



Review

Decontamination of soils containing PAHs by electroremediation: A review

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ABSTRACT

During the last years, the anthropogenic sources have contributed to organic compound penetration into the environment. One large group of persistent and toxic contaminants is the hydrophobic organic contaminants. Among them, polycyclic aromatic hydrocarbons (PAHs) have been recognized as a representative group of these pollutants with low solubility. In this paper, it is showed the electroremediation of soil contaminated with PAHs as an alternative, to organic compound removal. This technique, mainly used for heavy metal extraction, applies the electric current to promote the movement of contaminants. Nowadays the application of this technique alone or combined with other techniques as for example Fenton or bioremediation is taking fine results to PAHs removal. Although the PAHs soil decontamination by means of the electric field is in an initial stage, many researchers have demonstrated the treatment effectiveness. This paper describes the foremost principles to carry out the electroremediation of soils contaminated with PAHs, just like the different alternatives to improve the electroremediation of PAHs and also the new methodologies of PAHs removal by using hybrid technologies.

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1. Introduction

During the last years, the anthropogenic sources have contributed to organic compound penetration into the environment. One large group of persistent and toxic contaminants is the hydrophobic organic contaminants (HOCs), and, obviously, the main characteristic that differentiates these pollutants from other

contaminants is their hydrophobicity, they are repelled from water [1]. In addition, these substances tend to exist as pockets at the soil subsurface location to which they have migrated [2]. From a technical point of view, it is particularly difficult to treat or remove contaminants possessing low water solubility and high octanol–water partition coefficients characteristics [3]. Furthermore, some environmental factors as soil type and structure, pH, temperature and the association with co-pollutants such as other hydrocarbons and/or heavy metals, can prolong their time in the environment [4]. New technologies are being developed to mobilize or solubilise these contaminants in order to improve

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Table 1
Properties and chemical structures of some commonly studied PAHs [85,86].

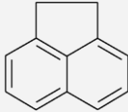
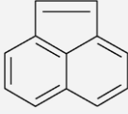
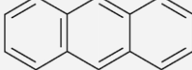
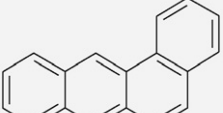
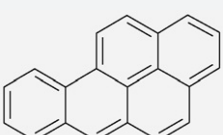
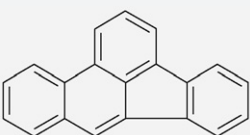
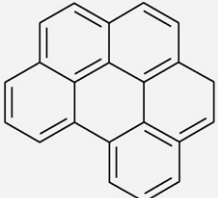
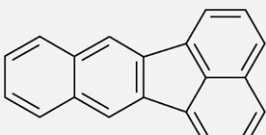
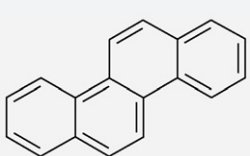
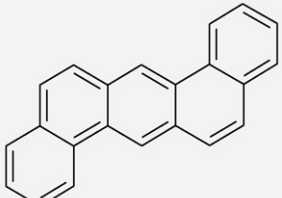
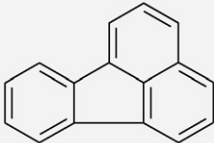
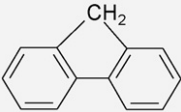
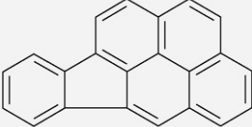
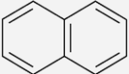
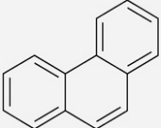
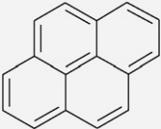
| Name | CAS | Chemical structure | Molecular weight (g/mol) | Boiling point (°C) | Melting point (°C) | Water solubility (mg/L) | Vapor pressure (mm Hg) | Partition coefficient, log K_{OW} | Henry's law constant, H (atm·m ³ /mol) |
|-----------------------------------|----------|---|--------------------------|--------------------|--------------------|--------------------------|------------------------|-------------------------------------|---|
| Acenaphthene | 82-32-9 |  | 154.21 | 277 | 95 | 1.93 | 4.47×10^{-3} | 3.98 | 7.91×10^{-5} |
| Acenaphthylene | 208-96-8 |  | 152.2 | 265–275 | 92–93 | 3.93 | 0.029 | 4.07 | 1.45×10^{-3} |
| Anthracene | 120-12-7 |  | 178.2 | 342–340 | 218 | 0.0076 | 1.7×10^{-5} | 4.45 | 1.77×10^{-5} |
| Benzo(a)anthracene | 56-55-3 |  | 228.29 | 435 | 162 | 0.010 | 2.2×10^{-8} | 5.61 | 1×10^{-6} |
| Benzo(a)pyrene | 50-32-8 |  | 252.3 | 495 | 179–179.3 | 0.0023 | 5.6×10^{-9} | 6.06 | 4.9×10^{-7} |
| Benzo(b)fluoranthene | 205-99-2 |  | 252.3 | 481 | 168.3 | 0.00125×10^{-7} | | 6.04 | 1.22×10^{-5} |
| Benzo(ghi)perylene | 191-24-2 |  | 276.34 | 550 | 273 | 0.00026 | 1.3×10^{-10} | 6.50 | 1.44×10^{-7} |
| Benzo(k)fluoranthene ^a | 207-08-9 |  | 252.31 | 481 | 215–217 | – | – | – | – |
| Chrysene | 218-01-9 |  | 228.3 | 448 | 255–256 | 0.0028 | 6.3×10^{-7} | 5.16 | 1.05×10^{-6} |
| Dibenz(a,h)anthracene | 53-70-3 |  | 278.35 | 524 | 262 | 0.0003×10^{-10} | | 6.84 | 7.3×10^{-8} |

