Electro-bioremediation of hydrophobic organic soil-contaminants: A review of fundamental interactions

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Abstract

In recent years, there has been increasing interest in employing electro-bioremediation, a hybrid technology of bioremediation and electrokinetics for the treatment of soil contaminated with hydrophobic organic compounds (HOC). Present electro-bioremediation approaches however mainly aim at pollutant extraction through transport over large distances and tend to neglect both the impact of direct current (DC) on organism–soil interactions and microscale HOC release rates. Accordingly, no data are available on bioavailability changes acting via DC-driven effects on organism–compound and organism–soil interactions. This is a serious gap of our current knowledge hampering the improvement of the electro-bioremediation methodology. This review establishes a conceptual framework of the various influences of DC on processes governing HOC-bioavailability in soil, in particular the DC influence on microbial physiology and the physico-chemistry of organism–soil and organism–compound interactions.

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1. Introduction

One of the major challenges in environmental biotechnology is the improvement of in situ soil decontamination efficiency. Present bioremediation of contaminated soil and groundwater is an empirical business often lacking an environmentally sound methodology that is based on mechanistic knowledge of the rate-limiting microscale processes. In recent years, there has been increasing interest in employing electro-bioremediation, a hybrid technology of bioremediation and electrokinetics for the treatment of soil contaminated with hydrophobic organic compounds (HOC). Several studies have indeed demonstrated improved removal of organic pollutants such as gasoline hydrocarbons, aromatic compounds, herbicides or trichloroethylene in electric fields [1–6] applied to soil. In electro-bioremediation, electrokinetics is the use of weak electric fields (ca. 0.2–2 V cm⁻¹ [7]) to soil. It can be used in situ and is particularly effective in (saturated and unsaturated [8]) fine-grained soils of low hydraulic conductivity, which are normally difficult to treat by other in situ methods [9]. Several comprehensive articles have summarized the state of the knowledge with foci on physical [10], physico-chemical [11], engineering [12] and remediation aspects [3,8,13] of electrokinetics in soil clean-up. However, sound data on the effect of weak electric fields on HOC-degrading soil microorganisms is missing [14]. This is surprising since (engineered) bioremediation of polluted soil significantly depends on microbial activity and aims at the stimulation of indigenous microorganisms capable of degrading the pollutants [15]. The ‘electro-bioremediation-tetrahedron’ depicted in Fig. 1a and b epitomize (···) the influences of DC on the relevant bioremediation processes of soil-bound HOC, i.e. its impact on the soil matrix, HOC, microorganisms and their mutual interactions: the tetrahedron’s base triangle A represents the interactions of soil, microorganisms and a (hydrophobic organic) compound that govern its bioavailability; triangle B relates direct current (DC) to abiotic compound–matrix interactions potentially leading to electrokinetic movement of HOC and concomitant improvement of HOC-bioavailability; whereas triangles C and D illustrate the impact of DC on the physiology, chemistry and physico-chemistry of organism–compound, and
organism–matrix interactions that may influence microbial HOC uptake and community dispersion, respectively.

The idea of electrokinetics is to stimulate mobilization of soil components, contaminants and/or microorganisms in order to either physically remove or to disperse them. For in situ electrobioremediation small scale dispersion of HOC is intended rather than ‘macroscopic’ HOC-transport (HOC-extraction), as bacteria are ubiquitous in soil [16]. Assuming average separation distances of ≤100 μm [17] between individual bacterial microcolonies, short-distance transport may drastically improve the contact between pollutant molecules and bacteria and, concomitantly, biodegradation [18,19]. However, present electro-
bioremediation approaches mainly aim at pollutant transport over large distances and tend to neglect both the impact of DC on organism–soil interactions and microscale HOC release rates. Accordingly, no data are available on bioavailability changes acting via DC-driven effects on organism–compound and organism–soil interactions. This is a serious gap of our current knowledge hampering the improvement of the electro-bioremediation methodology. This review will therefore try to establish a conceptual framework of the various influences of DC on processes influencing HOC-bioavailability in soil, in particular the DC influence on microbial physiology and the physico-chemistry of organism–matrix and organism–compound interactions.

