

This research work studied the effect of pH on the degradation of PHCs from soil polluted using the electro-Fenton process. The airflow rate was 10 mL/minute. A 2.0 V voltage was applied, and 1 g/L of Na_2SO_4 was used as a supporting electrolyte (T1). Results showed that the initial pH was 3.0 during the electro-Fenton process. However, it rapidly rose to 5.5 in the initial 12 h. At the end of the experiment, pH reaches a value of 7.0 (Fig. 4). An increase in pH during the electro-Fenton process can be attributed to three factors: (i) electrolysis produces $^{\bullet}OH^-$ and H^+ on the cathode and anode, respectively, and H^+ is used to produce H_2O_2, while $^{\bullet}OH^-$ is produced concurrently with $^{\bullet}OH$ radicals during the Fenton-reaction (Quiroz et al., 2014). (ii) The oxidation potential of generated reactive oxygen species (ROS), mainly $^{\bullet}OH$, is strongly influenced by the solution pH, which explains why different solutions have varying degradation efficiency. (iii) Also, at higher pH, H_2O_2 decomposition can be inhibited by the absence of protons, thereby reducing the production of hydroxyl radicals, which reduces the efficiency of the Fenton process with increasing pH. Moreover, the evolution of hydrogen gas at lower pH would bring down the efficiency, as it would reduce the generation of hydrogen peroxide (Periyasamy et al., 2022).

Furthermore, this study showed that a lower pH, *i.e.,* 3, promotes oxidation-reduction reactions and favours the decomposition of H_2O_2. A pH range of 5–9, ideal for bacterial development, is required during bioslurry processes following the electro-Fenton process for degrading PHCs. These findings are consistent with those reported by Wang et al. (2010). They found the highest rates of contamination degradation by electro-Fenton treatment at pH values between 2 and 4. According to this study, when the electro-Fenton process was completed, the slurry pH attained a value adequate for the bioslurry process (pH 5–7). As a result, if the biological process was used after the electro-Fenton procedure, it was not essential to alter pH.

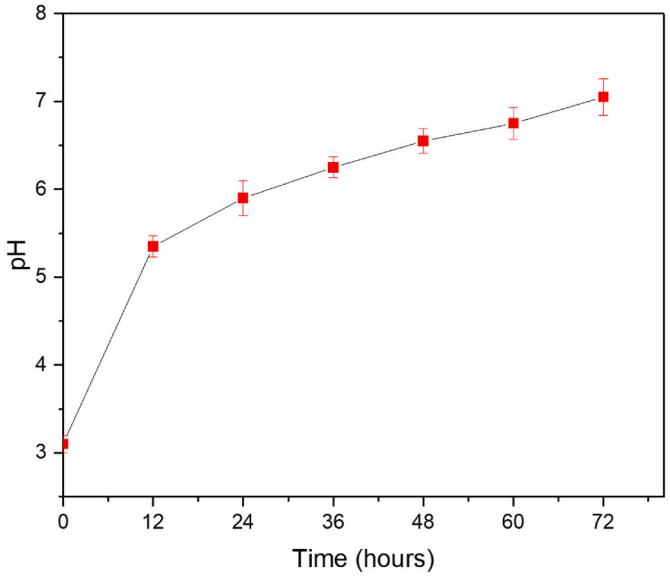


Fig. 4. Changes in pH during the operation of the electro-Fenton process.

3.4. Evaluation of integrated electro-Fenton and bioslurry treatment for PHCs degradation

Biotreatment and the electro-Fenton process are effective remediation techniques for soil polluted with PHCs. However, the electro-Fenton process caused secondary pollution in the soil environment, and biotreatment is typically incapable of effectively removing very harmful contaminants. That prompted the development of an integrated approach to Fenton and biotreatment methods for the remediation of PHC-polluted soil. Huang et al. (2017) demonstrated that an integrated approach to Fenton and biotreatment methods had greater treatment efficacy than either method alone.

In this study, four scenarios (T4-T7) were developed by selecting the highest rate time interval in the electro-Fenton process (48 h), as shown in Fig. 2. This investigation was performed with the combination approach of electro-Fenton with different periods (12, 24, 36, and 48 h) with bioslurry for the degradation of soil polluted with PHCs. As shown in Fig. 5, after 72 h of incubation, the removal efficiency of PHCs reached 93.6, 70.12, 64.02, and 61.03%, respectively. It demonstrates that organic pollutants can be chemically broken down into more biodegradable intermediates via the electro-Fenton process, resulting in lower concentrations (Ambaye and Hagos, 2020).

