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Published in:
Reviews in Environmental Science and Bio/technology

Document Version:
Publisher's PDF, also known as Version of record

Queen's University Belfast - Research Portal:
Link to publication record in Queen's University Belfast Research Portal

MINI-REVIEW

Stability and performance enhancements of Electrokinetic-Fenton soil remediation

Y. S. Ng · B. Sen Gupta · M. A. Hashim

Abstract Electrokinetic process is a potential in situ soil remediation process which transports the contaminants via electromigration and electroosmosis. For organic compounds contaminated soil, Fenton's reagent is utilized as a flushing agent in electrokinetic process (Electrokinetic-Fenton) so that removal of organic contaminants could be achieved by in situ oxidation/destruction. However, this process is not applied widely in industries as the stability issue for Fenton's reagent is the main drawback. The aim of this mini review is to summarize the developments of Electrokinetic-Fenton process on enhancing the stability of Fenton's reagent and process efficiency in past decades. Generally, the enhancements are conducted via four paths: (1) chemical stabilization to delay H_2O_2 decomposition, (2) increase of oxidant availability by monitoring injection method for Fenton's reagent, (3) electrodes operation and iron catalysts and (4) operating conditions such as voltage gradient, electrolytes and H_2O_2 concentration. In addition, the types of soils and contaminants are also showing significant effect as the soil with low acid buffering capacity, adequate iron concentration, low organic matter content and low aromatic ring organic contaminants generally gives better efficiency.

1 Introduction

Electrokinetic soil treatment is a remediation process that operates under a low direct current gradient in soil, as opposed to a hydraulic pressure gradient, which promotes the migration of water and various contaminants under coulombic forces (Shenbagavalli and Mahimairaja 2010). This process produces an electrical gradient that acts as a driving force for the transport of various pollutants in soil, which makes it suitable for both saturated and unsaturated soil (Acar et al. 1995; Yang and Liu 2001; Shenbagavalli and Mahimairaja 2010; Tsai et al. 2010). The main feature of the electrokinetic process is in situ soil contaminant removal, and it may be considered as a preferable treatment option compared to some conventional ex situ treatment processes, such as solidification/stabilization and soil washing. Electrokinetic soil treatment has been studied for the removal of a wide range of contaminants, such as heavy metals, phenols,

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petroleum oils/hydrocarbons and radioactive substances (Acar et al. 1995; Doering et al. 2001; Korolev 2006; Shenbagavalli and Mahimairaja 2010; Kim et al. 2011a). In spite of normal flushing agents, Fenton's reagent has also been used in electrokinetic process as a flushing agent for removing organic contaminants from soil by providing in situ oxidation/destruction and this process is known as Electrokinetic-Fenton. Electrokinetic-Fenton process has been studied experimentally in laboratory scale using both column and box designs. This process has been successfully applied not only for artificial spiked soil, but also contaminated soil from real site (Isosaari et al. 2007). However, the applicability of Fenton's Reagent in electrokinetic process is always in doubt as the stability of this reagent is inconsistent and is highly dependent on the environment. This mini review summarizes the efforts applied to enhance the process efficiency for Electrokinetic-Fenton soil remediation via Fenton's Reagent's stability, oxidant availability, electrodes operations, solid iron catalyst and operating conditions.

2 Electrokinetic process description

There are two mechanisms of contaminant transport in soil; the first occurs as water transport, whereby contaminants are flushed towards the electrode chambers from anode to cathode or vice versa, whilst the second mechanism involves the migration of ions towards their respective electrodes. These mechanisms may consist of three main phenomena; namely electrolysis, electromigration for removing metal ions, and electroosmosis for removing organic compounds (Acar and Alshawabkeh 1993; Acar et al. 1995; Ma et al. 2010; Shenbagavalli and Mahimairaja 2010; Kim et al. 2011a).

Figure 1 illustrates the mechanisms for the electrokinetic process in soil. In general, two electrodes, namely an anode and a cathode, are introduced into the soil together with two porous chambers (the anode chamber and the cathode chamber). The aqueous solutions in the chambers, which act as electrolytes/flushing agents, undergo electrolysis when a direct current is induced. The hydrogen ion (H^+) is produced in the anode chamber and the hydroxide ion (OH^-) is produced in the cathode chamber during the

electrolysis process, as shown in Eqs. (1) and (2), respectively (Acar and Alshawabkeh 1993) while the oxygen and hydrogen gases generated are often vented out from the chambers.
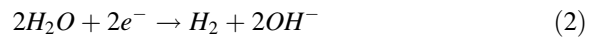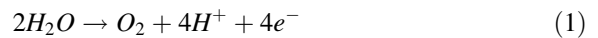
$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{1}$$

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{2}$$

Figure 1 shows that the induced electric field influences H^+ to migrate towards the cathode through the soil. As the movement of H^+ in the soil towards the cathode (acid front) is approximately 1.75–2 times higher than OH^- movement towards the anode (Acar and Alshawabkeh 1993; Acar et al. 1995; Chung and Kang 1999; Gioannis et al. 2008; Park et al. 2009; Kim et al. 2011b), a net acid front advancement from the anode region to the cathode region will progress along the soil normally, consequently affecting the pH and properties of the soil from the anode to the cathode region.

As the acid/base front advances, the electrical field can induce cation and anion migration in the soil. This mechanism is known as electromigration and it governs the removal of metal ions from soil under the electrokinetic process. Metal cations are transported towards the cathode and vice versa for anions, following a similar trend for the acid and base fronts, as shown in Fig. 1. It is also important to note that, unlike electroosmosis, electromigration of the ions will still occur as long as an electric field is induced. This process may continue despite the cessation of electroosmosis (Acar et al. 1995).