Table 1 (Continued)

| Name | CAS | Chemical structure | Molecular weight (g/mol) | Boiling point (°C) | Melting point (°C) | Water solubility (mg/L) | Vapor pressure (mm Hg) | Partition coefficient, log K_{OW} | Henry's law constant, H (atm·m ³ /mol) |
|--------------------------|----------|--|--------------------------|--------------------|--------------------|-------------------------|------------------------|-------------------------------------|---|
| Fluoranthene | 206-44-0 |  | 202.26 | 375 | 111 | 0.20–0.26 | 5.0×10^{-6} | 4.90 | 6.5×10^{-6} |
| Fluorene | 86-73-7 |  | 166.2 | 295 | 116–117 | 1.68–1.98 | 5.0×10^{-6} | 4.90 | 6.5×10^{-6} |
| Indeno(1,2,3-cd)pyrene | 193-39-5 |  | 276.3 | 530 | 163.6 | 0.062 | 10^{-11} – 10^{-6} | 6.58 | 6.95×10^{-8} |
| Naphthalene ^a | 91-20-3 |  | 128.17 | 218 | 80.5 | – | – | 3.37 | – |
| Phenanthrene | 85-01-8 |  | 178.2 | 340 | 100 | 1.20 | 6.8×10^{-4} | 4.45 | 2.56×10^{-5} |
| Pyrene | 129-00-0 |  | 202.3 | 393 | 156 | 0.077 | 2.5×10^{-6} | 4.88 | 1.14×10^{-5} |

^a Ref. [86].

this performance. Several processes have attracted considerable attention for remediation of HOCs contaminated soils. These new techniques utilize model pollutants to validate the HOCs removal, and under this concern, it is well recognized that PAHs are an excellent representative group of HOCs. Furthermore, 16 specific PAHs: acenaphthene, acenaphthylene, anthracene, benz(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(ghi)perylene, benzo(k)fluoranthene, chrysene, dibenz(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, naphthalene, phenanthrene, and pyrene (Table 1) are listed by the Environmental Protection Agency to be among the 126 priority pollutants and 5 of them are listed among the 25 hazardous substances thought to pose the most significant potential threat to human health at the superfund sites [5].

Soils and sediments can be treated for PAHs contamination by *in situ* and *ex situ* methods. However, from an economic and environmental point of view the *in situ* decontamination is taking high importance, so that, at the present time, many research efforts have been expanded to find suitable methods for remediation by using no invasive techniques.

The technologies to *in situ* PAHs soil decontamination can be mainly classified in two types: physical-chemical and biological. The former ones are based on the ability for several microorganisms, to degrade some organic compounds and these processes have been proven successfully in specific environments [6]. Nevertheless, as a result of PAHs properties the main techniques used to PAHs decontamination are based on physical-chemical technologies. Thus, PAHs decontamination is leaching remediation

as surfactant solubilisation, solvent extraction, supercritical fluid extraction and hot water extraction [7–9].

The electroremediation of soil contaminated with PAHs arises as an alternative, to produce the leaching remediation. This technique, mainly used for heavy metal extraction, applies the electric current to promote the movement of contaminants. Nowadays, the application of this technique alone or combined with others techniques as for example Fenton or bioremediation is taking fine results to PAHs removal. Although the PAHs soil decontamination by means of the electric field is in an initial stage, many researchers have demonstrated the treatment effectiveness. This paper describe the foremost principles to carry out the electroremediation of soils contaminated with PAHs, just like the different alternatives to improve the electroremediation of PAHs and also the new methodologies of PAHs removal by using hybrid technologies.

2. PAHs soil contamination

PAHs constitute a class of organic substances which consist of two or more fused benzene rings made up of carbon and hydrogen atoms. They are formed during the thermal decomposition of organic molecules and their subsequent recombination. Incomplete combustion at high temperature (500–800 °C) or subjection of organic material at low temperature (100–300 °C) for long periods results in PAHs production [10]. These compounds exhibit recalcitrant and strong mutagenic/carcinogenic properties for the living beings [11]. The common sources of PAHs in environment include natural, as well as anthropogenic. Natural sources are forest and

rangeland fires, oil seeps, volcanic eruptions and exudates from trees [10]. The main anthropogenic sources are burning of fossil fuel, coal tar, wood, garbage, refuse, used lubricating oil and oil filters, municipal solid waste incineration and petroleum spills and discharge [7,10]. The typical PAHs concentration found near sources zones of contaminates sites are 500 mg/kgds [8].

PAHs occur as colorless, white/pale yellow solids with low solubility in water, high melting and boiling points and low vapour pressure (Table 1) [10]. With an increase in molecular weight, their solubility in water decreases; melting and boiling point increase and vapour pressure decreases [12,13]. Toxic PAHs are persistent and difficult to remove from low permeability clayey soils because these contaminants have a low aqueous solubility and a tendency to strongly bind with the clay minerals and organic matter present in these soils [14].

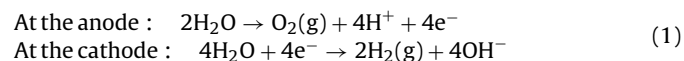
3. Electroremediation to PAHs soil decontamination

Over the years, the electroremediation technology has been applied successfully in the remediation of inorganic contaminant in soils, wastes and sediments [15–20]. However, at the present time, as a result of the high industrialization and the new industrial processes, elevated amounts of organic pollutant are released into the environment. Thus, the decontamination of organic compound, in special PAHs, is receiving more and more attention. As a result of these novel contaminants appearance, several strategies must be analyzed to remove these new pollutants. Among the different alternatives, electroremediation seems to be an adequate technique to remove organic compounds. Nevertheless, some technique modifications are essential to apply this technique to remove PAHs, pollutants with low water solubility. In Table 2, the different technologies developed and the results obtained by different pollutants are summarized.

