



Review

A review on techniques to enhance electrochemical remediation of contaminated soils

Albert T. Yeung^{a,*}, Ying-Ying Gu^{b,1}^a Department of Civil Engineering, The University of Hong Kong, Pokfulam Road, Hong Kong^b Department of Environmental Science & Engineering, College of Chemical Engineering, China University of Petroleum (East China), 66 West Changjiang Road, Qingdao 266555, People's Republic of China

ARTICLE INFO

Article history:

Received 20 June 2011

Received in revised form 15 August 2011

Accepted 15 August 2011

Available online 22 August 2011

Keywords:

Electrochemical remediation

Soil remediation

Enhancement techniques

Contaminant solubilization

Soil pH control

Coupling of remediation technologies

ABSTRACT

Electrochemical remediation is a promising remediation technology for soils contaminated with inorganic, organic, and mixed contaminants. A direct-current electric field is imposed on the contaminated soil to extract the contaminants by the combined mechanisms of electroosmosis, electromigration, and/or electrophoresis. The technology is particularly effective in fine-grained soils of low hydraulic conductivity and large specific surface area. However, the effectiveness of the technology may be diminished by sorption of contaminants on soil particle surfaces and various effects induced by the hydrogen ions and hydroxide ions generated at the electrodes. Various enhancement techniques have been developed to tackle these diminishing effects. A comprehensive review of these techniques is given in this paper with a view to providing useful information to researchers and practitioners in this field.

© 2011 Elsevier B.V. All rights reserved.

Contents

| | |
|-------------------------------------------------------|----|
| 1. Introduction | 12 |
| 2. Classification of enhancement techniques | 12 |
| 3. Techniques to solubilize contaminants | 12 |
| 3.1. Lowering of soil pH | 12 |
| 3.2. Introduction of enhancement agents | 13 |
| 3.2.1. Chelants | 13 |
| 3.2.2. Complexing agents | 14 |
| 3.2.3. Surfactants and cosolvents | 14 |
| 3.2.4. Oxidizing/reducing agents | 15 |
| 3.2.5. Cation solutions | 15 |
| 4. Soil pH control | 16 |
| 4.1. Electrode conditioning | 16 |
| 4.2. Use of ion exchange membrane | 18 |
| 5. Coupling with other remediation technologies | 18 |
| 5.1. Oxidation/reduction | 18 |
| 5.2. Bioremediation | 20 |
| 5.3. Permeable reactive barriers | 21 |
| 5.3.1. Lasagna process | 21 |
| 5.3.2. Zero-valent iron (ZVI) PRB | 22 |
| 5.3.3. PRBs of different reactive media | 23 |

* Corresponding author. Tel.: +852 28598018; fax: +852 25595337.

E-mail addresses: yeungat@hku.hk (A.T. Yeung), guyong99hg@yahoo.com.cn (Y.-Y. Gu).¹ Tel.: +86 532 86984668; fax: +86 532 86984668.

| | |
|-------------------------------------------|----|
| 5.3.4. PRB – summary | 24 |
| 5.4. Phytoremediation | 24 |
| 5.5. Ultrasonication | 25 |
| 5.6. Other remediation technologies | 25 |
| 6. Conclusions | 26 |
| Acknowledgements | 26 |
| References | 26 |

1. Introduction

Electrochemical remediation is a promising technology to remediate fine-grained soils contaminated by inorganic, organic, and mixed contaminants. A direct-current (dc) electric field is imposed on the contaminated soil. The contaminants are migrated by the combined mechanisms of electroosmosis, electromigration, and/or electrophoresis. Detailed description of these fundamental electrokinetic phenomena in soil is given by Yeung [1] and Yeung and Gu [2]. As a dc electric field is a much more effective force in driving fluid through fine-grained soils than a hydraulic gradient [3], electrochemical remediation is particularly applicable to fine-grained soils of low hydraulic conductivity and large specific area. Milestone developments and future research directions of the technology are given in Yeung [4]. However, as the soil-chemical fluid system is an electrochemical system [5], many electrochemical reactions are occurring simultaneously during electrochemical remediation of contaminated soil [6]. Moreover, the large specific area of the fine-grained soil provides numerous sites for soil-contaminant interactions. These interactions are soil specific, contaminant specific, dynamic, reversible, and pH-dependent. The coupling of electrochemical reactions with the soil-contaminant interactions makes the electrochemical remediation process extremely complex.

Similar to most remediation technologies, electrochemical remediation can only extract mobile contaminants from soil [7,8]. Contaminants can exist as sorbed species on soil particle surfaces, sorbed species on colloidal particulates suspended in soil pore fluid, dissolved species in soil pore fluid, or solid species as precipitates. Only contaminants exist as dissolved species in the soil pore fluid or sorbed species on colloidal particulates suspended in soil pore fluid can be extracted by most remediation technologies, and electrochemical remediation is no exception [7]. Therefore, enhancement techniques are developed to solubilize contaminants in soil and to keep them in a mobile chemical state.

Electrolytic decomposition of electrolytes occurs at the electrodes, generating H^+ ions at the anode (the positive electrode) and OH^- ions at the cathode (the negative electrode). These ions are migrated into the contaminated soil, resulting in changes in soil pH as a function of time and space. The change in soil pH can change the chemical states of contaminants, rendering them immobile. It can also change the magnitude and direction of electroosmotic flow, affecting the advective transport of contaminants in soil pore fluid by electroosmosis. Moreover, these ions can polarize the electrodes and reduce the effectiveness of the dc electric field imposed. Therefore, controlling soil pH is very important for the success of electrochemical remediation.

In many cases, application of electrochemical remediation alone is not adequate to remediate the contaminated soil to the required acceptance level. Therefore, the technology is enhanced by coupling with other remediation technologies as part of a remediation train of processes. The synergy can achieve results that are better than the sum of technologies applied individually.

Many techniques to enhance the extraction efficiency of electrochemical remediation of contaminated soil have been developed throughout the years. A comprehensive review of these techniques

is given in this paper to facilitate effective applications of these enhancement techniques by researchers and practitioners in the field of electrochemical remediation of contaminated fine-grained materials such as clay, sediment, and sludge.

2. Classification of enhancement techniques

The primary objectives of these enhancement techniques are: (1) to solubilize contaminants in soil and to keep them in mobile states; (2) to control the soil pH within a range of values favoring the application of electrochemical remediation; and (3) to destruct, breakdown, or transform the contaminants simultaneously or sequentially. Therefore, the enhancement techniques are broadly classified into three groups: (1) techniques that solubilize contaminants and keep them in mobile states; (2) techniques that control soil pH; and (3) remediation techniques that can be coupled with electrochemical remediation synergistically to destruct, breakdown, or transform the contaminants simultaneously or sequentially. However, these three groups of techniques are inter-related. Detailed classification of these techniques is presented in Fig. 1.

3. Techniques to solubilize contaminants

Contaminants in soil can be sorbed on soil particle surfaces or exist as precipitates in soil pores under certain environmental conditions, rendering them immobile. These contaminants may go into dissolved phases again when the environmental conditions change. Therefore, the temporary immobility of contaminants cannot be considered as permanent containment. However, it does create a difficult hurdle for the remediation process. Enhancement techniques have been developed to solubilize contaminants during electrochemical remediation including: (1) lowering of soil pH; and (2) introduction of enhancement agents.

3.1. Lowering of soil pH

Most metals can be solubilized in a low pH environment. During the electrochemical remediation process, H^+ ions are generated at the anode and migrated towards the cathode, an acid front is thus developed. A low pH environment can be generated in soil of low acid/base buffer capacity and extraction of metals can be achieved with a reasonable degree of success.

For natural soils of high acid/base buffer capacity, strong acids and weak acids have been used as enhancement agents to neutralize the OH^- ions generated at the cathode and to lower of the soil pH. Weak acids, such as acetic acid CH_3COOH and citric acid, can also serve as a complexing agent and a chelant, respectively. Strong acids are observed to be more effective than weak acids in many studies.

However, it should be noted that when the soil pH is lower than the point of zero charge (PZC) [9], the direction of electroosmotic flow is reversed, i.e., from the cathode towards the anode. The advective transport of contaminant by electroosmosis would diminish the electromigration of cations towards the cathode. Moreover, a very low pH environment developed during the

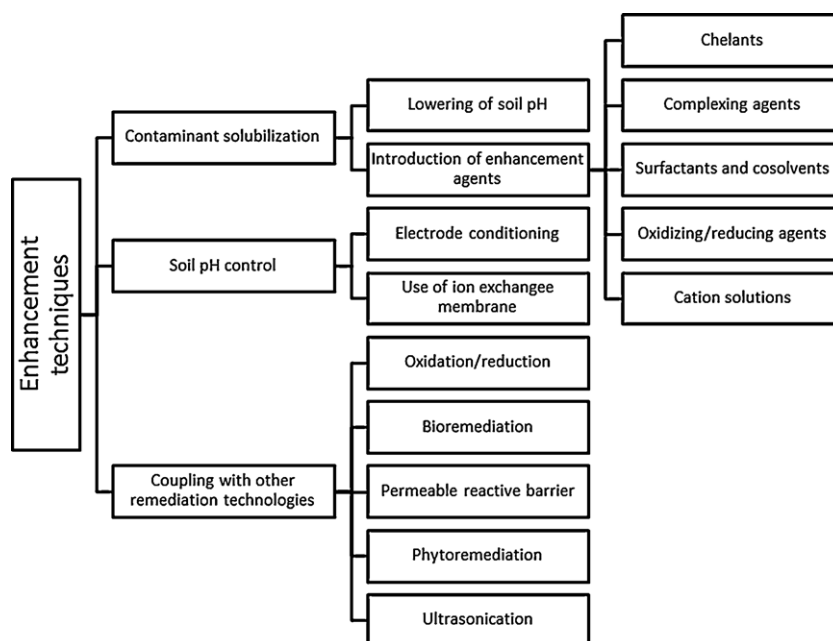


Fig. 1. Classification of enhancement techniques for electrochemical remediation.

remediation process may impact the environment adversely and render the remediated soil not readily arable afterwards.

More details on lowering of soil pH are presented in Section 4 later in this review paper.

3.2. Introduction of enhancement agents

When the acid/base buffer capacity of soil is high, i.e., the resistance of soil to pH change is high, it is very difficult to lower the soil pH by the H^+ ions generated by electrolysis or introduction of acid to the soil. Therefore, other enhancement agents have to be utilized to desorb contaminants sorbed on soil particle surfaces and to keep them in the dissolved phase. These enhancement agents include: (1) chelants or chelating agents; (2) complexing agents; (3) surfactants and cosolvents; (4) oxidizing/reducing agents; and (5) cation solutions.

3.2.1. Chelants

Chelation is the formation or presence of two or more separate bonds between a bi-dentate or multi-dentate ligand, i.e., the chelant, and a single metal central atom or ion. Chelants can thus desorb toxic metals from soil particle surfaces by forming strong water-soluble complexes which can be removed by the chelant-enhanced electrochemical remediation. An example on how ethylenediamine-*N,N'*-disuccinic acid (EDDS), a biodegradable chelant, solubilizes sorbed Pb from soil particle surfaces is illustrated in Fig. 2 [10]. The chelant-enhanced electrochemical remediation is thus a four-step process: (1) injection of the chelant into the contaminated soil by electroosmosis and/or electromigration; (2) formation of soluble Pb–EDDS complex on soil particle surfaces; (3) dislodgement of Pb–EDDS complex from soil particle surfaces to soil pore fluid; and (4) extraction of Pb as Pb–EDDS complex by electroosmosis and/or electromigration.

Chelants, such as carboxylates, organophosphonates, polyamines, and industrial wastewaters [11], have been used or investigated as enhancement agents in electrochemical remediation. Among all the chelating agents, aminopolycarboxylates, such as ethylenediaminetetraacetic acid (EDTA) and (diethylenetriamine)pentaacetic acid (DTPA), and hydroxycarboxylates, such as citric acid, have been most frequently used in electrochemical

remediation. A detailed review of use of chelants in electrochemical remediation is given by Yeung and Gu [2], and will not be repeated in this review paper.

In addition to solubilizing sorbed contaminants from soil particle surfaces, chelants also change the zeta potential of soil particle surfaces. In general, chelants lower (becomes more negative) the zeta potential of soil particle surfaces [12]. The lowering of the zeta potential of soil particle surfaces increases the positive electroosmotic volume flow rate of soil pore fluid, i.e., from the anode towards the cathode, facilitating the advective transport of contaminants by electroosmosis towards the cathode.

Post-remediation of treatment and disposal of the used extraction fluid is a problem as it is rich in metal-chelant complexes.

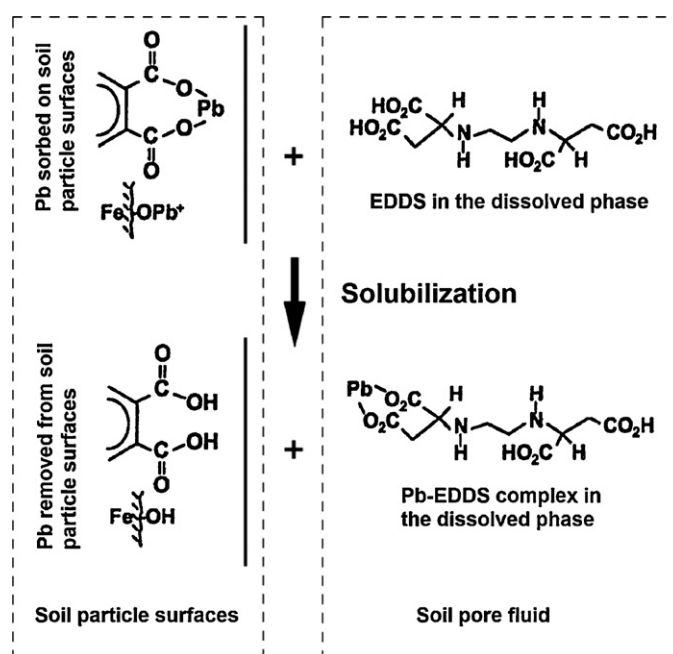


Fig. 2. Solubilization of sorbed Pb from soil particle surfaces by EDDS.

Some chelants, such as EDTA, are toxic, especially in their free forms [13,14], and are poorly photo-, chemo-, or biodegradable in the environment [15]. Different methods to handle used extraction fluids are presented by Lestan et al. [16]. The methods currently available to recover chelants from used extraction fluids still encounter operational difficulties and they work well only for a few contaminants and soil types [2,16]. The development of more robust recycling methods for used chelants would greatly increase the economic value of chelant-enhanced electrochemical remediation.

3.2.2. Complexing agents

Complexing agents are chemicals which form coordination complexes with metal ions. Coordination complexes differ from chelate complexes by the formation of only a single bond between the metal central atom or ion and the complexing agent.

Some complexing agents, such as I^- , Cl^- , NH_3^- , and OH^- , are introduced into soil as conditioning acids or bases during electrochemical remediation process. These ligands can form soluble complexes with metals such as $[HgI_4]^{2-}$, $[CuCl_2]^-$, $[CuCl_4]^{2-}$, $[Cu(NH_3)_4]^{2+}$, $[Zn(OH)_4]^{2-}$, $[Cr(OH)_4]^-$, and $[Cr(OH)_3]^{2-}$. It has been demonstrated by many researchers [17–20] that mercury could be efficiently extracted by iodide-enhanced electrochemical remediation as soluble complex HgI_4^{2-} . Sulfate reducing bacteria were shown to be a viable tool for treatment of the acidic and oxidative Hg-contaminated iodide waste solution resulting from the enhanced electrochemical remediation [21].

Acetic acid, CH_3COOH , is a complexing agent frequently utilized to enhance electrochemical remediation [22–24]. Although it is not as effective as strong acid such as HNO_3 , it is preferred in soil remediation. It can neutralize the electrolysis product at the cathode to reduce energy consumption, and keep the electrolyte pH within a certain range by its acid/base buffer capacity. Moreover, it is relatively cheap, biodegradable, and environmentally safe. Similarly, lactic acid was used to enhance electrochemical remediation of Cu-contaminated soil [25].

Cyclodextrins are nontoxic, biodegradable, and have low affinity of sorption onto the soil particle surfaces in a wide pH range [26]. Moreover, they have the ability to form inclusion complexes with many substrates in aqueous solutions. Hydroxypropyl- β -cyclodextrin, carboxymethyl- β -cyclodextrin, β -cyclodextrin, and methyl- β -cyclodextrin have been utilized to enhance electrochemical remediation of soils and sediments contaminated with organic compounds and heavy metals [26–32], with varying degrees of success.

Ammonium acetate, CH_3COONH_4 , was used as anolyte by Chen et al. [33] in their bench-scale experiments on electrokinetic removal of Cu from soil using a constant electrical current density of $1.33 A/m^2$. Their results reveal that a concentration of CH_3COONH_4 of higher than 0.1 M was needed to sustain the electroosmotic flow. The apparent electrical conductivity of the specimen was controlled by the 10-mm thick layer of soil close to the cathode. The high pH condition in the vicinity of the cathode favors copper-ammonia complex reactions, thus increasing the solubility and removal rate of Cu during electrochemical remediation. The extraction efficiency of Cu increased with the concentration of CH_3COONH_4 used. When 0.5 M CH_3COONH_4 was used, the proportion of soil containing Cu was less than 10% after treatment.

3.2.3. Surfactants and cosolvents

Cationic, anionic, or non-ionic surfactants are amphiphilic compounds containing both hydrophilic groups (heads) and hydrophobic groups (tails). There are both synthetic and natural surfactants. Natural surfactants are also known as biosurfactants, as they are biologically produced from yeast or bacteria from various substrates including sugars, oils, alkanes, and wastes [34].