Moreover, when compared to individual treatments of electro-Fenton (T1) and biolsurry (T2), the combined approach increased degradation by 21.02 and 22.78%, respectively, and this result is in line with Xu et al. (2015). Furthermore, they claimed that electro-Fenton's pretreatment process increased the reduction rate from 50% (individual bioslurry and electro-Fenton) to 91% (integrated approach). They also reported that pyrene removal increased significantly in the hybrid system. Therefore, an integrated approach is an effective way to remediate soil polluted with PHCs.

The results also demonstrated that T4 showed maximum performance compared to the other treatments (Fig. 5). After 72 h, the total removal efficiency reached 93.6%, and as time increased, the PHCs-degradation rate enhanced. However, it gradually declines with time (Xu et al., 2015). This indicates that some competing processes may have occurred, resulting in the opposite of the predicted effect. During the experiment, organic matter in the soil and intermediates would have acted as competitors. Therefore, for this integrated approach, the best time to use the electro-Fenton process had to consider changes in the organic matter composition of soil polluted with PHCs. Table 1 compares the treatment of petroleum hydrocarbon-contaminated soil by combining electro-Fenton and biological processes in recent years. This table also details the type of PH treated and its initial concentration, their operating conditions, and the observed improvement in soil remediation as reported in the literature. The present work shows a higher yield in terms of pollution reduction. However, the method needs further research and investigation concerned with optimizing electrolysis time and dose of biosurfactant for large-scale soil remediations.

3.5. Effect of bacterial population on best treatment selection for EF-bioslurry process

The biodegradation of oil-contaminated soil is highly dependent on viable microorganisms (Ambaye et al., 2022). Therefore, this experiment investigated the effect of the heterotrophic bacterial population by

