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Efficacy of Coupled Electrokinetic Remediation Techniques for Soil Decontamination- A Review

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ABSTRACT: *Traditional technologies for removal of numerous contaminants in fine grained soils have not been very effective when the soil has high absorptive properties and low hydraulic conductivity. These traditional technologies which are mainly ex-situ are also associated with high cost and very long remediation time. Electrokinetic Remediation (EKR) has proven to be an effective means of removing various contaminants from a matrix with high salinity, low permeability and high buffering capacity. These contaminants include organic compounds, heavy metals, radionuclides, organic waste and some mixed inorganic species. The working components for electrokinetic systems such as electrodes, electrolytes, contaminant concentration which impact on the effectiveness of the process and the overview of the principles of this technique in different soils are discussed through this review. Also, many researches have revealed that electrokinetics in combination with other techniques improves remediation efficiency of polluted soils. These other techiques such as bioremediation, fenton technique, phytoremediation have positive coupling effect when combined with electrokinetics unlike results obtained when individual techniques are used alone. Merits and demerits of the coupled techniques are also outlined. Overall, a well-articulated experimental design for the application of electrokinetics should be employed to greatly improve the efficiency of the technique and combination of techniques is advised for synergy and hence optimum remediation results.*

KEYWORDS: electrokinetic, remediation, coupling techniques, synergistic effects, fine-grained soils

INTRODUCTION

Soil which is largely an immobile key component of the environment is often a receptor of accumulated contamination from urban, agricultural, industrial and maritime activities, and so can be said to be an indispensable part of the human environment. As a non-renewable resource and a very dynamic system which aids ecosystem survival, soil contamination and remediation has been obtaining serious considerations around the world. Voiciante *et al* (2021) states that the boisterous industrial boom that started at the latter part of the 19th century had brought forth innumerable cases of environmental pollution inclusively marked with the discharge of large quantities of organic and inorganic contaminants which can adversely affect ground water and public health. More so, since soil produces food for most living beings, soil pollution is highly economically important and critical due to fundamental effects on human health and biological resources (Thuy, 2014). Different kinds of pollutants are found in sediments and soil, such as bulk organics like grease and oil, halogenated hydrocarbons, polycyclic aromatic hydrocarbons (PAHs), nutrients like phosphorus and nitrogen compounds, phytoxic metals such as nickel, lead, chromium; carcinogenic chemicals like benzene, cyanide, inorganic contaminants (Jamal & Alamddine ,2009). With soils been contaminated, the important points in the agenda of environment professionals will be soil remediation and the most appropriate technique to use, which should be cost effective, safe and less time consuming. The research on the remediation of contaminated soils is therefore currently a hotspot in environmental science although it is also one of the most challenging fields of research (Huang *et al*, 2012). Soil remediation is the use of a technology that can eliminate or remove the contaminants, followed by restoring the site to original state (Mohammed, 2014). The soil properties and/or the remediation technology employed most times causes the impossibility of the site being restored to the original state. Iman & Azadeh (2012) recounted that the outcome of degree of success of soil remediation depends pivotally on the contaminant type, contaminated soil nature, concentration of pollutants on the subsurface, therefore the feasible objective in soil remediation is to reduce the pollutants to a state appropriate for common soil uses (Cameselle *et al*., 2013). The quest for pollutant-free soils over time, has led to a green, novel technique, Electrokinetics, which has proven its value, especially in soils with low permeability. This review therefore demonstrates the effectiveness of electrokinetics in low permeability soils and efficacy of coupled electrokinetic remediation techniques for soil decontamination.

Genesis/Development of Electrokinetics

Electrokinetics has been identified since early 1800, when a DC current was applied to a clay-water mixture by Ferdinand Friedrich Reuss and he observed that under the influence of the induced electric field, water molecules moved towards the cathode (Mohammed, 2014). The earliest theoretical article on electrokinetics was authored by Hermann von Helmholtz in 1879 where he presented the first analytical description of the elecotroosmotic phenomenon. His theory was then at a later time modified and expanded by Marian Smoluchowski in 1921, this birthed the familiar Helmholtz-Smoluchowski (HS) theory which relates electric constant in a porous medium that is charged under an electric gradient (Saichek & Reddy, 2005). For Newtonian fluids, the HS equation still fairly enjoys usage in the quantification of the electroosmotic flows (Lyklema, 2000). Leo Casagrande in 1949 induced the consolidation of fine grained soils using electroosmosis. He designed a model for the determination of osmosis in clay from the HS equation taking into accounts the effects of tortuosity and porosity on electromotive flow in soils. From the 1980s, electrokinetics has suited remediation purposes (Lageman *et al*., 1989). Most studies during these period were channelled towards dispelling water for soil stabilization and were concentrated after the electroosmotic dewatering of fine-gravel soils. Several Russian researchers prospected for metals using electro migration in the 1960s (Shenbagavalli & Mahimairaja, 2010). Early 1980s involved the exploitation of electrokinetic technologies across all boards concerning the removal of toxic contaminants in the soil in form of chemical ionic species in Europe and the US (Lageman *et al*., 1989). A great deal of work was carried out in the 1990s when a lot of publications and studies were been shaped, which birthed the advancement in understanding of electrokinetic phenomena in soils (Acar *et al*., 1990; Acar & Alshawabkeh, 1993; Probstein & Hicks, 1993; Acar *et al*., 1995), in modelling (Yeung, 1990; Choi, & Lui, 1995; Yeung & Datla, 1995; Alshawabkeh & Acar, 1996; Yu & Neretnieks, 1996) and field applications (Lageman, 1993; USEPA, 1998; Ho *et al*., 1997; USAEC, 2000). In recent years, electrokinetic remediation has been engaged successfully in the treatment for groundwater, sediments and soils polluted with vast types of contaminants such has radionuclides, heavy metals and organic compounds (Virkutyte, *et al*., 2002; Reddy & Camselle, 2009; Yeung, 2011; Ribeiro *et al*., 2015). There is a handful of areas in which electrokinetics has successfully being applied to a good extent namely: stability of soil during excavation, removal of salts from agricultural soils, injecting of grouts, barriers and leak detection systems in clay liners, microorganisms and nutrients into the subsoil strata of low permeability, increasing pile strength, removal of metallic objects from the ocean bottom, increasing flow rate of petroleum production, dewatering of clayey formations during excavation (Mohammed, 2014; Shenbagavalli & Mahimairaja, 2010). Electrokinetics has shown, in comparison to other methods, good potential in remediating polluted materials under complicated conditions, e.g., when sample is either characterised by high heterogeneity or low permeability. Undoubtedly, soil remediation of fine grained matrices is challenging due to the low hydraulic conductivity which impedes the movement of water through the porous medium of the soil. This makes hydraulic-based techniques (such as soil-washing, soil-flushing or pump-and-treat) non-effectual. Generally, fine-grained soil particles are characterized by a large amount of reaction sites and a high specific surface area of soil particles, these involves intense interactions between solid soil matrix and contaminants Among the several feasible treatment options available, electrokinetic remediation is reputed as the most effective for low permeability porous matrices because the applied direct current goes between the grain pores of the soil, where other techniques cannot reach. Also, electrokinetics can be used in both ex-situ and in-situ forms for various range of contaminants, and can also be exploited in combination with other techniques for an even more effective result.

Basis and Applications of Electrokinetics

The need for removal of contaminants in sediments, sludge and soil is catered for by a remediation technique called Electrokinetic Remediation (EKR). Electrokinetic remediation works on the principle of application of a direct electric current of low intensity on to the porous matrix to be decontaminated (Acar & Alshawabkeh, 1993; Shenbagavali & Mahimairaja, 2014). Transportation and mobilization of contaminants are effected by the electric field applied and these move through the porous matrix in the direction of the electrodes (cathode and anode) where they are accumulated, impelled out and treated. The contaminants due to several transportation mechanisms facilitated by the created electric field are moved out of the soil (Acar *et al*, 1990, 1995). Three major transport phenomena occur with the application of the electric field namely electroosmosis, electromigration and electrophoresis. They cause the movement of the pollutants to the electrodes (Shenbagavalli & Mahinairaja, 2010, Lindgen *et al*, 2010). Quite a handful of factors determine the direction of the movement of the pollutant, such as soil type, contaminant concentration, contaminant type, soil structure, current density in the soil pore water, interfacial chemistry of the soil-water mixture. These transport phenomena are greatly controlled and determined by the surface charge densities of the soil aggregates and therefore by the mineralogical soil composition.

