Bioelectrochemical Remediation for the Removal of Petroleum Hydrocarbon Contaminants in Soil

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Abstract: Consistent accumulation of petroleum hydrocarbon (PH) in soil and sediments is a big concern and, thus, warrants a static technology to continuously remediate PH-contaminated soil. Bioelectrochemical systems (BESs) can offer the desired solution using the inimitable metabolic response of electroactive microbes without involving a physiochemical process. To date, a wide range of BES-based applications for PH bioremediations under different environmental conditions is readily available in the literature. Here, the latest development trend in BESs for PH bioremediation is critically analyzed and discussed. The reactor design and operational factors that affect the performance of BESs and their strategic manipulations such as designing novel reactors to improve anodic reactions, enhancing soil physiology (electrical conductivity, mass diffusion, hydraulic conductivity), electrode modifications, operational conditions, microbial communities, etc., are elaborated to fortify the understanding of this technology for future research. Most of the literature noticed that a low mass diffusion condition in soil restricts the microbes from interacting with the contaminant farther to the electrodes. Therefore, more research efforts are warranted, mainly to optimize soil parameters by specific amendments, electrode modifications, optimizing experimental parameters, integrating different technologies, and conducting life cycle and life cycle cost analysis to make this technology viable for field-scale applications.

Keywords: bioelectrochemical systems; petroleum hydrocarbon; bioremediation; microbial communities

1. Introduction

Bioelectrochemical systems (BESs) have shown enormous potential for a wide range of energy and environmental applications [1]. For example, a microbial electrolysis cell (MEC) can generate green hydrogen [2,3], a microbial electrosynthesis cell (MES) can be used for biochemical, and fuel synthesis via the CO2 reduction reaction [4–6], and, similarly, microbial desalination cells (MDCs) and microbial fuel cells (MFCs) have been considered a low-cost device to recover water from saline water and contamination treatment from soil and wastewater, respectively, and generate electricity [7–10]. Despite the different outcomes, these BESs share a common design aspect and inoculum (mostly electroactive bacteria), which makes BESs a versatile device for several applications. In particular, different BES designs have been tested for treating a wide range of wastewater, groundwater, and solid matrices, such as soil and sediments, from lab to field scale [11]. In particular, the application of BESs for petroleum hydrocarbon (PH) treatment in soil has been found effective and environmentally sustainable with no requirement for chemical additives [12,13].

An air cathode MFC-type BES is typically used for PH removal from soil and sediment. However, the BES setup used in the case of PH-contaminated soil treatment is fairly different from conventional MFCs used for wastewater treatment (Figure 1). The most common design of BES utilized for PH degradation consists of a snorkel column-based membrane electrode assembly (MEA) [14,15]. This special MEA is usually fabricated around a hollow polyvinyl chloride (PVC) rigid architecture. The cathode and anode
electrode, made with flexible carbon materials, faces inside and outside the PVC pipe. The MEA hollow column is then inserted in the PH-contaminated area to fabricate a fully functional BES. This specific BES design has many advantages, such as cheap to fabricate, high scalability, and flexible to install at the point source (deep into the ground) [16]. Naturally thriving microbes at the contaminated sites can remove the PH but at a slow rate due to the limited availability of electron acceptors [17,18]. In the presence anode (electron acceptor), the electroactive bacteria in the consortium of PH-degrading microbes utilize the end products of PH activation and fermentation, such as acetate and butyrate, and generate electrons, which are then captured at the anode and transferred externally to the cathode [16]. At the cathode, oxygen accepts the electrons and completes the redox cycle. Therefore, this process, along with PH degradation, also generates a sustainable electrical current that can be harvested. However, the power density obtained from soil PH-degrading BESs, is mostly in the µ to mW range (Table 1), which is low compared with conventional MFCs, and can be utilized to operate onsite low-power-consuming sensors and alarming devices [19]. In fact, the main goal of such BESs is not to generate power but rather to focus mostly on PH degradation.

Recently, a few attempts have been made to analyze the recent advancements and outlooks in BES-based PH bioremediation technologies. For example, Jin and Fallgren explained the feasibility of BES for environmental bioremediation with a specific focus on the organic and inorganic, and harmful metal-contaminated medium [37]. Ambaye et al. presented recent progress in BES-based technologies for PH bioremediation with a general overview of the electron transfer mechanism and integration of different technologies [38]. Thus, there is scope to critically analyze the process and comprehend its readiness of BESs for full-scale application by exploring fundamental mechanisms and limitations. Therefore, the main aim of this review is to critically analyze past developments in BES technologies for the treatment of PH-contaminated soil and understand the current major limitations that need to be addressed for field-scale implementation of this technology. Under different subsections, we have evaluated the fundamentals to advanced aspects of BES working principles and design, microbial metabolism and interactions, soil properties, environmental factors, etc., in the context of PH contamination. Finally, a future perspective section is included to guide future research needs for field-scale implementation of BESs for PH bioremediation in a wide range of environmental conditions.

Figure 1. Schematic diagram of BES applied for PH bioremediation in soil samples.

In addition, many environmental and operational challenges directly hamper the field scale of BESs for PH removal [20]. Foremost, the physicochemical feature of soil directly imparts the effect of BES performances, especially the radius of influence (ROI) and PH degradation efficiency [21]. For example, electrical conductivity, hydraulic conductivity, porosity, availability and type of microbes, the bioavailability of minerals, organic matters, etc., can regulate redox reactions at the anode directly or indirectly. Therefore, in order to incline them toward a favorable range, soil amendments have been conducted in the past [22,23]. Moreover, electrode materials, serving as an electron sink for microbial metabolic electrons, have also been tailored via activation (improving surface area), surface modification (nanoparticle treatments), and functionalization (incorporating hydrophilic functional groups) to make them more biocompatible for biofilm development and enhance current exchange [20,24,25]. BES operating conditions have not been investigated thoroughly except for operating the BESs at different time intervals (for example, most studies
preferred to examine PH removal for over 100 days). Moreover, it is expected that cathode performance (as a terminal electron acceptor) will also have direct implications on anode performance and, thus, PH bioremediation [26,27]. Most studies used an air cathode BES due to the high redox potential of the oxygen reduction reaction (ORR, 1.229 V vs. SHE) and sustainability for field-scale implementation (Table 1). However, ORR is sluggish due to the high overpotential demand to activate [28]. To overcome this issue, different types of ORR catalysts have been investigated and employed to enhance BES performance [29,30]. In particular, in soil BESs, only a few reports demonstrate the application of cathode catalysts, such as biochar or activated carbon [31,32], and Pt-modified carbon cloth [33–35], but none were evaluated for their effect on the PH degradation rate at the anode side.

