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Abstract

Soil and groundwater are key components in the sustainable management of the subsurface environment. Source contamination is one of its main threats and is commonly addressed using established remediation techniques such as in-situ chemical oxidation (ISCO), in-situ chemical reduction (ISCR; most notably using zero-valent iron [ZVI]), enhanced in-situ bioremediation (EISB), phytoremediation, soil-washing, pump-and-treat, soil vapour extraction (SVE), thermal treatment, and excavation and disposal. Decades of field applications have shown that these techniques can

successfully treat or control contaminants in higher permeability subsurface materials such as sands, but achieve only limited success at sites where low permeability soils, such as silts and clays, prevail. Electrokinetics (EK), a soil remediation technique mostly recognized in in-situ treatment of low permeability soils, has, for the last decade, been combined with more conventional techniques and can significantly enhance the performance of several of these remediation technologies, including ISCO, ISCR, EISB and phytoremediation. Herein, we discuss the use of emerging EK techniques in tandem with conventional remediation techniques, to achieve improved remediation performance. Furthermore, we highlight new EK applications that may come to play a role in the sustainable treatment of the contaminated subsurface.

Keywords: electrokinetics, remediation, subsurface contamination, plume migration, phyto-remediation, bioremediation, ISCO, nano zero valent iron (nZVI), landfill

1. Introduction

Soils, sediments and aquifers are fundamental bases for global environmental sustainability and provide essential resources to humans and nature alike (Godfray et al., 2010; Koch et al., 2013; McBratney et al., 2014). Anthropogenic impacts through land-use changes have affected, to differing degrees, the capacity of these geological features to maintain their basic functionality. Nutrient cycling, water retention, provision of physical/chemical stability, storage/filtering/transformation of compounds and sustaining biodiversity are some of the key functions that are an integral part of groundwater and food security (Godfray et al., 2010; Seto et al., 2011; United Nations, 2009). Most fresh water reserves (98-99%) occur in the subsurface; this means that 8-10 million km^3 of freshwater is contained or in direct contact with rock and soil (Margat, 2008; Shah et al., 2007). In an increasingly populated and urbanized world, pollution is widely recognized as a significant challenge to soil and groundwater resources management (FAO, 2003). Efforts to quantify groundwater pollution (Giuliano et al., 1998; Zaporozec, 2002) are scarce and the actual scale of the problem is not well known. Point-source pollution (i.e., the source of many groundwater plumes) is often difficult to accurately locate and address, as depicted in Figure 1. The causes of point-source contamination may be varied: industrial leakage (Gent et al., 2004; Lima et al., 2012a), backfill in construction works (Laethem and Legrand, 1993), or overall urbanized environments (Callender and Rice, 2000; Yongming et al., 2006). Source pollution treatment (A in Figure 1) is key to limiting contaminant transport to the vadose zone environment (Dresel et al., 2011) and subsequent migration to the groundwater zone (B in Figure 1). When present, low permeability lenses (Figure 1), initially act as a sink for contaminants however with time can switch to being a source of long-term contamination.

Contamination in low permeability materials remains a significant and unresolved remediation challenge. A large contaminant source has the potential to generate a significant plume in groundwater, and presents a risk to potential downgradient receptors (A in Figure 1). A unique form of contaminant transport occurs with dense non-aqueous phase liquids (DNAPLs), including chlorinated solvents, polychlorinated biphenyls (PCBs), coal tars etc. since they tend to sink to the bottom of aquifers due to their density (Macdonald et al., 2000). Contaminants in the context of groundwater exposure pathways are varied, and can consist of organic molecular compounds, nano-substances, pharmaceuticals, immiscible liquids, and are often toxic at very low (part per billion) concentrations. New ingenious approaches are needed for in-situ (and ex-situ) remediation of soils, sediments and aquifers, particularly when they are comprised of low permeability materials.

Recent successes in electrokinetic (EK) or EK assisted remediation programs have demonstrated that the technique may be a viable and versatile remediation tool for low permeability soils and sediments. EK approaches generally consist of the application of a direct current (DC) electric field to the subsurface through electrodes to move porewater or migrate contaminants or remediation amendments. EK approaches have wide applicability, from soil dewatering (Lockhart and Stickland, 1984; Yang et al., 2005) to desalination of built environments (Ottosen and Rorig-Dalgaard, 2009), removal of soil metal contaminants (Jensen et al., 2007; Ottosen et al., 1997; Pamukcu et al., 1997; Pamukcu and Wittle, 1992) or degrading/removing soil organic contaminants (Lima et al., 2012a; Lima et al., 2011; Pamukcu, 1994; Reddy et al., 2011; Saichek and Reddy, 2004, 2003), including immiscible oil constituents (Ghazanfari and Pamukcu, 2014; Pamukcu et al., 2016). First used at the beginning of the last century for dewatering and stabilizing clays (Casagrande, 1949; Reuss, 1809), EK was intensively studied in the 1990s for removing metals from soils (Acar and Alshawabkeh, 1993; Lageman, 1993; Ottosen et al., 1997; Ottosen and Hansen, 1992; Schultz, 1997), as well as radionuclides and other inorganic species(Acar et al., 1995). More recently EK has been used in various formulations for the removal of organic contaminants (Lima et al., 2011; Pamukcu, 1994; Ribeiro et al., 2005). The approach has been highly successful at the laboratory scale for both inorganic and organic contaminants and in recent field trials for organic contaminants. Field-scale in-situ applications are becoming more common, and have demonstrated the potential of the approach. In spite of promising early results at a variety of scales, the technology has not yet advanced to a commonly-accepted commercial status.