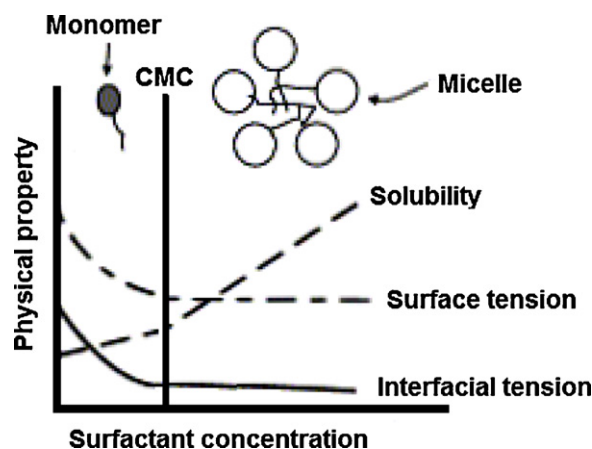


Fig. 3. Variation of surface tension, interfacial tension, and contaminant solubility with surfactant concentration (after Mulligan et al. [35]).

Surfactants can lower the surface tension of a liquid to allow easier spreading, and the interfacial tension between two liquids, or between a liquid and a solid. Therefore, they may act as adhesives, flocculating agents, wetting agents, foaming agents, detergents, de-emulsifiers, penetrants, and dispersants. Typical desirable functions of surfactants include solubility enhancement, surface tension reduction, critical micelle concentration, wetting ability, and foaming capacity [35]. Surfactant monomers form spheroid or lamellar structures with organic pseudo-phase interiors, which lowers surface or interfacial tensions. The minimum concentration at which any added surfactant molecules appear with high probability as micellar aggregates is called the critical micelle concentration (CMC) [36]. The variation of surface tension, interfacial tension, and contaminant solubility with surfactant concentration is schematically shown in Fig. 3.

Both synthetic surfactant and natural surfactants can be used as additives in the phase separation processes for remediation of organic compound-contaminated soils by enhancing the aqueous solubility and mobility of organic contaminants [35,37–40]. Moreover, surfactants have been observed by many researchers to be feasible in enhancing heavy metal extraction from soil and sludge [41].

Several factors can adversely affect the efficiency of soil flushing using surfactants including: (1) hardness of groundwater; (2) sorption of surfactants onto clay particle surfaces; (3) inactivation of surfactants due to rapid biodegradation; and (4) difficulties in recovering the surfactant from used flushing solution [42]. Therefore, factors that need to be considered in the selection of surfactants in electrochemical remediation include: (1) efficiency and effectiveness of the surfactant in remediating the contamination; (2) biodegradability of the surfactant and degradation products; (3) toxicity of the surfactant and its degradation products to humans, animals, plants, and the ecology; (4) ability to be recovered, recycled, and reused; (5) public perception and regulatory restrictions; (6) functionality of the surfactant at different pHs; (7) electrical charges, if any, carried by the surfactant; and (8) cost.

Overall, desirable surfactant characteristics for soil remediation include biodegradability, low toxicity, solubility at groundwater temperatures, low sorption onto soil particles, effective at concentrations lower than 3%, low soil dispersion, low surface tensions, and low CMC. Anionic and non-ionic surfactants are less likely to be sorbed onto soil particle surfaces but anionic surfactants may precipitate. However, co-injection of an anionic surfactant with a non-ionic surfactant can reduce precipitation and also CMC values [43].

Biosurfactants or natural surfactants are known for their biodegradability, reduced toxicity, and environmental-friendliness [44], and they may be less expensive in some cases [45]. Moreover, their efficiency is often higher than those of synthetic surfactants, i.e., a similar surface tension reduction can be achieved by introduction of a smaller quantity of biosurfactant [46]. They are proven to be more tolerant to extreme variations in temperature, ionic strength, and pH [47–49]. Moreover, they may potentially be produced *in situ* using the organic contaminants as substrates for their production. Biosurfactants are essentially classified either as low- or high-molecular-mass. High-molecular-mass biosurfactants consist of particulate and polymeric amphiphiles. Low molecular-mass biosurfactants can broadly be classified into three groups: (1) glycolipids or lipopolysaccharides, such as rhamnolipids, trehalolipids [50], and sophorolipids [51,52]; (2) lipoproteins–lipopeptides, such as acyclic [53], and cyclic ones (cyclolipopeptides) [54,55]; and (3) hydroxylated cross-linked fatty acids (mycolic acids) or phospholipids [46].

Both synthetic surfactant and natural surfactants have been reported to be efficient in mobilizing organic contaminants during electrochemical remediation of soil contaminated by organic compounds. The feasibility of using synthetic surfactants such as alkyl polyglucoside (APG), sodium dodecyl sulfate (SDS), sodium dodecylbenzenesulfonate (SDBS), Pannox 110, Brij 30, Triton X-100, Griton ALM 100, Calfax 16L-35, Igepal CA-720, Tergitol 15-S-7, Tergitol NP-10, and Tween 80 have been studied by many researchers to enhance electrochemical remediation of soils contaminated by petroleum hydrocarbons [56], polycyclic aromatic hydrocarbons (PAHs) [27,57–64], 1,2-dichlorobenzene (1,2-DCB) [65], hexachlorobenzene (HCB) [29,63], dichlorodiphenyltrichloroethane (DDT) [66], ethylbenzene [67], chlorobenzene [68], trichloroethylene (TCE) [68], and diesel oil [69,70]. The viability of these synthetic surfactants in enhancing electrochemical remediation of soils contaminated by various organic compounds has been established.

However, few studies have been carried out on the use of natural surfactants to enhance electrochemical remediation. Nonetheless, rhamnolipid is the most frequently used biosurfactant as an enhancement agent for electrochemical remediation of soils contaminated by organic contaminants. Chang et al. [61] compared the performance of rhamnolipid with Triton X-100, a synthetic surfactant, in enhancing the extraction of phenanthrene from unsaturated soils by electrochemical remediation. Their results indicate that rhamnolipid was more efficient in removing phenanthrene from soil than Triton X-100. Moreover, the electroosmotic flow rate in the rhamnolipid system was higher than that in Triton X-100. In addition to the higher electroosmotic flow rate, the higher remediation efficiency may also be attributed to the promotion of microbial growth in the soil–water system in the presence of rhamnolipid. Gonzini et al. [71] also studied the effects of rhamnolipid on enhancing electrochemical remediation of a gasoil-contaminated soil. Their results indicate that the remediation efficiency of gasoil could be increased up to 86.7% by increasing the dose of rhamnolipid. Moreover, the lower concentration of the gasoil in the liquid phase at the higher concentration of the biosurfactant demonstrated evidently that rhamnolipid could enhance gasoil biodegradation, possibly through two mechanisms: (1) increasing the aqueous solubility of hydrocarbons and thus their bioavailability to microorganisms; and (2) interacting with microorganisms to make their cell surfaces more hydrophobic and thus easier to associate with hydrophobic substrates. They also identified the need for future development on surfactant production by autochthonous microorganisms, so as to reduce the surfactant cost for field application of the technology.

Groboillot et al. [72] studied the feasibility of using amphisin, a biosurfactant, to enhance electrochemical remediation of dredged

harbor sediments contaminated by PAHs. Their results indicate pure amphisin from *Pseudomonas fluorescens* DSS73 was more effective in solubilizing and mobilizing PAHs strongly sorbed to sediments than a synthetic anionic surfactant. Amphisin production by bacteria in natural environment was also considered. Although the growth of *P. fluorescens* DSS73 was weakened by the three model PAHs above saturation, amphisin was still produced.

Kaya and Yukselen [73] studied the effects of anionic, cationic, and non-ionic surfactants on the zeta potential of soil particle surfaces of kaolinite, montmorillonite, and quartz powder in the presence of Li^+ , Ca^{2+} , Cu^{2+} , Pb^{2+} , and Al^{3+} . Understanding the variations of zeta potential of soil particle surfaces with the introduction of surfactants is important because the zeta potential controls the direction and rate of electroosmotic flow which impact the contaminant extraction efficiency of electrochemical remediation [1,2]. Their results indicate that the presence of cationic surfactant significantly increases (becomes less negative) the zeta potential of soil particle surfaces in an acidic environment (pH ~4). The presence of the anionic surfactant makes the zeta potential of soil particle surfaces more negative. However, the non-ionic surfactant has little effect on the zeta potential of soil particle surfaces. They recommended the determination of zeta potential of soil particle surfaces prior to electrochemical remediation to maximize the remediation efficiency of the technique.

However, the results of using surfactants to enhance the extraction efficiency of metal contaminants from soil by electrochemical remediation are mixed. Some researchers reported positive results [74,75], while other researchers reported insignificant enhancement [64,76,77].

Cosolvent is a second solvent added in small quantity to the primary solvent to form a mixture that may greatly enhance the solvent power of the primary solvent due to synergism. They can enhance the aqueous solubility of many organic contaminants through cosolvent effect. Several cosolvents, such as ethanol [78,79], *n*-butylamine [80–82], *n*-propanol [70], acetone [80], and tetrahydrofuran [80], have been examined for their ability to enhance the solubilization of organic compounds such as PAHs and diesel oil in soil during the electrochemical remediation process.

3.2.4. Oxidizing/reducing agents

Oxidizing or reducing agents can be injected into contaminated soil to manipulate the *in situ* chemistry and microbiology, so as to enhance extraction of contaminants or to reduce their toxicity through oxidation or reduction reactions. Oxidizing agents may include air or oxygen, or chemical oxidants, such as hydrogen peroxide H_2O_2 , potassium permanganate KMnO_4 or sodium permanganate NaMnO_4 , ozone, chlorine, or oxygen releasing compounds. Contaminants are chemically or microbially oxidized. Similarly, reducing agents such as Fe^{2+} , Fe^0 , calcium polysulfide, or sodium dithionite can be used to reduce contaminants in soil.

The injection of oxidizing/reducing agents during electrochemical remediation of contaminated soil is equivalent to coupling electrochemical remediation with oxidation/reduction to remediate contaminated soil. Therefore, the subject will be treated in Section 5.

3.2.5. Cation solutions

Coletta et al. [83] used natural solutions containing clay extracts and synthetic solutions with varying concentrations of Al^{3+} , Ca^{2+} , and Na^+ as anodic flushing solutions to investigate the feasibility of enhancing electrochemical remediation of Pb-contaminated clay of initial Pb concentration of 340–410 mg/kg dry clay (dry) and moisture content of 80–83%. Natural flushing solutions were prepared by mixing water and clay in ratios varying from 2:1 to 40:1 by weight, and the supernatant was used as an anodic flushing solution. The 7:1 natural solution was observed to be most effective

for Pb removal. The solution was composed of 2.289, 0.314, 1.464, 0.803, and 0.908 ppm of Ca^{2+} , Al^{3+} , Na^+ , Mg^{2+} , and K^+ , respectively. Synthetic solutions were prepared using AlCl_3 , $\text{Ca}(\text{NO}_3)_2$, and NaCl solutions. The Pb extraction efficiency was highest when the solution ionic strength was approximately 0.001 M for each element group, and with trivalent Al^{3+} and divalent Ca^{2+} ions at concentrations of 0.064 and 0.31 mM, respectively. Moreover, the 0.31 mM Ca synthetic solution exhibited the highest overall Pb extraction efficiency due to its high ionic mobility, large hydrated ionic radius, and near optimum ionic strength. Energy requirement was determined to be 8–31 kWh/m³ of soil.

Reddy and Chinthamreddy [84] investigated the feasibility of enhancing electrochemical remediation of glacial till spiked with Cr^{6+} , Ni^{2+} , and Cd^{2+} of concentrations of 1000, 500, and 250 mg/kg, respectively by simultaneous injection of 0.1 M NaCl from the anode and 0.1 M EDTA from the cathode. Their experimental results indicate that the presence of NaCl sustained the electric current and electroosmotic flow. The remediation efficiency of Cr was increased considerably to 79%. Ni and Cd were migrated significantly towards the anode but eventually accumulated in the soil near the anode. The accumulation of these metals was attributed to the preferential complexation of EDTA with H^+ ions in an acidic environment.

The thickness of the diffuse double layer around soil particles $1/\kappa$ (m) is given by

$$\frac{1}{\kappa} = \sqrt{\frac{\varepsilon RT}{2000 \times c F^2 z^2}} \quad (1)$$

where ε is the permittivity of soil pore fluid (F/m); R is the universal gas constant (8.314 J/mol K); T is the absolute temperature (K); c is the concentration of cations in the diffuse double layer (mol/L); F is the Faraday constant (96,485 C/mol); and z is the valence of cations in the diffuse double layer. The electroosmotic volume flow rate is given by

$$Q = k_e i_e A \quad (2)$$

where Q is the electroosmotic volume flow rate (m³/s); k_e is the coefficient of electroosmotic conductivity (m²/V s); i_e is the electrical gradient (V/m); and A is the total cross-sectional area perpendicular to the direction of flow (m²).

It should be noted that the polyvalent cations injected into contaminated soil may replace contaminant ions or H^+ ions in the diffuse double layer of the soil. Cation exchange in clay follows a replaceability series that favors the adsorption of cations of higher valence. If two atoms have the same valence, the larger cation is favored. The order of adsorption is shown with corresponding ionic radii in Å as follows [3],

$$\text{Al}^{3+} > \text{Pb}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+ > \text{Na}^+ > \text{Li}^+$$

0.57 1.19 1.06 0.78 1.33 0.98 0.7

In addition to valence and ionic radius, ion concentration is another important factor affecting cation exchange. A cation of high concentration and low replacing power may be preferred to a cation of low concentration and high replacing power [3].

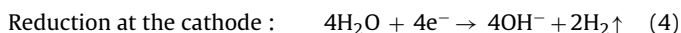
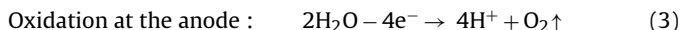
Adsorption of cations of high valence in the diffuse double layer of clay particle surfaces causes a decrease in the thickness of the diffuse double layer around clay platelets as predicted by Eq. (1) [85,86]. Moreover, a high concentration of cations in the soil pore fluid causes further decrease in the thickness of the diffuse double layer and an increase in ionic strength of the system.

The decrease in thickness of the diffuse double layer decreases the repulsive forces among clay particles and allows the van der Waals attractive forces among clay platelets to dominate, resulting in flocculation of clay particles. The flocculated structure in the clay fabric causes an increase in porosity and decrease in tortuosity of flow paths, leading to an increase in tortuosity factor, and resulting in increases in the hydraulic conductivity and coefficient of electroosmotic conductivity of the clay, and the effective

ionic mobilities of the ionic species in the soil pore fluid. However, an increase in ionic strength (electrolyte concentration) of the soil pore fluid increases the electrical conductivity of soil and energy consumption of the process. Conversely, a decrease in ionic strength (electrolyte concentration) increases the thickness of the diffuse double layer, leading to a decrease in the coefficient of electroosmotic conductivity and a reduction of electroosmotic flow rate and electromigration of ions. However, the electric current flowing through the soil is reduced, leading to lower energy consumption. As the electroosmotic flow rate and electromigration are the dominant transport mechanisms in electrochemical remediation, there is an optimized ionic strength to maximize the overall remediation efficiency of electrochemical remediation.

4. Soil pH control

As a result of electrolytic decomposition of electrolytes at the electrodes, H^+ and OH^- ions are generated at the anode and the cathode, respectively during the electrochemical remediation process as follows:



The generated H^+ and OH^- ions are migrated into the soil by the dc electric field imposed on the soil. As a result, the soil pH near the anode is lowered and that near the cathode is raised. Different techniques have been developed to condition the electrode reservoir solutions, i.e., the anolyte and catholyte, so as to eliminate the adverse impacts of electrode reactions. The primary purpose of electrode reservoir conditioning is to maintain the pHs of anolyte and/or catholyte within appropriate ranges specific to the contaminants being remediated. In most cases, the pH of anolyte is raised and that of catholyte is lowered. The conditioning is particularly important for electrochemical remediation of soils of low acid/base buffer capacity, as the resistances to pH change of these soils are low. Specific objectives of reservoir conditioning include [87]: (1) precipitation of metal contaminants should be avoided and/or precipitates should be solubilized and mobilized; (2) electrical conductivity of the specimen should not be increased excessively in a short duration so as to avoid diminishing of the advective transport of contaminant by electroosmosis prematurely; (3) the electrolysis reaction at the cathode should possibly be depolarized to avoid the generation of OH^- ions and their transport into the specimen; (4) the depolarization would also assist in decreasing the electrical potential difference across the specimen and reduce energy consumption of the process; (5) if any chemical is used, the metal precipitate with this new chemical should be soluble within the pH ranges maintained by reservoir conditioning; (6) any special chemicals introduced should not result in any increase in toxic residue in the soil; and (7) the additional cost of chemicals and/or equipment for reservoir conditioning should not increase the overall cost of the electrochemical remediation process significantly.

The most frequently used reservoir conditioning techniques in electrochemical remediation are: (1) electrode conditioning by conditioning agents; and (2) use of ion exchange membranes.

4.1. Electrode conditioning

Weak acids may be introduced to neutralize the OH^- ions generated at the cathode during the electrochemical remediation process. However, improper use of some acids in the process may pose a health hazard. For example, the use of HCl may pose a health hazard as: (1) it may increase Cl^- concentration in groundwater; (2) it may promote the formation of some insoluble chloride salts,

for example, PbCl_2 ; and (3) Cl_2 gas will be generated by electrolysis if it reaches the anode.

Organic acids, such as CH_3COOH or citric acid, are weak acids that undergo partial dissociation in water. There are several advantages in using these weak acids to depolarize the OH^- ions generated at the cathode: (1) they are environmentally safe and biodegradable; (2) they possess certain acid/base buffer capacities so that they can maintain the electrolyte pH to some extent; (3) they are complexing agents that can form soluble complexes with metals to enhance solubilization of heavy metals sorbed on soil particle surfaces and to maintain mobility of heavy metals in soil; (4) the concentration of ions generated by acid dissociation is very low as their pK_a values are relatively high, the resulting increase in the electrical conductivity of soil and thus the power consumption are small; and (5) these weak acid ions prevent the formation of other insoluble salts in the vicinity of the cathode, preventing the development of a low electrical conductivity zone and dissipation of excessive electrical energy in the soil near the cathode [2].

