Tampere University of Applied Sciences

Bioremediation Enhanced by Electrokinetic Remediation

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ABSTRACT

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This study was carried out to give an overview of the applicability of electrokinetic methods in soil remediation. The main focus was on using pulsed electrical current with reverse polarity combined with bioremediation in treating soils contaminated with PAHs and PFAs. Methods used to gather information were based mainly on literature review from online sources and previous case studies of EKOGRID.

EKOGRID is the company that commissioned the theme of this thesis and provided baseline knowledge related to electrokinetic remediation methods.

Results indicate that pulsed current with reverse polarity can be efficiently used in removing PAHs, PFAs and other type of contaminants from soil. This method proved to be more efficient that the other electrokinetic remediation methods because of the better mobilization of contaminants facilitating the efficient biodegradation of the contaminants, including PAHs and PFAs. By consuming less electricity, the energy efficiency that this electrokinetic system withholds is a major advantage over other remediation techniques. However, further research is required to find out the effects of different remediation conditions and parameters, especially with respect to PFAs decomposition.

Key words: Pulsed current under reverse polarity, PAHs, PFAs, EKOGRID

CONTENTS

GLOSSARY

AC	Alternating Current
Cd	Cadmium
Cu	Copper
DC	Direct Current
DNAPL	Dense nonaqueous phase liquids
EC	Electrical Current
EK	Electrokinetic
Mg	Manganese
MgSO4	Magnesium Sulphate
PAHs	Polyclinic aromatic hydrocarbons
PC	Pulsed Current
PEC	Pulsed electrical current
PEF	Pulsed electroosmotic flow
PFAs	Polyfruoroalkyl substances
PFCs	Perfluorinated chemicals
PFOs	Perfluorooctane Sulfonates
PFOA	Fluorooctanoic acid
POP	Persistent Organic Pollutants
RNA	Ribonucleic acid
TAMK	Tampere University of Applied Sciences
TCE	Trichloroethylene
Zn	Zing

1 INTRODUCTION

The past century ecosystems have witnessed a large increase in pollution, first and Second world war have had dramatic consequences on people's life quality and ecosystems. Industrial evolution initiated in 20th century and until today it is one of the main sources of air, water and soil pollution as vast variety of chemicals are released and bioaccumulate from low food chains to higher food chains (Philp et al. 2005).

Various industries have caused short term as well long-term consequences from large increase in the diversity of organic compounds that are industrially produced. Oil industries are responsible for causing short and long-term consequences to ecosystems and humans, as they pose a threat of exposure to petroleum gases which contain various toxic substances, one of those being PAHs (polyclinic aromatic hydrocarbons) which will be investigated in this study (Industrial Safety & Hygiene News. 2019). In addition to PAH, PFA (per- and polyfluoroalkyl substance) is a contaminant relatively new to humans, which is found mostly in man-made products (Adam M. 2021).

PAHs and PFAs pose a threat to human health and wild life, they have been found in the most remote places, in animal tissues and can be biomagnified in food chains. PAHs have existed longer and pose a higher threat as they can be found in large concentrations, caused from oil spillages and oil slicks. Although awareness has been risen lately from scientists regarding the threat that PFAs pose to humans and animals. Techniques such as in situ and ex situ have been tested in fields to decontaminate polluted soils, some have been successful and some less. In situ technologies have been found to be more sustainable, cost efficient and energy efficient compared to 'old fashioned' treating techniques such as excavation and other ex situ methods. (Mohammadi M. 2015)

Bioremediation process, which is described as the use of microorganisms to detoxify or remove pollutants is an in-situ technology naturally occurring in soil environments which can be enhanced by other technologies for instance remediation, chemical surfactants etc., this way the biodegradation of contaminants can be improved. Bioremediation enhanced by electrical current (electrokinetic) will be studied in this bibliography and more precisely pulsed electrical current with reversing polarity of the system.

1.1 Electrokinetic methods

Electrokinetic remediation is a technique that includes the introduction of electrical current in soil, electrodes are inserted in soil and an external monitor controls the application of electricity introduced to the soil by the electrodes (figure 1). The current can be either direct (DC), pulsed (PC) or direct/pulsed current with reversed polarity.

1.1.1 DC (Direct Current)

Direct current is the continuous current applied in a single direction from negative to positive electrode. Half of the electrodes are negatively charged, and half are positively charged. Introducing electrical current in soil enhances natural bioremediation treatment as it delivers more efficiently nutrients to indigenous bacteria thereby providing a significant large potential for treating also low conductivity soils which pose a challenge due to the finer grains. In addition, electrical current mobilizes pollutants in soil and enhances phenomena such as electromigration, electroosmotic flow and electrophoresis. It can gather pollutants into one area depending on the nature of the pollutants and contributes in transforming them into less harmful substances and degradation (Hassan et al. 2015).

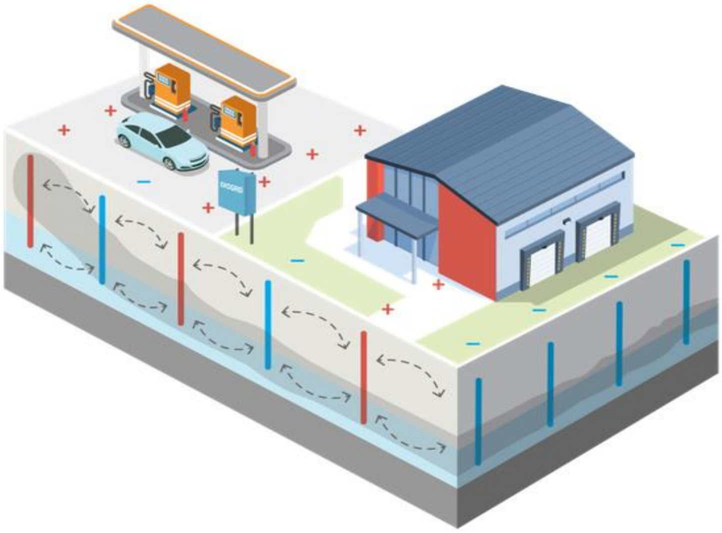

Figure 1. Schematic representation of electrokinetic system (Lindberg)