1.1. Pollutant bioavailability as a limiting factor of soil bioremediation

Various studies have shown that the sequestration of organic contaminants in the solid soil phase by sorption and entrapment reduces their bioavailability depending on the contaminant’s physico-chemical characteristics [19–21]. Due to their high solid-water distribution ratios \( K_d \), HOC typically are associated with carbon phases of particles and are very slowly released from soil, sediments and aquifer solids by diffusive transport processes [19,22]. A sequence of three potential bottleneck processes of diffusive mass-transfer controlling HOC release have been described: (i) diffusion of the sorbate within the molecular nanoporous network of natural organic matter (OM) [20], (ii) pore or surface diffusion in aggregated minerals constituting natural particles [21], and (iii) diffusion of the sorbate across an aqueous boundary layer at the exterior of soil particles [23]. As a consequence of progressive binding with soils, residual HOCs may become less leachable and thus unavailable to microbes as bacteria appear to degrade chemicals only in proportion to their dissolved phase chemical activity [24–28]. Two factors have been considered necessary to determine a chemical’s bioavailability: (i) the rate of mass transfer of the compound from the soil to the catabolically active cells and (ii) the rate of the compound’s uptake and metabolism by the cells, which in turn acts as driving force for the mass transfer to the cell. The bioavailability of a chemical has been defined as the rate of mass transfer relative to the intrinsic activity of the soil biota [17,18] and thus may vary between different species [29–31]. Semple et al. define the term ‘bioavailability’ as the fraction of a chemical in a soil that can be taken up or transformed immediately by living organisms, whereas the term ‘bioaccessibility’ refers to the fraction of a substance that could become available with time [32]. Experimental evidence and theoretical considerations [28] show that better substrate bioavailability can be achieved by enabling faster contaminant transport to the bacteria or by mobilizing the bacteria. Theoretically, only short-distance movement of either the pollutant or the bacteria within the soil would be needed to overcome mass-transfer limitations. The principle of electro-bioremediation is thus to make bioaccessible HOC-fractions bioavailable by dispersing both soil-bound microorganisms and HOC.

1.2. Influence of DC on physico-chemical soil–compound interactions

1.2.1. Physico-chemical phenomena

When a DC field is applied to a wet soil matrix, it invokes electroosmosis, electromigration and electrophoresis (for a review cf. [4,33]). Electrophoretic flow emerges because excess ions migrate in a plane parallel to particle surfaces toward the oppositely charged electrode. As they migrate, they transfer momentum to the surrounding fluid molecules via viscous forces. Consequently, electroosmosis is the mobilization of surface-near pore fluids in an electric field, usually from the anode toward the cathode (because cations accumulate near particle surfaces of negative charge). Electroosmotic flow is able to take free-phase dissolved matter toward the cathode [11]. For non-ionic substances, electroosmosis is the predominant transport mechanism. Electrophoretic flow rates vary from \( 10^{-4} \) to \( 10^{-6} \) cm\(^2\) V\(^{-1}\) s\(^{-1}\), depending on the morphological properties of the porous medium, such as the porosity, flow path radius, pore width, as well as the physico-chemical properties of the solid and the liquid phases. In general electroosmosis is more efficient in fine-grained soils (with \( \mu \)m or smaller pores) and at higher water contents [34]. Electromigration is the active movement of ionic species in a DC field to the electrode of opposite charge [35]. Since the electromigration rate is at least one order of magnitude higher than the electroosmotic flow [8], electromigration generally dominates mass transport of ions and charged molecules. Electrophoresis is defined as the transport of charged particles such as clay platelets or bacterial cells toward the electrode opposite in polarity in a DC field. Furthermore, a competition between buoyancy, hydrodynamics, and electroosmosis/electromigration may influence the microfluidics and lead to distinct flow regimes and concomitant solute transport within pores [36]. Electrokinetically induced flow processes may further result in steepened chemical concentration gradients and concomitantly enhanced transfer of surface-associated contaminants. The effective chemical diffusion in general, depends on the molecular diffusion coefficient, the concentration gradient, and the porous medium micromorphology (porosity and tortuosity).