EK applications in recent years have integrated chemical surfactants, chemical amendments and chelating agents to enhance metals or organics desorption from soil (Bolan et al., 2014; Lima et al., 2012b; Ottosen et al., 2012), or to degrade contaminants at their source. Migration of these chemical enhancers in low permeability soils is possible due to four key phenomena occurring when a direct current is applied to soil: electromigration (movement of charged ions), electro-osmosis (movement of pore water), electrophoresis (movement of colloids) and electrolysis (water splitting) (Acar and Alshawabkeh, 1993). Coupling these phenomena with the aforementioned conventional remediation techniques has been the focus of recent EK research (Cameselle et al., 2013a; Lageman and Godschalk, 2007; Pamukcu et al., 2004). In addition to coupling with existing approaches, EK has been demonstrated to be capable of stripping micropollutants, especially non-polar compounds including heavy oils, from low permeability soils and sediments, where other treatment methods may fail (Alcántara et al., 2012; Ghazanfari et al., 2012; Lima et al., 2012b; Pamukcu, 2009; Pazos et al., 2010). Other EK applications are currently being researched for instance the off-site removal of soil metals (Jensen et al., 2007; Ottosen et al., 2012) and a stand-alone technique for oil transport and recovery from geological media including soils, sediments and rock formations (Chilingar et al., 1968; Ghazanfari et al., 2014; Ghazanfari and Pamukcu, 2014; Ghosh et al., 2012; Pamukcu, 1994; Pamukcu et al., 2016; Wittle et al., 2011).

EK approaches face some unique engineering challenges mainly due to the side effects associated with this technique, such as alteration of natural pH levels near the electrodes, potential enhanced weathering of the porous media during long-term applications, hydrogen and chlorine gas generation at the electrodes and/or other unpredicted redox reactions (Acar and Alshawabkeh, 1993; Ottosen et al., 2000). Some of these side-effects (Acar and Alshawabkeh, 1993) have been engineered to advantage as synergistic effects beneficial for other traditional soil techniques, such as ISCO (USEPA, 2006), EISB (Mao et al., 2012; Niqui-Arroyo and Ortega-Calvo, 2007) and phytoremediation (Aboughalma et al., 2008; Cameselle et al., 2013a; Kubiak et al., 2012). Field scale application of EK-combined remedies has recently been demonstrated at sites in Denmark and the USA (Mao et al., 2012; Riis et al., 2012).

EK has been the topic of a number of review papers, each of which focused on one facet or another of this technique. Yeung (Yeung, 2011) takes a historical approach, Cameselle et al. (Cameselle et al., 2013b) focused on the combination of phytoremediation and EK, Pamukcu (Pamukcu, 2009) on electrochemical treatise, others on specific contamination (Gomes et al., 2015; Saichek and Reddy,

2005). EK is an approach with the capacity of overcoming traditional problems in soil remediation practices. The technique can be applied in-situ in a manner that avoids soil excavation and minimizes the disturbance of soil texture, porosity and biodiversity (Saichek and Reddy, 2005; Virkutyte and Sillanpaa, 2002). Treatment costs are variable depending on the contaminant, approach, and other site-specific factors, but are in line with other intrusive in-situ approaches (Virkutyte and Sillanpaa, 2002). Due to low soil disturbance, low water and energy usage, EK is often less expensive than other remedial techniques (Alshawabkeh and Acar, 1992; Gomes et al., 2015; Higgins et al., 2008; Wittle et al., 2011; Yang et al., 2011). Herein, we discuss the strength of EK as a complement to traditional soil and groundwater remediation techniques and explore future avenues for EK as a sustainable subsurface remediation approach.

2. Conventional soil remediation techniques for source control and their limitations

Commonly practiced technologies for soil and groundwater remediation include permeable reactive barriers (PRBs) (Benner et al., 2002), bioremediation (Guerin, 1999; Tromp et al., 2012), i.e. the use of either plants (phytoremediation) or microorganisms (bioremediation) to degrade, accumulate or reduce/oxidize chemical contaminants, soil-washing (Meuser, 2012), pump-and-treat (Meuser, 2012), in-situ chemical oxidation (ISCO) and in-situ chemical reduction (ISCR), the use of chemicals to oxidize or reduce redox sensitive contaminants in high porosity soils and sediments, vapour-technologies to volatilize organic contaminants, thermal approaches to vapourize organic contaminants and remove them through vacuum extraction, and "dig-and-dump". The majority of these approaches (with the exception of thermal and dig-and-dump) have significant limitations when contaminants to be treated reside in low permeability regions. Table 1 summarizes the main characteristics and main challenges of bioremediation, phytoremediation, nano-particles, ISCO, thermal, and landfilling (dig-and-dump). As mentioned previously, a number of these techniques can be combined with EK to increase their suitability for treatment of contaminants in low permeability regions. A summary of the techniques that can be enhanced using EK, and a brief synthesis of the target contaminants and major limitations is presented in the next sections.

Bioremediation is a cost-effective technique for treating a variety of contaminants, including chlorinated solvents, BTEX, selected inorganic substances (e.g., perchlorate and nitrate) and polycyclic aromatic hydrocarbons (PAHs) (Liebeg and Cutright, 1999; Sturman et al., 1995; Vidali, 2001). Major bioremediation techniques broadly fall into two categories: biostimulation and bioaugmentation. Biostimulation most commonly refers to the addition of nutrients, such as electron

acceptors or electron donors, to promote biodegradation of contaminants by indigenous microbes. Bioaugmentation most commonly refers to the addition of microbes possessing specific capabilities to biodegrade contaminants. A number of factors can hinder bioremediation processes, including limited physical interaction between microorganisms and substances (contaminant bioavailability and/or bioaccessibility) (Semple et al., 2004); adverse site conditions (temperature, high co-contamination(Straube et al., 2003), pH, salts, oxygen, etc.) that may be inhibitory or toxic to microorganisms (Wick et al., 2011); and lastly, absence of bacterial species that can degrade the target contaminant.

Phytoremediation is a low-cost and environmentally acceptable solution for the remediation of shallow soils, soil water and runoff for both metals and organic contaminants e.g., (Chaney et al., 1997; McCutcheon and Schnoor, 2004; Tromp et al., 2012). Phytoremediation is highly suitable for metals contamination as plants are capable of concentrating metals and extracting them from soils (Pilon-Smits, 2005). However, remediation occurs at a shallow soil depth (root zone) and may require extended remediation time. Solutions may include deep planting of trees in boreholes (tree-wells), and the use of polluted groundwater for plant irrigation (Pilon-Smits, 2005).