1.1.2 Pulsed Current

Electrokinetic remediation utilizing pulsed electrical current is relatively new, it has been applied in wide range of soil contaminations providing scientists with good removal rate results. During the treatment low voltages are applied with on and off time intervals. Pulsed electrical current provides the time interval ions need to be discharged, providing the opportunity to soil environment to get from saturated into unsaturated phase and this assists soil particles to regain their ability receiving positively and/or negatively charged ions. In more simple words the electrical current is turned on and off every few second or minute intervals figure 2b). In addition, pulsed electrical current (EC) aims to create a more violent movement is soil pores which enhances the interaction between contaminants and microbes and increases the number of free ions that will operate as receptors to migrate toward the electrodes. (Sun et al. 2012)

1.1.3 Pulsed Current with Reverse Polarity

Pulsed current with Reverse polarity is described as the application of pulsed current while the electrode's polarity is switched from positive to negative and

vies versa, this aims to neutralize the acidic and alkali conditions that are created during remediation process, favouring microorganisms during their decomposing process, figure 2a). As in pulsed current the drastic change of polarity creates a 'shock' to soil particles and contaminants that are highly bonded to soil pores creating more vulnerable conditions for their decomposition and migration. (National Research Council 1993)
Introduction of electrical current can cause drastic change in soil environment which can therefor affect negatively biodegrading microbes, some of those parameters that can affect the degrading efficiency are pH, nutrients availability, O2 availability, moisture etc.. (Philp et al 2005)

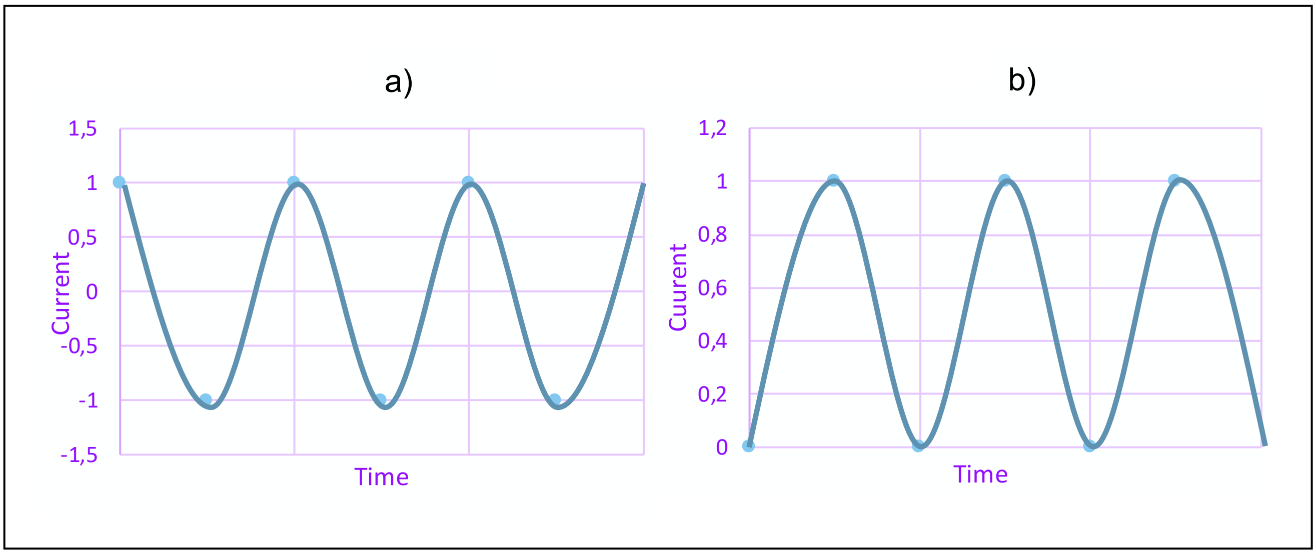

Figure 2. a) Pulsed current with reverse polarity/alternating current, b) Pulsed current (EKOGRID OY)

1.2 Bioremediation combined with electrokinetic methods

Electrokinetic bioremediation is the technique that combines physical mechanisms that occur in soil with the enhancement mechanisms caused by the introduction of electrical current, this technique is also called Bioremediation enhanced by electrokinetics. In situ Bioremediation includes the use of microbes and bacteria to remove contaminants and pollutants from soil, it stimulates their growth utilizing as energy source contaminants such as oil, pesticides and solvents while at the same time breaking down contaminants.

These natural processes that occur in soil are multiple and complex, it is difficult to define all the processes and identify the exact remediation process that occurs for each type of contaminant. (EKOGRID OY)

Electrical current creates slightly acidic conditions suitable for microbes' survival, provides free cations and anions that contribute in removal of contaminant ions via electromigration to the electrodes (anode and cathode), removes contaminants with electro-osmosis phenomena that are caused by charge difference and electrophoresis. In addition, it creates violent movements in soil particles which unblocks contaminant ions that are strongly stick in soil particles and can now be decomposed by microbes or transported away with electro-osmosis or electromigration. Besides the immediate consequences that are caused, electrical current can cause secondary changes during the remediation for example in moisture content, oxygen availability etc which can affect the degradation negatively, this will not be studied in this bibliography. (Hassan et al. 2015)

1.3 Some key contaminants

1.3.1 PAHs

PAHs are found mostly in petroleum products, they are released into the nature by incomplete combustion of fossil fuels, wood processing, manufacture of gas and coal tar, escaped automobile gasoline, fuel-burning kitchen stove and the incineration of waste. PAHs differ in the number of carbons they consist, simplest ones consist of 4-6 carbons atoms for example pyrene, benzopyrene, coronene and the more complex ones have 7 and more carbons. PAHs consisting up to 6 carbon atoms are described as small PAHs whereas PAHs with 7 and more are described as large PAHs, large PAHs pose a higher threat to environment and humans as they are more toxic and harmful compared to smaller PAHs and they are more difficult to be extracted and decomposed. They are one of the most common and widespread organic contaminants in soil, their nonpolar and hydrophobic character poses a further challenge in extracting them and they tend to accumulate in food chains. Hundreds of different PAHs exist although during this study mostly PAHs ranging from 4-7 carbon atoms will be examined. (Fernadez-Luqueno et al. 2010)