Despite these enormous research efforts, BES-based PH bioreduction technologies are not yet fully commissioned in fields, except for a 50 L pilot study in which a column-type BES with different anode materials (graphite granules, GG, and biochar, BC) was used for the treatment of PH-contaminated soils [36]. The PH removal efficiency was noted to be in the range of 82.1–89.7% at 35 cm away from the anode after 120 days of operation. Based on the statistical evaluation and some extrapolation, they expected that the ROI could be further increased up to 90 cm if the ratio of ROI and radius of BES (ROB) (i.e., the radius of the column) is maintained at 12 in the case of BES using GG as an anode. If this hypothesis is true, then a smaller number of columns with slightly high ROB will be needed to install in field trials. However, this speculation warrants a full-scale investigation.

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Table 1. Recent advancements in BES-based bioremediation strategies for PH-contaminated soil.

| Soil Type                          | BES Type          | Anode         | Experiment Days | Microbial Communities                                                                 | Petroleum Hydrocarbon (PH)                  | Power/Current Generation | Degradation Efficiency | Ref         |
|-----------------------------------|-------------------|---------------|-----------------|----------------------------------------------------------------------------------------|---------------------------------------------|--------------------------|------------------------|-------------|
| Saline soil                       | U-tube            | Carbon mesh   | 25              | *Desulfobulbus*, *Geobacteraceae*, and uncultured * Archaea*                           | PAHs                                        | 125 ± 7 C, 0.85 ± 0.05 mW m⁻² | 15.2 ± 0.6%         | [33]        |
| Diesel and engine oil             | Tubular           | Carbon cloth  | 64              | *Comamonas testosteroni*, *Pseudomonas putida*, and *Ochrobactrum anthropi*            | TPH                                         | 86 ± 0.1 mA             | 78.7%                  | [13]        |
| Contaminated soil                 | Two columns       | Graphite granules | 120              | *n*-alkanes                                                                            | TPH                                         | 70.4 ± 0.2 mA m⁻²       | (8.8 ± 0.3 mW m⁻²)  | 89.7%       | [12]        |
| Peat moss and soil                | Rectangular cuboid| Electroactive biofilm | 7               | Sulfate                                                                                | TPH                                         | 286.7 mW m⁻²             | 46.15%                 | [21]        |
| Soil from oil recovery machine    | Cylindrical       | Carbon cloth and activated carbon | 182              | *Alcanivorax*, *Marinobacter*, *Pontibacillus*, *Sediminimonas*, *Georgenia*          | TPHs, alkanes, and aromatics                | 46 C d⁻¹ & 8283 C       | 52%, 38%, and 136%   | [39]        |
| PHC-contaminated soil oil production | Graphite rod and activated carbon | -                  | 150              | TPHs                                                                                    | 120.5 mA m⁻², 17.3 mW m⁻², and 5398 C      | 55 ± 2%                 |                       | [40]        |
| Sediment from lake                | Columnar glass reactor | Graphite felt        | 110              | *Proteobacteria*, *Chloroflexi*, *Acidobacteria*, *Bacteroidetes*, *Planctomycetes*, and *Firmicutes* | Polycyclic aromatic hydrocarbons (phenanthrene and pyrene) | 43.74 ± 1.2, 53.90 ± 6.0, 48.30 ± 2.4, 56.71 ± 8.6 mV and 0.98 ± 0.14, 0.87 ± 0.04, 0.57 ± 0.06, 0.49 ± 0.07 kJ | 64.5, 73.4, 78.3, and 80.8% | [41]        |
| Aged soil                         | Horizontal or vertical | Carbon mesh and activated carbon | 135              | *α*, *β*, and *γ*-Proteobacteria and *Escherichia* sp.                                | PHC                                         | -                        | 21%                    | [33]        |
| Sandy sediment                    | Three columns     | Carbon cloth and carbon brush | 66               | TPH                                                                                   | 190 mV (2162 mW m⁻³)                        | 2% and 24%               |                       | [42]        |
| Alluvial plain soil               | Multichamber      | Graphite felt and graphite felt | 25               | TPHs                                                                                    | 20 mA m⁻²                                  | 50%                     |                       | [43]        |
| Petroleum-hydrocarbon-contaminated soils | Carbon mesh and activated carbon | -                  | 223              | *Proteobacteria*, *Actinobacteria*, *Chloroflexi*, *Verrucomicrobia*, *Verrucomicrobia*, *Nitrospirae*, and *Firmicutes* | TPHs, alkanes, aromatics, polar material, asphaltene, high-molecular hydrocarbons and nonmetallic derivatives, and 16 PAHs | 12.9 ± 0.2 mV and 207.2 ± 6.9 mV | 68-78%, 49-79%, 26-44%, and 32-57% | [44]        |
| Soil Type                        | BES Type          | Anode                  | Experiment Days | Microbial Communities                                      | Petroleum Hydrocarbon (PH) | Power/Current Generation | Degradation Efficiency | Ref |
|---------------------------------|-------------------|------------------------|------------------|-----------------------------------------------------------|---------------------------|--------------------------|------------------------|-----|
| Saline–alkali soil              | Two-layered       | Carbon mesh and        | 65               | *δ*-Proteobacteria (Proteobacteria), Flavobacteria (Bacteroidetes), or Clostridia (Firmicutes) | TPH, n-alkanes, and 16 PAHs | 81 to 304 mA m⁻²         | 59-92%                 | [45]|
|                                 |                   | activated carbon       |                  |                                                           |                           |                          |                        |     |
| Aged soil                       | Three-layered     | Carbon mesh and        | 135              | Alcanivorax, Geobacteraceae sp., Proteobacteria, Gammaproteobacteria, and Escherichia sp. | TPH and n-alkanes         | 2.56 ± 0.13 10⁻⁴ m W m⁻² | 54 ± 7.5%              | [35]|
|                                 |                   | activated carbon       |                  |                                                           |                           |                          |                        |     |
| Soil-contaminated (aged PHC)    | Three-layered     | Carbon mesh and        | 182              | Proteobacteria, Firmicutes, Bacteroidetes, Actinobacteria, Chloroflexi, Planctomycetes, and Acidobacteria | Long-chain alkane fatty acids | 61.5 ± 0.8 mA m⁻² and 0.321 C d⁻¹ g⁻¹ | >90%                   | [12]|
|                                 |                   | activated carbon       |                  |                                                           |                           |                          |                        |     |
| Raw contaminated soil           | Tubular           | Carbon cloth and       | 110              | -                                                         | TPH                       | 80 ± 5 mA m⁻²            | 21-37%                 | [46]|
|                                 |                   | carbon felt             |                  |                                                           |                           |                          |                        |     |
| Crude-oil-contaminated soil     | Bottle-type       | Carbon fiber brush     | 137              | -                                                         | n-alkane and (C10–C20) alkanes | 322 ± 6 mA cm⁻³         | n-alkane: 27-45%; (C10–C20) alkanes: 60-75% | [47]|
|                                 | dual-chamber      |                        |                  |                                                           |                           |                          |                        |     |
| Saturated soil                  | Column-type       | Graphite felt          | 50               | Gammaproteobacteria, Vibrionales, and Clostridia          | Benzo[a]pyrene            | 3766.15 ± 120.37 C and 0.36 ± 0.08 kJ | 52.52 ± 4.23           | [48]|
| Aged saline soil                | Three-layered     | Carbon mesh            | 180              | γ-Proteobacteria, Alcanivorax sp., Firmicutes, Geobacteraceae sp., and Escherichia sp. | PAHs and total n-alkanes (C8–C40) | 37 mW m⁻²               | 18, 36, and 29          | [49]|
| Petroleum-contaminated soil     | Horizontal or     | Carbon mesh            | 135              | -                                                         | TPH, alkenes, and PAHs    | 0.282 ± 0.015 and 0.285 ± 0.025 V | 12.5 ± 0.6% and 8.3%  | [13]|
|                                 | Vertical          |                        |                  |                                                           |                           |                          |                        |     |
| Waterlogged paddy soil          | Single chamber    | Carbon felt            | 14               | -                                                         | Phenol                    | 29.45 mW m⁻²             | 90.1%                  | [50]|
| Sandy soil, clay soil           | Tubular           | carbon felt/carbon      | 248              | Acidobacteria, Actinobacteria, Bacteroidetes, Chloroflexi, Firmicutes, and Proteobacteria | TPH                       | 55–58 mA cm⁻², 120 mW m⁻² | 48-59% and 42-45%       | [23]|
|                                 |                   | cloth                  |                  |                                                           |                           |                          |                        |     |
| Sandy soil, clayey soil         | Column-type       | carbon felt/carbon      | 230              | -                                                         | Diesel                    | -                        | 41% and 39%             | [21]|
|                                 |                   | cloth                  |                  |                                                           |                           |                          |                        |     |
Table 1. Cont.