ISCO for groundwater remediation was first introduced in the 1990s as an aggressive in situ technique to address groundwater contamination without requiring soil excavation (Innocenti et al., 2014; Schnarr et al., 1998; Yukselen-Aksoy and Reddy, 2012). Four oxidants have been commonly used: hydrogen peroxide (Fenton's reagent), ozone, permanganate, and persulfate (USEPA, 2006). Permanganate and persulfate oxidant stability in the subsurface is high, and natural soil oxidant demand for these particular oxidants is potentially low, making ISCO an attractive, cost-effective remediation technique, especially in high hydraulic conductivity material (Ferrarese et al., 2008; O'Mahony et al., 2006; USEPA, 2006). The major limitations of ISCO are related to the hydrogeological conditions: ISCO is more effective in medium to high permeability material, while less effective in low permeability soils (such as clay, loams, glacial tills, hydromorphous soils) as advective transport of oxidants is dramatically decreased (USEPA, 2006). A high content of reduced substances, such as Fe(II), in the soils to be treated may trigger oxidant activation before delivery to the contaminant location (Benner et al., 2002; Petri et al., 2011).

Nano zero valent iron (nZVI) application is a relatively recent remediation technology (Bennett et al., 2010; Elliott and Zhang, 2001; He et al., 2010; Johnson et al., 2013; Kocur et al., 2014) suitable for

198 contaminants that can be treated by chemical reduction. Several laboratory-scale experiments have
199 shown that nZVI can remediate a wide range of contaminants such as nitrate anions (Suzuki et al.,
200 2012; Yang and Lee, 2005), heavy metals (Boparai et al., 2011), pesticides (Satapanajaru et al., 2008;
201 Sayles et al., 1997), PCBs (Wang and Zhang, 1997), chlorinated volatile organic compounds (cVOCs)
202 (Sakulchaicharoen et al., 2010; Song and Carraway, 2005) and radionuclides (Roh et al., 2000). Field-
203 scale studies have used commercially available nZVI (Henn and Waddill, 2006; Krug et al., 2010; Wei
204 et al., 2010) or onsite synthesized nZVI (Bennett et al., 2010; Elliott and Zhang, 2001; He et al., 2010;
205 Kocur et al., 2014; Wei et al., 2010; Zhang, n.d.) that were either unstablized (Elliott and Zhang, 2001;
206 Zhang, n.d.) or polymer coated (0.10%-0.80%, weight/volume) to increase suspension stability
207 (Bennett et al., 2010; He et al., 2010; Henn and Waddill, 2006; Kocur et al., 2014; Wei et al., 2010). A
208 major challenge for nZVI is delivery time: it needs to be delivered to the target treatment zone while
209 reactive and in suspension (e.g. days to a few weeks) (Kocur et al., 2014, 2013; Sakulchaicharoen et
210 al., 2010). As with other chemical in-situ remediation techniques, most successful field studies have
211 been performed in highly permeable soils. Fine grained soils limit nZVI travel distances (Chowdhury
212 et al., 2012).
213
214 ***Landfilling***, often referred to as a "dig-and-dump" approach, is considered one of the least
215 sustainable remediation approaches (EEA, 2009). Excavation and landfill disposal of contaminated
216 soil resolves site problems immediately and can be used widely regardless of pollution type and soil
217 characteristics. From a sustainability standpoint, landfills should be considered a last resort for
218 waste. They are expensive in terms of land (area that is allocated for this purpose, with few examples
219 of rehabilitation post-exploitation); fees for hazardous waste disposal are high (US EPA, 2014); and
220 the environmental cost is also considerable, since leachate emission poses an additional threat to
221 groundwater quality. Additionally, landfills constitute a subsurface legacy, transferring waste and
222 groundwater contamination issues to future generations (Bai and Sutanto, 2002; EEA, 2009).
223
224 The following section examines how EK approaches can be used to enhance bioremediation,
225 phytoremediation, ISCO and nZVI, since these are already tried-out combinations. Particular focus is
226 given to bioremediation enhanced by EK (EK-BIO) which has been demonstrated to be highly
227 effective in field-scale studies, and ex-situ soil remediation for metals.
228
229 **3. EK in combination with conventional techniques: How is EK overcoming limitations?**

An electric field is applied to a porous media, including saturated soil or sediment, that (i) drives ions present in the media towards one of the electrodes – electromigration, (ii) moves pore water when soil porosity and zeta potential is conducive – electro-osmosis, (iii) mobilizes colloids when soil macropores are sufficiently large to enable their passage – electrophoresis, and that (iv) instigates electrolysis, i.e. generation of an acidic front from the anode and alkaline front from the cathode (Acar and Alshawabkeh, 1993; Lageman, 1993; Mitchell, 1993; Ottosen et al., 2000; Pamukcu and Wittle, 1992). Due to the many different phenomena that may occur during the use of an EK approach, EK requires sound engineering to control potential side-effects. Early applications of EK technology did not effectively manage potentially negative processes and hindered early field applications (Alcántara et al., 2012; Gent et al., 2004; Lima et al., 2012b; Reddy and Cameselle, 2009; Simons, 1984). More recent research and field experience has overcome early difficulties. EK approaches are significantly favoured over most other in-situ techniques when it comes to low permeability soils(Cameselle and Reddy, 2012; Ghazanfari et al., 2012; Paillat et al., 2000) due to the increased ability to drive remediation amendments to the contaminants, extract contaminants directly, and its limited impacts on soil structure.

3.1. Sustainability of EK Approaches

Sustainability principals are being increasingly recognized as important considerations in the remedy selection process (Hadley and Ellis, 2009). SURF (Sustainable Remediation Forum) defines sustainable remediation as those practices that reduce global impacts at the same time as minimizing local atmospheric effects, potential impacts on worker and community safety, and/or the consumption of natural and energy resources that might be attributable to remediation activities (Hadley and Ellis, 2009; ITRC (Interstate Technology Regulatory Council), 2011). As presented in Table 1, even the most promising techniques present limitations.

