DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

ELECTROKINETIC REMEDIATION OF CONTAMINATED SOILS

by
Melayib BİLGİN

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İZMİR

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Ph.D. THESIS EXAMINATION RESULT FORM

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ELECTROKINETIC REMEDIATION OF CONTAMINATED SOILS

ABSTRACT

Recently, soil pollution has gained importance among the main environmental problems in the world. In developed countries, as well as water and air pollution, soil pollution has become a big issue. This commonly encountered contaminants heavy metals, chlorinated organic compounds, total petroleum hydrocarbons (TPH) and polycyclic aromatic hydrocarbons (PAH).

In the presented study, remediation studies were conducted to determine the effectiveness of electrokinetic method on the treatment of natural soil contaminated with petroleum hydrocarbons, in laboratory scale reactors. Electokinetic remediation of agricultural soil with an initial TPHs concentration of 10000 ppm was investigated under 20 V or 40 V direct current by using NaOH, pure water, Acetic Acid and Ethanol as electrolyte solution, treatment efficiencies were observed according to the distance from the anode chamber and the applied electrical potential. The effect level of electrokinetic remediation on PAHs, which were announced by EPA as in high toxicity group and present in engine oil that was used as contaminant, was also included in the framework of the study. It was observed that high treatment efficiencies for PAHs and TPHs were achieved according to the distance from the anode and the electrical potential applied to the system. Additionally, the operational costs of the systems were also evaluated and it was seen that the applied conditions resulted with lower costs compared with the previous electrokinetic studies reported in the literature and with the other treatment technologies, despite the data exhibit higher treatment efficiencies.

Keywords: Electrokinetic Remediation, Electrolyte Solution, Total Petroleum Hydrocarbons, Polycyclic Aromatic Hydrocarbons (PAHs).

KİRLETİLMİŞ TOPRAKLARIN ELEKTROKİNETİK ARITIMI

ÖZ

Son zamanlarda dünyada temel çevre sorunları arasında toprak kirliliği büyük önem kazanmıştır. Gelişmiş ülkelerde su ve hava kirliliğinin yanı sıra toprak kirliliği de büyük bir sorun haline gelmiştir. Kirlenmiş toprakta organik veya inorganik olmak üzere birçok kirletici bulunabilir. Bu kirleticilerden ağır metaller, klorlu organik bileşikler, Toplam Petrol Hidrokarbonları (TPH) ve Çokhalkalı Aromatik Hidrokarbonlar(PAH) yaygın olarak karşılaşılanlardır.

Sunulan çalışmada elektrokinetik yöntemin petrol hidrokarbonları ile kirletilmiş doğal toprağın arıtımındaki etkinliğinin belirlenmesi amacıyla laboratuar ölçekli reaktörlerde arıtım çalışmaları yürütülmüştür. Başlangıç TPH konsantrasyonu 10000 ppm kuru madde (km) olan tarım toprağının 20 V ve 40 V doğru akım altında, elektroliz sıvısı olarak NaOH, saf su, Asetik asit ve Etanol kullanılarak elektrokinetik arıtımı araştırılmış, anottan olan mesafeye ve uygulanan elektrik potansiyeline bağlı olarak giderim verimleri incelenmiştir. Kirletici olarak kullanılan motor yağı içinde bulunan ve EPA tarafından yüksek toksisite grubunda olduğu belirtilen onaltı adet Çokhalkalı Aromatik Hidrokarbonun (PAH) elektrokinetik arıtımdan etkilenme seviyeleri de çalışma kapsamında araştırılmıştır. PAH ve TPH arıtım verimleri değerlendirildiğinde, anottan olan mesafeye ve uygulanan elektrik potansiyeline bağlı olarak yüksek giderim verimlerinin söz konusu olduğu gözlenmiştir. Bunlara ilaveten sistemlerin işletme masrafları da değerlendirmiş olup, uygulanan şartların, elde edilen daha yüksek arıtma verimlerine rağmen, literatürde yayınlanan önceki elektrokinetik çalışmalar ve diğer arıtma teknolojilerine göre daha düşük işletme masrafları oluşturduğu belirlenmiştir.

Anahtar Kelimeler: Elektrokinetik Arıtım, Elektroliz Sıvısı, Toplam Petrol Hidrokarbonları, Çokhalkalı Aromatik Hidrokarbonlar (PAH)

CONTENTS

CHAPTER ONE
INTRODUCTION

1.1 The Problem Statement

Recently, soil pollution has gained importance among the main environmental problems in the world. In developed countries, as well as water and air pollution, soil pollution has become a big issue. Soil is contaminated by many reasons such as developing industry, mining, oil pipeline leaks and accidents, the highways and anthropogenic sources(Atlas, 1995), and that pollution has reached alarming. Many organic or inorganic contaminants can be found in contaminated soil. This commonly encountered contaminants heavy metals (Kim et al., 2009), chlorinated organic compounds (Zoeteman, 1985, Palmer et al., 1988, Şirin, 1998), total petroleum hydrocarbons (TPH) (Huang et al., 2005) and polycyclic aromatic hydrocarbons (Alcántara et al., 2008; Alcántara et al., 2009).

Heavy metals in the soil began to accumulate more with the development of industry and mining. One of the reasons for raising the quantity of the heavy metals in the soil is utilization of waste waters as irrigation water and application of treatment sludge in the field to be used as fertilizer.

Polycyclic aromatic hydrocarbons (PAHs) are common contaminants in the environment and they are composed of two or more benzene rings (Alcántara et al., 2009; Pathak et al., 2009).

PAHs sources may be both natural and anthropogenic. Emissions from anthropogenic activities predominate, but some PAHs in the environment are originated from natural sources. Anthropogenic ones are oil spills, urban runoff, domestic and industrial wastewater discharges and vehicle exhaust (Doong & Lin, 2004). PAHs are a group of chemicals that are formed during the incomplete burning of coal, oil, gas, wood, garbage, or other organic substances, such as tobacco and charbroiled meat PAHs generally occur as complex mixtures (for example, as part of combustion products such as soot), not as single compounds. They are also toxic, mutagenic and carcinogenic properties due to their serious environmental problems constitute (Alcantara et al., 2008; Pathak et al., 2009; Alcantara et al., 2009).

As pure chemicals, PAHs are usually colorless, white or pale yellow-green solids. There are more than 100 PAH in the environment, but only 16 of them are included in the priority pollutants list of U.S. EPA based on a number of factors including toxicity, extent of information available, source specificity, frequency of occurrence at hazardous waste sites, and potential for human exposure (ATSDR, 1995).

The chemical structures of the most common PAHs are presented in Figure 1.1. and some properties of the most common PAHs are illustrated in Table1.1

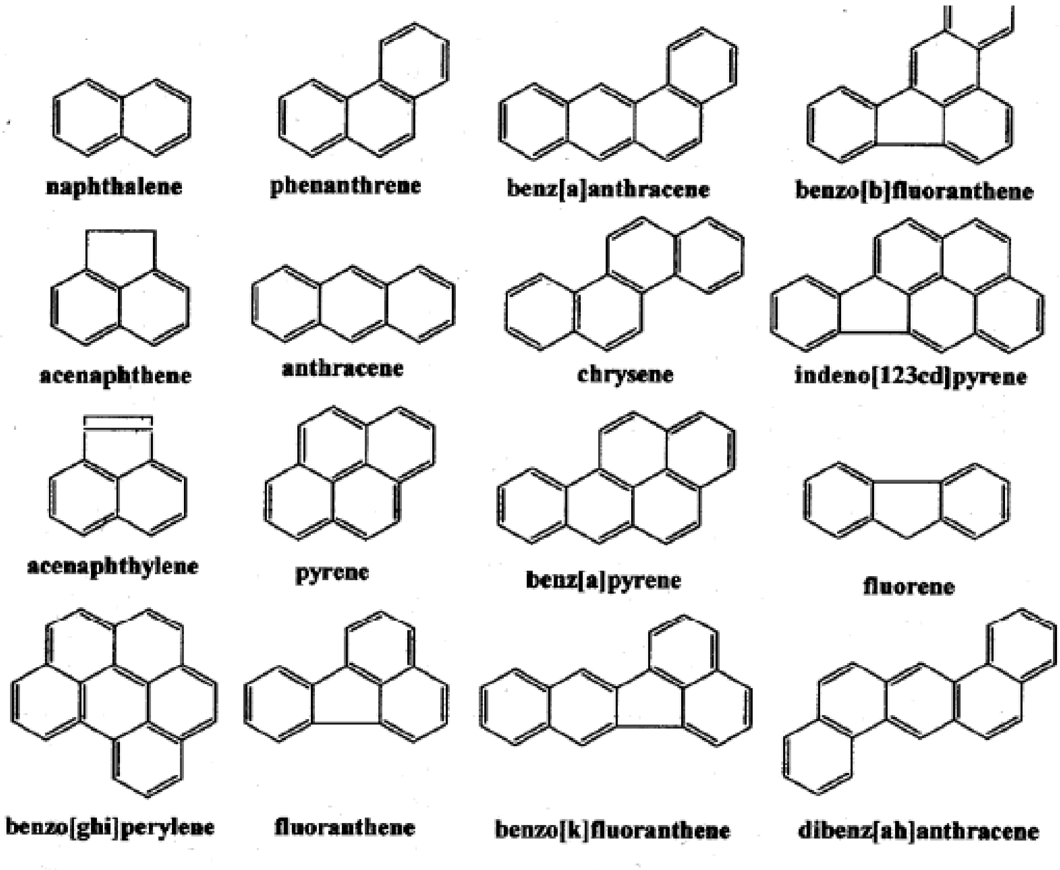


Figure 1.1 The chemical structures of the most common PAHs (Manoli & Samara, 1999)

Table 1.1 Some properties of the most common PAHs

PAHs	Number of Rings	Number of Carbon	Molecular Weight, g/mole	Boiling Point, °C	Solubility in Water, mg/L
Acenaphthylene	3	12	152.2	270	3.93
Acenaphthene	3	12	154.21	96	1.93
Fluorene	3	13	166.2	295	1.83
Phenanthrene	3	14	178.2	340	1.2
Anthracene	3	14	178.2	342	0.076
Carbazole	3	12	167.21	351	0
Fluoranthene	4	16	202.26	375	0.23
Pyrene	4	16	202.3	393	0.077
Benz (a) anthracene	4	18	228.29	159	0.01
Chrysene	4	18	228.3	448	0.0
Benzo (b) fluoranthene	5	20	252.3	168	0.0012
Benzo (k) fluoranthene	5	20	252.3	550	0.00076
Benzo (a) pyrene	5	20	252.3	179	0.0023
Dibenz (a.h) anthracene	5	22	278.35	524	0.0005
Benzo (g.h.i) perylene	6	22	276.34	480	0.00026
Indeno (1.2.3-cd) pyrene	6	22	276.3	530	0.062

1.2 Soil Pollution in Turkey

Turkey has contaminated soil problems although they do not yet have high priority among other environmental problems. The causes of contaminated soil problems in Turkey may be summarized as follows:

Industrialization: In Turkey, industrialization has started in about 1930's. For a long time, no environmental considerations were taken into account. Even today, water and air pollution problems are discussed in more detail and soil contamination to a lesser extent. Industrial wastes causing soil contamination also include oil pollution in many cases.

Leaking tanks and pipes*:* Since Turkey is located between Europe and Middle East, transportation of goods is very important. A considerable amount of oil is transported. Thousands of filling stations use buried underground tanks. Many kilometers of underground pipelines carry petroleum products. Although there are no studies about the leakage from these tanks and pipelines, it is known that they start to leak after some time.

Accidental spills: 90% of transportation is performed by motorway in Turkey. Accidental spill is an important contamination source for oil because of the occasional tanker trucks accidents**.**

Midnight dumping: During to the application of removal of cesspool contents in some areas, sometimes the wastewaters and hazardous waste are discharged to uninhabited areas.

1.2.1 Contaminated Sites in Turkey

Some examples of the identified contaminated sites and major soil and groundwater problems associated with these sites in Turkey are as follows:

Beykan Oil Field Site*:* At this site, petroleum hydrocarbon pollution of surface soils, surface and groundwater caused by oil production activities of the Beykan Oil Field is of concern. The Beykan Oil Field is enclosed by the watershed of a medium size dam constructed during early-sixties for irrigation purposes. A total of 38 oil producing wells are placed within the various protection zones surrounding the dam's reservoir; 13 of them being in the immediate vicinity, within the first 300 m of the reservoir shore called the "*absolute protection zone.*" Oil spills at these wells and along pipelines connecting wells and other facilities are considered as potential pollution sources effecting the reservoir water quality. Spill records revealed that, during the peak oil production years, 95 tons of annual average spill occurred, resulting in an average total petroleum hydrocarbons (TPHs) concentration of 20,300 ppm in contaminated soils (NATO/CCMS Pilot Study, 1998).

Incirlik PCB Contaminated Soils Site*:* At this site, soil contamination by polychlorinated biphenyls (PCB), oil leaking from storage drums at a military reutilization yard occurred during the operation of the yard between the years of 1970 and 1988. Estimated PCB-contaminated soil volume is 1,600 m3. PCB concentrations measured in composite contaminated soil samples range up to 750 ppm (NATO/CCMS Pilot Study, 1998).

***Chromium Ore Processing Residue Dump Site**:* At this site, soil and groundwater contamination by Cr(VI) leaching from chromium ore processing residue (COPR) is of concern. COPR is produced by a chromate production factory providing mostly the needs of leather tanning industry. Due to high chromium content (25,000 ppm), COPR is partly recycled by mixing with chromium ore at a ratio of roughly 1:20 (NATO/CCMS Pilot Study, 1998).

1.3 Remediation Techniques for Contaminated Soils

Several technologies exist for the remediation of metals-contaminated soil and water. These technologies are contained within five categories: isolation, immobilization, toxicity reduction, physical separation and extraction (Evanko & Dzombak, 1997). These are the same general approaches used for many types of contaminants in the subsurface (LaGrega et al., 1994).

1.3.1 Isolation

Isolation technologies attempt to prevent the transport of contaminants by containing them within a designated area. Contaminated sites may also be isolated temporarily in order to limit transport during site assessment and site remediation. Capping systems are used to provide an impermeable barrier to surface water infiltration to contaminated soil for prevention of further release of contaminants to the surrounding surface water or groundwater (Evanko & Dzombak, 1997). Subsurface barriers may be used to isolate contaminated soil and water by controlling the movement of groundwater at a contaminated site. These barriers are designed to reduce the movement of contaminated groundwater from the site, or to restrict the flow of uncontaminated groundwater through the contaminated site (Rumer & Ryan, 1995).

1.3.2 Immobilization

Immobilization technologies are designed to reduce the mobility of contaminants by changing the physical or leaching characteristics of the contaminated matrix. A variety of methods are available for immobilization of metal contaminants, including those that use chemical reagents and/or thermal treatment to physically bind the contaminated soil or sludge (Evanko & Dzombak, 1997).

1.3.2.1 Solidification/Stabilization

Solidification and stabilization (S/S) immobilization technologies are the most commonly selected treatment options for metals-contaminated sites (Conner, 1990). Solidification involves the formation of a solidified matrix that physically binds the contaminated material. Stabilization, also referred to as fixation, usually utilizes a chemical reaction to convert the waste to a less mobile form. The general approach for solidification/stabilization treatment processes involves mixing or injecting treatment agents to the contaminated soils. Inorganic binders, such as cement, fly ash, or blast furnace slag, and organic binders such as bitumen are used to form a crystalline, glassy or polymeric framework around the waste (Evanko & Dzombak, 1997). The dominant mechanism by which metals are immobilized is by precipitation of hydroxides within the solid matrix (Shively et al., 1986).

1.3.2.2 Vitrification

The mobility of metal contaminants can be decreased by high-temperature treatment of the contaminated area that results in the formation of vitreous material, usually an oxide solid (Evanko & Dzombak, 1997). Most soils can be treated by vitrification and a wide variety of inorganic and organic contaminants can be targeted. Vitrification may be performed ex situ or in situ, although in situ processes are preferred due to the lower energy requirements and cost (U.S. EPA, 1992a).

Typical stages in ex situ vitrification processes may include excavation, pretreatment, mixing, feeding, melting and vitrification, off-gas collection and treatment, and forming or casting of the melted product. The energy requirement for melting is the primary factor influencing the cost of ex situ vitrification. Different sources of energy can be used for this purpose, depending on local energy costs. In situ vitrification (ISV) involves passing electric current through the soil using an array of electrodes inserted vertically into the contaminated region. Each setting of four electrodes is referred to as a melt (Evanko & Dzombak, 1997).

1.3.3 Chemical Treatment

Chemical reactions can be initiated that are designed to decrease the toxicity or mobility of metal contaminants. The three types of reactions that can be used for this purpose are oxidation, reduction, and neutralization reactions. Chemical oxidation changes the oxidation state of the metal atom through the loss of electrons. Commercial oxidizing agents are available for chemical treatment, including potassium permanganate, hydrogen peroxide, hypochlorite, and chlorine gas. Reduction reactions change the oxidation state of metals by adding electrons. Commercially available reduction reagents include alkali metals (Na, K), sulfur dioxide, sulfite salts, and ferrous sulfate. Changing the oxidation state of metals by oxidation or reduction can detoxify, precipitate, or solubilize the metals (NRC, 1994). Chemical neutralization is used to adjust the pH balance of extremely acidic or basic soils and/or groundwater. This procedure can be used to precipitate insoluble metal salts from contaminated water, or in preparation for chemical oxidation or reduction. Chemical treatment can be performed ex situ or in situ. However in situ chemical agents must be carefully selected so that they do not further contaminate the treatment area (Evanko & Dzombak, 1997).

1.3.4 Treatment Walls (Permeable)

Treatment walls remove contaminants from groundwater by degrading, transforming, precipitating or adsorbing the target solutes as the water flows through permeable trenches containing reactive material within the subsurface (Vidic & Pohland, 1996). Several methods are available for installation of permeable treatment walls, some of which employ slurry wall construction technology to create a permeable reactive curtain. Several types of treatment walls are being tried for arresting transport of metals in groundwater at contaminated sites. Trench materials being investigated include zeolite, hydroxyapatite, elemental iron, and limestone (Vidic & Pohland, 1996). Trenches filled with elemental iron have shown promise for remediation of metals contaminated sites. While investigations of this technology have focused largely on treatment of halogenated organic compounds, studies are being performed to assess the applicability to remediation of inorganic contaminants (Powell et al., 1994). The use of limestone treatment walls has been proposed for sites with metals contamination, in particular former lead acid battery recycling sites which have lead and acid contamination in groundwater and soil (Evanko & Dzombak, 1997).

1.3.5 Biological Treatment

Biological treatment technologies are available for remediation of metals-contaminated sites. These technologies are commonly used for the remediation of organic contaminants and are beginning to be applied for metal remediation, although most applications to date have been at the bench and pilot scale. Biological treatment exploits natural biological processes that allow certain plants and microorganisms to aid in the remediation of metals (Evanko & Dzombak, 1997). These processes occur through a variety of mechanisms, including adsorption, oxidation and reduction reactions, and methylation(Means & Hinchee, 1994).

*Bioaccumulation; B*ioaccumulation involves the uptake of metals from contaminated media by living organisms or dead, inactive biomass. Active plants and microorganisms accumulate metals as the result of normal metabolic processes via ion exchange at the cell walls, complexation reactions at the cell walls, or intra- and extracellular precipitation and complexation reactions (Evanko & Dzombak, 1997).

Phytoremediation; Phytoremediation refers to the specific ability of plants to aid in metal remediation. Some plants have developed the ability to remove ions selectively from the soil to regulate the uptake and distribution of metals (Evanko & Dzombak, 1997). Potentially useful phytoremediation technologies for remediation of metals-contaminated sites include phytoextraction, phytostabilization and rhizofiltration. Phytoextraction employs hyperaccumulating plants to remove metals from the soil by absorption into the roots and shoots of the plant. Phytostabilization involves the use of plants to limit the mobility and bioavailability of metals in soil. Rhizofiltration removes metals from contaminated groundwater via absorption, concentration and precipitation by plant roots. This technique is use to treat contaminated water rather than soil and is most effective for large volumes of water with low levels of metal contamination.

Bioleaching; Bioleaching uses microorganisms to solubilize metal contaminants either by direct action of the bacteria, as a result of interactions with metabolic products, or both. Bioleaching can be used in situ or ex situ to aid the removal of metals from soils. This process is being adapted from the mining industry for use in metals remediation. The mechanisms responsible for bioleaching are not fully defined, but in the case of mercury bioreduction (to elemental mercury) is thought to be responsible for mobilization of mercury salts.

1.3.6 Physical Separation

Physical separation is an ex situ process that attempts to separate the contaminated material from the rest of the soil matrix by exploiting certain characteristics of the metal and soil. Physical separation techniques are available that operate based on particle size, particle density, surface and magnetic properties of the contaminated soil. These techniques are most effective when the metal is either in the form of discrete particles in the soil or if the metal is sorbed to soil particles that occur in a particular size fraction of the soil (Evanko & Dzombak, 1997).