| Soil Type                        | BES Type            | Anode                          | Experiment Days | Microbial Communities                          | Petroleum Hydrocarbon (PH) | Power/Current Generation | Degradation Efficiency | Ref  |
|----------------------------------|---------------------|--------------------------------|-----------------|-----------------------------------------------|-----------------------------|--------------------------|------------------------|------|
| Sandy soil                       | Multichamber        | Graphite plate/graphite felt   | 63              | *Deltaproteobacteria, Geobacter, Pseudomonas*  | Atrazine                    | 0.30 to 0.17 mA           | 1.38 ± 0.33 a mg/(kg day) and 91.69 ± 2.70 a | [51] |
| Paddy soil                       | Vertical            | Graphite plate/graphite felt   | 14              | *P. subcapitata and Salmonella typhimurium*    | Atrazine                    | 66 mA m⁻²                 | 83%                    | [50] |
| Paddy soil                       | Horizontal          | Carbon cloth/carbon cloth      | 25              | *Desulfotomaculum and Geobacter*               | Pentachlorophenol (PCP)     | -                        | 35.2% and 60.7%          | [52] |
| Paddy soil                       | Two-chamber         | Carbon felt/carbon felt        | 10              | *Geobacter, Shewanella, and Dehalobacter*      | PCP                         | -                        | -                      | [53] |
| Saline soil (refractory organic pesticide) | Vertical          | Carbon cloth and granular activated carbon | 60              | -                                              | Hexachlorobenzene (HCB)     | 70.8 mW m⁻²               | 71.14%                 | [12] |
| Refractory organic pesticide     | Vertical            | Carbon cloth and granular activated carbon | 60              | *Geobacter sulfurreducens, Beta Proteobacteria* | HCB                         | 77.5 mW m⁻²               | 39.33% and 0.543 mg/(kg d) | [47] |
| Black, chao, yellow, brown, and red soil | Cylindrical         | Graphite rod/Activated carbon | 53              | -                                              | Tetracycline                | CS (946 ± 307 C) BS (340 ± 43 C) YBS (134 ± 34 C) RS (50 ± 46 C) | BS (75 ± 2%), RS (65 ± 5%), YBS (61 ± 7%), CS (52 ± 10%) | [54] |
2. Petroleum Hydrocarbons (PHs): Contamination Hazard in the Environment and Current Bioremediation Technologies

