



Review

Electrokinetic-enhanced bioremediation of organic contaminants: A review of processes and environmental applications



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HIGHLIGHTS

- We investigate the influence of geological matrices on EK-enhanced mixing.
- Mechanisms of EK-BIO at the field-scale including several novel applications.
- Review of the physicochemical processes that effect EK-BIO in the environment.
- Summary of design options available to enhance EK-BIO treatment at the field-scale.
- Spreadsheet model that applies EK-BIO treatment to a contaminant plume scenario.

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ABSTRACT

There is current interest in finding sustainable remediation technologies for the removal of contaminants from soil and groundwater. This review focuses on the combination of electrokinetics, the use of an electric potential to move organic and inorganic compounds, or charged particles/organisms in the subsurface independent of hydraulic conductivity; and bioremediation, the destruction of organic contaminants or attenuation of inorganic compounds by the activity of microorganisms *in situ* or *ex situ*. The objective of the review is to examine the state of knowledge on electrokinetic bioremediation and critically evaluate factors which affect the up-scaling of laboratory and bench-scale research to field-scale application. It discusses the mechanisms of electrokinetic bioremediation in the subsurface environment at different micro and macroscales, the influence of environmental processes on electrokinetic phenomena and the design options available for application to the field scale. The review also presents results from a modelling exercise to illustrate the effectiveness of electrokinetics on the supply electron acceptors to a plume scale scenario where these are limiting. Current research needs include analysis of electrokinetic bioremediation in more representative environmental settings, such as those in physically heterogeneous systems in order to gain a greater understanding of the controlling mechanisms on both electrokinetics and bioremediation in those scenarios.

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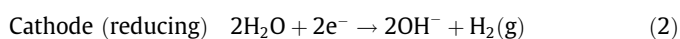
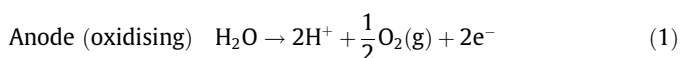
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1. Introduction

Land contaminated by anthropogenic activities is of global concern and where exposure to harmful substances occurs there is potential for unacceptable risks to human and environmental health. Bioremediation is a well-established technology used to treat biodegradable contaminants, according to concepts based in general on *ex situ* treatment of excavated material (mainly used in pollutant source removal), and *in situ* treatment of sites with restricted access (where less disturbance is desirable and extended remediation timescales are acceptable) (CIRIA, 2002). Bioremediation requires environmental conditions which are favourable for the particular biochemical process and interaction between microorganisms, contaminants, nutrients and electron acceptors/donors (Sturman et al., 1995). *In situ* biodegradation can be limited by contaminant bioavailability: the immediate contact between microorganisms and substances required for contaminant biodegradation, and bioaccessibility: the fraction of these components accessible to microorganisms in the environment (Semple et al., 2004). Consequently, biodegradation processes may occur in the subsurface environment, but not at a rate to mitigate risks at a particular site.

These limitations can be overcome by coupling bioremediation with electrokinetics (EK), a remediation technology where direct current is applied within subsurface porous media to induce specific transport phenomena (Fig. 1), namely: (1) electroosmosis – the bulk movement of fluid through pores; (2) electromigration – the movement of ions in solution; and (3) electrophoresis – the movement of charged, dissolved or suspended particles in pore fluid. It is also characterised by the electrolysis of water at the electrodes (Virikutyte et al., 2002):



The reaction products, hydrogen (H^+) and hydroxyl (OH^-) ions migrate towards their oppositely charged electrode, generating acid and base fronts (Acar et al., 1993). Electromigration and electroosmosis are independent of hydraulic conductivity and EK can be used to generate mass flux in zones impervious to advective

transport (Jones, C.J.F.P et al., 2011). The principles of electrokinetics have been reviewed by Acar and Alshawabkeh (1993), Virikutyte et al. (2002), Yeung and Gu (2011).

Factors which limit the performance of *in situ* bioremediation are often highly site-specific (Boopathy, 2000) and commonly include: (1) mass transfer of electron acceptors and nutrients to microorganisms responsible for biodegradation (Simoni et al., 2001), (2) limited bioaccessibility of contaminants (e.g. partitioning to aquifer material) for biodegradation (Lohner et al., 2009), and (3) adaptation of the indigenous microorganisms for biodegradation of a particular contaminant (Mrozik and Piotrowska-Seget, 2010). The aim of coupling EK to bioremediation is to overcome these limitations, increasing the effectiveness of remediation measures. This review covers a number of related topics: (1) EK-bioremediation (EK-BIO) processes at the micro and macroscale (e.g. Wick et al. (2007), Lohner et al. (2009), Wick (2009)), but with greater focus on the interactions between EK-BIO processes and the subsurface environment; (2) mechanisms supporting field application, considering the practical aspects of using EK-BIO in specific cases such as the direct influence of environmental factors on EK (e.g. Page and Page (2002)) with a critical focus on bioremediation; and (3) up-scaling EK-BIO at the field-scale. An analysis of coupled electrokinetic/bioremediation processes and the potential for application of EK-BIO as a sustainable remediation technique is also presented.

2. EK-BIO processes in the subsurface environment

The processes and mechanisms that constitute EK-BIO operate at the micro and the macroscale (Sturman et al., 1995). Micro-scale (<10 mm) processes occur at pore-level and include interactions between contaminants, microorganisms and their surrounding subsurface environment. At the macro-scale (>10 mm) these processes are manipulated for application to plume-scale management and remediation.

2.1. Micro-scale

2.1.1. Substance transport by EK

EK enhances bioremediation by making bioaccessible contaminants, nutrients, electron acceptors (EAs) and electron donors