Several techniques are available for physical separation of contaminated soils including screening, classification, gravity concentration, magnetic separation and froth flotation. Screening separates soils according to particle size by passing the matrix through a sieve with particular size openings. Classification involves separation of particles based upon the velocity with which they fall through water or air. Gravity concentration relies on gravity and one or more other forces (centrifugal force, velocity gradients, etc.) that may be applied to separate particles on the basis of density differences. Magnetic separation subjects particles to a strong magnetic field using electromagnets or magnetic filters and relies on differences in magnetic properties of minerals for separation (Evanko & Dzombak, 1997).

1.3.7 Extraction

Metals-contaminated sites can be remediated using techniques designed to extract the contaminated fraction from the rest of the soil, either in situ or ex situ. Metal extraction can achieved by contacting the contaminated soil with a solution containing extracting agents (soil washing and in situ soil flushing) or by electrokinetic processes. The contaminated fraction of soil and/or process water is separated from the remaining soil and disposed or treated.

1.3.7.1 Soil Washing

Soil washing can be used to remove metals from the soil by chemical or physical treatment methods in aqueous suspension. Soil washing is an ex situ process that requires soil excavation prior to treatment (Evanko & Dzombak, 1997). Particle size separation techniques may not be successful if fine particle, e.g., metal oxide, coatings are present on particles in larger size fractions(Van Ben Schoten et al., 1994).

1.3.7.2 Soil Flushing

In situ soil flushing is used to mobilize metals by leaching contaminants from soils so that they can be extracted without excavating the contaminated materials. An aqueous extracting solution is injected into or sprayed onto the contaminated area to mobilize the contaminants usually by solubilization (Evanko & Dzombak, 1997).

1.3.7.3 Electrokinetic Treatment

The success of various electrokinetic remediation technologies has been illustrated for removal of metals from soils via bench and pilot scale experiments. Currently, several of these technologies are being implemented in comprehensive demonstration studies to further the use of electrokinetic techniques at contaminated sites (Evanko & Dzombak, 1997).

Electrokinetic remediation technologies apply a low density current to contaminated soil in order to mobilize contaminants in the form of charged species. The current is applied by inserting electrodes into the subsurface and relying on the natural conductivity of the soil (due to water and salts) to effect movement of water, ions and particulates through the soil. Water and/or chemical solutions can also be added to enhance the recovery of metals by this process. Positively charged metal ions migrate to the negatively charged electrode, while metal anions migrate to the positively charged electrode (Evanko & Dzombak, 1997). This technique will be explained in detail in the next chapter.

1.4 Purpose of the Study

The general objective of this research is to experimentally investigate the effectiveness and feasibility of using electrokinetic extraction technique to mobilize and/or remove organic contaminants detected frequently in polluted sites. In the literature, reporting studies on electrokinetic remediation of contaminated soil has started in 1993 (Acar & Alshawabkeh, 1993). In the following years, the data from researches that explain the electrokinetic phenomenon on the treatment of contaminated soils has published, especially about the soils contaminated with metals and heavymetals (Jensen et. al., 1994, Li et. al., 1996, Reddy & Chinthamreddy 1999 Lee et. al., 2000, Saichek & Reddy, 2003, Altin & Degirmenci, 2005, and Alcantara et. al., 2010). In these studies, the application of co-solvents (electrolyte solutions) and the voltage applied has varied to observe the changes in treatment efficiencies. After 2003, the treatment of organic contaminants (mainly hydrophobic) by electrokinetic method was started to be studied by a limited number of researchers (Saichek & Reddy, 2003, Ricart et. al., 2008, Alcantara et. al., 2010) under different electrical potentials by using various co-solvents. The literature survey on electrokinetic method application on contaminated soils exhibited that the major lack of information on the application of this method is unknown effectiveness of the method on natural soils, since research groups achieve the experiments on the inert soils with determined granular distribution, such as kaolinite and glacial till. Furthermore, the investigations on the treatment of organic contaminants are deficient, since the most of the researchers prefer to treat only one organic compound (pentadecane, ethylbenzene, etc.) in the systems, which is contrary to the fact that common organic contaminants such as gasoline, engine oil, and crude oil, are the mixtures of many compounds.

According to the literature survey, the objectives of this study are stated and can be summarized as follows;

1. To investigate the efficiency of electrokinetic treatment on natural soils contaminated with petroleum hydrocarbons.

2. To collect evidence to interpret some phenomena observed during electrokinetic remediation experiments such as electroosmotic flow, generation of gases at the electrodes, change of soil pH, and change of pH in anode and cathode chamber, etc. according to the applied voltage and electrolyte solution used.

3. To examine removal of contaminants by electrokinetic remediation techniques under different electrical potential and different electrolyte solution for investigating and discussing the operational costs.

CHAPTER TWO
ELECTROKINETIC APPLICATION

The demand for innovative and cost-effective in situ remediation technologies in waste management stimulated the effort to employ conduction phenomena in soils under an electric field to remove chemical species from soils (Acar & Alshawabkeh, 1993).

The use of electrokinetics for containment or treatment of sites with inorganic contaminants has attracted considerable attention, partly because of previous experiences with electro-osmotic procedures in soil dewatering, and partly because of the relatively “simplicity” of the field application method. This is generally considered a physico-chemical technique because of the field application methods, i.e., the use of electrodes and current energy. For the more granular types of soils (silts), the procedure can be effective (Yong, 2001). A typical Electrokinetic Remediation System is shown in Figure 2.1.

2.1 Electrokinetic Remediation Process

In this technology, a direct current (DC) is passed through the contaminated soil, causing contaminating species to be transported towards the electrodes and then removed from the soil. Three principal mechanisms of contaminant movement in electrical field are involved in this technology: electromigration, electroosmosis, and electrophoresis (Li et al, 1997).

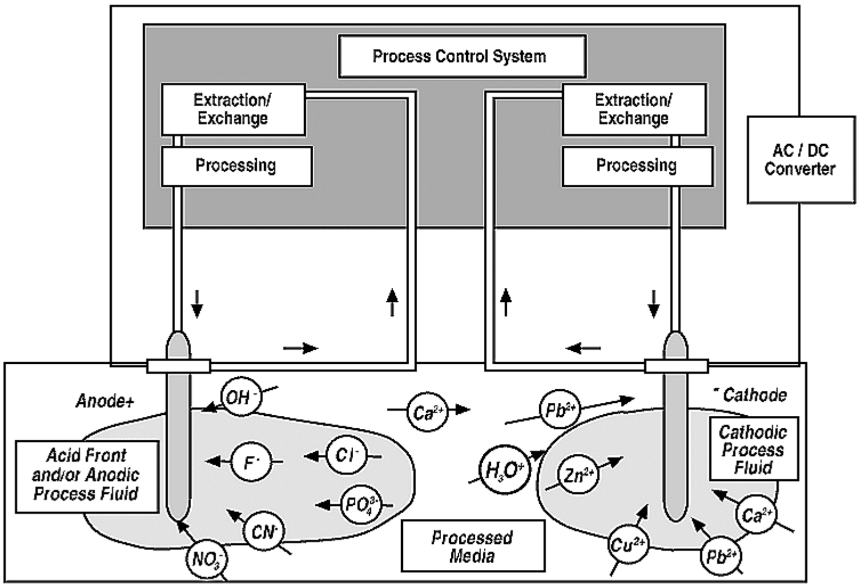


Figure 2.1 Typical Electrokinetic System (Acar & Alshawabkeh, 1993)

a) Electromigration

Electromigration is the migration of ionic species, which are present in the soil void fluid, in an electric field. Cations move towards the cathode, while anions move towards the anode. The triggering mechanism in action is electrolysis of the fluid in the system.

b) Electroosmosis

Electroosmosis in a pore occurs due to the drag interaction between the bulk of the liquid in the pore and a thin layer of charged fluid next to the pore wall that, like a single ion, is moved under the action of the electric field in a direction parallel to it. The thin layer of charged fluid, or electric double layer, has a typical thickness between 1 and 10 nm (Li et al, 1997). This action is directly related with the presence of anions and the cations present in the system which affect the zeta potential of the soil that controls the liberty and direction of the pore fluid.

c) Electrophoresis

Electrophoresis is the migration of charged colloids in a soil-liquid mixture. Electrophoresis could be important in a system where the contaminants are bound to colloids. But in the systems with low soil porosity and permeability, electrophoresis becomes a recessive action.

In conventional use of the technology, the cathode is directly inserted in the soil being treated. Therefore, the hydroxyls generated at the cathode are transported into the soil, causing an increase in pH near the cathode. Because heavy metals precipitate at high pH and, furthermore, a high pH favors the sorption of heavy metals onto the soil surface, most heavy metals can be found in the cathode half of the soil after remediation (Li et al, 1997).

Electrokinetic (EK) processing, the applied current leads to water electrolysis at both anode and cathode, and the equations are as follows (Li et. al. 1997, Chang & Liao 2006, Shen et al. 2007):

At the Anode; $2H_2O - 4e^- = 4H^+ + O_{2(g)}$ (Eq. 1)

At the Cathode; $4H_2O + 4e^- = 4OH^- + 2H_{2(g)}$ (Eq. 2)

As seen from these equations, the electrolysis reactions cause an acidic solution to be generated at the anode and an alkaline solution to be generated at the cathode.

CHAPTER THREE

LITERETURE REVIEW

A number of studies were reported in literature for the electrokinetic remediation of contaminated soils. Major studies may be summarized as follows:

Acar & Alshawabkeh firstly introduced the electrokinetic treatment of metal contaminated soils in their article published in 1993, which explains the transfer of the process fluid and ionic species under an electric field (Acar & Alshawabkeh, 1993).

Jensen et.al. (1994) developed a new concept for electrokinetic remediation of soils polluted with heavy metals. In the new concept two strong ion exchange membranes are used to separate the soil from the electrode chambers. This construction ensures high effectivity of the current with respect to removal of charged species - i.e. heavy metal ions - from the soil (Jensen et. al., 1994).

Li et. al. (1996) proposed a new technique in which a conductive solution is inserted between the cathode and the soil to be treated. By this approach, the pH in the soil can be kept low so that no metal precipitation will occur. The experimental results show that metal removal efficiencies depend on the duration of the treatment and the content of electrolytes in the solution. Metal removal efficiencies of > 96% can be reached for both copper and zinc (Li et. al., 1996).

Li et. al. (1997) presented the results of a new electrokinetic soil remediation technique in which a conductive solution is inserted between the cathode and the soil being treated. In this arrangement, the heavy metals will no longer precipitate in the treated soil. They are transported out of the soil and precipitated in the conductive solution. The experimental results show that metal removal efficiencies higher than 90% can be reached (Li et. al., 1997).

Puppala et. al. (1997) investigated the feasibility of enhanced extraction of metals from high sorption capacity soils by the use of acetic acid to neutralize the cathode electrolysis reaction and also the use of an ion selective (Nafion™) membrane to prevent back-transport of the OH- generated at the cathode. Acetic acid and Nafion enhancement resulted in better removal efficiencies and lead electrodepositions at the cathode compared to unenhanced tests (Puppala et. al., 1997).

Reddy & Chinthamreddy (1999) investigated the migration of hexavalent chromium, Cr(VI), nickel, Ni(II), and cadmium, Cd(II), in clayey soils that contain different reducing agents under an induced electric potential. Bench-scale electrokinetic experiments were conducted using two different clays, kaolin and glacial till, both with and without a reducing agent. The reducing agent used was either humic acid, ferrous iron, or sulfide, in a concentration of 1000 mg/kg. These soils were then spiked with Cr(VI), Ni(II), and Cd(II) in concentrations of 1000, 500 and 250 mg/kg, respectively, and tested under an induced electric potential of 1 VDC/cm for a duration of over 200 h. The reduction of chromium from Cr(VI) to Cr(III) occurred prior to electrokinetic treatment. The extent of this Cr(VI) reduction was found to be dependent on the type and amount of reducing agents present in the soil (Reddy & Chinthamreddy 1999).

Lee et. al. (2000) conducted saturated kaolinite specimens loaded with lead (II). using an electrolyte circulation method to control electrolyte pH. As a result, the operable period was extended and the removal efficiency for lead (II) was also increased (Lee et. al., 2000).

Roulier et. al. (2000) developed an integrated soil remediation technology called Lasagna that combines electrokinetics with treatment zones for use in low permeability soils where the rates of hydraulic and electrokinetic transport are too low to be useful for remediation of contaminants. The technology was developed by two groups, one involving industrial partners and the DOE and another involving US EPA and the University of Cincinnati, who pursued different electrode geometries. The Industry/DOE group has demonstrated the technology using electrodes and treatment zones installed vertically from the soil surface (Roulier et. al., 2000).

Saichek & Reddy (2003) investigated to improve the remediation of low acid buffering soils by controlling the pH at the anode to counteract the electrolysis reaction. Six bench-scale electrokinetic experiments were conducted, where each test employed one of three different flushing solutions, deionized water, a surfactant, or a co-solvent. For each of these solutions, tests were performed with and without a 0.01 M NaOH solution at the anode to control the pH. Controlling the pH was beneficial for increasing contaminant solubilization and migration from the soil region adjacent to the anode, but the high contaminant concentrations that resulted in the middle or cathode soil regions indicates that subsequent changes in the soil and/or solution chemistry caused contaminant deposition and low overall contaminant removal efficiency (Saichek & Reddy 2003).

Yuan & Weng (2004) investigated the remediation efficiency and electrokinetic behavior of ethylbenzene contaminated clay by a surfactant-aided electrokinetic (SAEK) process under a potential gradient of 2 V cm^{-1}. The removal efficiency of ethylbenzene was determined to be 63–98% in SAEK system while only 40% was achieved in an electrokinetic system with tap water as processing fluid (Yuan & Weng 2004).

Zhou et. al. (2004) evaluated the effect of enhancement reagents on the efficiency of electrokinetic remediation of Cu contaminated red soil. The enhancement agents were a mix of organic acids, including lactic acid+ NaOH, HAc–NaAc and HAc–NaAc +EDTA. The soil was prepared to an initial Cu concentration of 438 mgkg_1 by incubating the soil with $CuSO_4$ solution in a flooded condition for 1 month. Sequential extraction showed that Cu was partitioned in the soil as follows: 195 mgkg_1 as water soluble and exchangeable, 71 mgkg_1 as carbonate bound and 105 mgkg_1 as Fe and Mn oxides. The results indicate that neutralizing the catholyte pH maintains a lower soil pH compared to that without electrokinetic treatment. The electric currents varied depending upon the conditioning solutions and increased with an increasing applied voltage potential (Zhou et. al., 2004).

Kim et. al. (2005) carried out ex situ electrokinetic (EK) bioremediation of a laboratory-prepared pentadecane-contaminated kaolinite. Extraneous bacteria and ionic nutrients were continuously supplied to the soil specimen by a new electrolyte circulation method, which controlled electrical pH change of electrolyte solution to keep bacterial activity. The highest removal efficiency (77.6%) was obtained at 0.63 mA/cm^2 for 1000 mg/kg pentadecane after 14 days (Kim et. al., 2005).

Zhou et. al. (2005) treated a Cu–Zn contaminated red soil by electrokinetics. When the catholyte pH was controlled by lactic acid and $CaCl_2$, the soil Cu and Zn removal percentage after 554 h of running reached 63% and 65%, respectively (Zhou et. al., 2005).

Kim et. al. (2005) supplied extraneous bacteria and ionic nutrients to the soil specimen by a new electrolyte circulation method, which controlled electrical pH change of electrolyte solution to keep bacterial activity. The highest removal efficiency (77.6%) was obtained at 0.63 mA/cm^2 for 1000 mg/kg pentadecane after 14 days (Kim et. al., 2005)

Altin & Degirmenci (2005) investigated the effect of the presence of minerals having high alkali and cation exchange capacity in natural soil polluted with lead (II) by means of the efficiency of electrokinetic remediation method. Eventually, lead (II) removal efficiencies for these samples varied between 60% and 70% up to 0.55 normalized distance. Under the same conditions, removal efficiencies in kaolinite sample varied between 50% and 95% up to 0.9 normalized distance (Altin & Degirmenci 2005).

Amrate et. al. (2005) tested electrokinetic extraction to remove lead from an Algerian contaminated soil ([Pb]=4.432±0.275 mg g^{-1}) sited near a battery plant. The effect of EDTA at various concentrations (0.05–0.20 M) on the enhancement of lead transport has been studied by applying a constant voltage corresponding to nominal electric field strength of 1 V cm^{-1} (duration: 240 h). Results of contaminant distribution across the experimental cell have shown efficient transport of lead toward the anode despite the presence of calcite (25%) and the high acid/base buffer capacity of the soil (Amrate et. al., 2005).

Zhou et. al. (2006) conducted a pilot-scale experiment for electrokinetic treatment of 700 kg of copper contaminated red soil using a constant voltage of 80 V. The results indicate that 76% of Cu was successfully removed from the soil after 140 d of treatment when lactic acid was used as enhancing reagent for adjusting the catholyte pH and dissolving soil Cu by complexation, and the pilot-scale electrokinetic experiment consumed electric energy of 224 kW h t^{-1} soil (Zhou et. al., 2006)

Ravera et. al. (2006) evaluated the feasibility of electrokinetic remediation of copper-contaminated soil following eight days of electroreclamation. The results indicate that electrokinetic reclamation of Cu is totally ineffective in soil composed primarily of clay minerals and organic matter (Ravera et. al., 2006).

Wang et. al. (2006) proposed an upward electrokinetic soil remedial (UESR) technology to remove heavy metals from contaminated kaolin. Unlike conventional electrokinetic treatment that uses boreholes or trenches for horizontal migration of heavy metals, the UESR technology, applying vertical nonuniform electric fields, caused upward transportation of heavy metals to the top surface of the treated soil. The main part of the removed heavy metals was dissolved in cathode chamber influent and moved away with cathode chamber effluent when 0.01M nitric acid was used, instead of distilled water (Wang et. al., 2006).

Pazos et. al. (2006) presented ‘‘polarity exchange’’ technique as a simple way to avoid the negative effect of OH^- on metal transportation. This technique lies in the operation during short time intervals at inverted polarity, so that the generation of H^+ ions from the oxidation of water neutralize in the alkaline zone where the metal is precipitated, favoring its dissolution. Successive polarity exchanges will yield with a complete decontamination of the soil with a moderate increment in the electric power consumption(Pazos et. al., 2006).

Wang et. al. (2007) treated kaolin contaminated with heavy metals, Cu and Pb, and organic compounds, *p*-xylene and phenanthrene, with an upward electrokinetic soil remediation (UESR) process. In the experiments with duration of 6 days removal efficiencies of phenanthrene, *p*-xylene, Cu and Pb were 67%, 93%, 62% and 35%, respectively(Wang et. al., 2007).

Kimura et. al. (2007) demonstrated the usefulness of the combined use of the electrokinetic (EK) remediation and a ferrite treatment zone (FTZ) for a treatment of the contaminated soil with heavy metal ions. Copper ions in contaminated soil were transferred into the FTZ by the EK technology and were ferritized in this system. The ratio of the ferritized amount of copper against total copper was 92% in the EK process with FTZ after 48 h (Kimura et. al., 2007).

Nam et. al. (2008) determined the levels and distribution of polynuclear aromatic hydrocarbons (PAHs) in soil samples from background locations in the UK and Norway, to investigate their spatial distribution and the controlling environmental factors. PAHs with 4 and more rings comprised ~90% of total PAHs in the UK soil, but only 50% in the Norwegian soil (Nam et. al., 2008).

Ricart et. al. (2008) investigated removal of organic pollutants and heavy metals in soils by electrokinetic remediation. They used soils which artificially polluted in the laboratory with chromium and an azo dye (Reactive Black 5). They studied the electromigration of Cr in a spiked kaolinite sample in alkaline conditions. The removal of Cr was improved compared to the experiment where Cr was the only pollutant, and RB5 reached a removal as high as 95%. RB5 was removed by electromigration towards the anode, where the dye was degraded upon the surface of the electrode by electrochemical oxidation (Ricart et. al., 2008).

Tran et. al. (2009) used expanded titanium (Ti) covered with ruthenium oxide (RuO_2) electrode to anodically oxidize polycyclic aromatic hydrocarbons (PAH) in creosote solution. Under optimal conditions, they removed 84% of petroleum hydrocarbon (C10–C50), (Tran et. al., 2009).

Genc et. al. (2009) investigated manganese removed from naturally polluted river sediment by applying an electrokinetic remediation technique. The removal efficiencies of metals were low and the highest removal efficiencies of manganese, copper and lead, were evaluated as 18%, 20% and 12%, respectively. Almost no removal of zinc was observed in all electrokinetic remediation experiments(Genc et. al., 2009).