EK inherently uses electrical energy, which can be from fuel sources (Lima et al., 2012a) or from renewable sources (solar, wind) (Zhang et al., 2015). Despite electric energy being at the base of the technique, the sustainability score for EK approaches is high, as the consumption of renewable resources, such as water, is low, use of electricity is small compared to other techniques, it generates minimal waste, and has limited impact on local surface activities. Recent field applications have used a closed water circuit for EK, where only groundwater is used and no external water input is necessary (Mao et al., 2012; Riis et al., 2012).

3.2. EK Enhancement of Traditional Approaches

Bioremediation presents a number of limitations, including the need to control abiotic conditions, mass transfer challenges, bioavailability, bioaugmentation and potentially high operation or long-term re-application costs (Vidali, 2001) (Table 1). EK has been used to surpass some of these challenges, such as control of physico-chemical conditions of soil (Niqui-Arroyo et al., 2006), decrease mass transfer limitations through nutrient transfer and stimulating bioactivity and controlling bacterial population (Mao et al., 2012; Tyagi et al., 2011). Deflaun & Condee (DeFlaun and Condee, 1997) first enhanced migration of bacteria through soil, while Mao et al. (Mao et al., 2012) applied the same principle as a bioaugmentation tool for the remediation of chlorinated solvents. Different EK principles have been used: electro-osmosis or electrophoresis to mobilize bacteria (Figure 2) (DeFlaun and Condee, 1997; Wick et al., 2004) and electromigration to drive nutrients in low porous materials (Gill et al., 2014; Mao et al., 2012). After successful lab trials, the patented EK-BIO has been applied in-situ (Luo et al., 2006) with considerable success (Riis et al., 2012). Some bioremediation drawbacks (primarily challenges with nutrient distribution in low permeability soils) may thus be addressed remarkably with EK, but evidently target contaminants still need to be biodegradable. EK-BIO has been used primarily on the degradation of organic contaminants, but can also be used for biodegradation of nitrates and perchlorate (Mao et al., 2012; Riis et al., 2012).

Phytoremediation has shown positive results for the in-situ remediation of both metals and organics. While promoting the degradation of organic contaminants (Kamath et al., 2004; Pilon-Smits, 2005), plants can assimilate and bioaccumulate metals (Ali et al., 2013; Chaney et al., 1997; Weis and Weis, 2004). An innovative, however as yet to be field-demonstrated EK combination, is EK-phyto (Figure 2) (Aboughalma et al., 2008; Cameselle et al., 2013a). EK can be used to mobilize and redistribute metals in situ, and therefore enhance their transport to the plant roots (Aboughalma et al., 2008). In addition, EK can help stimulate plant growth by mobilizing (micro)nutrients in/to the root zone. Cameselle et al. (Cameselle et al., 2013a) summarized the state-of-the-art regarding the combination of phytoremediation and EK and concluded that laboratory studies yielded the best results with the application of an alternate current (AC) electric field or low direct current (DC) voltage. Therefore, electromigration is used to transfer ions and metals to the root zone while the development of heat (AC electric field) may create ideal assimilation conditions for the plant. Since a low DC field stimulates electroosmosis (Lima et al., 2011), this might explain the improved plant performance under such conditions (Cameselle et al., 2013a).

Nano-ZVI shows potential to treat redox sensitive contaminants (i.e. organic contaminants in general, or redox sensitive metals) but also stable metal ions, such as divalent Cd^{2+} (Boparai et al., 2011). Polymer stabilized nZVI particles have a net negative surface charge (zeta potential of -48 to -56 mV) (Chowdhury et al., 2012; Kocur et al., 2013) and can adsorb positively charged species. EK has the potential to enhance nZVI transport by electrophoresis. Studies have reported the enhancement of nZVI delivery through coarse and medium grained soils (Chowdhury et al., 2012) while others found that electroosmosis can enhance nZVI delivery through clayey soil (Figure 2) (Gomes et al., 2013; Krishna R. Reddy, 2007). These studies suggest that EK has the potential for enhanced nZVI delivery throughout a number of different soil types to enable subsequent contaminant degradation resulting from nZVI oxidation. EK-nZVI laboratory studies have shown great potential, but field trials are needed.

Like the other techniques mentioned in this review, ISCO performance in low permeability or highly heterogeneous soils is often a significant unresolved challenge. Commonly used chemical oxidants (permanganate, persulfate) are negatively charged, and highly mobile through electromigration in low permeability soils (Figure 2) (Alshawabkeh, 2009; Nieto Castillo et al., 2012). Electroosmosis or electromigration may also help mobilize specific contaminants (non-charged hydrophobic organics or metals, respectively) by encouraging desorption or transport to different phases (Isosaari et al., 2007; ITRC, 2001). ISCO is a highly commercialized technology, with many different approaches and patented techniques (Table 1; see e.g. (Virkutyte and Sillanpaa, 2002)). EK-TAP (thermal activated persulfate) (Reynolds, 2015) has recently been developed and is currently undergoing field testing at a number of locations in Europe and the USA (ITRC, 2000; Roach and Reddy, 2006; Siegrist et al., 2001). EK-TAP uses a standard DC electric field to migrate persulfate into the contaminated region and then switches to AC to slightly increase the soil and groundwater temperature in the treatment zone ($<40^0$C) to activate the persulfate.