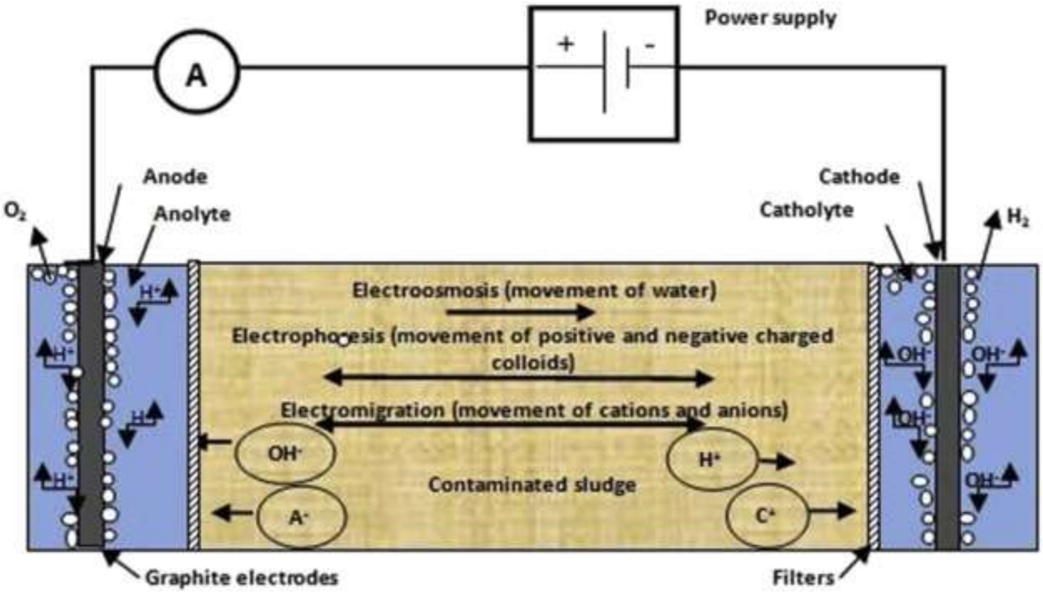

Figure 1: Principles of Electrokinetic Remediation Process

Transport Phenomena in Electrokinetic Remediation

A driving force that could cause mass movement of particle is provided when an electric field is introduced across a volume sample of a soil and this force can be likened to other driving forces such as thermal gradient, concentration gradient and pressure gradient. The major target of electrokinetic remediation is to initiate and sustain the movement of subsurface pollutants when subjected to an electric field using channels like electrophoresis, electromigration and electroosmosis (Virkutyte *et al*., 2002).

Electromigration

This is the first and major channel of movement of ions in the pore solution with the driving force generated from the supplied electric field. Anions migrate towards the anode while the cations move to the cathode. The result of electromigration is that the ions tend to gather around the oppositely charged electrode with respect to their respective charges (Reddy *et al*., 2006; Elisa, 2008). This electromigration of anions and cations is proportional to the concentration of the ion in the pore water solution and also proportional to the electric strength (Kim *et al*., 2005). The rate of the migration of a specific ion species is described by a term called ionic mobility when the ions are under a unit electric field. The effective ionic mobility better describes the rate of ionic migration in soils, this also accounts for tortuosity and the soil porosity, which greatly influence ion migration (Alshawabkeh, 2001). Electromigrative velocity (v_{em}) mostly is governed by the ionic valence (*zi*), ion mobility (*ui**) and electric gradient (E), this can be mathematically expressed roughly as:

$$v_{em} = u_i^* z_i F E \qquad (1)$$

where F is the Faraday constant (in Cmol-1).

Ion mobility i.e *ui** is a parameter associated to the ion diffusion coefficient (Di) as shown by the Nernst-Townsend-Einstein equation and their relationship is expressed by Yeung (2011). The pivotal parameters above such as T, n, D and τ are usually seen and used as constants, these constants by the way show discrepancies from time to time in EKR process. Significant errors therefore can occur due to usage of these constants when used to explain the temporal and spatial distribution of pollutants in EKR process.

Electroosmosis

This is the transport of moisture or pore fluid under the influence of an electric field from the anode to the cathode. It is a flow through the soil of a bulk of water as a result of electric field (Lynch *et al*., 2007). This phenomenon is controlled by the pH of the system, applied voltage, and electrolyte and zeta potential of the soil medium (Annamalai & Sundaram, 2020). The predominance of a negative charge on the surfaces of the particles, forces most of the migration of the fluid from the anode to the cathode and these movements of both water molecules and ions of these species (hydration shells) cause a net strain as a whole on the pore fluid surrounding the hydration shell. The generated net strain is built up into a shear force due to the pore fluid viscosity. The synopsis of all these effects is that most times there is an excess of cations in proximity to the soil particles and towards the cathode, the electric field builds up a net force which causes pore fluid flux to it (Acar *et al*., 1995). Therefore, the flow of pore fluid from the anode to the cathode compartment is caused by the electric field, producing a flux that forces the water level to rise in the cathode compartment. Mahmoud *et al* (2010) states that three distinct layers can be separated out of this electrical double layer and they are namely: outer Helmoltz plane including diffuse layer, inner Helmoltz plane, and the slip plane bearing the zeta potential (found in the diffuse layer). There is then a generation of osmotic flow and the flow of ions hydrated in EDL under the influence of the electric field with respect to a charged surface which drive water molecules to undergo a viscous force induced directional flow. Some cations with high valence including H^+ in the diffuse double layer of surfaces of the soil particles are adsorbed near the anode area and this reduces the diffuse double layer thickness. This reduced double layer is able to alter the balance between the forces of repulsion and van der waals forces of attraction in the clay particles, this can lead to the flocculation of clay particles (Li *et al*., 2016). The flocculated structure is susceptible to low tortuosity of the flow paths and high porosity which can further enhance efficiency of the electromigration. A number of theories have been posited to explain and describe the behaviour of electroosmosis. The Helmoltz-Smoluchowski theory is centred on the zeta potential concepts and electric diffuse layer; it is widely adopted and employed by scholars. The theory of electroosmotic flow rate (qe) was developed by Choi & Lui (1995), Sunderland (1987) and reported by Masi *et al* (2017b). Despite the fact that the transmission effect of electroosmosis is not higher than that of electromigration, it can also increase transmission of the ions when the zeta potential of the soil particles surface is negative. Generally, acidic conditions have proven to be helpful for electromigration of most heavy metals due to the desorption effect but the electroosmotic flow direction is reversed when the point zero charge is higher than the pH at the soil particles. As a result, the soil pH range that may balance the two opposing effects is necessarily sought for to sustain a greater transport efficiency of contaminants in the soil.

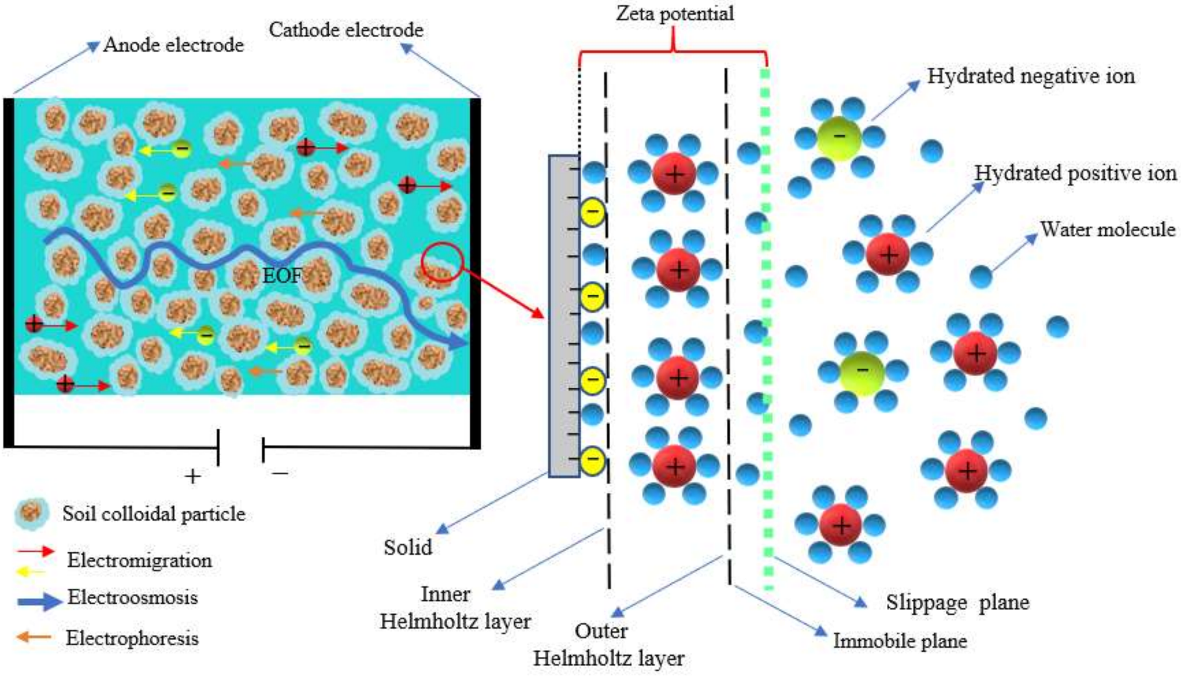

Figure 2: The Schematic diagram that shows the transport phenomena in electrokinetic processes (Wen *et al*, 2020).

Electrophoresis

Electrophoresis is the transport of charged colloids and particles driven by the force of an electrical field. When a colloidal suspension is subjected to a direct current (DC) electric field which is applied across the suspension through the use of electrodes, charged colloids and particles suspended in the pore fluid are attracted to either the cathode or anode electrostatically and repelled from the other (Shenbagavalli & Mahaimaraja, 2010). Negatively charged particles incline towards the anode while the positively charged particles towards the cathode (Ahmad, 2004). Normally, its application for environmental purposes is largely inconsequential and therefore less important as compared to electromigration and electroosmosis in terms of the flux despite the fact that in some rare cases, electrophoresis is seen to contribute major roles in decontamination. A typical example of this scenario is when the movable colloidal particles and the contaminants are bound together or when contaminants are adsorbed on the migrating colloids, the contaminants will be moved with the colloidal particles (Shin *et al*., 2017). This happens in reality when the particle size is small enough, here; electrophoresis is bound to contribute significantly to the pollutants transport. Therefore, electrophoresis generally has a very little effect especially on inorganic matters transport in less permeable soil systems in contrast to electroosmosis and electromigration and as a consequence, it is sometimes said to be insignificant in EKR process.