Oonnittan et. al. (2009) investigated the feasibility of enhanced electrokinetic Fenton process for the remediation of hexachlorobenzene (HCB) in low permeable soil. Results show that the position of electrodes in the system and the way in which Fenton's reagent was added to the system has a significant influence on the treatment efficiency (Oonnittan et. al., 2009).

Giannis et.al. (2009) conducted an integrated experimental program to remove Cd, Pb and Cu from contaminated soil. The chelate agents nitrilotriacetic acid (NTA), diethylenetriamine pentaacetic acid (DTPA) and ethyleneglycol tetraacetic acid (EGTA) were used as washing solutions under different pH conditions and concentrations. The removal efficiency for Cd was 65–95%, for Cu 15–60%, but for Pb was less than 20% (Giannis et.al., 2009).

Gomez et. al. (2009) developed an innovative process that combines soil electrokinetic remediation and liquid electrochemical oxidation for the degradation of organic compounds present in a polluted soil was and evaluated by using benzo[a]pyrene spiked kaolin. When no pH control was used, around 17% of initial contaminant was detected in the cathode chamber; however, when pH control was applied, the recovery of benzo[a]pyrene could be higher than 76%, when the pH control in the anode chamber was set at 7.0 (Gomez et. al., 2009).

Cang et. al. (2009) investigated the change of enzyme activities of a heavy metal contaminated soil before and after electrokinetic (EK) treatments at lab-scale and the mechanisms of EK treatment to affect soil enzyme activities. The results showed that the average removal efficiencies of soil copper were about 65% and 83% without and with pH control of catholyte, respectively, and all the removal efficiencies of cadmium were above 90% (Cang et. al., 2009).

Yuan et.al. (2009) investigated an enhanced electrokinetic (EK) remediation process coupled with permeable reaction barrier (PRB) of carbon nanotube coated with cobalt (CNT-Co) for As(V) removal from soil under potential gradient of 2.0 V/cm for 5 days treatment. Results showed that removal efficiency of As(V) was greater than 70% in EK/CNT-Co system with EDTA as processing fluid (Yuan et.al., 2009).

Rocha et. al. (2009) presented an investigation of electrokinetic bacterial mobilisation in a residual soil from gneiss. The experimental program aimed at assessing the efficacy of electrophoresis against the electro-osmotic flow to transport endospores of *Bacillus subtilis* LBBMA 155 and nitrogen-starved cells of *Pseudomonas* sp. LBBMA 81. Electrokinesis was performed on a low hydraulic reconstituted clayey soil column submitted to a 5mA electrical current for 24 h. The higher transport efficiency of *B. subtilis* endospores was attributed to their higher negative charge on cell surface (Rocha et. al., 2009).

Hyun et. al. (2010) measured the effect of the sorption of phenanthrene and 2,20,5,50-polychlorinated biphenyl (PCB52) by five differently weathered soils in water and low methanol volume fraction ($f_c \leq 0.5$) as a function of the apparent solution pH. For phenanthrene sorption at the natural pH, the empirical constant (a) ranged between 0.95 and 1.14, and was in the order of oxisols (A2 and DRC) < alfisols (Toronto) < young soils (K5 and Webster). The results revealed an unexplored relationship between the cosolvent effect on the sorption and the properties of the soil organic matter (a primary sorption domain) as a function of the degree of soil weathering (Hyun et. al., 2010).

Zhang et al. (2010) designed and tested contrasting experiments using four operation modes (none, solely horizontal, solely vertical and 2D crossed electric field) at the bench-scale with the practical sample of chromium contaminated soil (1.3×105 mg/kg) from a chemical plant to investigate Cr(VI) migration downward in each test and the effectiveness and feasible of the new design. During the tests, Cr(VI) could migrate deep into the soil in the solely horizontal mode. Cr(VI) migration downward could be prevented by vertical barrier in the solely vertical mode(Zhang et al., 2010).

Li et. al. (2010) examined hydroxypropyl-_-cyclodextrin (HPCD) enhanced electrokinetic (EK) remediation of aged sediment contaminated with hexachlorobenzene (HCB) and heavy metals (Zn and Ni) in bench-scale. Deionized water, 5 and 20% HPCD were used as anodic flushing solutions, respectively, with constant voltage gradient of 1.0Vcm−1. The experimental results showed that HCB migration and removal from sediments was significantly affected by HPCD concentrations and cumulative electroosmotic flow (EOF). This study indicated that EK process combined with HPCD flushing and pH buffering was a good alternative for HCB removal from sediments, and other enhancement was needed for heavy metals removal (Li et. al.,2010).

Ouhadi et. al. (2010) investigated on the effect of “calcite or carbonate” ($CaCO_3$) on removal efficiency in electrokinetic soil remediation. Bench scale experiments were conducted on two soils: kaolinite and natural-soil of a landfill in Hamedan, Iran. The results showed that an increase in the quantity of carbonate caused a noticeable increase on the contaminant retention of soil and on the resistance of soil to the contaminant removal by electrokinetic method (Ouhadi et. al., 2010).

Ma et. al. (2010) designed an in situ electrokinetic remediation technique by combining the uniform electrokinetic technology with a new-type of bamboo charcoal as adsorbent. A bench-scale experiment was conducted to investigate the application of this technique for simultaneous removal of 2,4-dichlorophenol (2,4-DCP) and Cd from a sandy loam at different periodic polarity-reversals. After 10.5 d of operation, about 75.97% of Cd and 54.92% of 2,4-DCP were removed from soil at intervals of 24 h, whilst only 40.13% of Cd and 24.98% of 2,4-DCP were removed at intervals of 12 h (Ma et. al., 2010).

Pazos et. al. (2010) studied the possibility for electrodialytic metal removal for sewage sludge ash from FBSC. A detailed characterization of the sewage sludge ash was done initially, determining that, with the exception of Cd, the other heavy metals (Cr, Cu, Pb, Ni and Zn) were under the limiting levels of Danish legislation for the use of sewage sludge as fertilizer. After 14 days of electrodialytic treatment, the Cd concentration was reduced to values below the limiting concentration (Pazos et. al., 2010).

Kim et. al. (2010) investigated on the effects of electrokinetic remediation on indigenous microbial activity and community within diesel contaminated soil. The main removal mechanism of diesel was electroosmosis and most of the bacteria were transported by electroosmosis. After 25 days of electrokinetic remediation (0.63 mA cm−2), soil pH developed from pH 3.5 near the anode to pH 10.8 near the cathode.

The results described here suggest that the application of electrokinetics can be a promising soil remediation technology if soil parameters, electric current, and electrolyte are suitably controlled based on the understanding of interaction between electrokinetics, contaminants, and indigenous microbial community (Kim et. al., 2010).

Alcantara et. al. (2010) proposed electroremediation for cleaning soil contaminated by organic compounds. Model samples of kaolin clay polluted with a mixture of PAHs (fluoranthene, pyrene, and benzanthracene) were treated. Electroremediation of kaolin contaminated with a mixture of these three PAHs was carried out using a solution of 1% Tween 80 and 0.1M Na_2SO4 as the processing fluid. Under these conditions, low removal was obtained. The results of this work reveal the high potential for the application of the electroremediation process on soil polluted with different PAHs (Alcantara et. al., 2010).

CHAPTER FOUR
MATERIALS AND METHODS

The sampling procedures for the soils, materials used for the study, the methods of the analysis, and the properties of the experimental setup are described in this section.

4.1 Soil Sampling

Agricultural soil used for the study was obtained from the Menemen Research Centre of Turkish Ministry of Agriculture from the sampling depth of 10 cm. The samples are stored in zip-lock plastic bags at 5°C until the experiments. The properties of soil sample are illustrated in Table 4.1.

Table 4.1 The properties of soil sample

Analysis of soil sample	**Value**
Grain size distribution (dry soil)	
2 mm>φ>300 µm ,%	68.85
300 µm> φ >45 µm ,%	27.55
45 µm> φ ,%	3.6
pH	6.43
Water Content , %	11.77
Organic Matter Content ,% **(dry soil)**	5.08
TOC ,ppm **(dry soil)**	1200
TN$_{\text{dissoluble}}$ **,ppm** **(dry soil)**	136
TPH (dry soil) ,ppm	1040

4.2 Materials Used

Engine oil was used to spike the soil samples in this study. The oil is the product of PETROFER Industrial Oils and Chemicals Company which is located in Çiğli, Izmir. The type of the oil is PETROFER Petrolube Lubrimax 20W/50 Four Seasons Engine Oil, API: SF-US MIL: 46152-B.

4.3 Experimental Set Up

As can be seen in Figure 4.1; the experimental setup used for electrokinetic remediation of engine oil contaminated soil mainly consists of; soil bed, electrolyte solution chambers, gas measurement systems attached to the electrolyte solution chambers, and power supply unit.

A 24 cm long Plexiglas cylinder with 75 mm internal diameter was used to obtain fixed soil bed for the experiment. The soil bed, which contaminated soil was placed into, has two graphite electrodes with 75 mm diameters and 3 mm thickness at the both ends connected to the electrolyte chambers. The chambers were made of industrial Teflon and each of has 66 ml of liquid volume. Gas measurement systems attached to the electrolyte chambers were made of two glass cylinders equipped with valves to control air and liquid entrance and exit.

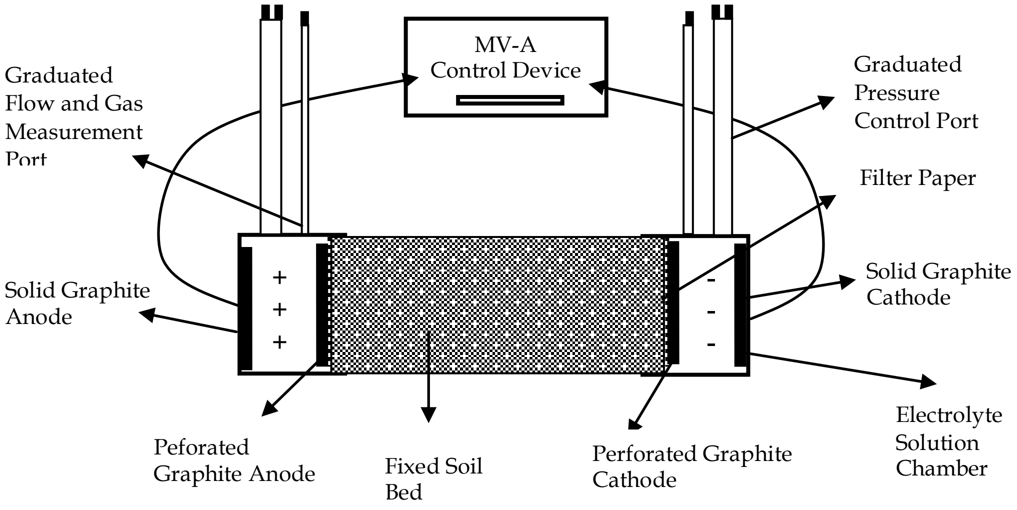


Figure 4.1 Major parts of the designed reactors

4.3.1 Fixed Bed Soil Preparation

Prior to the experiments, Menemen Soil was dried and sieved under 2 mm to remove larger particles and then autoclaved to stop microbial activity. The required amount of engine oil was dissolved in Petroleum Ether (PE) and added to 1.25 kg of Menemen Soil to obtain 10000 ppm dry weight (dw) of TPHs in the soil. After PE was evaporated under the fume hood, the electrolytic solution used in the electrolytes was applied to the soil sample to obtain humidity that equals to the soil field capacity (31%). Then, the soil electrolyte solution mixture was placed into the soil bed and compressed by using shaking table to avoid empty spaces in the samples that may inhibit the electrical conductivity along the sample.

The systems were operated constantly for 192 hours under 20 V or 40 V DC electrical potentials. The electrical intensity during the experiments were arranged to 0.01 A and remained constant. The summary of the experimental conditions are given in Table 4.2.

4.4 General Characterization Studies

4.4.1 pH

The pH values of the soil sample were determined by using wet sample according to the EPA Method 9045 C (USEPA, 1995). 20 grams of sample is mixed with 20 ml of distilled water for 5 minutes and centrifuged at 4000 rpm for 10 minutes. The pH value of the supernatant is measured. The values were monitored by using a WTW pH 720 pH meter.

4.4.2 Water Content

Water content was determined via gravimetric analysis by drying the wet soil sample overnight at 105 °C. The moisture content of the sample is determined by using the difference between the weight of wet and dry soils.

Table 4.2 The summary of the current work

Solvent	**Voltage(V)**	**Concentration (M)**	**Time(hour)**
NaOH	20	1	192
NaOH	20	0.5	
NaOH	40	0.5	
Acetic Acid	20	1	
Acetic Acid	20	0.5	
Acetic Acid	40	1	
Acetic Acid	40	0.5	
Ethanol	20	1	
Ethanol	20	0.5	
Ethanol	40	1	
Ethanol	40	0.5	
Distilled water	20	na	
Distilled water	40	na	

na: not applicable

4.4.3 Organic Matter Content

The determination of organic matter content of the soil sample was conducted according to the Standard Methods (Franson et al., 1992). This method depends on the ignition of dry soil sample in an oven at 500±50 °C.

4.4.4 Grain Size Distribution

The grain size distributions of the soil sample were determined by sieving 1000 g of soil from the sieves with different screen sizes. Particles larger than 2000µm were eliminated since they are counted as rock and gravels. The detected size fractions are given with Table 4.3.

Table 4.3 Fractions used to determine grain size distribution

Fraction	Soil Type
$2000\mu m > F_A > 300\ \mu m$	Sand
$300\ \mu m > F_B > 90\ \mu m$	Sand
$90\ \mu m > F_C > 45\ \mu m$	Sand+Silt
$45\ \mu m > F_D$	Silt+clay

4.4.5 Gas and Electroosmotic Flow Measurement

Fluid levels variations in the flow volume and gas volume measurement devices are illustrated in Figure 4.2. which is used to derive Eq. 3 and Eq. 4.

$$n_P = \frac{n_0}{L-x}\left[h + \frac{(H+h)(L-x+h)\rho_{sol}\, g}{P_0}\right] \qquad \text{Eq. 3}$$

where n_P: amount of gas produced between $t = t_0$ and $t = t_0 + T$ (mol); n_0: amount of air in the small cylinder at t_0 (mol); L: length of the cylinders (m); x: fluid level in both cylinders at t_0 (m); h: drop in fluid leveling the small cylinder from t_0 to $t_0 + T$ (m); H: rise in fluid level in the large cylinder from t_0 to $t_0 + T$ (m); P_0: atmospheric pressure (Pa); d: diameter of the small cylinder (m); D: diameter of the large cylinder (m); ρ_{sol}: density of the purging solution (kg/m^3); g: acceleration of gravity (= 9.8 m/s^2); t_0: starting time for collection of electroosmotic flow volume and gas volume (s); and T: total period of collection (s).

$$V_{eo} = \frac{\pi}{4}(HD^2 - hd^2) \qquad \text{Eq. 4}$$

where V_{eo}: volume of electroosmotic flow collected from t_0 to $t_0 + T$ (m^3).

4.4.6 Hydrometer Analysis

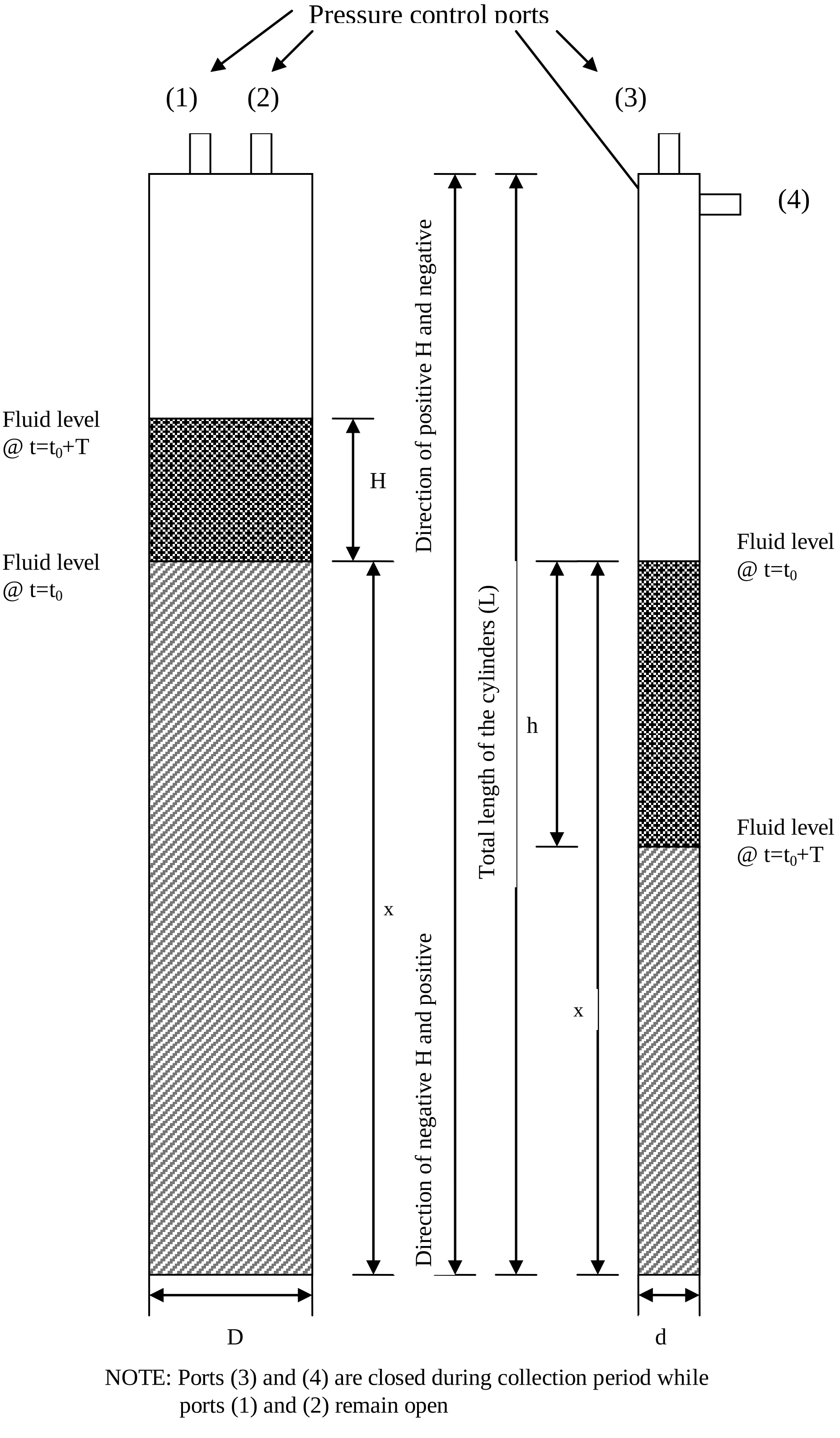
Hydrometer analysis is the procedure generally adopted for determination of the particle size distribution in a soil for the fraction that is finer than No.200 sieve size (0.0075mm). The lower limit of particle-size determined by this procedure is about 0.001 mm(ASTM D 422).

4.4.7 Total Petroleum Hydrocarbons Analysis

EPA Method 3550 is modified for Total Petroleum Hydrocarbons determinations. EPA Method 3550 is a procedure for extracting nonvolatile and semi volatile organic compounds from solids such as soils, sludges, and wastes and it is a gravimetric method. The ultrasonic process ensures intimate contact of the sample matrix with the extraction solvent.

Here, the described procedure is modified to allow fast measurements. Five grams of contaminated soil was mixed with Na_2SO_4 and extracted with solvents by using ultrasonic extractor. 20 ml solvent was used for each of the experiments and the analysis were quadruplicated.

After the extraction, the solvent containing dissolved contaminant was allowed to be evaporated in a water bath (50ºC) under the fume hood and the recovery rate was determined by gravimetric method. Different solvents, ultrasonic powers, temperatures, extraction times, and amount of sample were applied to find the highest recovery rate for the spiked contaminant. In Table 4.4, the recovery rates for studied parameters are given.



NOTE: Ports (3) and (4) are closed during collection period while
ports (1) and (2) remain open

Figure 4.2. Fluid Level in the Electroosmotic Flow and Gas Volume Measurement Devices during the Collection Period

Table 4.4 TPH recovery rates by using ultrasonic extraction for spiked clean soil medium

Set #	**Solvent Used**	**Initial Contaminant Conc., ppm**	**Ultrasonic Power**		**Extraction**		**Amount of Sample, g**	**Recovery Rate, %**
			%	**Watt, W**	**Temp. °C**	**Time min**		
1	Hexane	50000	70	98	**20**	10	5	58
	Methanol							26
	Acetone							38
	Petroleum Ether							**94**
2	Petroleum Ether	50000	70	98	**20**	5	5	62
						10		**94**
						15		87
						20		80
3	Petroleum Ether	50000	50	70	**20**	10	5	79
			60	**84**				**97**
			80	112				60
4	Petroleum Ether	50000	60	84	**20**	10	**5**	**97**
							10	79

As can be seen in Table 4.4, the optimum recovery rate was obtained for the solvent “Petroleum Ether” at 20°C with 60% ultrasonic power (84 W) and 10 minutes of extraction time for 5 g of soil sample. The determined recovery rate for Petroleum Ether was 97 %.