1.3.2 PFAs

PFAs can be found under different names such as Perfluorinated chemicals (PFCs), Perfluorochemicals (PFCs), Perfluoroalkyls, etc. PFAs are exclusively man-made chemicals characterized as very stable, highly hydrophobic, and oleophobic which can accumulate and biomagnified in nature and are classified as highly toxic and carcinogenic. They have been used to create oil and water repellents such as GoreTex products, Teflon products, Stain carpets, fluoropolymer coatings, used in surfactants in firefighting foams and other products such rubber, plastic, take-out containers, pizza boxes, dental floss, etc. Their chemical structure consists of 4-16 carbon atoms surrounded by fluorine atoms, 4-7 carbon atoms are characterized as short-chain whereas more than 8 atoms are long-chain. They migrate in nature and have been found globally in the atmosphere, water sources, soil, as well as in food. PFAs pose a further threat as they are not metabolized by humans nor excreted when they are found as long-chain compounds and can take years for the human body to get rid of the compounds, dissimilar to some animals that can excrete the chemicals relatively fast. (Sheets et al. 2015)

2 Scope

The aim of this study was to perform a review on the applications of electrokinetic remediation methods in treating contaminated soils. The focus was on the applications of pulsed electrical current with reverse polarity in combination with bioremediation and treatment of soils contaminated with PAHs and PFAs. Additionally, the real remediation cases done by EKOGRID company were included in this study in order to have a broader basis in concluding on the efficiency of soil remediation with pulsed current under reverse polarity in treating PAHs and PFAs.

3 Materials and Methods

This work is based on review of scientific publications on the field of applicability of electrokinetics in treating soil contaminants. The gathering of information was based on quantitative and qualitative methods, mainly on literature review.

For the literature review the following group of articles were used:

- Articles investigating the effect of electrokinetics to soil microbial communities
- Investigation of articles testing the applicability of pulsed current in removing various contaminants, mainly hydrocarbons and heavy metals
- Articles studying the removal efficiency of various types of contaminants (heavy metals and oil-based pollutants) under pulsed current with reverse polarity
- Articles investigating the removal of PAHs and PFAs utilizing electrokinetic remediation methods

Information gathered from each article was adjusted accordingly to the relevance of the study, details irrelevant to the objective of the study were not included. Laboratory experiments and case studies were the main source of information used.

Vast availability of articles regarding electrokinetic remediation provided significant amount of information, although there was limited number of scientific articles and case studies regarding removal of PAHs and PFAs with electrokinetic methods.

Information on EKOGRID technology applications was gathered from 3 case studies conducted in the past utilizing EKOGRID technology, provided confidentially by the company. Focus of case studies was the removal of PAHs and aliphatic hydrocarbons utilizing pulsed current with reverse polarity, although detailed description of case studies' data is not presented as it is classified as confidential. (EKOGRID OY)

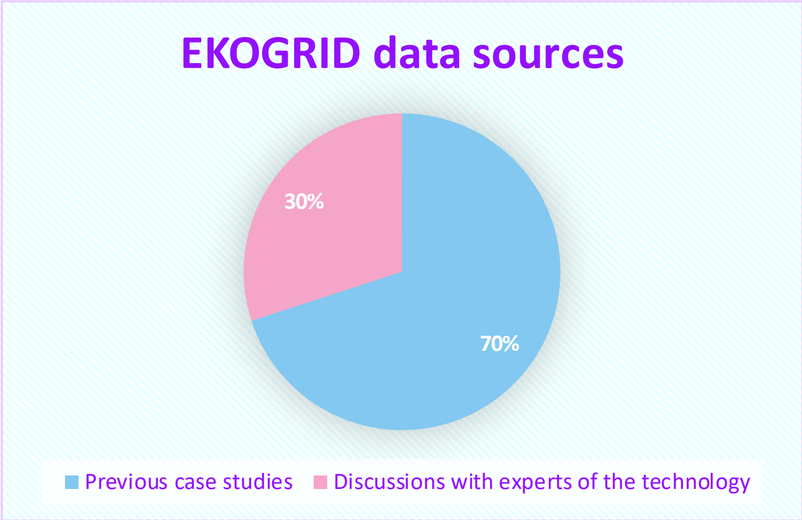

Figure 3. EKOGRID research data source

Main source of the articles were scientific websites such as Andor (TAMK's online library) and Science Direct. Andor includes vast variety of scientific articles, from which most are linked to Science Direct. Articles from both websites provided relevant information regarding the applicability of electrokinetics in soil. Other tools that were used to present and analyze data were Microsoft Excel and Microsoft Word to create graphs, tables and figures to present the data. (Andor)

Key words used during data collection from Andor and Science Direct:

- Electrokinetic remediation
- Direct current
- Pulsed current under reverse polarity
- PAHs
- PFAs

The gathering and presentation of information followed the process presented in figure 4. Based on the findings of the articles studied and EKOGRID's case studies results the applicability of pulsed current with reverse polarity electro-kinetics in treating PAHs and PFAs was tested.

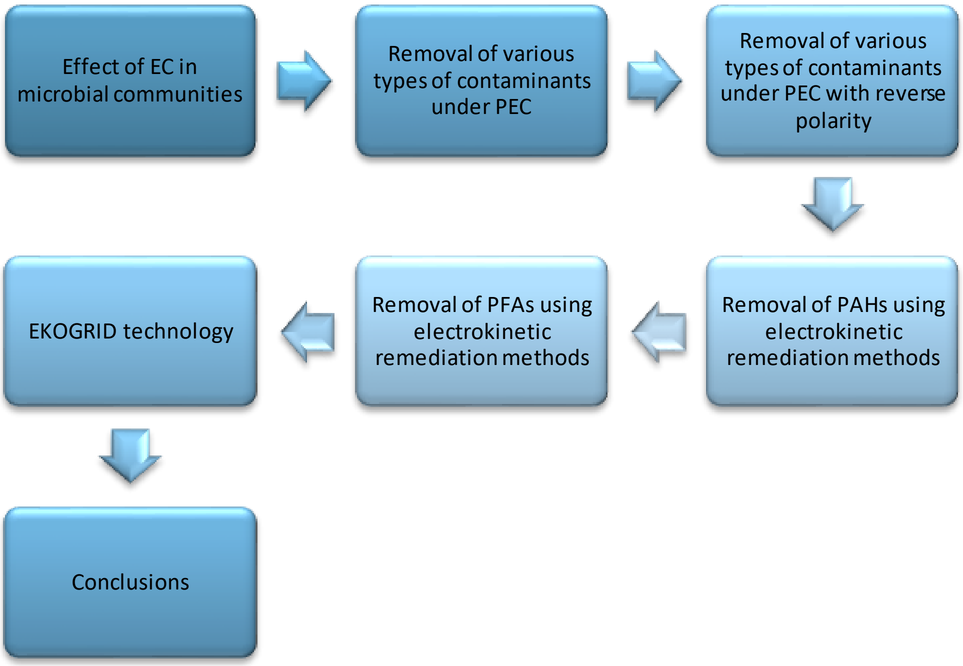

Figure 4. Gathering information process

4 Results

4.1 Studies on the application of electrokinetic methods for various purposes

Electrokinetic remediation utilizing pulsed electrical current under low voltages and reverse polarity is a treatment technique that limited information is known, application of this technology around the world has not evolved considerably and this impedes companies and municipalities to invest in this technology which has the potential to provide an efficient, cost effective and sustainable removal of soil contaminants.

