

The Influence of Electrokinetic Remediation Process on the Removal of Cationic and Anionic Dyes from Kaolinitic Soils

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ABSTRACT

Low permeability soils possess specific mineralogical properties such as particle size, high buffer capacity, and high sorption capacity, which make them difficult to remediate and so pose serious environmental problems when polluted. The grain pores of these low permeability soils trap in pollutants tightly, which are inaccessible and non-responsive to traditional technologies during remediation. Traditional technologies, some of which are ex-situ remediation techniques further compound these environmental problems through logistics and economic infeasibility. Electrokinetic Remediation (EKR) can offer certain advantages for treatment of various contaminants which include organic compounds, heavy metals, radionuclides, organic waste and some mixed inorganic species from a matrix with high salinity, low permeability and high buffering capacity. In addition, (EKR) is a clean and novel technique which accesses the grain pores of low permeability soils such as clays and silts, which have proven non-responsive to other soil remediation technologies such as soil flushing and soil washing. Among these fine soils, it has been proven that (EKR) is more effective on clay soil with particle size <2mm, moderate plasticity, lower cation exchange capacity (CEC) and lower buffering capacity which can be found in this order: kaolinite > illinite > bentonite.

Keywords: *Electrokinetic, Remediation, Synergistic Effects, Kaolinitic Soils, Dyes*

Introduction

Globally, the environment is indeed under great stress, due to increased industrialization, manufacturing processes, urbanization as well as population pressure on the limited natural resources.

Voiciante *et al* (2021) states that the unstoppable industrial progress that began at the end of the 19th century has generated countless cases of environmental contamination, with the release of large quantities of inorganic and organic pollutants. The unsustainable habits and lifestyles of the population, compounds all the forms of environmental pollution, one of which is soil pollution.

Soil is essentially a non-renewable resource and a very dynamic system which performs many functions and delivers services vital to human activities and ecosystem survival. Soil is not only a resource, but also an indispensable part of the human environment. As a key component of the environment, soil is often a receptor of accumulated contamination from industrial, agricultural, urban and maritime activities and due to the interconnection in the natural cycles and in the web of life, soil contamination can lead to water and air pollution and vice versa (Thuy, 2014). Hence, soil contamination has been obtaining serious considerations around the world, been one of the most expensive and time consuming issues faced by environmental professionals. It is considered a serious problem since it affects not only the environment, living organisms and human health, but also the economic activities associated with the use of soil. Gill *et al* (2014) opines that soil contamination by anthropogenic activities is of global concern and where exposure to harmful substances occurs, there is potential for unacceptable risks to humans. Soil can therefore be said to be contaminated, when it presents a hazard in the form of material that has the potential for harm. For example, a landfill site may contain contaminated soil while the assessment of the risk of harm is based on the likelihood, frequency and seriousness of adverse consequences. Jamal & Alamddine (2009) reported the main types of contaminants identified as (i) Toxic or carcinogenic chemicals such as cyanide, benzene; (ii) Toxic or phytotoxic metals such as lead, chromium, nickel (iii) Organic contaminants such as oils, solvents, phenols, tanneries, textile works and dye works. Contaminated soil is a critical environmental issue, as a threat to ground water, poor quality of agricultural products which harms human health through the food chain and in general leads to the disruption of natural terrestrial ecosystems (Cameselle *at al.*, 2013). Contaminants can be washed off the soil by rain and groundwater, resulting in the dissemination of the contaminant. The public and the environment are being exposed to these pollutants through different pathways to unacceptable dosages. Therefore, soil contamination is a serious problem that requires a rapid solution in order to prevent more environmental damages. Similarly, a pollutant is a substance or energy introduced into the environment that has undesired effects, or adversely affects the usefulness of a resource. Pollutants could be in the gaseous, liquid or solid forms. Pollutants in the air include carbon monoxide, sulphur dioxide, nitrogen dioxide etc. Pollutants in water include pesticides, industrial solvents while pollutants in the soil include oils, organic chemicals, construction activities etc. These various pollutants present adverse effects on the environment. Organic pollutants which include oxygen demanding wastes, synthetic organic pollutants and oil, deplete dissolved oxygen in the water bodies to below 4.0mg/L which adversely affect aquatic life and coastal plants. In the presence of organic matter in water, thermal pollutants increase the bacterial action due to rise in temperature which also results in rapid decrease of dissolved oxygen. Radioactive pollutants are toxic to life forms while inorganic pollutants which include metal compounds, trace elements, mineral acids etc have adverse effect on aquatic flora and fauna. The two major types of colorants or dyestuffs produced today are dyes and pigments.

Dyes are organic colorants used in textile industries, pharmaceuticals, cosmetic, food and other industries for imparting different shades of colour. Dyes are coloured organic (i.e., they contain carbon) compounds that are used to impart color to various substrates, including paper, leather, fur, hair, drugs, cosmetics, waxes, greases, plastics and textile materials. Pigments which are finely ground solids dispersed in a liquid, such as paint or ink, or blended with other material pigments may be inorganic compounds (i.e., they do not contain carbon) or organic compounds

they generally give brighter colours. Dyes possess colour because they absorb light in the visible spectrum. The visible spectrum is the portion of the electromagnetic spectrum that is visible to the human eye. It contains the colours- Red, Orange, Yellow, Green, Blue, Indigo and Violet and are within the range of 400-700nm. A dye has an unsaturated (multiple bond) group attached to it. When the unsaturated group is reduced, the dye loses colour, when oxidized, it regains colour. This unsaturated group is known as chromophore and the substance having chromophores are known as chromogens. The presence of many chromophores produce deeper colour. Dyes usually have at least one chromophore colour bearing group for example retinal, and have a conjugated system (a structure with alternating double and single bonds). They also exhibit resonance of electrons, which is a stabilizing force in organic compounds. The properties of dyes are based on the following factors. They include shade (brightness or dullness), ease of application, and durability of colour, resistance to sunlight and chemicals and high affinity to substrate. The dye has a colour due to the presence of chromophores (Effendi & Shunitz, 2015) while the auxochrome (group of atoms attached to a chromophore which modifies the ability of that chromophore to absorb light for example carboxylic acid, hydroxyl group) makes the dye water soluble and binds the dye to the substrate by interaction with the oppositely charged groups of the substrate structure. Auxochromes are not responsible for colour, their presence can shift the colour of a colorant and they are most often used to influence dye solubility. They can either be acidic or basic, the important being OH, NH₂, NHR and NR₂. These radicals which bring about deepening of colour are known as bathochromic group and those posing opposite effect are known as hypochromic group (Bhatia, 2011). The presence or absence of the various chromophores, auxochromes and bathochromes, determine the acidic, basic and complexing nature of dye which, in turn, decides applicability of the dye. There are several classifications of dyes according to Aspland (1992). They include (i) Classification based on the source or origin (ii) Classification based on the dyeing process (iii) Classification based on the chromophore present (iv) Classification based on the charge on the chromophore.