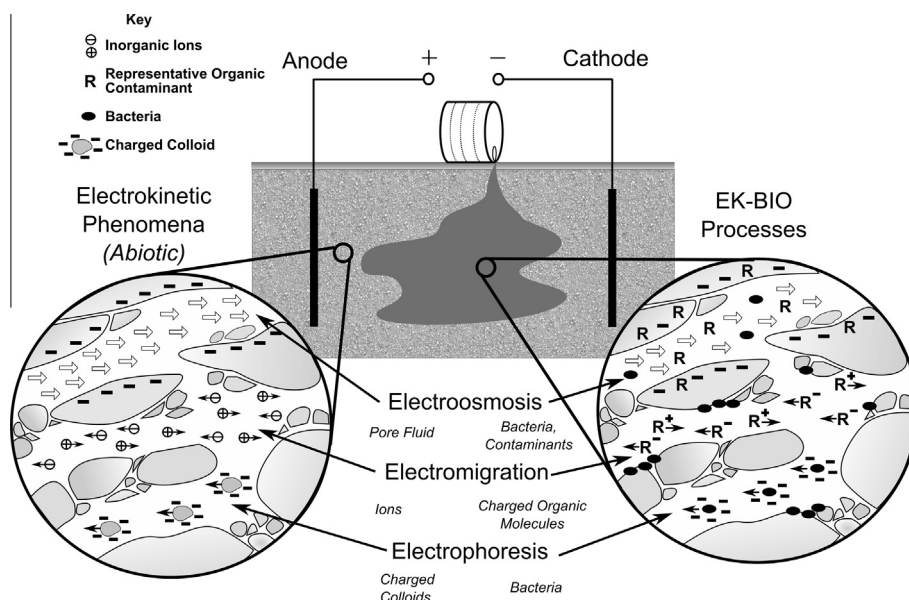


Fig. 1. Conceptual model of electrokinetic processes which can enhance the biodegradation of dissolved-phase organic substances in the saturated zone under an applied direct current, known as EK-BIO. Expanded bubbles detail the abiotic and biotic effects of electrokinetic bioremediation.

(EDs) more bioavailable to catabolically active microorganisms (Wick, 2009). This is achieved by EK phenomena reducing spatial barriers to encourage greater contact between substances and releasing bound contaminants from the porous matrix (Wick et al., 2007). The relative influence of these phenomena depend on the nature of the substances present and their specific properties (Fig. 1), broadly: microorganisms – electroosmosis and electrophoresis dominate (Wick et al., 2004), contaminants – electromigration and electroosmosis dominate (Luo et al., 2005a; Niqui-Arroyo et al., 2006), and ionic nutrients and EAs/EDs – electromigration dominates (Thevanayagam and Rishindran, 1998).

Biodegradation in the subsurface can be controlled by the supply of limiting substances via advection, dispersion and infiltration (Aksu and Bülbül, 1998). Solute advection in low permeability porous media is limited by hydraulic mechanisms but transport velocities can be increased for various substances under an applied EK field (Table 1). In general the electromigration of microorganisms and nutrients/EAs/EDs is fastest in high permeability media, where the pore spaces are larger with less occlusion and reduced tortuosity (Rowe and Badv, 1996). Desorbed hydrophobic contaminants are more mobile in lower permeability clays, where electroosmosis is the primary transport mechanism. In contrast the electromigration of hydrophilic compounds such as phenols is much less than for inorganic single ions due to their high mass to charge ratio (Table 1). The large variation in velocities through different materials for microbes (e.g. clay $0.05\text{--}0.15\text{ cm}^2\text{ V}^{-1}\text{ h}^{-1}$) and hydrophobic contaminants ($0.001\text{--}0.26\text{ cm}^2\text{ V}^{-1}\text{ h}^{-1}$) is due to substance-specific properties. For example, microbe distribution is influenced by cell surface charge and tendency for attachment to sediments (Wick et al., 2004; Da Rocha et al., 2009), whereas increased contaminant transport relates to the water partition coefficient of the specific compound; more soluble compounds have greater mobility under an electric field (Bruell et al., 1992). Differences between the transport rates of single inoculum and mixed consortia can be explained by variation in the velocity of individual populations in consortia. Genetic profiling can be used to distinguish microbes that travel faster from those that adhere preferentially to sediment.

There are two mechanisms developed by EK which enhance contact between substrates when the combined transport rate of

microbes, contaminants, nutrients, EAs and EDs are considered. These are: (1) substances travel in opposite directions, e.g. for negatively charged ions and particles electroosmosis creates a flux counter to that of electromigration or electrophoresis; and (2) migration velocities for substances travelling in the same direction differ, creating longitudinal mixing. The relative importance of different EK processes, and therefore enhancement of solute/microbe migration is determined by the physical properties of the porous media and the dominant transport mechanism. For example, in clays there is an increased likelihood of contact between substances as microbes and contaminants mobilised by electroosmosis migrate in the opposite direction to negatively charged ions moving by electromigration. However, the absence of a significant electroosmotic flux in sands means that contact between substances moving in opposite directions is controlled more by electromigration of negative and positive ions; thus contact in sands occurs primarily by overlapping migration paths.

2.1.2. Contaminant desorption by EK

Electrokinetics can aid the release of organic contaminants bound to clay particles and organic matter in soils and sediments (Maini et al., 2000; Luo et al., 2005a). Shi et al. (2008a) proposed that this is due to disruption of the surface charge that binds molecules to soil particle surfaces by the advective flux resulting from electroosmosis. While studies show that this mechanism does not achieve complete contaminant extraction without facilitating agents (e.g. surfactants) (Saichek and Reddy, 2005), bioavailability and subsequently biodegradation can be enhanced (Niqui-Arroyo et al., 2006). However, it is unclear if electroosmosis-assisted desorption without facilitating agents can effectively enhance biotransformation of contaminants at large scales, due to the heterogeneity that occurs naturally in electroosmotic flow from spatial changes in pH, voltage gradient and electrical conductivity (Eykholt, 1997; Alshawabkeh et al., 2004).

2.1.3. Influence of EK on microbial community viability

Maintaining the viability of an active degrader species (e.g., bacteria, archaea) is important for bioremediation in the natural environment, where microbial populations exist as diverse

Table 1
Migration velocities of substances under an electric field determined in laboratory experiments.