Remediation of fine grained soils contaminated with metals has historically been performed through landfilling(Reddy, 2010). Landfilling costs are generally higher and less sustainable in the long-term than any in-situ soil remediation (Table 1), in addition to the environmental costs and sustainability considerations addressed elsewhere in this review. When there is no in-situ solution in sight, an alternative to soil landfilling is off-site treatment of soil. This occurs often where brownfields are considered, either for metal (Merkx et al., 2013) or organic pollutants (Gomes et al., 2015; Lima et al., 2012a; Pamukcu, 1994). The electrodialytic remediation (EDR) method has been proposed as a fast

and continuous in-situ or off-site alternative to landfilling for excavated soil. Promising results through the application of EDR for heavy metal polluted harbour sediment (Nystroem et al., 2005) have been obtained by treating a stirred suspension instead of a stationary matrix. The stirred system for EDR was adapted for the soil remediation, and the soil was suspended in water during the remediation (Gomes et al., 2013; Jensen et al., 2007; Lima et al., 2012b; Ottosen et al., 2012; Sun et al., 2012). Advantages of off-site EDR treatment involve (i) transient and nonlinear changes during remediation that are overcome by the continuous mixing; (ii) the removal rate of heavy metals is faster, as stirring enables mixing and desorption; (iii) easy handling for adding chemical desorbing solutions; and (iv) stirred EDR can be combined with soil washing for minimizing the volume to be treated. In this case the clean coarser fraction and the highly polluted fine fraction are separated during the soil washing and only the fine fraction is treated by EDR. Successful removal rates have been obtained for both metals (Jensen et al., 2007; Ottosen et al., 2012; Sun et al., 2012) and organics (Gomes et al., 2013; Lima et al., 2012b).

Besides aiding traditional technologies, EK has been applied as:

- landfill liner enhancement tool, for contaminant confinement (Ouhadi et al., 2010)
- Extraction of nutrients, like phosphorus, from waste materials (Guedes et al., 2014).
- Radionuclides control in soils/clays (Maes et al., 1999)
- EK as enhancement technology for oxidation of emerging contaminants and pesticides (Linley et al., 2014; López-Vizcaíno et al., 2017);
- And remediating soil by stabilizing/precipitating contaminants in a stable iron-rich band (Cundy and Hopkinson, 2010)

Landfill-liner enhancements have undergone developments since its first patent (Wittle and Bell, 2002). Most recent studies aim at combining chemical stabilisers, such as calcium carbonate, to increase landfill liner contaminant adsorption, with an addition of 28% weight mass of carbonates (Ouhadi et al., 2010). Clay liners are normally used in landfilling. Combining EK with clay liners has been the focus of numerous studies, from predicting the behaviour of swelling clays under such hydro-electric conditions (Lima et al., 2010; Moyne and Murad, 2002) to removing radioactive elements in clays (Kim et al., 2003; Maes et al., 1999; Valdovinos et al., 2016). The latter approach focused on radioactive liquid organic waste (Valdovinos et al., 2016), ^{24}Na (15h) and ^{99m}Tc (6h) (with 71.8% and 61% removal rates respectively) (Valdovinos et al., 2016), and Uranium (23% removal rate) (Kim et al., 2003). Alternatively, more technical aspects have been used regarding EK. For

362 instance, electric fields have been used to generate pH and Eh gradients to induce in situ
363 precipitation of a stable iron-rich band (Cundy and Hopkinson, 2010), or to engineering stabilise soil
364 by dewatering/rewatering soils, (Cundy and Hopkinson, 2010).
365
366 **4. Future avenues for environmental EK**
367 In the decades since EK was first applied to soil with the intention of removing pollutants
368 (Alshawabkeh and Acar, 1992; Hansen et al., 1997; Lageman, 1993; Pamukcu, 1994), EK has
369 developed into a viable alternative for remediation of source contamination, particularly when
370 combined with other conventional techniques for application to low permeable soils. EK approaches
371 have numerous strengths, such as minimizing land disturbance when applied in-situ, reduced costs
372 in terms of energy and transportation, and as an auxiliary tool to a number of new applications
373 (section 3).
374
375 Most site remediation initiatives concern point source pollution. However sources of anthropogenic
376 groundwater pollution are numerous and, many times, diffuse. Plume migration concerns a
377 challenging issue regarding pollution dispersion (B in Figure 1). While the Permeable Reactive
378 Barrier (PRB) concept is currently the leading technology to target downstream pollution effects,
379 previous combination of EK with PRB (EK-PRB) has proven advantageous in terms of treatment, PRB
380 material longevity and cost reduction (Ramírez et al., 2015). The idea was tested at bench and field
381 scale in the 1990ies and coined as the Lasagna Technology (Ho et al., 1995; Sa V. Ho et al., 1999a,
382 1999b). A wealth of experimental studies have been conducted in EK-PRB (Chung and Lee, 2007;
383 Huang and Cheng, 2012; Moon et al., 2005; Vieira dos Santos et al., 2017; Weng et al., 2007; Zhou et
384 al., 2016) with a rekindled interest in the last 2-3 years. The older studies showed that standard PRBs,
385 including zero valent iron filing for the treatment of chlorinated hydrocarbons and chromate in
386 aquifer settings, can be significantly enhanced by coupling to EK. Recent studies show original
387 combinations of pollutants and PRB treatment materials. In particular, the development of biological
388 reactive barriers is proposed (Mena et al., 2016; Ramírez et al., 2015). In these studies bacterial
389 cultures of active sludge from an urban WWTP and coarse mineral soil (kaolinite, gravels) are used
390 as biobarriers. Biological growth was observed in the biobarrier, and under the effect of the electric
391 field, bacteria from the biofilm became detached and were transported through the diesel
392 contaminated soil in both directions (Ramírez et al., 2015). Added surfactant was transported across
393 the treatment zone due to electromigration and electroosmosis, which resulted in diesel
394 emulsification. After two weeks of operation, the combination of biological and EK phenomena

resulted in 39% removal of the diesel biodegradable fraction (Ramírez et al., 2015). In fact, EK has proven great applicability in addressing organic contamination, contrary to the attested regarding its first applications for metal contamination. Further studies are expected in addressing LNAPL and DNAPL plumes and exploring solutions for the interface unsaturated-saturated zones (Dresel et al., 2011). There is a need for sustainable solutions to treat these deep locations and EK-PRB can be the answer to these groundwater issues.