4.4.8 Polycyclic Aromatic Hydrocarbons Analysis

For GC-MS analysis of PAHs, soil extractions are completed according to the EPA Method 3550A- Ultrasonic Extraction. 1 g of soil is placed into a 40 mL vial and 25 mL 1:1 acetone:hexane mixture was added. Prior to extraction, all samples were spiked with PAH internal surrogate standards to monitor analytical recovery efficiencies. 0.5 mL PAH internal standard (Accustandard- 8000 mg/L each: Naphthalene-d8, Acenaphthene-d10, Phenanthrene-d10, Chrysene-d12, and Perylene-d12) was added into the vial and retained overnight. The vial, then, has extracted in ultrasonic extractor for 30 min with 380 Watt, filtered from glass wool and transferred to another vial.

The samples were cleaned up on an alumina-silicic acid column containing 3 g of silicic acid (3% water) and 2 g of alumina (6% water) (EPA Method 3610B). The column was pre-washed with 20 mL of DCM followed by 20 mL of petroleum ether.

Then, 20 mL DCM was added to the column and the strain containing PAHs was collected in another 40 mL vial.

This strain was transferred into the Kuderna-Danish Apparatus (water temperature 65°C, DCM boiling point: 40°C) and the volume of the extract reduced to 10 mL. 10 ml hexane was added to the system once more and the volume was reduced to 5 mL final volume by arranging the water bath to 65°C until the first 10 mL collected (for DCM collection) and then by arranging it to 95°C (Hexane boiling point: 69°C) for hexane collection. 1 mL of final volume was placed in a 1.5 mL glass vial and used for GC-MS analysis.

All extracts were analyzed for 15 PAHs including acenaphthene (ACT), fluorene (FLN), phenanthrene (PHE), anthracene (ANT), carbazole (CRB), fluoranthene (FL), pyrene (PY), benz[a]anthracene (BaA), chrysene (CHR), benz[b]fluoranthene (BbF), benz[k]fluoranthene (BkF), benz[a]pyrene (BaP), indeno[1,2,3-cd]pyrene (IcdP), dibenz[a,h]anthracene (DahA), and benzo[g,h,i]perylene (BghiP) with a gas chromatograph (GC) (Agilent 7890A) equipped with a mass selective detector (Agilent 5975C inert MSD). A capillary column (HP5-ms, 30 m, 0.25 mm, 0.25 µm) was used. The initial oven temperature was held at 50°C for 1 min, was raised to 200°C at 25°C min^{-1} and from 200 to 300°C at 8°C min^{-1}, and was held for 5.5 min. The injector, ion source, and quadrupole temperatures were 295, 300, and 180°C, respectively. High purity helium was used as the carrier gas at constant flow mode (1.5 mL min^{-1}, 45 cm s^{-1} linear velocity). The MSD was run in selected ion-monitoring mode. Compounds were identified on the basis of their retention times, target and qualifier ions and were quantified using the internal standard calibration procedure.

CHAPTER FIVE
RESULTS AND DISCUSSION

The results obtained from the electrokinetic treatment tests conducted by using engine oil contaminated agricultural soil are presented in this section.

Electrokinetic treatment of an agricultural soil which is contaminated by engine oil in laboratory was investigated according to the parameters such as applied electrical potential, the type of the electrolyte solution used and solution concentration. The operated electrokinetic treatment systems were observed for the pH changes and gas generation in electrolytic chambers, and the electroosmotic flow generated during the treatment. At the end of the treatment period, the soil in the reactor column was detected for its pH value, TPHs concentration and PAHs concentration. The data are presented below.

5.1 pH Changes in Electrolytic Chambers

The pH values of electrolytic solutions were started to be measured in every 24 hours after the operation starts until the treatment period (192 h) was over. The results are presented for anode chambers and cathode chambers separately for each of the electrolytic solutions [NaOH, pure water, CH_3COOH (Acetic Acid), and Ethyl Alcohol (EtOH)] by indicating the applied direct current and the concentration of the solution.

5.1.1 pH Changes in Anode Chambers

In Figure 5.1, the pH changes in the anode chambers are given for the DC applied and the NaOH concentration used in the systems.

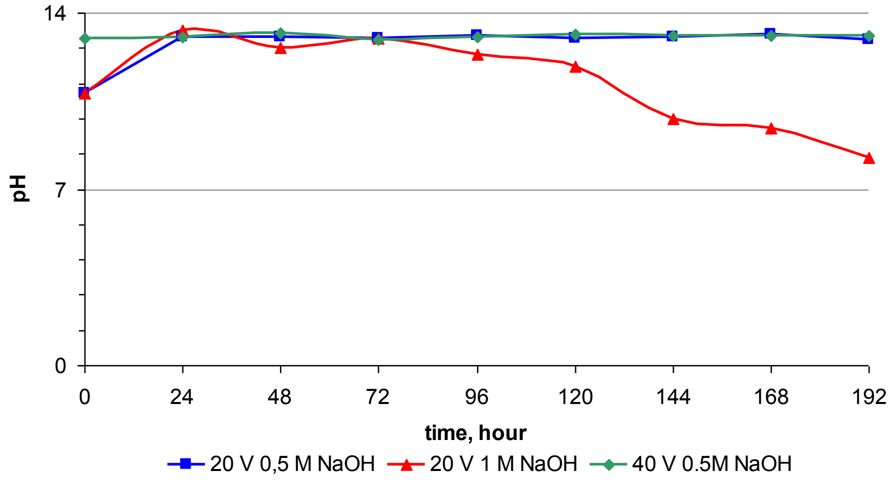


Figure 5.1 pH changes in anode chamber when NaOH used as electrolytic solution

In all of the three experiments conducted with NaOH, the pH in anode chambers were in alkaline levels when the systems were initiated. The pH levels were steady and around 13 in the cases with 0.5 M NaOH concentration, while it started to drop down after the first 72 hours and reached to the level of 8.4 at the end of the treatment period with 1 M of NaOH .

In the experiments conducted with pure water as electrolyte solution, the effect of applied current on anode electrolyte solution pH level can be seen in Figure 5.2.

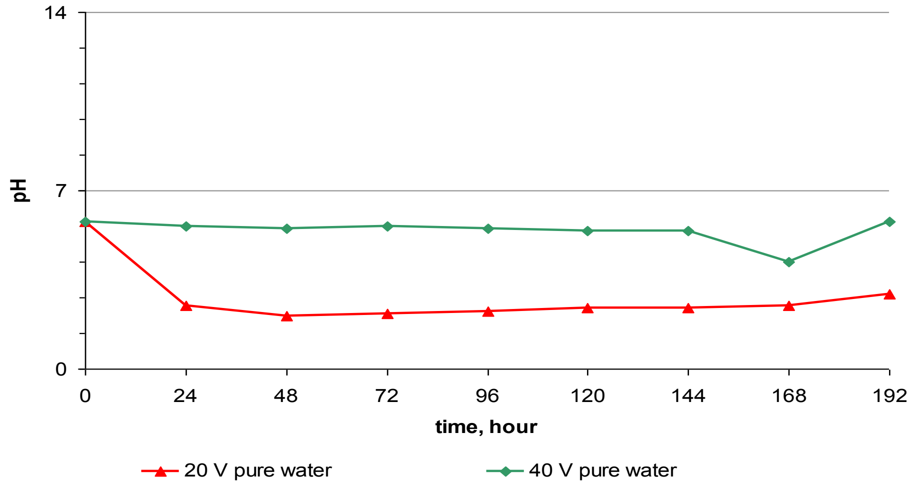


Figure 5.2 pH changes in anode chamber when pure water used as electrolytic solution

The initial pH levels in the anode chambers were below neutral level (5.8). As 20 V DC was applied to the system, pH level in anode chamber decreases to 2.5 in the first 24 h and kept this level until the end of the experiment, while 40 V DC application resulted with a slight and steady decrease in pH during the treatment period.

Two different initial concentrations could be applied to the system under 20 V and 40 V DC when Acidic acid was used as the electrolyte solution. Figure 5.3 displays the pH levels in anode chambers obtained from these systems.

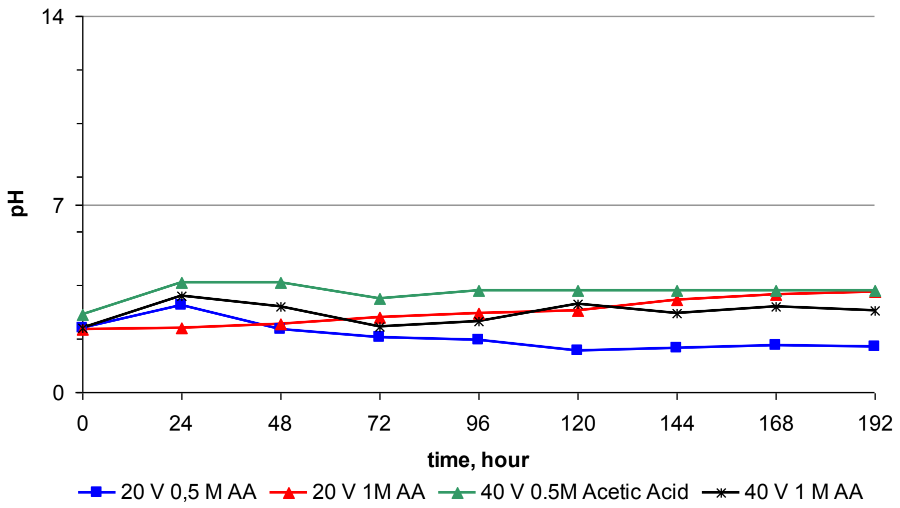


Figure 5.3.pH changes in anode chamber when Acetic Acid (AA) used as electrolytic solution

The initial pH level in the anode chamber solutions were below 3.0 and the pH levels fluctuates between 2.3 and 3.8 during the test period after a slight increase in the first 24 hours, except the experiment conducted with 0.5 M Acedic acid under 20 V DC which displayed a steady decrease after the 24^{th} hour to reach a pH level of 1.67 in anode chamber.

The pH levels in anode chambers were also monitored in the experiments conducted with ethyl alcohol (EtOH). The data is given in Figure 5.4 for the DC applied and the EtOH concentration used.

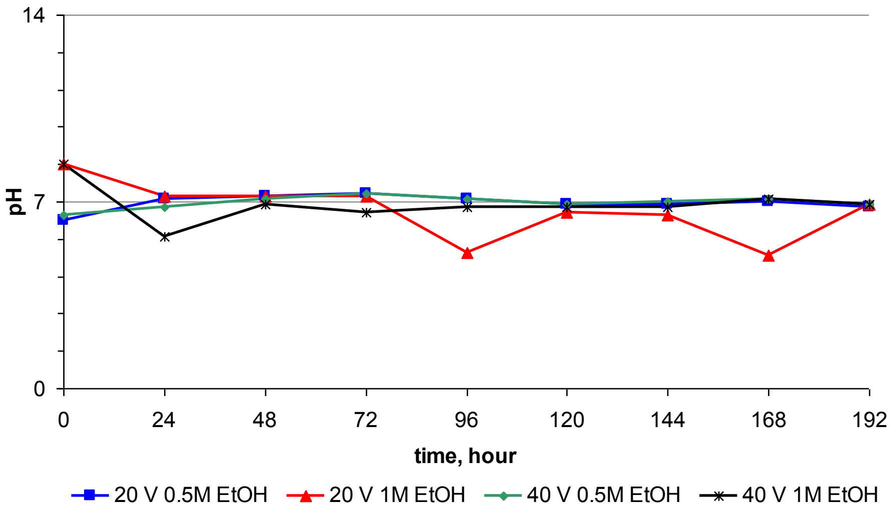


Figure 5.4.pH changes in anode chamber when Ethyl Alcohol (EtOH) used as electrolytic solution

Even though the initial pH levels in anode chambers were between 6.5 and 8.5 in the tests conducted with ethyl alcohol, pH values are aligned to neutral level (7.0) in first 48 hours and only small fluctuations has seen during the rest of the experimental period for all of the different EtOH concentrations and DC applications.

5.1.2 pH Changes in Cathode Chambers

Changes in pH level in the cathode chambers are presented in Figure 5.5 for the tests conducted with NaOH solutions. As can be seen from the figure, the initial pH levels in the cathode chambers were strongly alkaline (>10) at the beginning of the experiments and they were aligned at 13.3 in first 24 hours and remained at this level until the end of the experiments in all of the cases.

In Figure 5.6, cathode chamber pH levels are given for the tests conducted with pure water as electrolyte solution. Initial pH in cathode chambers were 5.8 for the tests conducted with 20 V and 40 V DC. In the case with 20 V DC application, pH level in cathode solution increased to 12.8 in first 72 hours, while it reached to 11.6 in first 48 hours with 40 V DC. pH values kept these levels until the end of the experimental period in both cases.

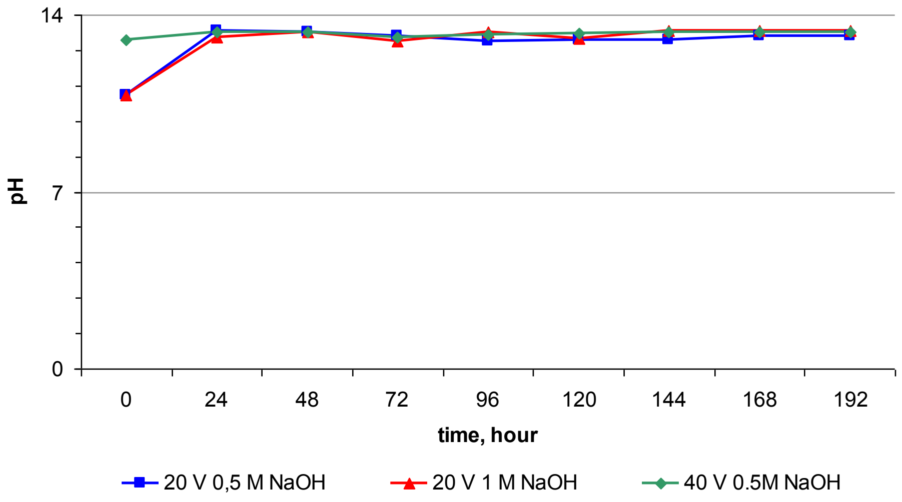


Figure 5.5 pH changes in cathode chamber when NaOH used as electrolytic solution

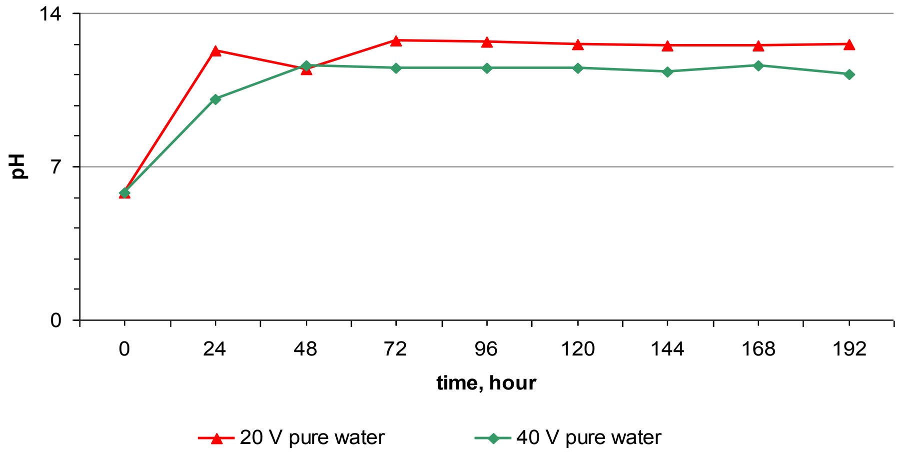


Figure 5.6 pH changes in cathode chamber when pure water used as electrolytic solution

pH changes in cathode chamber, when Acetic acid used as electrolyte solution, can be seen in Figure 5.7.

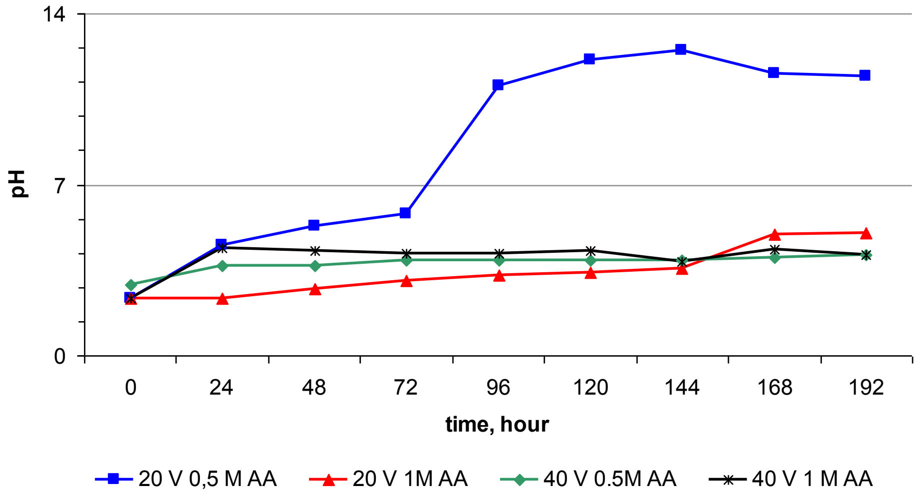


Figure 5.7 pH changes in cathode chamber when Acetic Acid (AA) used as electrolytic solution

As can be seen from the figure, the initial pH values in the chambers were between 2.4 and 2.9. In the tests conducted under 40 V DC (0.5 M AA and 1 M AA) and in the test conducted with 1 M AA under 20 V DC, pH levels slightly increased during the tests and reached to a range between 4.4 and 5.2 at the end. In the test conducted with 20 V DC with 0.5 M AA, pH level in cathode chamber showed a sharp increase up to 11.0 in first 96 hours and then reached to 11.4 with a slight raise.

In the tests conducted with EtOH, similar with the findings in anode chamber, pH levels were between 6.3 and 8.4 at the beginning of the experiment, all they aligned to 7.0 in first 48 hours and then kept this level until the end of the experiment (Figure 5.8).

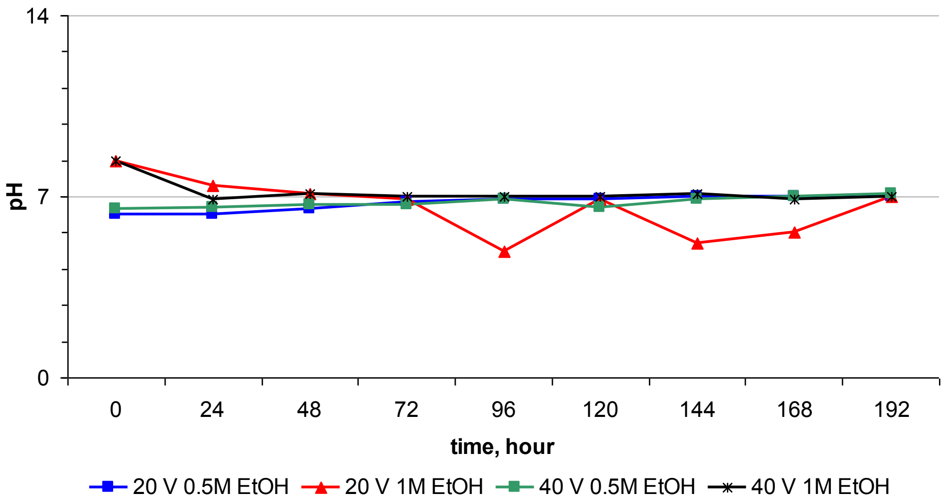


Figure 5.8 pH changes in cathode chamber when Ethanol (EtOH) used as electrolytic solution

5.2 Gas Measurements

The gases produced in anode (O_2) and cathode (H_2) chambers were measured daily during the experimental studies. The measurements are presented on a cumulative basis for anode and cathode chambers according to the electrolytic solution used for different DC applications and solution concentrations.

5.2.1 Oxygen Gas Productions in Anode Chambers

Cumulative oxygen productions in anode were lower in the experiments under 20 V DC with 0.5 and 1M NaOH solutions (~ 0.005 mol) than the experiment under 40 V DC with 0.5 M NaOH. (0.012 mol) (Figure 5.9). The oxygen productions with 20V DC were not distinctive before the first 96 hour of the experiment, but a significant O_2 production has started at the end of the first 24 hours in the experiment with 40 V DC.