4.1.1 Effect of EC in microbial communities

Two studies are presented in Table 1, investigating the impacts caused on microbial communities during remediation. The effect on microorganisms is determined in both experiments by the strength of electrical field that is applied and the treatment duration. An important observation that was made in study 2 was that the interaction of bacteria and pulsed electrokinetic flow (PEF) led to a decrease in respiratory activity of active cultures of bacteria whereas bacteria that had already a decreased respiratory activity a restoration and increase in their respiratory activity was observed. This study underlines the complexity of bacteria cells and the challenge of unblocking the transfer of electrons under electric fields (Podolska et al. 2009). In a greater picture the changes caused in study 2 were insignificant and both studies reveal the innocence of low electric fields when treating contaminated soils.

Table 1. Case study 1 & Case study 2

Topic of the study	Followed	Microbes studied	Soil type	Pollutant studied	Condition	Results	References
Study 1: Changes in microbial communities	Degradation kinetics and bacterial cell surface properties	fluorene-degrading Sphingomonas sp.LB126	-	Fluorene	Laboratory	No changes on microbe communities, soil particles homogenized, and immobile pollutants were mobilized	Shi et al 2007
Study 2: Respiratory activity of microbes (response of bacterial cells to the first electrical currents)	- Electric field of 20-40 V/cm - Unipolar pulses with duration of 1ms - Repetition frequency of 100Hz - Duration of experiment 30 min	Cyanide-resistant strains	-	Cyanide	Laboratory	Between time frame of 5-15 minutes a positive respiratory reaction was caused, first 5 minutes and last 10 minutes caused a decrease	Podolska et al. 2009

4.1.2 Removal of various types of contaminants (mobilization, decomposition) under Pulsed Electrical Current

Case studies and experiments that have been conducted to investigate the feasibility of pulsed electrical current in treating various types of contaminants (hydrocarbons and heavy metals) are presented (Table 2). Detailed information and parameters are not presented as they are irrelevant to the study which aims to present the applicability of pulsed EC. Both studies in Table 2 reveal that pulsed current is a more efficient method in removing heavy metals compared to direct current and more energy efficient as study 4 revealed that during direct current the energy consumption was 3 times higher than pulsed current. (Ryu et al. 2009a)

Table 2. Case study 3 & Case study 4

Topic of study	Followed	Microbes studied	Environment of samples	Heavy metals studied	Condition	Results	References
Study 3: Operating efficiency of pulsed EC	Manganese removal was tested under 2 different current applications, direct current and pulsed current.	-	Electrolytic manganese residue in solid waste	Mg	Laboratory	Mg had a removal efficiency of 41.21% under direct current and 45.57% under pulsed current	Shu et al. 2019
Study 4: Pulsed electrical current to treat contaminated soil with heavy metals	2 experiments conducted. Constant voltage of 1V/cm was applied for 14 days. For Experiment A normal DC was used and for experiment B pulsed current with ''on/off'' time duration of 1s for each phase. MgSO4 of concentration 0,1M was used as an anolyte	-	Rice field nearby abandoned mine	Zn	Laboratory	Removal rate of 2.1% Zn and 14.0% Zn for Experiments A and B respectively. Energy consumption for exp. A is 269.2 Wh and for exp. B 92.9Wh	Ryu et al. 2009a

A comparative study done by Geng et al. (2020) on the removal and energy efficiency was studied between alternating current (AC) and pulsed current (PC) and revealed that for treating DNAPL, trichloroethylene (TCE) contaminant and migrating it out of low permeability soil (kaolin), PC is more efficient, consuming less energy. The comparison was done at 3 different voltage gradients, 3V cm-1, 3.5V cm-1 and 3,75V cm-1 and was found that PC managed to migrate TCE more efficiently than AC out of the low permeability soil. In addition, there was a significant difference in energy consumption which was around one-sixth for the PC compared to AC at low voltage gradients and the overall removal of TCE in average was 8.4 times higher during PC compared to AC (Geng et al. 2020). Even though AC had not equal removals to pulsed current the combination of the two methods could provide potential improvement in degradation process of contaminants.

Byung-Gon Ryu investigated the removal of heavy metals under pulsed current using two different cycle frequencies per hour. The two frequencies used were 1800 (cycles/h) with voltages between 1-2 V/cm and 1200 (cycles/h) with voltages ranging between 1-3 V/cm. After the experiments were completed it was found that higher pulse frequency (1800 cycles/h) increased the removal of Cd and Zn when comparing to lower frequency of 1200/h and greater electrical strength enhanced the removal efficiency under constant pulse frequency (Ryu et al. 2009b). Electro-osmotic flow which was influenced by the frequency of pulses was the factor that caused the higher removal of contaminants.

The last study concerning treatment of various types of contaminants under pulsed current investigated the application of electrokinetic remediation in treating oil spillages (light hydrocarbons 820kg/$m^3$and heavy hydrocarbons 930kg/m^3). Utilizing two currents, direct current and pulsed current. After the first four days it was observed that pulsed current (PC) maintained a higher electrical intensity in the soil compared to direct current having also a higher removal efficiency. Electrical resistance of soil was also lower during PC compared to DC which is an indication of the good conductivity of soil hence more efficient transportation of ions towards the cathode and anode. (Kariminezhad & Elektorowicz 2017)

4.1.3 Removal of various types of Contaminants (mobilization, decomposition) under Pulsed Electrical Current with reverse polarity

Applications of pulsed current under reverse polarity and reverse polarity to treat heavy metals and oil-based pollutants are presented. Rojo et al. (2015) revealed the efficiency of reversing the polarity in treating soils contaminated with copper. The experiment included two different electric field applications, direct current (DC) and DC with AC (alternating current) (AC+DC). AC+DC consisted of periodic polarity reversal which created a cyclic process consisting of two stages, one stage with direct polarity followed by a reverse polarity, direct stage was greater resulting to a positive net charge in system. The voltages applied during DC varied from 10 to 20 V whereas during AC from 15 to 25 and frequencies of polarity switch varying from 50 to 2000 Hz.