Experimental results on removal of Pb from kaolinite by Lee and Yang [88] indicate that external circulation of the electrolyte solution from the cathode reservoir to the anode reservoir could control pore fluid pH, and prevent excessive H^+ from decreasing electroosmotic flow rate and excessive OH^- from increasing heavy metal precipitation. Saichek and Reddy [89] demonstrated that the use of NaOH to control pH at the anode could improve the extraction efficiency of phenanthrene from kaolin by electrochemical remediation.

Experimental results of Hicks and Tondorf [90] on removal of Zn from Georgia kaolinite, a soil of low acid/base buffer capacity, reveal that problems related to isoelectric focusing could be prevented by rinsing away the OH^- ions generated at the cathode, achieving an extraction efficiency of 95%. The experimental results of Puppala et al. [87], Rødsand et al. [91], and Reed et al. [92] indicate that the addition of CH_3COOH to the cathode reservoir prevented the development of alkaline conditions in the soil. The technique could improve the extraction efficiency of Pb, as the soil pH nearest to the cathode was lowered to prevent precipitation of $\text{Pb}(\text{OH})_2$.

Zhou et al. [93] studied the performance of electrochemical remediation of the low pH Chinese red soil contaminated by Cu and Zn enhanced by catholyte conditioning. Without catholyte conditioning, the soil pH near the cathode was increased from 4.2 to above 6, resulting in accumulation of large quantities of Cu and Zn precipitates in the vicinity of the cathode. Application of lactic acid as catholyte pH conditioning agent improved the extraction efficiency of Cu and Zn from the soil. Increasing the ionic strength of the conditioning agent by adding 10 mM CaCl_2 further enhanced Cu removal, but did not cause a significant improvement for Zn extraction.

The feasibility of using reservoir conditioning to enhance electrochemical remediation of heavy Cd-contaminated soil was investigated by Gidarokos and Giannis [94]. 0.01 M CH_3COOH or 0.01 M citric acid was used as catholyte to prevent Cd from precipitating as hydroxide. Their results reveal that when the catholyte pH was controlled to be lower than 4, significant amounts of H^+ ions produced at the anode could be migrated throughout the specimen, resulting in desorption of Cd from soil particle surfaces and a very high extraction efficiency.

Ryu et al. [95] studied the performance of laboratory-scale electrochemical remediation on Cu-, As-, and Pb-contaminated soil enhanced by electrolyte conditioning. Their results reveal that catholyte conditioning using HNO_3 increased the removal of Cu and Pb from the soil, and the maximum removal was 60.1% for Cu and 75.1% for Pb. Anolyte conditioning using NaOH enhanced the migration of As which exists in an anionic form and 43.1% of As was removed.

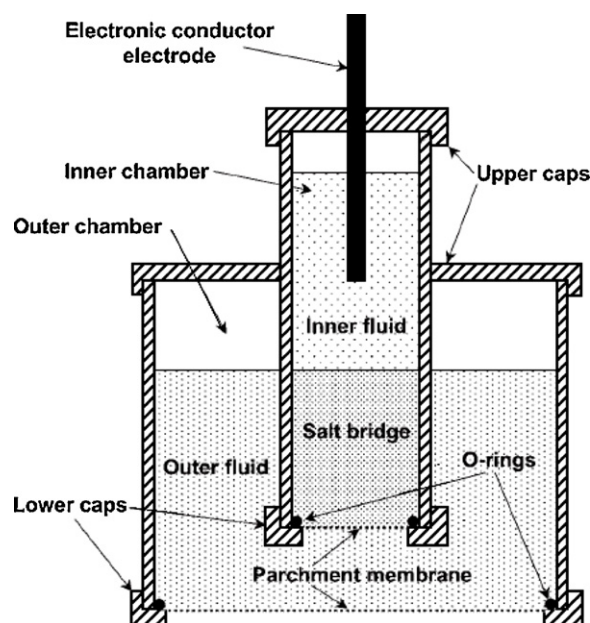


Fig. 4. The NEOCHIM electrode (after Leinz et al. [100]).

Genc et al. [96] used CH_3COOH to keep both the anolyte and catholyte at $\text{pH} \leq 4$ in their laboratory study on electrochemical remediation of contaminated sediment from Cuyahoga River, OH, USA. The river sediment was contaminated by Mn, Cu, Zn, and Pb. However, the low pH of catholyte generated reverse electroosmotic flow, i.e., from the cathode towards the anode. As a result, they observed the accumulation of Mn near the cathode. However, other metals, such as Cu, Zn, and Pb were mostly in the middle section of the specimen. Moreover, as a result of reverse electroosmotic flow, the extraction efficiencies of metals were low. The highest extraction efficiencies of Mn, Cu, and Pb observed were 18%, 20% and 12%, respectively, and no removal of Zn was observed in all their experiments.

Buffer solutions, such as CH_3COOH and NaHCO_3 , have also been successfully used to control the pH of electrode reservoir electrolytes so as to control the electroosmotic flow direction and to maintain the electroosmotic volume flow rate during the electrochemical remediation of Pb- or Cd-contaminated Milwhite kaolinite, a natural clay of high acid/base buffer capacity [97,98].

The NEOCHIM technology was developed by the U.S. Geological Survey on the foundation of Russian scientists' research results on CHIM, a method of electrogeochemical sampling for use in the exploration of buried mineral deposits. A schematic of the NEOCHIM electrode is shown in Fig. 4. The technology solves the problems associated with the presence of H^+ and OH^- ions in the vicinity of electrodes by using an electrode made of two compartments linked by a salt bridge [99]. The power electrode is immersed in a conducting fluid in the inner compartment where H^+ and OH^- ions produced by electrolysis are retained and prevented from reaching the outer compartment by the salt bridge. The salt bridge is retained by a semipermeable parchment membrane at the base of the inner compartment. A further conducting fluid is retained by the outer compartment. Electrical contact of the electrode with soil is made through a semipermeable parchment membrane at the base of the outer compartment. The membrane allows the passage of ions from the conducting fluid into the soil and from the soil into the fluid, while retaining the fluid in the compartment. The experimental results of Leinz et al. [100] on electrochemical remediation also indicate the high potential of the NEOCHIM process for the monitoring and remediation of hazardous waste sites.

4.2. Use of ion exchange membrane

Another technique of reservoir conditioning is the use of ion exchange membranes or ion-selective membranes to isolate specific ions generated by electrode reactions from the contaminated soil. Cation exchange membranes essentially allow only cations to pass through, and anion exchange membranes allow only anions to pass. Therefore, a cation exchange membrane installed between the cathode and contaminated soil can prevent the OH^- ions generated at the cathode from migrating into the contaminated soil and precipitating with metal contaminants as hydroxides. The metal contaminant cations can be migrated from the soil through the cation exchange membrane into the catholyte to precipitate with the OH^- ions on the membrane surface or in the catholyte. However, precipitation with the OH^- ions on the membrane surface causes fouling of the membrane. The deterioration of the membrane performance is essentially caused by deposition of foulants on the membrane surface, resulting in an increase in flow resistance of the membrane and decreases in fluxes flowing through the membrane. Nonetheless, the technique is promising as it does not introduce any additional chemicals into the system [101]. However, membrane fouling remains one of the most crucial factors limiting the use of ion exchange membranes in electrochemical remediation [102]. Moreover, the experimental results of Rødsand et al. [91] indicate that the membrane extraction technique did not enhance the extraction of Pb from spiked Norwegian marine clay by electrochemical remediation as expected.

Puppala et al. [87] studied the use of NafionTM membrane to limit the transport of OH^- ions into soil during electrochemical remediation of an illitic deposit contaminated by Pb. The advantage of the membrane technology is that it would not be necessary to neutralize the cathode by continuous introduction of acid, resulting in considerable saving of acid cost. However, the energy consumption of the process was increased by the electrical resistance of the membrane. Lower expenditures are anticipated if: (a) the membrane is changed periodically and cleaned to prevent fouling, and/or (b) the post-membrane catholyte is removed frequently for precipitation. Moreover, the relative high cost of NafionTM membrane may increase the cost of *in situ* electrochemical remediation unless the system can be engineered and optimized to decrease the cost during real-life field implementation. Therefore, cost-efficient field techniques should be devised.

The results of Li et al. [103] indicate the use of a cation selective membrane installed at the front of the cathode to prevent OH^- ion migration towards the anode could greatly enhance the extraction efficiency of Cu by electrochemical remediation. However, they observed that very little Cu ions could penetrate the cation-selective membrane to precipitate in the cathode compartment. Although a cation selective membrane should ideally not permit anions, such as OH^- , to enter, most of the Cu precipitated as hydroxides in the compartment between the soil and the membrane, indicating the membrane was not 100% effective and some OH^- ions still entered the compartment and precipitated the Cu ions there.

Kim et al. [104] installed an anion exchange membrane between the anode and contaminated soil specimen and a cation exchange membrane between the cathode and the soil specimen to enhance electrochemical remediation of a Cd- and Pb-contaminated kaolinite. Moreover, an auxiliary solution cell was installed between the cation exchange membrane and the contaminated soil. Small holes were punched in the membrane to allow OH^- ions to move into the auxiliary solution cell from the catholyte so that metal contaminants were precipitated in the auxiliary solution cell instead of at the catholyte. Their results indicate the overall extraction efficiencies of membrane-enhanced electrochemical remediation were improved tremendously due to the prevention of hydroxide

precipitation in the soil and increase in electric current efficiency. Moreover, the installation of the auxiliary solution cell could nullify the fouling problem within the cation exchange membrane and thus improve the overall effectiveness of the electrochemical remediation process.

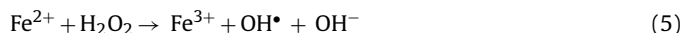
5. Coupling with other remediation technologies

There are many technologies available for remediation of contaminated soil and groundwater [8,105]. They all have their advantages and disadvantages. Some of these technologies can be coupled with electrochemical remediation synergistically so that the coupled remediation efficiency is higher the sum of the individual technologies applied individually. Some of the remediation technologies with feasibility of coupling with electrochemical remediation are presented here. However, the feasibility of many other remediation technologies coupling with electrochemical remediation has yet to be investigated and it should be noted that there are numerous opportunities of coupling these remediation technologies with electrochemical remediation to improve the remediation efficiency of contaminated soil and groundwater drastically for the benefit of mankind and the environment.

5.1. Oxidation/reduction

The oxidation/reduction remediation technologies focus on modifying the chemistry and microbiology of the environment by injecting selected reagents into the subsurface to enhance degradation and extraction of contaminants by *in situ* chemical oxidation/reduction reactions [8]. The technologies are applicable for a wide range of inorganic, organic, and mixed contaminants.

The most widely studied and utilized oxidation technology in environmental engineering is probably the Fenton process. All processes that involve catalytic reaction between hydrogen peroxide H_2O_2 and Fe^{2+} ions can be denoted as Fenton processes [106]. The Fenton process involves two major steps: (1) oxidation of Fe^{2+} ions to Fe^{3+} ions with decomposition of H_2O_2 and generation of hydroxyl radicals, as illustrated in Eq. (5); and (2) degradation of organic contaminants by hydroxyl radicals through oxidation as illustrated in Eqs. (6) and (7),



By-products of the chemical reactions presented in Eq. (7) can be further degraded by radical mechanism to complete mineralization. Although Eq. (5) is often referred as the Fenton reaction, other important reactions, such as the occurrence of the Fenton catalytic cycle, also occur:



The presence of Fe is catalytic. The hydroxyl radicals so generated are strong and relatively unspecific oxidants that react with most organic contaminants. Therefore, the Fenton process is widely used for the destruction of biorefractory organic contaminants such as benzene, phenols and chlorophenols in wastewater or drinking water. The radicals oxidize the organic molecule by abstracting hydrogen atoms as illustrated in Eq. (6) or by adding themselves to double bonds and aromatic rings. The hydroxyl radicals are only active in aqueous form and thus cannot attack contaminants sorbed

on soil particle surfaces [107]. However, it has been demonstrated that it is technically feasible to use high concentration H_2O_2 to oxidize contaminants sorbed on soil particle surfaces [108,109], as high concentration H_2O_2 favors the generation of highly reactive species, such as HO_2^\bullet (hydroperoxyl radicals), $\text{O}_2^{\bullet-}$ (superoxide anions), and $\text{HO}_2^{\bullet-}$ (hydroperoxide anions), other than hydroxyl radicals. The generation of these non-hydroxyl and highly reactive radicals in the presence of high concentration H_2O_2 leads to aggressive reactions that ultimately oxidize the contaminants sorbed on soil particle surfaces [110,111]. However, the Fenton process is effective only at low pHs of 3–5. Therefore, pH adjustment may be required during the remediation process.

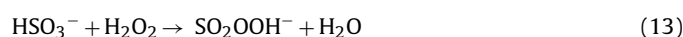
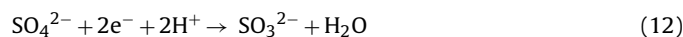
Recently, there are many investigations into the Fenton-like processes for the degradation of organic contaminants. These processes can be broadly classified into three groups: (1) processes that use ferric salts as catalyst to incite the Fenton reaction, i.e., Eq. (5); (2) processes that use heterogeneous Fenton type catalysts such as iron powder, iron-oxides, iron-ligands, or iron ions doped in zeolites, pillared clays or resins; and (3) processes that use other metal ions, e.g., copper, manganese or cobalt, as catalyst. The major advantages of the Fenton type processes are: (1) they are able to degrade many organic contaminants to harmless or biodegradable products; (2) they use relatively cheap reagents; and (3) the reagents are safe to handle and environmentally benign [106].

The bench-scale laboratory experimental results of Yang and Long [112] and Yang and Liu [113] indicate that it is technically feasible to couple the Fenton-like process with electrochemical remediation using a permeable reactive barrier of granular scrap iron powder to extract and degrade phenol and trichloroethylene (TCE) *in situ*, respectively. The overall contaminant remediation efficiency is contributed by two mechanisms: (1) destruction of organic contaminants by the Fenton-like process; and (2) extraction of contaminants by electrochemical remediation. Their experimental results also reveal that the percentage of organic contaminant destruction increased with the quantity of scrap iron powder used in the process. However, a larger quantity of scrap iron powder embedded in soil would decrease the coefficient of electroosmotic conductivity, resulting in lower efficiency of advective transport of the contaminant by electroosmosis and thus lower contaminant extraction efficiency. Moreover, the smaller was the size of the scrap granular iron powder, the higher was the destruction efficiency, but the lower was the overall contaminant remediation efficiency.

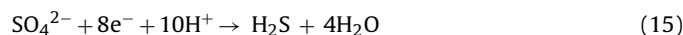
Kim et al. [114] explored the feasibility of coupling the Fenton process with electrochemical remediation to remediate phenanthrene-contaminated EPK kaolinite, using the iron minerals on soil particle surfaces as catalyst. Their results reveal that the intermediate anions, i.e., HO_2^- and $\text{O}_2^{\bullet-}$, generated by the Fenton-like reactions changed the electrical current intensity significantly. The addition of 0.01 N H_2SO_4 to the anode reservoir improved the stability of H_2O_2 and treatment efficiency of phenanthrene in the soil specimen. More than a half of the spiked phenanthrene was destructed or extracted after 21 days of treatment. Therefore, the use of H_2O_2 and dilute acid, as an anode purging solution, is a feasible technology for the remediation of halogenated organic compound-contaminated soil of low hydraulic conductivity, low acid/base buffer capacity, and high iron content. Kim et al. [115] attempted to remediate phenanthrene-contaminated Hadong clay similarly, however, the acid/base buffer capacity of Hadong clay is high due to its high carbonate content. Their results reveal that the presence of carbonates of high acid/base buffer capacity reduced the stability of H_2O_2 and treatment efficiency of phenanthrene, and confirmed that the Fenton reaction is effective only at low pHs of 3–5.

Different methods have been attempted to overcome the problem of high acid/base buffer capacity of soil. Kim et al. [116] studied the stabilizing effects of phosphate and sodium dodecyl sulfate (SDS) on H_2O_2 during electrochemical remediation of phenanthrene-contaminated Hadong clay coupled with the Fenton-like process. Both stabilizers decreased (becomes more negative) the zeta potential of soil particle surfaces due to complexation of phosphate and SDS with oxides, resulting in increase of electroosmotic volume flow rate. Complexation with phosphate hindered the migration of dissolved Fe ions towards the cathode significantly. However, SDS could dissolve the Fe ion from the Fe oxide of soil and transport the dissolved Fe ions towards the cathode. Nonetheless, transition metal complexation with phosphate and SDS improved the stability of H_2O_2 , in particular, in the high pH region near the cathode by SDS. The increase of H_2O_2 stability allowed more reaction time for the Fenton-like process, resulting in better treatment efficiency of phenanthrene.

Kim et al. [117] studied the performance of H_2SO_4 and HCl injected from the anode for pH control in the remediation of phenanthrene-contaminated Hadong clay by electrochemical remediation. When H_2SO_4 was utilized, the reduced species of sulfate may increase the decomposition rate of H_2O_2 near the anode significantly as follows:



Moreover, reduced sulfur species, such as H_2S and HS^- , accumulated in the region near the cathode due to the reducing environment of the region. The generation of these sulfur species is accompanied by a significant stoichiometric decrease of H^+ ions in the soil pore fluid,



resulting in a sharp increase in soil pH, rapid decomposition of H_2O_2 , and generation of O_2 gas. Such decomposition of H_2O_2 was not observed in experiments using HCl as the pH control agent. Moreover, H_2O_2 may be re-generated near the cathode by the reaction,



The remediation efficiency of phenanthrene-contaminated soil by the Fenton-like process is dependent on both the extent of degradation and migration by electroosmosis.