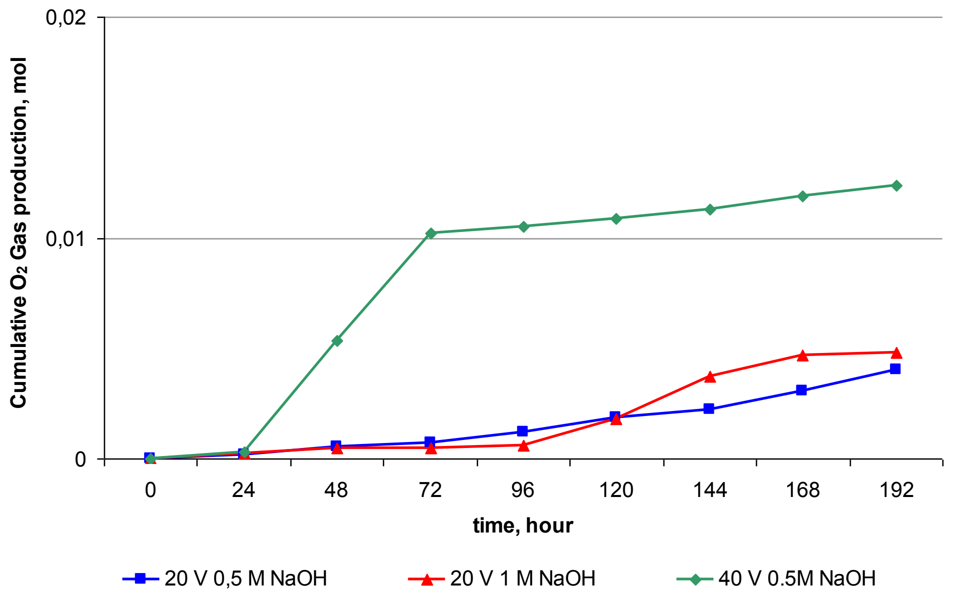


Figure 5.9 Cumulative oxygen gas production in anode chamber when NaOH used as electrolytic solution

When pure water has used as electrolytic solution, any difference between the cumulative oxygen gas productions were not be detected in the cases with 20 V and 40 V DC applications (~ 0.004 mol), (Figure 5.10).

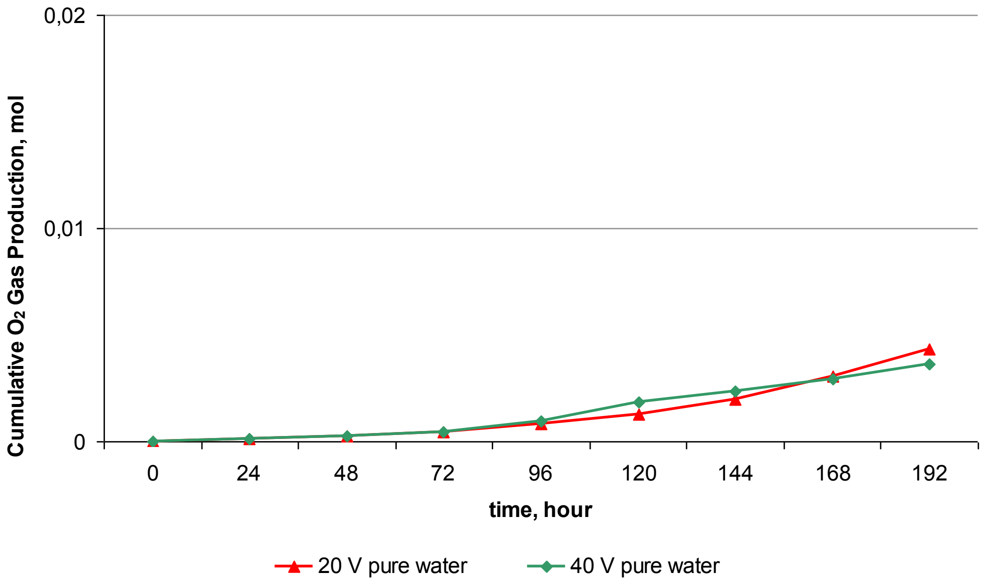


Figure 5.10 Cumulative oxygen gas production in anode chamber when pure water used as electrolytic solution

When Acetic acid was used as electrolytic solution, the experiment under 40 V DC with 1 M of AA showed a distinctive oxygen production (0.07 mol) which has started in the first 24 hours of the experimental period (Figure 5.11). The experiments with 20 V DC and the experiment under 40 V DC with 0.5 M AA resulted with cumulative oxygen productions between 0.002-0.006 mol.

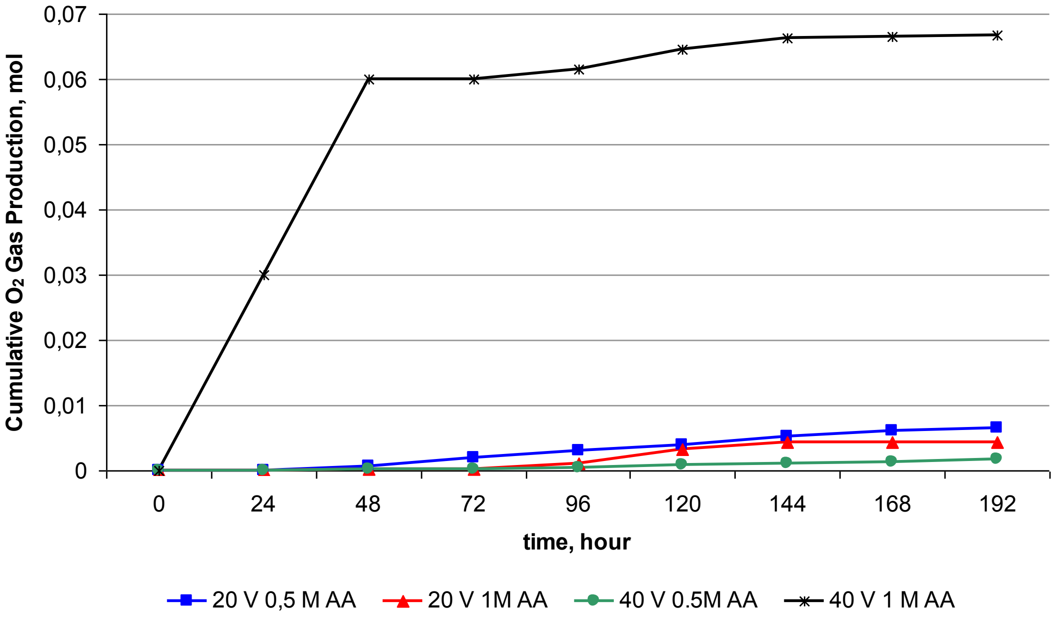


Figure 5.11 Cumulative oxygen gas production in anode chamber when Acetic acid (AA) used as electrolytic solution

The oxygen productions in anode chamber in the experiments conducted with ethyl alcohol (EtOH) were low (0.001-0.009 mol). The higgest cumulative oxygen production was observed in the experiment under 20 V with 1 M EtOH (Figure 5.12).

5.2.2 Hydrogen Gas Productions in Cathode Chambers

When the cumulative hydrogen productions in the cases with NaOH as electrolyte solution in cathode chamber were considered, it was seen that the highest production has occurred in the experiment under 20 V DC with 1 M NaOH as 0,12 mol (Figure 5.13) lower in the experiments under 20 V DC with 0.5 and 1M NaOH solutions (~

0,005 mol) than the experiment under 40 V DC with 0.5 M NaOH. (0.012 mol) (Figure 5.9).

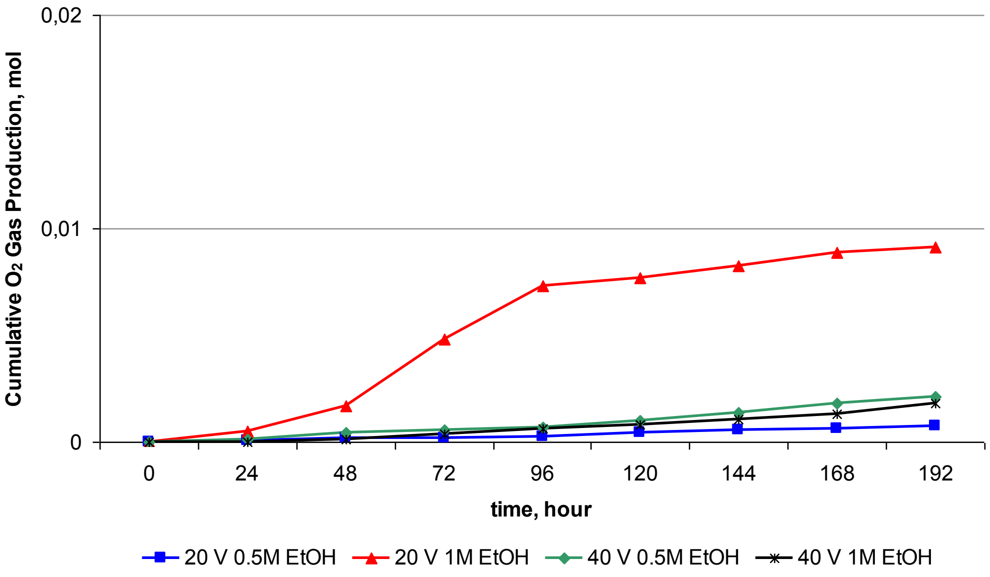


Figure 5.12 Cumulative oxygen gas production in anode chamber when ethanol (EtOH) used as electrolytic solution

The experiments conducted with 0.5 M NaOH under 20 V and 40 V DC resulted with 0.01 and 0.013 mol cumulative hydrogen gas generation, respectively.

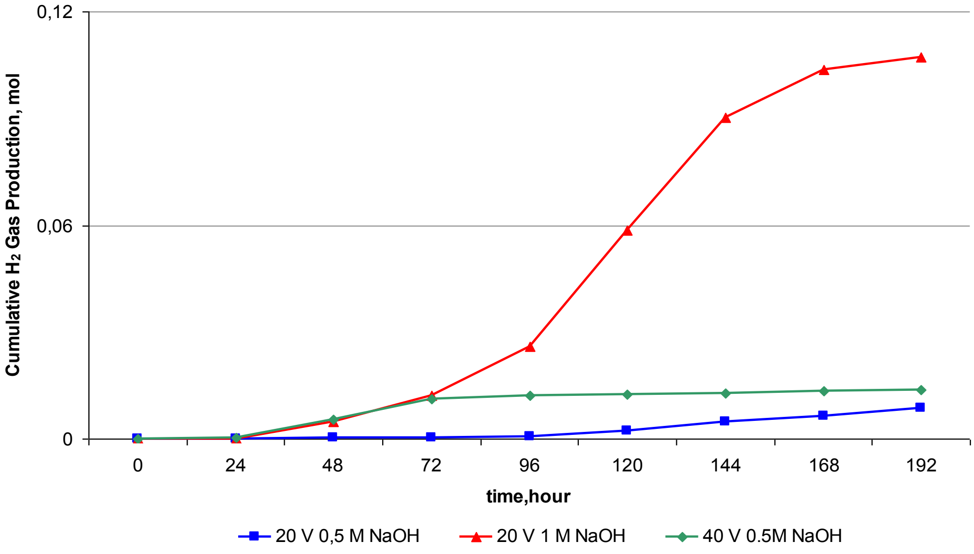


Figure 5.13 Cumulative hydrogen gas production in cathode chamber when NaOH used as electrolytic solution

In the experiments conducted with pure water as electrolyte solution, the cumulative hydrogen productions from cathode chambers were not distinctive before the first 48 hours (Figure 5.14) and the final values are 0.004 and 0.012 mol hydrogen for the experiments with 20 V DC and 40 V DC, respectively.

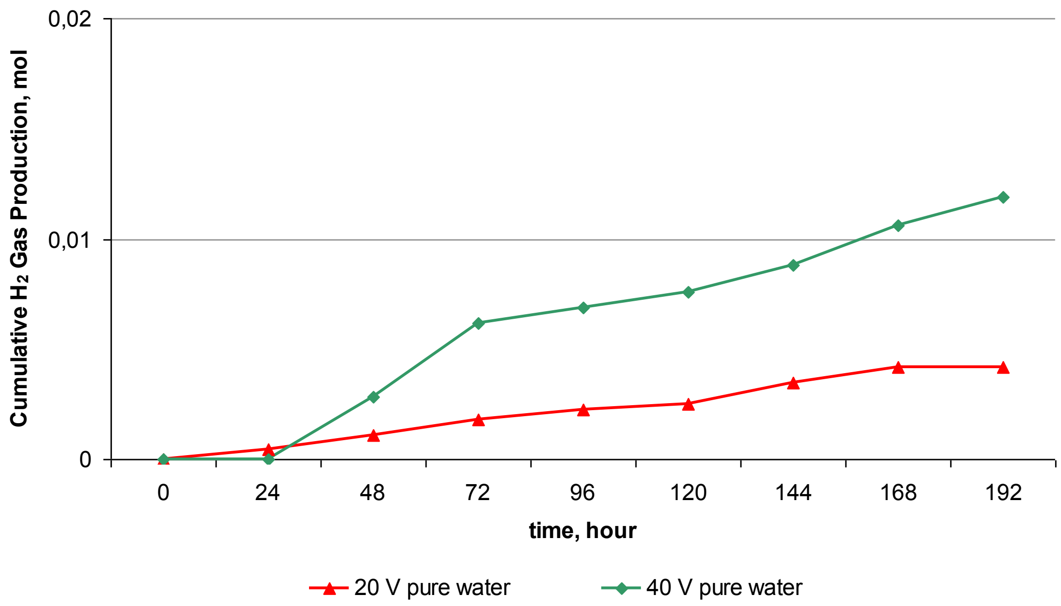


Figure 5.14 Cumulative hydrogen gas production in cathode chamber when pure water used as electrolytic solution

The cumulative hydrogen productions in the experiments with acetic acid as electrolyte solution showed a small difference for the cases under 20 V and 40 V DC (Figure 5.15). Cumulative hydrogen production in the experiments with 20 V was around 0.001 mol, while it was observed as 0.004 mol for the experiment under 40 V DC.

In the experiments conducted with ethanol solutions, the hydrogen productions under 20 and 40 V DC were very low and close to each other (~0.003) (Figure 5.16).

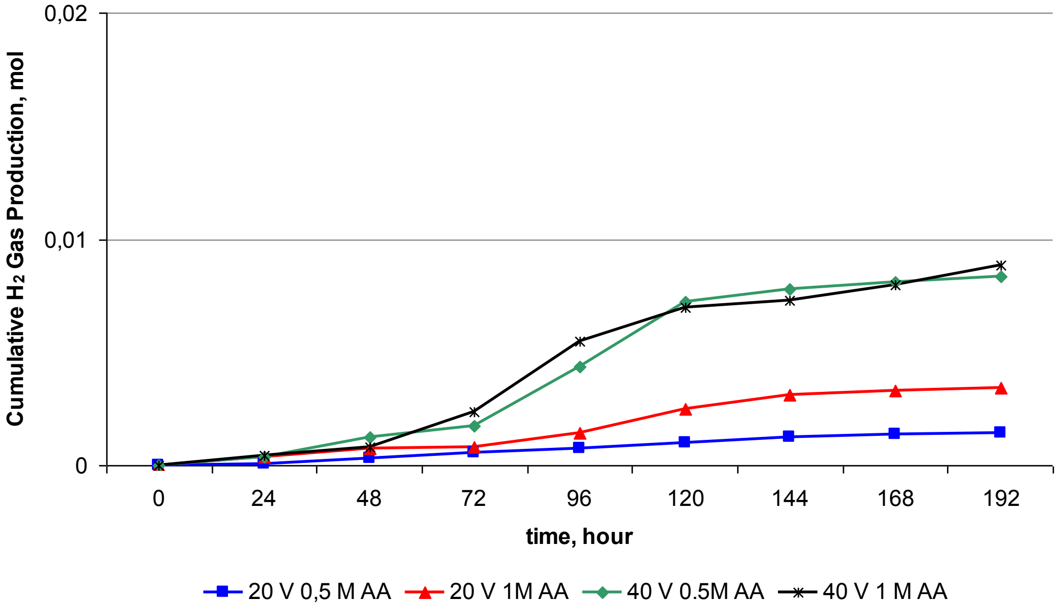


Figure 5.15 Cumulative hydrogen gas production in cathode chamber when Acetic acid (AA) used as electrolytic solution

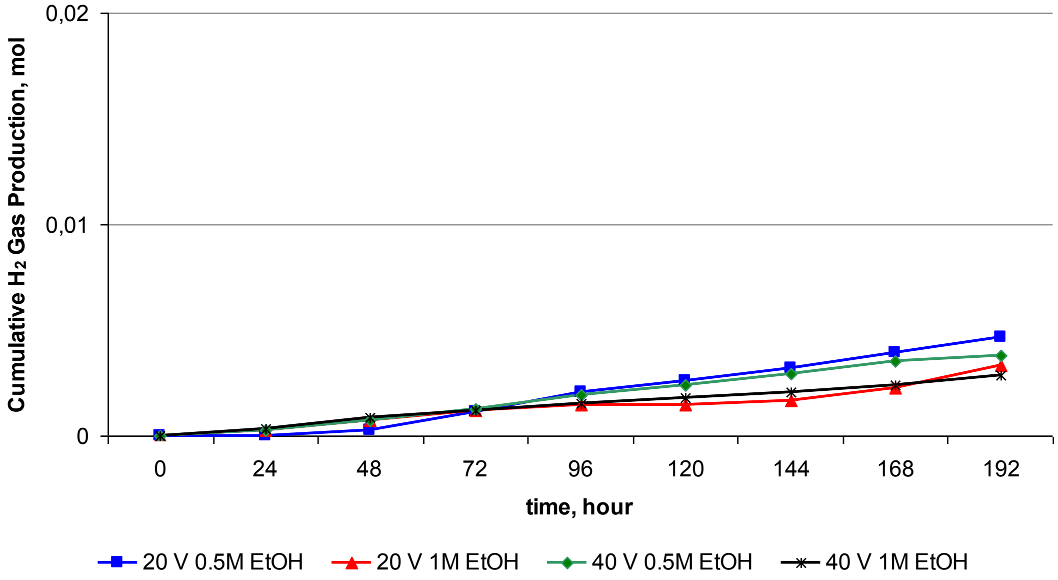


Figure 5.16 Cumulative hydrogen gas production in cathode chamber when Ethyl Alcohol (EtOH) used as electrolytic solution

5.3 Electroosmotic Flow

Electroosmotic flow was varying with the type and concentration of the electrolyte solution, as well as the applied electrical potential on to the soil. Below, the electroosmotic flow measured during the conducted experiments, with different electrolyte solutions having 0.5 or 1 M concentration, are presented on a cumulative basis covering the 192 hour of experimental period.

In the experiments with NaOH solutions, lower concentrations performed positive electroosmotic flows; 152 cm^3 and 77 cm^3 for 20 V and 40 V DC with 0.5 M NaOH, where negative values were measured during the experimental period in the experiment under 20 V DC with 1 M NaOH (-119 cm^3) (Figure 5.17).

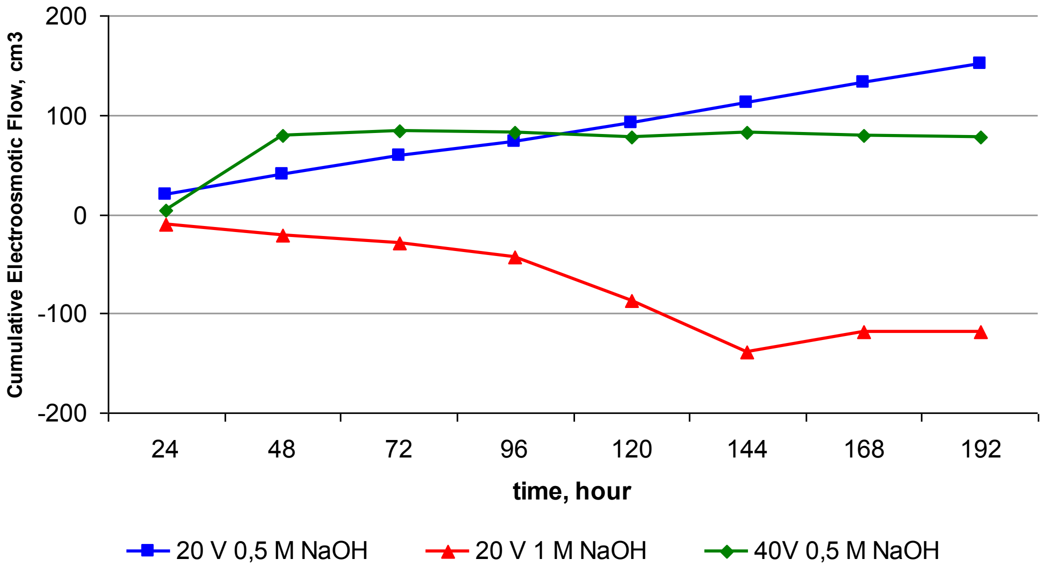


Figure 5.17 Cumulative electroosmotic flow in the experiment which NaOH was used as electrolytic solution

In the experiments with pure water, the electroosmotic flow measured under 40 V DC showed positive values and the cumulative score was about 17 cm^3 (Figure 5.18). But, the experiment under 20 V DC started with a negative electroosmotic flow and at the end of the first 24 hours it represented a positive trend which continued until the end of the experimental period obtaining a cumulative score of 7.38 cm^3.