Electroosmosis is another mechanism in the electrokinetic process that mainly governs the transport of neutral organic compounds in soil treatment. Electroosmosis can be defined as the movement of pore water that also transports neutral compounds in soil due to the movement of ions, as shown in Fig. 1. A schematic diagram illustrating this mechanism is shown in Fig. 2. Soil normally contains a high negative surface charge, due to imperfection in the mineral lattice, which attracts cations in the soil close to the soil surface (Acar et al. 1995). When an electric field is induced, excess cations, close to the soil surface (diffuse double layer), tend to move towards the cathode. According to Acar et al. (1995), the movement of the cations and their associated water molecules yield a net strain on the pore fluid and thus transform into a shear force through the viscosity of

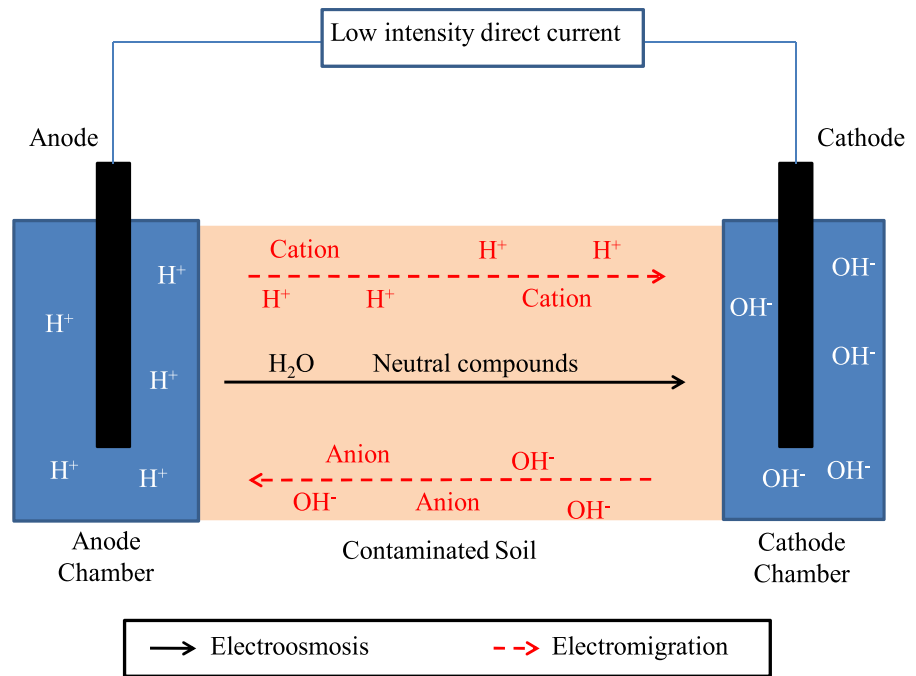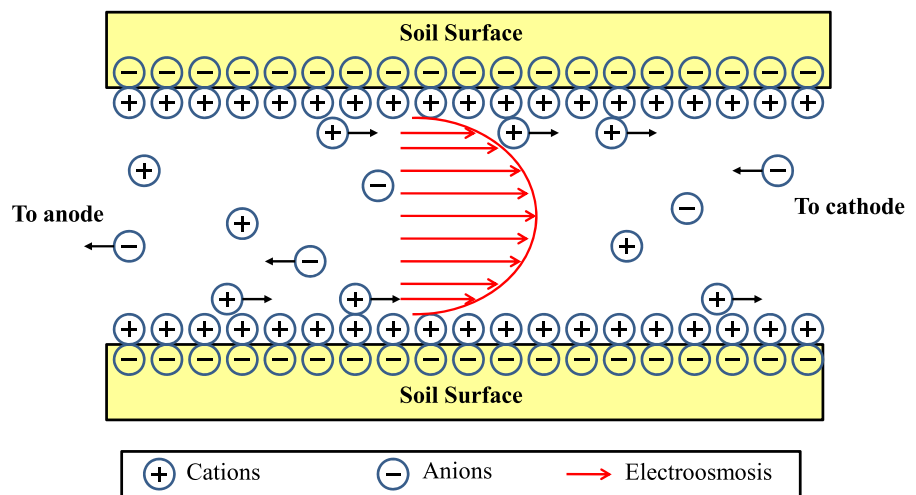**Fig. 1** Electrokinetic process in soil treatment

Fig. 2 Schematic diagram for electroosmosis process

the fluid. As the surface charge of the soil is normally negative, the force for the pore fluid is likely to be cationic and the transport of the pore fluid will be directed towards cathode region, as shown in Fig. 2. However, it is worth noting that the transport of neutral organic compounds by electroosmosis is dependent on their availability in the pore water/flushing agent. This is strongly governed by the sorption strength of the compounds on soil (Lima et al. 2011), number of sorption sites/organic matter on the soil (Reddy and Saichek 2003) and partition coefficient of the compounds between the soil and the flushing agent (Reddy and Saichek 2003; Reddy et al. 2006; Oonnittan et al. 2008; Reddy et al. 2010; Lima et al. 2011).

3 Electrokinetic-Fenton in soil treatment

In spite of favourable contaminant removal efficiency, the electrokinetic process has a major disadvantage, which is the necessity for further treatment of the flushed contaminants, in particular the organic compounds. This can further increase capital and operating

costs. In order to overcome this, the possibility of in situ oxidation of contaminants by combining electrokinetic process and oxidants has been investigated. One of the most promising oxidants is Fenton's reagent.