Classification of dyes based on origin

Dyes can be classified as natural or synthetic according to their sources or origin. Natural dyes are derived from nature through organic and inorganic materials or sources. Natural dyes are produced from different plant and animal sources such as roots, leaves, bark, barriers, and wood. Examples of such dyes are logwood and tyrian purple. Synthetic dyes are dyes obtained by adding chemicals to natural dyes or as feedback petrochemicals or by adding chemicals to chemicals (Lee, 2011). Example, artificial alizarin is a synthetic dye synthesized from coal tar and anthracene. Synthetic dyes are easy to use, less expensive and have wider range of colours. The first synthetic dye “Mauveine” by Perkin was made from coal tar.

Classification of dyes based on the dyeing process

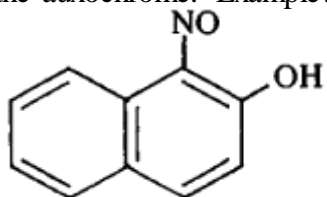
Dyeing process is accomplished by dissolving or dispersing the colorant in a suitable solution (usually water) and bringing this system into contact with the material to be dyed: Acid Dyes are anionic dyes soluble in water, Basic Dyes are water soluble cationic dyes, Mordant Dyes are dyes with no natural affinity. They require a mordant which improves the fastness of the dye against water and light. Reactive Dyes utilize a chromophore containing a substituent that is capable of directly reacting with the substrate, Direct Dyes are neutral dyes usually used as pH indicators and biological stains. Vat Dyes are dyes soluble in water but insoluble in sodium

hydrosulfide (Na-S-H), Disperse Dyes are water insoluble but forms colloids for the dyeing of cellulose acetate. Sulphur Dyes are two part developed dyes. Initially imparts a yellow colour and later oxidized to produce the dark colour.

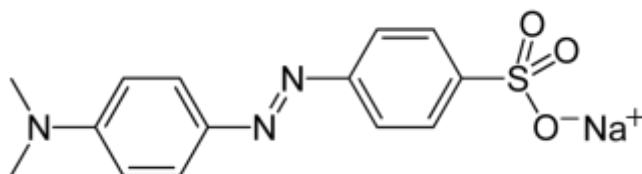
Classification of dyes based on the Chromophore present

Dyes may be classified according to the type of chromophores present in their structures. Chromophore is an atom or group that is responsible for the colour of the compound.

Nitro and Nitroso Dyes: - These dyes contain nitro or nitroso group as the chromophore and –OH as the auxochrome. Example: Naphthol yellow 5 and mordant green 4.

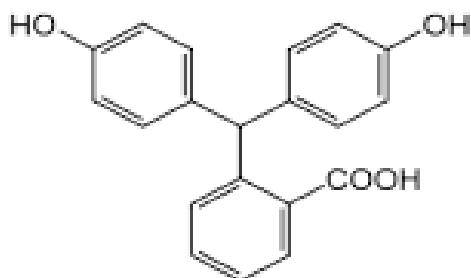


Azo Dyes: - These are a large class of synthetic dyes that contain nitrogen as the azo group –N=N–

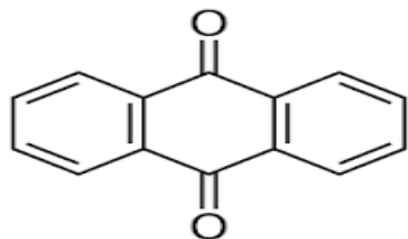


Example is methyl orange

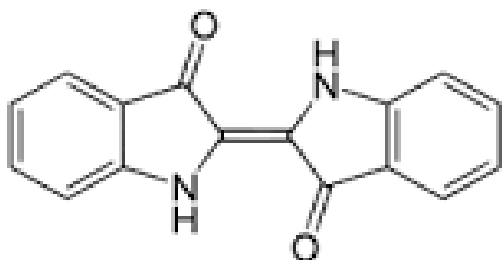
Triarylmethane Dyes: - These are synthetic organic compounds containing triphenylheptane backbone. In these dyes, a central carbon is bonded to three aromatic rings e.g. Malachite Green, phenolphthalein



Anthraquinone Dyes: - Any group of organic dyes having molecular structures based upon that of anthraquinone. Alizarin is the main ingredient



Indigo Dyes: - These are dyes that contain carbonyl and -NH-chromophore.



Classification of dyes based on the charge on the chromophore

Dyes may be classified pending on the charge carried on their chromophores. Some are cationic in nature; some are anionic while some are non-ionic/neutral.

Cationic dyes: - Are dyes that possess positive charge on its molecules and attach to anionic surfaces. They are also called basic dyes and ionize into cations in a solution. Examples are methylene blue, crystal violet

Anionic dyes: - Are dyes that possess negative charge on its molecules and attach to cationic surfaces. They can also be called acid dyes. They are usually acid, direct or reactive dyes. Example; methyl orange, eriochrome black T.

Non-ionic/Neutral dyes: - Are dyes without a net negative or positive charge (Aspland, 1992). Non-ionic dyes do not appear to form aggregates in aqueous solution.

Dyes are seen in the effluent of most industries such as textile, tannery, printing, paper, plastics etc. This has resulted in large volumes of waste water containing dyes being discarded annually, creating a major environmental problem. Around 10^6 tons of dye waste are produced annually worldwide and used extensively in textile dyeing/finishing and also in food, paper and cosmetic industries (Pazos *et al.*, 2008). Also, Effendi & Shunitz, (2009) stated that billions of litres of dyes are produced everyday around the world and most of the dye manufacturers and users, release massive quantities of waste water containing dye to the extent of 0.001-0.7% w/v. Tannery industry is one of the major users of dye and they produce tons of dye waste and effluents. Estimation shows that out of 700,000 tons of dyes used, over 15-20% is left in the effluent during the dyeing process. The discharge of these highly coloured wastewaters into the ecosystem involves major environmental problems. Pazos *et al* (2008) further stated that there are more than 10,000 of chemically different synthetic dyes. Among them, azo dyes are a major class of synthetic, coloured organic compounds and account for about half of the textile dyestuffs used today. Percolation of the contaminated surface water to subsurface strata and rupture of

underground storage tanks are some of the processes through which dye waste gets into the soil. Other processes include the leaching of wastes from landfills, spillage during transportation and direct/deliberate discharge of industrial wastes to the soil. Wang & Zhou (2019) opined that most of these waste dyes in the environment are stable against temperature, light, detergents and microbial attack and are believed to be toxic and non-biodegradable in nature, which inevitably poses many severe hazards on both human health and ecological systems. Human health is not left out, methylene blue, a thiazine dye which is most commonly used for dyeing cotton and silk, give rise to harmful effects on humans such as severe headache, diarrhoea, vomiting on long exposure (Effendi & Shunitz, 2016). High concentrations of methyl orange, an azo dye can possibly lead to intestinal cancer, while direct or indirect contact with Phenol Red, a triarylmethane dye leads to irritation of the eye, the respiratory system and skin. This compound is also toxic to the muscle fibres and has mutagenic effects.