Petroleum hydrocarbons (PHs) contain complex aliphatic and aromatic compounds composed of carbon and hydrogen [35]. The aliphatic PHs can be divided into alkanes composed of hexane, heptane, octane, and cycloalkanes, e.g., methylcyclopentane and ethylcyclopentane, and alkenes that contain ethane and propane. Conversely, aromatic PHs can be subdivided into two broad categories such as monoaromatics (e.g., benzene, toluene, ethylbenzene, and xylene) and polyaromatics (e.g., naphthalene, biphenyl, fluorene, and many other complex aromatic compounds) [55]. PHs are further halogenated by adding a fraction of halogen such as F, Cl, Br, and I to use for different purposes, such as refrigerants, pesticides, and herbicides. Both halogenated and nonhalogenated PHs can cause a seriously detrimental effect on the environment [56,57]. In particular, PH contamination in soil and sediments is a global problem that poses short- and long-term effects on the environment as well as human and animal health [58,59]. A recent survey conducted by Panagos et al. identified over a million contaminated sites in Europe, among which at least 50% of the site could be potentially contaminated with PHs [60]. However, PH contamination in the subsurface environment could be linked to a natural phenomenon, but in the terrestrial ecosystem, PH contamination is widely linked to the oil exploration and transportation process as well as heavy industrial applications [61,62]. Once PH is spilled over the surface, it intrudes into unsaturated zones and reaches groundwater resources [63]. However, the PH contamination spectrum in surface and subsurface ecosystems mainly depends on the physiochemical properties of PH, for instance, density, water solubility, vapor pressure, sorption characteristics, biodegradability, etc., and soil characteristics, e.g., composition, texture, organic matter, and moisture content, etc. [64]. In general, PHs with a high degree of water solubility, volatility, and biodegradability is not a persisting problem, as these can be naturally removed with time; however, in the case of PHs with the opposite to these characteristics, it is problematic due to the long-lasting behavior [61].

PHs can be removed from the contaminated zones via distinct methods, that is, physiochemical, electrochemical, and biological (bioremediation) [65–67]. The physiochemical technique can include physical and/or chemical processes such as excavation of contaminated soil/sediments, pumping and throwing groundwater, washing with solvents and/or surfactants, thermal desorption, and redox disruptions using chemical agents [68]. However, physiochemical techniques need a great deal of effort, investment, and, most importantly, potential byproduct hazards after chemical treatment. In contrast, bioremediation technologies utilize the versatile metabolic pathways of microbes, in which the PHs serve as an energy source [69–71]. Therefore, bioremediation can offer complete mineralization of PHs with no hazardous byproducts to be dealt with in the downstream process [72]. Bioremediation can be applied both ex situ (off-site treatment) and in situ (in-site treatment), which is yet another attractive feature of this technology. In situ treatment could be as simple as injecting the right microbial communities into the contaminated zones, whereas ex situ treatment could be achieved under controlled environmental conditions [72]. However, bioremediation technology is a slow process [68]. Moreover, one needs to select a better approach to stimulate the growth of microbial communities under contaminant stress conditions, which can otherwise prevent PH mineralization [68]. Anaerobic PH biodegradation and the microbial aspects have been comprehensively reviewed and also addressed existing correlations between target microbial groups and PH degradation efficiencies [73,74]. However, a common strategy to improve PH biodegradation has been to supply electrons via suitable electron donors to microbes to stimulate reduction reactions (of halogenated compounds) or electron acceptors to stimulate oxidation reactions (of nonhalogenated compounds) [75–77]. This interesting discovery prompted the utilization of poised electrodes to either supply or uptake electrons to stimulate redox reactions for PH removal, i.e., BES-assisted bioremediation of PHs [78]. However, in this case, the microbes should be electrochemically active (i.e., capable of accepting or transferring extracellular electrons), as discussed in the following subsection.
3. Bioelectrochemical Systems for PH-Contaminated Soil Treatment

3.1. Microbial Interaction with Electrodes While PH Degradation and Strategies for Improvements

The interaction of microbes with electrodes to perform a bidirectional extracellular electron transfer (EET) is the prime requirement to conduct PH degradation in BESs. In general, microbes can interact with a poised electrode either via direct connections (using electrically conductive extracellular protein networks) or via indirection connections (using electron shuttles) [79]. A few microbial communities such as Geobacter sulfurreducens and Shewanella oneidensis are known to have electron conductive proteins, such as pili or cytochromes or both, on their cell wall, which they use to connect with the electrode for electron exchange [80,81]. In contrast, other electroactive microbes use electron shuttles secreted by themselves (e.g., phenazines of Pseudomonas spp.) or are added externally (e.g., flavins, hydrogen) [82,83]. Therefore, microbial community composition can play a pivotal role in the BES-assisted bioremediation of PHs, and moreover, complex syntrophic and/or cooperative interactions among community members are of prime importance. However, a single microbial community can perform initial PH oxidation to small molecules with subsequent mineralization to CO$_2$ using electrodes as an electron sink. For example, *G. metallireducens* could completely mineralize small-molecular-weight PHs such as benzene, phenol, and toluene [84]. Palma et al. further confirmed that *Geobacter* sp. grown at graphite electrodes could oxidize PHs into smaller molecules for further oxidation [85–88]. In this scenario, *G. metallireducens* can directly interact with electrodes via cytochromes or pili to transfer electrons to the poised anode.