In addition, there are series of complex effects that change the chemical composition of a system which has its porous matrix subjected to an electric field. One of such effects in water electrolysis. Water electrolysis is the production of OH^- at the cathode and H^+ at the anode, it happens exclusively at the electrodes. The transport phenomena aforementioned i.e. electroosmosis, electrophoresis, and electromigration create species gradients along the material, OH^- and H^+ species inclusive. It is imperative that the pH be strictly controlled to avoid the formation of precipitation species (e.g., hydroxides or carbonates) and other inimical effects which can impede the transport processes thereby reducing the system performance. The addition of acid/base at either or both of the electrode compartments is a workable strategy for maintaining the system pH level. Another approach involves improving the system metal solubility by either the addition of chelating agents or application of alternating or pulsed electric fields. Controlling the pH/redox conditions is undoubtedly a key factor in regulating the efficiency of pollutant removal because the boundary conditions for transport are defined by the electrolytes. Unfortunately, the electrolyte composition varies continuously due to the ionic species flux which consequently varies the H^+-OH^- balance in the system, these cause a transient and non-linear behaviour in the setup (Alshawabkeh, 2009). Electrical conductivity distribution and non-uniform geochemistry profiles are also results of this non-linearity. These effects are broadly interdependent because all variables involved are inter-related. The moistening of porous matrix by supply of electric field also starts off chemical reactions in the soil and at the electrodes and these significantly drive the chemical transportation and speciation of the pollutants and other species in the soil. Notable chemical reactions that take place include adsorption-desorption reactions, redox reactions, acid-alkaline reactions and dissolution-precipitation reactions. These types of reactions decisively affect the speciation of the pollutants, the flux and efficiency of pollutant removal (Yeung, 2009). The decomposition of water is the major reaction in electrochemical/electrokinetic systems and it generates both hydrogen and oxygen gases from the respective reduction half-reaction at the cathode and oxidation half-reaction at the anode as shown in equations 1 and 2.

At Anode (Oxidation):

$$2H_2O_{(l)} + 4e^- \rightarrow \ 4H^+{}_{(aq)} + O_{2_{gas}} \qquad E = -1.229V \tag{1}$$

At Cathode (Reduction):

$$4H_2O_{(l)} + 4e^- \rightarrow \ 2H_{2_{gas}} + 4OH^-{}_{(aq)} \qquad E = -0.828V \tag{2}$$

Basically, alkaline solution is produced at the cathode while acid is produced at the anode, this consequently increases the pH at the cathode while the pH at the anode decreases. Dynamic changes in the soil are sparked up by these chemically driven movements of the H^+-OH^-system of ions. Hydrogen ion is noticed to be averagely twice as mobile as hydroxyl ion, therefore, the protons override in the movement on ions predicating the movement of the acid front across the soil particles till it contacts the hydroxyl front in a region close to the cathode and at this point, the ions may react to generate water. Thus, the soil is variegated into two different zones with a very sharp pH gradient between them: a low pH zone on the anode side (longer) and a high pH zone close to the cathode (shorter). The geochemical characteristics and most importantly the extent of interchange of OH^- and H^+ ions determine the actual soil pH values and since the pH values greatly impact the rate of absorption/desorption of the contaminants, the degradation of the contaminants, chemical speciation, and the dissolution/precipitation reactions; it is consistent to state that these electrolysis reactions are highly influential in the electrokinetic treatment. Moreover, the other quantities affected by the pH changes are the evolution of the electroosmotic flow (this plays a vital role in removal of non-charged organic contaminants) and the contaminant migration as well (Reddy & Cameselle, 2009). The dissolution and transportation of the contaminants can be improved by the addition of chemicals and these enhancing chemicals which can react with both pollutants and the soil, making it expedient to determine the soil geochemistry and the other reactions capable of occuring while as well putting into perspective concomitantly the pH effects to be able to arrive at an optimum technique that keeps the natural properties of the soil intact during pollutant removal to preserve its usefulness even after the remediation. The electrolysis reactions are also controlled by electrode types and arrangement, electric potential supplied during the remediation and in particular, the chemical species used (Emenike, 2013). In summary, fluid is induced to flow through the soil pores due to a difference in fluid potential internally generated or externally applied (Istrate *et al*, 2007), advection of fluid through the pores facilitated by electroosmotic flow, movement of protons generated through the soil by migration of ions from which are driven by electrical gradient and lastly, diffusion caused by concentration gradients.

Diffusion which is another of these complex effects simply refers to the mass transport driven by individual species, concentration gradients and the movement through hydraulic gradients generated by advection (Lindgen, 2010). Diffusion appears as a consequence of concentration gradients developed by the electroosmosis and electromigration of pollutants during electrokinetic remediation of contaminated soils. Electroosmosis and electromigration effects often overshadow the effect of diffusion, considering its low velocity which makes diffusion to be considered negligible most times.

Operating parameters used in electrokinetic remediation

A number of factors are considered during electrokinetic remediation of contaminated soils, some of which are electrolytic reactions at the electrodes, pH and soil-surface chemistry, geo-technical/hydrological characteristics of the porous medium and equilibrium chemistry of the aqueous system (Alshawabkeh, 2001). It is safe to conclude that the parameters which impact the contaminant removal efficiency of polluted soils are: soil type, soil structure, contaminant concentration, system pH, remediation time, electrode types and spacing, processing fluid and applied current density. Alshawabkeh *et al*. (1990) indicated three significant problems to any possible remediation technology. They are namely large specific surface area that gives room for a number of active sites that facilitate surface reactions, low hydraulic conductivity that impedes the flow rate of fluid volume, the dynamics of the process which is not well understood.

Contaminant Concentration The type and concentration of the contaminant to be removed is of great importance during electrokinetic remediation, although Alshawabkeh *et al* (1990) suggests that contaminant type does not restrict or limit the remediation process significantly provided the pollutant is not in the sorbed state. On the other hand, existing data reveal that removal of contaminants having high concentrations is not impossible. Although high concentration levels on ions in the pore field will also heighten the electrical conductivity of the soil thereby reducing the electroosmotic fluid flow and reducing removal efficiency indeed. High concentration of pollutants cause ionic species movement to additionally influence the transport process and in effect, the time rate and efficiency of removal will be reduced. At lower concentrations, the migration and advection will together participate in the extraction of the pollutants which tends to better and higher removal efficiency of pollutants. Zhou *et al*

(2004) studied the extraction of copper and chromium from polluted soils using EKR by lactic acid addition in the catholyte. It was reported that higher dye removal rates at low initial concentration and an increase of liquid flow rate and current density could significantly improve the dye removal. Zhou *et al* (2010) carried out a study on electrochemical remediation process for degradation of chlorophenol (CP) presented in soil. The operating parameters used include flow rate, initial pH, current density and initial CP concentration. These were all found to affect the removal efficiency. It was opined that an increase of liquid flow rate and current density significantly improves the CP removal. Higher CP removal rate was observed at lowest initial CP concentration.

Electrolytes/Processing fluid Cameselle *et al* (2020) studied optimization and analysis of manganese (Mn) extraction from polluted solid matrixes by EKR. The eletrokinetic treatment of Mn polluted kaolinite clay specimen was studied in conjuction with other system influences like current density, pH, voltage influence, moisture content, and some other facilitating agents on energy consumption and metal removal. 100ml of concentrated manganese sulphate solution was added with 120g of kaolinite. The electrodes of the cell had a constant direct current applied on them for 7 days. The Mn removal from the kaolinite model was analysed using four organic acids that possess complexing capacities, i.e., EDTA, tartaric acid, citric acid, and oxalic acid. At 0.1M concentration of the manganese in the solution, the complexing organic acids were added before mixing the solution with kaolinite. The range of the final pH of the mixture was discovered to be between pH 5 (for EDTA) down to pH 3 (for oxalic acid). The possible speciation of complexes was determined by the pH of the mixture which between the organic acids and Mn^{2+} ions. The speciation of anionic complexes was not favoured in the pH range used in this particular test, cationic or neutral complexes are the most probable complex species in the pH range used in these tests. Therefore, it was anticipated that the manganese could have been moved by electromigration towards the cathode (for cationic species) and electroosmosis (for neutral species). The detailed result of this research work indicated that the transportation of manganese towards the cathode was favoured by addition of organic acids which decreases the accumulation in section S5 of the kaolinite specimen. Therefore, there was a lower amount of manganese accumulated in section S5 than what was accumulated with no facilitating agent involved and the manganese was driven to the cathode chamber. When citric acid was used, the manganese content was completely extracted from the polluted soil solution and was also collected in the cathode chamber due to the development of a strong electroosmotic flow and also the complexing capacity of citric acid with manganese that was able to transfer all the soluble species in the fluid to the cathode side. Overall, facilitating agents in electrokinetic treatment are believed to be most efficient for the pollutants removal in electrokinetics. Cameselle & Pena (2017) studied the extraction of zinc pollutants from a contaminated agricultural soil using citric acid as the agent. The most occuring species in the mixture solution, zinc citrate (L – ligand citrate), was the negative species ZnL^- at pH greater than 6; the positive complex ZnH_2L^+ at pH 3 and the neutral complex ZnHL at pH 3.5. When the pH was lower than 3, the most occuring species was the Zn^{2+} cation. The species moved towards the cathode or anode (by electroosmosis or electromigration) determined by the charge carried or the soil pH. The efficiency of the facilitating agents and pH was well depicted by the results in the removal of metals from real soil samples. Acar *et al* (1995) investigated the results of delivering chemical conditioners at the cathode or the anode of an EKR system in the removal of pollutants from contaminated soil. These conditioners have the ability to alter the electrode reactions and also improve the efficiency of the system. In the research, the processing fluid used at the cathode was acetic acid, 50ml was added to 100g of kaolinite at 30V, 10A for 24 hours. The major reaction was the evolution of hydrogen and the reduction of proton. The creation of soluble complexes was facilitated by the migration of acetate anions into the system. This was made possible because acetic acid depolarizes the reaction in the cathode which aided in the successful solubilisation of the contaminant since most acetate salts are soluble. Other related researches were carried out on clays contaminated with thorium at concentration levels of 1500 to 2000mg/k Ωm (Virkutyte, 2002). Thorium ions possess four charges and agglutinates very strongly with the clay. It was opined that formation of the upstream bone which forms the precipitates of insoluble metal hydroxide that blocks the interstitial holes or passage ways of the clay is achievable by conditioning the cathode with acetic acid. Pazos *et al* (2008) made a study on remediation of dye-polluted kaolinite using the blends of both electrochemical treatment and EKR. It was depicted in this research that the EKR method, on addition of a sufficient electrolyte as disodium hydrogen phosphate, the process was greatly improved. The dye decolourization rate is noticeably improved if disodium hydrogen phosphate concentration is increased. Processing fluids are used during EK to either enhance or condition the mobility and solubility of organics in the soil. Emilio (2010) also demonstrated that the recovery rate was highest in electrokinetic cells where electrolytes were added. Alshawabkeh *et al* (1999) stated that enhancement agents are required in the determination and regulation of the soil chemistry and promote transport and solubilisation of the pollutant species. These enhancement/facilitating agents are required to show the following characteristics:

i. they should be stable chemically over a wide range of pH,
ii. they are not to produce insoluble salts within the range of pH values expected to occur during the remediation with the contaminant and
iii. They should not leave behind toxic residue in the soil after treatment.

Ricart *et al* (2008) studied heavy metals and organic pollutants removal in contaminated soils by electrokinetic remediation process. The research work employed desorption of a dye, Reactive Black 5(RB5) using potassium sulphate as the enhancing agent. The inclusion of this enhancing agent in the interstitial fluid aided the dissolution and desorption of RB5 which in turn led to a 95% extraction of the dye from the polluted soil. This shows that the use of stable salts does not in any way give undesirable speciation and products at the anode and cathode during the electrokinetic treatment. Pazos *et al.* (2008) also confirmed that potentiality in the processing fluids when potassium sulphate was used in the removal of the dye pollutant from the kaolinite sample. This achieved 91%-96% removal efficiency in all of the clay samples. However, heavy hydrocarbons which are examples of insoluble organics are not decisively ionised and the soils in contact with these insoluble organics are uncharged. Therefore, the separation of insoluble organics by the electrokinetic process is limited to their transport out of the soil by electroosmotic flushing of the liquid, either using surfactant or water to make the compounds dissolved or push the compounds ahead by a water front (Probstein *et al*., 1993).

Electrode Type: Electrically conducting materials that are chemically inert such as platinum, stainless steel, coated titanium, or graphite should be preferred as electrodes in electrokinetic remediation processes. The use of these materials prevents the generation of unwanted corrosion products when in acidic range of operation and the operational dissolution of the electrodes (Alshawabkeh *et al*, 1999). Electrodes should also be hollow and porous which facilitates the removal of contaminated solutions from below the surface. The electrodes can either be installed vertically or horizontally and the spacing between the electrodes should also be considered. Other factors to consider for the selection and design of electrode materials include: ease of fabrication, availability of the material, electrical conductivity of material and ease of installation.

Current and Voltage: Cameselle *et al* (2020) studied the optimization and analysis of Manganese (Mn) removal from polluted solid matrixes by EKR. The analysis of the influence of different factors such as moisture content, current density, influence of voltage, facilitating agents, and pH on metal removal and energy consumption was carried out on the treatment of the manganese contaminated kaolinite clay specimen. It was discovered that in this experiment that manganese, just like a number of organic acids form stable complexes with heavy metals over a wide range of pH thus allowing the electrokinetic transport of these metals into the cathode chamber. It was concluded that an alternative method to overcome unsolicited early precipitation of manganese is the application of complexing agents. The test was carried out at a constant electric current intensity of 1.5 A/m^2, an intermediate value registered at 30V in the previous test of the current intensity. The value selected was used to enable the comparison of results of this test on the same current intensity and constant voltage of 30V. The result of this operation at a constant current intensity was the production of less accumulation in Section S5 and a higher removal rate of manganese collected at the cathode. The removal of manganese was only 65% from Sections S1-S4 while for the use of lower current intensities, there were pronounced drops in the electric potential between the cathode and anode; this caused slower development of alkaline zone in the cathode side and reduced rate of electrolysis of water than at the constant voltage of 30V. Alshawabkeh *et al* (1999) states that the most efficient electric current density demonstrated for the EKR process is in the range 1 A/m^2 to 10 A/m^2. The fact that the higher the electric current density the more the generated acid and the faster the pollutant removal process is counterbalanced by more power consumption as the square of the electric current is proportional to the power consumption. Pazos *et al* (2008) carried out an experiment with an electric current with maximum values of 30V or 10mA. Annamalai *et al* (2014) and Istrate *et al* (2013) carried out a study which revealed the technical optimum current density to be 10 A/m2 as increase to this value significantly improved contaminant removal. Parameters monitored during these experiments were current, pH and pollutant concentration. In the first two days of treatment, current increased followed by a decreasing in the next 3 days and at the end the steady state value of 10m/A was reached. Greiciute & Vasarevicius (2017) carried out a research that bordered on remediation of heavy metal contaminated soil using the electrokinetic approach. It was discovered from the study that a higher cleaning efficiency is reached when applying 29V rather than 24V.

Remediation Time: Istrate *et al* (2010) carried out a research on the electrochemical remediation- efficiency vs treatment configuration of three different soil types (kaolin, sand and mixed matrix-kaolin+sand). These soil types were artificially contaminated with diesel fuel. It was observed that the removal percentages obtained during the test performed on a sand sample are smaller compared with removal percentages reached in kaolin. It was also noted that the contaminant removal increases significantly as the time increase i.e. the more time, the better the removal results.

Coupled Electrokinetic Techniques

One of the advantages of electrokinetic remediation processes is the ability to combine with other techniques for synergistic effect/efficiency on remediation of the polluted media.

Electrokinetics with Fenton Technique

Yang & Long (1999) were first to adapt the electrokinetic process of phenol polluted process with facilitation of the Fenton technique which is an adaptation of the oxidation-reduction methods. This Fenton technique had been previously shown by researchers to also remove pollutants from soil media or wastewater. Fenton + Electrokinetics is a proven in-situ efficient refining method utilized when a vast body of soil is largely polluted most especially low permeability fine-grained soils such as clay soils. The use of Fenton technique alone cannot solve problems of low permeability and production of hydroxyl radicals from the decomposition of chemical species, thus in combination with electrokinetics, there is a significant increase in the efficiency of the removal efficiency (Bocos *et al*, 2015). Electrokinetics remediation of low permeability soil contaminated with organics was substantively aided when correctly integrated with Fenton and other oxidation processes (Yang & Liu, 2001; Kim *et al*., 2006; and Ren *et al*., 2014). Fenton process amidst all other oxidation processes has received much interest in the degrading of organic pollutants that are biofractory in media because of their high oxidizing capacities (Kang *et al*., 2005 and Sun & Yan, 2007). The reactions of Fe^{2+} ions against hydrogen peroxide (H_2O_2) are termed as Fenton process. Kim *et al*., 2006, 2005, Kim *et al*., 2007; and Huang *et al*, 2012 have demonstrated in the past that organic pollutants including phenols, polycyclic aromatic hydrocarbons, and halogenated hydrocarbons can be treated by this method. The crucial principle of the Fenton process is maintaining the operational pH near 3 around the anode area of the cell. During the process, organic pollutants and heavy metals in the system migrate through electromigration and electroosmosis initiated by the electric field, then the hydroxyl free radicals degrade them at the anode area of the cell in the Fenton reactions. According to Yeung & Giu, (2011), the Fenton process can be stratified into two steps:

The first and initiating part is the Fe^{2+} oxidation to Fe^{3+} ions made possible producing hydroxyl radicals in the process of the reaction which breaks down hydrogen peroxide too (Equation 1). The second part which is rather a group of similar reactions include the degradation of organic pollutants when attacked by the hydroxyl radicals produced in the first part all the way to oxidation. (Eqns 2 and 3).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\cdot + OH^- \quad (3)$$

$$RH + OH\cdot \rightarrow H_2O + R\cdot \quad (4)$$

$$OH\cdot + Fe^{3+} \rightarrow Fe^{2+} + products \quad (5)$$

There are additional reactions termed the Fenton catalytic cycle, they occur as listed here in Equations 6 to 8.