| Substance subjected to transport | | EK transport velocity ($\text{cm}^2 \text{V}^{-1} \text{h}^{-1}$) | | | References |
|----------------------------------|-----------------|---|---------------------|--|--|
| | | Sand | Silt | Clay | |
| Microorganisms | Single inoculum | 0.1 ^[1] , 0.5 ^[2] | – | 0.05 ^[2] , 0.08 ^[1] , 0.15 ^[1] | ^[1] Wick et al., 2004; ^[2] Suni and Romantschuk, 2004 |
| | Mixed consortia | 0.24 ^[3] | 0.99 ^[4] | 0.84 ^[4] | ^[3] Maillacheruvu and Chinchoud, 2011; ^[4] Mena et al., 2012 |
| Organic contaminants | BTX | – | – | 0.16 ^[5] , 0.26 ^[5] , 0.22 ^[5] | ^[5] Bruell et al., 1992 |
| | TCE | – | – | 0.15 ^[5] | ^[5] Bruell et al., 1992 |
| | Hexane | – | – | 0.1 ^[5] | ^[5] Bruell et al., 1992 |
| | Isooctane | – | – | 0.001 ^[5] | ^[5] Bruell et al., 1992 |
| | Phenols | 0.02 ^[6] , 0.04 ^[6] | – | 0.06 ^[6] | ^[6] Luo et al., 2005a |
| Nutrients, EA and ED | Nitrate | 0.57 ^[7] , 0.67 ^[8] | – | 0.94 ^[9] | ^[7] Lohner et al., 2008a; ^[8] Lohner et al., 2008b; ^[9] Thevanayagam and Rishindran, 1998 |
| | Sulphate | 0.67 ^[9] , 0.96 ^[7] | – | 0.42 ^[9] | ^[9] Acar et al., 1997; ^[7] Lohner et al., 2008a |
| | Ammonium | 0.2 ^[7] , 0.36 ^[9] | – | 0.38 ^[9] | ^[9] Acar et al., 1997; ^[7] Lohner et al., 2008a |
| | Lactate | 0.21 ^[10] | – | 0.13 ^[10] , 0.15 ^[11] , 0.17 ^[12] | ^[10] Wu et al., 2007; ^[11] Wu et al., 2012; ^[12] Mao et al., 2012 |

communities (Megharaj et al., 2011) and utilise a network of compound and metabolite exchanges between members to biodegrade contaminants (Abraham et al., 2002). Understanding how they respond to contaminants is necessary to evaluate the suitability of bioremediation for a particular site (Kleinsteuber et al., 2012; Palival et al., 2012).

The application of a low intensity direct current (0.3–1 mA cm⁻²) has no overall effect on the microbial community; localised negative effects result from pH changes close to the electrodes which can cause stress responses such as selection and catabolic pressures (Lear et al., 2004; Wick et al., 2010). These pH changes can alter the properties of some contaminants, for example pentachlorophenol is more lipophilic at pH 2 and may increase the system toxicity close to the anode (Lear et al., 2007). In addition, secondary electrode reactions can generate chlorine (Cl₂) and hydrogen peroxide (H₂O₂) which may inhibit the microbial community adjacent to the electrodes (Thrash and Coates, 2008). Positive effects associated with EK include the generation of oxidising and reducing zones favourable for biodegradation of contaminants close to the electrodes (Kim et al., 2010; Lohner et al., 2011). At the single cell level, low intensity electric field can stimulate ATP production (Shi et al., 2008b; Velasco-Alvarez et al., 2011) and have minimal effect on the cell surface charge (Shi et al., 2008b). At high intensities (>40 mA) the cell surface becomes more hydrophobic and can cause the cell to change shape (Luo et al., 2005b). Hence, for successful bioremediation direct current should be applied at low intensities to maintain the viability of active microorganisms.

A mechanism that may initiate a stress response, which is overlooked in current studies, is the pressure exerted by electromigration where the distributions of trace ions required for growth are disrupted (Pazos et al., 2012). This is particularly relevant in oligotrophic environments, such as groundwater, where the ability to replenish nutrients from the geological matrix is limited over long time periods (Goldscheider et al., 2006). The implication is that measures (such as pH control) may limit the negative effects of EK but stresses on microbes will still occur. Microbes which are more tolerant to these stresses may be more useful in EK-BIO applications (Kim et al., 2010). The impact of various EK-BIO treatments on the viability of the microbial community requires further research to minimise the negative effects of EK and enhance the biodegradation capacity.

2.2. Macro-scale

At the field-scale bioremediation can be applied within a range of techniques (Table 2) (Coulon et al., 2012). Each may be limited by contaminant – microbe – EA/ED contact and mixing, or hydraulic transport issues. EK can be used to develop alternative flow fields to increase contact between microorganisms and contaminants or deliver a required amendment to a specific zone that is limited under ambient conditions. Table 2 summarises the mechanisms by which EK can enhance bioremediation techniques and frames these in the context of field-scale scenarios.

2.2.1. EK-Bioattenuation

Bioattenuation is a low impact and cost effective remediation technique, but is limited to sites where the contaminant is biodegradable and there is adequate mixing of contaminants, electron acceptors and microorganisms for biodegradation to occur at a suitable rate (Thornton and Rivett, 2008). Natural mixing can be enhanced with EK and optimised by increasing the number of electrodes, reversing the electrode polarity, placing electrodes in a radial configuration and rotating the polarity (Luo et al., 2005; Luo et al., 2006; Harbottle et al., 2009; Yuan et al., 2013). This is in order to (1) increase the diversity and connectivity of flow-paths for potential contact and mixing between microorganisms and contaminants (Luo et al., 2006), (2) maintain more uniform pH and moisture conditions (Fan et al., 2007) as well as microorganism distribution (Huang et al., 2013), and (3) increase the area over which the electric field and enhanced biodegradation is effective.

An important control on biodegradation under EK is the voltage gradient that limits the migration rate of substances *in situ*. This gradient can vary spatially and temporally and when highest maximises contact between substances, and therefore enhances biodegradation (Li et al., 2010). However this spatial and temporal variability can lead to uneven biodegradation of contaminants within the matrix (Luo et al., 2006).

Demonstrated and potential applications of EK-bioattenuation include:

- *Ex situ* bioremediation treatment where electrodes are inserted into an excavated soil pile. Studies show EK-bioattenuation is an effective polishing treatment for oil-contaminated soil that

Table 2Potential influence of electrokinetic processes on *in situ* bioremediation (adapted from Boopathy (2000)).

| Bioremediation process and limitations | Electrokinetic influence |
|--|--|
| <i>Bioattenuation</i> – transformation of pollutants by natural means (aka natural attenuation), mixing limited by hydrodynamic dispersion <i>in situ</i> | <i>EK-Bioattenuation</i> – EK transport processes increase bioavailability of contaminants and naturally occurring nutrients and electron acceptors |
| <i>Biostimulation</i> – increased biodegradation by the addition of nutrients and/or oxygen or other electron acceptors to optimise the P:K:N ratio, improve redox conditions and increase bioavailability. Limited by hydraulic delivery and access to low permeability zones | <i>EK-Biostimulation</i> – EK transport processes allow addition and delivery of nutrients, electron acceptors and surfactants into contaminated zones regardless of permeability to increase bioavailability of limiting substances |
| <i>Bioaugmentation</i> – introduction of allochthonous or cultured microbial species adapted to the biodegradation of a particular contaminant. Limited by hydraulic delivery and access to low permeability zones | <i>EK-Bioaugmentation</i> – EK transport of bacterial population to specific zones regardless of permeability where indigenous community is not adapted |
| <i>Phytoremediation</i> – use of plants and or microbes in root zones to effect remediation. Limited by access to contaminants | <i>EK-Phytoremediation</i> – EK transport processes increase the bioavailability of contaminants |

had previously been land-farmed; the benefit of the EK treatment included increased biodegradation of more recalcitrant PAHs (Acuña et al., 2010).