3.1. Electroremediation principles

Electroremediation or electrokinetic remediation is an *in situ* technology that consists of the controlled application of low intensity direct current through the soil between appropriately distributed electrodes. One of the most important advantages of the electrokinetic technique is its efficacy for the treatment of low hydraulic permeability soils, where other techniques as natural attenuation or traditional remediation efforts such as pump-treat are not adequate [21,22].

During the electroremediation, the electrolysis of water occurs at the electrodes according to the following reactions:



Therefore, these reactions cause an acidic solution to be generated at the anode and an alkaline solution to be generated at the cathode. Furthermore, substances in solution are transported towards the electrodes by the electric field action. The main transport mechanisms are electromigration, migration of ions towards the opposite charged electrode, and electro-osmosis, movement of liquid through the soil matrix relative to the charged particles (Fig. 1). The electrolysis of water affects the remediation process because the ionic products (H^+ and OH^-) may electromigrate and/or be transported by electro-osmosis towards the oppositely charged electrode location. Thus, an acidic (H^+) front of solution may move from the anode towards the cathode, and/or an alkaline (OH^-) front of solution may move from the cathode towards the anode. In the case of organic compounds, usually uncharged species, they are transported with the electro-osmotic flow of the aqueous solution. After the treatment, contaminants are recovered in the electrode chambers and can be treated more easily.

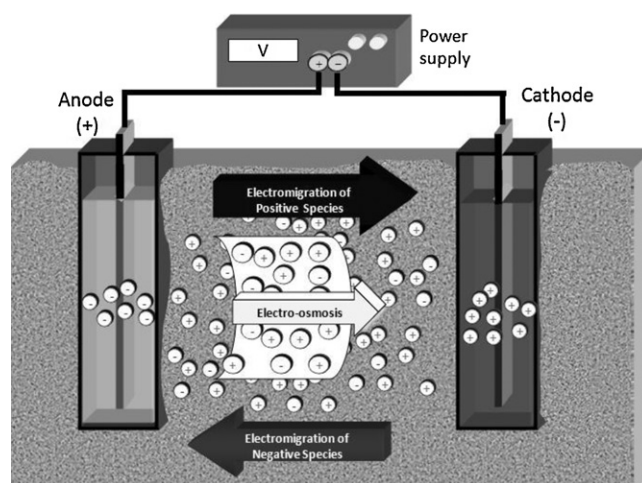


Fig. 1. Transport mechanisms during electroremediation.

Recently, electrokinetic remediation has been applied in the remediation of organic species, especially water-soluble compounds [23–28]. Nonetheless, the efficiency of the process is severely limited when the pollutants are organic compounds with low solubility, e.g. PAHs. The hydrophobicity and slow desorption rates of PAHs make it difficult to remove from subsurface environments using traditional electrokinetic remediation technology (*vide supra*). To improve the electrokinetic process, it is necessary to enhance PAHs desorption from the polluted soil and create a favorable environment to transport towards the electrode chambers. Besides, organic compound removal can be enhanced by increasing the electro-osmotic flow with the presence in the processing fluid of electrolytes (Na_2SO_4 , NaNO_3 , etc.) and also applying pH control at the electrode chambers [25,29].

3.2. Electroremediation with solubilising agents

Solubilising agents are commonly used as flushing solutions to substantially increase PAHs desorption and solubilisation through micellisation and surface tension reduction [30]. During the electroremediation process, these agents can be added directly into the soil or to the electrode chamber solutions and then they are introduced into the soil by electro-osmosis and/or electromigration (Fig. 2). The most common solubilising agents, utilized in the electrokinetic technique, are co-solvents, surfactants and cyclodextrins (Table 2).

3.2.1. Co-solvents

Co-solvents are water-miscible organic compounds as a result of their polar structure. They can promote contaminant removal in two ways. The first is by increasing the apparent solubility of the contaminant in water, which improves the mass removal per pore volume. The second way is by reducing interfacial tension between the water and the contaminant, which may result in direct mobilization of PAHs. Furthermore, co-solvents that microbes can use as

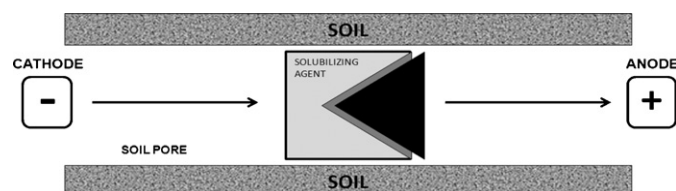


Fig. 2. Solubilising agents.

Table 2
Electroremediation of PAH-contaminated soil.