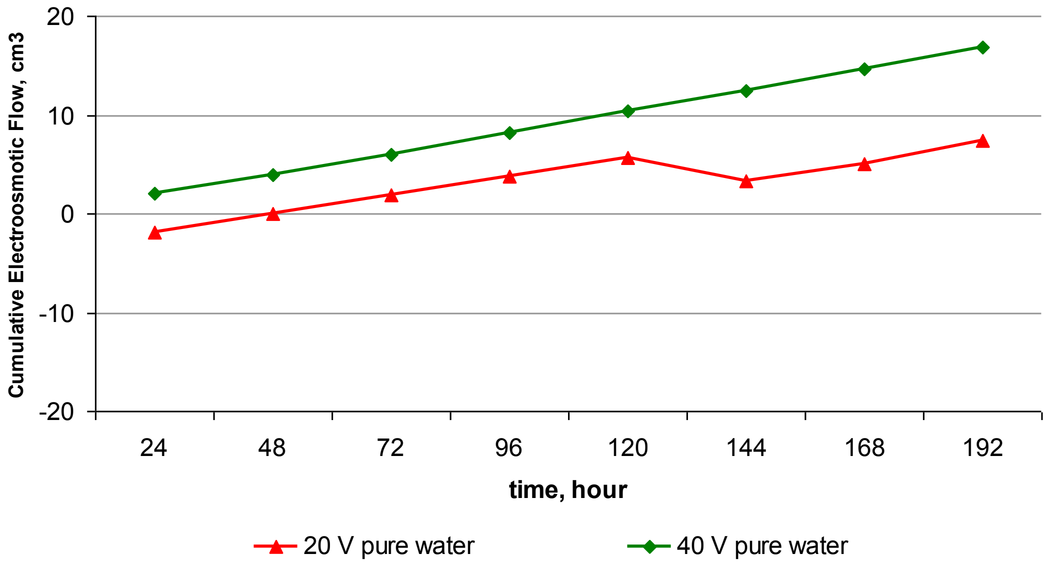


Figure 5.18 Cumulative electroosmotic flow in the experiment which pure water was used as electrolytic solution

Four different experimental conditions were applied by using Acetic acid solution. The results for the cumulative electroosmotic flow are given in Figure 5.19.

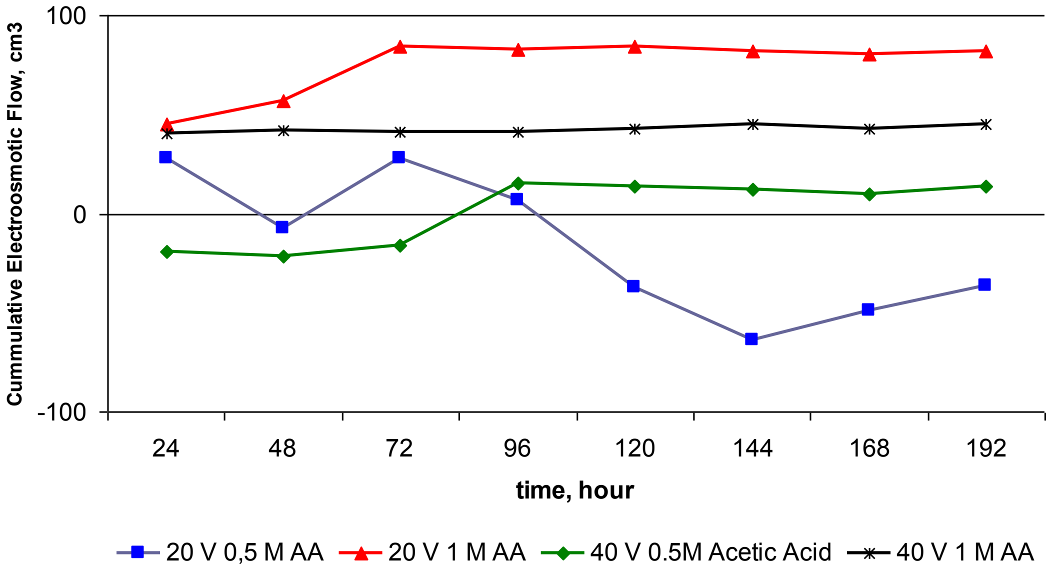


Figure 5.19 Cumulative electroosmotic flow in the experiment which Acetic acid (AA) was used as electrolytic solution

In the first 24 hours, the direction of electroosmotic flow was negative in the experiment with 0.5 M Acetic acid under 20 V DC, it reversed to positive in the 48th hour, and then again backward for the next 72 hours, and finally again moved backwards until the end of the experiment by obtaining -36.4 cm^3 of cumulative electroosmotic flow. The movements of electroosmotic flow in the experiments under 20 V (1 M Acetic acid) and 40 V (0.5 M Acetic acid) showed similar trends; moved forward in the first 96 hours and then moved backward and forward until the end of the experimental period by obtaining 82 cm^3 and 14 cm^3 cumulative scores. In the experiment with 1M Acetic acid under 40 V DC, any distinct movement of electroosmotic flow could not be observed during the experimental period.

In Figure 5.20, the cumulative electroosmotic flows for the use of ethanol (EtOH) as electrolyte solution were given for different experimental conditions. As can be seen from the figure, measured electroosmotic flow values were quite low for EtOH for all of the experiments. The low direction deviates backwards and forwards and final cumulative scores are between -5.0 and 3.2 cm^3.

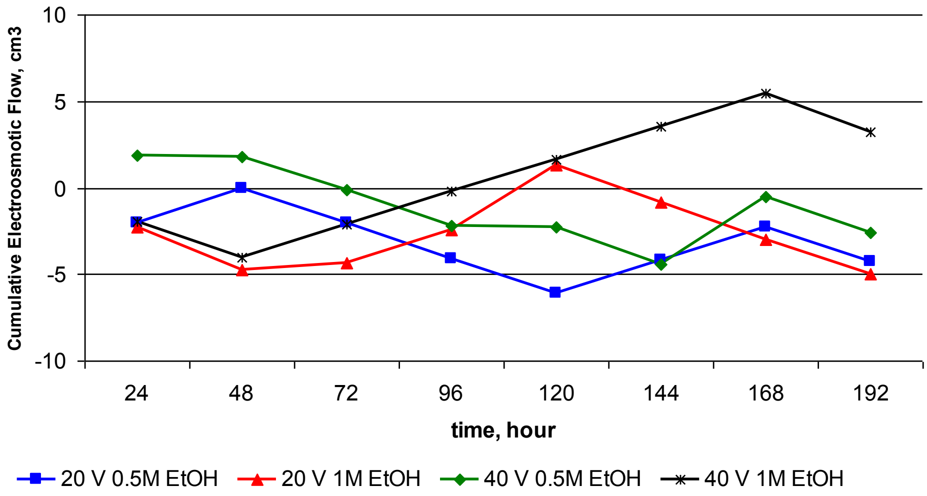


Figure 5.20 Cumulative electroosmotic flow in the experiment which Ethyl Alcohol (EtOH) was used as electrolytic solution

5.4 Soil pH values at the end of the experimental period

The soil in the reactor column was removed and pH values were detected in equivalent soil slices with the width of 4 cm at the end of the each experiment. The results are presented in below figures according to the soil slice distance from the anode.

After the experiments conducted with NaOH as electrolyte solution, the soil pH values were alkaline through the column and between 10.1 and 11.2 (Figure 5. 21).

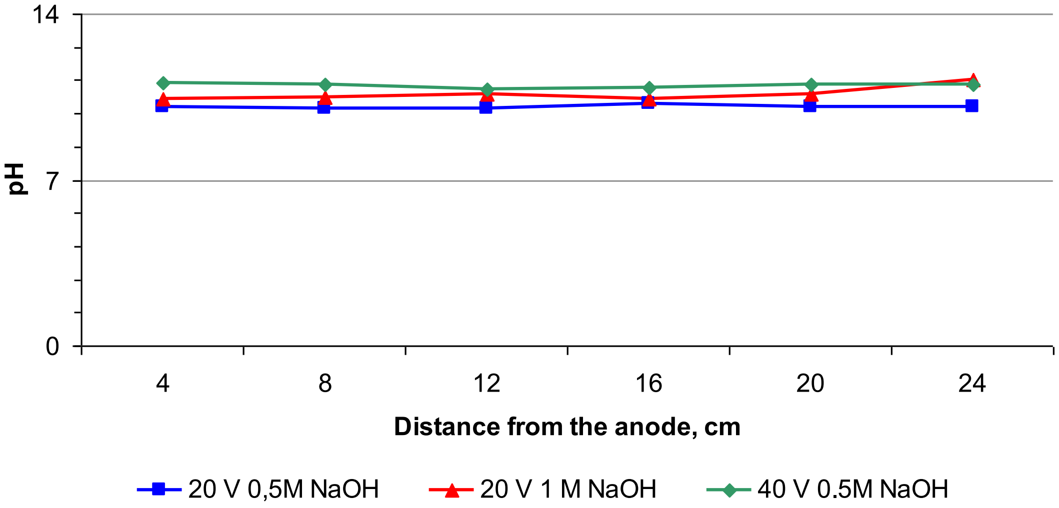


Figure 5.21 Soil pH levels after the experiments with NaOH solutions

Soil pH levels were above neutral levels after the experiments conducted by using pure water as the electrolyte solution. The values were among 8.2 with 8.9 through the soil column for 20 V DC application and between 7.5 and 8.0 for the DC application of 40 V (Figure 5.22).

When Acetic acid was used as electrolyte solution, pH of the soil column slightly raises from anode to cathode, (Figure 5.23) except the experiment conducted with 1 M Acetic acid under 40 V DC, that the soil shows neutral levels through the reactor column.

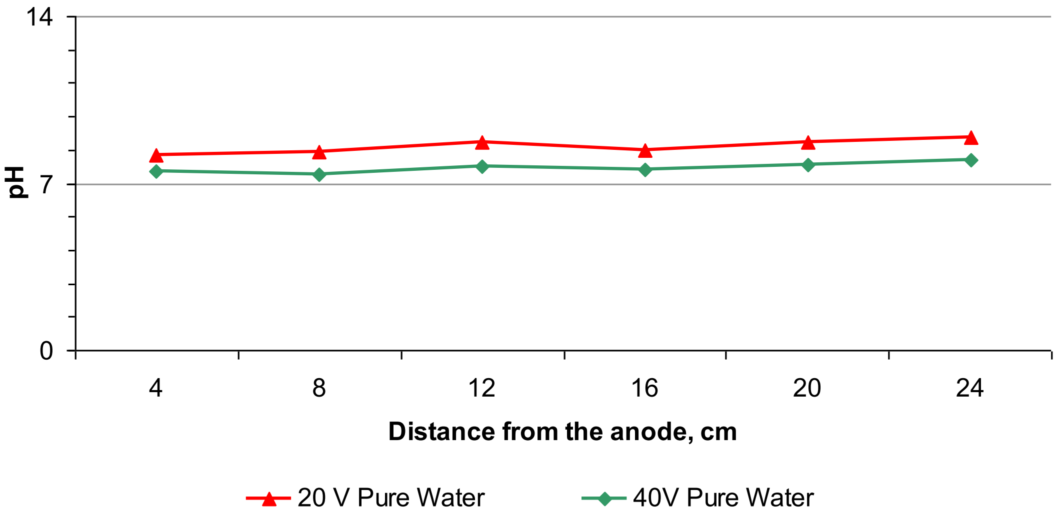


Figure 5.22 Soil pH levels after the experiments with pure water

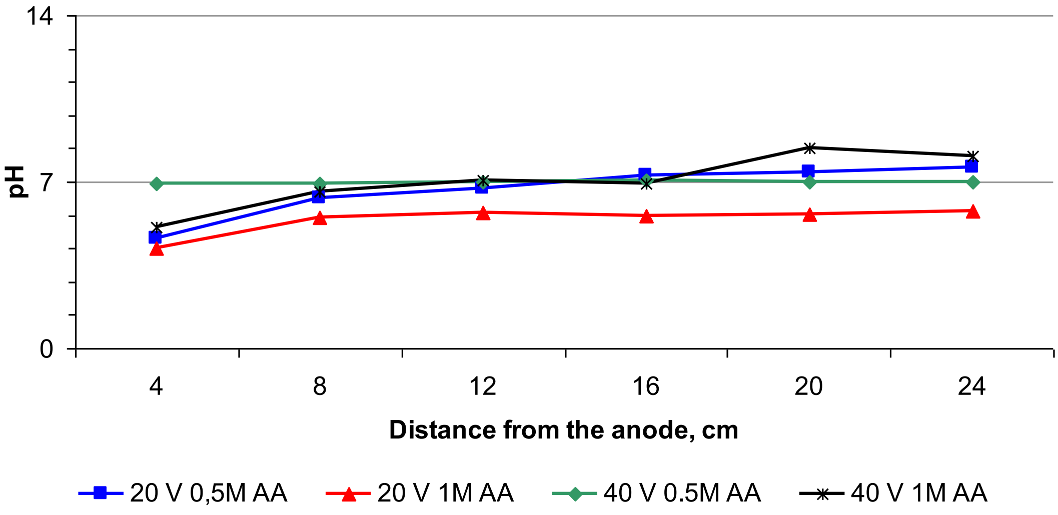


Figure 5.23 Soil pH levels after the experiments with Acetic acid solutions

Under the conditions of the other experiments with Acetic acid the soil pH in front of the anode was between 4.6 and 5.1, which rises slowly and reaches relatively slight alkaline levels (8.1) in front of the cathode.

In the experiments conducted with EtOH, the soil pH was generally around 7.5 after treatment(Figure 5.24). In the case with 0.5 M EtOH use under the 40 V of DC apply resulted with alkaline pH levels after the first half of the soil column (in front of the cathode) as high as 10.2.

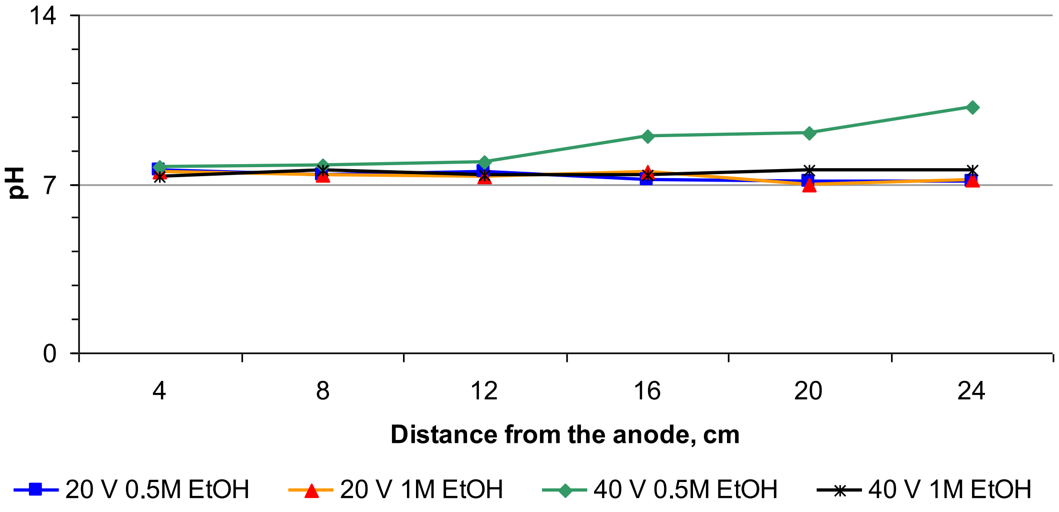


Figure 5.24 Soil pH levels after the experiments with EtOH solutions

5.5 TPHs Concentrations and Treatment Efficiencies Obtained in Soil after the Treatment Period

TPHs concentrations in the soil column were detected after the treatment period and the treatment efficiencies were determined according to the initial concentration. Below the average results are presented for each of the electrolyte solution used as well as the treatment performances in soil sections according to the distance from the anode.

Figures 5.25, 5.26, and 5.27 present the final TPHs concentrations in the soil sections and treatment efficiencies in the case of NaOH use as electrolyte solution. In the experiment with 0.5 M NaOH and 20 V DC application, TPHs treatment efficiencies are lower (76-78 %) in the soil sections close to anode than the efficiencies obtained in the soil sections in front of the cathode(91-98%). The average TPHs treatment efficiency is 85 % in this experiment.

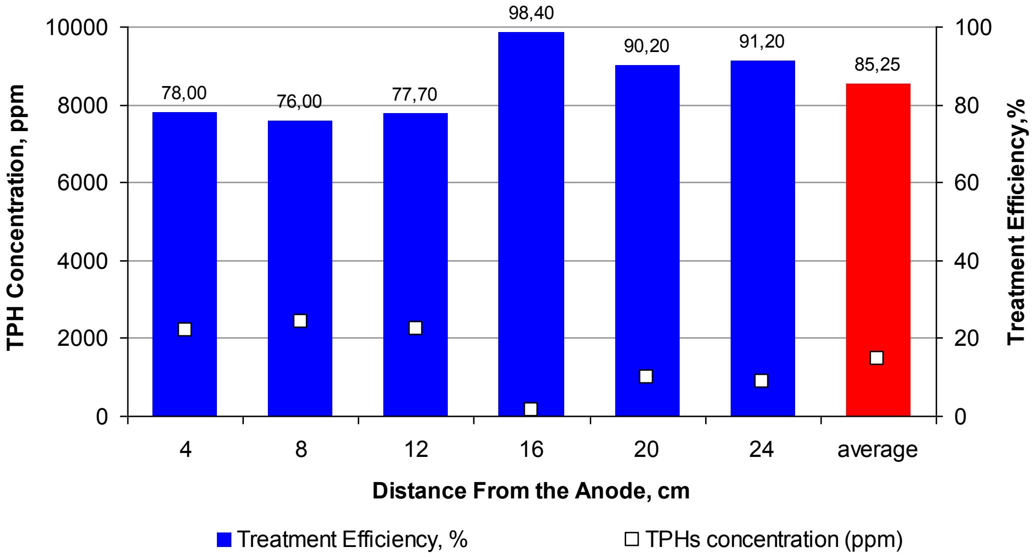


Figure 5.25 The TPHs concentrations and Treatment Efficiencies in Soil Sections After the Electrokinetic Remediation According to the Distance from the Anode (20 V 0.5 M NaOH)

In the experiment with 1 M NaOH, 20 V DC electrical potential resulted with lower treatment efficiencies than the 0.5 M NaOH concentrations under the same DC (average treatment efficiency: 72.6%).

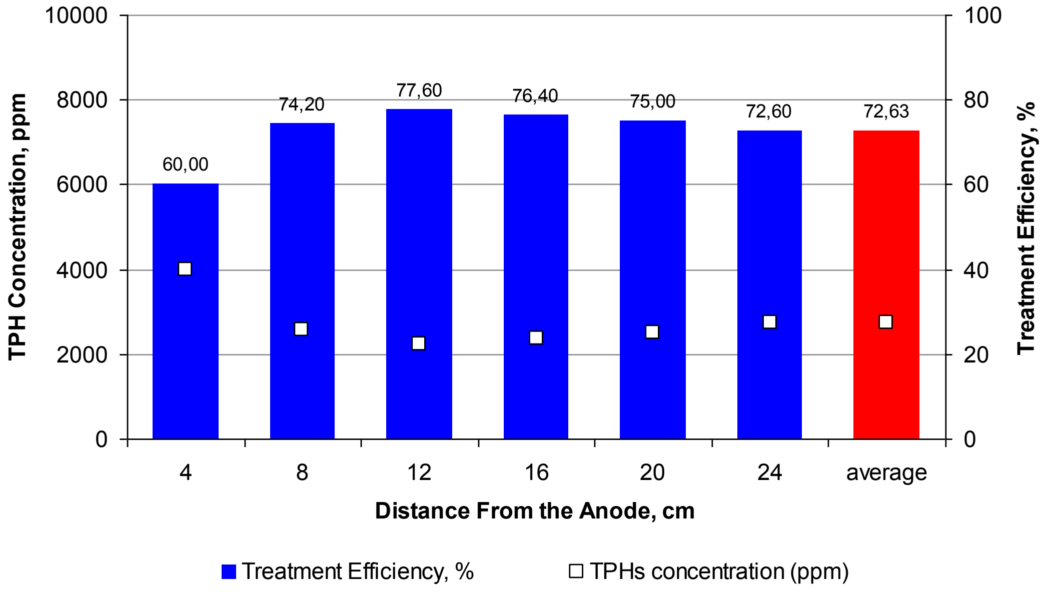


Figure 5.26. The TPHs concentrations and Treatment Efficiencies in Soil Sections After the Electrokinetic Remediation According to the Distance from the Anode (20 V 1 M NaOH)

With 0.5 M NaOH and 40 V DC electrical potential the TPHs removal through the soil column has decreased and the average treatment efficiency was determined as64.6%.