Electrokinetic-Fenton is an electrokinetic process that utilizes Fenton's reagent as a flushing solution. This process has been introduced as one of the in situ oxidation methods for soil treatment, which reduces the necessity of a second treatment for highly contaminated effluent. In comparison to normal soil oxidation, Electrokinetic-Fenton eliminates the difficulty of normal Fenton's reagent when treating soil with high clay content, as low permeability soil tends to prevent Fenton's reagent from penetrating through the soil and oxidizing the contaminants during normal mechanical flushing. H_2O_2 often decomposes before reaching the contaminated site due to a slow transport rate in the soil. Unlike the normal transport mechanism, elevated concentration of H_2O_2 in Fenton's reagent is transported via electroosmosis, rather than by a hydraulic pressure difference (Park et al. 2005; Kim et al. 2006). This ensures the effective penetration of Fenton's reagent through the soil and oxidation of 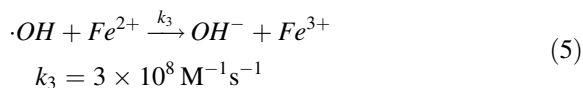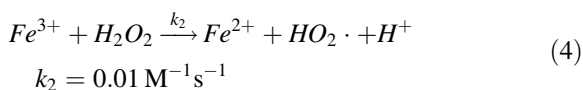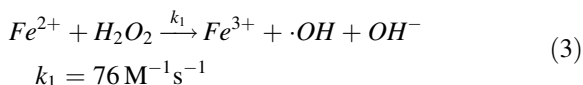organic compounds through a reaction with the hydroxyl radicals. The mechanisms for hydroxyl radical generation/regeneration are given in Eqs. (3–7), and the oxidation processes are as shown in Eqs. (8) and (9), where R· is an organic radical (Flotron et al. 2005; Oonnittan et al. 2008; Anotai et al. 2010; Khamaruddin et al. 2011).

$$Fe^{2+} + H_2O_2 \xrightarrow{k_1} Fe^{3+} + \cdot OH + OH^-$$
$$k_1 = 76\,M^{-1}s^{-1} \tag{3}$$

$$Fe^{3+} + H_2O_2 \xrightarrow{k_2} Fe^{2+} + HO_2 \cdot + H^+$$
$$k_2 = 0.01\,M^{-1}s^{-1} \tag{4}$$

$$\cdot OH + Fe^{2+} \xrightarrow{k_3} OH^- + Fe^{3+}$$
$$k_3 = 3 \times 10^8\,M^{-1}s^{-1} \tag{5}$$

$$\cdot OH + H_2O_2 \xrightarrow{k_4} H_2O + HO_2 \cdot$$
$$k_4 = 3.3 \times 10^7\,M^{-1}s^{-1} \tag{6}$$

$$\cdot OH + \cdot OH \xrightarrow{k_5} H_2O_2 \quad k_5 = 5.2 \times 10^9\,M^{-1}s^{-1} \tag{7}$$

$$RH + \cdot OH \xrightarrow{k_6} R \cdot + H_2O \tag{8}$$

$$R \cdot + Fe^{3+} \rightarrow Fe^{2+} + \text{Oxidised organic substrates} \tag{9}$$
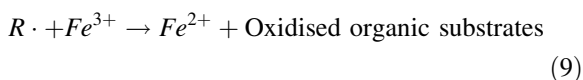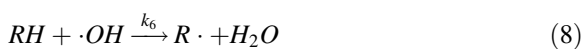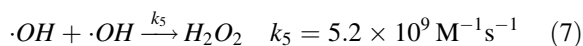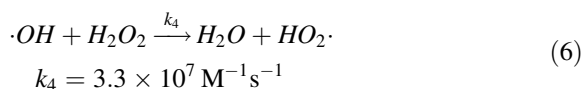
In addition to a normal reaction scheme, Fenton-like reaction is another possible reaction pathway mediated by the iron oxides in the soil as ferrous sources (Flotron et al. 2005; Oonnittan et al. 2009; Garrido-Ramírez et al. 2010). The Electrokinetic-Fenton process not only enhances the transport rate of Fenton's reagent through a low permeability soil, but also eliminates the necessity of secondary treatment for the effluent. However, it is worth noting that there are still a number of wastes that could be produced among the reactions such as CO_2, water and incomplete oxidation products of the organic contaminants. The most notable waste that could be observed is iron sludge especially when the ferrous source is in excess and near cathode region.

Figure 3 shows the general direction of flow within the Electrokinetic-Fenton process. Similar to the electrokinetic process, the system mainly consists of two electrode poles; the anode chamber and the cathode chamber. When a low intensity direct current is applied, acid front progresses at a rate of 1.75–2 times faster than the base front (Acar and Alshawabkeh 1993; Acar et al. 1995; Chung and Kang 1999; Gioannis et al. 2008; Park et al. 2009; Kim et al. 2011b), leading to electroosmosis from the anode to cathode. Electroosmosis acts as a driving force to transport Fenton's reagent in the anode chamber through the soil and towards the cathode chamber, as shown in Fig. 3. Fenton's reagent oxidises the organic contaminants that are available in the soil through hydroxyl radical generation, leading to an in situ oxidation process.

4 Applications of Electrokinetic-Fenton in soil treatment for organic compounds removal

The Electrokinetic-Fenton method has been studied extensively for the treatment of organic compounds, such as phenol (Yang and Long 1999; Kim et al. 2005; Babuponnusami and Muthukumar 2012), chlorophenoxyl acid, aromatic herbicides (Aaron and Oturan 2001), phenanthrene (Kim et al. 2005; Park et al. 2005; Kim et al. 2006; Reddy and Karri 2006; Kim et al. 2007; Alcántara et al. 2008; Kim et al. 2009; Park and Kim 2011), hexanchlorobenzene (HCB) (Oonnittan et al. 2008, 2009, 2010), diesel (Tsai et al. 2010), H-acid/RB5 (Rao et al. 2006), trichloroethane (Yang and Liu 2001) and PAHs (Isosaari et al. 2007). A