In mixed microbial inoculum, both electroactive and nonelectroactive microbes live in a symbiotic relationship, helping each other to thrive in environmentally stressed conditions [89]. PH biodegradation under this scenario is mainly driven by syntrophic metabolism, in which PH is first activated via fumarate addition and hydroxylation followed by partial oxidation by nonelectroactive bacteria (PH-degrading fermentative bacteria such as *Achromobacter*, *Acinetobacter*, *Marinobacter*, *Mycobacterium*, *Pseudomonas*, *Staphylococcus*, *Streptobacillus*, *Streptococcus*, and *Rhodococcus*) to CO$_2$/H$_2$ and acetate [90–94]. Then, electroactive bacteria, e.g., *Geobacter* sp., scavenge the produced H$_2$ and acetate utilizing a poised anode as a terminal electron acceptor. This syntrophic relation is believed to be established via the cohesive connection between the PH-degrading and electroactive bacteria in the form of sludge granules or anodic biofilms [95]. However, the recent discovery of interspecies electron transfer via conductive nanomaterials (such as iron oxides or carbon) or even cable bacteria established the possibility for a long-distance syntrophic relationship between the PH-degrading and electroactive bacteria [96]. This prospect was partially confirmed by the addition of conductive particles in PH-contaminated soils to extend the influence of electrodes for PH biodegradation [97,98]. Sulfate-reducing bacteria (SRB) have been widely documented for their specific role in the natural bioremediation of PH-contaminated sediments and aquifers [99,100]. In this scenario, SRBs degrade PH using sulfate as an electron acceptor in the bulk soil and generate HS-. The anode then oxidizes sulfide into sulfate, helping to maintain the metabolic electron acceptor and reduce the accumulation of HS- in the systems, which otherwise can act as an SRB inhibitor [14,101].

In almost all the experiments, PH-contaminated soil with natural microbial flora within the soil matrix was used for BES operation. However, at the end of the experimental period, microbial diversity analysis demonstrated significant enrichment of phylum *Proteobacteria*, *Chloroflexi*, *Acidobacteria*, and *Firmicutes* [102]. Under these bacterial phyla, many bacterial species such as *Clostridium* sp., *S. oneidensis MR-1*, *P. aeruginosa*, *Escherichia coli*, *G. sulfurreducens*, etc., were identified as electroactive and utilized in MFCs for wastewater treatment and energy generation [6,103,104]. The EET promoted by electroactive bacteria is the foundation of bioelectrochemical processes, and, as discussed above, the bioelectroremediation of PH-contaminated soil has taken leverage of this process. So far, there has been significant progress in the past to search for new microbes capable of conducting EET, such as the discovery of cable bacteria [105], and also to augment EET in known bacteria. EET has been augmented via electrode modifications, bacterial genetic engineer-
ing, and chemical treatment [106]. Recently, Li et al. observed the selective relocation of bacterial distribution in PH-contaminated soil while using a different type of surfactant as an additive [51]. They noticed an average influence degree of sodium dodecyl sulfate (36%) > glycerol monostearate (14%) > cetrimonium bromide (10%) > chembetaine LEC (1%) on microbial distribution in the soil. Furthermore, some other additives such as Tween-80, polyethyleneimine, and EDTA have been shown to promote higher EET in BES while treating PH-contaminated soil [51,107]. However, the accumulation of these chemical additives in the soil, in the long run, could be toxic for the bacteria and, thus, could potentially hamper biofilm formation [108]. Instead, biologically viable surfactants such as rhamnolipids (RLs) derived from \textit{Pseudomonas} were noted to be effective in improving EET in BES for energy generation [109–111]. In this line, Ambaye et al. produced long-chain RL from low-cost carbon winery waste through nonpathogenic \textit{Burkholderia thailandensis E264} strains and used it as an additive to enhance EET for PH electrobioremediation [112]. A higher dose of RL (100 mg/L) could assist in removing 72% PH in just 20 days, while microbial community analysis showed specific enrichment of electroactive bacteria such as \textit{Geobacter}, \textit{Desulfovibrio}, \textit{Klebsiella}, and \textit{Comamonas} at the anode surface [108,113].

Despite the solid knowledge of microbe–electrode and microbe–microbe interactions and microbes responsible for PH degradation in soil and water, the application of this knowledge to manipulate BES-based PH bioremediation strategies is still limited and needs more practical investigation. Moreover, the major challenge in such BESs is to establish an electroactive biofilm at the anode electrode due to the high toxicity of PHs and certain metabolic intermediates with high solubility generated from the PH activation step by PH-fermenting bacteria [90,114,115]. In addition, soil texture and water content impact the electron transport [116], which also affects microbial metabolism and BES performance. In recent years, some research efforts have been made to address these issues, as discussed in detail in the following sections.