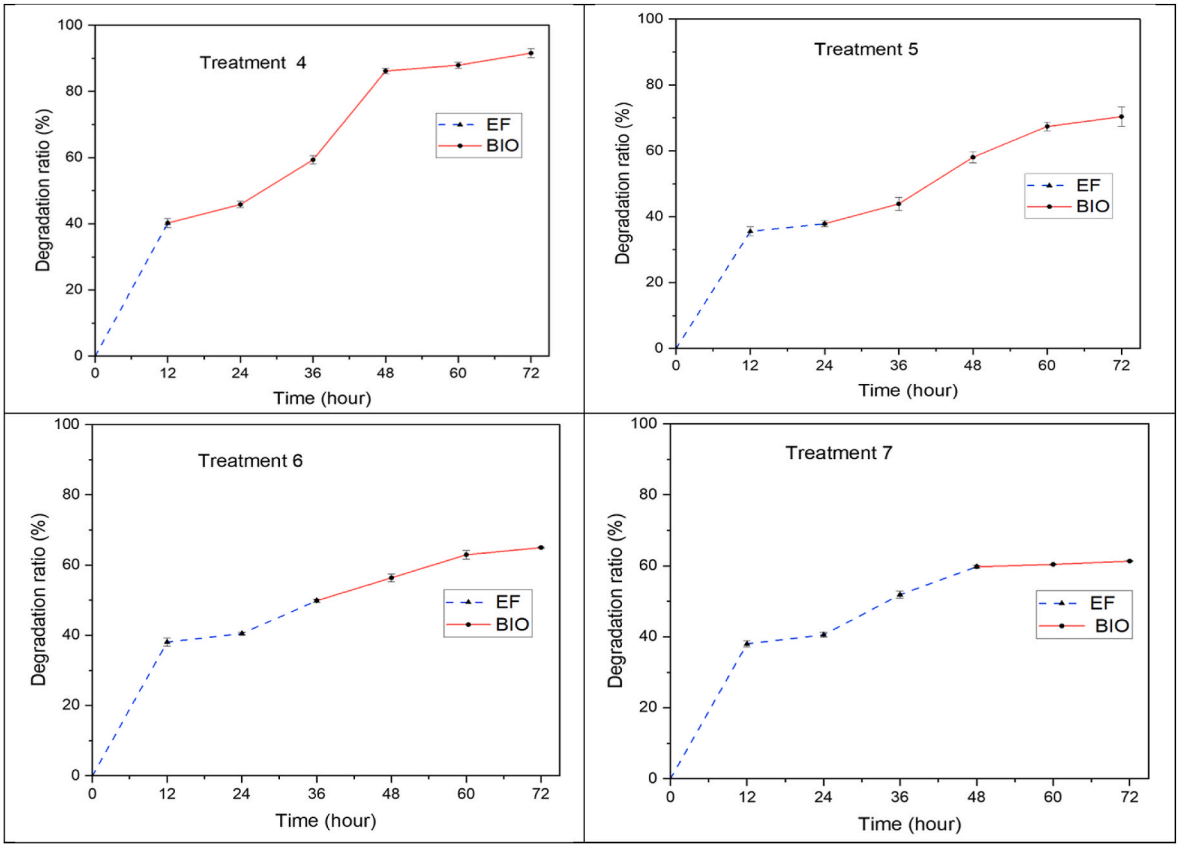


Fig. 5. TPH degradation ratio between electro-Fenton and bioslurry process and effect of incubation time (T4: 12 h, T5: 24 h, T6: 36 h, T7: 48 h): Data are means of duplicates, and error bars show standard deviations.

Table 1
Comparison with previous work studies on the combination of electro-Fenton and biological process for petroleum hydrocarbon polluted soil treatment.

Type of pollutant	Initial concentration	Treatments	Conditions	Performance (%)	Ref.
Petroleum-contaminate ted soil	Total dichloromethane-extractable organics (TEO) 32,400 mg/kg	Electro-Fenton- with biological process	The optimum molar ratio of H_2O_2 and Fe^3+ was 300/L, determined in batch experiments. Following the Fenton-like pretreatment, biological treatment was carried out in the same reactor. A mixed culture, isolated from the contaminated soil, was used as an inoculum	50.6	Lu et al. (2010)
Petroleum oil-contaminated soil	38,300 mg/kg	Electro-Fenton with biostimulation	A modified Fenton oxidation, using Fe (III) chelated with nitrilotriacetic acid in a molar ratio of 1:1 as a catalyst, followed by biostimulation of indigenous microbes by adding peanut hull as a bulking agent.	88.9	Gong (2012)
Oil contaminated soil	17400 mg/kg	Fenton with biological process	The degradation of oils in Fenton-like treatment was carried out in a slurry with different H_2O_2/ contaminant weight ratios (w/w) under batch conditions followed by aerobically incubating without shaking at 20 °C in the dark.	74	Goi et al. (2006)
Diesel contaminated soils	25.4 g mg/kg	Chemical oxidation with indigenous microorganisms	Chemical oxidation with Fenton's reagent Following chemical oxidation, bioremediation was stimulated through oxic incubation with nutrient amendment followed by biostimulation of residual microbial populations was conducted in the micrococosms by adding nutrients and air mixing to provide optimal aeration	59	Sutton et al. (2014)
Linear alkylbenzene polluted soil	2563 mg/kg	Coupling chemical oxidation and biostimulation	Modified Fenton's reaction at various dosages and of permanganate on the microbiota over 4 weeks were assessed.	65	Martínez-Pascual et al. (2015)
Pyrene-contaminated soil	144.70 mg/kg .	Electro-Fenton with bioaugmentation	Direct electro-Fenton process followed by bioaugmentation	91	Xu et al. (2015)
Petroleum hydrocarbon-contaminated soil	4500 mg/kg g	Electro-Fenton and biosurfactant-assisted bioslurry process	Electro-Fenton (with a boron-doped diamond as an anode electrode) and biological processes stimulated with long-chain rhamnolipids	93.6	Present study

applying the electro-Fenton process as a pretreatment during the combination of EF and bioslurry. Results showed that the number of bacteria grew faster after inoculation in electro-Fenton with the bioslurry process until T7, which was 36 h of electro-Fenton and 36 h of bioslurry, then gradually declined at the end of the experiment with different incubations of the electro-Fenton process. Furthermore, the total heterotrophic bacterial population's 16S rRNA gene copy number changes over time in the combined electro-Fenton and bioslurry process, as shown in Fig. 6. This finding demonstrated that more PHCs were dissolved into the aqueous phase during the integration processes of electro-Fenton with the bioslurry process, making hydrocarbons more bioavailable. It also showed that the bacterial population expanded more rapidly following a combined electro-Fenton and bioslurry process (Usman et al., 2016).