- Groundwater contaminant plumes can persist due to inadequate mixing between contaminants and EA at the plume fringe for effective biodegradation (Thornton et al., 2001a) and a depletion of favourable electron acceptors in the plume core (Huang et al., 2003). EK could be used to increase mixing at the plume fringe with electrodes located transverse to the plume flow path and applying an electric field to drive electromigration of background EAs normal to (and into) a contaminant plume.

2.2.2. EK-Biostimulation

EK can enhance the delivery of nutrients (e.g. phosphate (Lee et al., 2007)), electron acceptors (e.g. nitrate and sulphate (Lohner et al., 2008a) and electron donors (e.g. lactate (Wu et al., 2007)) through different materials at rates greater than diffusion. EK-biostimulation in soils has been demonstrated for PCE (Mao et al., 2012; Wu et al., 2012), toluene (Tiehm et al., 2010), diesel (Pazos et al., 2012) and PAHs (Xu et al., 2010). In addition to chemical amendments the gaseous products of water electrolysis (H_2 and O_2) can be used to stimulate reductive dechlorination of PCE and oxidation of VC, respectively (Lohner and Tiehm, 2009). This process has been demonstrated in a sequential column experiment where contaminated groundwater was first reduced as it passed through the cathode then oxidised in the anode column (Lohner et al., 2011).

Biostimulation can also be achieved through the addition of solubilising agents, to increase the dissolution and bioavailability of hydrophobic contaminants into the aqueous phase (Mulligan, 2005). EK phenomena enhance contact between surfactants and bound contaminants at the micro-scale and can deliver surfactants to polluted zones at the plume-scale (Saichek and Reddy, 2005). These modifications have been demonstrated with synthetic surfactants (Saichek and Reddy, 2003), biosurfactants (Gonzini et al., 2010), co-solvents (Gómez et al., 2009) and cyclodextrin (Ko et al., 2000). Experiments that combine EK-BIO with solubilising agents use surfactants or biosurfactants that are biodegradable (Mulligan, 2005). After addition of solubilising agents an increase in the bioaccessible fraction of the contaminant was reported (Niqui-Arroyo and Ortega-Calvo, 2010), leading to enhanced biodegradation (Gonzini et al., 2010). These studies also showed that variation in EK properties such as field strength and polarity reversals had limited effect on biodegradation over the presence of a surfactant (Gonzini et al., 2010; Niqui-Arroyo and Ortega-Calvo, 2010). However the soil samples contained a uniform distribution of surfactants at the start of the experiment; the implication is that macro-scale delivery of surfactants, either by EK or other means, is required to enhance biodegradation. Karagunduz et al. (2007) achieved the best macro-scale distribution in a soil with low

electroosmotic permeability using anionic surfactants transported by electromigration, alternative surfactants may be more suitable in soils with a higher electroosmotic permeability.

Demonstrated and potential applications of EK-biostimulation include:

- In a contaminated groundwater plume the concentrations of the contaminant and substance limiting biodegradation are inversely proportional to each other (Bauer et al., 2008). EK could be used to migrate the limiting substance into the plume regardless of the subsurface permeability. The concept has been demonstrated at the lab scale by Tiehm et al. (2010), where nitrate was migrated laterally into a toluene plume to stimulate biodegradation.
- Contaminants can diffuse into low permeability matrices rendering them inaccessible and difficult to treat. Once sequestered the contaminant can diffuse back into the host matrix and pose a pollution risk over long timescales (Reynolds and Kueper, 2002), extending the remediation period. EK-biostimulation could add an amendment at a rate greater than diffusion to stimulate bioremediation in these low permeability matrices.

2.2.3. EK-Bioaugmentation

EK can enhance the migration of microorganisms through low permeability soils (Wick et al., 2004; Mao et al., 2012; Mena et al., 2012), despite potential occlusion of cells due to small pore throat size in fine grained materials (DeFlaun and Condee, 1997). This enhancement has been attributed to movement of microorganisms preferentially along a flow path through macro-pores within the soil by electroosmotic flow (Wick et al., 2004). EK-bioaugmentation has been used within sequential treatment of contaminated soil conditioned with an active degrader species. Mao et al. (2012) used EK to firstly distribute lactate, then the dechlorinating strain *Dehalococcoides* for treatment of PCE-contaminated soil. EK-Bioaugmentation can also be effective at redistributing bacteria as a pre-treatment step for soils contaminated with heavy metals (Lee and Kim, 2010).

Microbes maintain their membrane integrity (Shi et al., 2008c) and functionality during transport by EK and effective biodegradation during migration has been observed for both dextrose (Mailacheruvu and Chinchoud, 2011) and diesel (Lee and Lee, 2001). Microbes have a strong tendency to attach to sediment and organic matter particles disrupting transport (Mrozik and Piotrowska-Seget, 2010), but this can be reduced when using EK by adding surfactants (Wick et al., 2004). It is often difficult to maintain the survival of exogenous microbes introduced to a foreign environment (Megharaj et al., 2011). A possible alternative could be the addition of endospores instead of active bacteria. Endospores are more robust and migrate faster under EK than bacteria due to a high associated surface charge (Da Rocha et al., 2009).

2.2.4. EK-Phytoremediation

Phytoremediation of recalcitrant organic contaminants in the shallow subsurface (soil and root zone) requires a symbiotic relationship between the plant and the soil microbial community (Teng et al., 2011). Most EK-phytoremediation studies focus on treatment of heavy metal-polluted soils (Cameselle et al., 2013) where the electric field accumulates contaminants around the plant roots increasing bioavailability (Cang et al., 2011). At present there are no reported studies coupling EK and phytoremediation of organic contaminants, however EK processes have not been shown to significantly hinder the mechanisms by which plants enhance their degradation. For example: (1) under EK the biomass of certain plant species (lettuce and ryegrass) has been increased under AC electric fields demonstrating plant health can be maintained (Bi et al., 2010, 2011), and (2) the respiration and biomass of the microbial community can be enhanced under EK-phytoremediation (Cang et al., 2012). Therefore further research should focus on using EK in combination with phytoremediation to treat organic contaminants.