EK techniques are based on the fundamental processes of EM, EO and EP. They had been recognised all by the middle of the XXth century (Casagrande, 1949; Reuss, 1809), but, as pointed out by Yeung (Yeung, 2011), research on the understanding of fundamental phenomena is still needed. Variability in osmotic flow rate, the means of transport of electric current through the soil are still not clearly understood. Here we stress that aspects of soil-contaminant interaction can benefit from further understanding when concerning contaminant removal. It has been shown that, under the influence of an electric field, the phenomena that take place at the interface between matrix and pore fluid are very complex and give rise not only to the dominating processes of EM, EO and EP but to subtle effects related to the complex nature of the solid-liquid and liquid-liquid interfaces present in the porous media. Effects such as diffuse double layer compression, electroosmotic drag or electroosmotically induced displacement give rise to refined or new strategies for soil extraction and remediation. Some new developments emerged that brink between laboratory and pilot scale research:

- In-situ manipulation of redox-state via EK for redox sensitive metals (e.g. Cr, As, Cu) (Brosky and Pamukcu, 2013; Pamukcu et al., 2004; Sun et al., 2015)

In a porous water saturated material, particles typically carry a surface charge that is compensated by the Electric Double Layer (EDL). As electric fields are imposed to this material, a faradaic current is induced which is responsible for electromigration of the unbound aqueous species in the pore water. However, because a conductivity difference exists between the outer part of the EDL and the free pore solution, that outer part – the Diffuse Double Layer (DDL) is compressed while the electric field is applied, leading to a potential difference which adds to the redox potential of the system and can contribute to its reactivity. This EK induced DDL phenomenon has been explored in a laboratory study of Cr(VI) reduction in clay. It showed that a 0.6 mA/cm2 applied current was able to increase the reduction rate of the system by a factor of 5 (Sun et al., 2015). While only Cr(VI)/Cr(III) and Cu(II)/Cu(I) redox couples have been studied experimentally up to date (Brosky and Pamukcu,

2013; Pamukcu et al., 2004; Sun et al., 2015)), many redox sensitive elements (uranium, selenium, etc) may be candidates for this treatment method.

- Application of EK in the field of oil extraction and oil transport in water wet porous media (Amba et al., 1964; Chilingar et al., 1968; Ghazanfari et al., 2014, 2012; Ghazanfari and Pamukcu, 2014; Haroun et al., 2013; Pamukcu et al., 2016; Shalabi et al., 2012; Wittle et al., 2011)

Viscous coupling between oil and water phase takes place when an electrical interface, similar to that of clay electric double layer, develops between the two phases, provided that the oil has polarity and possesses some functional groups (i.e., O, N, S compounds, carboxylic acids, amides). Electrokinetic transport of hydrocarbon liquids in water wet porous media is governed by the principles of two-phase flow. As the water phase moves by electro-osmosis through water wet porous media, the neighboring oil phase is also transported, to an extent, depending on the strength of the viscous coupling developed between the two phases. More so, in water wet systems of clay/saline water/oil, the reactions of the electrolysis products of saline water (i.e., hydroxyl ions) with the carboxylic acids of oil result in the formation of surfactants at the water/oil interface. This, in turn, reduces significantly the interfacial tension between oil and water further aiding the oil transport by electroosmosis (Ghazanfari et al., 2012; Pamukcu et al., 2016). Another interesting phenomenon is observed when the water and oil phases are strictly immiscible and viscous coupling does not take place (Pamukcu et al., 2016). Then the electroosmotic flow of the water can pass by the nonconductive liquid ultimately displacing the oil in opposite direction of flow. This liquid separation process is shown to be particularly efficient when pore space it restricted. Also it favors increase of permeability of the porous media.

Laboratory and field applications research show EK as capable of separate and recover oil from water, aqueous sediments and high clay rock formations, advancing EK to be used as a stand-alone or integrative technique for:

- remediation of oil contaminated soils and sediments where spills have occurred (i.e., coastal sediments, coal gasification sites, abandoned oil production or refinery sites);
- change in physical properties can be triggered via electrokinetic methods as the classic soil consolidation (Adamson et al., 1966) with the aid of calcium carbonate producing bacteria (Keykha et al., 2014);
- product extraction, with special interest for mobilization of crude oil in enhanced oil recovery (EOR) processes (Al Shalabi et al., 2012; Amba et al., 1964; Haroun et al., 2013; Shalabi et al.,

2012; Wittle et al., 2011) from formations where other extraction methods (i.e., drilling) may not be feasible or environmentally viable.

As a final remark, we would like to observe that EK is increasingly used in the remediation of emerging contaminants such as pesticides (López-Vizcaíno et al., 2017; Vieira dos Santos et al., 2017), perfluorinated chemicals and radionuclides (control in soils/clays (Maes et al., 1999)). Novel approaches reside in using new catalytic materials (Linley et al., 2014) or as a means for element recycling in waste materials such as phosphorous (Guedes et al., 2014). Because EK acts as a transport tool for dissolved and colloidal particles, as well as solvent through porous media, the possibilities for futures applications are varied and only limited by inventiveness and possibly limited research funds. Therefore, we highlight how EK can act as a versatile and manifold tool for the sustainable treatment of contaminated soil.