Total Copper removal percentage during DC with 20V was found 8.8% whereas during AC+DC with 14.6V and frequency of 1000Hz was found 24.5%, almost three times greater than DC. When the frequency of AC+DC was increased to 2000Hz the removal efficiency of copper decreased. Increasing the frequency after a certain point results in sustained decrease in the net charge of the system which leads to decrease in the removal rate of the contaminant which in this case was Copper. This study is a good representation of frequency's importance when switching polarity and the potential when combined with pulsed current. (Rojo et al. 2015)

Rotation of electrode reactors is a technique that has been used since 1906 to enhance the biodegradation of contaminants in soil and the idea behind is corelated to the one investigated in this study, that utilization of reverse polarity in combination with pulsed EC can create a violent movement in soil leading in unblocking the contaminants from soil pores. The rotation of electrodes is a good example of how mass transfer at the electrodes can accelerate electrochemical reactions occurring in soil. (Almeira et al. 2012)

Almeira et al. (2012), in a study testing the rotation of the electrodes found that the rotation speed between 0.25r/m and 1.25r/m resulted in increase of mass transport towards cathode region, but then electromigration saw a decline when the rotation speed exceeded 1.25r/m. The explanation to this phenomenon is that fast change of electrical field, results in a constant change of the force acting over the ions, therefore the ions are unable to make any significant displacement in the direction of the cathode.

The conclusion of this study is that circulation of electrodes results in reduction in the electrical resistance of the porous matrix leading to an efficient migration of cations towards the cathode. The violent and rapid change of electrical field can have adverse results in transportation and biodegradation of pollutants.

Two case studies presented in Table 3 revealed the importance of polarity change in remediation systems. Polarity change provides a stable pH environment for microorganisms creating more favorable conditions for their growth, this is extremely vital for the biological processes that occur during the remediation time as drastic changes in pH can be catastrophic. Uniform polarity change enhances biological processes increasing the decontamination rate of pollutants in soil.

In addition, conductivity of soil is critical in remediation as it determines the mobility of charged ions in soil. Electromigration of pollutants is a major removal mechanism that occurs and is highly depended on the conductivity of soil which was showed to be stabilized and improved when lower voltage gradients were applied. Higher voltages resulted in higher removal of contaminants, although in the long run the effect can be reversed due to the saturation of soil with charged ions that will create a resistance, which will therefore reduce the conductivity of soil (Rodrigo & Camacho 2015).

Table 3. Case study 5 & Case study 6

Topic of the study	Followed	Microbes studied	Soil type	Pollutant studied	Condition	Results	References
Study 5: Combination of reversing electrodes polarity with pulsed current	- Three experiments with three different Voltages applied 0.5V/cm,1.0V/cm,1.5V/cm. - Duration of treatment two weeks and the polarity were reversed every 24h.	-	Clay	Diesel	Laboratory	- pH maintained at neutral levels except in 1.5V/cm, a small increase. - Microbial concentration same as initial except in 1.5V/cm, increase. - Conductivity increased in 0,5V/cm and decreased in 1V/cm, 1,5cm/V. - 1,5V/cm highest removal efficiency 35,4%, highest energy consumption. - 0,5V/cm and 1V/cm removal efficiency higher than normal bioremediation.	Rodrigo & Camacho. 2015
Study 6: Efficiency removal of periodic polarity switching and pH change	- 1.0V/cm tests with EC, treatment lasted 100 days Test 1: Reference Test 2: Bacteria, Bioremediation Test 3: EC Test 4: Bacteria, EC, Bioremediation Test 5: Switch polarity, Bioremediaiton Test 6: Bacteria, Switch polarity, Bioremediation	oil-degrading bacteria	24,8% clay, 62,6% silt, 13,6% sand	Oil	Laboratory	- Tests 3,4 massive difference in pH, at anode pH 3,2 and at cathode pH 12,5. - pH difference in tests 5,6 between 5,5 and 7,3. - Removal efficiency of test 4 was 2,4 and 1,3 times higher than tests 2 and 3 respectively. - Test 6 has the highest removal with 72.6%	Li et al. 2010

4.2 Removal of PAHs from soil using electrokinetic remediation methods

PAH is a group of contaminants that can be found nearly anywhere in the world, there are hundreds of different PAHs existing, some of them more hazardous and some less, PAHs with less aromatic rings are less toxic and easier to extract from nature and be decomposed unlike PAHs with more aromatic rings which are toxic and carcinogenic and much more difficult to extract from nature due to their highly hydrophobic nature (Cheng et al. 2016). An experiment studying the removal of PAHs with initial concentration of 720mg/Kg revealed that in 23 days 94% of PAH was managed to be remediated with electrokinetic remediation. The removal efficiency of electrokinetic remediation was found much more efficient compared to other remediation techniques which will be justified furthermore in this chapter (Pazos et al. 2010).

Studies 7 and 8 investigated the efficiency of decontaminating PAH polluted soils (Table 4). In study 7(Isosaari et al., 2006) the potential of oxidants used in remediation can be seen in combination with various electrical currents to treat pollutants Electrokinetic (EK) persulphate has the highest removal efficiency while the other methods have relatively lower. In study 8(Wang et al., 2013), polarity change enhanced the removal of PAHs at both voltages applied 1 and 2V/cm, with lower voltage having higher removal efficiency. In study 8 fungal RNA analysis suggested that high voltages can be lethal to soil microbes and altered operation of electrical current is more suitable for microbe's growth and sustain. (Wang et al. 2013)