3. Practical aspects of applying EK-BIO

3.1. Influence of subsurface environmental processes on EK-BIO

EK phenomena and success of EK-BIO treatment depend on environmental variables; therefore tailoring the treatment to the environment in which it is applied is important for managing electrode effects and predicting and sustaining EK phenomena. The principal environmental properties that influence EK-BIO are the electrolyte (i.e. groundwater chemistry or soil moisture) through which the current travels, the geological strata that influence EK phenomena, hydrodynamics that introduce advection as an additional transport vector, physical heterogeneity that can alter transport rates and the mixed nature of contaminants found at many sites.

3.1.1. EK and electrolyte properties

When an electric field is applied to a porous medium (e.g. soil or aquifer) the pore water acts as an electrolyte. The capacity of a system to accommodate an electric field is proportional to the concentration of ions in solution (Alshawabkeh and Acar, 1996). These ions are primarily derived from dissolution of minerals originating in the surrounding geological matrix (Paillat et al., 2001) but also anthropogenic sources. Thus, the soil or rock type imparts ionic characteristics that affect the electrochemical properties of the system (Reddy and Saichek, 2003). Similarly, soil and rock type heterogeneities can be reflected by electrolyte conductance heterogeneities and can lead to zones exhibiting a low voltage gradient that can slow electromigration (Li et al., 2013). At constant voltage, high concentrations of dissolved ions will allow more electric current to be transferred through the system, which in turn increases the rate of electrolysis reactions at the electrodes (Kim and Han, 2003) and increases power consumption (Wu et al., 2012a).

In unsaturated soils the electric current follows a more tortuous path than in saturated soils due to the gas-filled pore space and will travel preferentially through more saturated zones with higher electrical conductivity (Mattson et al., 2002). Electroosmosis can induce pore fluid flux and alter the moisture content, shifting the distribution towards the cathode (Elektorowicz and Boeva, 1996; Luo et al., 2005c; Fan et al., 2007; Harbottle et al., 2009; Ouhadi et al., 2010). This has the effect of increasing the electrical resistance and/or impeding the migration of an amendment by increasing the volume of pore space occupied by pore gas (Mattson et al., 2002; Kim et al., 2012). Moreover, for EK-BIO applications, electro-dewatering by electroosmosis can initiate water stress

and impede the growth and survival of microorganisms (Li et al., 2012). These effects can be mediated by applying EK in rotational or bidirectional modes to better distribute moisture (Luo et al., 2005c; Li et al., 2012).

3.1.2. EK interactions with geological strata

The proportion of fine-grained sediments with net surface charge in a geological matrix determines the extent of electroosmotic flow. Electroosmosis requires a net charge on the surface of sediment and soil grains, hence clays and silts have the highest electroosmotic permeability due to a high surface charge density (Acar et al., 1995). The zeta potential, a measure of that charge, is susceptible to changes in pH and electrolyte conductivity (Vane and Zang, 1997). At neutral pH the zeta potential is often negative and indicates flow towards the cathode, if the pH drops (e.g. below pH 2 for kaolinite (Vane and Zang, 1997)) the zeta potential becomes positive and flow changes towards the anode (Yeung, 2006). Similarly, as electrical conductivity increases the zeta potential is closer to zero and is sensitive to the valence state of ions in solution (Yukselen-Aksoy and Kaya, 2010). The implication for EK-BIO is that electroosmosis presents a counter flux that hinders the migration of negatively charged amendments. Suppressing electroosmotic flow by acidification can have a negative impact on the microbial community, therefore increasing the electrical conductivity of the pore fluid is more effective for EK-BIO applications (Wu et al., 2007).

The pH buffering capacity of a soil is primarily controlled by the carbonate mineral content. Implications for EK-BIO include mediation of the acid front from the anode, which has been shown in soils with 15% carbonate content (Ouhadi et al., 2010). Minimising pH changes at the electrodes can reduce stress responses in microorganisms (Lear et al., 2004). It also ensures a more sustained and uniform electroosmotic permeability by maintaining neutral pH conditions favourable for a negative zeta potential (Eykholt, 1997; Reddy and Saichek, 2003). However, heterogeneous distribution of carbonate minerals in the subsurface could lead to spatial variability in the soil buffering capacity and therefore should not be relied upon to moderate pH changes at electrodes. To a lesser extent cation exchange in a soil can affect pH buffering and is a function of the clay type and organic matter content (Andrews et al., 2005). The presence of more exchange sites in a soil can result in greater sequestration of contaminants (Reddy and Saichek, 2003), potentially reducing the fraction that is bioavailable or bioaccessible.

3.1.3. EK and hydrodynamics

In scenarios where EK is applied in saturated medium to high permeability zones, groundwater flow can significantly affect EK processes by introducing another transport vector. Complimentary applications of EK and hydraulic flow include using a perpendicular electric field to disperse nutrients upstream of contaminated groundwater (Godschalk and Lageman, 2005) or to deliver electron acceptors directly into a mobile contaminant phase (Tiehm et al., 2010). Electromigration against hydraulic gradients is effective at retaining substances close to the electrodes, but this decreases as hydraulic flow rate increases (Eid et al., 1999). An electromigration rate for nitrate of $2.4 \text{ cm}^2 \text{ V}^{-1} \text{ h}^{-1}$ has been achieved under perpendicular hydraulic flow (30 cm h^{-1}) (Tiehm et al., 2010). This is higher than in previous studies ($0.57\text{--}0.67 \text{ cm}^2 \text{ V}^{-1} \text{ h}^{-1}$) of nitrate migration in a static system with deionised water and groundwater at (Lohner et al., 2008a, b). The difference is proposed to result from dilution of the pH changes at the electrodes by the hydraulic flow (Tiehm et al., 2010). In either case the electromigration of nitrate transverse to advective flow is rapid relative to hydrodynamic dispersion and diffusion.

3.1.4. EK and physical heterogeneity

To date the majority of EK literature has focused on treatment of homogeneous material such as uniform clays and sands. Studies where EK is applied to physically heterogeneous systems include movement of charged substances into low permeability zones by electromigration (Reynolds et al., 2008) and where electroosmosis is used to remove organic contaminants (e.g. phenanthrene) from clay (Saichek and Reddy, 2005). In layered systems the migration of substances can be disrupted by electroosmotic flow through low permeability clay layers. This can cause a pressure difference between layers and introduces an alternative transport vector, which may disrupt the flow path of the target substance (Alshawabkeh et al., 2005).