3.2. Characteristics of the Soil and Physical Amendments

The physiochemical features of soil play a vital role in establishing the interaction between bacteria and electrodes (Figure 2). The foremost characteristic could be identified as electrical conductivity (EC), which is the primary measure of ionic mobility inside the soil matrix. It means that soil with a high EC value enhances BES-based PH biodegradation due to low internal resistance for electron transport. Soil EC can be directly improved by the addition of sodium ions, which, eventually, can enhance BES performance in terms of HP biodegradation [117]. However, the externally added salt could significantly increase the treatment cost as well as elevate soil stress by creating high osmotic pressure, which may have a long-term detrimental effect on microbial ecology [118]. Therefore, as an alternate approach, natural EC manipulation techniques have been employed. For instance, it is quite understood that EC can be affected by several factors such as moisture, texture, and salinity [116]. Increasing the water content in soil could be a strategy to increase conductivity [118]. For example, it was observed that an increase in moisture content from 23% to 28% could significantly decrease the internal resistance from 42 Ω to 7.4 Ω in a U-tube soil MFC, which, in turn, improved PH biodegradation by 120%. This observation was further confirmed in a later study, in which a higher water saturation level of 48% compared with a 20% saturation level was noted to enhance the PH biodegradation rate at the anodic zone.
Soil texture heavily affects PH biodegradation in BESs. For a given water saturation, PH degradation in sandy soil was noted better than in clay soil. In a study, the BES with sandy soil could remove 48–59% of HP at a water saturation level of 48% compared with 42–45% in clay soils at a similar water saturation level [44]. This enhanced performance of BES with sandy soil could be attributed to the improved mass transport process through the porous texture. Typically, sandy soil contains 57.14 ± 0.03% sand, 28.93 ± 0.06% silt, and 13.93 ± 0.05% clay; in the case of clay soil, these constituents significantly vary (33.12 ± 0.08% sand, 35.46 ± 0.06% silt, 31.42 ± 0.04% clay). Due to high hydraulic conductivity, sandy soil also increases the ROI of HP biodegradation near the anode of BESs [119]. For example, after 60 days of the experimental period, the BESs with sandy soil could remove 41% of HP within the 5 cm ROI and 35% within 39 cm, whereas only 23% and 17% removal in HP was noted within the similar ROI using BES with clay soil [48]. Therefore, Li et al. amended PH-contaminated soil by mixing it with sand and evaluated the performance of MFC for PH biodegradation [21]. They observed decreased conductivity of soil with an increase in sand content in the soil. For instance, the original soils had an EC of 1.52 ± 0.03 mS cm$^{-1}$ and amended soil with soil-to-sand ratios of 5:1 and 2:1 showed an EC of 1.40 ± 0.19 mS cm$^{-1}$ and 1.10 ± 0.19 mS cm$^{-1}$, respectively. This low EC in sandy soil is possible because of the high insulating properties of sand. However, the amended soil, namely, 5:1 and 2:1, demonstrated a higher porosity of 49.8% and 51.3% compared with the pristine soil (44.5%), which enhanced mass transport across the matrix of the amended soil; thus, an improved PH degradation of 22% was noted in the case of 2:1, followed by 15% in 5:1 and 12% in pristine soil. This study thus indicates that even if a higher EC promotes microbial electron transfer reactions, it is not alone responsible for improved PH biodegradation in BESs.

The application of external additives such as conductive materials, nutrients, and electron acceptors has shown a positive impact on PH biodegradation. In fact, the effect of these additives on the performance of BES, in general, has been widely documented [120,121]. In particular, the addition of conductive biochar in soil promoted electron transfer from microbes to the electrode, which eventually enhanced degradation efficiency and also current generation [23,42,49,51]. Moreover, biochar provides a porous matrix and extensive surface

Figure 2. Physiochemical features of soils and their impact on microbial interaction for electron exchange: (a) clay soil with high cation exchange capacity; (b) nanoparticle-amended soil; (c) sandy-amended soil with high hydrohalic conductivity; (d) application of cable bacteria for long-distance electron transfer.
area for both substrate diffusion and microbial colonization, which could be one of the reasons for enhanced BES performance. Cai et al. demonstrated seven-time higher pentachlorophenol removal in BES with biochar-amended soil compared with BES with original soil [122]. In addition, biochar could enhance the ROI for PH biodegradation by four times (i.e., 4 cm in original soil to 16 cm in biochar-amended soil). However, a study revealed that 79–86% of the total charge in BES with biochar-amended soil could be generated after 5 months, which might implicate the requirement of a long start-up time. To reduce the start-up time, carbon fiber was mostly used for soil amendments to PH remediation in BESs [23,42,51]. When carbon fiber was mixed at a rate of 1% w/w dry weight, the power density of MFC could be increased up to 10% with a 58% decrease in internal resistance compared with the MFC without additive-containing soil [42]. The BES with carbon-fiber-amended soil showed a quick start-up time of 0.5 h with a peak current density of 200 mA/cm$^2$ after 3 days of operation. During 144 days of operation, the BES with carbon fiber demonstrated a 329% (at 5% overall removal rate) enhanced PH removal compared with the BES without carbon fiber. Recently, Zhang et al. created conducive networking inside a soil matrix using magnetite nanoparticles to enhance the interaction of microflora and PH in plant–rhizosphere (Iris tectorum) BES [123]. This novel approach accelerated direct interspecies electron transfer, which resulted in 174–232% enhanced PH removal (at 24.1–29.2% removal rate) in BES with magnetite compared with the control BES (at 8.8% removal rate).

3.3. Reactor Design and Electrode Materials

The PH-contaminated soil is a complex matrix, and thus, the design of BES should also be particular for its treatment. In general, air-cathode-based BESs with a typical arrangement of the anode and the cathode have been utilized for PH remediation, for instance, multianode with vertical and horizontal stacking, a single graphite rod, snorkel-column-based, U-type, and insertion-type (Figure 3; Table 1). Compared with the BES with an active aeration cathode (air diffusion via a pump in the catholyte), an air cathode with a passive aeration system (via exposed air) is cost-effective for field-scale applications. Single or multianode BES systems are the simplest design, which can be fabricated by inserting graphite columns as the anode in the soil material, whereas cathodes made with either flexible carbon or graphite plate can be attached to the soil surface exposed to air. The anode and the cathode can be connected to the external resistance. The multianode system is generally used to provide a high surface to the microbes for enhanced current density. For example, a three-anode system (made with carbon meshes) stacked horizontally in a BES could achieve a net removal rate of total PH, polycyclic aromatic hydrocarbons, and n-alkanes (C8–C40) of 18%, 36%, and 29%, respectively [47]. Similarly, Zhang et al. fabricated BES with both horizontal (HA) and vertical arrangements (VA) of four pieces of carbon meshes as anodes and evaluated the performance for PH biodegradation [54]. HA demonstrated a 50.6% higher PH removal (12.5% removal) compared with VA during 135 days of the operational period. The higher PH degradation in HA is perhaps due to low mass transfer resistance compared with VA.