$$Fe^{2+} + OH\cdot \rightarrow Fe^{3+} + OH^- \quad (6)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2\cdot + OH^- \quad (7)$$

$$Fe^{2+} + HO_2\cdot \rightarrow Fe^{3+} + OH_2^- \quad (8)$$

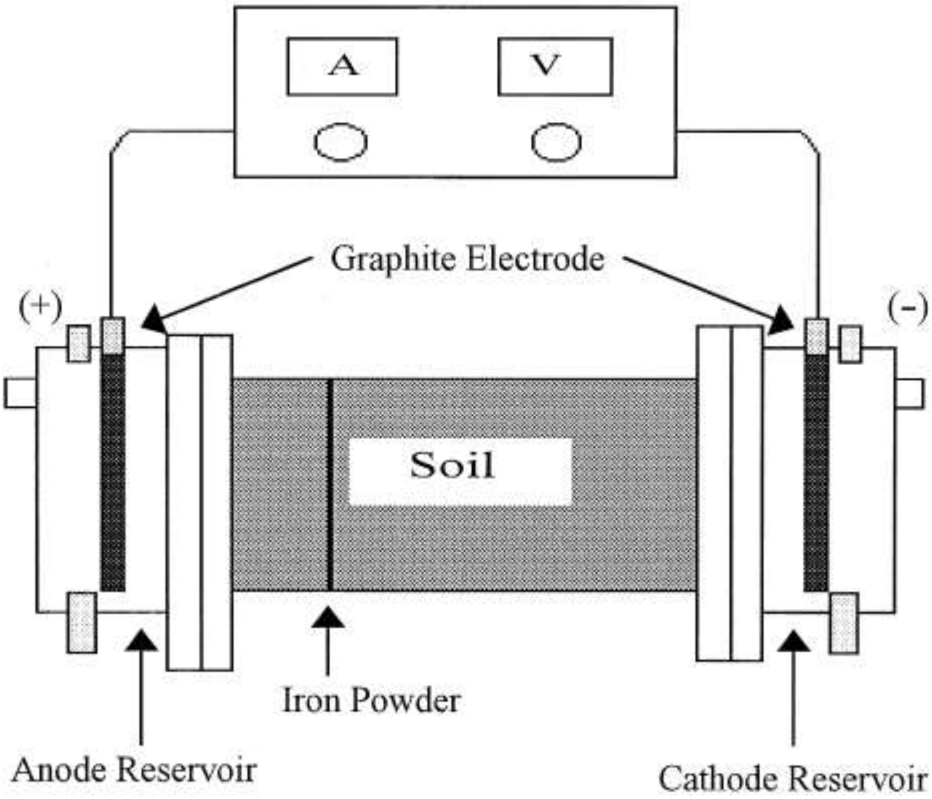

Figure 3: Diagrammatic representation of a set-up for treating pollutant contaminated soils by the Electrokinetic – Fenton process (adopted from Yang *et al*, 1999).

A number of reports have been made on the use of the Electrokinetic–Fenton combination technique. In most of them, the electrokinetic process had been used to instil oxidizing agent into the matrixes. Yukselen-Aksoy & Reddy (2012) made use of sodium persulfate as the oxidizing agent to degrade the PCB organic pollutant in the contaminated soil through the electrokinetic process. The study reported 77.9% as the maximum removal of PCB from the contaminated kaolin soil. Kim *et al* (2005) employed the EK-Fenton (EK-F) combination procedure to separate phenanthrene from contaminated kaolin soil. The research work revealed the influence of a number of parameters on the process, the parameters studied include remediation time, hydrogen peroxide stability, type of controlling & remediating fluids. The optimum conditions were achieved using EK-F process and hydrogen peroxide with 7% volume concentration of sulphuric acid for a duration of 312 hours. The work further concluded that the more the amount of acid used, the greater the removal efficiency. Sandu *et al*, (2016) remediated soils polluted with hydrocarbons using the EK-F procedure. Tween 80 surfactant was applied to the cell and this jumped up the removal rate by 45% as compared to the case without the addition of any surfactant. The pH was reported as a major influencer of the removal efficiency and this was caused by the selective solubility of metals at varying pH values and in consequence, hydrogen peroxide stability. The feasibility of the EK-F technology enhanced by surfactants in the treatment of real hydrocarbons contaminated soil was also examined by this same author and the discovery made was that the EK-Fenton method was improved. Paixao *et al* (2020) used the EK-Fenton in a different mode to make contaminated soil hydrocarbon-free when the soil has low hydraulic conductivity. The types of soils that exhibit this characteristic contain high levels of kaolin and using citric acid as a pH regulating agent increased the ease of the oxidation process such that iron electrode and H_2O_2 caused the removal of 89% of TPH from kaolin. Isossari *et al* (2007) built on the bases aforementioned, by studying the separation of PAHs from polluted clay by applying low DC/AC voltage with the use of Sodium Persulphate (or Fenton's reagent). The removals obtained for the PAHs were 11% after 8 weeks in Electro-Fenton and 19% from the same duration for Electro-Persulphate. It was reported that the limited removal was due to lack of optimization of the process conditions used for both methods such as increase duration, reagent dosages, and the pH which was supposed to be regulated at about 3 which was also not put into consideration by the authors.

Several compounds are added to the EK-F process in some cases to promote the efficiency of the Fenton reaction and to support an acidic operating condition. Kim *et al.* (2005) utilized 0.01N H_2SO_4 and 7% of H_2O_2 for the EK-F treatment of phenanthrene-polluted kaolin in the anode chamber and discovered that after duration of 21 days, above half of the phenanthrene in the clay had been extracted. They maintained that the stability of H_2O_2 and consequentially the treatment of the entire clay was improved by the presence of H_2SO_4. However, when Kim *et al.* (2009) used the exact flushing solution during the remediation of phenanthrene from clay with heightened buffering power, dismal removal was observed. They asserted that, although enhancing fluids were applied to the process, the clay carbonate content led to the reduction of H^+ concentration in the clay, thereby reducing the Fenton reaction efficiency. Their work affirmed that carbonates lower the treatment efficiency due to its reduced stabilization of H_2O_2. It is therefore proven that the addition of specific compounds in the soil matrixes plays a significant role in the efficiency of EK-Fenton process. Recently, experiments to examine the influence of the oxidant dosage in the EK-Fenton process were carried out by Reddy & Karri (2009), the set-up was polluted with phenanthrene and nickel. The effect of the oxidant dosage during the EK-Fenton treatment was closely monitored. The Ni movement towards the cathode was favoured by H_2O_2 though high amount of metal was held up in the soil close to cathode chamber and the result was an oxidation of around 56% of the phenanthrene when 30% H_2O_2 was used. This emphasizes that the control of the pH is as important as the optimization of the voltage gradient and H_2O_2/Fe concentrations for increase in the removal efficiency of nickel along with the oxidation of phenanthrene. Alcantara *et al* (2010) also discovered that when cathode and anode chambers are filled with 30% H_2O_2, the pH of the kaolin is maintained averagely at an acid value of 3.5 without pH control. In 14 days, a removal efficiency of 99% phenanthrene was achieved. Applicability studies on EK-F process revealed that the H_2O_2 stability and transfer rate of acid front are proportional to the phenanthrene degradation yield. This makes the injection of acid customarily included to efficiently treat sorbed pollutant on soils during the process while ensuring the acid is not too much to decrease the electroosmotic flow rate Several chlorophenols like PCP, 2,4-dichlorophenol (2,4-DCP), 4-chlorophenol (4-CP), 2,4,6-trichlorophenol (2,4,6-TCP) were used to study the relationship between their degradation rates and the chlorine content of contaminant molecules and the sequence of degradation was 2,4-DCP>2,4,6-TCP>PCP>4-CP(Kim *et al.*, 2005). The EK-F process was used in the removal of hexachlorobenzene (HCB) from kaolinite soil. The study revealed that under several different conditions tested, the process proved effective. Such conditions and results were high concentration of hydrogen peroxide (30% H_2O_2) gave 76% HCB removal with iron in the kaolin and without cyclodextrin, using beta cyclodextrin as flushing agent gave

64% HCB removal. In the absence of cyclodextrin, the oxidation was faster but the anode chamber had contaminants clogged up around it with varying addition method of Fenton's reagent into the cell. Also changing the distance between the electrodes significantly affected the remediation efficiency. Using Tween 80 and EDTA separately as flushing solutions in the EK-Fenton remediation for dredged petroleum hydrocarbons (TPH)-polluted marine sediment within 30 days of remediation, revealed EK-Fenton-EDTA had better effectiveness with the highest removal rate for metals and TPH (Pazos *et al*, 2013).

EK with Surfactants/Co-solvents Technique

This is yet another form of combined technique but instead of relying on oxidation reactions co-solvents or surfactants are added within the soil, which combines with the contaminants to eventually form compounds that can be transported due to the physicochemical characteristics of chelation, desorption, complexation or dissolution that they exhibit. The organic pollutants that have formed movable compounds are transported to the electrodes for further treatment by electrokinetics (Huang *et al.*, 2012). This combined process exploited ideas from various fields such as electrochemistry, environmental chemistry, soil chemistry, surfactant chemistry, and colloid chemistry. According to Huang *et al*. (2012), the surfactants utilized in this combined process can be broadly classified into these major categories; biological surfactants, such as rhamnolipid, carboxymethyl-β-cyclodextrin (CMCD), hydroxypropyl-β-cyclodextrin (HPCD), and β-cyclodextrin; anionic surfactants, such as Calfax 16L-35, 2,20-Azino-bis-(3-ethylbenzthiazoline sulfonate) (ABTS), and sodium dodecyl sulfonate (SDS); non-ionic surfactants, such as alkyl polyglucosides (APG), PANNOX 110, Brii 35, Igepal CA-720, Triton X-100, and Tween 80; and lastly cationic surfactants, such as CTAC.