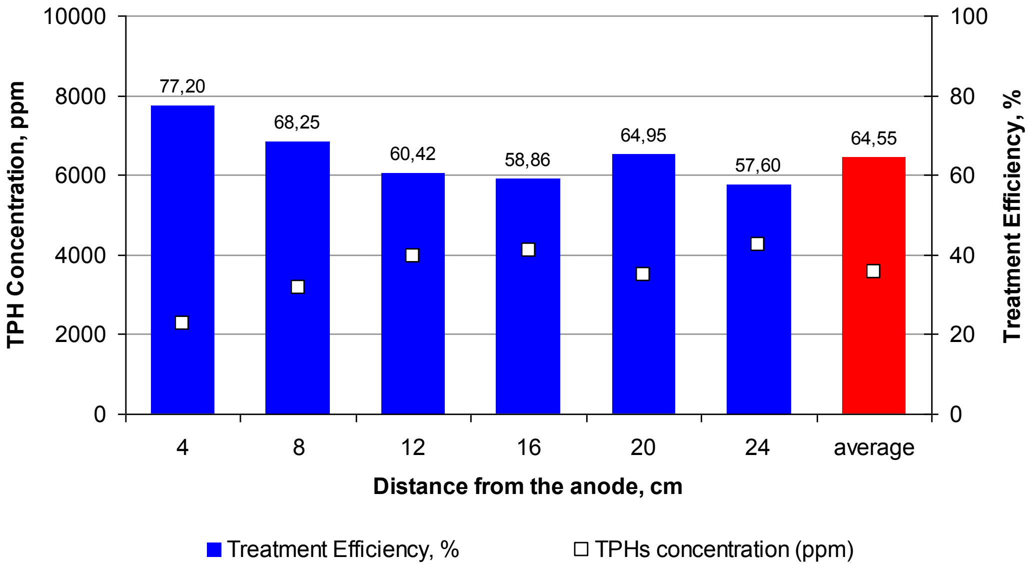


Figure 5.27 The TPHs concentrations and Treatment Efficiencies in Soil Sections After the Electrokinetic Remediation According to the Distance from the Anode (40 V 0.5 M NaOH)

It is seen that neither the raise in NaOH concentration nor the raise in DC gives higher treatment efficiencies.

In the experiments with pure water, increasing DC resulted with higher TPHs treatment efficiencies through the soil column (Figures 5.28 and 5.29). When 20 V DC applied to the system, the treatment efficiencies in the anode half of the reactor were between 70-94% and the efficiencies in the cathode half were between 55-84%, with an overall treatment efficiency of 74.7 %. In the 40 V DC application, the difference in the treatment efficiencies obtained in anode and cathode halfs are not as distinct as it was observed in 20 V DC application and the overall treatment efficiency was 89.5%.

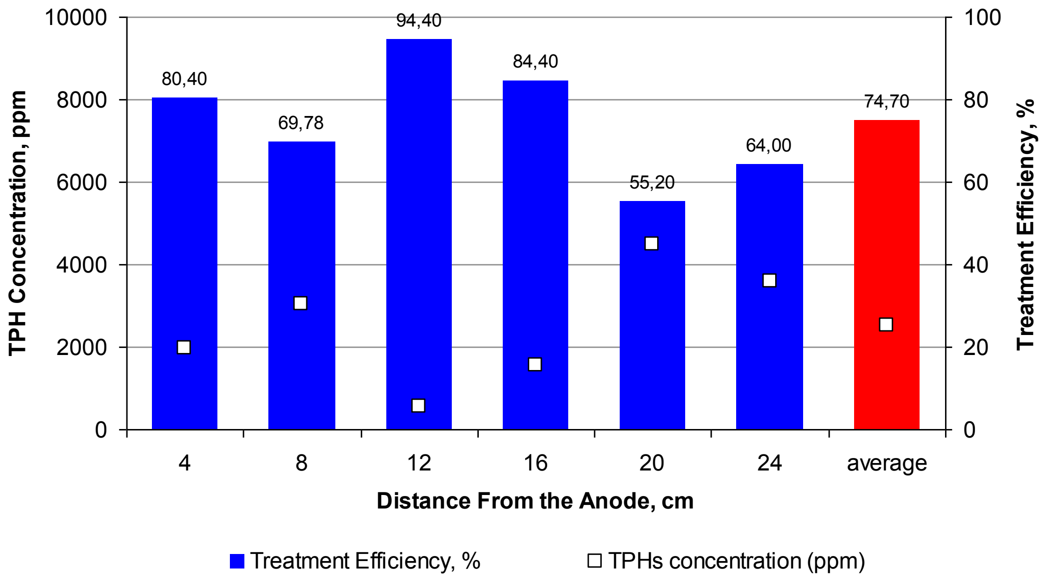


Figure 5.28 The TPHs concentrations and Treatment Efficiencies in Soil Sections After the Electrokinetic Remediation According to the Distance from the Anode (20 V Pure Water)

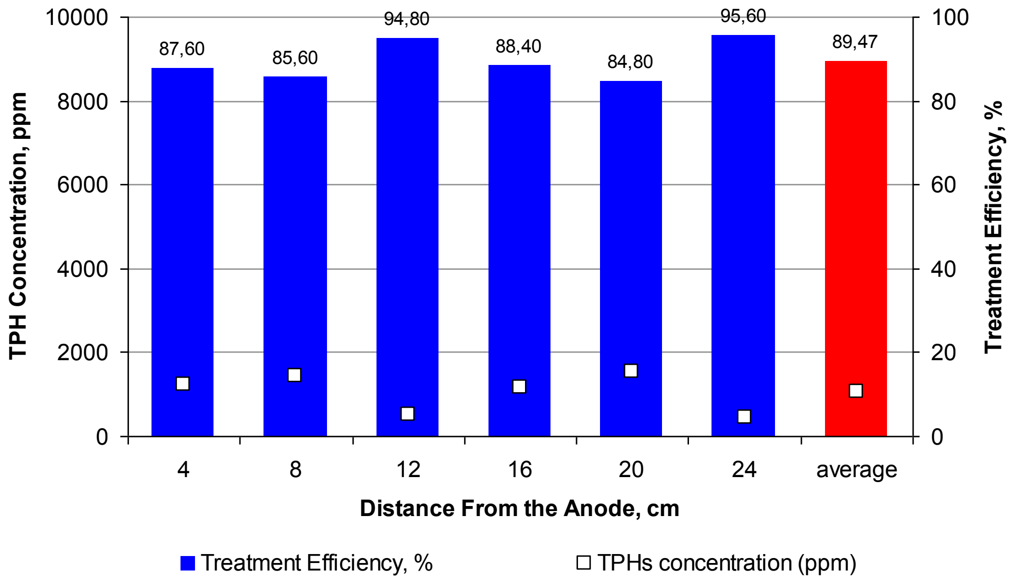


Figure 5.29 The TPHs concentrations and Treatment Efficiencies in Soil Sections After the Electrokinetic Remediation According to the Distance from the Anode (40 V Pure Water)

The treatment efficiencies with Acetic acid solutions are presented in Figures 5.30, 5.31, 5.32, and 5.33. With the 0.5 M of Acetic acid, the final TPHs treatment efficiencies in anode half (78.4-97.8 %) is relatively higher than the efficiencies obtained in the cathode half (70-78.5%) of the reactor. The overall treatment efficiency for TPHs was 82.7%.

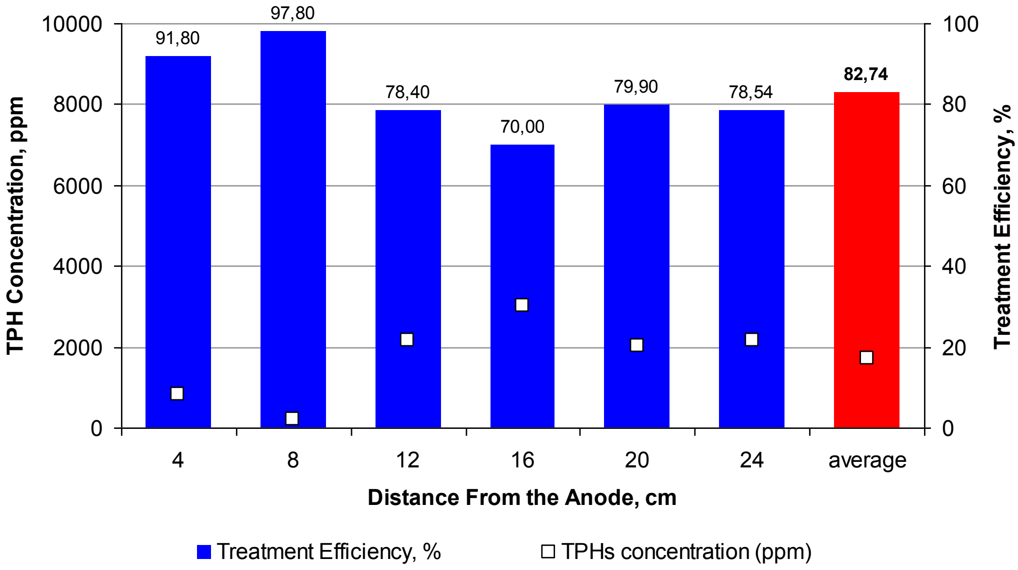


Figure 5.30 The TPHs concentrations and Treatment Efficiencies in Soil Sections After the Electrokinetic Remediation According to the Distance from the Anode (20 V 0.5 M Acetic Acid)

By increasing the Acetic acid concentration under 20 V DC, treatment efficiency increased (91.4%) and the deviations between the concentrations observed in anode (90.5-93.7) and cathode (87.7-93.3) halfs became insignificant.

Increasing voltage from 20 V to 40 V in the case of 0.5 M Acetic acid application also increased the overall treatment efficiencies, which were found as 82.7% for 20 V and 89.99% for 40V. But, the TPHs treatment efficiencies just in front of the anode and cathode reservoirs (70% and 81.2 % respectively) were significantly lower than the other sections of the soil column.

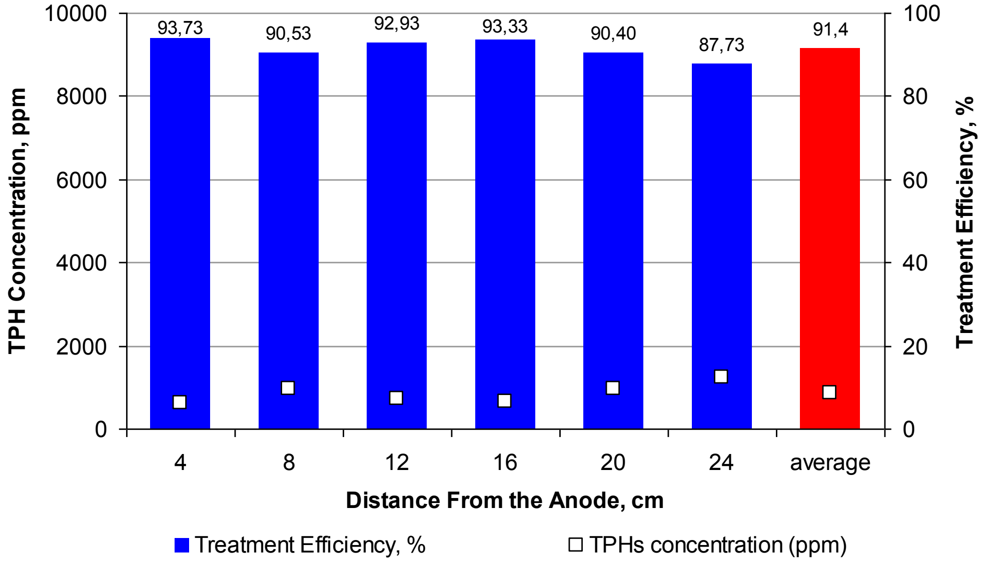


Figure 5.31 The TPHs concentrations and Treatment Efficiencies in Soil Sections After the Electrokinetic Remediation According to the Distance from the Anode (20 V 1 M Acetic Acid)

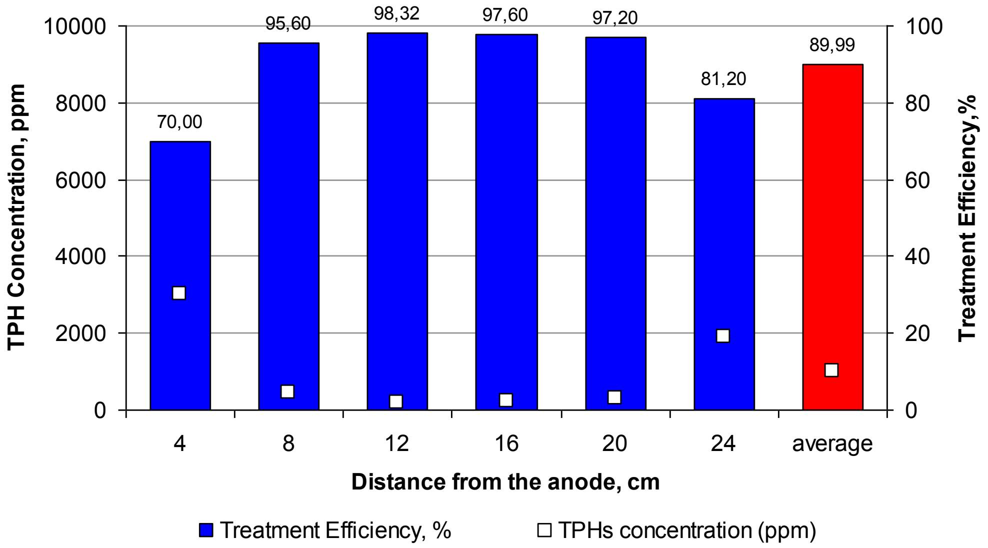


Figure 5.32 The TPHs concentrations and Treatment Efficiencies in Soil Sections After the Electrokinetic Remediation According to the Distance from the Anode (40 V 0.5 M Acetic Acid)

As 1 M Acetic acid was used as electrolyte solution under 40 V DC electric potential, both the overall treatment efficiency (44.5%) and the treatments in soil sections (17.9-71.2%) decreased. Furthermore, distinctive treatment efficiencies have seen in sequential soil sections of the column.

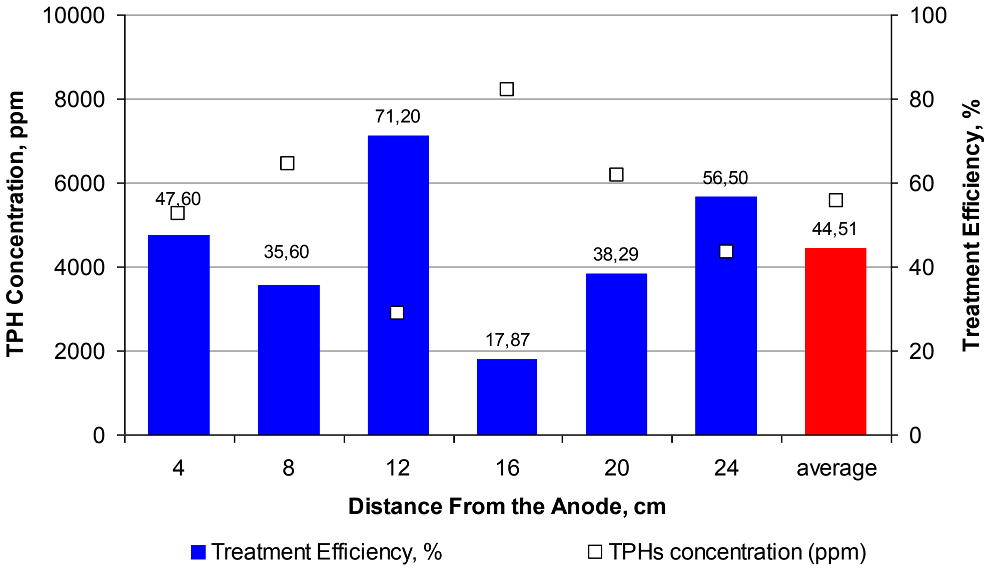


Figure 5.33 The TPHs concentrations and Treatment Efficiencies in Soil Sections After the Electrokinetic Remediation According to the Distance from the Anode (40 V 1 M Acetic Acid)

The experiments conducted by using EtOH solutions resulted with high treatment efficiencies. In the experiment conducted with 0.5 M EtOH under 20 V DC, overall treatment efficiency was 89.3% and the removal efficiencies in soil sections were also high except the section in front of the anode (53.2 %), (Figure 5.34).

1 M EtOH concentration gave an overall treatment efficiency of 94.2% (Figure 5.35)with quite small distinctions in soil sections (min: 89.2%, max: 99.4%).

Increase in applied electrical potential resulted with lower treatment efficiencies (Figures 5.36 and 5.37). When 0.5 M EtOH used the overall treatment efficiency was 82.3 % and it was 91.97% as 1 M EtOH was used as electrolyte solution under 40 V DC electrical potential.

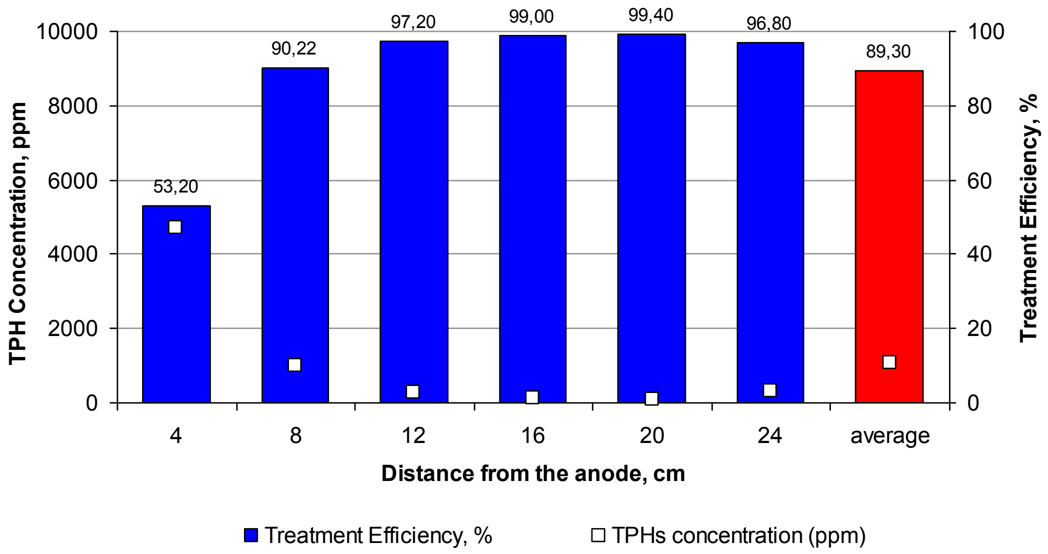


Figure 5.34 The TPHs concentrations and Treatment Efficiencies in Soil Sections After the Electrokinetic Remediation According to the Distance from the Anode (20 V 0.5 M Ethanol)

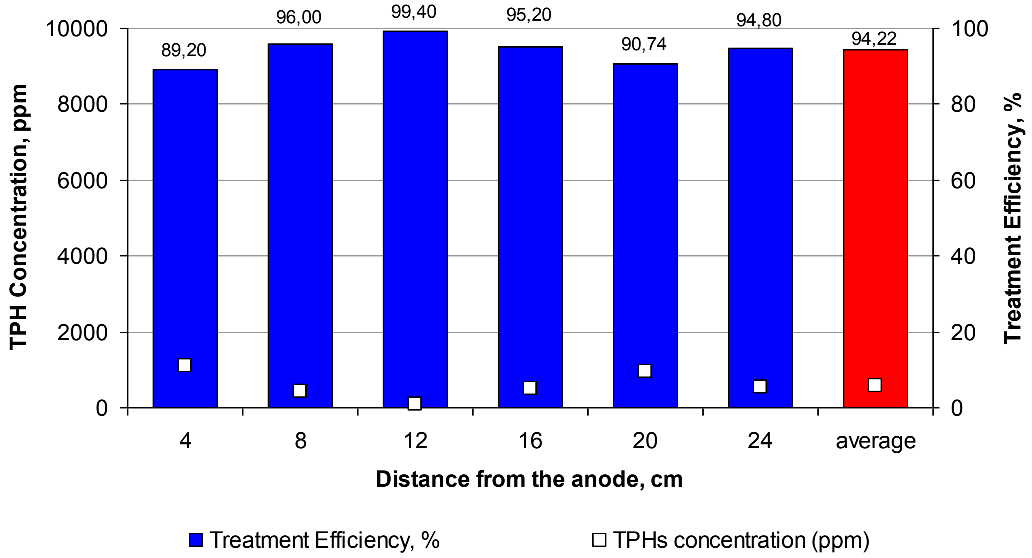


Figure 5.35 The TPHs concentrations and Treatment Efficiencies in Soil Sections After the Electrokinetic Remediation According to the Distance from the Anode (20 V 1 M Ethanol)