Fig. 3 General transport process in Electrokinetic-Fenton
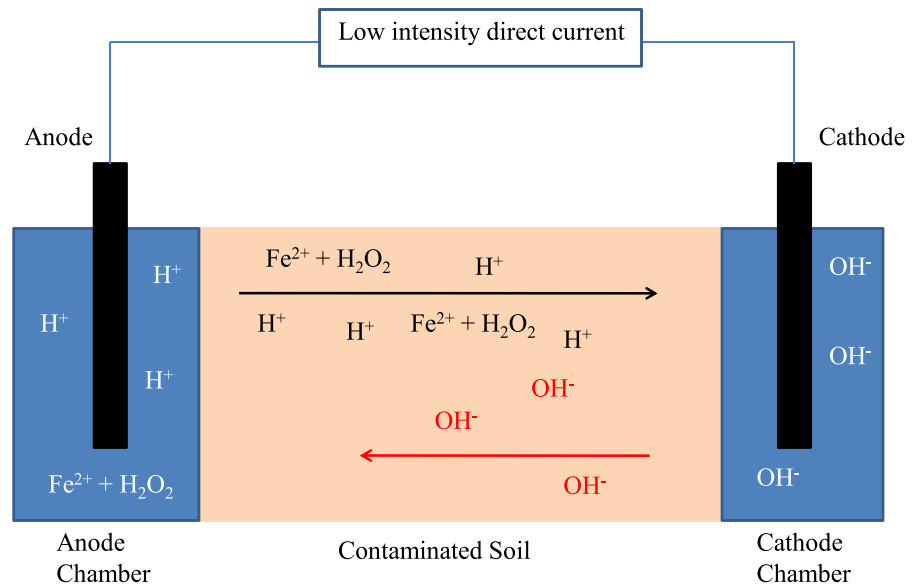
summary of the studies concerned with the Electrokinetic-Fenton process to remove organic compounds in soil is provided in Table 1.

Table 1 confirms that the treatment efficiency for different organic compounds using the Electrokinetic-Fenton process is in the range of 26–99.70 %. The large deviation in efficiency is mainly due to the difference in the types of organic compounds, types of soil and their operating conditions. In general, Electrokinetic-Fenton process is found to provide better treatment efficiency than normal soil oxidation and electrokinetic process. This is justified by Tsai et al. (2010) that the use of 8 % H_2O_2 in electrokinetic process shows a high treatment efficiency for artificial diesel contaminated soil at 97 % in comparison to electrokinetic process at 55 % and normal soil oxidation at 27 %. Compared to normal electrokinetic process, Electrokinetic-Fenton not only reduces contaminants concentration in the effluent/cathode chamber (Yang and Long 1999), but also provides in situ oxidation for recalcitrant contaminants, as observed in the work of Kim et al. (2005) for removing phenanthrene from kaolin whereby significant removal efficiency is reported in this process whilst phenanthrene fails to mobile in the normal electrokinetic process. However, it is worth noting that higher contaminant removal is normally observed in the anode region soil section compared to the cathode region, due to a higher H_2O_2 concentration in the

anode region. This is caused by the reduction in stability of Fenton's reagent when progressing to the cathode region, as a result of higher pH in the cathode region and longer transportation time. Efforts have been made to compensate for the low stability issue through the use of H_2O_2. These can be categorized into: (1) chemical stabilization (H_2O_2 stabilization, complexing agents addition), (2) oxidant delivery mode, (3) electrodes operation and solid iron catalysts, and (4) operating conditions (electrolytes, voltage gradient, H_2O_2 concentration).

4.1 Enhancement of Electrokinetic-Fenton via chemical stabilization

Lower pH conditions in the anode chamber are found to enhance the stability of H_2O_2 and increase the acid front advancement (Kim et al. 2005, 2006, 2007). The use of acid to depolarize cathodes has also been found to enhance H_2O_2 stability and treatment efficiency (Alcántara et al. 2008). Under low pH conditions (pH 2–4), stable H_2O_2 is capable of yielding higher levels of free radicals. This increases the stability of Fenton's reagent in the system, and thus increases the treatment efficiency. It is worth noting that the choice of acid is important in governing H_2O_2 stability. The work of Kim et al. (2009) reports that the use of H_2SO_4, as an anode purging acid, results in the increase of the H_2O_2 decomposition rate in comparison to HCl, as a result of

Table 1 Summary of major modifications on Electrokinetic-Fenton process for organic compounds removal in soil treatment and their operating conditions

Type of modifications	Main feature	Contamination				Operating condition				Best treatment efficiency (%)[a]	References
		Case study	Type of soil	Types of contaminants	Initial Concentration, mg kg^{-1}	Durations, days	Voltage gradient, V cm^{-1}	H$_2$O$_2$ concentration, %	Iron source (concentration, M)		
H$_2$O$_2$ stabilization	Addition of acid in anode solution	Spiked	Kaolin	Phenol / Phenanthrene	200 / 200	10–20.25	1.5	0–7	Soil	≈74[b]	Kim et al. (2005)
	Addition of acid in anode solution	Spiked	Kaolin/ Hadong clay	Phenanthrene	200	10–22	1.5	7	Soil	≈74[b]	Kim et al. (2006)
	Acid and H$_2$O$_2$ stabilizer K$_2$HPO$_4$ and SDS	Spiked	Hadong clay	Phenanthrene	200	10–22	1.5	7	Soil	<40[b]	Kim et al. (2007)
	Different anode purging acid solutions	Spiked	Hadong clay	Phenanthrene	200	10	1.5	7	Soil	<40[b]	Kim et al. (2009)
	Use of acid and surfactant SDS	Spiked	Youngdong clay	Phenanthrene	200	10–18	1.5	7	Soil	70–80[b]	Park and Kim (2011)
Oxidant delivery mode	Different H$_2$O$_2$ injection points along the soil	Spiked	Kaolin	HCB	100	10–20	1.5–2	8–12	Not mention	≈60[b]	Oonnittan et al. (2010)
	Injection wall for maintaining redox potential of soil and expansion of oxidation zone	Real case	Clay	PAHs	420	56	0.53 + 0.047AC at 90 Hz	3	Solution (0.74 × 10^{-3})	26	Isosaari et al. (2007)
	Injection of H$_2$O$_2$ at different chambers	Spiked	Kaolin	Phenanthrene	500	10	3	10	Soil	≈90[b]	Alcántara et al. (2008)
Electrodes Operations	Types of electrode materials	Spiked	Silty clay	Diesel	10,000	60	1.33	0–8	Iron electrode	95	Tsai et al. (2010)
	Electrode polarity exchange	Spiked	Youngdong clay	Phenanthrene	200	10–18	1.5	7	Soil	70–80[b]	Park and Kim (2011)
	Types of electrode materials	Spiked	Loam/sand	Trichloroethane	184–283	10	1	<4,000 mg L^{-1}	Solution (0.0196–0.098)/ iron powder	88.91	Yang and Liu (2001)