Besides these transport processes many other reactions may occur in a DC field such as desiccation due to heat generation, gas generation due to electrolysis of water, decomposition or precipitation of salts and minerals, ion exchange, development of pH gradients, sorption processes and electrochemical transformations. Electrokinetically induced soil–contaminant interactions are particularly important in fine-grained soils because of the large surface to volume ratio and the large specific surface area. Such interactions include: (1) change of Zeta potential (\( \zeta \)) at the soil particle/pore fluid interface; (2) the capacity to buffer pH changes; and (3) sorption/desorption of reactive contaminants onto or from the soil particle surface and precipitation/dissolution of metallic contaminants in the pore fluid. Electrolysis of pore fluids at both electrodes in wet soils according to the reactions: \( 2H_2O \rightarrow 4H^+ + O_2(g) + 4e^- \) (at the anode) and \( 2H_2O + 2e^- \rightarrow 2OH^- + H_2(g) \) (at the cathode) has important secondary effects [11]. The anode reaction will generate an acid front, while the reduction at the cathode produces alkalinity.
These acids and bases will advance through the soil matrix by diffusion, electromigration and/or electroosmosis, and thus may locally change soil pH [8] potentially influencing biodegradation of organics in soils. Concomitant electrochemical redox-reactions may lead to a series of electrochemical reactions, such as the production of reactive oxygen species and other energy-rich intermediates. Previous studies have further indicated the significance of the Zeta potential of soil on electrokinetic remediation efficiency [37–39]. Zeta potentials of kaolinite, montmorillonite and quartz powder with Li\(^+\), Ca\(^{2+}\), Cu\(^{2+}\), Pb\(^{2+}\) and Al\(^{3+}\) in the presence of anionic surfactants were found to be negative, whereas non-ionogenic and cationic surfactants produced both positive and negative ζ potentials depending on soil type and ions present in the system [39]: ζ potentials of kaolinite and quartz powder in presence of surfactants showed similar trends, with the absolute magnitude of ζ of quartz powder being higher than that of kaolinite. The ζ potential of montmorillonite commonly shows a different trend from those of kaolinite and quartz powder. Based on the test results, these authors recommended that ζ potential of soils should be determined before the electrokinetic decontamination in order to maximize the efficiency of the technique.