Plate 1: Dye contaminated sites

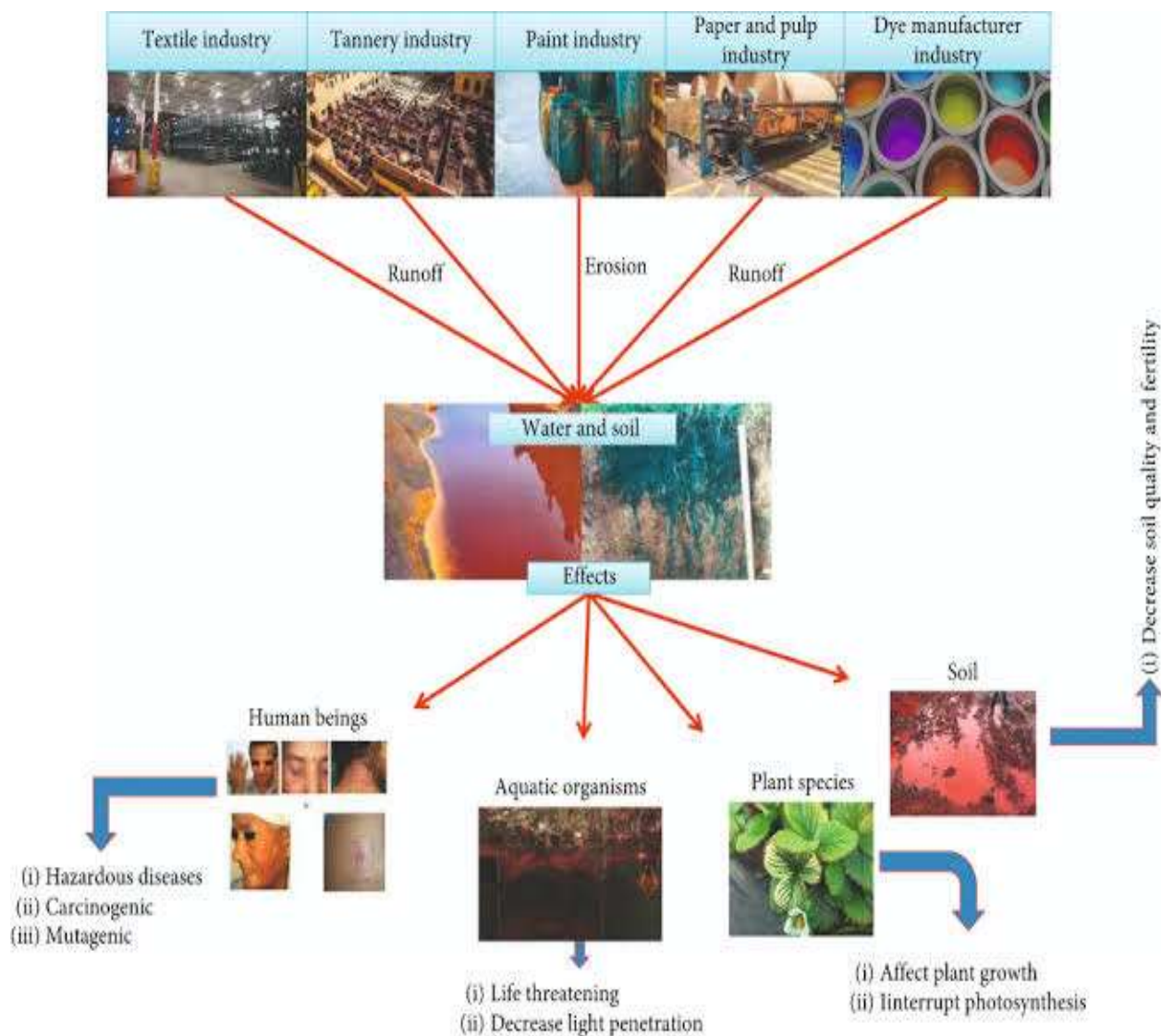


Figure 1: The hazardous effects of synthetic dyes on the environment from different industries (Uduma, 2021)

Review of the Efficacy of Electrokinetic Remediation Technique

Effendi *et al* (2016) studied the removal behavior of hydrophilic and hydrophobic dyes from organic contaminated kaolinite soil by an electrokinetic remediation system. 120g of kaolinite clay minerals were mixed with 40ml of Methylene Blue (MB), Methyl Orange (MO), Phenol Red (PR) dye solutions and mixture of 100mg dye/kg was obtained. The mixture stood for 24h for the drying procedure, an initial pH of 4 and a moisture content of 30% was obtained. pH in both chambers was controlled under the applied voltage of 30V. After the completion of the