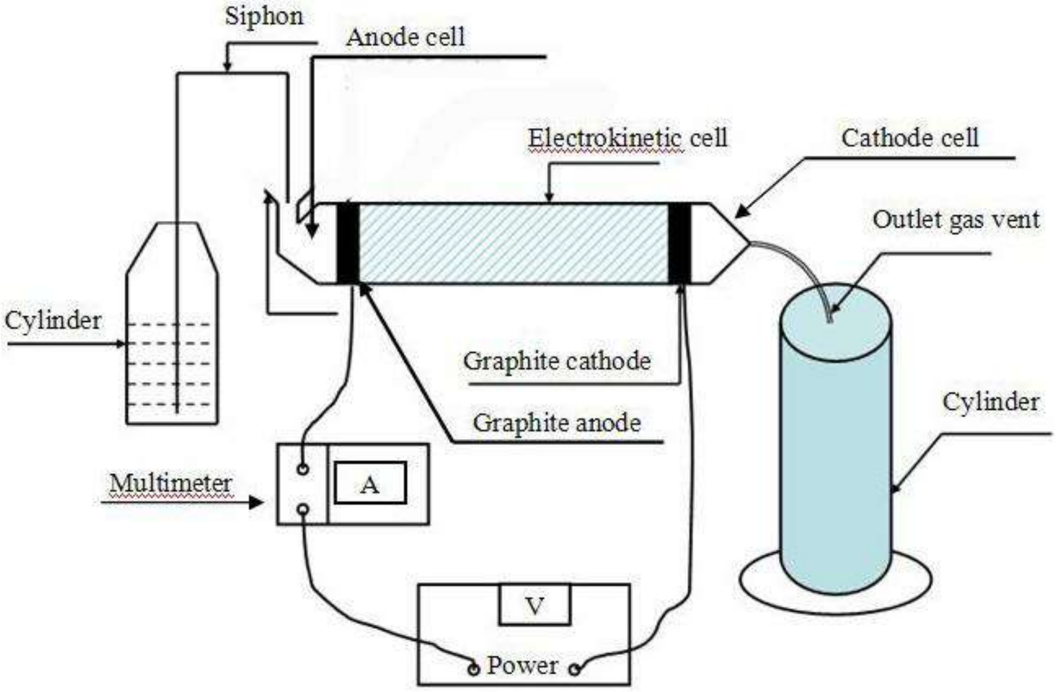

Figure 4: The Schematics of an Electro-Kinetic reactor enhanced by surfactants (Yuang *et al*, 2006).

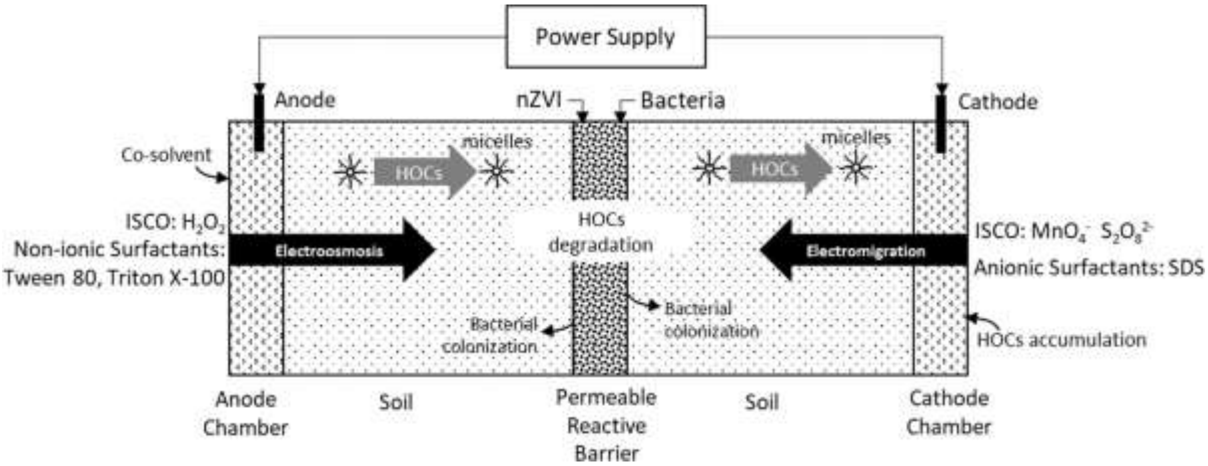

Figure 5: Diagram showing the enhanced removal of organics using Electrokinetic Remediation (Cameselle & Gouveia, 2018).

The biological or non-ionic surfactants are often selectively preferred of the aforementioned groups of surfactants because anionic surfactants tend to move pollutants towards the anode (which is in contrary direction to the trend of electro-osmotic flows) while cationic surfactants exhibit high toxicity levels. Generally, in this type of remediation, the currently used co-solvents include acetone, ethanol, propanol, methanol and tetrahydrofuran (Saichek *et al*, 2005). The widely used ones are propanol, ethanol, and methanol because of ease of use due to their high water solubility and polarity in water thereby making electro-osmotic flow more powerful. Lukman *et al* (2013) made use of the combination technique of EK and adsorption procedures to carry out simultaneous removal of organics (kerosene) and heavy metals from natural saline-sodic soil. This was done in a 21-day procedure of continuous electrokinetic-adsorption and the efficiency for kerosene and phenol removal was found to be 49.8% and 100% respectively. L'opez-Vizcaino *et al* (2014) in the same vein, scaled up to a pilot plant in order to evaluate the combined technique of EK and surfactant (SDS) of natural phenanthrene-polluted soil. Notwithstanding the excessive energy consumption that was more than 500 kWh/m^3 and protracted processing time of 2800 hours, the removal was at an average of only 25%. The effectiveness of surfactants in the EK remediation for anthracene or n-hexadecane polluted soil had the order: SDS>Tween 80>Triton X-100 in the demonstration of Boulakradeche *et al* (2015). Qiao *et al* (2018) also used these same three surfactants (Triton X-100, SDS, and Tween 80) in the anode chamber for curing of the clayey soil spiked with 1,2,4-trichlorobenzene. The discovery made was that Tween 80 when used as the anode flushing solution, gave the best flush efficiency with 5067ml cumulative EOF. Estabragh *et al* (2019) opined from evidence of their research that the use of ionic surfactants (SDS) yields a better efficiency of remediation when compared with non-ionic surfactants (Tween 80 and Poloxamer 407). A preceding work showed that the highest mass concentration of 84 g/L of bio-surfactant gave the most efficient biodegradation while 56g/L of bio-surfactant gave the most efficient extraction of oil from the soil bed (Gidudu & Chirwa, 2020). These studies have been done using EK in conjunction with surfactant enhancement methods to cure soils polluted with complex and heavy hydrocarbon compounds (e.g., diesel, and petroleum) or single simple pollutants (e.g., anthracene or phenanthrene) as HOCs. The heavy hydrocarbons used included engine oil, crude oil, lubricants, diesel, and a whole lot of wide range compounds that differ in composition. Another research was carried out by the same author to determine the effect of electrokinetics on the curing of a soil polluted with kerosene with the aid of two prevalent surfactants, the usage of 0.01M and 0.005M SDS in EK-SDS-1 and EK-SDS-2 respectively increased the separation efficiency to 55% and 50% in the anode. Moreover, the application of Tween 80 in EK-Tw80-1 and EK-Tw80-2 with the concentrations 1% and 0.1% raised kerosene removal steadily from 45% to 52% towards the chamber of the cathode. The results conclusively revealed that the addition of surfactants gives an additional advantage to the removal of kerosene when compared with the outcome of just the traditional EK test. It is worthy of note that the energy consumption for Tween 80 and SDS experimentations were less and more respectively as compared to their concurrent application. The use of EK coupled with surfactants as an eco-friendly technology has a possibility of curing natural polluted soil and reinstating the balance between ecosystem and ecology in the areas polluted when augmented with the best environmental management strategy available.

EK with Biological Technique

Electrokinetic remediation combined with biological techniques was first practiced for the treatment of soils polluted with heavy metals. The most widely used microorganisms are Mycobacterium frederiksbergense LB501TG, Sphingomonas *sp*. L138, Burkholderia cepacia G4, Thiobacillus ferroxidans, Pseudomonas *sp*. strain PNP1, Burkholderia *sp*. RASC c2, and Pseudomonas mendocina KR1 (Huang *et al*, 2012). Organic contaminants which are responsible for polluting soils are possible source of nutrients(carbon) to some microorganisms, which are the fundamental components used to provide the energy and the electrons essential for their growth as well as to develop the new-born cells (Kim & Yang, 2006; Niqui-Arroyo & Ortega-Calvo, 2007). This can be exploited to rid a contaminated soil of its pollutants by introducing microorganisms that would assimilate the pollutants for their metabolism. This biological technique is so efficient that it not only decomposes complex pollutants into less toxic materials but it also oxidizes them into water and carbon-dioxide (CO_2) eventually, mobility of the contaminants can also be modified to make them settled or coagulated in a region in the system. This is an environmental-friendly substitute for the other widely accepted treatment techniques with a number of merits such as safety, cost effective and shorter remediation time. The activities of the microorganisms in degradation of pollutants can nevertheless be controlled by environmental factors like water content, metal ions, pH, soil temperature, and other organic pollutants. In addition, the contaminants have to be degradable by microorganisms while the metabolic ability of the microorganisms should be strong enough. Factors such as soil mechanism, existence of inhibitory substances to microorganisms, and variation of pollutant nature can all affect the efficiency of the degradation in real-life applications thereby limiting its application. Biological technique can however complement the EK remediation method, improving remediation efficiency and reducing energy costs. Also for underground situations, the bioavailability of organic contaminants can be enhanced by the combination strategy through employing a number of EK effects induced by the application of a direct electric field (Olszanowski & Piechowiak, 2006; Arantxa *et al*, 1999). Another viable option is to degrade organic pollutants through the use of electric thermal effects which convey various additives to the contaminated area. The organic pollutants can be degraded using electrode reactions to generate suitable pH, temperature, and reduction-oxidation conditions for bio-transfer in underground processes after which the organic contaminants are degraded with biological techniques.