Table 4. Case study 7 & Case study 8

Topic of the study	Experimental process	Microbes studied	Soil type	Pollutant studied	Condition	Results	References
Study 7: Efficient remediation methods to decontaminate PAHs	- Five different experiments conducted for 8 weeks. - Direct current (DC) applied 53V/m and alternating current (AC) 4,7V/m with frequency 90Hz. - DC&AC = Direct current+ alternating current - EK Fenton= DC&AC+ mixture 35mM of ferrous iron+ fesh 3% hydrogen peroxide - EK Persulphate=DC&AC+ mixture 35mM of ferrous iron+1.7M sodium peroxodisulphate - Fenton only= mixture 35mM of ferrous iron+ fesh 3% hydrogen peroxide - Persulphate only= mixture 35mM of ferrous iron+1.7M sodium peroxodisulphate	PAH degrading microbes	Clay	PAHs	Laboratory	**1-2 ring PAHs removed** DC&AC 22% EK Fentom <22% EK Persulphate 50% Fentom only 35% Persulphate only <22% **4-6 ring PAHs removed** DC&AC13% EK Fentom <13% EK Persulphate 28% Fentom only <13% Persulphate only<13%	Isosaari et al. 2006
Study 8: Effect of altered directional and unidirectional electric fields on PAH-contaminated soils	- Two different voltages applied 1V/cm and 2V/cm for altered directional and unidirectional applications for 23 days. - Polarity switched for altered every 12 hours. - Concentration of PAHs in soil 220.1mg/Kg.	PAH degrading microbes	Clay loam	PAHs	Laboratory	High ring PAHs degraded to low ring, removal efficiency during 1V/cm was higher and even higher during altered directional (figure 10)	Wang et al. 2013

Reddy & Saichek(2016) studied the application of direct and pulsed current at two different voltages 1VDC/cm and 2VDC/cm in treating PAHs. Pulsed EC was found much more efficient for longer period, it had sustained more flow rate for over 250 days whereas in DC the flow was decreased after the first 25 days. The flow rate for DC was 13mL/day for the first 25 days and afterwards the average flow dropped to 1mL/day whereas in PC the average flow for the whole treatment time of 275 days maintained at 7mL/day. The concentration of phenanthrene after direct current was found higher compared to pulsed current which had lower than 150mg/Kg. Optimal conditions for contaminant removal found in this experiment consist of switching the electrical current on and off, generating a pulse electroosmotic flow and a pulse of electromigration which results in mobilizing phenanthrene from soil pores. (Saichek & Reddy 2006)

Another study (Yuan et al. 2016) had a main objective to investigate whether microbial degradation of cyclododecane (PAH) can be enhanced by electro-kinetics and if so, what is the microbial degradation pathway and enhancement mechanism. The soil tested was sandy loam. Three tests were conducted, in Test 1 bioremediation was introduced without the application of electric field, in Test 2 electro-bioremediation was performed with constant voltage of 1.3V/cm and Test 3 had the same voltage but with electrode's polarity switching every 2h. Treatments lasted 25 days and the initial concentration of cyclododecane was 1000mg/Kg.

Electric field contributed in removal of the contaminant, although in Test 2 the continuous application of electrical current resulted in a large pH difference, at the anode it was 3.1 and at the cathode was 9.6. In test 3 the pH of the soil was uniform in most of the soil maintaining a value around 6.5 which was approximately the initial pH value of the soil. Ring breaking mass was calculated, as it is a critical step in the biodegradation of cycloalkanes, in Test 2 ring-breaking products comprised 15.8% of the initial cyclododecane and in Test 3 23.5%. These results indicate that electric field and reverse polarity increased the removal efficiency of cyclododecanone. pH was found to play a significant role in bioremediation, lower pH values (more acidic conditions) favor the biodegradation of contaminants, although too acidic conditions can pose a threat to microorganisms that are sensitive to pH changes and can lead to their death. (Yuan et al. 2016)

Voltage and frequency are key parameters when utilizing pulsed electrical current for the removal of contaminants. A study conducted by Cheng et al. (2016) for remediation of PAH-contaminated soils with pulsed electrokinetic, reveals that voltage and frequency influence the removal rate of PAH's significantly. When frequency increased from 50 to 90 Hz Phenanthrene degradation rate increased also from 61% to 67% after 40 minutes of treatment. The results obtained from this study reveal that higher frequencies boost physical mechanisms as electro-osmosis to occur and mobilize contaminants better when utilizing pulsed current. (Cheng et al. 2016)

4.3 Removal of PFAs from soil using electrokinetic remediation methods

PFAs (perfluoroalkyl substances) have been manufactured and used for over 60 years in various industries and belong to the group of Persistent Organic Pollutants (POP) as they are highly persistent in nature and difficult to be decomposed. Studies have shown that plants that have been irrigated by PFAs have absorbed it through their photosynthesis process and transport it through the food chain up to humans, they have been detected in human blood, plasma and breast milk (Stahl et al. 2012). Studies and investigations regarding the biodegradation of PFAs are extremely limited as they are relatively new to humans and limited information is known for their characteristics, although several case studies have been found and will be presented in this chapter.

Niarcho et al. (2021) conducted three experiments for 21 days, the field samples tested were taken from an airport in Sweden which was contaminated with PFAs. Direct current was utilized with voltages varying from 0.19 to 0.39 mA/cm. Results revealed that removal efficiency of PFAs with less than 8 carbon atoms was much higher compared to compounds with more than 8 Carbon atoms. Application of higher current densities didn't result in increase in removal efficiency of PFAs, instead PFAs that were not present in the reference sample were found after the treatment, which leads to the conclusion that long-chain PFAs pose a challenge. (Niarcho et al. 2021)

Söregard et al. (2019) came to the same conclusions in an experiment aiming to asses for the first time the effect of electrokinetic remediation process on PFAs. Lower current (0.19mA/cm) resulted in a greater degradation of short-chain PFAs near the cathode compared to higher current of 0.38mA/cm. PFAs tested were ranging from 3 to 11 Carbon atoms, samples investigated were collected from a fire-fighter training site, soil was characterized as clay and was known to be contaminated with PFAs. Two electrical experiments were conducted with two different current densities of 0.19 mA/cm (8.5V) and 0.38 mA/cm (20V) for 21 days. Results reveal that higher current does not apply to better transportation of PFAs hence better removal, despite the fact that results showed that at 0.38mA/cm the concentrations of majority of PFAs were lower compared to the 0.19mA/cm. (Sörengard at al. 2019)