EKR process, soils samples in the chamber were divided into sections S_1 , S_2 , S_3 , S_4 and S_5 and samples analyzed for pH, EC and dye concentrate for the thiazine dye MB, the concentration distribution in all sections varied from 5-15 % with the lowest concentration remaining in S_1 , the concentration increased in S_2 and S_3 . The highest concentration was in S_4 , almost thrice the amount in S_1 . In S_5 , the amount decreased again. Most of the MB accumulated in the cathode. It was found clearly that MB migrates from the anode to the cathode chamber since it has a positive charge, same as the EOF with electrolysis of water being the main reaction which takes place during the process and no significant difference of increasing pH in S_2 , S_3 and S_4 recorded. The distribution of MB concentration and the pH value during the process, clearly states that the removal direction of MB was from anode to cathode. Phenol Red (PR) a triarylmethane dye, represented the neutral hydrophilic dye because PR has both the positive and negative dye and the net charge of the whole molecule is neutral. This means that PR dye movement during EK under electric field was restricted to electroosmosis phenomena. With the use of distilled water, 40% of PR still remained in the soil, 29% in the cathode chamber and 30% in the EOF receives. PR dye had the highest concentration in S_4 when sodium sulphate and monosodium dihydrogen sulphate were used as electrolyte in the process. Electrolysis which is the main reaction in the EK process for dye removal yields an acidified kaolinite which led to the creation of current intensity around the wins. This depends on the current voltage applied and also the electrical conductivity of the electro kinetic treatment solution. The amount of dye which remains in each section is affected by the electrical conductivity, the higher the electrical conductivity, the bigger the amount of dye removed. During the experiment, 0.1M sulphuric acid around pH 7 was used in the anode chamber to avoid the pH jumping and to avoid the formation of H^+ ions and the acid front by using a base solution such as 0.1 sodium hydroxide at a pH of almost 7. For the methyl orange (MO), an azo dye that has a negative charge, without controlling the pH it was found that the distribution amount of the dye migrated towards the anode. MO dye has its highest concentration in S_4 and MO dye remained in the soil section at 43%. When the controlling pH was applied in the cathode chamber, total MB concentration decreased to 24.2%. The distribution concentration decreased from the cathode to the anode chamber and the MB dye was present in its highest concentration in S_1 . Same trend was found when controlling pH in the anode. For PR a neutral molecule, without controlling and concentrated in S_4 and when controlling pH in the cathode chamber, 87% of the PR dye was removed from the soil sections. The amount of dye remains in each section is controlled by the electrical conductivity. It was observed from the study, that the higher the electrical conductivity, the larger the amount of dye removed. In conclusion, the study showed that the addition of electrolyte for hydrophilic dyes or surfactant for hydrophobic dyes and controlling the pH during the treatment could reveal the optimum condition for the EKR process. The dye removal was increased from the kaolinite section and the process improved addition of adequate electrolytes. Moving directions of dye, pH value charges, EC, concentration after the EKR process for the sections S_1 - S_5 were different for any kind of dye contaminant. Characteristic and behaviour of the removal system was different among all tested dye contaminants since there were differences of the dye structures and the charge of dyes. It also showed that pH values into the kaolinite chamber soil sample are decisive parameters to achieve the best remediation process.

Voccinate *et al* (2021) reviewed the sustainability in electrokinetic remediation processes, an overview on application and technical solutions and focusing more on their sustainability. The

most relevant phenomena induced in a soil by applied electric field include electroosmosis, electromigration, electrolysis and electrophoresis. Since soils are usually characterized by a high ionic resistance, an increase in temperature is usually observed (Joule-Thompson effect). The review also states that the main challenge of EK technology is the conversion of low solubility pollutants into mobile forms in order to extract them; this is overcome through the addition of enhancing agents added to the process fluids. Coupling of the electrokinetic approach with bio-remediation and phytoremediation was argued to represent a more sustainable approach. This is because their energy requirement is low, the addition of chemicals is often not necessary and the characteristics of the soil at the end of the treatment are improved compared to the initial situation. EK treatment also increases the bioavailability of organic pollutants by facilitating contact between microbes and/or pollutants. In addition, EK application can improve their growth and respiration of plants (which in turn facilitates the removal of metals) and also facilitate the spread of microorganisms of the rhizosphere. Suitable operating conditions must be selected to ensure the survival and development of microorganisms and/or plants. The two most critical parameters for keeping microorganism active are extreme pH values and high temperatures, these two are also produced during the process, making optimization of both EK and biological processes very challenging. Application of EK also causes negative effects to plants such as growth inhibition and death of plants located near the electrodes (O' Connor *et al*, 2003). Other negative effects include phyto-toxicity due to the increasing bioavailability of metals. For the thermal effects of EK, much of the energy supplied when an electric field is applied is dissipated as heat due to the resistivity of soils. The greater the resistivity of soil, the greater the potential required to induce a given amount of current and then the greater the associated thermal effect. Differences are usually found in the spatial distribution of temperature in the soil with a marked increase near the cathode. This is due to the alkaline front originating from the cathode. Alkalinity thereby reduces the mobility of metal species through the formation of the respective hydroxide hence decreasing the hydraulic conductivity. Precipitation of insoluble compounds especially those of calcium and magnesium were seen to influence the electrochemical reactions that allow the passage of electric current. Precipitation of poorly soluble compounds reduces porosity, increase tortuosity and resistivity of the soil and prevents the transportation of pollutants. At high temperatures, strong alkaline environment causes precipitation of salt in the cathode region. This problem can be overcome by adjusting the pH at the cathode through the addition of acids. Other proposed solutions could be the use of a solution of citric acids and polyaspartic acid as electrolytes to destroy the CaCO_3 deposits formed on the cathode. Voccianti *et al* (2021) further reviewed that the choice of the positive electrode (anode) may represent a problem because if the electrode is unsuitable, it can be quickly corroded, corrosion can cause an undesirable increase in the voltage required to generate the current, thus increasing energy consumption.

Xu *et al* (2020) found similar effects in the use of stainless steel and graphite when treating a soil contaminated with cadmium (Cd). During the EK process, stainless steel releases metal ion including chromium, causing a secondary pollution problem. To prevent this, electrically conductive polymers such as polypyrrole (PPy) was used as a coating to protect stainless steel electrode from corrosion but it did not provide long term protection in chloride containing environment.

Kim *et al* (2013) proposed that stable electrodes coated with titanium are the best solution especially for energy optimization because focusing effect occurs where the acid and alkaline fronts meet during an EK process acting as barrier to the migration of those species (especially heavy metals) that are able to form poorly soluble hydroxide. The most common method to counteract the focusing effect is to control the pH at the cathode by keeping it at low level or by preventing the alkalinity produced by the cathode from entering the soil through the use of ion exchange membrane. The action of electroosmotic flow (EOF), causes water in the soil to move from anode to cathode under the application of the electric field. EOF helps in removal of pollutants although excessive dehydration must be prevented. Dehydration causes the precipitation of salts originally dissolved in the pore water and interruption of electrical contact between the soil and anodes. These effects lead to the use of electrolyte solutions because increasing soil moisture content improves the soil conductivity and promotes electromigration. This led to Shin *et al* (2017) reporting in past scientific literature that optimal condition of 50% soil moisture for EKR of soil contaminated by Arsenic had lower removal rate compared to a 35% soil moisture. Hence a correlation between dehydration, precipitation and focusing effect was created thus. Precipitation of insoluble compounds and focusing effect occurring at the cathode result in high resistance in the region which induces local high temperature and a lot of soil moisture evaporate. A significant amount of the cost of implementing an EKR technology is related to electricity consumption.

Alshwabkeh *et al* (1999) presents that, the cost of electricity represents 10 – 15% of the total cost and 25% of the operating costs. However, specific engineering choices can reduce cost such as a different arrangement and a reduced number of electrodes. Another strategy is to increase the conductivity of the system through the addition of appropriate electrolytes as shown in Fu *et al* (2017) where 0.1M citric acid was added to improve the efficiency of energy use in the treatment of a soil contaminated with chromium (Cr).