| Pollutant | Sample | Process fluid | | Observations—best results | Reference |
|-----------------------------------|--|---|--|--|-----------|
| | | Anode | Cathode | | |
| PHE 26 mg/kgds | Glacial till | 20% n-butylamine 20% acetone 20% tetrahydrofuran | H ₂ O | <i>Best results:</i> 43% PHE removal by using 20% n-butylamine after 127 days. | [35] |
| PHE 500 mg/kgds Ni 500 mg/kgds | Kaolin | 10% and 20% n-butylamine 0.01 M NaOH | H ₂ O | <i>Observations:</i> periodic voltage gradient of 2 V/cm (5 days on and 2 days off). <i>Best results:</i> Ni precipitation no removal, 7% PHE removal by using 20% n-butylamine and 0.01 M NaOH after 37 days. | [36] |
| PHE 500 mg/kgds | Kaolin | 3% Tween 80 with/without 0.01 M NaOH 40% ethanol with/without 0.01 M NaOH | H ₂ O | <i>Observations:</i> 1 V/cm. <i>Best results:</i> low removal in all cases. Best results with 40% ethanol without NaOH after 250 days. | [27] |
| PHE 500 mg/kgds | Kaolin | 40% ethanol 0.1 M Na ₂ SO ₄ 3% Tween 20 0.1 M Na ₂ SO ₄ | 40% ethanol 0.1 M Na ₂ SO ₄ 3% Tween 20 0.1 M Na ₂ SO ₄ | <i>Observations:</i> 3 V/cm, two-stage process (electrokinetic remediation followed by liquid electrochemical oxidation). <i>Best results:</i> 95% PHE removal by using 40% ethanol and 0.1 M Na ₂ SO ₄ after 60 days. | [29] |
| BTEX, PAHs Heavy metals | Soil from a former gasworks site | 2 M formic acid 1/500 dilution Hydrobreak | 8 M acetic acid | <i>Observations:</i> 1.28–3.2 A/m ² hexagonal electrode configuration anodes surrounding a central tubular cathode. <i>Best results:</i> 99% PAHs removal no metal neither BTEX significant removal after 118 days. | [50] |
| Mixture of heavy metals and PAHs | Organic silty sand from former manufactured gas plant soil | EDTA Non-ionic surfactant | – | <i>Observations:</i> sequential flushing EDTA and a non-ionic surfactant. <i>Best results:</i> effectively removed heavy metals and PAHs. | [51] |
| PHE 500 mg/kgds | Kaolin | 3% and 5% Igepal CA-270 0.01–0.1 M NaOH | H ₂ O | <i>Observations:</i> 1 and 2 V/cm. <i>Best results:</i> in all conditions low removal was reached after 60–70 days. | [52] |
| PHE 500 mg/kgds | Kaolin | 5% Igepal CA-720 0.01–0.1 M NaOH | H ₂ O | <i>Observations:</i> periodic voltage 1 and 2 V/cm (5 days on and 2 days off). <i>Best results:</i> 90% PHE removal by using periodic 2 V/cm, 0.01 M NaOH and 5% Igepal CA-720 after 275 days. | [53] |
| PHE 500–800 mg/kgds | Kaolin | 5–30 g/L alkylpolyglucosides 5–30 g/L Calfax 16L-35 | H ₂ O | <i>Observations:</i> 0.8 mA/cm ² . <i>Best results:</i> 98% PHE removal by using 30 g/L alkylpolyglucosides after 14 days. | [54] |
| BAP ≈300 mg/kgds | Kaolin | 1% Brij 35 40% ethanol | 1% Brij 35 40% ethanol | <i>Observations:</i> 3 V/cm two-stage process (electrokinetic remediation followed by liquid electrochemical oxidation). <i>Best results:</i> 76% BAP removal by using 1% Brij 35 and pH control at 7 in the anode after 33 days. | [55] |
| PHE | Clayey soil | Rhamnolipids | H ₂ O | <i>Observations:</i> introduction of biosurfactant produced by <i>P. aeruginosa</i> to solubilised PHE | [57] |
| NPH and 2,4-DNT | Loam and sandy loam | 2 and 5 g/L CMCD 0.01N NaNO ₃ | H ₂ O | <i>Observations:</i> 5–10 V/cm. <i>Best results:</i> 83% NPH and 89% 2,4 DNT by using 2 g/L CMCD 10 V/cm. | [60,61] |
| PHE 1.9 mg/kgds | Kaolin | 1.37 and 6.85 mM HPCD Na ₂ CO ₃ buffer | 0.01 M NaCl | <i>Observations:</i> 1.4 V/cm. <i>Best results:</i> 75% PHE removal by using 6.85 mM HPCD prepared in the Na ₂ CO ₃ buffer solution after 6 days. | [62] |
| PHE 500 mg/kgds Ni 500 mg/kgds | Kaolin | 1 and 10% HPCD 0.01 M NaOH | H ₂ O | <i>Observations:</i> periodic voltage 2 V/cm (5 days on and 2 days off). <i>Best results:</i> in all cases lower removal of PHE and negligible removal of Ni. | [63] |
| PAHs Heavy metals | Creosote-contaminated clay | 0.05 M phosphate buffer 3% H ₂ O ₂ , 35 mM Fe ²⁺ , Fenton reagent and 0.05 M phosphate buffer | 0.025 M phosphate buffer | <i>Observations:</i> 0.48 V/cm, DC/0.047 V/cm, AC combination. Fe ²⁺ and Na ₂ S ₂ O ₈ were distributed in soil as oxidants. <i>Best results:</i> 11% removal Electro-Fenton and 19% removal in Electro-Persulphate after 48 days. | [65] |
| PHE 200 mg/kgds | Kaolin | 3.5% and 7% H ₂ O ₂ 7% H ₂ O ₂ , 0.01N H ₂ SO ₄ | H ₂ O | <i>Observations:</i> 1.5 V/cm, 4163 ppm of Fe are native on the kaolin. <i>Best results:</i> ≈50% PHE removal by using 7% H ₂ O ₂ and 0.01N H ₂ SO ₄ after 21 days. | [3] |

Table 2 (Continued)