Knowledge of how EK processes develop within physically heterogeneous systems is crucial to field-scale application of the technology. EK-enhanced migration of substances across permeability boundaries is greater than advective-dispersion and diffusion (Reynolds et al., 2008) because they are controlled by different mechanisms. For example, advection across permeability contrasts is controlled by the ambient flow field and diffusion is limited by the solute concentration gradient and diffusion coefficient, whereas electrokinetic migration is determined by the positioning of the electric field which can be orientated independent of the permeability field. However additional factors also apply. EK theory suggests that the velocity of substance migration from high to low permeability falls due to spatial changes in porosity and tortuosity, combined with a higher opposing electroosmotic flux in the low permeability section (Wu et al., 2012a). A spatial variation in ion migration speeds would lead to a redistribution of ions across a permeability boundary leading to an accumulation of ions in the low permeability section based on (1) the slower migration rates; and (2) a drop in the voltage gradient associated with the increased electrical conductivity of the pore fluid.

3.1.5. EK and mixed contaminants

Contamination in the natural environment often occurs as mixtures of organic and inorganic contaminants that may require treatment by different remediation technologies. EK has been applied to remove both simultaneously. However, the removal of organics and heavy metals without facilitating agents can be problematic as both require different conditions for mobilisation, i.e. electromigration of metal ions under acidic conditions and electroosmotic flow of hydrophobic organics under neutral conditions (Maini et al., 2000). Successful removal of mixed contaminants from soils has required the use of cyclodextrin (Maturi and Reddy, 2006) or non-ionic surfactants and EDTA (Colacicco et al., 2010; Alcántara et al., 2012).

Remediating mixed contaminants with EK-BIO is poorly studied but could involve sequential processes in which inorganic contaminants are first removed by EK followed by EK-BIO treatment for the organic contaminants. Heavy metals can inhibit microbial growth, especially as their extraction using EK requires mobilisation into solution thereby increasing their bioavailability (Cang et al., 2007). Studies show that microbial communities remain functional following heavy metal removal by EK (Wang et al., 2009), although the use of facilitating agents such as EDTA can decrease microbial cell number and activity (Kim et al., 2010). It may be possible to enhance community viability by the pH control used to remove heavy metals, for example, using lactic acid as an electrode conditioning solution that reduces pH at the cathode to favour acid conditions for metal extraction, while simultaneously providing microbes with a carbon source (Zhou et al., 2006).

3.2. Design of field-scale EK-BIO

3.2.1. Electrochemical optimisation of amendment addition

EK related electrochemical factors can be modified to enhance the migration and mass flux of an amendment. A linear relationship between the voltage gradient applied and electromigration rate has been demonstrated in homogenous sandy soils (Lohner et al., 2008a; Tiehm et al., 2010). In clay, Wu et al. (2007) demonstrated that a minimum voltage gradient was required to ensure penetration of lactate ($>0.8 \text{ V cm}^{-1}$). This is due to the counter flux from electroosmosis (Wu et al., 2007) and the higher tortuosity of fine grained sediment (Jones, E.H. et al., 2011). pH control at the electrodes can enhance amendment migration and distribution because it prevents the combination of acid and base fronts creates a band of water with a low associated electrical conductivity (Acar et al., 1993). This produces a zone where the amendment migration is increased significantly, resulting in non-uniform distribution of an amendment. It also stops the precipitation of the amendment out of solution, for example, permanganate used for chemical oxidation precipitates below pH 3.5 preventing it from reaching the target location (Hodges et al., 2013).

Ions are often added in mixtures when applied as nutrients (Gonzini et al., 2010; Xu et al., 2010; Pazos et al., 2012). This can reduce the effective ionic mobility and mass flux of an ion relative to a system where it is the only or dominant ion (Alshawabkeh and Acar, 1996). In mixtures, ions are subject to competitive transport due to the need to maintain electrical neutrality in the system (Lohner et al., 2008a). In addition, the chemical form in which the amendment is transported can affect its migration; Lee et al. (2006) compared inorganic phosphate (K_2PO_4) to organic phosphate (triethyl phosphate) and found greater losses of the inorganic form due to reactions with available metal ions.

Mass transport of an amendment can be enhanced by increasing the inlet concentration (Lohner et al., 2008a), but this may result in a disproportionate amount of the amendment being retained within the soil between the inlet and target location (Thevanayagam and Rishindran, 1998). This is due to the increased electrical conductivity of the pore fluid caused by the amendment, which drops the voltage gradient, subsequently reducing the rate of electromigration. Thus the concentration of an amendment at a target location is reduced relative to an increase in the inlet concentration (Wu et al., 2012b). For EK-BIO applications the amendment must be added into the system at a rate which exceeds the microbial capacity in the contaminated zone to ensure an even distribution (Rabbi et al., 2000). Therefore if a biological amendment is to be applied it should be at a concentration that accounts for microbial consumption and the amount retained in the soil mass. Enhancing the concentration at the target locations can be achieved by moving the electrode or the inlet location closer to the target to reduce the distance the amendment needs to travel (Wu et al., 2012b).

3.2.2. Electrode optimisation

The application of EK-BIO determines the electrode material that should be used. For systems where an amendment is added under constant voltage, a material that reduces the voltage drop at the soil–electrode interface is preferable to retain a higher average voltage gradient in the rest of the soil. Mohamedelhassan and Shang (2001) noted the electrode material related to a significant drop in the voltage profile at the soil–electrode interface adjacent to the anode and was highest for materials with a high surface potential (e.g. carbon) relative to steel. Durability is also a factor; metal electrodes corrode more easily especially at low pH (Sun et al., 2007) and should therefore be used with pH control or with an

appropriate surface coating to reduce corrosion. However, electrode coatings that raise the surface potential of the electrode will generate more secondary products from electrochemical reactions, such as: chlorine (Cl_2), hydrogen peroxide (H_2O_2) or high energy free radicals (e.g. O_2^- or $\cdot\text{OH}$), which inhibit microorganisms adjacent to the electrode (Li et al., 2002; Tiehm et al., 2009). This is important in EK-BIO applications where the electrodes are in close proximity to the degrading microorganisms. Hence, metal electrodes may be most suitable for small-scale application whereas metal electrodes engineered to resist corrosion are more suitable for large-scale applications where long distances are involved. Titanium and stainless steel are noted as effective electrode materials at the field-scale because they are reliable with a low associated economic cost (Virkutyte et al., 2002).