Gidudu & Chirwa (2020) investigated the effect of variation in voltage, variation in electrode spacing and application of a bio surfactant in the EKR process. Soil composed of 71% sand, 20% silt, 9% clay obtained from Pretoria was spiked with engine oil to achieve 150mL/kg soil contamination. Strain PAH was obtained from AP1 tank sludge characterization of the bio surfactant was done by FTIR, TLC. For the EK set up, 2000g of soil spiked with oil was mixed with 30g of bacterial cells grown for 24h and 300ml of 28g/l of the bio surfactant using an overhead stirrer. Voltages were varied as 30V, 10V and the distance between electrodes were varied as 185mm, 335mm having four main experiments of (30V - 185mm) (30V - 335mm) (10V-185mm) and (10V-335mm) Distilled water was used as the electrolyte, pH, bacterial counts, TOC, EOF, current were measured after every 24h. Results showed that the bio surfactant produced, reduced the surface tension of water from 71mN/m to 30.35mN/m. The current was low in the first 48h then gradually increased but later decreased in all experiments. The gradual increase in current from low values in the initial stages of the experiment were due to electrolysis that occurs at the cathode and anode leading to the dissociation of water producing OH⁻ ions at the cathode and H⁺ ions at the anode (Cameselle *et al.*, 2013). Production of these ions in the electrode compartments increased the ionic strength of the system leading to a subsequent increase in the current. The different electrode spacing, even though at the same voltage made a difference in resistance. This is because with larger electrode spacing, the

charged ions have a longer distance to travel as compared to shorter electrode spacing. For the electroosmotic flow, its direction was observed to be from the anode compartment to the cathode. The experiments operated with 30V had the highest electroosmotic flow, this validates Helmholtz - Smoluchowski theory where voltage is directly proportional to electroosmotic flow. In conclusion, the results showed that by combining the highest voltage of 30V with the lowest electrode spacing of 185mm and use of a bio surfactant as the process enhancement additive, the highest oil extraction and the overall removal of hydrocarbons is achieved.

Rosales *et al* (2009) studied the influence of operational parameters on electro-Fenton degradation of organic pollutants from soil. In this work, two organic compounds (Lissamine Green B (LGB) dye and Phenanthrene) were used to obtain model polluted soils. 0.15kg of Kaolinite clay was mixed with LGB solutions at several concentrations. On the other hand, real soil was mixed with a phenanthrene solution in hexane. Steel and graphite bars were used. In all experiments, 50g of polluted model soil per litre of liquid solution (5% w/v) were employed. Na₂SO₄ was used as the electrolyte. Samples were taken periodically from the electrochemical cell to be analyzed for pH and contaminant concentration. Result obtained showed that in the absence of an electrolyte, low degradation rates are obtained, high electrolyte concentration increases the electric current densities, the reaction rate is also increased and so the total decoloration of the solution is reached in a shorter treatment time. From the results, soil polluted by LGB dye could be remediated quickly and efficiently by electro-Fenton process, attaining a better decoloration degree than by conventional electrochemical oxidation. The use of anode and cathode made of graphite or stainless steel bars led to the highest LGB decoloration rate by contrast when the combination anode-stainless steel and cathode-graphite was employed. A lower initial concentration of the contaminants obtained better decoloration percentages unlike when the initial concentration was increased. A relationship between the dye concentration and the decoloration rate shows that at high dye concentrations, the decoloration rate is reduced, since the amount of hydroxyl radicals is not enough to oxidize the pollutant present, thus decreasing the removal efficiency.

Pazos *et al* (2008) studied the remediation of dye polluted kaolinite by combination of electrokinetic remediation and electrochemical treatment (decolonization). 150g of kaolinite clay was mixed with 150ml of a solution of Lissamine Green B (LGB). The mixture stood for 24h with an initial pH of about 4. 80g of the spiked Kaolinite was put into the electrokinetic cell with the addition of 0.1M Na₂HPO₄. Upon completion of each experiment, samples S₁-S₅ were taken from anode to cathode and they were analyzed for moisture content, pH and LGB concentration. When water was used as the processing fluid, no significant LGB removal was obtained in the unenhanced electrokinetic treatment. LGB was partially removed from S₁ and accumulated in S₄. When water is used as the processing fluid, electrolysis takes place and yields H⁺ and OH⁻ ions at the anode and cathode respectively. LGB having both positive and negative charges is a neutral molecule and therefore its transportation is limited to electroosmosis. The electrolyte increases the electric conductivity and favors the desorption of dye from the clay particle which is transported mainly by electroosmosis towards the corresponding electrode chamber. Electrolyte favours the electron transfer between the electrode and the organic pollutants, increasing the decolonization rate. Addition of Na₂HPO₄ prevents the acidification of the kaolinite (making pH over 7). The basic front penetrated at the cathode penetrated into the sample increasing pH of the

fluid. At the end, sample reached a pH profile almost flat between S_1 and S_4 increasing to almost 10.6 in the last section due to alkaline front from the cathode. Accumulation of LGB in S_4 was very low due to the quick removal of the dye, so a high removal was achieved before the developing of the pH jump. The electrokinetic treatment of the kaolinite sample polluted with a colored compound was followed visually. In the beginning the colour intensity was uniformly distributed along the sample. The application of the electric field mobilized the organic compound. The movement of LGB results in the appearance of white zones on both sides of the kaolinite sample with the rest of the kaolinite coloured. A sharp line separated both zones. The thickness of the white layer increased during the treatment and after 2 days, the dye was removed from the kaolinite sample and was concentrated in the cathodic solution and after that treated electrochemically.

Annamalai *et al* (2015) investigated the optimization of electrolyte for sulphate removal in textile effluent contaminated farming soil. The study also investigated the challenges of removal of sulfate from the soil stating that past research works obtained removal efficiency as low as 22.3% within 14 days. This low removal efficiency was attributed to the presence of calcium and magnesium distribution in the soil which forms metal sulphate complexes in the soil hence this investigation of the removal of sulphate in a mineral complex farming soil by the EK process. The polluted farming soil had its initial physicochemical characteristics determined by the standard procedure, the sulphate concentration was determined by turbidimetric method. Two EK cells having different distance of electrodes were used. EK.A and EK.B had the length of middle chambers as 3 and 10cm respectively. Soil sample was mixed with water to obtain soil moisture of 20% using titanium as cathode and IrO_2 - RuO_2 - TiO_2 /Ti as anode at $3.3 Vcm^{-1}$. In EK process, sulphate was moved towards anolyte through the soil with pH of about 4.5 throughout the experiment. After 24h, only 5% of sulphate was removed from the soil to the anolyte chamber. pH of the soil changed due to the production of H^+ ion at the anode and OH^- ions at the cathode. These H^+ ions react with sulfate minerals and lead to release sulphate ions which can move freely towards the opposite direction and so sulphate desorption increases when pH is reduced. The average removal percentage of sulphate was 96.2% after 96h using $3.3 Vcm^{-1}$ voltage gradients. The present study reached higher removal at low voltage gradient within shorter duration (96h) with hydrogen chloride (HCl) as an electrolyte. The study concluded that electric field permits the efficient inclusion of sulphate into the soil. The removal process was optimized by evaluating the electrolyte composition and pH. Maximum removal of sulphate from the contaminated farming soil was around 96% using 0.01M HCl at pH 4.5.