| Pollutant | Sample | Process fluid | | Observations—best results | Reference |
|---|------------------------|---|---------|-----------------------------------|--|
| | | Anode | Cathode | | |
| PHE 200 mg/kgds | Hadong clay and kaolin | 7% H ₂ O ₂ and 0.01N H ₂ SO ₄ | | H ₂ O | <i>Observations:</i> samples with differing buffering capacity, 4163 ppm and 3147 ppm of Fe are native on the kaolin and Hadong clay respectively. <i>Best results:</i> ≈50% PHE removal after 21 days in kaolin Hadong clay low removal. [72] |
| PHE 500 mg/kgds Ni 500 mg/kgds | Kaolin | 5–30% H ₂ O ₂ | | H ₂ O | <i>Observations:</i> 1 V/cm 805 ppm Fe is native in the clay. <i>Best results:</i> 56% PHE oxidation by using 30% H ₂ O ₂ after 28 days. Ni was mobilized towards the cathode but was retained in the soil as precipitated. [73] |
| PHE 500 mg/kgds | Kaolin | 10% H ₂ O ₂ | | 10% H ₂ O ₂ | <i>Observations:</i> 3 V/cm <i>Best results:</i> 99% PHE removal after 14 days. [74] |
| PHE 500 mg/kgds Pb 500 mg/kgds | Natural clay | H ₂ O | | H ₂ O | <i>Observations:</i> 0.5 mA/cm ² electrokinetic couple ultrasound 30 kHz. <i>Best results:</i> 90% PHE and 91% Pb removal after 15 days. [75] |
| HCB, PHE and FLU 100 and 500 mg/kgds | Kaolin | 0.01 M NaOH 0.01 M Na ₂ CO ₃ | | H ₂ O | <i>Observations:</i> 1.5 V/cm electrokinetic couple ultrasound 24 and 30 kHz. <i>Best results:</i> 74% HCB, 88% PHE and 90% FLU by using 24 Hz coupled 1.5 V/cm with initial concentration 100 mg/kgds after 10 days. [76] |
| PHE 895 mg/kgds PXY 895 mg/kgds Cu 740 mg/kgds Pb 820 mg/kgd | Kaolin | – | | 0.01 M HNO ₃ | <i>Observations:</i> 0.39 mA/cm ² . Upward electrokinetic soil remediation. <i>Best results:</i> 67%, PHE, 93% PXY, 62% Cu and 35% Pb removals after 6 days. [77] |
| 2,4-DCP 811 mg/kgds | Silt soil | 0.5 M Na ₂ HPO ₄ | | 0.5 M HNO ₃ | <i>Observations:</i> 0.89 A/m ² , <i>Burkholderia</i> sp. bacterium inoculated in the soil movement of organic compound and degradation. <i>Best results:</i> 87.1% 2,4-DCP removal after 22 days. [79] |
| PHE | Creosote-polluted clay | 1 M phosphate buffer | | 1 M phosphate buffer | <i>Observations:</i> 0.5–0.6 V/cm (77 h) and 0.2–0.3 V/cm (260 h) in alternate periods. <i>Novosphingobium</i> sp. LH128 bacterium inoculated in the soil. <i>Best results:</i> the treatment promoted the microbial activity and PHE removal after 14 days. [80] |

PHE, phenanthrene; FLU, fluoranthene; PXY, p-xylene; BAP, benzo(a)pyrene; HCB, hexachlorobenzene; CMCD, carboxymethyl-β-cyclodextrin; DNT, dinitrotoluene; DCP, dichlorophenoxyacetic acid; HPCD, hydroxypropyl-β-cyclodextrin; NPH, naphthalene.

substrates may have the added advantage of promoting bioremediation if they are used at non-toxic levels [31].

Several researches have demonstrated the high influence of miscible organic solvent on the sorption and mobility of PAHs [32–34]. Based on this ability, diverse electrokinetic treatments have utilized co-solvents to enhance the PAHs removal. Li et al. [35] carried out electrokinetic experiments by using different co-solvents (acetone, tetrahydrofuran, and n-butylamine) to extract phenanthrene from glacial till soil. They found that after 127 days of treatment the most effective co-solvent, n-butylamine at a 20% concentration, removed 43% of the initial phenanthrene. Although these results showed a moderate success, the initial concentration of phenanthrene employed by the authors was too low, 26 mg/kgds. Thus, when Maturi and Reddy [36] utilized the same co-solvent, during the treatment of kaolin contaminated with phenanthrene (500 mg/kgds), a low removal was obtained. Despite that in their experiments an alkaline environment was favored to increase the electro-osmotic flow, no enhancements were detected and, after 37 days only 7% of phenanthrene was removed.

On the other hand, the toxicity of some co-solvents, as n-butylamine may be an environmental concern [37], and for this reason water-miscible alcohols can be more adequate by environmental applications. Among them, ethanol has been used

extensively because it is environmental friendly and with a moderate cost. Saichek and Reddy [27] conducted bench-scale electrokinetic experiments to extract phenanthrene from kaolin employing different flushing solutions: 3% Tween 80 and 40% ethanol. Although a pH control was used, they found that lower phenanthrene removal was obtained in all experiments. Furthermore, the lowest electro-osmotic flow was obtained when 40% ethanol was used as flushing solution.

Often the results obtained in the treatments not only depend on the co-solvent employed. Some substances, e.g. electrolytes, can be added to the flushing solution to enhance the electro-osmotic flow. Consequently, Alcántara et al. [29] found that when a solution of 40% ethanol and 0.1 M Na₂SO₄ was introduced in the soil by electric field action, the desorption of phenanthrene from kaolin particle surfaces was improved. They also reported a higher electro-osmotic flow towards the cathode chamber. After 16 days, more than 95% of initial phenanthrene was removed from the soil and recovered into the cathode chamber.

3.2.2. Surfactants

Surface active agents (surfactants) are chemical compounds that consist of a strongly hydrophilic group, the head of the molecule, and a strongly hydrophobic group which is the tail.

The hydrophilic group causes surfactants to exhibit high solubility in water, while the hydrophobic group prefers a hydrophobic phase, such as PAHs. This fact enables surfactants to enhance the solubility of the contaminant through micellar solubilisation. In this process, aggregations of surfactant monomers form a micelle; its interior becomes a hydrophobic region suitable for PAHs, and, as a result, PAHs solubility is greatly enhanced [5]. The minimum concentration of the surfactant needed to produce the micelle is called the critical micelle concentration [38].