Alcantara et al. [118] studied the electrochemical remediation of phenanthrene-contaminated kaolinite of initial concentration of 500 mg/kg of soil. Electrochemical remediation alone resulted in negligible remediation of phenanthrene. Fenton-like reaction was thus generated in kaolinite which was also contaminated by Fe. When both the anode and cathode reservoirs were filled with 10% H_2O_2 , an overall extraction and destruction efficiency of phenanthrene of 99% was obtained in 14 days by applying an electrical gradient of 300 V/m across the soil specimen. It should be noted that the soil pH was maintained at approximately 3.5 without pH control, favoring the Fenton-like processes.

Reddy and Karri [119] applied electrochemical remediation enhanced by the Fenton-like process to kaolin contaminated with a mixture of Ni and phenanthrene each at a concentration of 500 mg/kg of dry soil. The objective of the coupled remediation processes was simultaneous oxidation of phenanthrene and extraction of Ni. Experiments were conducted using H_2O_2 solution in concentrations of 5%, 10%, 20%, and 30% and deionized water as control. Native Fe was used as catalyst for the Fenton-like process. A dc electrical gradient of 1 V/cm was applied and H_2O_2 solution was

introduced at the anode for 4 weeks. The volume of electroosmotic flow was substantial in all the experiments, approximately one pore volume in the control experiment and 1.2–1.6 pore volumes in the H_2O_2 experiments. Oxidation of phenanthrene increased with concentration of H_2O_2 and a maximum of 56% oxidation was observed with 30% H_2O_2 . Nickel was migrated from the anode towards the cathode but it was precipitated near the cathode as a result of the high pH environment. They concluded that optimization of H_2O_2 /catalyst concentration and electrical gradient applied, and control of soil pH are required to improve the efficiency of oxidation of phenanthrene and extraction of Ni simultaneously.

Oonnittan et al. [120] studied the feasibility of electrochemical remediation of hexachlorobenzene (HCB)-contaminated kaolin enhanced by the Fenton process with and without using β -cyclodextrin to enhance the solubility of HCB in the soil pore fluid. The initial concentration of HCB in kaolin was 100 mg/kg of soil. The native iron in kaolin was utilized to catalyze the Fenton-like reaction and no soluble iron was added during the process. After 15 days of treatment, a maximum remediation efficiency of 76% was observed when 30% H_2O_2 was used in the absence of β -cyclodextrin. However, the introduction of β -cyclodextrin as an enhancing agent led to a slower rate of oxidation.

Tsai et al. [121] studied the feasibility of electrochemical remediation of diesel-contaminated soils enhanced by the use of 0.1 M NaCl as purging solution and corroded iron electrodes. Their experimental results indicate the concentration of total petroleum hydrocarbon diesel in the contaminated soil was reduced from 10,000 to 300 mg/kg by electrokinetically enhanced oxidation in the presence of both 8% H_2O_2 and Fe_3O_4 (corroded iron electrodes), i.e., remediation efficiency of 97%. However, individually applied electrochemical remediation and Fenton oxidation can only yield remediation efficiencies of 55% and 27%, respectively. The synergistic effect of the two remediation technologies is thus evident.

Oonnittan et al. [122] identified the importance of efficient oxidant delivery methodologies for effective contaminant oxidation to occur. The success of electrochemical remediation coupled with the Fenton process depends heavily on the good contact between the contaminant and the oxidant facilitated under optimized reaction conditions.

Isosaari et al. [123] coupled persulfate oxidation with electrochemical remediation to cleanup creosote-contaminated soil for 8 weeks. Their results reveal that electrokinetically enhanced oxidation with sodium persulfate $\text{Na}_2\text{S}_2\text{O}_8$ resulted in remediation efficiency of creosote removal of 35% which is better than that of electrochemical remediation of 24% or persulfate oxidation of 12% individually. The oxidant generated more positive redox potential than electrochemical remediation alone. Moreover, the persulfate treatment decreased the electroosmotic volume flow rate. The results of elemental analyses indicate decrease in the natural Al and Ca concentrations, increase in Zn, Cu, P, and S concentrations, and migration of several metal cations towards the cathode.

The effectiveness of electrokinetically enhanced persulfate oxidation for destruction of TCE spiked in a sandy clay soil was evaluated by Yang and Yeh [124]. Their experimental results indicate that electroosmosis could greatly enhance the transport of the injected $\text{Na}_2\text{S}_2\text{O}_8$ from the anode reservoir to the cathode reservoir via the contaminated soil, enhancing the *in situ* chemical oxidation of TCE. Moreover, the injection of nano-scale Fe_3O_4 was observed to have a profound impact in the activation of persulfate oxidation.

Reddy and Chinthamreddy [125] studied the electromigration of Cr^{6+} , Ni^{2+} , and Cd^{2+} in clayey soils containing different *in situ* reducing agents in bench-scale experiments. Two different clays, kaolin and glacial till, were used with or without a reducing agent. Kaolin is a soil of low acid/base buffer capacity and glacial till is a soil of high acid/base buffer capacity. The reducing agent used was humic acid, ferrous sulfate, or sodium sulfide of concentration of

humic acid, Fe^{2+} , and S^- of 1000 mg/kg soil. The soils were then spiked with Cr^{6+} , Ni^{2+} , and Cd^{2+} in concentrations of 1000, 500, and 250 mg/kg, respectively, and treated by an electrical gradient of 1 V/cm for more than 200 h. The reduction of chromium from Cr^{6+} to Cr^{3+} was completed prior to electrochemical remediation. Their results indicate that the extent of Cr^{6+} reduction was dependent on the type and quantity of reducing agent in the soil in the order of sulfide > ferrous iron > humic acid. Moreover, electromigration of Cr^{6+} was significantly retarded in the presence of sulfide because of: (1) the opposite directions of migration of Cr^{6+} and Cr^{3+} ; (2) sorption and precipitation of Cr^{3+} in high pH regions near the cathode in kaolin and throughout the glacial till; and (3) sorption of Cr^{6+} in low pH regions near the anode in both soils. Both Ni^{2+} and Cd^{2+} were migrated towards the cathode in kaolin. However, the migration was significantly retarded in the presence of sulfide due to the pH increase throughout the soil. The initial high pH conditions within the glacial till caused Ni^{2+} and Cd^{2+} to precipitate, so the effects of reducing agents were inconsequential. The study demonstrated evidently that the reducing agents, particularly sulfide, in soils may affect the redox chemistry and pH of the soil, ultimately affecting the remediation efficiency of electrochemical remediation.

Weeks and Pamukcu [126] conducted a study to demonstrate the feasibility of *in situ* reduction of Cr^{6+} to Cr^{3+} by introducing ferrous iron Fe^{2+} , a reducing agent, to the contaminated soil electrokinetically. Their results indicate that the Cr^{6+} in soils could be effectively reduced to Cr^{3+} by electrochemical remediation. Moreover, they demonstrated that the Nernst equation may be applicable to model the soil-water system to estimate the concentrations of different Cr species after electrochemical remediation.

5.2. Bioremediation

Bioremediation is the use of microorganisms (mainly bacteria) to decompose hazardous contaminants, transform them to less harmful forms, and/or immobilize them under suitable environmental conditions [8]. The success of bioremediation requires the simultaneous existence of microorganisms, contaminants (food for the microorganism), electron acceptors, and essential nutrients for the microorganisms to grow. In fine-grained soils of low hydraulic conductivity, it is difficult to supply microorganism and the required electron acceptors or nutrients to the contaminants, or to supply the contaminants to natural occurring microorganisms. Electrokinetics-enhanced bioremediation or bioelectrokinetics is the technology that couples bioremediation with electrochemical remediation by supplying the microorganisms, electron acceptors, or nutrients to the contaminants, or migrating the contaminants to the microorganisms by electrokinetic flow processes. The ability to directionally transport bacteria from injection points into zones of contamination is a distinct advantage of electrokinetics-enhanced bioremediation for *in situ* remediation [127].

Electroosmosis and/or electrophoresis have been utilized successfully to inject a *Pseudomonas* strain (bacterial cell capable of degrading diesel) into diesel-contaminated soil [128]; *Sphingomonas sp. L138* and *Mycobacterium frederiksbergense LB501TG* (polycyclic aromatic hydrocarbon-degrading bacteria) into model aquifers made of glass beads, alluvial sand from Lake Geneva, and historically polluted clayey soil in the laboratory [129]; *Pseudomonas putida*, *Bacillus subtilis*, and *Klebsiella pneumoniae* to stimulate bacterial cell migration and biodegradation of crude oil in soil [130]; *Sphingomonas sp. LB126* (fluorene-degrading bacteria) into a laboratory model aquifer [131]; *Bacillus spp.* (nitrate reducing bacteria) to remove nitrate from soil [132]; *B. subtilis LBBMA 155* and nitrogen-starved cells of *Pseudomonas sp. LBBMA 81* into a residual

soil [133]; and *Acidithiobacillus thiooxidans* (sulfur-oxidizing bacteria) into tailing soil contaminated by Cd, Cu, Pb, Zn, Co, and As [134]. However, it was observed that electrokinetic transport of strongly charged and highly adhesive cells of *M. frederiksbergense* LB501TG in different model aquifers was poor [129].

Lee and Kim [135] injected *A. thiooxidans* (sulfur-oxidizing bacteria) into shooting range soil contaminated by Cu, Zn, and Pb. The bioleaching process improved the extraction efficiencies of Cu and Zn by electrochemical remediation. However, PbSO₄, a byproduct of sulfur oxidation, existed as precipitates and was immobile. Nonetheless, the problem was overcome by subsequent injection of EDTA.

Electrokinetics was used successfully to inject ammonium nitrogen into fine-grained soil [136], benzoic acid cometabolite into TCE-contaminated soil [137], acetate and phosphate amendment into Cr⁶⁺-contaminated soil [138], KH₂PO₄ and triethyl phosphate into kaolin soils [139], oxygenated and nutrient-rich liquid into creosote-contaminated soil [140], and nitrate to toluene-contaminated soil under denitrifying conditions [141].

The results of Schmidt et al. [142] indicate the feasibility of injecting nitrate and ammonium into a very humid clayey silt of high plasticity, high electrical conductivity, low hydraulic conductivity, low density, high acid/base buffer capacity, and high cation exchange capacity. However, injection of phosphorous into this type of soil did not prove to be successful.

Lohner et al. [143,144] studied the distributions of microbial electron acceptors nitrate and sulfate and of the nutrients ammonium and phosphate by electrokinetics in a model sandy soil. Their results reveal that the ion distribution in the soil was significantly influenced by the pH profile and the imposed electrical gradient. The results of Xu et al. [145] reveal that ammonium and nitrate ions could be distributed more uniformly in phenanthrene contaminated-soil by reversal of electrode polarity.

The results of Jackson et al. [146] indicate electrokinetics could enhance the bioremediation of 2,4-dichlorophenoxyacetic acid-contaminated soil by increasing the bioavailability of the contaminant to microorganism. Similar observation was made by Fan et al. [147] during their study on *in situ* bioremediation of 2,4-dichlorophenol-contaminated soil.

Wu et al. [148] demonstrated experimentally that electrokinetic injection of lactate, a negatively charged biodegradable organic, in sand was dependent on electric current density. However, the increase in electric current intensity did not result in a proportional increase in lactate transport due to development of an appreciable electroosmotic flow from the anode to the cathode. Tiehm et al. [149] observed that the microbial activities of vinyl chloride degrading microorganisms were inhibited by electrochemical reaction products when stainless steel electrodes and titanium electrodes with mixed oxide coating type DN201 were used. However, when the electrodes were separated from the microorganisms by bipolar membranes, no inhibition by the electric field was observed. Li et al. [150] demonstrated that a dc electric current could stimulate microbial activities and accelerate the biodegradation of petroleum, and there is a strong positive correlation between the electric intensity and the bioremediation efficiency of petroleum. The results of Wick et al. [151] suggest that the presence of an electric field, if suitably applied, would not influence the composition and physiology of soil microbial communities and hence would not affect their potential to biodegrade subsurface contaminants. The results of Kim et al. [152] also suggest that the application of electrokinetics could be a promising soil remediation technology if soil parameters, electric current, and electrolyte were suitably controlled based on the understanding of interaction between electrokinetics, contaminants, and indigenous microbial community. Moreover, the increase in soil temperature during electrochemical remediation promotes microbial activities in general.

However, the microbial activities can also be inhibited if the soil temperature is higher than 45 °C.

5.3. Permeable reactive barriers

A permeable reactive barrier (PRB) is an engineered barrier made of reactive treatment media placed across the flow path of a contaminant plume in aquifer that removes or degrades contaminants in the groundwater flowing through it [153]. It relies on the flow of contaminants through the barrier. The use of granular zero-valent iron (ZVI) mixed with soil to construct PRBs for entrapping or decomposing contaminants in the subsurface has gained widespread acceptance by the environmental remediation and regulatory communities in recent years. Considerable investigation has been conducted to understand the interfacial chemistry of granular iron, and the sorption and degradation mechanisms of contaminants.

When a PRB is coupled with electrochemical remediation, the flow of contaminants through the barrier is not provided by the advective transport of contaminants driven by the natural hydraulic gradient of groundwater. It is driven by the electroosmotic flow of soil pore fluid, electromigration of charged species, and/or electrophoresis of charged particulates. In most cases, particularly in fine-grained soils, these transport mechanisms are far more significant than that driven by the natural hydraulic gradient of groundwater. The sorption characteristics of most solid particle surfaces are pH-dependent. The degradation reactions of many contaminants are also pH-dependent. As a result, the pH gradient generated by the electrochemical remediation process in the PRB may affect the sorption and degradation mechanisms of the reactive medium in the PRB. The use of enhancement agents in electrochemical reaction would further complicate the situation. Moreover, it is possible to construct a PRB in the subsurface by electrokinetic flow processes. Therefore, there are many additional aspects that need to be considered when a PRB is coupled with the electrochemical remediation process to improve the remediation efficiencies of organic, inorganic, and mixed contaminants.

5.3.1. Lasagna process

Electrochemical remediation is coupled with sorption/degradation of contaminants in treatment zones installed directly in contaminated soils in the Lasagna process. The Lasagna process is an *in situ* remediation technique that applies the concept of Integrated In situ Remediation [154]. A dc electric field is applied to migrate the contaminants from soil into treatment zones where the contaminants are removed by sorption, immobilization, or degradation as shown in Fig. 5. The technique is called “Lasagna” because of the layered appearance of electrodes and treatment zones. Theoretically, it can remediate organic, inorganic, and mixed contaminants.

Electrodes and treatment zones can be of any orientation depending upon the emplacement technology used and the characteristics of the site and contaminant. The treatment process is composed of these key steps [154]:

- (1) Highly permeable zones in close proximity of the contaminated soil are created by hydrofracturing or similar technologies. Appropriate materials such as sorbents, catalytic agents, microbes, oxidants and buffers are introduced to these highly permeable zones to transform them into treatment zones.
- (2) Electrokinetic flow processes are utilized to migrate contaminants from soil into treatment zones. Since these zones are located close to each other, the time taken for the contaminants to move from zone to zone can be very short.
- (3) For highly non-polar contaminants, surfactants can be introduced into the fluid or incorporated into the treatment zones

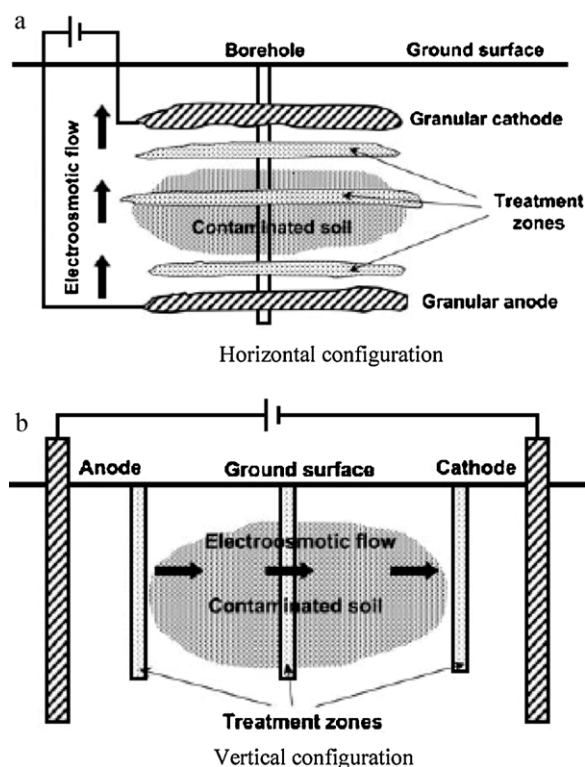


Fig. 5. Principle of Lasagna Process (after Ho et al. [154]).

to solubilize the organics. For a mixture of organics and metals, the treatment zones can contain sorbents for binding the metals and/or microbes or catalysts for degrading the organics.

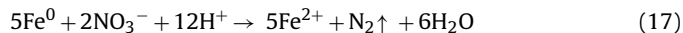
(4) If needed, the fluid flow direction can be reversed periodically by switching the electrical polarity. The operation would enable multiple passes of the contaminants through the treatment zones for complete sorption/destruction. The polarity reversal also serves to minimize complications associated with long-term operation of uni-directional electrokinetic flow processes. The high pH cathode effluent can be re-circulated through the contaminated soil when the polarity of the electric field applied is reversed, i.e., the cathode has been reversed to become the anode and vice versa. The recycling of effluent provides a convenient means for pH neutralization of the contaminated soil and minimization of wastewater generation.

The technique has been proved to be technically feasible in bench-scale laboratory experiments on the degradation of par-nitrophenol in kaolinite [154] and field-scale experiments on remediation of TCE-contaminated soils at various sites [155–158]. Jackman et al. [159] demonstrated the feasibility of migrating 2,4-dichlorophenoxyacetic acid in contaminated silt soil by electrokinetic flow processes into microorganism active treatment zone for biodegradation of organic contaminants.