**1.2.2. Effect of DC on compound mass transfer processes**

It has been demonstrated manifold that electroosmosis efficiently removes water-dissolved phenol, α-nitrophenol [33], hexachlorobenzene [4], benzene, toluene, ethylene and xylene (BTEX) [40,41], hexane, isooctane and trichloroethylene (TCE) from clay [2]. It appears, however, that electroosmotic long-distance transport of HOC is significantly enhanced when they are present as droplets, or colloidal particles [7,42,43] or when solubilization is assisted by surfactants, cyclodextrins or chelating agents [7,44–49] (for a comprehensive review on electrokinetic removal of soil-bound HOC cf. [11]). Estimations by Bruehl et al. [40] showed that electroosmotic removal efficiencies of organic chemicals from a given kaolin clay depend on the compound’s Freundlich constant (\(K_d\) (mL g\(^{-1}\))) and, to a lesser extent, to its aqueous solubility (\(c_{\text{sat}}^w\) (mol L\(^{-1}\))) leading to the following electrokinetic mobilization efficiency: toluene (\(-\log c_{\text{sat}}^w = 2.25\); \(K_d = 0.6\)) > TCE (\(-\log c_{\text{sat}}^w = 2.04\); \(K_d = 0.84\)) > benzene (\(-\log c_{\text{sat}}^w = 1.64\); \(K_d = 0.89\)) > m-xylene (\(-\log c_{\text{sat}}^w = 2.77\); \(K_d = 1.6\)) > hexane (\(-\log c_{\text{sat}}^w = 3.15\); \(K_d = 2.5\)) > (\(-\log c_{\text{sat}}^w = 4.52\); \(K_d = 24\)). It should be noted however, that equilibrium isotherm models, such as the Freundlich isotherm, are based on the assumption that the contaminant is sorbed to the soil particle surface and that the dynamic chemical equilibrium in the dissolved phase is reached instantaneously at all times. This may be adequate when the flow velocity of the groundwater is low. However, as the electrokinetically driven migration velocity of the contaminant is relatively high, the validity of using equilibrium isotherms to describe sorption/desorption processes may not be adequate. Other studies have described the electrokinetic transport of PAHs in coal tar contaminated soil covering a wide range of aqueous solubility (\(-\log c_{\text{sat}}^w = 3.6–8.22\)) [50,51] with PAH removal efficiencies of 44–70% [50] within 21 days and ≤90% [51] within 23 days, respectively. Some selectivity was observed in the transport of PAH compounds in clayey specimens, probably owing to the preferential retention of some compounds by clay [50]. Interestingly, there was little or no selectivity in the transport of PAHs in granular specimens. Naphthalene was the most consistently transported compound while the lowest removal rate was observed with chrysene [50]. To our knowledge however, no mechanistic studies on the impact of DC on the microscale flow and desorption processes of HOC exist for soil environments. Electrokinetically enhanced mass transfer in situ may be relevant at the micro and the macroscale. On the macroscale, electrokinetically enhanced introduction of nutrients, co-substrates, water, electron acceptors or bacteria into soil [2,52–55], pollutant-degrading bacteria into polluted areas [56], and inversely, mobilization of contaminants into biologically active treatment zones [1,2,57] have been described. On the microscale, intra-particle diffusional mass-transfer resistances often impose serious limitations on the rate biotransformation in soil. Electrically driven mass-transfer processes such as electromigration of charged species and electroosmotic solute transport may be convenient and efficient to stimulate chemical fluxes in soil matrices. Particularly, electroosmosis is likely to overcome mass-transfer bottlenecks in low permeable soil matrices by (i) increasing the release of sorbates by inducing liquid flow at the immediate exterior of soil particles, (ii) creating flow in nanopores in the organic sorbent phase, which are inaccessible by hydraulic flow, and (iii) influencing the pore or surface diffusion among aggregated minerals.