In general, surfactants are classified in anionic, cationic and non-ionic by the ionic characteristics of the hydrophilic head groups. Despite having high solubilisation capacities for PAHs, cationic surfactants are not suitable for soil remediation because of their low biodegradability on soil; these compounds are strongly retained in the soil matrix due to negative charge of the soil surface [39]. Therefore, anionic surfactants must show a higher remediation capacity due to a low degree of adsorption. Nevertheless, since anionic surfactants migrate toward the anode, they could be detrimental to the electrokinetic remediation process, because they would tend to counteract the electro-osmotic flow, which is usually toward the cathode [40]. Thus, non-ionic surfactants are often chosen because of their higher solubilisation capacities and furthermore they are more economical than the cationic and anionic ones. In addition, non-ionic surfactants are safer to use due to their higher biodegradability in the natural environment [41,42].

During the last years, the ability of non-ionic surfactants to remove PAHs has been studied. Several researches have tested non-ionic surfactants (e.g. Igepal CA-720, Tween 80, Tween 20, Triton X-100, Brij 30, Brij 35 and Tyloxapol) to remove single PAHs or PAHs mixtures from soil [43–49].

Based on the former studies, removal characteristics of PAHs from soil using a surfactant-enhanced electrokinetic process have been investigated for several researchers. Maini et al. [50] used Hydrobreak, a non-ionic surfactant, for electroremediation of a historically contaminated soil from a former gasworks site. The main contaminants of this soil were PAHs, BTEX and heavy metals. Although they utilized a hexagonal array of tubular anodes surrounding a central tubular cathode to favor the acid medium, no metal removal was obtained. However, at the end of the treatment, 99% of PAHs removal was obtained. Reddy and Kumar [51] reported a bench-scale electrokinetic remediation of a former manufactured gas plant site contaminated with a mixture of heavy metals and PAHs. The research found that sequential flushing with EDTA and a non-ionic surfactant, combined with the electrokinetic enhancement, removed effectively heavy metals, and PAHs. The addition of Igepal CA-720 during the electrokinetic remediation of phenanthrene in kaolin was tested by Saichek and Reddy [52]. Despite basic pH was favored inside the systems, low removal was obtained. Their results are attributed to surfactant sorption and phenanthrene partitioning to the sorbed surfactant molecules as well as the lower dielectric constant of the surfactant solutions. On the other hand, the periodic voltage application, 5 days on and 2 days off, was developed by Reddy and Saichek [53] demonstrated that 5% Igepal CA-720 was able to remove more around 90% of phenanthrene from kaolin in 275 days. The use of the surfactant alkyl polyglucosides (APG) during the electrokinetic treatment was reported by Yang et al. [54]. Their research determined that 98% phenanthrene removal could be achieved when a solution of 30 g L^{-1} of APG was used. In addition, it was found that when surfactants were applied to the process, the electrical potential gradient was lower than that of water. Thus, the electro-osmotic flow decreased as the concentration of surfactant increased. It is clear that the electrokinetic movement of PAHs is mainly due to the electro-osmotic flow, thus, in order to favor

the removal some enhancements must be carried out. Gómez et al. [55] reported that when a solution of surfactant Brij 35 1% was used during the electrokinetic treatment, benzo(a)pyrene was transported successfully through kaolin clay towards the cathode chamber. They found that the extent of this recovery depended on the pH profile on the soil. When no pH control was used, around 17% of initial contaminant was detected in the cathode chamber; though, when pH control in the anode chamber was set at 7.0, the recovery of benzo(a)pyrene could be higher than 76%.

Currently new surfactants, so-called biosurfactant, have been studied. These compounds are biologically produced from yeast or bacteria of various substrates such as sugars, oils, alkanes and waste. In most cases, they are synthesized as metabolic by-products. [56]. Ju and Elektorowicz [57] developed the on-site production and electrokinetic introduction of non-toxic, biodegradable surfactants produced from natural microorganisms to remediate PAH-contaminated soil. Their experiments demonstrated that rhamnolipids (biosurfactants) produced by *Pseudomonas aeruginosa*, increased the solubility of phenanthrene into the aqueous phase. Even though the use of these compounds in the electrokinetic treatment was proved successfully, no more recent researches were found.

3.2.3. Cyclodextrins

Cyclodextrins are cyclic oligosaccharides of glucopyranose units with a lipophilic cavity in the centre. They are produced by the action of a group of enzymes called cyclodextrin glycosyltransferases on starch. The natural product consists of a mixture of various cyclodextrins, mainly α -cyclodextrin, β -cyclodextrin and γ -cyclodextrin, which consist of six, seven, and eight glucopyranose units, respectively (Fig. 3). Cyclodextrins are capable of forming inclusion complexes with contaminants by taking up a whole contaminant molecule, or some part of it, into the cavity. Cyclodextrins offer some advantages over organic solvents, then these compounds appear as promising complexing agents to enhance organic compounds solubility, while minimizing environmental impact because of their non-toxic nature and biodegradability [58,59]. Jiradecha [60] was one of the first researchers introducing cyclodextrins in the electrokinetic treatment. In his research used two field soils, loam and sandy loam and employed carboxymethyl- β -cyclodextrin (CMCD) to remediate the laboratory spiked organic contaminants, naphthalene and 2,4-dinitrotoluene. After the electrokinetic experiments, it was determined that the CMCD enhanced electrokinetic process increased naphthalene removal to 83% [61]. Ko et al. [62] carried out the removal of phenanthrene from saturated low-permeability subsurface environments using hydroxypropyl- β -cyclodextrin (HPCD). They determined that pH control in the anode reservoir with a Na_2CO_3 buffer was necessary to keep electro-osmotic flow and charge flow rates higher. After 6 days of treatment, approximately 75% phenanthrene removal was obtained by flushing the anode reservoir with a 6.85 mM HPCD prepared in the Na_2CO_3 buffer solution. Following this research, Maturi and Reddy [63] studied the feasibility of using HPCD in electrokinetic remediation for the simultaneous removal of heavy metals and polycyclic aromatic hydrocarbons (PAHs) from low permeability soils. Bench-scale electrokinetic experiments were conducted using HPCD at low (1%) and high (10%) concentrations and using deionized water in control test. 0.01 M NaOH was added during the experiments to maintain neutral pH conditions at anode. They determined that the selected cyclodextrin enhanced phenanthrene migration from anode to cathode. On the other hand, it did not remove phenanthrene completely from the soil into the cathode solution either due to low electro-osmotic flow or due to low solubilisation.