In another study the degradation of perfluorooctane sulfonates (PFOs) a subgroup of PFAs, used in metal plating, semiconductor manufacturing and contained in a wide variety of products was investigated. Different current densities and temperatures were tested utilizing a rotating disk electrode reactor and a parallel plate flow-through reactor. 5 different currents were utilized in the treatment 1, 5, 10, 15 and 20 mA/ sq.cm. Degradation of PFOs was found greater at lower currents 5 and 10 mA/sq.cm, indicating that current density is not proportional to degradation efficiency. (Kimberly et al. 2007)

Per- and polyfluoroalkyl substances have properties of strong stability, hydrophobicity, lipophobicity and high surface activity. The most common PFAs found are fluorooctanoic acid (PFOA) and perfluoroctane sulfonic Acid (PFOs) which are the most stable conversion product of their environmental precursors and derivatives. They are difficult to be degraded hence increasing the risk of bioaccumulation and toxicity in environment. In a recent study (Hou et al., 2021) low intensity electrical current has been applied to remediate these contaminants. PFOA and PFOs were managed to be degraded efficiently in saturated environment under low-voltage direct current, with degradation efficiencies reaching 51.7% and 33% respectively for PFOA and PFOs. (Hou et al. 2021)

4.4 EKOGRID Technonolgy

Pulsed electrical current has been applied at EKOGRID OY consultant company, which has been investigating this technology (EKOGRID technology) the last decade, utilizing pulsed electrical current at low voltages while the same time reversing the polarity of electrical current in time intervals of 2-4 seconds (figure5). Case studies presented in Table 5, reveal how EKOGRID technology is been applied in the field and managed to remediate successfully soil contaminants PAH's, BTEX(benzene, toluene, ethylbenzene, xylene) etc. in a sustainable and ecological manner. (Jääskeläinen)

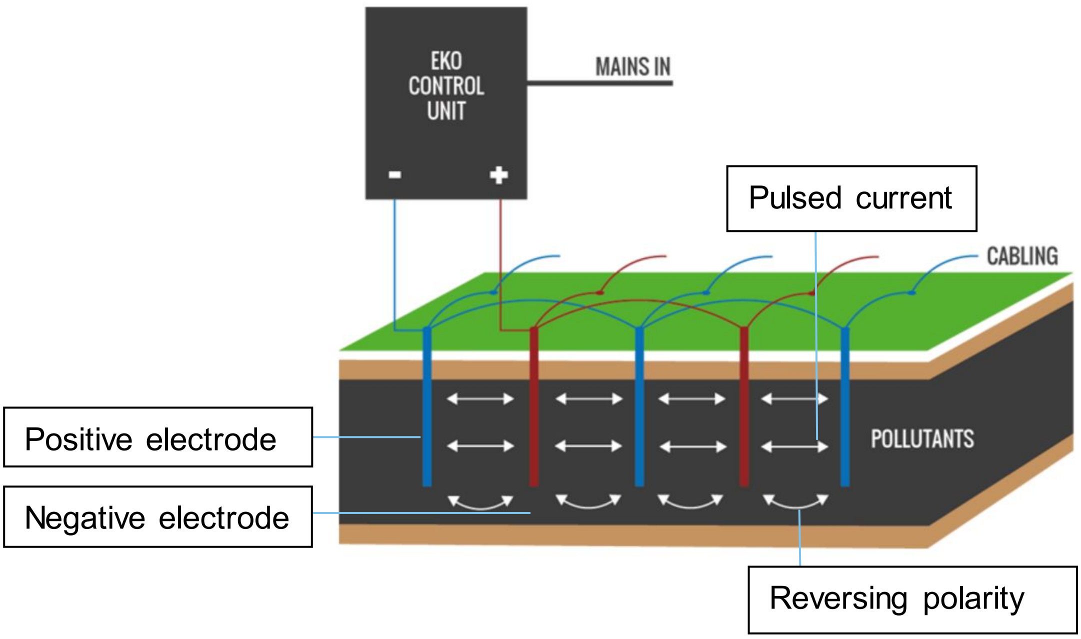

Figure 5. Schematic representation of EKOGRID system (Lindberg)

Table 5. EKOGRID's case studies

Studies	Characteristics	Pollutant	Pollution depth	Soil	Technology	Results	References
Case study 1	14 different PAH contaminants investigated	PAHs	1-2m	Characterized as humid with high nutrient content	EKOGRID	PAHs concentration well below limit (figure 6)	Humala S.
Case study 2	Sewage lagoon consisting of petroleum hydrocarbons	Lube oil, consisting of PAHs	0-2,5m	Sandy silt, Gravely sandy clay	EKOGRID	Lube oil (PAHs) concentration below remediation legal requirements (figure 7)	Humala S.
Case study 3	Pollution of bottom sediment with hydrocarbons varying from 5-35 carbon atoms	Aliphatic hydrocarbons	Below lake water (0-2 m)	-	EKOGRID	Concentration of aliphatic hydrocarbons reached target values (figure 8) and EKOGRID technology managed to compact and harden the sediments	Humala S.

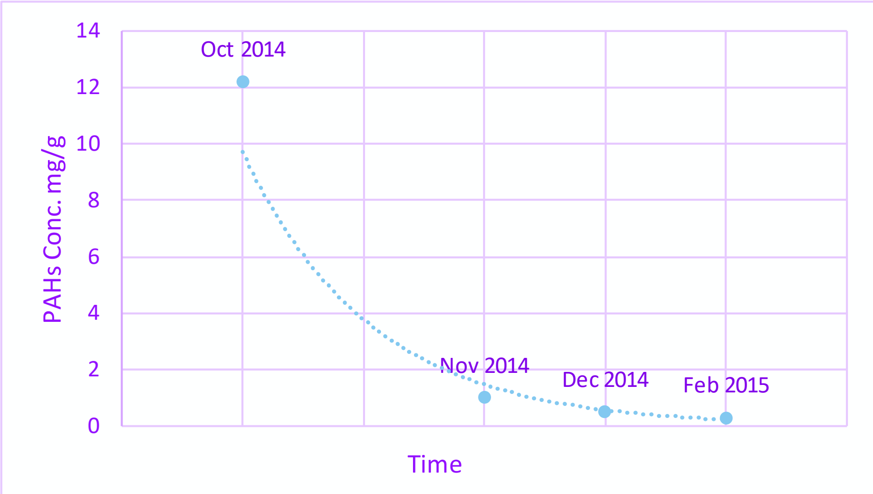

Figure 6. EKOGRID's Case study 1 (Humala S.)