3.2.3. Electrode configuration

Electrodes can be installed in different configurations, for example: unidirectional, bidirectional, radial – pairs or radial – bidirectional (Fig. 2). These can be applied to achieve different outcomes. For example, a bidirectional or radial – bidirectional setup is suitable for the migration of amendment evenly and at high concentration (Wu et al., 2013), whereas a radial – pairs configuration is suitable for mixing substances *in situ* (Luo et al., 2006). Additional factors to enhance electrode configuration include:

- Polarity reversals – effective at maintaining uniform pH conditions (Harbottle et al., 2009) and enhancing mixing of substances *in situ* by alternating the migration path (Luo et al., 2006). It is also effective to achieve a more even distribution of amendment in a unidirectional setup (Kim and Han, 2003; Xu et al., 2010). This technique may also be effective at removing the products of electrochemical reactions deposited on the electrode surface, which can reduce the active surface area of the electrode and therefore its efficiency over time.
- Electrode spacing – reducing the distance between electrodes increases the intensity of the electric field over an smaller area and in modelling simulations reduced remediation timeframes by enhancing oxidant distribution (Wu et al., 2013). However, it can lead to increased power consumption and cost through heating (Kim et al., 2012).
- Injection wells – adding an amendment into a well placed within or adjacent to a contaminated zone reduces the migration distance of the amendment compared with adding this via the electrode chamber (Wu et al., 2012a; Wu et al., 2013).
- Absence of metal debris – ensuring the subsurface is free of electrically conductive objects such as metal pipe networks or storage tanks prevents short-circuiting (Mattson et al., 2002).

A by-product of an EK setup in the field is ohmic heating caused by the soil acting as an electrical resistor when an electric current

is passed through it. Increasing soil temperature to ca. 30 °C is beneficial for microbial growth (Killham, 1994). For EK-BIO treatments it is an additional mechanism to enhance bioremediation, and in a field trial Suni et al. (2007) observed a temperature increase from ambient 6 °C to 16–50 °C with 1–1.5 A. However, for EK applications close to the surface, ohmic heating may increase evaporation leading to reduced moisture content and increased electrical resistance (Page and Page, 2002).

3.3. Additional techniques to develop the application of EK-BIO

3.3.1. Permeable reactive barriers

Permeable reactive barriers (PRBs) are an established technology typically used for the *in situ* treatment of groundwater contaminated with organic chemicals and heavy metals (Smith et al., 2003). The engineered treatment zone in PRBs implemented with EK include zero valent iron (Moon et al., 2005), activated carbon (Ma et al., 2010) and atomising slag (Chung and Lee, 2007). The role of EK in this context includes one or more of the following: (1) to migrate the contaminants into the PRB (Li et al., 2011), (2) to generate oxidising and reducing conditions at the anode and cathode, respectively, by electrolysis of water at these electrodes, to enhance the efficiency of zero valent iron PRBs (Moon et al., 2005), or (3) to electrochemically construct a PRB *in situ* using a sacrificial anode that will precipitate out of solution upon reaching the base front from the cathode (Faulkner et al., 2005). Bioremediation has been successfully integrated into PRBs (also known as ‘bio-barriers’). Examples include Teerakun et al. (2011) where a zero valent iron PRB was coupled with an anaerobic and aerobic biobarrier to treat TCE, and Yeh et al. (2010), where the bioavailability of electron acceptors was increased by constructing a barrier of oxygen release compounds to enhance the aerobic biodegradation of BTEX compounds. To date there have been few EK-BIO combinations with PRBs. Fonseca et al. (2012) compared two bio-barriers to treat hexavalent chromium (Cr^{6+}) made from zeolite and activated carbon placed before the anode in the path of the contaminant moving by electromigration and achieved removal rates of 60% and 79%, respectively. Areas for further research include enhancing bio-barriers with EK by the addition of electrodes that could generate a limitless source of electron donors and acceptors (shown in Lohner et al. (2011)).

3.3.2. *In situ* chemical oxidation and reduction

Coupling EK transport mechanisms with the delivery of substances into soils and sediments to oxidise or reduce contaminants has been demonstrated in the literature and includes the use of: permanganate ion to oxidise DNAPLs (Thepsithar and Roberts, 2006; Wu et al., 2012a), Fenton’s reagent where H_2O_2 migrates with electroosmosis and is catalysed by either introduced or native Fe to oxidise PAHs (Kim et al., 2005; Reddy and Chandhuri, 2009),

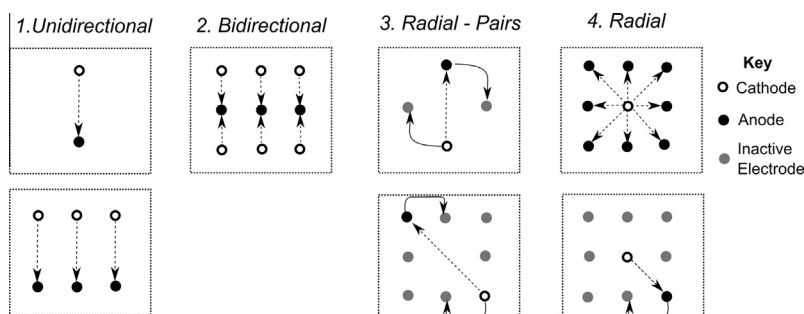


Fig. 2. Illustration of different electrode configurations in the literature (polarity of electrodes is assumed to be reversible), e.g. 1. Unidirectional: Harbottle et al. (2009), Xu et al. (2010), 2. Bidirectional: Alshwabkeh et al. (2005); Li et al. (2010), 3. Radial pairs: Luo et al. (2006), and 4. Radial: Fan et al. (2007); Suni and Romantschuk (2004).

Table 3

Results from the CORONAScreen and EK-BIO treatment model to predict the time to reach steady-state plume length for a BTEX-contaminated groundwater scenario (n/a = not applicable).

| Scenario | Cathode – plume distance (m) | Amendment solution (g L ⁻¹) | | Time until plume ED = EA (days) |
|---|------------------------------|---|-------------------------------|---------------------------------|
| | | NO ₃ ⁻ | SO ₄ ²⁻ | |
| Base case ^a | n/a | n/a | n/a | 241 |
| EK migration of background EAs ^b | 1 | n/a | n/a | 191 |
| | 5 | n/a | n/a | 166 |
| | 10 | n/a | n/a | 140 |
| EK migration of background and amendment EAs ^c | 1 | 1 | 0 | 37 |
| | 1 | 0 | 1 | 32 |
| | 1 | 1 | 1 | 19 |

^a Base case for development of plume with no EK treatment.

^b Enhanced migration of dissolved EA into plume from background groundwater.