Table 1 continued

| Type of modifications | Main feature | Contamination | | | | Operating condition | | | | Best treatment efficiency (%)[a] | References |
		Case study	Type of soil	Types of contaminants	Initial Concentration, mg kg⁻¹	Durations, days	Voltage gradient, V cm⁻¹	H_2O_2 concentration, %	Iron source (concentration, M)		
Solid iron catalysts	In situ Fe^{2+} generation using scrap iron powder as iron source for Fenton's reagent	Spiked	Loam	Phenol	200	10	1	0.3	Iron powder (1.5–32.69 g)	99.7	Yang and Long (1999)
	Effect of scrap iron on removal efficiency and destruction efficiency	Spiked	Loam/sand	Trichloroethane	184–283	10	1	<4,000 mg L⁻¹	Solution (0.0196–0.098)/iron powder	88.91	Yang and Liu (2001)
Complexing agents on enhancing contaminants desorption	β-Cyclodextrin	Spiked	Kaolin	HCB	100	15	1.5	5–30	Soil	76	Oonnittan et al. (2009)
	β-Cyclodextrin	Spiked	Kaolin	HCB	376.4	14	1.5	15	Solution (0.56×10^{-3})	64	Oonnittan et al. (2008)
	Surfactant SDS	Spiked	Hadong clay	Phenanthrene	200	10–22	1.5	7	Soil	<40	Kim et al. (2007)
	Surfactant SDS	Spiked	Youngdong clay	Phenanthrene	200	10–18	1.5	7	Soil	70–80[b]	Park and Kim (2011)
Other	Presence of NaCl as electrolyte	Spiked	Silty clay	Diesel	10,000	60	1.33	3	Iron electrode	95	Tsai et al. (2010)

[a] Treatment efficiency = flushing efficiency + oxidation efficiency

[b] Estimated from the data provided

Fig. 4 Schematic diagram on the effect of stabilizers on metals diffusion (Kim et al. 2007; Park and Kim 2011)
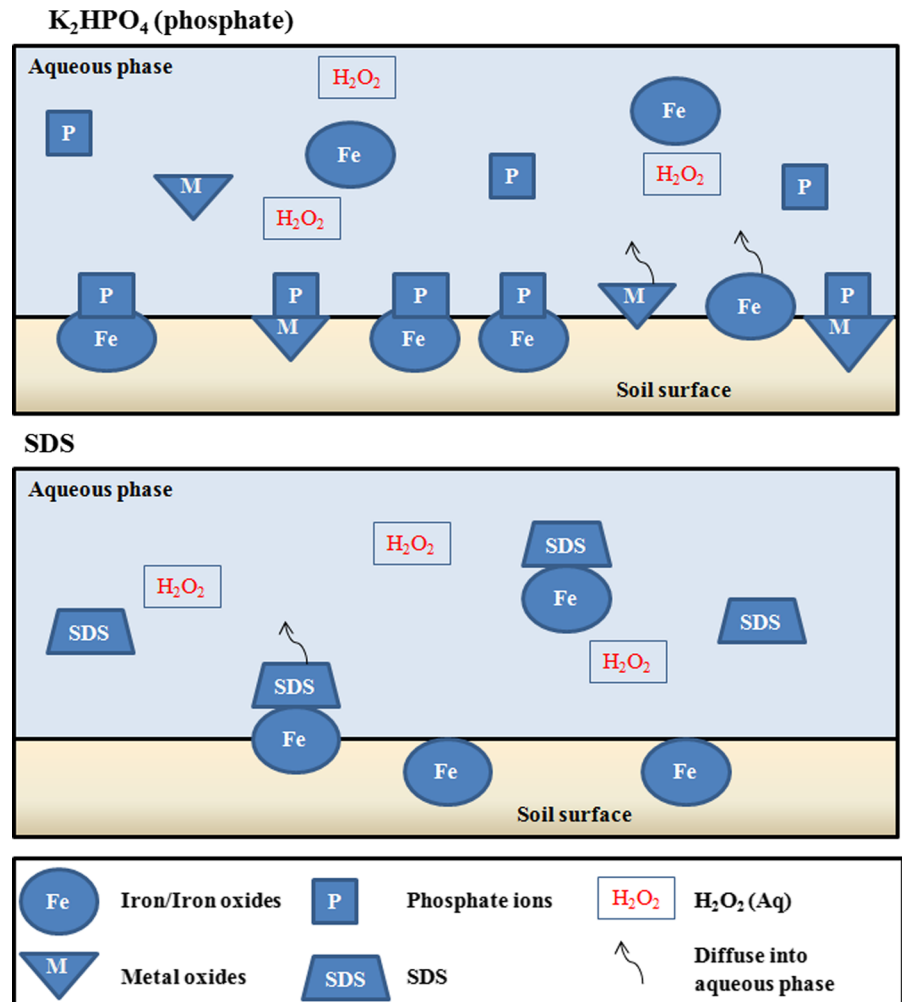
the reduction of sulphate at the anode region and the formation of H_2S and HS^- species in the soil. This causes higher soil pH and consequently decreases H_2O_2 stability.