Park *et al* (2009) conducted a research on the electrokinetic remediation of contaminated soil with waste-lubricant oils and zinc. Two different enhancement methods were applied to treat the mixed waste contaminated soil because the major removal mechanism for organic and inorganic waste is different. In EK, the purpose of enhancement is to increase the desorption of the pollutants from the contaminated matrix and to activate the transport of the pollutants desorbed from the soil. Surfactants are used to increase desorption of organic pollutants while acid or pH buffer solution is used for heavy metals. The alkaline conditioning of the anode is one way to enhance the transportation of organic pollutants because the high pH of the soil increases the electroosmotic flow. 20g of soil was mixed with 100ml of dichloromethane and oil extracted by ultrasonic-enhanced solvent extraction. Extractants were purified by silica gel and concentrated

by rotator evaporator. Amount of lubricant oil in the final solution was analyzed using GC fitted with Flame Ionized Detector (FID). Aqua regia extraction was applied to analyze Zn from the soil. Concentration of Zn in the extractant was analyzed using Atomic Adsorption Spectroscopy (AAS). For the experiment, a platinum coated titanium and carbon plate were used for the anode and cathode respectively, 0.1M HNO₃ was added periodically to the catholyte reservoir. The effects of voltage gradient 0.5, 1.0, 2.0V/cm was determined. Electric current was measured at regular time interval and electro-osmotic flow was calculated from the difference in volume of the catholyte reservoir. The operation lasted for 17 days after which the soil was sliced into 5 sections. Results showed that the current density was proportional with the voltage gradient applied to EK cell. The values of the current density were almost constant for 0.5 and 1.0 V/cm but increased gradually in the case of 2.0V/cm. As the applied voltage gradient increased, electromigration and EOF increased. Catholyte conditioning with HNO₃ may have also increased the high current density. Generally, the direction of the electro-osmotic flow pattern is towards the cathode from the anode because the surface charge of the soil has a negative value. For 0.5V/cm and 1.0V/cm, the electroosmotic flow moved from the anode to the cathode throughout the experiment. For 2.0V/cm., the accumulated electro-osmotic flow changed towards the anode and the pH distribution of the sample was most acidic. The initial concentration of lubricant oil in the soil was found to be 8700mg/kg. In the case of 2.0V/cm, concentration of lubricant oil from the anode was lower than the value in the case of 1.0V/cm while concentration near the cathode was slightly higher than that at 1.0V/cm. the surfactant transported by the electro-osmotic flow enhanced the solubilization of lubricant oil from the soil into pore water, and then the solubilized- lubricant oil was moved towards the cathode by the electro-osmotic flow. The overall removal efficiency of lubricant oil was between 45 and 55% for 0.5-2.0V/cm. Electro migration effect was higher than the electroosmotic movement of zinc because electromigration is proportional to applied voltage gradient. Overall direction of zinc removal was toward the cathode from the anode with removal efficiency of between 22-25%. The energy expenditure also increased with the voltage gradient. The conditioning enhanced desorption of zinc However, the EOF decreased and changed toward the anode from the cathode. Reverse osmotic flow inhibited zinc removal due to electromigration and the EK treatment over 17 days did not meet Korean regulation level.

Cameselle *et al* (2020) carried out a research on the analysis and optimization of manganese (Mn) removal from contaminated solid matrixes by electrokinetic remediation. The work focused on the assessment of the influence of the electric field strength and its mode of application to the soil in the electrokinetic removal of heavy metals. A model soil composed of kaolinite clay contaminated with manganese sulphate was selected for this work. Two disks of graphite of 50mm diameter were used as main electrodes (anode and cathode). 3 auxiliary electrodes P₁, P₂, P₃ from anode to cathode in the central tube were used to measure the electric gradient along the soil specimen. The flow control panel was used to measure the EOF through the soil specimen. The model soil had an average particle size of 3cm and x-ray diffraction analysis showed 85% kaolinite clay, 14% mica and 1% quartz. The matrix was prepared by mixing 100ml of concentrated manganese sulphate solution with 120g of dry kaolinite. The spiked kaolinite was introduced into the EK cell using the consolidation unit. The initial pH of the contaminated kaolinite was 4. A DC electric potential (10 to 30V) was applied for 7days. Periodic readings of electric current were recorded. The pH of the electrode solution was measured. At the end of the

test, the electrode solutions were collected and analyzed for pH and metal concentration. The kaolinite specimen was extruded from the central tube and divided into 5 equal portions S₁-S₅. Results showed that at 30V, Mn was transported towards cathode by electromigration and accumulated at S₅ with average removal of 83%. Amount of the Mn at the anode was negligible. The precipitation of manganese (MnO(OH)) was clearly in the cathode chamber. At the beginning of the test, the electric current intensity was low because there were no ions in the liquid in the electrode chambers. With electrolysis and immobilization, it increased to a maximum of 2.3mA and then decreased due to immobilization at the cathode side. The high pH in the cathode was responsible for the concentration of the voltage gradient in the cathode and increase of electric resistance in the cathode solution. The electric power consumption of the EK Treatment in 7days was 7.18Wh. About 1/3 of the electricity was spent in the electrolysis of water. The electric conductivity of the system (total flux of ions/total charge through the system varies along the treatment time). The lower removal of Mn in S₁-S₅ was due to lower driving force (electric potential difference) developed in the system because of the use of such a low electric current intensity which also led to lower electric power consumption. Voltage increases the driving force for the transportation of cations from the anode to the cathode at the same time increases power consumption due to electrolysis of water. Decrease of voltage also favored accumulation of Mn in the cathode, decreasing Mn in the S₅ soil section. This is due to the lower extension of the electrolysis of water at lower voltage. Test 1 with 40% moisture content resulted in 83% of the removal in S₁-S₄. The accumulation of the metal also increased up to 95% at 60% moisture. The result showed that 60% moisture was appropriate to remove Mn in the kaolinite sample. Electric power consumption also increased with moisture content because the presence of water decreased the resistance of the soil sample to the electrokinetic transport of charge. The main limitation in the removal of Mn from the kaolinite specimen was the development of an alkaline environment in the cathode side that precipitated the Mn in the last section of kaolinite. To avoid this, there is the addition of an acid, H₂SO₄ to keep an acid environment at selected pH. An acid which does not form insoluble salts with the contaminated metal is usually chosen. Lower pH increases the conductivity of the system and energy consumption. The power consumption was due to electrolysis of water. The most appropriate pH to achieve a complete removal with moderate power consumption is close to neutrality (pH = 6 to 7). To overcome the premature precipitation of Mn, there is need for the use of complexing agents. The organic acids were added at the concentration of 0.1M to the Mn solution before mixing it with kaolinite in the pH range from 3 to 5. The complex species formed were neutral or cationic, thus it was expected that Mn will be transported by electromigration (for cationic species) and electroosmosis (for neutral species). Of the five facilitating agents used, citric acid was the most appropriate, having a 99.99% of Mn removed from the soil and accumulated in the cathode chamber.