| Cyclodextrin (CD) | n | Internal diameter (Å) | External superior diameter (Å) | Height (Å) |
|-------------------|---|-----------------------|--------------------------------|------------|
| α-CD | 1 | 5.7 | 13.7 | 7.8 |
| β-CD | 2 | 7.8 | 15.3 | 7.8 |
| γ-CD | 3 | 9.5 | 1.9 | 7.8 |

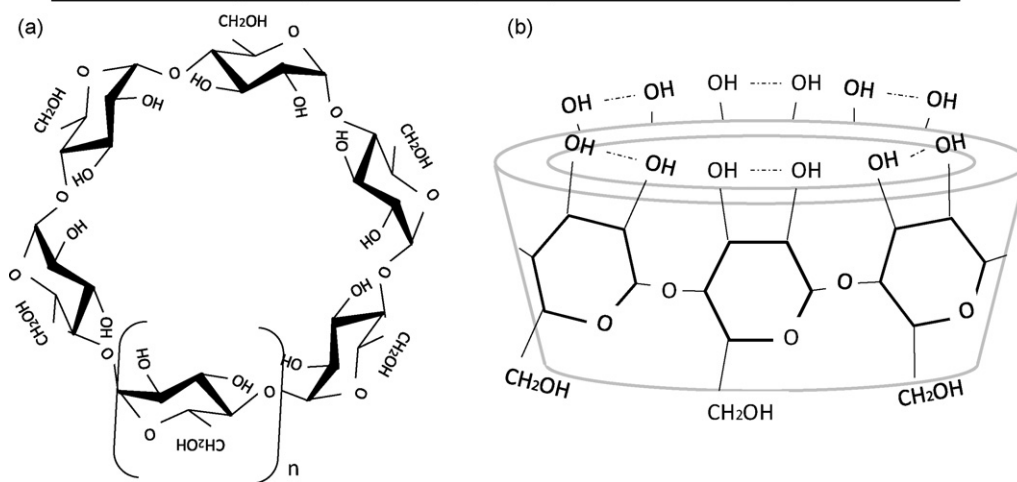


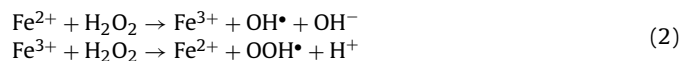
Fig. 3. Structure of cyclodextrins: (a) chemical and (b) tropoidal.

3.3. Hybrid technologies

3.3.1. Electro-Fenton

Fenton's reagent in conjunction with electroremediation treatment could be an environmentally friendly approach for organic compounds degradation in soil [3,64]. The electrokinetic treatment can facilitate oxidant delivery and activation of oxidizing radicals and simultaneously can induce oxidative/reductive reactions directly in soil [65].

Under this hybrid methodology organic compound oxidation takes place inside the soil by the use of hydrogen peroxide catalyzed by ferrous (Fe^{2+}) or zero-valent iron (Fe^0). The hydroxyl radicals generated in the Fenton reaction (Eq. (2)) are strong, relatively unspecific oxidants that react with most organic contaminants, including PAHs, at near diffusion-controlled rates in water (10^9 – $10^{10} \text{ M}^{-1} \text{ s}^{-1}$) [66,67]. The radicals oxidize the organic molecule by abstracting hydrogen atoms or by adding to double bonds and aromatic rings [68,69]. However, the Fenton reaction is effective only at low pH values (around 3), which require pH adjustment during the remediation [70]:



The Electro-Fenton technology was developed by Yang and Long [64]. They determined that an incorporation of Fenton reaction with scrap iron powder in the electrokinetic remediation system was beneficial to the chemical degradation of phenol in a saturated flow. In their experiments, a sandy loam soil saturated with phenol solution was treated by Electro-Fenton process incorporated with a permeable reactive wall of scrap iron powder next to the anode chamber. The addition of H_2O_2 (0.3%) was done in the anode reservoir. After 10 days, an overall removal and destruction efficiency of phenol of 99.7% was obtained. Although this treatment showed successful results, it must be taken into account that the

partial solubility of phenol in water played a key role in the removal process. When the solubility of the pollutant is low, e.g. PAHs, the process must be modified and the Electro-Fenton treatment must be carried out in a different way. Contaminants must be degraded inside the soil without their movement, thus the flushing solution must contain the oxidant. Following these bases, Isosaari et al. [65] studied the removal of PAHs from contaminated clay by integrating a low DC/AC voltage with the injection of Fenton's reagent or sodium persulphate. The PAHs removals obtained after 8 weeks were 11% in Electro-Fenton and 19% in Electro-Persulphate. The authors indicated that the limitation of the removal was mainly in the apparent need to optimize the reagent dosages and to lengthen the treatment time. Conversely, in the Electro-Fenton experiment, the authors did not take into account the adequate pH to favor the Fenton reaction. It is well reported that Fenton reaction must be carried out at pH around 3 [71] and the authors did not take this fact into consideration.