^c Enhancement as per ^b with additional input of EAs via amendment at electrodes.

and nanozero valent iron migrated by electrophoresis to reduce chlorinated solvent DNAPLs (C.J.F.P. Jones et al., 2011; E.H. Jones et al., 2011). The sequential treatment of contaminants with chemical oxidants followed by bioremediation is well documented for less biodegradable compounds, as the chemical oxidation step enhances the bioaccessibility of the contaminants to the microbes (Goi et al., 2006; Palmroth et al., 2006). However, chemical oxidants are typically aggressive and negatively impede microbial activity and growth (Palmroth et al., 2006). As a combination, EK-ISCO-BIO could have significant potential to remediate less biodegradable compounds sequestered in low permeability zones, by first adding oxidants then following with EK-BIO methods to replenish and/or rejuvenate the native microbial population and complete the remediation process.

4. Simulating the performance of EK-BIO at field-scale

To explore the potential of EK-BIO applications at the field-scale a spreadsheet model was developed to simulate the effect of EK on the supply of dissolved EA for biodegradation of BTEX in groundwater. This analysis was based on outputs from the electron balance model in CORONAScreen, developed by Thornton et al. (2001b). CORONAScreen predicts the steady-state length of a contaminant plume in groundwater according to the balance of EA and ED flux into the plume from all sources. The EK element introduces an additional flux of dissolved EA, migrating normal to groundwater flow, into the plume. The model simulated electromigration of NO₃⁻ and SO₄²⁻ in the background uncontaminated groundwater into the plume and, separately, migration of NO₃⁻ and SO₄²⁻ amendments added at the electrodes.

The conceptual scenario developed evaluated the potential contribution of EK-BIO to reduce the remediation timescale of a plume in which monitored natural attenuation (MNA) is the management option, but where biodegradation is limited by transverse dispersion of dissolved EA. This is a very common limitation on biodegradation of organic contaminants in plumes (Thornton et al., 2001a, b). The contribution from EK was the enhancement of the dissolved EA flux into the plume by electromigration, for biodegradation. The reference condition is a BTEX plume at steady-state, where the contaminant and EA flux into the plume are balanced. The model assumes the contaminant source has been removed and predicts the time taken until number of EDs in the plume is equalled by the flux of EAs in the absence of EK and by EK mechanisms. This is a suitable descriptor of remediation performance because management costs increase with remediation timescales.

The scenario was created using relevant information for the contaminant source, aquifer properties, groundwater and plume chemistry taken from a BTEX-contaminated aquifer (see [Supporting information](#)). The electrokinetic variables used include: voltage

gradient (100 V m⁻¹), area of the electrode array (equivalent to 10% of the plume section along the flow path (9.4 m²) and a bidirectional electrode configuration where the anode is located in the centre of the plume, with cathodes placed outside the plume (Fig. 2). A bidirectional configuration allows electron acceptors to be introduced into the plume transverse to the flow path. Several set-up parameters were varied to assess the effectiveness of the EK treatment, these were the distance between the cathode and plume and the concentrations of NO₃⁻ and SO₄²⁻ in the amendment solutions.

The results show that the time required to balance the ED and EA budgets within the plume and reach the steady state length is considerably reduced when using EK (Table 3). It implies that the treatment may also be effective in scenarios where MNA is not able to mitigate risk as the only management option, either to increase the natural flux of EAs into a plume for biodegradation or to supplement this with amendments. The benefits for introducing EAs by EK over hydraulic mechanisms in this scenario is EK-enhanced mixing of substances at the micro-scale and independence of EK phenomena to hydraulic conductivity controls.

Treatments where EAs from the background groundwater are migrated into the plume by EK require large distances between the electrode array and the plume to increase the catchment volume for EAs. This supports a higher mass flux of EAs for a longer period, but the treatment is no longer effective once the background EAs are depleted. A considerable reduction in treatment time compared to the base case could be achieved when adding amendment solutions at the electrodes. There is a small difference between the addition of nitrate and sulphate as single ions. This is due to the differences in the ionic mobility of the individual ions (NO₃⁻: 7.4 × 10⁻⁸ m² s⁻¹ V⁻¹ and SO₄²⁻: 8.3 × 10⁻⁸ m² s⁻¹ V⁻¹) (Thevanayagam and Rishindran, 1998).

The array area is expressed as a percentage of the plume area. As such, the treatment can only reach the section of the plume within that area. Therefore, it is important to know the best way to apply the technology in a certain situation. Several options include: (1) a fence of electrodes perpendicular to groundwater flow that supply EAs at a rate equivalent to the plume velocity (Godschalk and Lageman, 2005), (2) treatment of the plume in sections with movement of the electrodes accordingly; and (3) a static electrode array that the plume moves through and treatment is initiated at regular time intervals.

5. Conclusions

EK-BIO is a promising technology for the *in situ* treatment and remediation of many organic and inorganic contaminants in soil and groundwater. It has the potential to effectively enhance bioremediation in physically heterogeneous or low permeability

matrices where alternative technologies may be ineffective. This review has focused on the factors associated with upscaling EK-BIO from the bench-scale to the field-scale. Conclusions drawn from the literature reviewed herein include:

- The mechanisms for EK-induced mixing to enhance bioremediation will vary depending on the host geological matrix.
- Novel field-scale applications of EK-BIO exist including the remediation of plume-scale contaminant scenarios and contaminants sequestered within zones of low permeability.
- When EK is applied in the natural environment, complex physicochemical processes generate non-uniform pH, voltage and moisture gradients that can affect bioremediation performance and need to be considered on a site-specific basis, for example, groundwater flow will influence amendment transport and pH changes at the electrodes.
- Numerous electrode material and configuration options exist to optimise the EK-BIO treatment.
- Simple modelling of a relevant contaminated groundwater conceptual scenario to illustrate the performance of EK-BIO at the field-scale indicates that a considerable reduction in the time for a plume to reach steady-state length can be achieved. Relative to timescales which may typically occur for sites managed using MNA, EK-BIO could reduce overall remediation costs significantly.

Research is needed to investigate how EK-BIO responds to the complexity of typical field-scale applications, these include:

- A better understanding of the effect of natural aquifer settings on EK-BIO processes including groundwater flow and physical, geological and electrolyte heterogeneity.
- The effectiveness of EK-BIO applied to novel contaminants as well as organic and inorganic contaminant mixtures.
- Combinations with other remediation technologies such as PRBs, chemical oxidation/reduction and phytoremediation.
- Electrode configurations and treatment optimisation to accommodate field-scale complexity and affects of EK on microbial communities.

Furthermore, good practice guidelines on EK-BIO implementation at the field-scale could be developed to support the application of well-designed and effective EK-BIO treatment, without unintended adverse effects.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2014.03.019>.

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