Suzuki *et al* (2013) conducted a mechanistic study of arsenate (As) removal from artificially contaminated clay soils by electrokinetic remediation. The study performed bench scale laboratory experiments to investigate the effect of the pH of anode/cathode wells and the applied voltage waveform on the efficiency of arsenate removal. Arsenate removal by EK consists of two steps which include the desorption of arsenate into interstitial water and the migration of dissolved arsenate towards the electrode via electromigration or electroosmosis. 90g of Kaolinite + 400ml of the aqueous solution were artificially mixed. The aqueous solution was 50mg As/L (Na₂HASO₄) and 0.01mol/L NaNO₃ as electrolyte. Desorption of arsenate into

interstitial water is a prerequisite for arsenate removal by ion migration. Therefore, batch experiments were performed to obtain information regarding pH dependence of arsenate desorption with an initial pH level of 7.2. In this order, $\text{pH } 7.2 < \text{pH } 2.0 < \text{pH } 10.5$. For the effect of anode/cathode pH on remediation efficiency at constant voltage of 20V, arsenate recovery in the cathode well was negligible (below 1%) while arsenate recovery in the anode well increased with time but the time efficiency depended on anode/cathode pH. The time efficiency was significantly improved by not controlling the cathode pH. For test 1, when anode and cathode pH were held constant at 7.2, soil pH was neutral and did not vary from initial pH. For test 2, when cathode pH was not held constant, pH in anode increased with increase in time, due to generation of hydroxyl ions through water electrolysis at the cathode. The pH increase improved desorption of As which then migrated toward the anode because As is negatively charged. For test 3, when the pH at the anode was not held constant, pH decreased with increase in time, having the proton ions migrate towards the cathode. It was also concluded that high soil pH is favourable for efficient remediation. It was recommended that the cathode pH should not be controlled in the neutral range during remediation to facilitate the increase in soil pH. It was also discovered that the desorption of arsenate from the contaminated soils is not an instant process, but a relatively slow one requiring 2-3hours to effectively reach equilibrium.

Cameselle and Gouveia (2018) reviewed an article on the electrokinetic remediation for the removal of organic contaminants in soils, it identified limitations in the removal of organic contaminants from soil as (i) neutrality of the molecules and (ii) the low solubility of most of the target contaminants. The removal by electromigration and electroosmosis requires charged molecules and/or the solubilization of interstitial fluid. The contamination of organics with high or moderate solubility in water can be removed by adjusting the physicochemical conditions of soil such as pH to enhance the desorption of the contaminants. Thus, solubilized compounds will be removed by electroosmosis or electromigration if the organic compound is ionic or ionizable. When dealing with Hydrophobic Organic Compounds (HOC) contamination in soil, the direct application of EK to the soil is ineffective because it is not possible to remove by electromigration or electroosmosis, a compound that is not in solution in the interstitial fluid. The solubility of HOC can be enhanced by using surfactants and co-solvents in the processing fluid. In general, ionic or non-ionic surfactants are preferred in soil remediation. Anionic surfactants are preferred because cationic surfactants interact with soil particles and reduce activity. Biodegradable surfactants are also preferred. The surfactants increase the bioavailability of the contaminants in the soil that are degraded by soil microflora, thus diesel oil, PAHs can be effectively degraded. The use of co-solvents decreases the solubility of salts & the EC. As a result of this, the EOF decreases, but the increasing solubility of HOCs results in higher removal efficiency. In Situ Chemical Oxidation (ISCO) involves introduction of oxidants that reacts with the contaminants transforming them into simpler or less harmful molecules. Common oxidants include ozone, hydrogen peroxide, persulfate. The use of persulfate for oxidation of organic contaminants leads to high redox potential and no formation of toxic products. Persulfate is relatively stable, allowing good distribution and contact time. Persulfate as an anion is added to the cathode and transported into the soil by electromigration. The efficiency of the persulfate activated remediation is highly dependent on the ratio of oxidant/activator. Zero valent iron nanoparticle (nZVI) are the most common nanoparticles used in EK due to its low cost and reduced risk to the environment. EK can be used to transport nZVI into the soil but there is

limitation due to agglomeration and settling. Dispersants are used to enhance nZVI transportation in soil. Permeable Reactive Barrier (PRB) can also be combined with nZVI under the effect of an electric field. In EK – bioremediation, a biological reactive barrier is placed in the middle of the soil. The bacterium in the barrier degrades the hydrocarbons transported by EK from the clay specimen towards the reactive barrier. The only challenge is the negative effect of the electric field in the microorganism population. The pH and temperature assured the survival of the bacteria. It is also important to note that the electric field intensity needs to be controlled to keep the appropriate conditions for bacterial survival and development. EK –Phytoremediation is easy to implement and improves the properties of the soil. Application of electric field mobilizes contaminants and nutrients, favoring growth of plants and its remediation capacity. Intensity of electric field, chemical nature of electrode must be selected to avoid damage to growing plants and soil microflora. The use of AC electric current does not induce dramatic changes in soil PH.