A bench-scale experiment was conducted by Ma et al. [160] to investigate the simultaneous removal of 2,4-dichlorophenol (2,4-DCP) and Cd from a sandy loam by the Lasagna process using a new-type of bamboo charcoal as sorbent and periodic polarity reversals at different intervals. Their results indicate that the Lasagna process was effective in the simultaneous extraction of 2,4-DCP and Cd from sandy soil. Moreover, the extraction efficiencies were higher when the electrical polarity was reversed at 24-h intervals.

5.3.2. Zero-valent iron (ZVI) PRB

Chew and Zhang [161] investigated the feasibility of electrochemical remediation coupled with a ZVI PRB installed at the anode to treat a nitrate-contaminated soil according to the chemical reaction,



The amount of nitrate-nitrogen transformed by electrochemical remediation was increased significantly by coupling with a ZVI PRB. The major transformation products were ammonia-nitrogen and nitrogen gas.

Moon et al. [162] investigated the mechanisms of TCE degradation during electrochemical remediation coupled with a ZVI PRB. Their results indicate the rate of reductive dechlorination of TCE was improved 1.3–5.8 times of that of a ZVI PRB alone. The most effective configuration of electrode and ZVI PRB for TCE removal was with the cathode installed at the hydraulic down-gradient. The enhancement was attributed to the availability of more electron sources including: (1) the dc power supply; (2) electrolysis of water; (3) oxidation of ZVI; (4) oxidation of dissolved Fe^{2+} ; (5) oxidation of molecular hydrogen at the cathode; and (6) oxidation of Fe^{2+} in mineral precipitates. Each of these electron sources was evaluated for their potential influences on the TCE removal capacity through the electron competition model and energy consumption. A strong correlation between the quantity of electrons generated, removal capacity, and energy-effectiveness was identified.

Yuan [163] investigated the effect of ZVI PRB position and ZVI quantity on the efficiency of electrochemical remediation of tetrachloroethylene (PCE)-contaminated clay coupled with a ZVI PRB. The PRB was composed of 2–16 g of ZVI mixed with Ottawa sand in a ratio of 1:2 by weight. Her results indicate that the best position of the PRB was at the cathode and the remediation efficiency of PCE was 2.4 times that of electrochemical remediation alone. The remediation efficiency also increased with the quantity of ZVI in the barrier. The highest remediation efficiency of 90.7% was observed when the quantity of ZVI in the barrier was increased to 16 g. Moreover, it was observed that the more was ZVI in the barrier, the higher was the electroosmotic flow rate, and the lower was final soil pH after treatment.

The effectiveness of a ZVI PRB barrier installed at the middle of the soil specimen during electrochemical remediation of hyper- Cr^{6+} -contaminated clay (2497 mg/kg) was investigated by Weng et al. [164]. The barrier was composed of 1:1 ratio of granular ZVI and sand by weight. Their results indicate that the migration of H^+ ions was greatly retarded by the strong opposite migration of anionic CrO_4^{2-} ions, resulting in a reverse electroosmotic flow and development of alkaline zone across the specimen. The alkaline environment promoted the release of Cr^{6+} from the clay. Chromium removal was indicated by the high Cr^{6+} concentration in the anolyte and the presence of Cr^{3+} precipitates in the catholyte. The reduction efficiency of Cr^{6+} to Cr^{3+} was increased by the ZVI PRB. The electrochemical remediation coupled with a ZVI PRB has transformed the contaminant in the hyper- Cr^{6+} -contaminated soil to the less toxic form of Cr^{3+} .

Yuan and Chiang [165] investigated the removal mechanisms of As from soil by electrochemical remediation coupled with a PRB made of ZVI and FeOOH . The extraction efficiency for As was increased by 60–120% by the PRB. The best performance was achieved when a FeOOH layer was installed at the middle of the soil specimen. The improvement was attributed to higher surface area of FeOOH and the migration of HAsO_4^{2-} towards the anode by electromigration. The presence of As on the surface of the reactive media of the PRB was confirmed by results obtained by SEM coupled with energy dispersive spectroscopy. Moreover, the extraction of As contributed by surface sorption/precipitation on the PRB reactive media was much more than that by the electrokinetic flow

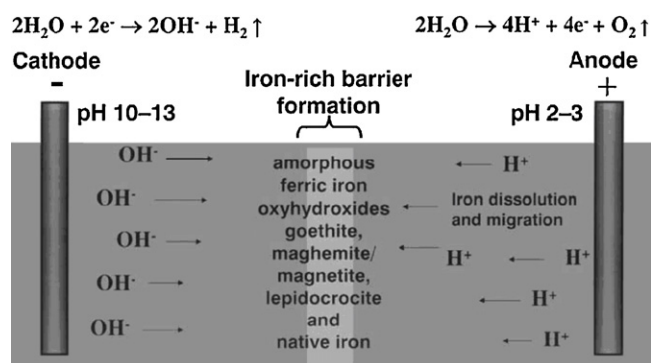
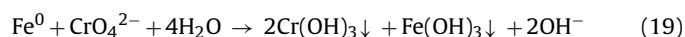
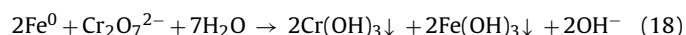


Fig. 6. Principle of iron-rich barrier generation by electrokinetics (after Faulkner et al. [169]).

processes. However, electromigration was a more dominant contaminant migration mechanism than the advective transport by electroosmosis.

Cang et al. [166] investigated the feasibility of treating a Cr-contaminated soil by electrochemical remediation coupled with a ZVI PRB. The reactions between Cr^{6+} in groundwater and the ZVI in the PRB are as follows:



ZVI is ultimately oxidized to Fe^{3+} which precipitates as $\text{Fe}(\text{OH})_3$, while Cr^{6+} is reduced to Cr^{3+} and also precipitates in the PRB. During the reactions, the OH^- ions released increases the soil pH and decreases the sorption capacity of Cr^{6+} on soil particle surfaces. Their results indicate that the technique was feasible for the remediation of Cr-contaminated soil. The maximum remediation efficiency of Cr achieved was 72%. The quantities of Cr in the anolyte and catholyte with a PRB were smaller than those without. The position of the PRB affected both the direction and rate of electroosmotic flow. The optimum positions of the PRBs are between the contaminated soil specimen and the electrodes.

Wan et al. [167] investigated the feasibility of surfactant-enhanced electrochemical remediation coupled with a PRB composed of microscale Pd/Fe for the treatment of a HCB-contaminated soil. The reduction kinetics of HCB by nanoscale Pd/Fe bimetallic particles was faster than that by nanoscale Fe particles. The degradation products of HCB using nanoscale Pd/Fe bimetallic particles have less chloro substituents than those using nanoscale Fe particles. The effects can be attributed to the catalytic effect of Pd on the Fe surface [168]. The nonionic surfactant Triton X-100 was selected as the solubility-enhancing agent. Their results indicate that HCB removal was generally increased by a factor of 4 as HCB was removed from soil through several sequential processes: (a) advective transport of HCB from the anode towards the cathode by electroosmosis; (b) complete sorption/degradation by the reactive Pd/Fe particles in the PRB; and (3) probable electrochemical reactions near the cathode.

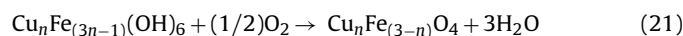
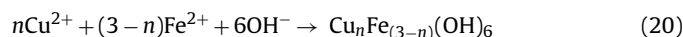
ZVI PRBs may be constructed *in situ* by electrokinetics. Faulkner et al. [169] have successfully generated subsurface barriers of continuous Fe-rich precipitates *in situ* by electrokinetics in their laboratory-scale experiments. Continuous vertical and horizontal Fe-rich bands up to 2 cm thick have been generated by applying a voltage of less than 5 V over a period of 300–500 h, using sacrificial iron electrodes 15–30 cm apart as shown in Fig. 6. The Fe-rich barrier is composed of amorphous iron, goethite, lepidocrocite, maghemite, and native iron. The applied dc electric field dissolved the sacrificial anode and injected the Fe ions into the soil. The Fe ions then re-precipitated in an alkaline environment to form the barrier. The thickness of the Fe-rich band increased with the applied

voltage. The hydraulic conductivity and unconfined compressive strength of the iron-rich band so produced were 1×10^{-9} m/s or less and 10.8 N/mm², respectively. The barrier may function as a PRB to degrade contaminants or an impervious barrier to contaminant transport. By monitoring the dc electric current intensity passing through the barrier, the integrity of the Fe-rich band may be assessed. Moreover, the barrier may 'self-heal' by continuing application of a dc electric current.

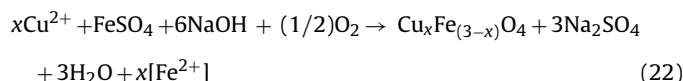
5.3.3. PRBs of different reactive media

Chung and Lee [170] investigated the potential use of atomizing slag as an inexpensive PRB reactive medium coupled with electrochemical remediation for simultaneous treatment of soil contaminated by TCE and Cd by laboratory-scale experiments. Their results indicate that the TCE concentration of the effluent through the PRB during electrochemical remediation were much lower than that of electrochemical remediation alone. Some of the TCE passing through the PRB would have been dechlorinated by the atomizing slag as indicated by the higher chloride concentration of the effluent. In general, both the remediation efficiencies of TCE and Cd achieved approximately 90%. The removal rate of Cd from the soil specimen was higher than that of TCE as a result of the additional transport by electromigration due to its positive charge.

Kimura et al. [171] investigated the possibility of coupling electrochemical remediation with a ferrite treatment zone (FTZ) to treat Cu-contaminated kaolinite. The FTZ was constructed between the cathode and contaminated kaolinite of soil containing polyferric sulfate solution so that the concentration of ferrite in the FTZ was 1000 ppm (mg/kg). Their results indicate 92% of Cu ions in contaminated kaolinite were migrated into the FTZ by electrochemical remediation and ferritized by the alkaline environment generated by the process after 48 h of treatment. The Cu ions were insolubilized by the ferrite reagent in the FTZ and accumulated as copper-ferrite through these chemical reactions [172],



Barrado et al. [173] suggested the co-precipitation mechanism for Fe^{2+} and divalent or polyvalent metal ions as follows,



The copper-ferrite precipitates are magnetic and can be separated from solution easily. Therefore, the advantages of coupling a FTZ with electrochemical remediation include: (1) it is possible collect the extracted heavy metals in a specific FTZ; (2) the treatment of a large quantity of Cu-rich wastewater produced by electrochemical remediation can be avoided; and (3) there is a possibility that copper-ferrite can be recovered by magnetic separation. It is envisaged in field implementation that the FTZ can be constructed near the cathode by injecting ferrite reagent into the soil, and the contaminated water is migrated to the FTZ by the electrochemical remediation process. Afterwards, the FTZ is excavated and the Cu is recovered by appropriate processes, such as soil washing using acid and magnetic separation.

The feasibility of electrochemical remediation of Cr-contaminated clay enhanced by a PRB made of transformed Red Mud (TRM) was investigated by De Giannis et al. [174] in bench-scale experiments. The TRM is primarily composed of micron-sized NaOH etched aggregates of (hydrated) Fe oxides (hematite and ferrihydrite 35% by weight) and hydrated alumina (boehmite and gibbsite 20% by weight). These are impregnated by newly formed and more or less soluble alkaline minerals, including sodalite (15% by weight), $\text{Ca}(\text{OH})_2$, hydroxycarbonates

and calcium aluminosilicates (portlandite, calcite, cancrinite, hydrocalumite and aluminohydrocalcite 15 wt%), $Mg(OH)_2$ and magnesium aluminosilicates (brucite and hydrotalcite 4 wt%). Their results reveal that the remediation efficiency of Cr^{6+} was proportional to treatment duration. The acidic environment near the anode generated by the electrochemical remediation process improved the sorption capacity of TRM for metal-oxyanions. Therefore, the PRB made of TRM installed near the anode improved the remediation efficiency of metal-oxyanions by electrochemical remediation.

Yuan et al. [175] investigated the feasibility of surfactant-enhanced electrochemical remediation of 1,2-dichlorobenzene (1,2-DCB)-contaminated soil coupled with a carbon nanotube (CNT) PRB installed at the middle of the specimen. CNT is becoming a prominent material being applied in the removal of aqueous and gaseous pollutants due to its high specific area, high reaction ability, and high electron transfer capacity [176–179]. It is highly expected that CNT will become an effective reactive medium in the PRB for removal of organic contaminants from the subsurface. Their results indicate the remediation efficiency of electrochemical remediation could be significantly improved by the introduction of SDS and coupling with a CNT PRB. Removal of 1,2 DCB was primarily contributed by surface sorption of the contaminant on CNT rather than by electrokinetic flow processes. However, electrophoresis of anionic SDS micelles towards the anode became a more critical contributor when the surfactant was used as processing fluid.

An enhanced electrochemical remediation process coupled with a PRB made of carbon nanotube coated with cobalt (CNT-Co) was investigated for As^{5+} removal by Yuan et al. [175]. Their experimental results indicate the PRB made of CNT did not contribute much to the remediation efficiency of As^{5+} . However, the PRB made of CNT-Co increased the remediation efficiency from 35% to 62%. The better remediation efficiency of electrochemical remediation enhanced by the PRB made of CNT-Co was attributed to the higher sorption of As^{5+} onto CNT-Co surfaces than CNT surfaces. Removal of As^{5+} was thus primarily contributed by the surface sorption of As^{5+} onto CNT-Co instead of the electrokinetic flow processes. The surface characteristics of CNT-Co, as revealed by SEM coupled with energy dispersive spectroscopy, evidently confirmed that As was adsorbed on the passive layer surface. The results of an investigation using sequential extraction revealed that the binding between As^{5+} and soil particles was shifted considerably from strong binding forms, i.e., Fe–Mn oxide, organic, and residual, to weak binding forms, i.e., exchange and carbonate, after electrochemical remediation.

Han et al. [180] investigated the feasibility of enhancing the electrochemical remediation of Cu-contaminated kaolinite by coupling with a PRB made of carbonized foods waste (CFW). The CFW is composed of more than 85% oxygen, calcium and carbon. The size range of the CFW is 75–150 μm within porous structures. The specific area, total pore volume, and average pore diameter of CFW were determined to be 14.16 m^2/g , 46.9 mm^3/g , and 132.4 \AA , respectively. The sorption efficiency of CFW used as a PRB reactive medium was found to be 4–8 times more efficient than that of zeolite. Throughout the experiment, an electrical gradient of 1 V/cm was implemented and acetic acid was injected from the anode to improve the remediation efficiency. Their results indicate the installation of a CFW PRB did not influence the electroosmotic flow. However, the electroosmotic flow was increased by the injection of CH_3COOH with time. The majority of Cu^{2+} extracted from kaolinite was sorbed by CFW.

5.3.4. PRB – summary

The remediation efficiency of electrochemical remediation can be enhanced by coupling with a PRB. Depending on the type of contaminant to be treated, different reactive media of the PRB can be utilized. However, experimental results from different researchers

to date indicate the remediation efficiency is primarily contributed by the sorption capacity of the reactive medium of the PRB. The role of electrochemical remediation lies in the migration of contaminants towards the PRB, generation of an acidic environment near the anode, and generation of an alkaline environment near the cathode. However, the sorption capacity of the reactive medium of the PRB can be promoted by the acidity or alkalinity of the environment to improve the remediation efficiency.

5.4. Phytoremediation

Phytoremediation is the use of plants to remove, degrade, or sequester inorganic and organic contaminants from soil and/or groundwater [8]. It is an emerging cost-effective alternative to conventional remediation technologies. However, contaminants may have limited bioavailability in the soil, methods to facilitate its transport to the shoots and roots of plants are thus required for successful application of phytoremediation.

O'Connor et al. [181] investigated the use of coupling phytoremediation with electrochemical remediation to decontaminate soils contaminated by Cu, Cd, and As. It can be observed in their results that the dc electric field could transport metal contaminants from the anode towards the cathode, and generate significant changes in soil pH. Moreover, perennial ryegrass could be grown in the treated soils to take up a proportion of the mobilized metals into its shoot system.

In their bench-scale studies, Lim et al. [182] demonstrated the effectiveness of Indian mustard (*Brassica juncea*) grown in contaminated soil in accumulating high tissue concentration of Pb, with the addition of EDTA in the soil and the application of a dc electric field around the plants. The accumulation of Pb in the shoots using EDTA and a dc electric field was increased by two- to fourfold that of using EDTA only. Similarly, the shoot Cu concentrations of ryegrass in the phytoremediation of contaminated soil enhanced by EDTA and EDDS was increased by 46% and 61%, respectively when coupled with electrochemical remediation [183].

Aboughalma et al. [184] studied the use of potato tubers to decontaminate soils polluted with Zn, Pb, Cu, and Cd in their laboratory-scale experiments using: (1) a dc electric field; (2) an alternating-current (ac) electric field; and (3) no electric field, i.e., the control. Their results reveal that metal accumulation in plant roots treated with electrical fields was generally higher than the control. The overall metal uptake in plant shoots treated with a dc electric field was lower than those treated with an ac electric field and the control, although there was a higher accumulation of Zn and Cu in the plant roots treated with electrical fields. The Zn uptake in plant shoots treated with an ac electric field was higher than that treated with a dc electric field and the control. Zn and Cu accumulation in plant roots treated with a dc electric field and an ac electric field were similar and higher than that of the control.

Bi et al. [185] studied the growth of rapeseed (*Brassica napus*) plants and tobacco (*Nicotiana tabacum*) plants under a dc electric field and an ac electric field and their abilities to decontaminate a soil contaminated by Cd, and a soil contaminated by Cd, Zn, and Pb. Their results reveal that the biomass production of rapeseed plants was enhanced by the ac electric field. However, the ac electric field has no effect on the biomass production of tobacco plants and the dc electric field even has a negative effect. Moreover, metal uptake by the rapeseed plant shoot was enhanced by the application of the ac electric field.