**1.3. Influence of DC on microorganism–soil interactions**

Capillary electrophoresis nowadays is an established tool for the separation and analysis of bacteria in the laboratory (for a review, see ref. [58]). Over the last few years several studies have demonstrated that microorganisms can be moved electrokinetically through soil [56,59–61], but little is known on the mechanisms by which microorganisms are electrokinetically dispersed in soil matrices. For bioremediation this is of great importance as most soil bacteria are normally immobilized in situ, i.e. they are attached to soil particles [62] and form microcolonies rather than releasing single cells into the soil water. This leads to the largely heterogeneous micro-scale-distribution of soil bacteria known to limit pollutant bioavailability [17]. Even macroscale (up to 0.4 m) electrophoretic transport of bacteria and NAPL-degrading yeast cells through sand, soil and aquifer sediments to the anode has been described. Depending on the microorganism and the subsurface matrix, electrophoretic transport rates (\(v\)) ranged from 0.019 to 0.023 cm\(^2\) h\(^{-1}\) V\(^{-1}\) for yeast cells [61] and 0.14 to 4 cm\(^2\) h\(^{-1}\) V\(^{-1}\) for bacteria [56,59]. In other studies however, electroosmotic transport of pollutant-degrading bacteria was the predominant mobilization mechanism with electrophoretic transport accounting for less than 20% of the observed bacterial dispersion in a soil matrix [59,60]. This is in good agreement with the observation that *Escherichia coli* moved in capillaries exclusively by electroosmosis at electrical field strengths of >0.3 V cm\(^{-1}\) over a wide range of pH values and ionic strengths tested [63]. The same investigators also found that bacterial motility is the predominant
mode of motion at voltages below 0.2 V cm\(^{-1}\), with bacteria moving at different mean speeds toward anode and cathode due to superimposed effects of electroosmotic flow, electrophoresis, galvanotaxis [64], and random motility. In model aquifer systems up to 90% of weakly negatively charged (\(\zeta = -7\) mV) and moderately adhesive Sphingomonas sp. L138 was transported by electroosmosis, whereas 0–20% were transported by electrophoresis. Electroosmotically transported bacteria (\(v = 0.1 - 0.4\) cm\(^2\) h\(^{-1}\) V\(^{-1}\)) were 50% slower than injected conservative tracers [59]. Poor electrokinetic transport of strongly charged (\(\zeta < -32\) mV) and highly adhesive Mycobacterium frederiksbengense LB501T [65,66] however occurred in the different model aquifers consisting of alluvial sand, clayey soil or glass beads pointing at a dominant influence of bacterial retention by the solid phase [59]. The strong affinity of the bacteria for these solid matrices could be partially overcome by treating the bacteria with the non-ionic surfactant Brij35 leading to up to 80% enhanced electrokinetic dispersion of both strains [59]. It thus can be concluded that the extent of the retardation in the subsurface depends on both the physics and the chemistry of the subsurface (e.g., the pore size distribution and the ionic strength of the pore water) as well as on biophysical factors (e.g., cell size, cell shape, cell surface charge and/or hydrophobicity).

No data however, are available on the influence of DC on the adhesion and detachment of bacteria in soil matrices. Some knowledge exists on bacterial attachment to medical devices under influence of DC. Several authors have described the electrokinetic inhibition of bacterial colonization on surfaces at low electric currents (17.2 \(\mu\)A cm\(^{-2}\)) [67]. A series of fundamental studies have been performed in parallel plate flow chambers [68], studying the influence of electric potential, electric current, and electric charge transfer on both bacterial deposition to and detachment from electrode surfaces. An external electric potential can be applied to a cell suspension in absence of electric current, when the surface in contact with bacterial suspension of at least one electrode consists of non-conductive material such as glass. No effect of the surface potential of glass surfaces on bacterial adhesion was found [69]. In other experiments both positive and negative electric currents were used to detach bacteria from salivary conditioning film on indium tin oxide (ITO) electrodes in order to compare the desorption forces acting parallel (electroosmosis) to forces acting perpendicularly, such as electrophoresis, electrostatics to the electrode surfaces [70]. From their experiments the authors concluded that parallel forces desorb bacteria more effectively than perpendicularly forces. It was also reported that current induced the detachment of 10 different bacterial strains. Although initial detachment rates increased with increasing electric current, the final extents of detachment were similar [71]. Bacterial adhesion to a semi-conducting ITO electrode changed the electric potential of the electrode without changing its capacitance, which was explained by charge transfer during bacterial deposition [72]. An average charge of about \(10^{-14}\) C per bacterium was found to be exchanged during initial adhesion corresponding to only a few percent of the total surface charge of a bacterium. Bacterial adhesion to the substrata with different specific resistivity where bacteria either donated or accepted electrons, led to conclude that bacteria adhered more strongly when they donated electrons to the substratum rather than inversely [73]. In conclusion, reported effects of electric fields on bacterial adhesion, detachment and biofilm formation to electrodes are thus likely to be attributed to the electric current rather than to the electric potential applied. As a consequence of bacterial adhesion, charge transfers were also observed between bacteria and conductive or semi-conductive surfaces, and meanwhile the direction of electron transfer was also demonstrated to affect the stability of bacterial adhesion.