Research findings also showed that prolonged exposure to the electro-Fenton process may have resulted in the formation of substances readily useable by bacteria. However, competition between petroleum-derived aromatic hydrocarbons and organic matter in soil and intermediates may have decreased the removal of PHCs if the electro-Fenton process had been applied for an extended period. While in bioslurry stimulated with biosurfactant-treated soil, hydrocarbons may have been depleted because of microbial consumption. Similar findings were also stated by Xu et al. (2015). They applied the direct electro-Fenton method before biotreatment to stimulate the degradation process of pyrene. Biosurfactant application in PHC-polluted soil is anticipated to emulsify hydrophobic pollutants and enhance their bioavailability by reducing the interfacial tension between soil media and the aqueous phase. In contrast, the electro-Fenton application may generate substances that bacteria can readily utilize (Whang et al., 2008).

Overall, PHC degradation is the highest in the first 36 during the whole remediation (shown Fig. 6). The highest PHC degradation efficiencies in the first 36 h indicated that the microbial community structure shift may be associated with the petroleum hydrocarbon degradation. This revealed that the success of oil-contaminated bioremediation depends on the presence of sufficient microorganisms with the appropriate metabolic capabilities. Simultaneously, prolonged soil application in the electro-Fenton process may have lowered PHC removal. This happened due to competition between PHCs and organic matter in soil and intermediates. Bacteria that can break down the PHCs have increased over time. That indicates native soil microflora has become acclimated to crude oil-contaminated soil's stressful conditions and can use complex hydrocarbons to grow.

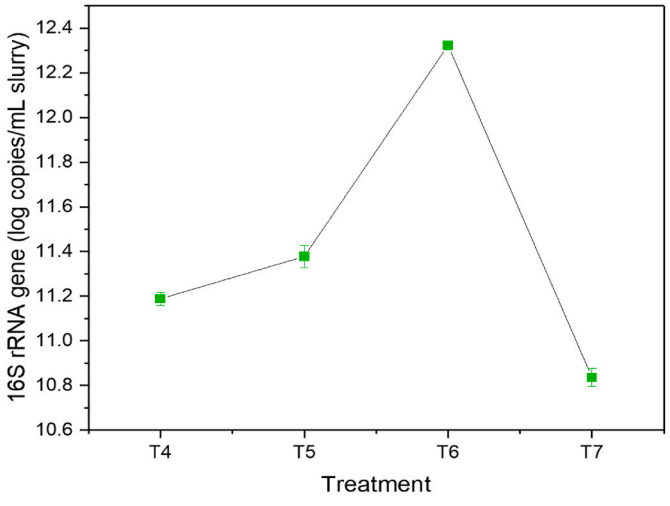


Fig. 6. Total heterotrophic bacterial population16S rRNA gene copy number changes in the EF-biological process.

3.6. Effect of intermediates on the selection of best treatment for EF-bioslurry process

Pretreatment with the electro-Fenton process yielded some low-molecular-weight substances with high bioavailability. When PHCs undergo the electro-Fenton process, $^{\bullet}OH$ can quickly ring-cleave them, resulting in low-molecular-weight by-products better suited for biodegradation. Organic pollutants decompose into aldehydes, alcohols, acids, carbon dioxide, and water due to either chemical oxidation or biological decomposition (Aboudalle et al., 2018). The lists of the most prominent intermediates identified by GC-MS in this investigation are shown in Table 2. Most byproducts of the electro-Fenton reaction are aliphatic and aromatic hydrocarbons, and exact species of intermediates were detected at varying concentrations throughout the experiment. Furthermore, the oxidation process increased the proportion of aliphatic to aromatic hydrocarbon byproducts. This showed that aliphatic and aromatic hydrocarbon intermediates, produced when rings were cleaved and hydroxylated, can be further chemically degraded (Pérez-Pantoja et al., 2019).

The percentages of aliphatic-aromatic hydrocarbon intermediates at 12, 24, 36, and 48 h were 3.63 ± 0.1, 4.48 ± 0.1, 5.78 ± 0.2, and 7.50 ± 0.1, respectively.