Cang et al. [186] studied the effects of dc electric current on the growth of Indian mustard (*B. juncea*) and speciation of soil heavy metals in pot experiments for 35 days. The soil was contaminated by Cd, Cu, Pb, and Zn. Their results indicate that plant uptake of metals was increased by the electrokinetics-assisted phytoremediation. Moreover, electrical gradient was identified to be the most

important factor in affecting the plant growth, soil properties, and metal concentrations in the soil and plant.

5.5. Ultrasonication

Acoustic waves or acoustic energy can enhance migration of contaminants in soil and facilitate their subsequent remediation and/or removal by these effects: (1) increase in kinetic energy of soil pore fluid, causing rise in temperature, and increase in volume and pressure of the soil pore fluid; (2) decrease in viscosity of soil pore fluid, increasing the volume flow rate of the soil pore fluid; (3) increase in molecular motion of contaminants, inducing disintegration and mobilization of contaminants sorbed on soil particle surfaces; and (4) cavitation (forming bubbles) in soil pore fluid, causing increase in porosity and hydraulic conductivity of soil [187].

Chung and Kamon [187] studied the performance of electrochemical remediation coupled with ultrasonication on simultaneous remediation of Pb and phenanthrene from contaminated natural clay. Their bench-scale experiments were conducted using specially designed and fabricated devices. Their experimental results reveal that both the fluid outflow rate and remediation efficiencies for both heavy metal and PAH were increased by the coupled remediation technologies in comparison to electrochemical remediation alone. The average outflow rate was increased from 120 mL/h to 143 mL/h, an increase of 19% by the coupling effects of electrokinetic and ultrasonic phenomena. The average remediation efficiency for Pb was increased from 88% to 91%, an increase of 3.4%; and the average remediation efficiency for phenanthrene was increased from 85% to 90%, an increase of 5.9%.

Chung [188] evaluated the performance of four remediation technologies, i.e., soil flushing, electrochemical remediation, ultrasonication, and electrochemical remediation coupled with ultrasonication, in the remediation of river sand from Korea contaminated by diesel fuel and Cd. His results indicate the coupled remediation technologies increased both the volume flow rate and contaminant extraction efficiencies. After 100 min, the final accumulated flow volume was 2200 mL, 2400 mL, 3800 mL, and 4000 mL by soil flushing, electrochemical remediation, ultrasonication, and electrochemical remediation coupled with ultrasonication, respectively. The final accumulated flow volume was thus increased by 9%, 73%, and 82% by electrochemical remediation, ultrasonication, and electrochemical remediation coupled with, ultrasonication, respectively. The remediation efficiencies for diesel fuel were 65%, 67%, 85%, and 87% by soil flushing, electrochemical remediation, ultrasonication, and electrochemical remediation coupled with ultrasonication, respectively. Similarly, the remediation efficiencies for Cd were 62%, 76%, 65%, and 83%, respectively. It is evident that electrochemical remediation coupled with ultrasonication is the most effective technique to extract heavy metal and hydrocarbon simultaneously from the contaminated sandy soil. Moreover, electrochemical remediation was observed to be the most effective method for the treatment of heavy metal, e.g., Cd, while ultrasonic remediation was the most effective for hydrocarbon, e.g., diesel fuel. As a result, the coupled techniques can be used effectively to extract both the heavy metal and hydrocarbon from contaminated soils simultaneously.

Pham et al. [189] studied the performance of electrochemical remediation enhanced by ultrasonication in the cleanup of kaolin contaminated by a mixture of three persistent organic pollutants: HCB, phenanthrene, and fluoranthene. Their bench-scale experimental results conclude that the remediation efficiencies for these three persistent organic pollutants by electrochemical remediation coupled with ultrasonication was higher than those of electrochemical remediation alone. Although the ultrasonic enhancement could increase both the electric current intensity and electroos-

motric volume flow rate, it could only increase the remediation efficiency for less than 10%. HCB is the most difficult contaminant to extract because of its high stability, while fluoranthene is the easiest contaminant to extract. Enhancement of electrochemical remediation by ultrasonication can be considered as one of the feasible technology to extract PAHs from contaminated soil.

Pham et al. [162] studied the feasibility of using electrochemical remediation enhanced by ultrasonication or the surfactant 2-hydroxypropyl- β -cyclodextrin to remediate soil contaminated by the hydrophobic compounds of HCB and phenanthrene. Their results indicate that both contaminants could be mobilized by electrochemical remediation enhanced by either ultrasonication or surfactant. However, it is more difficult to extract HCB because of its stability and low water-solubility. Moreover, remediation of phenanthrene enhanced by ultrasonication was more efficient than that by surfactant, as ultrasound can degrade the contaminant through oxidation by free radicals.

Shrestha et al. [190] utilized electrochemical remediation coupled with ultrasonication to treat kaolin contaminated by chrysene of concentrations of 25, 50, 75, and 100 mg/kg. Their results indicate the coupled technologies could improve the remediation efficiency of electrochemical remediation. Moreover, the remediation efficiency decreased with increase in the initial concentration of chrysene.

5.6. Other remediation technologies

There are many mature remediation technologies for contaminated soil and groundwater [8,105], and they can potentially be coupled with electrochemical remediation to enhance their individual remediation efficiencies synergistically. However, these possibilities have yet to be investigated.

For example, production of electrochemical oxidation equivalents *in situ* by inserting anodes in contaminated soil appears to be a promising idea, but the approach is proven to have poor remediation efficiency and the effects are much localized in soil. However, *in situ* production of oxidants has many advantages: (1) oxidants of short lifetimes can be used in the remediation process; (2) no stabilization of peroxides is necessary; (3) the hazard of storing large quantities of chemicals is avoided; and (4) logistics of handling chemicals is much simpler. A new approach is being investigated by Wesner et al. [191] to separate the *in situ* production of tailored oxidants and the transport of the oxidants by electrokinetics.

Thermal desorption is a technology that heats contaminated soil or sludge *in situ* or *ex situ* to volatilize the contaminants and remove them from soil [8]. Volatile and semi-volatile organics are removed from contaminated soil in thermal desorbers at 100–300 °C for low-temperature thermal desorption, or at 300–550 °C for high-temperature thermal desorption [192]. When a dc or ac electrical current is flowing through a contaminated soil, resistive or ohmic heating occurs. The heating can be used to accelerate many chemical and biological reactions occurring in the contaminated soil, and to modify many physical properties of contaminants. For example, heating can be used to increase desorption of many organic contaminants from soil particle surfaces and to remove dense non-aqueous phase liquids. Increased temperature may increase the aqueous solubility, decrease the density, decrease the viscosity, and increase the volatilization of organic contaminants, facilitating their transport in soil. Elevated temperatures not exceeding the temperature tolerance of microbial consortia can increase their metabolic activity and bioavailability, resulting in enhancement of biodegradation of organic contaminants. However, these thermal effects during electrochemical remediation have not been well studied to date [193].

6. Conclusions

Electrochemical remediation is a promising technology for the remediation of fine-grained soil contaminated by inorganic, organic, and mixed contaminants. However, enhancement techniques are often required to improve the remediation efficiency of the technology. A comprehensive review on techniques to enhance electrochemical remediation of contaminated fine-grained materials is given in this paper. A comprehensive and updated list of references is also provided for the reader who is interested in a particular enhancement technique to perform further study.

Acknowledgements

The sabbatical leave of the first author in California supported by the Faculty of Engineering of The University of Hong Kong to complete these review papers is appreciated. The financial support for the doctoral study of the second author provided by The University of Hong Kong is gratefully acknowledged.

References

- A.T. Yeung, Electrokinetic flow processes in porous media and their applications, in: M.Y. Corapcioglu (Ed.), *Advances in Porous Media*, vol. 2, Elsevier, Amsterdam, 1994, pp. 309–395.
- A.T. Yeung, Y.-Y. Gu, Use of chelating agents in electrochemical remediation of contaminated soil, in: D.C.W. Tsang, I.M.C. Lo (Eds.), *Applications of Chelating Agents for Land Decontamination Technologies*, ASCE Press, Reston, 2011.
- J.K. Mitchell, K. Soga, *Fundamentals of Soil Behavior*, 3rd ed., John Wiley & Sons, Hoboken, 2005.
- A.T. Yeung, Milestone developments, myths, and future directions of electrokinetic remediation, *Sep. Purif. Technol.* 79 (2011) 124–132.
- A.T. Yeung, Fundamental aspects of prolonged electrokinetic flows in kaolinites, *Geomech. Geoenviron. Eng.* 1 (2006) 13–25.
- A.T. Yeung, Geochemical processes affecting electrochemical remediation, in: K.R. Reddy, C. Cameselle (Eds.), *Electrochemical Remediation Technologies for Polluted Soils, Sediments and Groundwater*, John Wiley & Sons, Hoboken, 2009, pp. 65–94.
- A.T. Yeung, Contaminant extractability by electrokinetics, *Environ. Eng. Sci.* 23 (2006) 202–224.
- A.T. Yeung, Remediation technologies for contaminated sites, in: Y. Chen, X. Tang, L. Zhan (Eds.), *Advances in Environmental Geotechnics*, Zhejiang University Press, Hangzhou, 2009, pp. 328–369.
- G. Sposito, On points of zero charge, *Environ. Sci. Technol.* 32 (1998) 2815–2819.
- D. Lestan, B. Kos, Soil washing using a biodegradable chelator, in: B. Nowack, J.M. VanBriesen (Eds.), *Biogeochemistry of Chelating Agents*, ACS Symposium Series 910, American Chemical Society, Washington, DC, 2005, pp. 383–397.
- Y.-Y. Gu, A.T. Yeung, Desorption of cadmium from a natural Shanghai clay using citric acid industrial wastewater, *J. Hazard. Mater.* 191 (2011) 144–149.
- Y.-Y. Gu, A.T. Yeung, A. Koenig, H.-J. Li, Effects of chelating agents on zeta potential of cadmium-contaminated natural clay, *Sep. Sci. Technol.* 44 (2009) 2203–2222.
- M. Sillanpaa, A. Oikari, Assessing the impact of complexation by EDTA and DTPA on heavy metal toxicity using Microtox bioassay, *Chemosphere* 32 (1996) 1485–1497.
- N. Dirilgen, Effects of pH and chelator EDTA on Cr toxicity and accumulation in *Lemna minor*, *Chemosphere* 37 (1998) 771–783.
- B. Nortemann, Biodegradation of EDTA, *Appl. Microbiol. Biotechnol.* 51 (1999) 751–759.
- D. Lestan, C.L. Luo, X.D. Li, The use of chelating agents in the remediation of metal-contaminated soils: a review, *Environ. Pollut.* 153 (2008) 3–13.
- C.D. Cox, M.A. Shoosmith, M.M. Ghosh, Electrokinetic remediation of mercury-contaminated soils using iodine/iodide lixiviant, *Environ. Sci. Technol.* 30 (1996) 1933–1938.
- K.R. Reddy, C. Chaparro, R.E. Saichek, Removal of mercury from clayey soils using electrokinetics, *J. Environ. Sci. Health A – Tox. Hazard. Subst. Environ. Eng.* 38 (2003) 307–338.
- P. Suær, T. Lifvergren, Mercury-contaminated soil remediation by iodide and electroreclamation, *J. Environ. Eng., ASCE* 129 (2003) 441–446.
- Z.M. Shen, J.D. Zhang, L.Y. Qu, Z.Q. Dong, S.S. Zheng, W.H. Wang, A modified EK method with an I⁻/I₂ lixiviant assisted and approaching cathodes to remedy mercury contaminated field soils, *Environ. Geol.* 57 (2009) 1399–1407.
- T. Hakansson, P. Suer, B. Mattiasson, B. Allard, Sulphate reducing bacteria to precipitate mercury after electrokinetic soil remediation, *Int. J. Environ. Sci. Technol.* 5 (2008) 267–274.
- O. Hanay, H. Hasar, N.N. Kocer, O. Ozdemir, Removal of Pb from sewage sludge by electrokinetics: effect of pH and washing solution type, *Environ. Technol.* 30 (2009) 1177–1185.
- G.N. Kim, Y.H. Jung, J.J. Lee, J.K. Moon, C.H. Jung, An analysis of a flushing effect on the electrokinetic-flushing removal of cobalt and cesium from a soil around decommissioning site, *Sep. Purif. Technol.* 63 (2008) 116–121.
- L.M. Rajic, B.D. Dalmacija, J.S. Trickovic, M.B. Dalmacija, D.M. Krcmar, Behavior of zinc, nickel, copper and cadmium during the electrokinetic remediation of sediment from the Great Backa Canal (Serbia), *J. Environ. Sci. Health A – Tox. Hazard. Subst. Environ. Eng.* 45 (2010) 1134–1143.
- D.M. Zhou, L. Cang, A.N. Alshawabkeh, Y.J. Wang, X.Z. Hao, Pilot-scale electrokinetic treatment of a Cu contaminated red soil, *Chemosphere* 63 (2006) 964–971.
- K. Maturi, K.R. Reddy, Simultaneous removal of organic compounds and heavy metals from soils by electrokinetic remediation with a modified cyclodextrin, *Chemosphere* 63 (2006) 1022–1031.
- S.O. Ko, M.A. Schlautman, E.R. Carraway, Cyclodextrin-enhanced electrokinetic removal of phenanthrene from a model clay soil, *Environ. Sci. Technol.* 34 (2000) 1535–1541.
- A.P. Khodadoust, K.R. Reddy, O. Narla, Cyclodextrin-enhanced electrokinetic remediation of soils contaminated with 2,4-dinitrotoluene, *J. Environ. Eng., ASCE* 132 (2006) 1043–1050.
- S.H. Yuan, M. Tian, X.H. Lu, Electrokinetic movement of hexachlorobenzene in clayed soils enhanced by Tween 80 and beta-cyclodextrin, *J. Hazard. Mater.* 137 (2006) 1218–1225.
- T.P. Li, S.H. Yuan, J.Z. Wan, L. Lin, H.Y. Long, X.F. Wu, X.H. Lu, Pilot-scale electrokinetic movement of HCB and Zn in real contaminated sediments enhanced with hydroxypropyl-β-cyclodextrin, *Chemosphere* 76 (2009) 1226–1232.
- T.P. Li, S.H. Yuan, J.Z. Wan, X.H. Lu, Hydroxypropyl-β-cyclodextrin enhanced electrokinetic remediation of sediment contaminated with HCB and heavy metals, *J. Hazard. Mater.* 176 (2010) 306–312.
- C.L. Wan, M.A. Du, D.J. Lee, X. Yang, W.C. Ma, L.N. Zheng, Electrokinetic remediation and microbial community shift of β-cyclodextrin-dissolved petroleum hydrocarbon-contaminated soil, *Appl. Microbiol. Biotechnol.* 89 (2011) 2019–2025.
- J.L. Chen, S.F. Yang, C.C. Wu, S. Ton, Effect of ammonia as a complexing agent on electrokinetic remediation of copper-contaminated soil, *Sep. Purif. Technol.* 79 (2011) 157–163.
- S.C. Lin, Biosurfactants: recent advances, *J. Chem. Technol. Biotechnol.* 66 (1996) 109–120.
- C.N. Mulligan, R.N. Yong, B.F. Gibbs, Surfactant-enhanced remediation of contaminated soil: a review, *Eng. Geol.* 60 (2001) 371–380.
- E. Ruckenstein, S. Nagarajan, Critical micelle concentration – transition point for micellar size distribution, *J. Phys. Chem.* 79 (1975) 2622–2626.
- W. Chu, C.Y. Kwan, Remediation of contaminated soil by solvent/surfactant system, *Chemosphere* 53 (2003) 9–15.
- C.N. Mulligan, F. Eftekhari, Remediation with surfactant foam of PCP-contaminated soil, *Eng. Geol.* 70 (2003) 269–279.
- D. Fabbri, A. Crime, M. Davezza, C. Medana, C. Baiocchi, A.B. Prevot, E. Pramauro, Surfactant-assisted removal of swep residues from soil and photocatalytic treatment of the washing wastes, *Appl. Catal. B – Environ.* 92 (2009) 318–325.
- C.N. Mulligan, Recent advances in the environmental applications of biosurfactants, *Curr. Opin. Colloid Interface Sci.* 14 (2009) 372–378.
- R.A. Doong, Y.W. Wu, W.G. Lei, Surfactant enhanced remediation of cadmium contaminated soils, *Water Sci. Technol.* 37 (1998) 65–71.
- J.H. Harwell, Factors affecting surfactant performance in groundwater remediation applications, in: D.A. Sabitini, R.C. Knox (Eds.), *Transport and Remediation of Subsurface Contaminants: Colloidal, Interfacial, and Surfactant Phenomena*, ACS Symposium Series 491, American Chemical Society, Washington, DC, 1992, pp. 124–132.
- D.A. Sabitini, R.C. Knox, J.H. Harwell, Emerging technologies in surfactant-enhanced subsurface remediation, in: D.A. Sabitini, R.C. Knox, J.H. Harwell (Eds.), *Surfactant-enhanced Subsurface Remediation: Emerging Technologies*, ACS Symposium Series 594, American Chemical Society, Washington, DC, 1995, pp. 1–9.
- D.G. Cooper, Biosurfactants, *Microbiol. Sci.* 3 (1986) 145–149.
- C.C. West, J.H. Harwell, Surfactant and subsurface remediation, *Environ. Sci. Technol.* 26 (1992) 2324–2330.
- J.D. Desai, I.M. Banat, Microbial production of surfactants and their commercial potential, *Microbiol. Mol. Biol. Rev.* 61 (1997) 47–64.
- E.Z. Ron, E. Rosenberg, Biosurfactants and oil bioremediation, *Curr. Opin. Biotechnol.* 13 (2002) 249–252.
- S. Mukherjee, P. Das, R. Sen, Towards commercial production of microbial surfactants, *Trends Biotechnol.* 24 (2006) 509–515.
- K. Muthusamy, S. Gopalakrishnan, T.K. Ravi, P. Sivachidambaram, Biosurfactants: properties, commercial production and application, *Curr. Sci.* 94 (2008) 736–747.
- G. Soberón-Chávez, F. Lépine, E. Déziel, Production of rhamnolipids by *Pseudomonas aeruginosa*, *Appl. Microbiol. Biotechnol.* 68 (2005) 718–725.
- Y. Uchida, R. Tsuchiya, M. Chino, J. Hirano, T. Tabuchi, Extracellular accumulation of mono- and di-succinoyl trehalose lipids by a strain of *Rhodococcus erythropolis* grown on n-alkanes, *Agric. Biol. Chem.* 53 (1989) 757–763.
- Y. Hirata, M. Ryua, Y. Odaa, K. Igarashia, A. Nagatsukaa, T. Furutaa, M. Sugiuraa, Novel characteristics of sophorolipids, yeast glycolipid biosurfactants, next term as biodegradable low-foaming surfactants, *J. Biosci. Bioeng.* 108 (2009) 142–146.
- G.S. Kiran, T.A. Thomas, J. Selvin, B. Sabarathnam, A.P. Lipton, Optimization and characterization of a new lipopeptide biosurfactant produced by marine