Sanroman *et al* (2015) investigated the decolourisation of textile indigo dye by DC electric current. Graphite electrodes were used as both the anode and cathode with an initial concentration of indigo dye as 0.5g/l. Sand matrix with 40% porosity was mixed with 0.5l of indigo dye and kept for 3 days and voltage was kept at 30V. For the decolourisation, the dye was extracted with ethanol at a ratio of 1g dry soil/ 1ml ethanol and its percentage calculated. It was found that the electrochemical process allowed a colour removal of 76% in 87h. The presence of an electrolyte in the textile effluent could increase the decolourisation rate. For this reason, experiments with low concentration of the electrolyte were used. The addition of electrolyte clearly increases the degradation rate. This work also showed a comparative study between two alternate technologies (direct and indirect treatments). The indirect process was carried out in two consecutive stages which include extraction of dye from the soil and electrochemical decolourisation of the liquid collection and the complete dye extraction from the soil was achieved when the ethanol solution volume was three-fold the soil volume. On the other hand, the electrochemical treatment was applied to the extracting solution with addition of 10g/l NaCl. When water was used as solvent, the decolourisation degree was slower as compared to the use of ethanol. This is because water has a high dielectric constant and is polarized whereas ethanol is not polarized. This reduces the reactions on the electrodes and therefore lowers the current intensity. Low pH in the anode area was associated with oxidation of water while reduction near the cathode provoked an alkaline environment. The pH of the soil in the beginning was 7. In 30 min, pH of the soil became 2 near the anode and 11 near the cathode. pH gradient was developed quickly because of the moisture content and high permeability of the soil. The pH drop seems to move towards the cathode due to higher mobility of H⁺ ions than OH⁻ ions. In conclusion, results obtained showed the great potential of electrochemical technology to decolourise wastewaters contaminated with dye such as textile indigo. It was also observed that NaCl addition enhances oxidation reactions and thus reduces treatment time.

Oonnittan *et al* (2009) conducted a research on the field applications of electrokinetic remediation of soils contaminated with heavy metals. Early field scale studies proved abortive which led to extensive laboratory scale studies and paved the way to understand the parameter effects and principles of the process. Field scale trials failed as a result of one or some of these factors, heterogeneities in the soil, presence of metallic objects, low moisture content, aging of

the contaminants and also due to the lack of experience in the implementation of the technology in the field. This research work identified some elements as essential materials for EK set up. These elements include electrode system which can be installed vertically and horizontally, placing considerations on the electrode material, optimum electrode spacing, layout and configuration. The right choices of these factors will result in achieving uniform voltage distribution. The power distribution system is also considered. Electric power is applied to the electrode system by a power supply. The electric field for transportation of ions remains constant and the electric current intensity evolves along the treatment time as a function of the electrical resistance of the seal and electrolytic solutions. A proper circulation control system is also necessary for field application of EK. This enables complete mixing of electrode solutions and sample withdrawal if needed. There is also the need for contaminant recovery and disposal. This system can help with the reuse of electrolytes, hence reducing amount of waste generated contaminants can then be recovered by other methods such as adsorption to the electrodes, use of ion exchange, electroplating etc. Factors that limit technology performance in the field where listed as soil heterogeneities in the form of rocks or other uncovered objects that cause discontinuity in the current flow path which results in poor remediation. Also, conducting materials in the soil act as preferential flow paths for the current leaving the surrounding soil unaffected. Dissolution of metallic objects into the soil can also act as new source of ions that generates more pollution and more electric power consumption. Remediation time in field application is difficult to predict due to the different conditions in the actual field. Formation of by products is also another factor to look out for. Any type of enhancement is a potential for generation of harmful by products therefore selection of inert chemicals should be considered. As for the choice of electrodes, the electrode material should stand the deteriorating conditions that develop during the process and should also not introduce any residues to the soil. Positioning of electrodes is also necessary to extract contaminants from the entire treatment area. Lastly, EK is applicable to both saturated and unsaturated soils. Soil moisture content must be high enough for electromigration to take place and at the same time less than saturation to avoid the effects of pore water content and tortuosity. The site for EKR must undergo the following laboratory screening tests before implementation; site screening, electrical conductivity surveys, pH (both soil and pore water) and chemical analysis of pore water and soil.

Gholami & Youssefi (2014) studied the electrokinetic remediation of perchloroethylene (PCE) contaminated soil and also investigated the effects of EKR with nonionic surfactant on PCE contaminated soil. PCE was the representative of pollutants with low solubility. Clay soil was artificially contaminated with 10,000 mg/kg and 30,000mg/kg PCE. Remediation was carried out under the D.C power supply with electric voltage (1 V/cm) used for 8-16 days. A negatively charged soil resulted in greater osmotic flow towards the cathode. The PCE was analyzed by Fourier Transform Infrared Spectroscopy Instrument (FTIR). Results showed that 74% and 89% PCE removal efficiency was achieved for 10,000 and 30,000 mg/kg respectively. Therefore, from the study, integration of EK for the remediation of PCE contaminated soil was effective. Emilio (2010) reviewed the electrokinetic process for soil remediation with specifics to the soil microstructure and the presence of the double layer in fine grained or clay soil. Introduction of an electric field induces electrochemical processes which promote mobilization of ionic contaminants as well as altering electrical charges in the soil. The dipolar nature of water leads to water being captured as “adsorbed” and absorbed layers (double layer) which aids the EK

process since electrochemical reaction can only happen in electrochemically active interfaces having a double layer structure. The charged orientation in this double layer aligns the individual clay structure to an electrode with polarization occurring naturally. EK technique uses low-level DC which results in physico-chemical and hydrological changes in the soil mass leading to species transport in the porous media through conduction phenomena which non-ionic species will be transported along with the electro osmosis induced water flow. This transport coupled with precipitation, dissolution, sorption make up the fundamental mechanism affecting EKR process. The open flow arrangement at the electrodes allows ingress and egress of the processing fluid or of the pore fluid into and out of the porous medium. Extraction and removal of the contaminant can then be accomplished through electrodeposition, precipitation, pumping of water at the electrode. Adsorption into the electrode may also be feasible because some ionic species will change valence near the electrode making them more likely to adsorb. Some factors affecting EK technology may include grain size, contaminant concentration, ionic mobility, current density and pH of soil, soil type and structure amongst other. EK can also be applicable in soils of low hydraulic conductivity particularly with high clay content and the technology is most efficient when the cation exchange capacity (CEC) and salinity are low.

Conclusion

Electrokinetic Remediation (EKR) has proven to be a sustainable approach to soil remediation provides a wide variety of benefits to the environment. It's a clean and novel technique which accesses the grain pores of low permeability soils such as clays and silts. When electrokinetics is coupled with other remediation techniques, very impressive results are obtained because of the synergistic effect of both techniques. As an in-situ remediation technique, EKR offers minimal land disturbance especially for remote locations where traditional "dig and dump" methods are logistically and economically infeasible. EKR also cuts across complex environmental polluted matrixes- soil, sediment, and sludge and has been successful with wide range of pollutants-organics, inorganics, heavy metals, radionuclides, making it a potential measure for sustainability.

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