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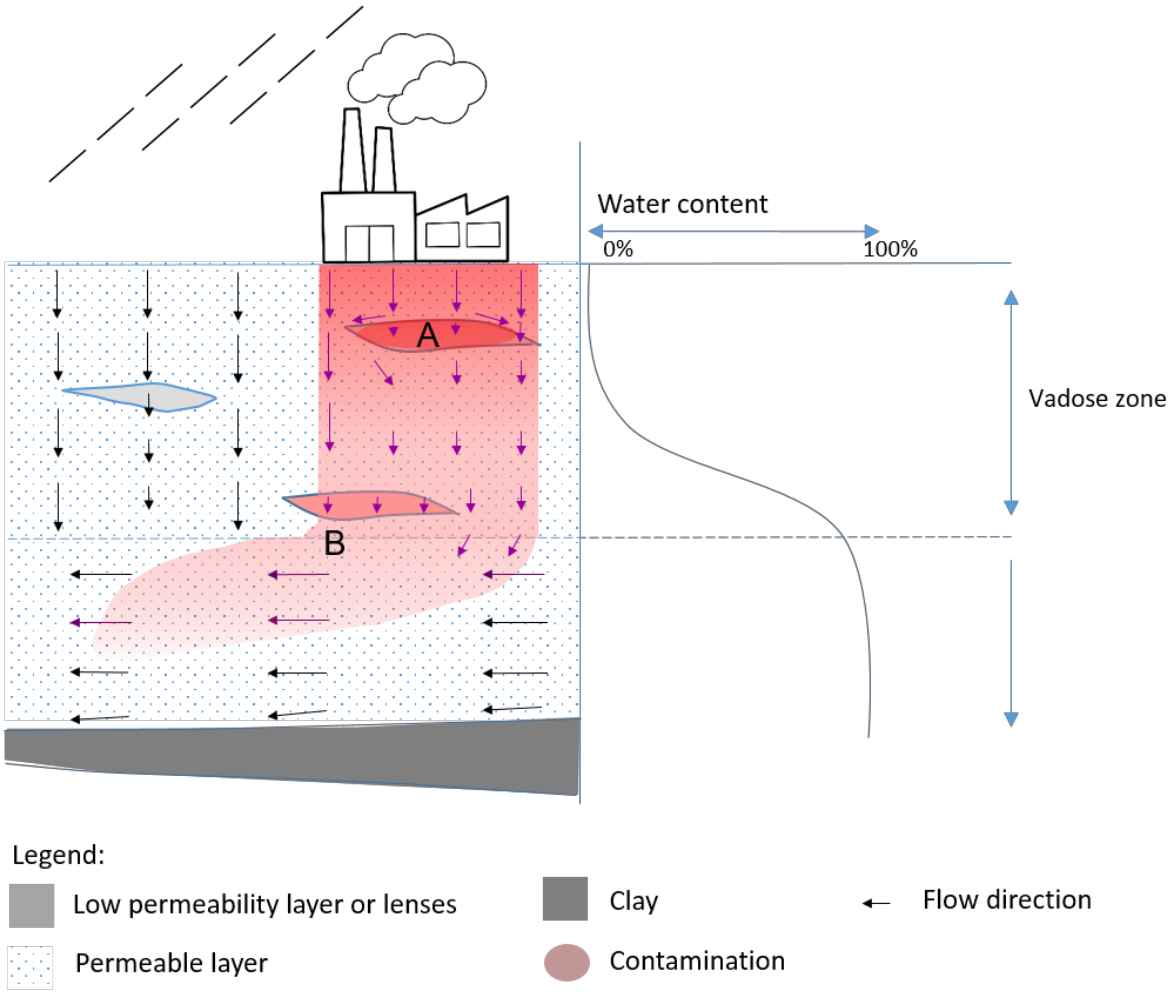

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946 Figure 1 – Schematics of a plume. A – source pollution; B – plume migration

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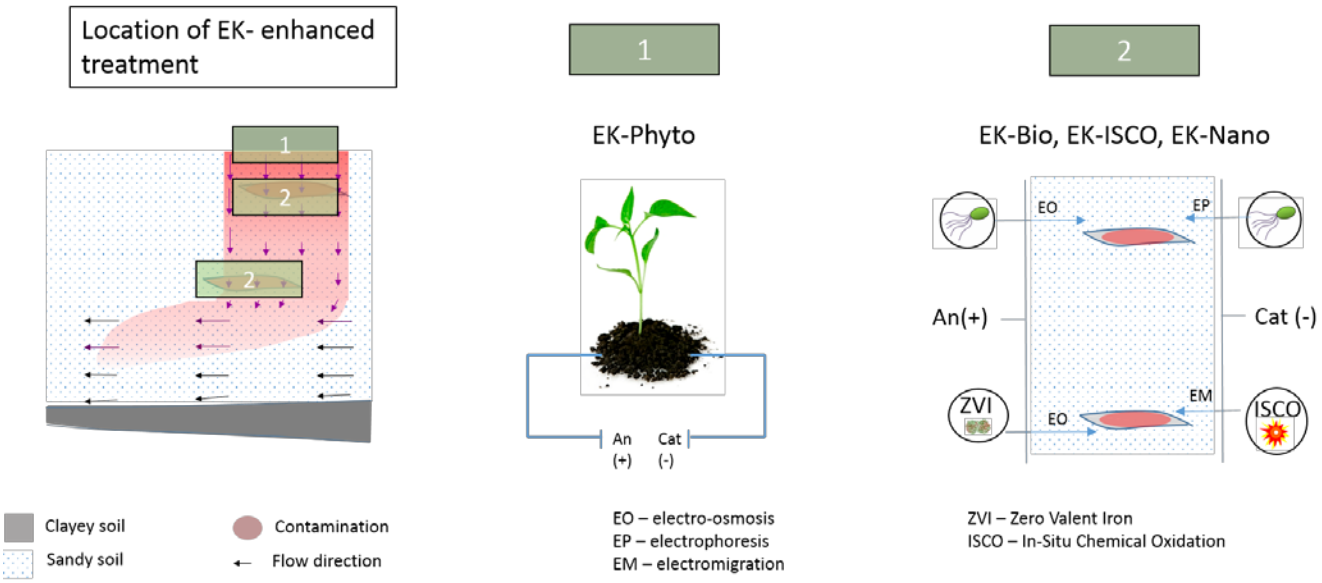

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950 Figure 2 – Schematic representation of electrokinetically enhanced remediation. The left most scheme
951 shows where, within the subsurface or underground, which EK-enhancement would be better suited.
952 Scheme 1 (middle frame) represents the combination of EK with phytoremediation. Scheme 2 (right
953 frame) summarizes how EK would enhance/transport/aid bioremediation, ISCO and nZVI applications.