Other than acids, the application of stabilizers, such as K_2HPO_4 and SDS, are also found to increase H_2O_2 stability (Kim et al. 2007; Park and Kim 2011). This can occur via altering the availability of iron catalyst for Fenton reaction. The work of Kim et al. (2007) and Park and Kim (2011) show that the use of phosphate can complex with metal oxides in the soil to prevent an undesirable Fenton-like reaction from other metals. This additive is more suitable for high iron content soil so that H_2O_2 decomposition could be slowed down. On the other hand, anionic surfactant SDS can be used to complex with iron oxides to form a water soluble

iron compounds to increase the concentration of iron catalyst in the aqueous solution, as illustrated in Fig. 4 and this is more suitable for low iron content soil (Kim et al. 2007; Park and Kim 2011). Furthermore, SDS is also reported to increase the availability of organic compounds in aqueous solution by enhancing the desorption of compounds from soil (Kim and Lee 1999; Park et al. 2007), which may further enhance the oxidation rate and treatment efficiency when SDS is utilized in Electrokinetic-Fenton process. However, it is worth noting that the efficiency enhancement by K_2HPO_4 and SDS is also strongly dependent on the pH of the soil region, acidity of the system and characteristic of the complexes formed (Kim et al. 2007; Park and Kim 2011), as the additives might cause drawbacks. For example, the use of surfactant SDS in

excess may act as a scavenger for hydroxyl radicals (Kim et al. 2007; Park and Kim 2011).

4.2 Enhancement of Electrokinetic-Fenton via oxidants delivery methods

As well as the addition of chemicals, several studies, concerned with the improvement of mechanical configuration to compensate for the effect of low H_2O_2 stability, were undertaken in the past. The delivery mode for Fenton's reagent is found to affect treatment efficiency. Isosaari et al. (2007) and Oonnittan et al. (2010) claimed that an H_2O_2 injection well in the middle of the soil, between anode and cathode chambers, could enhance treatment efficiency by increasing oxidant availability in the soil. The example for the configuration is as shown in Fig. 5. Based on a similar concept, the injection of H_2O_2 in both the anode and cathode chambers resulted in more than 90 % total mineralization of phenanthrene, which is more effective than H_2O_2 injection in any single chamber (Alcántara et al. 2008).

The effect of Fenton's reagent addition method in the anode chamber has been reported by several authors. The work of Oonnittan et al. (2010) indicates that greater treatment efficiency rates can be obtained when the system is operated using Fe^{2+} solution as an anolyte for 2 days before the addition of H_2O_2 solution. Simultaneous addition of Fe^{2+} and H_2O_2 solutions into the anode chamber is not recommended, as part of H_2O_2 is consumed in the anode chamber before electroosmosis, leading to lower oxidant availability (Oonnittan et al. 2010). This argument is supported by Yang and Liu (2001) who observed that Fe^{2+} in the anode chamber reduced the oxidizing capacity of the hydroxyl radicals generated before they entered the soil. Thus, destruction efficiency was found to be reduced.

In addition to the delivery sequence mentioned above, another delivery mode using H_2O_2 solution as the only flushing agent in the anode chamber is also used by researchers. Native iron oxides attached to the soil are used as the iron source (Park et al. 2005; Kim et al. 2005, 2006, 2007 Reddy and Karri 2006; Alcántara et al. 2008; Kim et al. 2009; Park and Kim 2011). The iron which is distributed in the soil at a concentration range of 805–11,644 mg kg^{-1} serves as on site catalyst for Fenton's oxidation. This prevents unnecessary H_2O_2 consumption in the anode chamber before it is transported across the soil in absence of iron catalyst in the chamber.
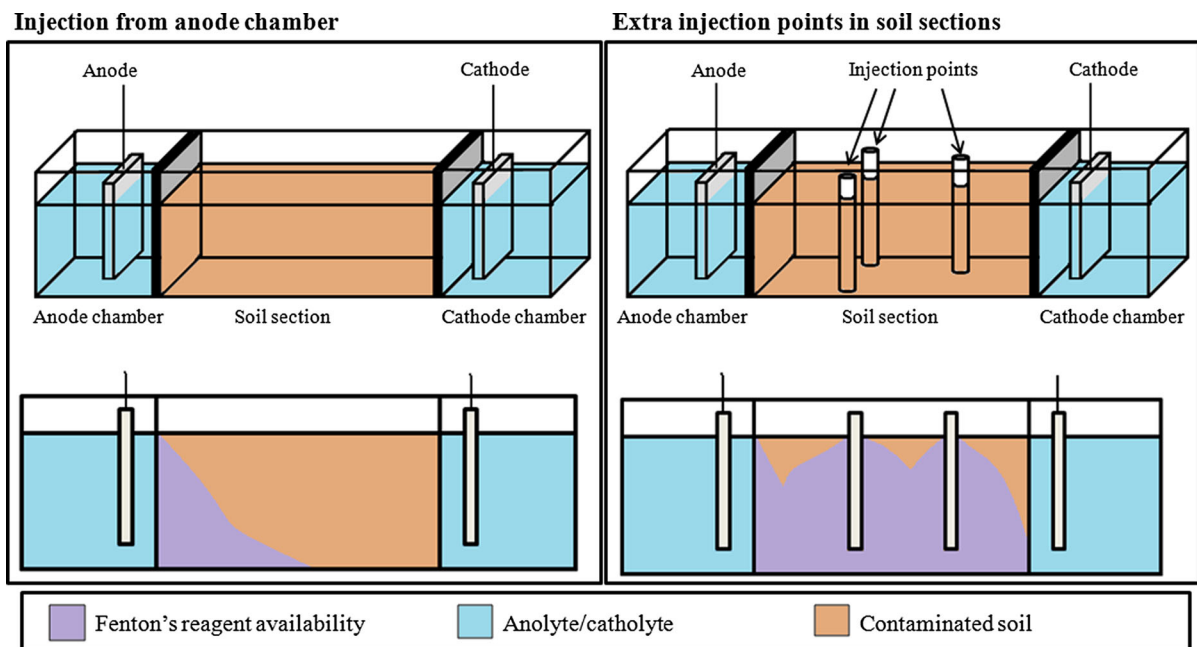