Recently, insertion- and snorkel-column-type MFCs have been mostly identical and simple to fabricate in waterlogged areas and have been increasingly utilized for PH removal from soil and sediments. The first insertion-type MFC was utilized for the removal of organics in waterlogged paddy soils [124]. In this design, a PVC tube was used as a rigid framework for membrane electrode assembly (MEA). MEA was fabricated by painting both sides of a Goretx cloth with conductive ink to serve as an anode and a cathode and wrapped across the PVC tube. The tube was then inserted in the paddy field, keeping the anode attached to the soil matrix and the cathode facing air in the hollow tube. The major advantage of this design is its portability, including other advantages based on performance indicators, such as decreasing the electrode spacing and reducing mass transport losses [119]. Therefore, this study laid a strong foundation to later develop snorkel-type MFCs for PH degradation in soils in a scale-up model. For example, a two-column-type MFC with a capacity of 50 L was fabricated using low-cost electrode materials, such as
biochar and graphite granules, for PH degradation. The MFC demonstrated an 82.1–89.7% PH removal within a radius of 1–34 cm in 120 days of operation, along with a current generation of 70 mA/m² [12]. This pilot-scale MFC demonstrated its potential application in existing groundwater monitoring wells with an ability to sense the contamination profile using electricity generated within the system.

Electrodes are the backbone of BESs and should possess certain features for their reliable application in PH-contaminated environments, for example, high biocompatibility, electronic conductivity, stability, and low cost [79,125–128]. Carbon-based electrodes fit well into these criteria and, thus, have been most commonly used in BES for PH bioremediation (Table 1). However, to fabricate the most widely used column-type BES for soil bioremediation, flexible carbon materials with 2D architecture and a defined surface area, such as carbon cloth, carbon felt, and carbon mesh, are a common choice [16,129] (Figure 4). Other types of rigid carbon electrodes, such as graphite plates and rods, have also been explored for the fabrication of single multianode soil BES at low cost. The 3D electrodes made with microfiber carbon brushes can provide additional surface area to the microbes for biofilm development, which are, however, utilized most commonly in benthic environments, such as marine sediments [130,131].

Figure 3. Different types of BES reactor designs developed for PH bioremediation: (a) snorkel-column-type; (b) U-type; (c) multiple anodes stacked vertically; (d) multiple anodes stacked horizontally.
which possibly stimulated microbial metabolism. In contrast, biochar obtained from wheat straw demonstrated a strong polar effect to improve aromatics removal. Among them, sawdust-derived biochar had a worse performance, which was attributed to the ability of this material to adsorb bioavailable minerals in the matrix and, thus, lessening the important nutrients for the microbes. This is a particular challenge to make the balance between sorption and bioavailability in the case of 3D materials, which need additional investigation [140]. Moreover, biochar is also reported to serve as an electron conduit in the interspecies electron transfer process. In an earlier study, Cai et al. observed an increased ROI of ~16 cm in BES with the application of biochar compared with 4 cm without biochar [122]. Lu et al. also noticed a similar PH removal efficiency of 82.1–89.7% in a pilot-scale BES with biochar and highly conductive graphite granules anode [12].

The above discussion hints that biochar could be an interesting material for scale-up applications due to its intrinsic physicochemical feature and most importantly, ease of synthesis from a wide range of waste raw materials.

Modification of the surface of electrode materials with conductive materials and functional groups has demonstrated promising results in the selective enrichment of microbes and enhanced extracellular electron exchange for the removal of pollutants (Figure 4) [43]. Carbon materials, such as carbon nanoparticles (CNP), nanotubes (CNT), and reduced graphene oxide (rGO) with high specific surface area and enhanced electronic conductivity,
serve as ideal materials to functionalize electrodes for BES applications [141]. For example, graphene (GR), graphene oxide (GO), carbon nanotubes (CNTs), and modified graphite felt (GF) anodes were used in BESs for polycyclic aromatic hydrocarbon (phenanthrene) removal from sediments [43]. The results showed an enhanced phenanthrene removal of 78% in BES with CNT-modified GF followed by BES with GR (73%), GO (71%), and least in the case of BES with pristine GF (45%). The enhanced surface area and conductivity of these three modified electrodes helped to increase microbial diversity at the anode and also enriched phenanthrene-degrading bacteria. Despite good results, the modified electrode has been employed so far in laboratory experiments, and thus, scale-up investigations need to be conducted to validate their applicability in field-scale applications.

3.4. Effects of Operating Conditions on PH Treatment by BES

As discussed in the previous sections, the physiochemical structure of soil imparts an effect on the performance of BES during PH treatment, and therefore, attempts have been made on soil amendments before BES treatment. In particular, soil EC has been more frequently tailored by manipulating water saturation and salt addition to enhance both the PH removal rate and the ROI. However, recent analyses demonstrated that a fold increase in EC is poorly correlated with an increase in BES performance [13,22]. Hence, other soil operating parameters such as the bioavailability of minerals in the soil, hydraulic conductivity, and mass transport within the soil matrix impart a higher impact than EC alone [22]. Furthermore, it can be noticed from the published results in the literature that the utilization of additives (sand, biochar, glucose, etc.) highly influences the PH degradation performance of BESs with similar design and substrate conditions rather than the total operational period of BESs (Figure 5). The addition of biochar and surfactants to the soil could achieve higher PH removal (up to more than 65%) than other soil amendments at a reduced operational period, regardless of reactor configurations. In general, batch mode operation was preferred in most studies to resemble the condition of field applications. The addition of a cosubstrate such as glucose and other organic wastes was noted as helpful in achieving a high PH degradation rate [142]. Li et al. reported three times higher PH removal (38%) in 0.1% w/v glucose-amended BES compared with the control (without glucose) [45]. PH removal could be further increased up to 48% using 0.5% glucose. The addition of glucose enriched the PH-degrading microbes, which could be confirmed by detecting increased dehydrogenase and polyphenol oxidase activities in the microbial consortium.