1.4. Influence of DC on microorganism–compound interactions

A series of studies has reported stimulation of bioremediation by electrokinetic processes [1,2,5,6,52–55,57,60]. Optimal biodegradation activity requires that DC has no negative effect on the physiology of the biocatalysts, i.e. the indigenous HOC-degrading bacterial communities in soil. To date only one work on the effect of DC on the soil microbes (i.e. the composition and structure of DC-exposed soil microbial communities) has been published [74]. In this study no direct effect of the applied current (0.314 mA cm\(^{-2}\)) on soil bacteria could be ascertained [74]. The application of DC to soil however, altered both the physico-chemical characteristics of the soil and changed the microbial community close to the anode due to anodic soil acidification. The authors concluded that, provided that factors such as soil pH and temperature were controlled, electrokinetics had no negative effect on ‘soil health’ [74]. Earlier studies in subsurface systems have shown that the application of 20 mA cm\(^{-2}\) to soils stimulated the activity of sulphur-oxidising bacteria [75] or the biological denitrification of nitrate-contaminated groundwater [55] due to the production of \(\text{H}_2\) and pH-changes, respectively.

When electric current is applied to living microbial cells, different responses, such as toxic electrode-effects, metabolic stimulation due to enhanced substrate mass-transfer processes to the cell and electrokinetic removal of inhibitory products [76], sublethal injuries [77] or changes in the physico-chemical surface properties [57,78] can be observed depending on the amperage, treatment time, cell type and medium characteristics [14]. Influences on cell-surface characteristics are of special interest in soil bioremediation as they influence bacterial adhesion to surfaces and concomitantly their mobility in the subsurface [79]. Over the last years several studies have investigated the effects of high- and low-amperage electric current on the inactivation of microorganisms for food processing or for wastewater hygenization. There are a few reports on antimicrobial activity of low amperage per se. It is postulated that the mechanism of action may be the disruption of bacterial membrane integrity, mechanical stress due to hydrodynamic drag [80] or the electrolysis of molecules on the cell surface. At properly selected conditions [81], the application of short electric pulses (electroporation [82]) causes transient or reversible membrane permeability changes that allow the electrorelease (electrolysis) of cell ingredients, such as intracellular proteins [83] or the uptake of foreign molecules, such as DNA, proteins or substances to which the cells is poorly or non-permeable. Matsunaga et al. [84,85] established that the electrochemical destruction of
microbial cells was based on the direct electron transfer between cells and an electrode, and demonstrated that coenzyme A was oxidized to dimers. The same authors also showed that the resulting inhibition of respiratory activity caused microbial cell death. The cytoplasm of cells is electrically conducting whereas the lipid bilayer of the cell membrane can be considered as dielectric. The application of electric fields to cells thus causes the buildup of electrical charge at the cell membrane, and consequently a change in voltage across the membrane. For externally applied electric fields leading to a transmembrane potential difference, $\Delta \Phi_m > 70–100 \text{mV}$, a value observed in eukaryotic cells in the absence of DC, the membrane permeability is expected to increase leading to a reversible or irreversible ‘dielectric’ breakdown [86] of $\Delta \Phi_m$. When the transmembrane potential differences exceed a critical value of usually 1 V, electromechanical cell membrane break down and concomitant cell death occurs [80].