Fig. 5 Increment in the availability of Fenton's reagent by multiple injection point (Isosaari et al. 2007)

4.3 Enhancement of Electrokinetic-Fenton via electrode operations and solid iron catalysts

A high pH condition in cathode region often causes iron and other metals to precipitate. The precipitation not only blocks the transport path for pore water flow, but also restricts availability of ferrous ion in the region for ·OH radicals generation when H_2O_2 is used. In order to solve this issue, Park and Kim (2011) observed that changing the direction of flow by switching electrode polarities periodically enhanced the treatment efficiency for phenanthrene, especially at the cathode region (after switching it became anode). The change of electrode polarities reduces the overall pH of the soil medium and this in turn increases the dissolution rate of the iron catalyst at the region which initially does not take part in Fenton's reaction due to precipitation. A higher H_2O_2 stability is also achieved by the generation of low pH in the entire soil column (Park and Kim 2011).

The nature of electrode materials is also found to influence treatment efficiency in Electrokinetic-Fenton processes. In general, when life span and the cost of the electrodes are not considered, treatment efficiency is controlled by the electrode material, where iron electrode > graphite electrode > stainless steel electrode (Yang and Liu 2001; Tsai et al. 2010). An iron electrode provides a higher treatment efficiency than a graphite electrode as the corrosion products of iron electrodes act as catalysts for Fenton's reaction (Tsai et al. 2010).

Other than iron electrode, Yang and Long (1999) and Yang and Liu (2001) utilized scrap iron powder (SIP) from the residue of an iron processing plant as solid ferrous sources. The use of zero valent iron powder as catalysts and permeable reactive walls along the soil to initiate Fenton-like oxidation showed higher phenol flushing efficiency when de-ionized water was used as a flushing agent and higher destruction efficiency when H_2O_2 was used (Yang and Long 1999). Ferrous ion solution was found to yield better flushing efficiency as a result of enhanced current density. However, in terms of destruction efficiency, SIP generally outperforms ferrous solution as the latter shows early consumption of H_2O_2 during flushing process (Yang and Liu 2001). Nevertheless, it is worth noting that the excess use of SIP may bring disadvantage. This is reported by Yang and Long (1999) that the treatment efficiency was reduced as the amount of SIP was increased. Theoretically, higher amounts of iron provide higher catalyst concentration, which increases the oxidation rate as well as the treatment efficiency. In actual fact, the use of large/excessive amounts of SIP may reduce treatment efficiency due to the reduction in the electroosmotic flow (EOF) and permeability, as it serves as a physical resistance/barrier that reduces H_2O_2 flow through the soil (Yang and Long 1999). For contaminants destruction, smaller size and larger quantities of SIP should provide more oxidation sites and thus, should enhance the oxidation process. However, it has been observed that there was a reduction in the flushing efficiency of the system as more $Fe(OH)_3$ precipitated, which offered resistance to electroosmosis (Yang and Liu 2001).

4.4 Enhancement of Electrokinetic-Fenton via operating parameters

Other than major modifications, operating conditions, such as voltage gradient, experimental duration, H_2O_2 concentration, introduction of NaCl and Na_2SO_4 in the electrolyte chambers generally have positive effects on the treatment efficiency (Park et al. 2005; Kim et al. 2005, 2006; Reddy and Karri 2006; Oonnittan et al. 2009; Tsai et al. 2010). The work of Park et al. (2005) showed the application of higher voltage gradient from 4 to 5.6 V cm^{-1} enhanced phenanthrene removal from 68.9 to 81.6 %, as a result of better H_2O_2 transport in the soil due to the increase in electroosmosis. However, unlike the work of Park et al. (2005) which was treating sandy soil, the increment of voltage gradient from 1 to 2 V cm^{-1} was found to slightly reduce the EOF when low permeable kaolin was treated, as reported by Reddy and Karri (2006). This could be attributed to relatively lower voltage gradient applied by Reddy and Karri (2006), which failed to maintain strong electroosmosis in lower permeability soil. Nevertheless, the oxidation process is found to perform better at higher voltage gradient. Moreover, in order to enhance H_2O_2 transport, NaCl and Na_2SO_4 were used as electrolytes in Electrokinetic-Fenton process (Park et al. 2005; Alcántara et al. 2008; Tsai et al. 2010). This is found to improve current intensity which can further enhance EOF of the system and thus gives better flushing efficiency (Alcántara et al. 2008; Tsai et al. 2010).