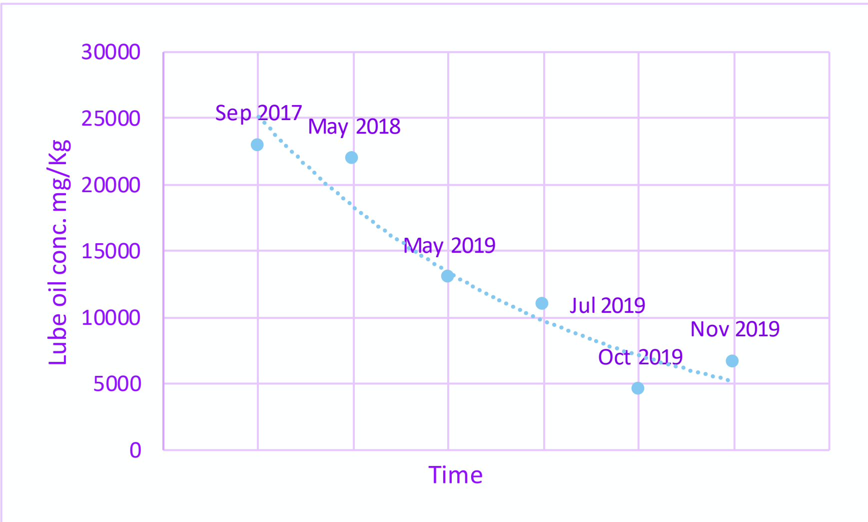

Figure 7. EKOGRID's Case study 2 (Humala S.)

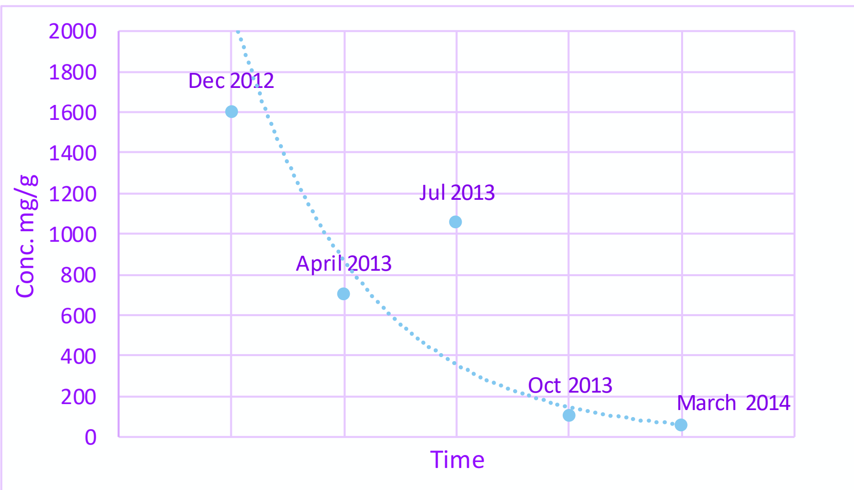

Figure 8. EKOGRID's Case study 3 (Humala S.)

5 DISCUSSION

This study reveals the capability and potential of electrical current specifically pulsed electrical current under reverse polarity in treating PAHs, PFAs and various types of contaminants. The innocence of low electrical currents to microbes is vital in soil environments, changes caused to microbial communities were insignificant which is major factor that affects the remediation process. (Kimberly et al. 2007).

The application of pulsed current and pulsed reversed current was seen to decontaminate efficiently heavy metals and hydrocarbons with significantly lower electrical energy consumptions compared to traditional direct current, which is a major advantage in large scale projects. Frequency of pulses enacts an important part in the removal of contaminants, higher frequencies enhance the removal rate up to a certain point, which when exceeded causes a decrease in the net charge of the system by the saturation of charged ions. (Cheng et al. 2016)

The surface charge of microorganisms is sensitive to variety of parameters including pH, composition of the nutrients, hydrogen index, growth phase, redox potential. Sometimes the decontamination of pollutants can pose a challenge to microbes, contaminants might exist in high concentrations being lethal to microbes or in very small providing not enough energy and this can be culminated further when the contaminants are strongly bonded to soil particles. That is why concentrations and type of pollutants should be identified before any treatment starts (Hassan et al. 2015). Critical factor is pH, which is stabilized with pulsed reverse polarity, as the constant change of polarity doesn’t allow any significant increase or decrease in pH, small decrease can be caused which can favour microbes.

PAHs and PFAs are highly hydrophobic posing a challenge for their remediation as was seen, pulsed current with reverse polarity was found to decompose efficiently these contaminants. Low voltages, constant pulses and constant change of polarity generate a pulse electroosmotic flow and pulsed electromigration which enhances the removal of contaminants. During periodic voltage the system gets charged and uncharged which allows the charged ions to get solubilized during ‘off time’ and when voltage is replied more ions are free to transport pollutant ions toward the electrodes (Reddy& Saichek 2016). Sometimes longer chain PFAs and higher ring PAHs as was seen due to their greater oleophilic nature pose a challenge of decontamination, although pulsed current with reverse polarity was found to enhance their degradation process.

Ekogrid technology case studies also revealed the potential of pulsed electrical current under reverse polarity in treating PAHs and other types of hydrocarbons. Low voltages applied, and constant change of polarity enhanced physical mechanisms to occur (electrophoresis, electromigration and electro osmosis). Rapid pulses of voltage applied create oxidative conditions which enhance the degradation of PAHs and PFAs, which are managed to be decomposed efficiently in finer and lower conductive soils as well.

Overall, this bibliography investigated the application of pulsed current under reverse polarity in treating contaminated soils with PAHs and PFAs, it revealed that the system is cost efficient consuming low energy supplies and efficient in treating and removing various contaminants including PAHs and PFAs . Various parameters and details though such as nutrient composition, oxygen demand, chemical structures, characteristics etc. which are important during remediation were not considered in the study. Therefore, a more detailed and experimental study should be conducted to access the capability of pulsed current under reverse polarity in treating PAHs and PFAs.

Ekogrid OY having utilized this remediation technique for several years, has revealed the efficiency and potential of the system, which can extract and remediate PAHs, PFAs and other types of contaminants in an efficient and sustainable manner. Electrokinetic remediation with pulsed current and reverse polarity constitutes major advantages that could give solutions to future soil decontamination projects.

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