- Brevibacterium aureum* MSA13 in solid state culture, *Bioresour. Technol.* 101 (2010) 2389–2396.
- [54] T.H. Nielsen, J. Sorensen, Production of cyclic lipopeptides by *Pseudomonas fluorescens* strains in bulk soil and in the sugar beet rhizosphere, *Appl. Environ. Microbiol.* 69 (2003) 861–868.
- [55] J.M. Raaijmakers, I. De Bruijn, M.J.D. De Kock, Cyclic lipopeptide production by plant-associated *Pseudomonas* spp.: diversity, activity, biosynthesis, and regulation, *Mol. Plant-Microbe Interact.* 19 (2006) 699–710.
- [56] C.S. Jeon, J.S. Yang, K.J. Kim, K. Baek, Electrokinetic removal of petroleum hydrocarbon from residual clayey soil following a washing process, *Clean-Soil Air Water* 38 (2010) 189–193.
- [57] K.R. Reddy, R.E. Saichek, Effect of soil type on electrokinetic removal of phenanthrene using surfactants and cosolvents, *J. Environ. Eng., ASCE* 129 (2003) 336–346.
- [58] R.E. Saichek, K.R. Reddy, Surfactant-enhanced electrokinetic remediation of polycyclic aromatic hydrocarbons in heterogeneous subsurface environments, *J. Environ. Eng. Sci.* 4 (2005) 327–339.
- [59] J.W. Yang, Y.J. Lee, J.Y. Park, S.J. Kim, J.Y. Lee, Application of APG and Calfax 16L-35 on surfactant-enhanced electrokinetic removal of phenanthrene from kaolinite, *Eng. Geol.* 77 (2005) 243–251.
- [60] J.Y. Park, H.H. Lee, S.J. Kim, Y.J. Lee, J.W. Yang, Surfactant-enhanced electrokinetic removal of phenanthrene from kaolinite, *J. Hazard. Mater.* 140 (2007) 230–236.
- [61] J.H. Chang, Z.M. Qiang, C.P. Huang, A.V. Ellis, Phenanthrene removal in unsaturated soils treated by electrokinetics with different surfactants-Triton X-100 and rhamnolipid, *Colloids Surf. A* 348 (2009) 157–163.
- [62] M.T. Alcántara, J. Gómez, M. Pazos, M.A. Sanromán, Electrokinetic remediation of PAH mixtures from kaolin, *J. Hazard. Mater.* 179 (2010) 1156–1160.
- [63] T.D. Pham, R.A. Shrestha, M. Sillanpaa, Removal of hexachlorobenzene and phenanthrene from clayey soil by surfactant- and ultrasound-assisted electrokinetics, *J. Environ. Eng., ASCE* 136 (2010) 739–742.
- [64] K.R. Reddy, C. Cameselle, P. Ala, Integrated electrokinetic-soil flushing to remove mixed organic and metal contaminants, *J. Appl. Electrochem.* 40 (2010) 1269–1279.
- [65] C. Yuan, C.H. Hung, W.L. Huang, Enhancement with carbon nanotube barrier on 1,2-dichlorobenzene removal from soil by surfactant-assisted electrokinetic (SAEK) process – the effect of processing fluid, *Sep. Sci. Technol.* 44 (2009) 2284–2303.
- [66] A. Karagunduz, A. Gezer, G. Karasuloglu, Surfactant enhanced electrokinetic remediation of DDT from soils, *Sci. Total Environ.* 385 (2007) 1–11.
- [67] C. Yuan, C.H. Weng, Remediating ethylbenzene-contaminated clayey soil by a surfactant-aided electrokinetic (SAEK) process, *Chemosphere* 57 (2004) 225–232.
- [68] A.Y. Kolosov, K.I. Popov, N.A. Shabanova, A.A. Artemeva, B.M. Kogut, A.S. Frid, V.Y. Zelvenskii, E.M. Urinovich, Electrokinetic removal of hydrophobic organic compounds from soil, *Russian J. Appl. Chem.* 74 (2001) 631–635.
- [69] J. Kim, K. Lee, Effects of electric field directions on surfactant enhanced electrokinetic remediation of diesel-contaminated sand column, *J. Environ. Sci. Health A – Tox. Hazard. Subst. Environ. Eng.* 34 (1999) 863–877.
- [70] H. Han, Y.J. Lee, S.H. Kim, J.W. Yang, Electrokinetic remediation of soil contaminated with diesel oil using EDTA-cosolvent solutions, *Sep. Sci. Technol.* 44 (2009) 2437–2454.
- [71] O. Gonzini, A. Plaza, L. Di Palma, M.C. Lobo, Electrokinetic remediation of gasoil contaminated soil enhanced by rhamnolipid, *J. Appl. Electrochem.* 40 (2010) 1239–1248.
- [72] A. Groboillot, F. Portet-Koltalo, F. Le Derf, M.J.G. Feuilloley, N. Orange, C.D. Poc, Novel application of cyclolipopeptide amphiphilic feasibility study as additive to remediate polycyclic aromatic hydrocarbon (PAH) contaminated sediments, *Int. J. Mol. Sci.* 12 (2011) 1787–1806.
- [73] A. Kaya, Y. Yukselen, Zeta potential of soils with surfactants and its relevance to electrokinetic remediation, *J. Hazard. Mater.* 120 (2005) 119–126.
- [74] C.H. Weng, C. Yuan, Removal of Cr(III) from clay soils by electrokinetics, *Environ. Geochem. Health* 23 (2001) 281–285.
- [75] P.W. Chang, Y.C. Tan, I.S. Wang, On-farm remediation and fertility enhancement of cadmium-contaminated silt loam by electrokinetic treatment process in Taiwan, *Irrigation Drain.* 57 (2008) 187–201.
- [76] A. Giannis, E. Gidarakos, A. Skouta, Application of sodium dodecyl sulfate and humic acid as surfactants on electrokinetic remediation of cadmium-contaminated soil, *Desalination* 211 (2007) 249–260.
- [77] R.K. Srivastava, R.P. Tiwari, P. Bala Ramudu, Removal of cadmium using electrokinetics – effect of enhancement agents, in: *Proc. 1st Sri Lankan Geotech. Soc. Int. Conf. Soil Rock Eng., Colombo*, 2007.
- [78] R.E. Saichek, K.R. Reddy, Effects of system variables on surfactant enhanced electrokinetic removal of polycyclic aromatic hydrocarbons from clayey soils, *Environ. Technol.* 24 (2003) 503–515.
- [79] J.Z. Wan, S.H. Yuan, J. Chen, T.P. Li, L. Lin, X.H. Lu, Solubility-enhanced electrokinetic movement of hexachlorobenzene in sediments: a comparison of cosolvent and cyclodextrin, *J. Hazard. Mater.* 166 (2009) 221–226.
- [80] A. Li, K.A. Cheung, K.R. Reddy, Cosolvent-enhanced electrokinetic remediation of soils contaminated with phenanthrene, *J. Environ. Eng., ASCE* 126 (2000) 527–533.
- [81] K.R. Reddy, P.R. Ala, S. Sharma, S.N. Kumar, Enhanced electrokinetic remediation of contaminated manufactured gas plant soil, *Eng. Geol.* 85 (2006) 132–146.
- [82] K. Maturi, K.R. Reddy, Cosolvent-enhanced desorption and transport of heavy metals and organic contaminants in soils during electrokinetic remediation, *Water Air Soil Pollut.* 189 (2008) 199–211.
- [83] T.F. Coletta, C.J. Bruell, D.K. Ryan, H.I. Inyang, Cation-enhanced removal of lead from kaolinite by electrokinetics, *J. Environ. Eng., ASCE* 123 (1997) 1227–1233.
- [84] K.R. Reddy, S. Chinthamreddy, Enhanced electrokinetic remediation of heavy metals in glacial till soils using different electrolyte solutions, *J. Environ. Eng., ASCE* 130 (2004) 442–455.
- [85] R.J. Hunter, *Zeta Potential in Colloid Science: Principles and Applications*, Academic Press, London, 1981.
- [86] A.T. Yeung, Diffuse double layer equations in SI units, *J. Geotech. Eng., ASCE* 118 (1992) 2000–2005.
- [87] S.K. Puppala, A.N. Alshawabkeh, Y.B. Acar, R.J. Gale, M. Bricka, Enhanced electrokinetic remediation of high sorption capacity soil, *J. Hazard. Mater.* 55 (1997) 203–220.
- [88] H.H. Lee, J.W. Yang, A new method to control electrolytes pH by circulation system in electrokinetic soil remediation, *J. Hazard. Mater.* 77 (2000) 227–240.
- [89] R.E. Saichek, K.R. Reddy, Effect of pH control at the anode for the electrokinetic removal of phenanthrene from kaolin soil, *Chemosphere* 51 (2003) 273–287.
- [90] R.E. Hicks, S. Tondorf, Electrorestoration of metal contaminated soils, *Environ. Sci. Technol.* 28 (1994) 2203–2210.
- [91] T. Rodsant, Y.B. Acar, G. Breedveld, Electrokinetic extraction of lead from spiked Norwegian marine clay, in: Y.B. Acar, D.E. Daniel (Eds.), *Characterization, Containment, Remediation, and Performance in Environmental Geotechnics*, *Geotech. Spec. Publ. No. 46, vol. 2*, ASCE, New York, 1995, pp. 1518–1534.
- [92] B.E. Reed, M.T. Berg, J.C. Thompson, J.H. Hatfield, Chemical conditioning of electrode reservoirs during electrokinetic soil flushing of Pb-contaminated silt loam, *J. Environ. Eng., ASCE* 121 (1995) 805–815.
- [93] D.M. Zhou, C.F. Deng, L. Cang, A.N. Alshawabkeh, Electrokinetic remediation of a Cu–Zn contaminated red soil by controlling the voltage and conditioning catholyte pH, *Chemosphere* 61 (2005) 519–527.
- [94] E. Gidarakos, A. Giannis, Chelate agents enhanced electrokinetic remediation for removal cadmium and zinc by conditioning catholyte pH, *Water Air Soil Pollut.* 172 (2006) 295–312.
- [95] B.G. Ryu, G.Y. Park, J.W. Yang, K. Baek, Electrolyte conditioning for electrokinetic remediation of As, Cu, and Pb-contaminated soil, *Sep. Purif. Technol.* 79 (2011) 170–176.
- [96] A. Genc, G. Chase, A. Foos, Electrokinetic removal of manganese from river sediment, *Water Air Soil Pollut.* 197 (2009) 131–141.
- [97] A.T. Yeung, C. Hsu, R.M. Menon, EDTA enhanced electrokinetic extraction of lead, *J. Geotech. Eng., ASCE* 122 (1996) 666–673.
- [98] A.T. Yeung, C. Hsu, Electrokinetic remediation of cadmium-contaminated clay, *J. Environ. Eng., ASCE* 131 (2005) 298–304.
- [99] R.W. Leinz, D.B. Hoover, D.L. Fey, D.B. Smith, T. Patterson, Electrogeochemical sampling with NEOCHIM – results of tests over buried gold deposits, *J. Geochem. Explor.* 61 (1998) 57–86.
- [100] R.W. Leinz, D.B. Hoover, A.L. Meier, NEOCHIM: an electrochemical method for environmental application, *J. Geochem. Explor.* 64 (1998) 421–434.
- [101] Z.M. Shen, X.J. Chen, J.P. Jia, L. Qu, W.H. Wang, Comparison of electrokinetic soil remediation methods using one fixed anode and approaching anodes, *Environ. Pollut.* 150 (2007) 193–199.
- [102] H.J. Lee, J.M. Choi, J.W. Cho, S.H. Moon, Characterization of anion exchange membranes fouled with humate during electro dialysis, *J. Membr. Sci.* 203 (2002) 115–126.
- [103] Z. Li, J.-W. Yu, I. Neretnieks, Electroremediation: removal of heavy metals from soils by using cation selective membrane, *Environ. Sci. Technol.* 32 (1998) 394–397.
- [104] W.S. Kim, S.O. Kim, K.W. Kim, Enhanced electrokinetic extraction of heavy metals from soils assisted by ion exchange membranes, *J. Hazard. Mater.* 118 (2005) 93–102.
- [105] F.A. Caliman, B.M. Robu, C. Smaranda, V.L. Pavel, M. Gavrilescu, Soil and groundwater cleanup: benefits and limits of emerging technologies, *Clean Technol. Environ. Policy* 13 (2011) 241–268.
- [106] N. Koprivanac, H. Kusic, AOP as an effective tool for the minimization of hazardous organic pollutants in colored wastewater; chemical and photochemical processes, in: A.A. Lewinsky (Ed.), *Hazardous Materials and Wastewater: Treatment, Removal and Analysis*, Nova Science Publishers, New York, 2007, pp. 149–200.
- [107] E. Neyens, J. Baeyens, A review of classic Fenton's peroxidation as an advanced oxidation technique, *J. Hazard. Mater.* 98 (2003) 33–50.
- [108] R.J. Watts, S. Kong, M. Dippre, W.T. Barnes, Oxidation of sorbed hexachlorobenzene in soils using catalysed hydrogen peroxide, *J. Hazard. Mater.* 39 (1994) 33–47.
- [109] R.J. Watts, P.C. Stanton, Mineralization of sorbed and NAPL-phase hexadecane by catalysed hydrogen peroxide, *Water Res.* 33 (1999) 1405–1414.
- [110] F.J. Rivas, Polycyclic aromatic hydrocarbons sorbed on soils: a short review of chemical oxidation based treatments, *J. Hazard. Mater.* 138 (2006) 234–251.
- [111] E. Ferrarese, G. Andreottola, I.A. Oprea, Remediation of PAH-contaminated sediments by chemical oxidation, *J. Hazard. Mater.* 152 (2008) 128–139.
- [112] G.C.C. Yang, Y.W. Long, Removal and degradation of phenol in a saturated flow by in-situ electrokinetic remediation and Fenton-like process, *J. Hazard. Mater.* 69 (1999) 259–271.