Furthermore, it has been found that exponentially growing cells are usually more sensitive to electric field treatment than cells in the stationary phase. Inactivation rates also depend on the medium’s conductivity and osmotic properties. However, it is believed that adverse electrochemical reactions are the main reasons for antimicrobial activity of low DC fields, especially in the vicinity of the electrodes [87]. For instance, no inhibition zone around the cathode was observed under anaerobic conditions as no $\text{H}_2\text{O}_2$ could be produced in the absence of oxygen and electrochemical reactions of chloride appeared to play a minor role [87]. Other studies have linked the antimicrobial activity of DC to electrochemically formed toxic substances, such as free chlorine [88], $\text{H}_2\text{O}_2$ [87,89] and metallic ions [90]. Some investigators [91] have attributed the lethal effect of electricity to a simple thermal effect called ohmic heating, whereas others excluded ohmic heating and production of $\text{H}_2\text{O}_2$ as causes for the lethal effect of electric treatment of Saccharomyces cerevisiae [92]. Low-field DC (1.5–30 V cm$^{-1}$) with current densities of 15 $\mu$A cm$^{-2}$ to 2.1 mA cm$^{-2}$ have been further shown to lead to a greatly increased antimicrobial activity of antibiotics against bacterial biofilms [93]. Relevant for bioremediation however may be electrokinetically enhanced mass-transfer processes due to the combined effect of electrophoresis and electroosmosis: in laboratory tests a growth stimulation of immobilized cell by 140% [94] due to the electrokinetic removal of inhibitory products and electroosmotically enhanced glucose-supply has been reported. It thus appears that a number of useful preparative electrochemical transformations can be accomplished by suitable selection of microorganisms and reaction conditions; Enhanced biotransformation of benzonitrile to benzoic acid and ammonia [95], electrically enhanced ethanol fermentation [96], reductive carboxylations [97], reduction of chloroppyruvate to chloroacetate catalyzed by a mediator-dependent $\alpha$-lactate dehydrogenase or the regeneration of pyridine nucleotides [98] have been reported. A recent study has further presented experimental observations that the natural electromagnetic field at the earth’s surface may be used by E. coli as supplemental energy source to sustain growth [99]. The authors argue that protons in liquid water can be excited at their natural resonance frequencies through Langmuir oscillations. By using electromagnetic energy the microorganisms thus may obtain enough kinetic energy to charge the transmembrane potential and, concomitantly may be capable of converting electromagnetic waves into chemical energy.

2. Outlook

The basic principles of electrokinetic extraction and the electrokinetically enhanced bioremediation of contaminants from fine-grained soil have been experimentally proven to be feasible. Although empirical electro-bioremediation appears to be safe, effective and economically interesting compared to other remediation techniques there is still a need for mechanistic understanding of the molecular processes affecting the release and transport of HOC in soil as well as the dispersion and physiology of HOC-degrading microorganisms before the technology can be fully exploited: Fig. 2 summarizes the molecular processes and interactions of bioavailability potentially influenced by DC: I represents the release of a chemical from an organic or inorganic matrix to a more accessible form and, inversely the adsorption of HOC to soil matrices; Processes II–IV describe the HOC’s transport to and uptake through the membrane of an organism and the processes of microbial

![Fig. 2. The influence of direct current (DC) on bioavailability of HOC as determined by various interactions of a compound or mixture with the solid phase matrix and the receptor organism (adapted from [32]): I represents the release of a chemical from an organic or inorganic matrix to a more accessible form and, inversely the formation of non-extractable so-called bound residues; II–IV describe the organism–compound and organism–matrix interactions in terms of transport to and uptake by the membrane of an organism and the processes of microbial adaptation to hydrophobic compounds; III and V describe interactions of the microbes with the matrix; whereas processes IV and VI include DC-related physiological and biochemical HOC-uptake and transformation processes.](image)
adaptation to hydrophobic compounds; III and V describe inter- 
actions of the microbes with the soil matrix, such as microbial 
translocation processes or the active improvement of bioavail- 
ability by altering bacterial cell surface properties. Up to date 
no data are available on the mechanistic understanding of the 
present electro-bioremediation approaches including the 
processes of association and dissociation of HOC from soil matrix 
(I), or to relate the HOC concentrations to the HOC release and 
transport over large distances. These studies furthermore neglect 
processes IV and VI, i.e. the influence of DC on bacterial cell 
surfaces, microscopic mass transfer at the cell surfaces and/or 
the bacterial physiology including the metabolism and degradation 
at the site of response within the cells. The main thrust of future 
research consequently lies in the establishment of a profound, 
conceptual and theoretical fundament for the processes taking 
place at a molecular and microscale level in soil environments.

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