![Figure 5](image_url)

**Figure 5.** Effect of reactor operation days and additives on PH removal. The results are derived from [12,21,44,47,48,122].
4. Current Challenges and Future Perspectives

Recent research efforts and the results so far on the application of BESs to remediate PH-contaminated soil/sediment and, in some cases, even groundwater have shown some potential for field-scale applications. For instance, a few findings revealed >70% HP removal in a reactor operation span of fewer than 120 days, whereas the majority of the findings showed relatively low removal efficiency (Table 1). Moreover, most experiments were conducted in lab-scale reactors, and to date, a single study demonstrated 50 L pilot-scale BES operations. In order to employ this technology on a field scale, snorkel-column-based BESs could be the best option. However, more research efforts are needed to improve the performance of such BESs to make them attractive for further commercialization. For in situ bioremediation of PH-contaminated sites, the radius of influence (ROI) is an important parameter by which one can decide how many numbers of BESs will be required for a given contaminated area [22]. A recent study noted a maximum ROI value of 35 cm with snorkel-column-based air cathode BESs having a carbon felt anode and an activated-carbon-coated carbon cloth cathode [44]. This reactor could remove ~48% and ~30% PH from saturated sandy and clay soil, respectively, within 248 days of reactor operation. If this design is to be utilized for field-scale applications, then a large number of snorkel columns will be required to insert in the ground at an interval of ~35 cm. Therefore, it is highly important to improve ROI by improving several parameters and adapting new approaches that directly or indirectly affect BES performance for scale-up applications in the near future (Figure 6).

As discussed above, ROI is synergistically influenced by the mass diffusion of PHs through soil pore spaces and, finally, their rate of degradation at the electrodes to create a healthy concentration gradient. Therefore, both processes should be well balanced as defined by the dimensionless Damkohler number (\(D_a\), a ratio of reaction rate and diffusive mass transport rate in a given process) [143]. In general, to achieve a 90% PH removal rate, the \(D_a\) value should be ~10 [144], which implies that the reaction rate is the limiting factor in soil BESs.

![Figure 6. An integrative approach and future research directions for improving BES performance.](image-url)
The rate of the reaction at the electrode can be improved by distinctive approaches, for example, by adding conducive nanoparticles to enhance the electron transport process between microbe-microbe and microbe–electrodes, improving anode electrode features, increasing the availability of supplements for the microbes, and enriching microbial diversity in the soil [123]. The utilization of microbes capable of conducting long-distance electron transfer using conductive materials as electron conduits can help improve the reaction rate [145, 146]. Although soil amendments with waste-biomass-derived carbon materials (e.g., biochar and activated carbon) showed improved microbial interactions, their electrochemical activity can be enhanced further by surface medications with hydrophilic functional groups and altering surface zeta potential. Further research efforts are needed to amend the soil with bioactive additives; for example, the application of leaf extracts with enriched bioactive compounds such as epigallocatechin-3-gallate (EGCG), gallocatechin, gallic acid, and anthocyanin could be a cost-efficient option to enrich the soil for enhanced microbial metabolism [147–150]. Excellent electrode materials with good stability and catalytic properties are required to be developed; biochar and activated-carbon-modified anode electrodes have shown promising results due to their high activated surface area, but their low electrical conductivity can hamper reaction kinetics at the anode [32]. Therefore, transition-metal (Fe, Co, and Mn)-doped biochar or activated carbon can address low electrical conductivity issues and can also significantly improve bioelectrochemical activity [151]. Moreover, electrodes modified with a hydrophilic functional group such as -NH₂, -COOH, -OH, etc., showed enhanced attachment with microbes via weak hydrogen bonding and electrostatic attraction, which promoted early-stage biofilm development in BES [44, 127]. Moreover, anodes modified with conductive polymers, such as polyaniline, polypyrrole, polymer dots, and low-cost transition metal oxides, have also shown enhanced activity toward microbial attachment and improvement in BES performance [128, 129]. Since these materials have not been utilized in BESs for soil bioremediation, it may thus be a good strategy to utilize them in BESs for PH remediation for enhanced performance. Moreover, an improved reaction rate at the cathode electrode (oxygen reduction reaction, ORR, in the case of air cathode BES) can also help maintain an anodic microenvironment for faster PH degradation. Therefore, sustainable ORR catalysts, such as platinum-group-metal (PGM)-free catalysts, should be applied on the air cathode side of BESs for enhanced ORR kinetics [152–154]. Experimental parameters such as the application of imposed potential and the addition of an organic cosubstrate in contaminated soil can further accelerate microbial metabolism and, thus, improve performance [142, 155]. The integration of an anodic Fenton process similar to that tested in MFCs for highly organic contaminated wastewater treatment could be helpful to oxidize higher-chain PHs to release stress in the soil [156]. Furthermore, the zerovalent iron (ZVI) treatment of PH-contaminated soil before BES application can also be tested to obtain a high PH degradation within a short period [157, 158]. Finally, it is highly important now to conduct a life cycle and life cycle cost analysis to evaluate the maturity and readiness of this technology for field-scale applications.

5. Conclusions

Recent advancements in BES-based environmental biotechnology for PH removal from soil (and sediments) were comprehensively reviewed and discussed. Based on the current knowledge of this technology, the insertion types of BES with snorkel columns as MEA can be more practical to develop static systems for continuous PH removal from contaminated soil. However, the major issues of BES-based PH bioremediation technologies are the low ROI and slow degradation rate, which practically hamper field-scale applications. Therefore, necessary amendments in soil physiology, operational parameters, and electrode design are warranted. The best possible way to enhance BES performance could be by improving mass diffusion and hydraulic conductivity of PH-contaminated soil by adding sand, mixing soil with conducive nanoparticles to improve electron exchange between the microbes and electrodes, utilizing an enriched microbial consortium, and integrating complementary technologies. Further, the optimization of reactor configurations and
operational conditions in the lab- and pilot-scale experimental trials are necessary to testify to the readiness of the advanced BES systems for the treatment of PH-contaminated soil at a large scale in the real field.

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