Table 2 also includes a percentage of the peak area occupied by intermediates of low molecular weight aliphatic and aromatic hydrocarbons. Following 12 h of electro-Fenton process application, the rate of these intermediates was slightly higher than 3%. As expected, increasing the electro-Fenton processing time to 48 h increased the yield by 8%. However, results of PHCs degradation rates during the integration of electro-Fenton with bioslurry treatment showed that the bioavailability of substrates produced initially within 12 h of the electro-Fenton process was adequate for the bioslurry phase.

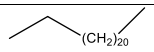
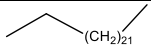
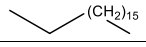
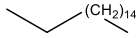
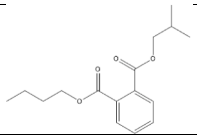
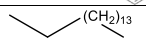
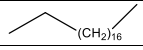
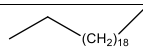
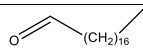
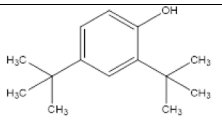
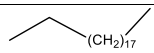
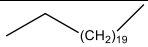
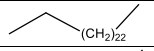
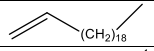
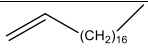
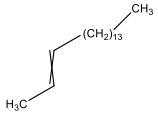
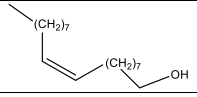
Moreover, since the electro-Fenton process improved PHCs removal by 26% during the electro-Fenton process phase, the overall reduction rate was 31% during the entire integration of electro-Fenton with the bioslurry process. The findings also revealed that there was no need to extend the application time of the electro-Fenton process. This demonstrates that organic pollutants' bioavailability and bacteria's activity were increased by employing an electro-Fenton process as a pretreatment before the biotreatment process. In addition, elect Fenton process-based further degradation of pollutants can generate low-molecular-weight by-products that function in the co-metabolism of substrates during the biotreatment phase.

In biological treatment, however, bacteria may favour using more readily metabolizable intermediates with a lower molecular weight and higher bioavailability. Because bacteria used high bioavailability intermediates at the start of the biological process, complete degradation of the pollutant was not possible through biological treatment due to competition between the intermediates (Lu et al., 2010; Abbas et al., 2022; Qian et al., 2022). Because of this, as can be seen in Fig. 5, the biological treatment process peaked in Treatment 4 and then declined in Treatments 6 and 7. Overall, PHC degradation was aided by an electro-Fenton application time of 12 h. In addition, applying the electro-Fenton process for 12 h reduced competition between intermediates, leading to improved biodegradation. However, more study is needed to determine the best way to use the combined electro-Fenton and biological treatment with a short incubation period on a commercial scale.

3.7. Effect of SOM composition on the selection of best treatment for EF-bioslurry process

Electrochemical reactions are potent, non-selective oxidant tools that affect many organic compounds. It is worth noting that SOM is a significant contaminant target during the anodic oxidation of polluted soils. The presence of SOM has been shown to affect contaminant removal negatively, positively impact indigenous microbe's survival

Table 2
Main fragmentation and percentages of fragmentation (aliphatic hydrocarbons and aromatic hydrocarbons).

S. No.	Detected main intermediates	Retention time (minutes)
1.	 tricosane	2.17
2.	 tetracosane	4.06
3.	 octadecane	4.64
4.	 heptadecane	5.54
5.	 butyl isobutyl phthalate	5.55
6.	 hexadecane	5.71
7.	 nonadecane	6.31
8.	 henicosane	6.42
9.	 Octadecanal	7.39
10.	 2,4-di-*tert*-butylphenol	8.03
11.	 icosane	8.18
12.	 docosane	8.39
13.	 pentacosane	9.38
14.	 henicos-1-ene	9.56
15.	 nonadec-1-ene	10.37
16.	 heptadec-2-ene	12.85
17	 (*Z*)-octadec-9-en-1-ol	20.63

during anodic oxidation, and significantly alter SOM's content, composition, and structure (Wang et al., 2012; Nidheesh et al., 2019). In this research, the changes of three humic fractions (humic acid, HA; fulvic acid, FA, and humin) in electro-Fenton treatment were evaluated for their effect on the degradation of soil polluted with PHCs. The best scenario for the integrated electro-Fenton and the bioslurry process is shown in Fig. 7. In the electro-Fenton process, total SOM content dropped from 3.25 to 1.61% after 48 h. The FA fraction's content decreased from 0.6% at the beginning to 1.6% at 12 h and then dropped to 0.4% at 48 h. It is only enhanced by 0.1% in electro-Fenton from 0 to 12 h.