954

Table 1 – Summary of the main defining characteristics of soil remediation techniques, the main application challenges and how EK can overcome them

	In-Situ Bioremediation	**Phytoremediation**	**Nano-scale Zero Valent Iron (nZVI)**	**ISCO**	**Landfilling**	**Thermal**(Lebrón et al., 2013; McGuire et al., 2016)
Target pollutants	Organic contaminants (chlorinated solvents, BTEX and other aromatic compounds, pesticides); some metals(Vidali, 2001)	Metals, metalloids (Ali et al., 2013) and organic contaminants (Seeger et al., 2013)	Organochlorines, nitroaromatics, dyes, phenols, heavy metals, pesticides, and anions (e.g., NO_3^{-1})	All oxidizable pollutants like organic pollutants (petroleum hydrocarbons, organochlorines, pesticides) and metals(Boparai et al., 2011; Nieto Castillo et al., 2012)	Metals, hazardous contaminants unamenable to in-situ remediation	Volatile organic compounds
Energy requirements	Low; depends on contaminant, bacteria, and technique. Laboratory scale experiments prior to field applications are often required, as well as treatability studies	Low. Plants are placed in-situ and some maintenance is required. Harvesting and replacement of plants	Low to moderate. It requires pumping and delivery of nano-particles to pollutant	Moderate to high; higher than other in-situ (non-thermal) remediation technologies. Electricity application from <0.22 – 44 kWh/ton of ozone activation; 33.33 kWh/m^3 for persulfate activation (USEPA, 2006; Yan et al.)	Moderate to high. Mainly for excavation and transportation	High. The approach requires heating of impacted soil and groundwater to (at a minimum) the boiling point of water)
Water usage	Low to moderate; depends on nutrient requirements	Low to moderate; depends on vegetative cover.	Moderate. ZVI needs to be diluted in water (e.g. 68 m^3 of water with a concentration of 2 g/L of nZVI(US	Moderate. Oxidant needs to be diluted in water (e.g. 8 – 14.5 m^3 of water for persulfate	Low. Landfill leachate needs to be treated, but does not add to water requirements	Low. Water may be used to increase contact with the soil to

			Continued irrigation is required	EPA and USEPA, 2000)). Intensive at the beginning stages	dilution(Yan et al.)). Intensive at the beginning stages		be treated or to cool electrodes.
Maintenance requirements		Low to moderate (nutrient additions); pH, oxygen content, nutrient regulation(Vidali, 2001)	Low to moderate. Maintenance requirements	Low	Low to moderate depending on oxidant choice, soil/site conditions	Moderate; landfill maintenance and leachate management	Moderate.
Duration		Long (can last years); depends on microorganisms, contaminant availability (US EPA and USEPA, 2000), and soil heterogeneity	Long (up to 30 years or more(Kamath et al., 2004))	Short (depends on transport of ZVI to target area). However recent studies suggest that nZVI can stimulate bioremediation (Kocur et al., 2015)	Short to moderate. Variable depending on nature of contaminant (sorbed, free phase, solubility, etc.)	Long. Waste is deposited in landfill, contamination transference	Short. Remediation programs are often on the order of weeks to months.
Disturbance of the subsurface	Mechanical	Low	Low	Low	Low	High	Moderate. Potential for changes to soil structure.
	Biological/ chemical	Moderate	Low	Moderate. Change of geochemical conditions	Moderate. Change of geochemical conditions	High	Moderate. Biological polishing following thermal treatment has been demonstrated as effective
Cost (all values in USD)		Wide range of low to high. From \$30 – 100/m^3 (aerobic degradation field demonstration);	Low. \$15 -25/m^3 (calculated based on the treatment of upper 1 m	High. \$255,000 to \$1,400,000 for 2987 ha (numbers based on a specific site)(Gavaskar et al.,	Moderate. Median cost of \$123/ m^3 based on 33 case studies (Krembs et al., 2010) but can	Low to moderate. Landfill disposal costs between \$250 – 350/m^3 (US EPA, 2014), and with possible total costs	High.

	$323,000 for a specific site of 480 $m^{2,}$ (based on project costs) (US EPA and USEPA, 2000; USEPA and US EPA, 1998)	layer)(McCutcheon and Schnoor, 2004)	2005). Nano-particles cost is $50/kg of nZVI	amount to $527/$m^3$ (Innocenti et al., 2014)	(excavation, transport, disposal, labour) amounting to $650/$m^3$ (personal communication, Geosyntec)	
Main challenge	Limited to biodegradable compounds, where degradation products may be more persistent or toxic than parent compounds. Long remediation times for some compounds (Singh and Ward, 2004)	Long remediation times. Address contaminant mainly at the relatively shallow subsurface (root zone)	nZVI particles need to be delivered to contaminant zone. Limited reactive lifetime of nZVI	Slow mass transfer, transport, and less control over oxidant due to limiting hydrogeological settings (USEPA, 2006). Rapid oxidant reaction rates (esp. H_2O_2, Fe^{2+}, and O_3) where oxidant demand may be high in some soils/aquifers	Contamination transference: environmental issues concerning soil are merely leachate transferred to landfill site	High energy costs and potential difficulties due to surface infrastructure requirements. Not suitable for inorganic contaminants
How EK can help	Electromigration and/or electro-osmosis can deliver nutrients, microorganisms to target zone	Electromigration can bring pollutants to roots for easier phytostabilisation, rhizofiltration or rhizodegradation(Aboughalma et al., 2008; Cameselle et al., 2013a)	Electrophoresis (if sandy soil) and/or electro-osmosis (if clayey soil) can enhance nanoparticle delivery to contaminated regions; faster nanoparticle transport than natural hydraulic conductivity	Oxidant delivery to contaminated regions; faster oxidant delivery than natural hydraulic conductivity	Electro-osmosis can be used to dewater soil/sediment/waste and reduce total residue weight/volume for landfilling; metals or organic contaminants can be extracted ex-situ through the electrodialytic method and avoid landfill all-together (Pernille E. Jensen et al., 2007; Ana T Lima et al., 2012;	Not amenable to improvement through EK approaches

					Nystroem et al., 2005; Ottosen et al., 2012; Sun et al., 2012)	