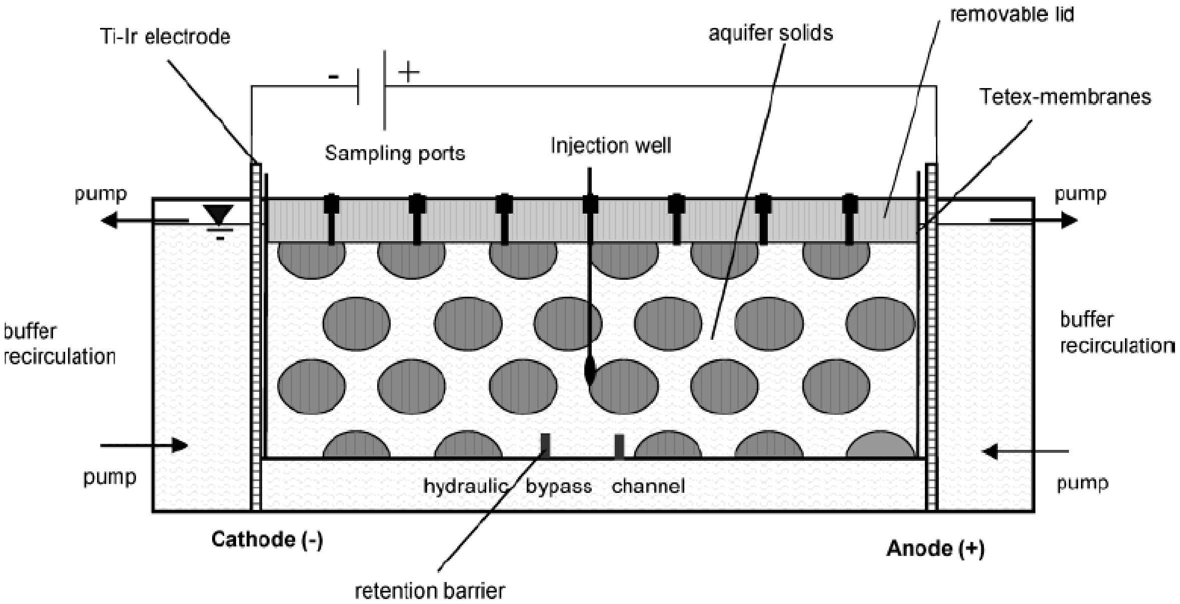

Figure 6: The Schematic diagram depicting EK reactor enhanced by biological techniques.

The Method of Lasagna

An innovative method for in-situ electrokinetic remediation of contaminated soils was developed at the Paducah site in Kentucky, USA and implemented in 1995. The technology was characterised by the formation of several layers of permeable treatment zones that are close to one another, addition of catalytic reagents, oxidising agents, sorbents, buffering solutions (these keep the layer separated), and the supply of an electric current to electrokinetically move the pollutants to the treatment zones formed. The technique due to its structural similarities and mannerism with the delicacy was called LasagnaTM. This novelty is efficient for the removal of heavy metal pollutants contained in heterogeneous, low permeability soils (Ho *et al*, 1999) and has a number of advantages when compared with other techniques. With this technique, fluid flow can be reversed through switching the polarity which enhances multiple pollutants to pass through the zones and also assists in reduction of the propensity of pH jumps and the non-uniform potential in the system. The cathode effluent can be recycled by targeting it back to the anode compartment where the pH is neutralized and in turn water management is simplified. Also, a wider range of soils can be remediated unlike most of the techniques that are streamlined to a particular soil structure. The schematic configuration of LasagnaTM models were suggested as vertical and horizontal forms (Ho *et al*, 1999) and for shallow contaminations which do not extend beyond 15m, the preferred treatment configuration is the vertical setup. The creation of horizontal fractures in over-consolidating soils as a result of vertical pressuring system exacted on the horizontal electrodes proves this technique especially efficient in the removal of pollutants from deeper layers of the soil system. All the same, there are several limitations which are technological or otherwise in nature which need to be worked on and the method itself improved in future studies. Potentially, LasagnaTM technology is able to treat multiple pollutants in clay and laden soils, though extended experiments and research still need to be carried out in order to guarantee that this process of remediation is well-suited for individual contaminants. Furthermore, one other adverse technology drawbacks is the formation of gas entrapments during electrolysis and also the necessity of excellent electrical contacts to the electrodes. The efficiency of this technology is opined to be increased by instilling bioremediation in ‘treatment’ zones. This would mean the combination of LasagnaTM and bioremediation techniques.

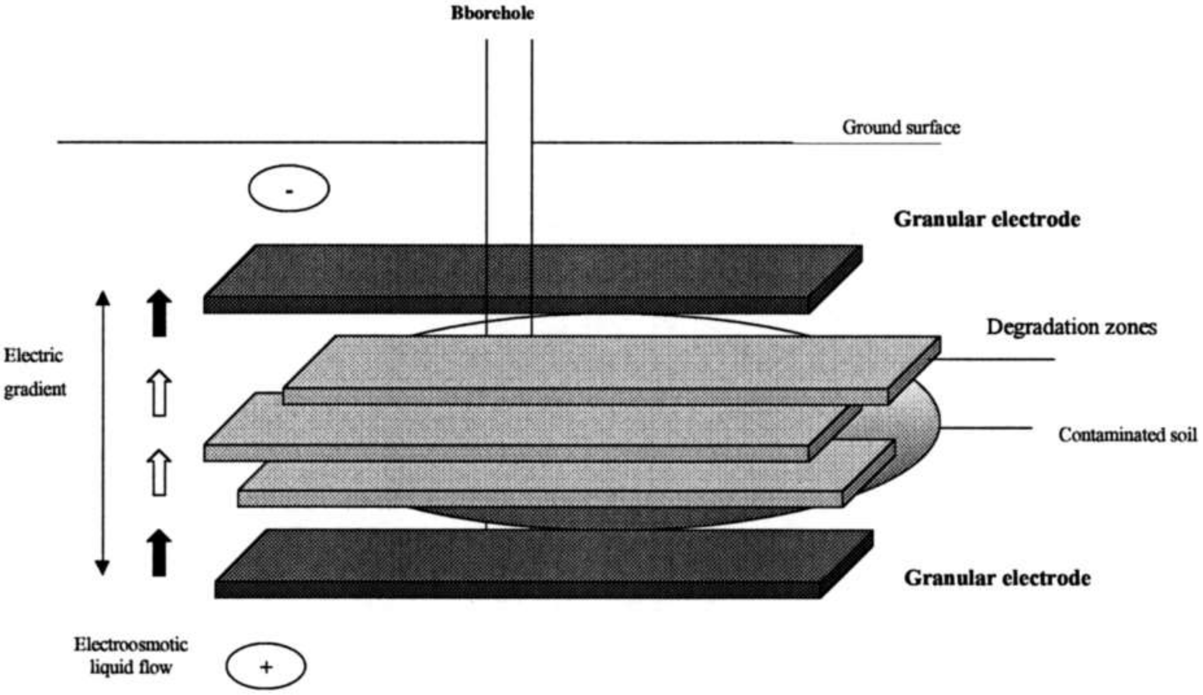

Figure 7: The diagrammatic representation of the configuration of Horizontal LasagnaTM (Ho *et al,* 1999)

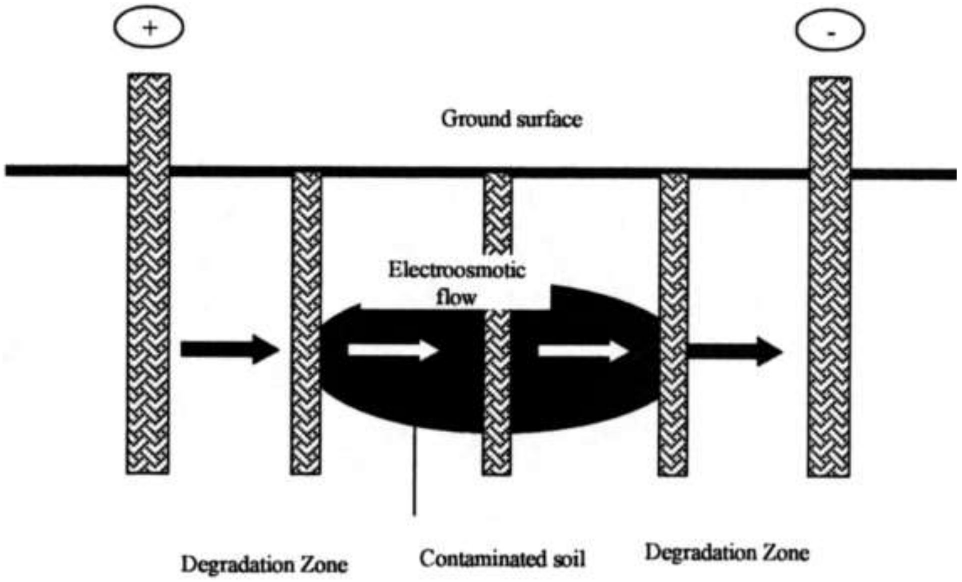

Figure 8: The diagrammatic representation of the configuration of Vertical LasagnaTM (Ho *et al,* 1999).