Fig. 7 showed that HA content decreased from 1.4% to 0.3%, while humin content dropped from 1.1% to 0.4%. An essential factor in the electro-Fenton process that led to the reduction of SOM was the non-selective nature of $^{\bullet}$OH radicals (Gao et al., 2020). The anodic oxidation process only oxidized about 1.9% of soil organic matter, despite competition for $^{\bullet}$OH between PHCs and organic matter. $^{\bullet}$OH, degraded a large portion of the organic material in the soil. SOM has undergone changes in content and structure, which can significantly affect its capacity to absorb and release organic contaminants such as petroleum-derived aromatic hydrocarbons (Gao et al., 2020).

In addition, this study showed that longer periods of anodic oxidation resulted in higher levels of fulvic acid (FA) and lower levels of humic acid (HA) and humin. It suggests that the oxidation process altered the structure of HA and converted at least some of it into FA. FA has a smaller molecular size than HA and is more effective at desorbing PHCs than HA (Velázquez-Vázquez et al., 2022). As a result, more PHCs in the soil will desorb into the liquid phase, facilitating their removal. Soil organic matter content and composition are affected by anodic oxidation, affecting PHCs absorption and desorption. Surfactants formed during chemical oxidation processes can also aid in the desorption of PHCs (Zhang et al., 2020). Soil organic matter fractions like FA and HA have been shown to play an essential role in the adsorption and degradation of petroleum hydrocarbons (Chen et al., 2019).

On the other hand, after 12 h, degradation rates slowed to the point where less HA could be converted to FA, and FA content began to decline. As we have seen, bacteria preferentially utilize FA as a carbon source, contributing to a more efficient bioslurry process. Hence, this result shows that using anodic oxidation as pretreatment for about 12 h, followed by bioslurry for about 60 h, enhanced the overall degradation of soil polluted with PHCs during the hybrid system, as shown in Fig. 5.

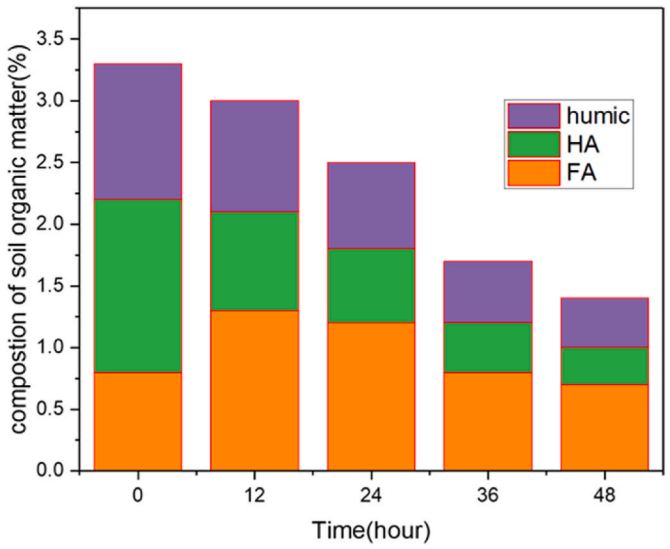


Fig. 7. Changes in SOM after different times of EF oxidation. Time 0 means raw soil.

3.8. Environmental implications of BDD anode in electro-Fenton process

It has been established that anodic oxidation can efficiently remove numerous organic contaminants in a short period. It can be easily adapted as a component of distributed wastewater treatment systems, which is another central selling point. Not only is it simple to automate, but it also takes up little space in design and does not require any additional chemicals (Jiang et al., 2021). Many studies have documented effective PAHs removal by using boron-doped diamond (BDD) electrodes as the anode (De Luna and Bensalah, 2022; Ltaïef et al., 2018; Olvera-Vargas et al., 2021). However, few researchers have observed drawbacks of anodic oxidation, such as alteration in SOM content, composition, and environmental impacts. SOM has been known to play a significant role in sequestering hydrophobic organic compounds in soil. However, the influence of chemical oxidation on SOM is a critical issue related to this technology (Wang et al., 2012).