- [113] G.C.C. Yang, C.Y. Liu, Remediation of TCE contaminated soils by in situ EK-Fenton process, *J. Hazard. Mater.* 85 (2001) 317–331.
- [114] S.S. Kim, J.H. Kim, S.J. Han, Application of the electrokinetic-Fenton process for the remediation of kaolinite contaminated with phenanthrene, *J. Hazard. Mater.* 118 (2005) 121–131.
- [115] J.H. Kim, S.J. Han, S.S. Kim, J.W. Yang, Effect of soil chemical properties on the remediation of phenanthrene-contaminated soil by electrokinetic-Fenton process, *Chemosphere* 63 (2006) 1667–1676.
- [116] J.H. Kim, S.S. Kim, J.W. Yang, Role of stabilizers for treatment of clayey soil contaminated with phenanthrene through electrokinetic-Fenton process – some experimental evidences, *Electrochim. Acta* 53 (2007) 1663–1670.
- [117] J.H. Kim, J.Y. Kim, S.S. Kim, Effect of H₂SO₄ and HCl in the anode purging solution for the electrokinetic-Fenton remediation of soil contaminated with phenanthrene, *J. Environ. Sci. Health A – Tox. Hazard. Subst. Environ. Eng.* 44 (2009) 1111–1119.
- [118] T. Alcántara, M. Pazos, S. Gouveia, C. Cameselle, M.A. Sanroman, Remediation of phenanthrene from contaminated kaolinite by electroremediation-Fenton technology, *J. Environ. Sci. Health A – Tox. Hazard. Subst. Environ. Eng.* 43 (2008) 901–906.
- [119] K.R. Reddy, M.R. Karri, Effect of oxidant dosage on integrated electrochemical remediation of contaminant mixtures in soils, *J. Environ. Sci. Health A – Tox. Hazard. Subst. Environ. Eng.* 43 (2008) 881–893.
- [120] A. Oonnittan, R.A. Shrestha, M. Sillanpaa, Effect of cyclodextrin on the remediation of hexachlorobenzene in soil by electrokinetic Fenton process, *Sep. Purif. Technol.* 64 (2009) 314–320.
- [121] T.T. Tsai, J. Sah, C.M. Kao, Application of iron electrode corrosion enhanced electrokinetic-Fenton oxidation to remediate diesel contaminated soils: a laboratory feasibility study, *J. Hydrol.* 380 (2010) 4–13.
- [122] A. Oonnittan, P. Isosaari, M. Sillanpaa, Oxidant availability in soil and its effect on HCB removal during electrokinetic Fenton process, *Sep. Purif. Technol.* 76 (2010) 146–150.
- [123] P. Isosaari, R. Piskonen, P. Ojala, S. Voipio, K. Eilola, E. Lehmus, M. Itavaara, Integration of electrokinetics and chemical oxidation for the remediation of creosote-contaminated clay, *J. Hazard. Mater.* 144 (2007) 538–548.
- [124] G.C.C. Yang, C.F. Yeh, Enhanced nano-Fe₃O₄/S₂O₈²⁻ oxidation of trichloroethylene in a clayey soil by electrokinetics, *Sep. Purif. Technol.* 79 (2011) 264–271.
- [125] K.R. Reddy, S. Chinthamreddy, Electrokinetic remediation of heavy metal-contaminated soils under reducing environments, *Waste Manage.* 19 (1999) 269–282.
- [126] A. Weeks, S. Pamukcu, Electrokinetically enhanced reduction of [Cr(VI)] in contaminated soils, in: *Proc. 15th Int. Conf. Soil Mech. Geotech. Eng.*, vols. 1–3, Istanbul, 2001, pp. 1935–1938.
- [127] M.F. DeFlaun, C.W. Condee, Electrokinetic transport of bacteria, *J. Hazard. Mater.* 55 (1997) 263–277.
- [128] H.S. Lee, K. Lee, Bioremediation of diesel-contaminated soil by bacterial cells transported by electrokinetics, *J. Microbiol. Biotechnol.* 11 (2001) 1038–1045.
- [129] L.Y. Wick, P.A. Mattle, P. Wattiau, H. Harms, Electrokinetic transport of PAH-degrading bacteria in model aquifers and soil, *Environ. Sci. Technol.* 38 (2004) 4596–4602.
- [130] A. Olszanowski, K. Piechowiak, The use of an electric field to enhance bacterial movement and hydrocarbon biodegradation in soils, *Polish J. Environ. Stud.* 15 (2006) 303–309.
- [131] L. Shi, S. Muller, H. Harms, L.Y. Wick, Factors influencing the electrokinetic dispersion of PAH-degrading bacteria in a laboratory model aquifer, *Appl. Microbiol. Biotechnol.* 80 (2008) 507–515.
- [132] J.H. Choi, S. Maruthamuthu, H.G. Lee, T.H. Ha, J.H. Bae, Nitrate removal by electro-bioremediation technology in Korean soil, *J. Hazard. Mater.* 168 (2009) 1208–1216.
- [133] U.N. Da Rocha, M.R. Totola, D.M.M. Pessoa, J.T. Araruna, J.C.L. Neves, A.C. Borges, Mobilisation of bacteria in a fine-grained residual soil by electrophoresis, *J. Hazard. Mater.* 161 (2009) 485–491.
- [134] K.Y. Lee, H.A. Kim, B.T. Lee, S.O. Kim, Y.H. Kwon, K.W. Kim, A feasibility study on bioelectrokinetics for the removal of heavy metals from tailing soil, *Environ. Geochem. Health* 33 (2011) 3–11.
- [135] K.Y. Lee, K.W. Kim, Heavy metal removal from shooting range soil by hybrid electrokinetics with bacteria and enhancing agents, *Environ. Sci. Technol.* 44 (2010) 9482–9487.
- [136] M. Elektorowicz, V. Boeva, Electrokinetic supply of nutrients in soil bioremediation, *Environ. Technol.* 17 (1996) 1339–1349.
- [137] M.F. Rabbi, B. Clark, R.J. Gale, E. Ozsü-Acar, J. Pardue, A. Jackson, In situ TCE bioremediation study using electrokinetic cometabolite injection, *Waste Manage.* 20 (2000) 279–286.
- [138] K.R. Reddy, S. Chinthamreddy, R.E. Saichek, T.J. Cutright, Nutrient amendment for the bioremediation of a chromium-contaminated soil by electrokinetics, *Energy Sources* 25 (2003) 931–943.
- [139] G. Lee, H. Ro, S. Lee, S. Lee, Electrokinetically enhanced transport of organic and inorganic phosphorus in a low permeability soil, *Geosci. J.* 10 (2006) 85–89.
- [140] S. Suni, E. Malinen, J. Kosonen, H. Silvennoinen, M. Romantschuk, Electrokinetically enhanced bioremediation of creosote-contaminated soil: laboratory and field studies, *J. Environ. Sci. Health A – Tox. Hazard. Subst. Environ. Eng.* 42 (2007) 277–287.
- [141] A. Tiehm, T. Augenstein, D. Ilieva, H. Schell, C. Weidlich, K.M. Mangold, Bio-electro-remediation: electrokinetic transport of nitrate in a flow-through system for enhanced toluene biodegradation, *J. Appl. Electrochem.* 40 (2010) 1263–1268.
- [142] C.A.B. Schmidt, M.C. Barbosa, M.D.S. de Almeida, A laboratory feasibility study on electrokinetic injection of nutrients on an organic, tropical, clayey soil, *J. Hazard. Mater.* 143 (2007) 655–661.
- [143] S.T. Lohner, D. Katzoreck, A. Tiehm, Electromigration of microbial electron acceptors and nutrients: (I) Transport in synthetic media, *J. Environ. Sci. Health A – Tox. Hazard. Subst. Environ. Eng.* 43 (2008) 913–921.
- [144] S.T. Lohner, D. Katzoreck, A. Tiehm, Electromigration of microbial electron acceptors and nutrients: (II) Transport in groundwater, *J. Environ. Sci. Health A – Tox. Hazard. Subst. Environ. Eng.* 43 (2008) 922–925.
- [145] W. Xu, C.P. Wang, H.B. Liu, Z.Y. Zhang, H.W. Sun, A laboratory feasibility study on a new electrokinetic nutrient injection pattern and bioremediation of phenanthrene in a clayey soil, *J. Hazard. Mater.* 184 (2010) 798–804.
- [146] W.A. Jackson, M.A. Jeon, J.H. Pardue, T. Anderson, Enhanced natural attenuation of perchlorate in soils using electrokinetic injection, in: *Bioremediation of Inorganic Compounds, Proc. 6th International In Situ On-Site Bioremediation Symposium*, vol. 9, San Diego, 2001, pp. 273–280.
- [147] X.Y. Fan, H. Wang, Q.S. Luo, J.W. Ma, X.H. Zhang, The use of 2D non-uniform electric field to enhance in situ bioremediation of 2,4-dichlorophenol-contaminated soil, *J. Hazard. Mater.* 148 (2007) 29–37.
- [148] X. Wu, A.N. Alshawabkeh, D.B. Gent, S.L. Larson, J.L. Davis, Lactate transport in soil by DC fields, *J. Geotech. Geoenviron. Eng.*, ASCE 133 (2007) 1587–1596.
- [149] A. Tiehm, S.T. Lohner, T. Augenstein, Effects of direct electric current and electrode reactions on vinyl chloride degrading microorganisms, *Electrochim. Acta* 54 (2009) 3453–3459.
- [150] T.T. Li, S.H. Guo, B. Wu, F.M. Li, Z.X. Niu, Effect of electric intensity on the microbial degradation of petroleum pollutants in soil, *J. Environ. Sci. – China* 22 (2010) 1381–1386.
- [151] L.Y. Wick, F. Buchholz, I. Fetzer, S. Kleinstueber, C. Hartig, L. Shi, A. Miltner, H. Harms, G.N. Pucci, Responses of soil microbial communities to weak electric fields, *Sci. Total Environ.* 408 (2010) 4886–4893.
- [152] S.H. Kim, H.Y. Han, Y.J. Lee, C.W. Kim, J.W. Yang, Effect of electrokinetic remediation on indigenous microbial activity and community within diesel contaminated soil, *Sci. Total Environ.* 408 (2010) 3162–3168.
- [153] P.L. Palmer, *Permeable treatment barriers*, in: *In situ Treatment Technology*, 2nd ed., Lewis Publishers, Boca Raton, 2001, pp. 459–482.
- [154] S.V. Ho, C.J. Athmer, P.W. Sheridan, A.P. Shapiro, Scale-up aspects of the Lasagna™ process for in situ soil decontamination, *J. Hazard. Mater.* 55 (1997) 39–60.
- [155] S.V. Ho, P.W. Sheridan, C.J. Athmer, M.A. Heitkamp, J.M. Brackin, D. Weber, P.H. Brodsky, Integrated in situ soil remediation technology: the Lasagna process, *Environ. Sci. Technol.* 29 (1995) 2528–2534.
- [156] S.V. Ho, C. Athmer, P.W. Sheridan, B.M. Hughes, R. Orth, D. McKenzie, P.H. Brodsky, A. Shapiro, R. Thornton, J. Salvo, D. Schultz, R. Landis, R. Griffith, S. Shoemaker, The Lasagna technology for in situ soil remediation. 1. Small field test, *Environ. Sci. Technol.* 33 (1999) 1086–1091.
- [157] S.V. Ho, C. Athmer, P.W. Sheridan, B.M. Hughes, R. Orth, D. McKenzie, P.H. Brodsky, A.M. Shapiro, T.M. Sivavec, J. Salvo, D. Schultz, R. Landis, R. Griffith, S. Shoemaker, The Lasagna technology for in situ soil remediation. 2. Large field test, *Environ. Sci. Technol.* 33 (1999) 1092–1099.
- [158] M. Roulier, M. Kemper, S. Al-Abed, L. Murdoch, P. Cluxton, J.-L. Chen, W. Davis-hoover, Feasibility of electrokinetic soil remediation in horizontal Lasagna™ cells, *J. Hazard. Mater.* 77 (2000) 161–176.
- [159] S.A. Jackman, G. Maini, A.K. Sharman, G. Sunderland, C.J. Knowles, Electrokinetic movement and biodegradation of 2,4-dichlorophenoxyacetic acid in silt soil, *Biotechnol. Bioeng.* 74 (2001) 40–48.
- [160] J.W. Ma, F.Y. Wang, Z.H. Huang, H. Wang, Simultaneous removal of 2,4-dichlorophenol and Cd from soils by electrokinetic remediation combined with activated bamboo charcoal, *J. Hazard. Mater.* 176 (2010) 715–720.
- [161] C.F. Chew, T.C. Zhang, In-situ remediation of nitrate contaminated groundwater by electrokinetics iron wall processes, *Water Sci. Technol.* 38 (1998) 135–142.
- [162] J.W. Moon, H.S. Moon, H. Kim, Y. Roh, Remediation of TCE-contaminated groundwater using zero valent iron and direct current: experimental results and electron competition model, *Environ. Geol.* 48 (2005) 805–817.
- [163] C. Yuan, The effect of Fe(0) on electrokinetic remediation of clay contaminated with perchloroethylene, *Water Sci. Technol.* 53 (2006) 91–98.
- [164] C.H. Weng, Y.T. Lin, T.Y. Lin, C.M. Kao, Enhancement of electrokinetic remediation of hyper-Cr(VI) contaminated clay by zero-valent iron, *J. Hazard. Mater.* 149 (2007) 292–302.
- [165] C. Yuan, T.S. Chiang, The mechanisms of arsenic removal from soil by electrokinetic process coupled with iron permeable reaction barrier, *Chemosphere* 67 (2007) 1533–1542.
- [166] L. Cang, D.M. Zhou, D.Y. Wu, A.N. Alshawabkeh, Coupling electrokinetics with permeable reactive barriers of zero-valent iron for treating a chromium contaminated soil, *Sep. Sci. Technol.* 44 (2009) 2188–2202.
- [167] J.Z. Wan, Z.R. Li, X.H. Lu, S.H. Yuan, Remediation of a hexachlorobenzene-contaminated soil by surfactant-enhanced electrokinetics coupled with microscale Pd/Fe PRB, *J. Hazard. Mater.* 184 (2010) 184–190.
- [168] Y.H. Shih, Y.C. Chen, M.Y. Chen, Y.T. Tai, C.P. Tso, Dechlorination of hexachlorobenzene by using nanoscale Fe and nanoscale Pd/Fe bimetallic particles, *Colloids Surf. A* 332 (2009) 84–89.

- [169] D.W.S. Faulkner, L. Hopkinson, A.B. Cundy, Electrokinetic generation of reactive iron-rich barriers in wet sediments: implications for contaminated land management, *Mineral. Mag.* 69 (2005) 749–757.
- [170] H.I. Chung, M. Lee, A new method for remedial treatment of contaminated clayey soils by electrokinetics coupled with permeable reactive barriers, *Electrochim. Acta* 52 (2007) 3427–3431.
- [171] T. Kimura, K.I. Takase, N. Terui, S. Tanaka, Ferritization treatment of copper in soil by electrokinetic remediation, *J. Hazard. Mater.* 143 (2007) 662–667.
- [172] S.S. Mandaokar, D.M. Dharmadhikari, S.S. Dara, Retrieval of heavy-metal ions from solution via ferritisation, *Environ. Pollut.* 83 (1994) 277–282.
- [173] E. Barrado, F. Prieto, M. Vega, F. Fernandez-Polanco, Optimization of the operational variables of a medium-scale reactor for metal-containing wastewater purification by ferrite formation, *Water Res.* 32 (1998) 3055–3061.
- [174] G. De Gioannis, A. Muntoni, R. Ruggeri, J.J.P. Zijlstra, Chromate adsorption in a transformed red mud permeable reactive barrier using electrokinesis, *J. Environ. Sci. Health A – Tox. Hazard. Subst. Environ. Eng.* 43 (2008) 969–974.
- [175] C. Yuan, C.H. Hung, K.C. Chen, Electrokinetic remediation of arsenate spiked soil assisted by CNT-Co barrier – the effect of barrier position and processing fluid, *J. Hazard. Mater.* 171 (2009) 563–570.
- [176] X.J. Peng, Y.H. Li, Z.K. Luan, Z.C. Di, H.Y. Wang, B.H. Tian, Z.P. Jia, Adsorption of 1,2-dichlorobenzene from water to carbon nanotubes, *Chem. Phys. Lett.* 376 (2003) 154–158.
- [177] Y. Yu, J.C. Yu, C.Y. Chan, Y.K. Che, J.C. Zhao, L. Ding, W.K. Ge, P.K. Wong, Enhancement of adsorption and photocatalytic activity of TiO₂ by using carbon nanotubes for the treatment of azo dye, *Appl. Catal. B – Environ.* 61 (2005) 1–11.
- [178] K. Yang, X.L. Wang, L.Z. Zhu, B.S. Xing, Competitive sorption of pyrene, phenanthrene, and naphthalene on multiwalled carbon nanotubes, *Environ. Sci. Technol.* 40 (2006) 5804–5810.
- [179] K. Yang, L.Z. Zhu, B.S. Xing, Adsorption of polycyclic aromatic hydrocarbons by carbon nanomaterials, *Environ. Sci. Technol.* 40 (2006) 1855–1861.
- [180] J.G. Han, K.K. Hong, Y.W. Kim, J.Y. Lee, Enhanced electrokinetic (E/K) remediation on copper contaminated soil by CFW (carbonized foods waste), *J. Hazard. Mater.* 177 (2010) 530–538.
- [181] C.S. O'Connor, N.W. Lepp, R. Edwards, G. Sunderland, The combined use of electrokinetic remediation and phytoremediation to decontaminate metal-polluted soils: a laboratory-scale feasibility study, *Environ. Monit. Assess.* 84 (2003) 141–158.
- [182] J.M. Lim, A.L. Salido, D.J. Butcher, Phytoremediation of lead using Indian mustard (*Brassica juncea*) with EDTA and electrokinesis, *Microchem. J.* 76 (2004) 3–9.
- [183] D.M. Zhou, H.F. Chen, L. Cang, Y. Wang, Ryegrass uptake of soil Cu/Zn induced by EDTA/EDDS together with a vertical direct-current electrical field, *Chemosphere* 67 (2007) 1671–1676.
- [184] H. Aboughalma, R. Bi, M. Schlaak, Electrokinetic enhancement on phytoremediation in Zn, Pb, Cu and Cd contaminated soil using potato plants, *J. Environ. Sci. Health A – Tox. Hazard. Subst. Environ. Eng.* 43 (2008) 926–933.
- [185] R. Bi, M. Schlaak, E. Siefert, R. Lord, H. Connolly, Influence of electrical fields (AC and DC) on phytoremediation of metal polluted soils with rapeseed (*Brassica napus*) and tobacco (*Nicotiana tabacum*), *Chemosphere* 83 (2011) 318–326.
- [186] L. Cang, Q.Y. Wang, D.M. Zhou, H. Xu, Effects of electrokinetic-assisted phytoremediation of a multiple-metal contaminated soil on soil metal bioavailability and uptake by Indian mustard, *Sep. Purif. Technol.* 79 (2011) 246–253.
- [187] H.I. Chung, M. Kamon, Ultrasonically enhanced electrokinetic remediation for removal of Pb and phenanthrene in contaminated soils, *Eng. Geol.* 77 (2005) 233–242.
- [188] H.I. Chung, Treatment of contaminated groundwater in sandy layer under river bank by electrokinetic and ultrasonic technology, *Water Sci. Technol.* 55 (2007) 329–338.
- [189] T.D. Pham, R.A. Shrestha, J. Virkutyte, M. Sillanpaa, Combined ultrasonication and electrokinetic remediation for persistent organic removal from contaminated kaolin, *Electrochim. Acta* 54 (2009) 1403–1407.
- [190] R.A. Shrestha, T.D. Pham, M. Sillanpaa, Electro ultrasonic remediation of polycyclic aromatic hydrocarbons from contaminated soil, *J. Appl. Electrochem.* 40 (2010) 1407–1413.
- [191] W. Wesner, A. Diamant, B. Schrammel, M. Unterberger, Electrosynthesis of oxidants and their electrokinetic distribution, in: K.R. Reddy, C. Cameselle (Eds.), *Electrochemical Remediation Technologies for Polluted Soils, Sediments and Groundwater*, John Wiley & Sons, Hoboken, 2009, pp. 473–482.
- [192] J.A. Soesilo, S.R. Wilson, *Site Remediation Planning and Management*, Lewis Publishers, Boca Raton, 1997.
- [193] G.J. Smith, Coupled electrokinetic-thermal desorption, in: K.R. Reddy, C. Cameselle (Eds.), *Electrochemical Remediation Technologies for Polluted Soils, Sediments and Groundwater*, John Wiley & Sons, Hoboken, 2009, pp. 505–535.