Other than voltage gradient and electrolyte, the use of higher H_2O_2 concentration is another way of enhancing treatment efficiency (Kim et al. 2005; Reddy and Karri 2006; Oonnittan et al. 2009; Tsai et al. 2010). At higher H_2O_2 concentration, the availability of oxidant in the soil is increased (Kim et al. 2005). Other than increase in oxidant availability, high H_2O_2 concentration (30 %) is also reported to generate non-hydroxyl radicals for oxidation of sorbed contaminants even in the absence of iron (Oonnittan et al. 2009). However, it is worth noting that an optimisation of all the operating parameters must be conducted with a view to efficiency, costing, as well as the environmental impact.

4.5 Other factors affecting Electrokinetic-Fenton efficiency

It is worth noting that the treatment efficiency of Electrokinetic-Fenton is also dependent on the types of soil as well as the types of contaminants. From the view of soil properties, Yang and Liu (2001) and Kim et al. (2006) suggested that an improved H_2O_2 stability and treatment efficiency could be achieved in a soil that has a low acid buffering capacity, abundant iron concentration and low organic matter content. Low acid buffering capacity enables more efficient acid front advancement and low pH conditions can be easily established in the soil. Besides that, high native iron concentrations in the soil augments Fenton oxidation by providing iron catalyst (Kim et al. 2006). Furthermore, soil with a lower organic matter content reduces inefficient consumption of H_2O_2 (Yang and Liu 2001), as the organic matter is reported to consume ·OH radicals and inhibit PAHs oxidation (Flotron et al. 2005). The above statement is generally true as the treatment efficiency for Electrokinetic-Fenton is lower for real contaminated soil which has higher organic matter content in comparison to spiked soil, as shown in Table 1. This trend is also observed in normal electrokinetic process, as shown in the work of Yuan et al. (2006) for removing HCB from both kaolin and real contaminated soil using β-cyclodextrin. The removal efficiency was found to be lower under real contaminated soil, which is probably due to relatively high organic matter content than kaolin (3.58 vs 0 %). The organic matter is responsible for adsorbing β-cyclodextrin in addition to provide strong

adsorption site for HCB; thus the removal is more difficult. Similar results can be observed from the work of Li et al. (2010) and Pham et al. (2010).

Other than treatment efficiency, soil zeta potential is another important parameter in Electrokinetic-Fenton process especially in determining the flow direction of electroosmosis. According to Helmholtz–Smoluchowski equation (Lee et al. 2009), an increasingly positive zeta potential will reduce the EOF towards cathode and vice versa. Zeta potential is strongly dependent on the pH of the system, whereby an acidic system will generally reduce or even reverse the direction of EOF (Baek et al. 2009). Since Fenton's reagent is commonly supplied under acidic condition, it is necessary to analyze the change in soil zeta potential and determine the direction of EOF so that the Fenton's reagent could be supplied under the right flow direction.

In addition, treatment efficiency is also dependent on the types of contaminant within the soil. This is supported by Isosaari et al. (2007) based on their investigation on the removal of PAHs. PAHs with a lower number of aromatic rings are found to be rapidly removed in comparison with PAHs with a higher number of aromatic rings whereby 32 % removal achieved for the former and 6.4 % for the latter. This is claimed to be related to the hydrophobicity of the PAHs in water whereby their solubilities in water decrease with the increase in molecular size, thus reduce in availability to Fenton's reagent (Isosaari et al. 2007). Moreover, the stronger sorption by more hydrophobic PAHs into the microporous structure of particulates may also reduce penetration rate of the oxidants which slow down the treatment efficiency (Valderrama et al. 2009). This is also supported by the work of Watts et al. (2000) on normal Fenton oxidation of monoaromatic hydrocarbons and aliphatic hydrocarbons in soil, whereby the less hydrophobic contaminants show better removal. Other than hydrophilicity, the oxidation preference and chemical properties of contaminants are also the important parameters for the treatment efficiency (Isosaari et al. 2007).

In contrast to the factors mentioned above, some soil properties such as soil permeability and conductivity are less critical in governing treatment efficiency in Electrokinetic-Fenton process. Soil permeability is less important in comparison to other properties as

electrokinetic process is generally suitable for both high and low permeability soil due to its electricity driven mechanisms, as discussed in Sects. 2 and 3. For soil conductivity, this properties is important in governing the current and electroosmosis process whereby low ion concentration in the system causes low electroosmosis (Acar et al. 1995; Shenbagavalli and Mahimairaja 2010) and thus the transport of Fenton's reagent. However, it is worth noting that the conductivity can be increased during the process by the use of electrolyte such as NaCl and Na_2SO_4 and thus better current and removal efficiency could be achieved (Park et al. 2005; Alcántara et al. 2008; Tsai et al. 2010). Nevertheless, a longer treatment time is expected for the soil with low permeability and conductivity.

5 Conclusions

Electrokinetic-Fenton process is found to be a promising technology for in situ organic compound degradation in soil. However, the primary concern for this technology is the stability of Fenton's reagent. Several enhancement methodologies have been reported that can compensate for this disadvantage. Popular options include H_2O_2 stabilization using acids and utilisation of different oxidant delivery point/methods for improved H_2O_2 coverage in the soil. However, it is worth noting that the dynamic change of soil properties, with respect to enhancing agents, may influence the removal efficiency. Soil properties, such as structure, pH, buffering capacity, zeta potential, permeability, conductivity, organic matter content, as well as metal concentration, can significantly affect the behaviour of Fenton's reagent. For example, soil pH affects the stability of Fenton's reagent and metal precipitation, which highly influences the transport of the reagent. In addition, soil permeability and conductivity are also important in governing the effectiveness and velocity of Fenton's reagent transport in the soil via electroosmosis. Moreover, soil organic matter, trace metals and various other contaminants compete for oxidation and result in unnecessary H_2O_2 and ·OH consumption as well as reduced treatment efficiency. Hence, soil properties should be analyzed prior to any enhancement process so that the Electrokinetic-Fenton oxidation process can be optimised and unnecessary chemical consumption can be limited.

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