The fate and transport of organic contaminants would be affected by shifts in the composition of SOM. Humin is the soil fraction most responsible for producing organic pollutants that cannot be extracted (Yang et al., 2010). In this study, anodic oxidation using a BDD electrode changed the sorption properties of soil by modifying soil organic matter and reducing humin content from 1.1 to 0.4%, as shown in Fig. 7. This demonstrates that the binding state of contaminants in soil could be altered by lowering humin content and increasing production of surfactant-like compounds under optimal conditions (Wang et al., 2012). Furthermore, the bioavailability of polyaromatic hydrocarbons in human acid was greater than that of humin (Chen et al., 2017; Zhang et al., 2009). It also suggested that lowering the total solvent extractable matter affinity in humin would increase the bioavailability of PHCs after anodic oxidation by BDD. Because of this effect, biodegradation can proceed well after chemical oxidation.

Studies conducted by Mansour et al., 2012; Ferrag-Siagh et al., 2013; Mousset et al., 2014; Ganzenko et al., 2020 shown that the use of BDD in the anodic oxidation process increases the biodegradation of soil polluted with PHCs. Even though BDD electrodes are excellent at maximizing oxidation efficiency, their widespread application is still debatable. Further study is required to reduce electrode costs, scale up fabrication while maintaining high physical stability, and find a solution to separating BDD film from the substrate surface and cracking issues. The process may also be hard to use on a large scale because soil polluted with PHCs in the real world has many different properties, such as low bioavailability of organic contaminants and the presence of other radical scavengers (Nidheesh et al., 2019).

The electro-Fenton process generally is based on an electron transfer between hydrogen peroxide (H_2O_2) and a homogeneous metal catalyst. Therefore, it is a good and promising alternative for soil treatment. However, the EF method still faces some problems that must be addressed. For example, in the EF process, the production of H_2O_2 is slow because oxygen has low solubility in water. In addition, the current efficiency under reduced pH (pH 2) is also low, and a large volume of iron sludge generation (Cheng et al., 2022).

On the other hand, combining the electro-Fenton process with other advanced oxidation methods has led to better results in removing contaminants. For example, the Ultrasonic (US) mechanism decomposes pollutants based on the creation of cavities or microbubbles resulting from acoustic cavitation in water. These cavities give rise to hydroxyl radicals and hydrogen radicals. Eventually, the combination of the electro-Fenton with the ultrasonic process, called sono-electro-Fenton, is reported to lead to an increase in cleaning the electrode surface, adaptability to the environment, and ultimately increase in the higher percentage of pollutants removal due to the chemical and physical reaction created (Babuponnusami and Muthukumar, 2012).

4. Conclusions

This study evaluated the performance of an integrated electro-Fenton and biodegradation process for removing soil polluted with petroleum-derived aromatic hydrocarbons (PHCs). As revealed from the total petroleum hydrocarbon reduction rate analysis, PHC was mineralized to a certain extent, and the removal ratio reached 71%. A change in oxidation conditions, such as radical $^{\bullet}OH$ and pH concentrations in the electro-Fenton process, was identified as counteractive to $^{\bullet}OH$ generation, leading to a low PHC removal rate. After being combined with biological treatment, the removal ratio of PHCs was elevated to 94%. As indicated by the results, the pretreatment of PHC pollutants increased the pH value from 3.0 to a suitable value for biodegradation. It also produced intermediates and a high flavunic acid content, a function of soil organic matter. The addition of biosurfactants increased bioavailability and resulted in PHCs with a lower molecular weight. Finally, combining electro-Fenton with biosurfactant-stimulated biological treatment was effective and feasible for removing PHCs from polluted soil. However, more research is needed to optimize key parameters for large-scale application.

Author contributions statement

Teklit Gebregiorgis Ambaye: Conceptualization, Writing – original draft& editing last version, Francesca Formicola: Reviewing, Silvia Sbaffoni: Reviewing, Shiv Prasad: Reviewing, Chiara Milanese: Reviewing, Francesco Saverio Robustelli Della Cuna: Reviewing, Andrea Franzetti: Conceptualization, Supervision, Writing – review & editing last version. Mentore Vaccari: Conceptualization, Supervision, Writing – review & editing last version.

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

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2023.138013.

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