In some cases, several compounds can be added to the Electro-Fenton process to enhance the Fenton reaction and favor an acid medium. Kim et al. [3] utilized 7% H_2O_2 and 0.01N H_2SO_4 in the anode chamber in the Electro-Fenton treatment of kaolin polluted with phenanthrene. They found that after 21 days more than half of the spiked phenanthrene in kaolin clay was removed. They stated that presence of H_2SO_4 improved the H_2O_2 stability and the treatment of phenanthrene in the entire clay. However, when Kim et al. [72] utilized the same flushing solution during the decontamination of phenanthrene from clay with elevate buffering capacity, very low removal was obtained. They established that, although enhanced flushing solution was used, the clay carbonate content resulted in the decrease of H^+ concentration inside the clay. Thus, the efficiency of Fenton reaction was reduced. Their research confirmed that carbonates reduce the H_2O_2 stabilization and treatment efficiency of phenanthrene by the Electro-Fenton reaction. It is evident that the presence of specific compounds and the soil matrix

has a great influence in the removal efficiency in the Electro-Fenton process.

Recently, Reddy and Karri [73] performed experiments to determine the influence of the oxidant dosage in the Electro-Fenton treatment of kaolin spiked with nickel and phenanthrene. They studied the effect of the oxidant dosage during the Electro-Fenton treatment. The presence of H_2O_2 favored the Ni movement towards the cathode but high amount of metal was retained in the soil close to cathode chamber. A maximum phenanthrene oxidation around 56% was observed working with 30% H_2O_2 . Their results emphasize that the optimization of H_2O_2 /Fe concentration and voltage gradient as well as the control of soil pH are required to increase the removal of nickel and the oxidation of phenanthrene.

On the other hand, the effectiveness of the Electro-Fenton technique to treat soils contaminated with PAHs has been proved by Alcántara et al. [74]. They found that when anode and cathode chambers were filled with H_2O_2 (10%), the kaolin pH is maintained at an acid value around 3.5 without pH control and an overall removal and destruction efficiency of phenanthrene of 99% was obtained in 14 days.

3.3.2. New approaches

Latterly, in order to obtain high effectiveness in the treatment of soil contaminated with PAHs several techniques have been coupled to electrokinetic remediation. Recently, Alcántara et al. [29] and Gómez et al. [55] have developed an environmentally friendly approach for PAHs soil remediation based on a two-stage process: electrokinetic remediation followed by liquid electrochemical oxidation. In their experiments after the electroremediation process and, in order to obtain the total degradation of mobilized PAHs from the contaminated soil, the liquid collected during electrokinetic remediation was oxidized by electrochemical treatment. This oxidation was accomplished via an electrochemical cell by using graphite as electrode material. The benzo(a)pyrene and phenanthrene were almost totally degraded in 1 day and 9 h, respectively.

The coupled effects of electrokinetic and ultrasonic techniques on migration as well as clean-up of contaminants in soils have been also researched. Chung and Kamon [75] found that the phenanthrene removal rate was average 85% for electrokinetic test and average 90% for electrokinetic couple with ultrasound. A mixture of three persistent organic pollutants: hexachlorobenzene, phenanthrene and fluoranthene from kaolin were investigated by Pham et al. [76]. Their results showed that ultrasonic enhancement can increase between 2% and 9% the pollutant removal rate. In both researches they found that, generally, ultrasound tests have higher electro-osmotic flow, current, permeability and contaminant removal rate than electrokinetic alone tests.

In some researches is stated that only a new cell configuration is enough to increase the PAHs removal. Under this stated, Wang et al. [77] determined that by using upward electrokinetic equipment and favoring an acid pH, it could reach a higher elimination. They developed a new cell configuration where a non-uniform upward electric field was created between an anode embedded in soil and a cathode placed on the soil surface. They found that in the experiments with duration of 6 days removal efficiencies of phenanthrene, and p-xylene were 67%, and 93% respectively. Their experiments demonstrated the feasibility of simultaneous removal of organic contaminants and heavy metals from kaolin using the upward electrokinetic soil remediation process.

The idea of that electrokinetic treatment of polluted soils can enhance biodegradation by spreading indigenous bacteria and added nutrients and raising soil temperature was proposed by Alshawabkeh et al. [78]. Conversely, there are few reports about the ability of this bio-electrokinetic process. Jackman et al. [79] studied the removal of PAHs using a radio-labelled model organic contaminant, 2,4-dichlorophenoxyacetic acid. After electric field

application, the pollutant movement from a contaminated region into a region inoculated with degradative bacteria was confirmed. Furthermore, the movement was correlated with 87.1% biodegradation *in situ*. Niqui-Arroyo et al. [80] promoted the microbial activity in a clay soil historically polluted with PAHs by using a specially designed electrokinetic cell with a permanent anode-to-cathode flow and controlled pH. They found that the rates of phenanthrene losses during treatment were tenfold higher in soil treated with an electric field than in the control cells without current or microbial activity. In a novel approach Shi et al. [81,82] presented electroremediation treatment mainly aims at macro scale pollutant extraction and tend to neglect possible impacts of direct current on the physiology of microorganisms. They studied the effect of weak electric fields (1 V cm^{-1}) on the fitness of electrokinetically dispersed fluorene-degrading *Sphingomonas* sp. LB126 in bench-scale model aquifers. Their findings suggest that electrokinetics is a valuable mechanism to transport PAHs-degrading bacteria in soil or sediments. On the other hand, recent researches determined that electric field can have adverse effects in soil microbial communities [83,84]. Their investigations concluded that it is necessary to select a proper voltage and take certain measures to control soil pH change in bio-electrokinetic process.

4. Conclusions

The present review shows the approaches to electroremediation of PAHs soil contaminated on the basis of significant recent original publications. The problems encountered in attempting to apply conventional technique and highlight the recent efforts that are being used in electroremediation in the decontamination of PAHs polluted soils were reported. Although the application of electroremediation in real soil is beginning, the results obtained in most of evaluated papers are encouraging. More researches are required to validate the techniques to decontaminate mixture of PAHs in real soil and carry out the treatment in field scale.

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