EK with Ultrasonic Technique

Many researches have revealed that electrokinetics in combination with ultrasonic technique, improves remediation efficiency of polluted soils (Thuy, 2014, Chung & Kamon, 2005, Kim, 2000). Thuy (2014) carried out a research on electrokinetic remediation with ultrasonic technique for low permeability soils polluted with organic contaminants. The study considered the complementary effect of the combination of these techniques – ultrasonication and electrokinetics in persistent organic pollutants (POPs) removal from polluted kaolin. To investigate the effects of parameters like frequency, moisture, initial concentration and remediation time on the treatment process, experiments were conducted at various sets of conditions and the result of these experiments revealed that ultrasonication has a potential to remove POPs. The experiment further distinguished performances between using electrokinetic process alone (EK) and the addition of ultrasonication to the process (EK+US). The result showed that though the level of improvement is insignificant, the combined electrokinetic and ultrasonic technique did show positive coupling effect as compared to individual processes alone. The function of ultrasonication in the process was to breakdown POPs from clayey soil through degrading the pollutants by oxidation and pyrolysis and increasing the mobility of hydrophobic organic compounds. Secondly ultrasonication increased the osmotic flow and sustained higher moving currents. The efficiencies of the removal of pollutants from EK+US tests showed from 2% to 17% higher than EK tests, subject to varying the pollutants and set-ups. There are additional merits to the use of ultrasound. These include transportable equipment, no generation of dangerous degraded products, allowing on-site treatment and compactness. Chung & Kamon (2005) discovered that ultrasound was applied to decontaminate organic pollutants mostly while EK remediation was applied to remove mostly heavy metals. So, these two techniques were combined to effectively remove phenanthrene and heavy metal (Pb) in natural clay and these two reaffirmed the synergistic effects on the decontamination as well as the contaminants migration. The removal efficiency for the combination of electrokinetic and ultrasonic technique at 30kHz, 200W gave 91% for Pb and 90% for phenanthrene which was higher than in the electrokinetic remediation alone which was 88% for Pb and 85% for phenanthrene. It was detected that ultrasound was responsible for increasing flow rate, increasing permeability; decreasing fluid viscosity, increasing porosity, as well as mobilizing sorbed pollutants. The overall effect of the integration of ultrasound to electrokinetic remediation yields positive synergistic effects most especially for the elimination of POPs and other organic contaminants in soils of low permeability.

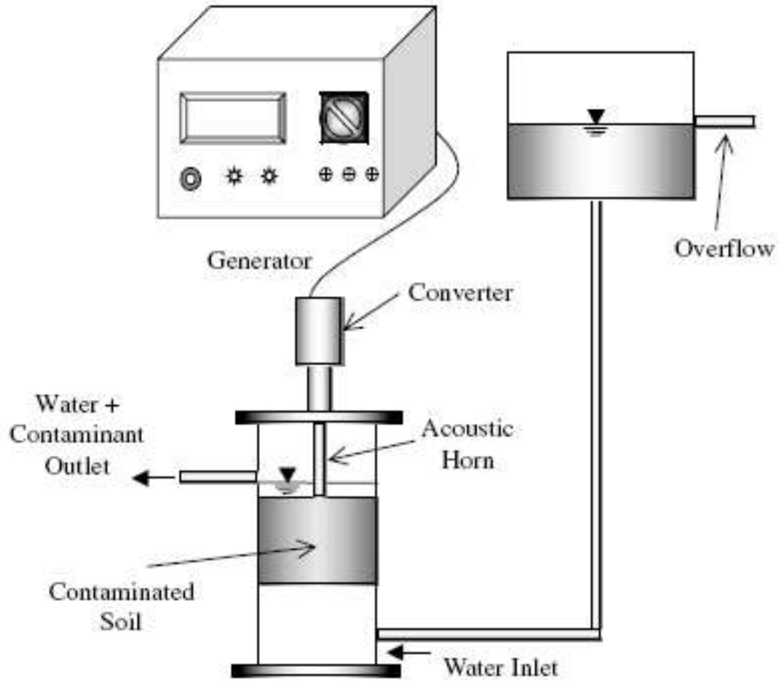

Figure 9: The schematic representation of the Electrokinetic and Ultrasonic Test Setup (Kim & Wang, 2003).

EK with Phytoremediation

Studies have also shown that electrokinetic remediation can be coupled with phytoremediation. Phytoremediation which is almost like bioremediation is the process of soil decontamination by the use of plants to absorb heavy metals or other contaminants. Phytoremediation is a plausible remediation technology in its own rights because it can run at low energy and cost, it has the advantage of ease of implementation on the field, and at the end of the process, the properties of the soil is improved. Electrokinetics, just like all other well established remediation combinations makes up for the limitations in the operations of the phytoremediation (Cameselle & Gouveia, 2018). For instance, the growth of plants and consequentially, phytoremediation capacity is favoured and improved by the application of an electric field on the system which mobilizes and disperses nutrients and contaminants throughout the system. The growing plants and soil microflora are very sensitive to electro-chemical changes therefore when trying to optimize the bioavailability of nutrients and contaminants, the chemical nature of the electrodes and the intensity of the electric field have to be regulated with utmost care to avoid counter productivity of the electrochemical constituent on the phytoremedial part of the system. With appropriate conditions, the combination technique termed “electro-phytoremediation” is capable of remediating soils containing mixed contamination. Acosta-Santovo *et al* (2012) discovered that very low electric field as little as 0.2 DCV/cm was efficient enough to enhance the germination of plants, and 1 V/cm of alternating current enhanced the plant to grow, and at the same time increased the remediation capacity. Oonitan *et al* (2009) elaborated the merits of electro-phytoremediation in a study on the decontamination of polyaromatic hydrocarbons (PAHs) and heavy metals polluted soil. As expected, the usage of alternating current did not bring up drastic dramatic changes in either nutrient concentration or soil pH, therefore the combination is suggested for large scale test.

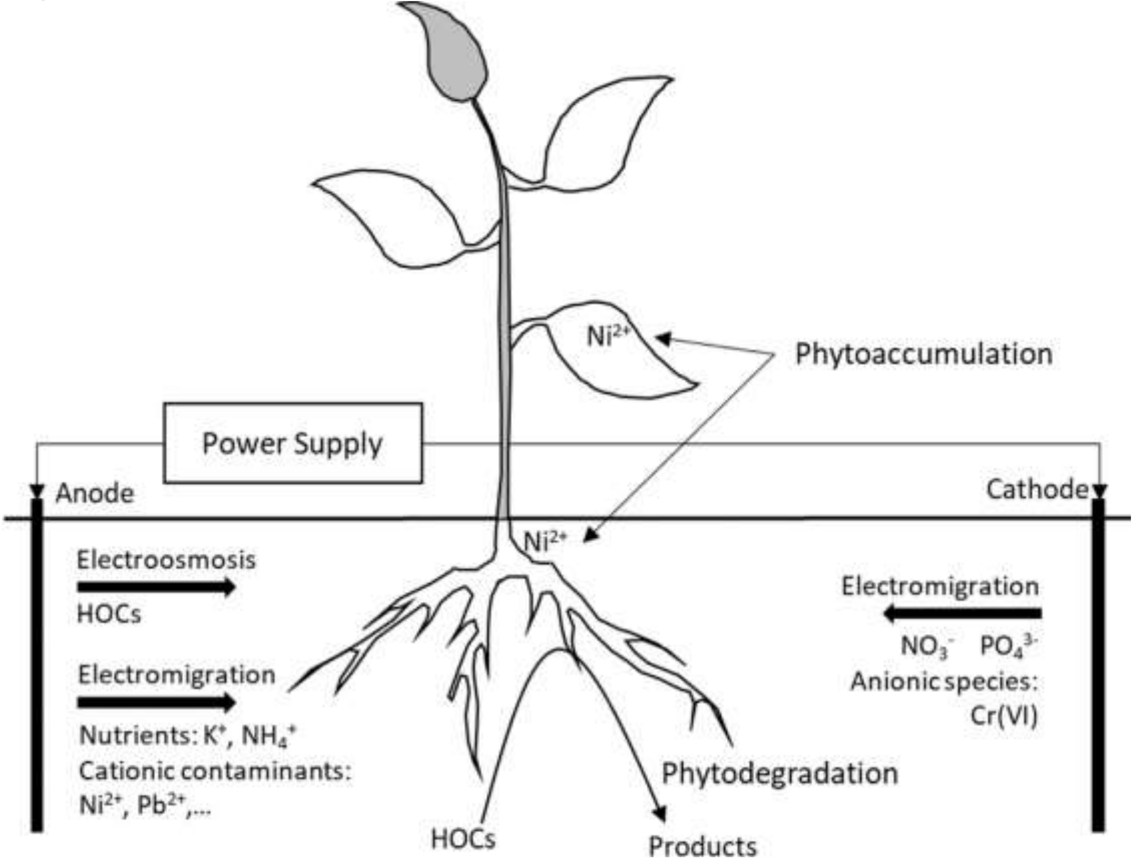

Figure 10: The schematic representation of Electrokinetic mechanisms in phytoremediation (Cameselle & Gouveia, 2018).

CONCLUSION

Electrokinetic remediation has proven to be a clean and promising substitute to traditional physicochemical processes used for the remediation of a wide range of contaminants at a polluted site, as it has proven to be more cost effective, decontaminating the soil effectively and still preserving the natural resource. For full remediation of polluted soils, best operational parameters must be put to use for optimum results. When electrokinetics is coupled with other remediation techniques, very impressive results are obtained because of the synergistic effect of both techniques. These coupled technologies, though with merits and demerits, have proven to be very effective in degrading contaminants in soil, require low energy consumption, and at the same time, conserve and enhance the properties of the soil been treated. However, to ensure maximum efficiency, the appropriate operating conditions of the coupled technologies must put in place as the technology continuously receives great attention to develop both the scientific and engineering theories, all for the safety of the environment.

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