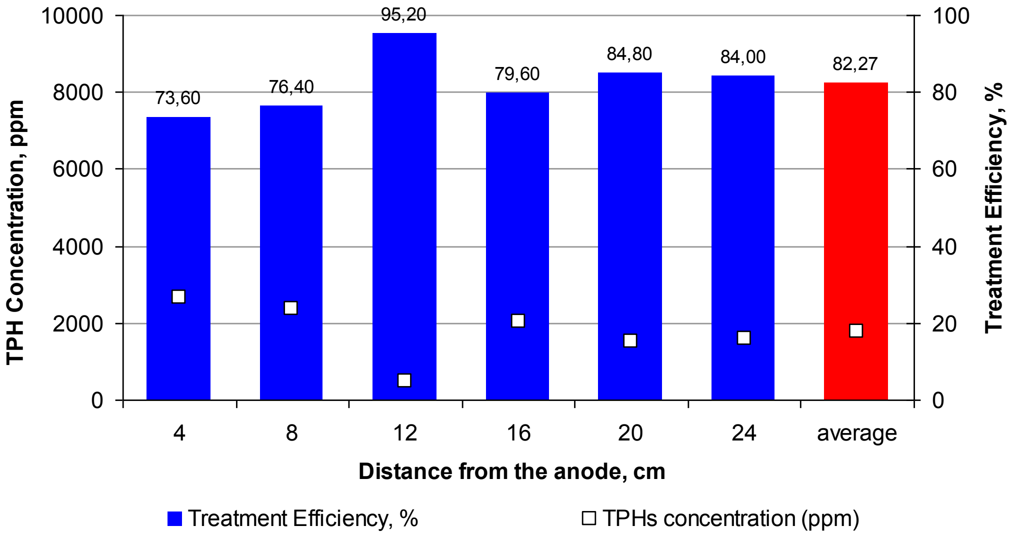


Figure 5.36 The TPHs concentrations and Treatment Efficiencies in Soil Sections After the Electrokinetic Remediation According to the Distance from the Anode (40 V 0.5 M Ethanol)

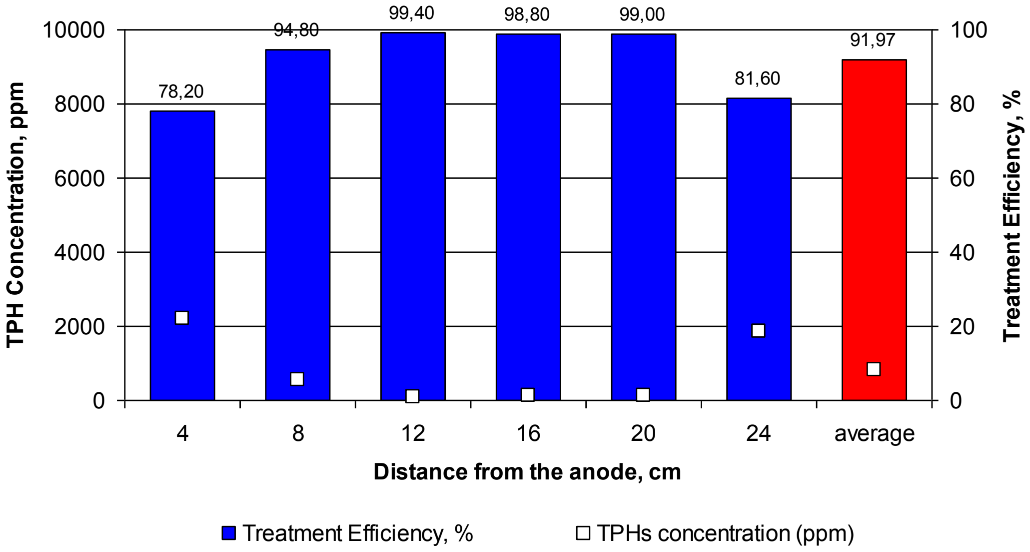


Figure 5.37 The TPHs concentrations and Treatment Efficiencies in Soil Sections After the Electrokinetic Remediation According to the Distance from the Anode (40 V 1 M Ethanol)

5.6 Total PAHs

The PAHs are also detected at the end of the electrokinetic remediation period in soil sections and the results are presented in this part of the thesis according to the electrolytic solution used.

Below, the PAHs average treatment efficiencies in soil sections by using NaOH solution are illustrated (Figure 5.38) according to the distance from the anode. It was seen that in the experiments conducted with 0.5 M NaOH resulted with higher PAHs treatment efficiencies.

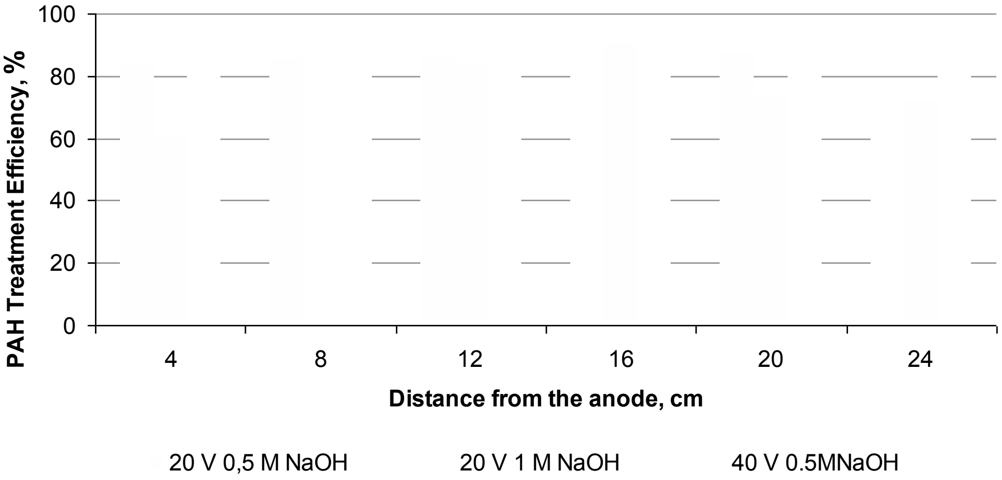


Figure 5.38 Average PAH treatment efficiency in soil sections by using NaOH as electrolyte solution

The experiments conducted with pure water as electrolyte solution resulted with very similar PAHs removal efficiencies for 20 V and 40 V DC electrical potential. It was seen that concentration differences between the soil sections were also insignificant (Figure 5.39).

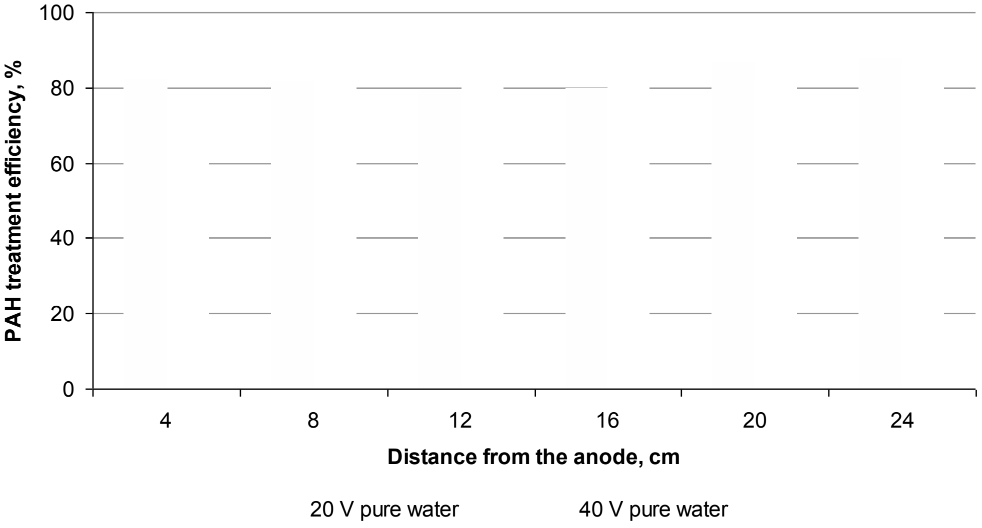


Figure 5.39 Average PAH treatment efficiency in soil sections by using pure water as electrolyte solution

In the experiments conducted with Acetic acid, the PAHs average treatment efficiency was low in all soil section when 20 V DC applied for the Acetic acid solution of 0.5 M. But, the same Acetic acid concentration gave the highest treatment efficiency when 40 V DC application is considered (Figure5.40).

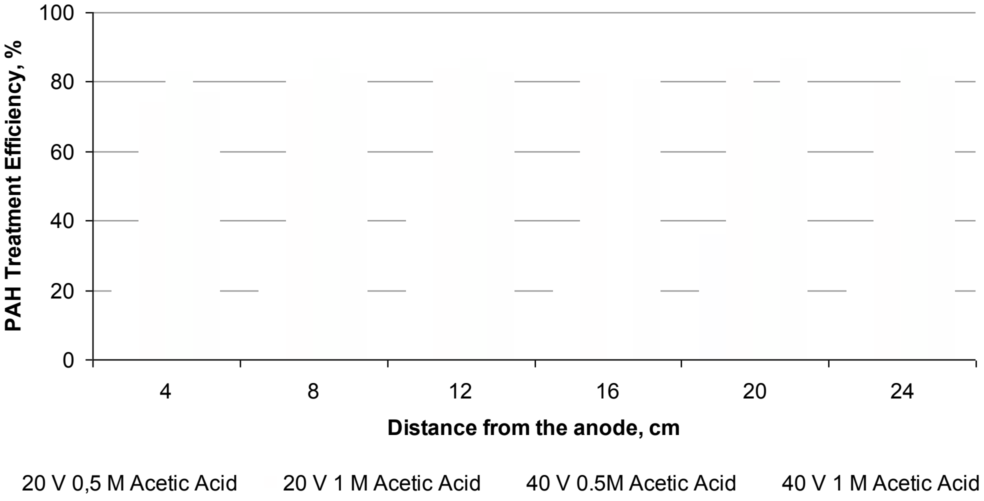


Figure 5.40 Average PAH treatment efficiency in soil sections by using Acetic acid (AA) as electrolyte solution

The PAHs average treatment efficiencies by using ethanol solutions are given in Figure 5.41. As can be seen from the figure, ethanol resulted with high treatment efficiencies especially in the cases conducted with 1 M solution. But concentration distinctions between the soil sections were lower when 40 V DC was applied to the system.

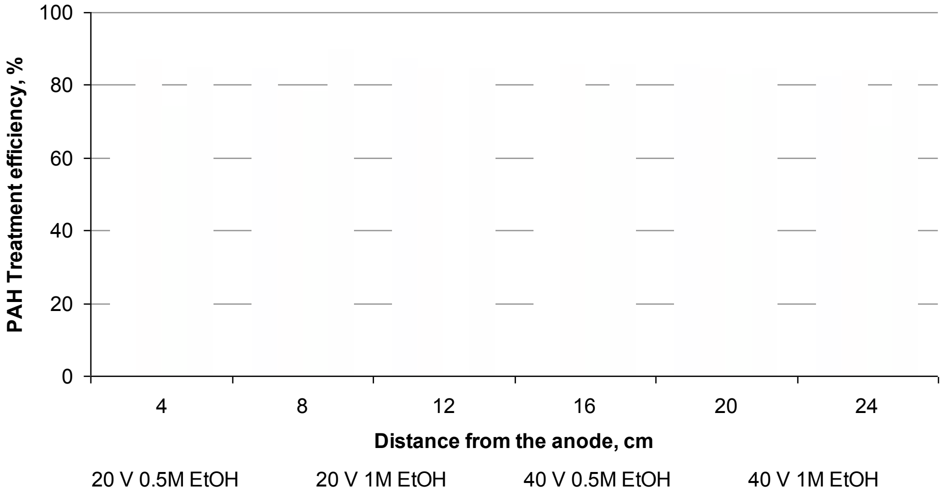


Figure 5.41 Average PAH treatment efficiency in soil sections by using Ethanol (EtOH) as electrolyte solution

Here, it should be known that the contribution of each PAH to their total concentration was different. Because of that reason, the evaluation of the data obtained from the treatment of PAHs was also completed according to the mass distribution of each PAH in contaminated soil in part 5.7.

5.7 The evaluation of the treatment efficiencies according to the PAHs Groups

As can be seen in Figure 5.42, the contribution of each PAH to their total concentration in soil was different. Depending on this fact, the studied PAHs were grouped according to their mass distribution. The first group has a total concentration of 251.38 ppm and represents the 6.72 % of the PAHs studied, the second group has a total concentration of 889.01 ppm with a mass portion of 23.75%, and the third group contributes 2602.48 ppm that represents 69.53% of the total PAHs in the system.

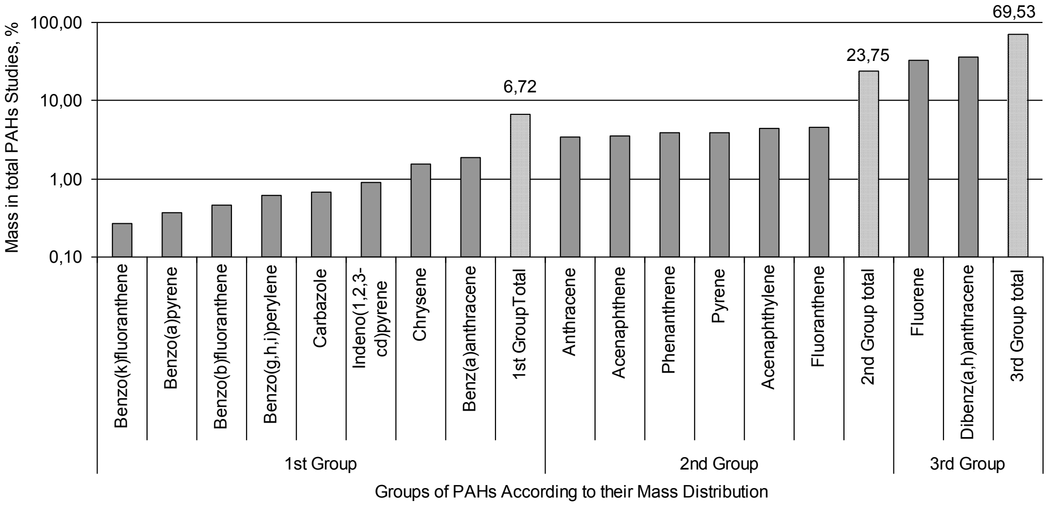


Figure 5.42 The mass distribution of studied PAHs and the groups constituted according to their mass distribution

In Table 5.1, the properties of the PAH compounds in each group and the average value of the groups are given. The average solubility of the in 2nd Group PAHs is higher than the other groups, where its average molecular weight, boiling point and number of benzene rings are lower than 1st and 3rd Group PAHs. The average properties of 1st and 2nd Group PAHs are similar, except their solubility, which is 0.00992 mg/L for 1st Group and 0.91525 mg/L for the 3rd Group PAHs.

Table 5.1. Properties of PAHs according to their mass groups

Group Number	PAH	Molecular Weight	Boiling Point, °C	Solubility in Water, mg/L	Number of Benzene Rings
1st Group	**Benzo(k)fluoranthene**	252.3	550.00	0.00076	5
	Benzo(a)pyrene	252.3	179.00	0.00230	5
	Benzo(b)fluoranthene	252.3	168.30	0.00120	5
	Benzo(g,h,i)perylene	276.34	480.00	0.00026	6
	Carbazole	167.21	351.00	0.00000	3
	Indeno(1,2,3-cd)pyrene	276.3	530.00	0.06200	6
	Chrysene	228.3	448.00	0.00280	4
	Benz(a)anthracene	228.29	159.00	0.01000	4
	1st Group Average	241.67	358.16	0.00992	4.75
2nd Group	**Anthracene**	178.2	342.34	0.07600	3
	Acenaphthene	154.21	96.20	1.93000	3
	Phenanthrene	178.2	340.00	1.20000	3
	Pyrene	202.3	393.40	0.07700	4
	Acenaphthylene	152.2	270.00	3.93000	3
	Fluoranthene	202.26	375.00	0.23000	4
	2nd Group Average	177.90	302.82	1.24050	3.33
3rd Group	**Fluorene**	166.2	295.00	1.83000	3
	Dibenz(a,h)anthracene	278.35	524.00	0.00050	5
	3rd Group Average	222.28	409.50	0.91525	4.00

The PAHs treatment efficiencies for to the groups constituted according to their mass distribution in the tests with NaOH solutions are given in Figure 5.43.

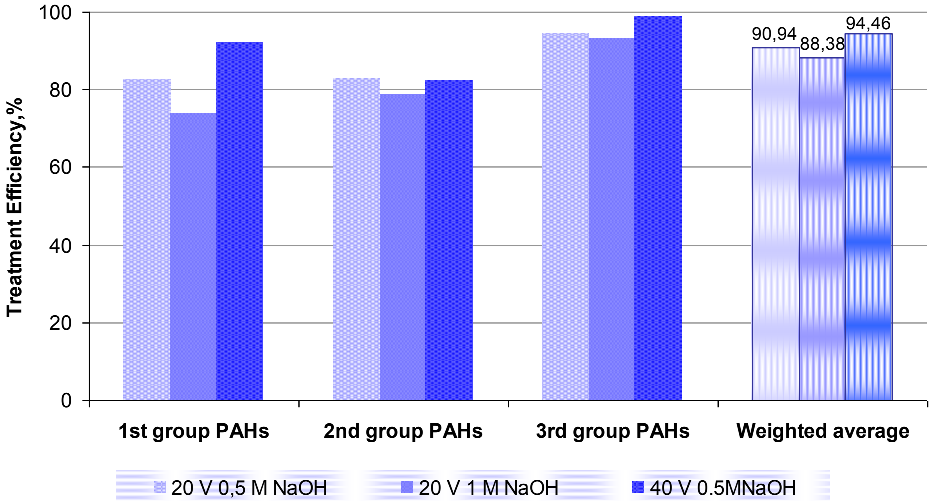


Figure 5.43 Treatment efficiencies of PAH groups with NaOH as electrolytic solution

As can be seen from the figure 3rd group PAHs' treatment efficiencies are higher with 0.5 M NaOH and the raise in electrical potential positively affected the treatment efficiency.

The results obtained with pure water were similar with the results obtained with NaOH; the treatment efficiency is highest in 3rd group PAHs (Figure 5.44). In that case, increase in applied electrical potential did not affect the treatment efficiency.

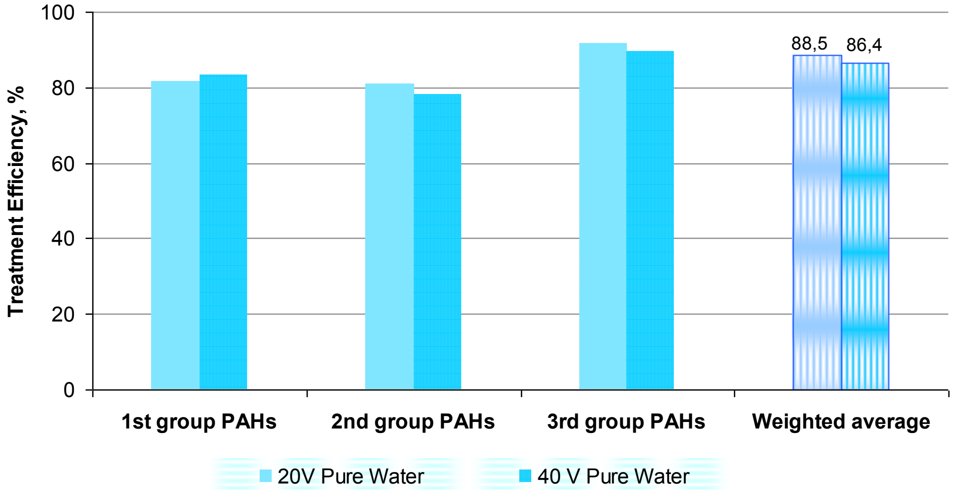


Figure 5.44 Treatment efficiencies of PAH groups with pure water as electrolytic solution

In the experiments with Acetic acid solutions, treatment efficiency with 0.5 M AA in 20 V electrical potential was quite low, where the tests conducted with 1 M AA were resulted with similar removal efficiencies (Figure 5.45). In this set of experiments, 0.5 M Acetic acid removed PAHs in the soil efficiently in 20 V DC electrical potential. The most effectively treated PAHs are the ones in the 3rd group.

Treatment efficiencies of PAH groups are very distinctive in the experiments conducted with ethanol (EtOH), (Figure 5.46). The treatment efficiencies of PAH group in decreasing order is as follows:

3rd Group> 1st Group>2nd Group

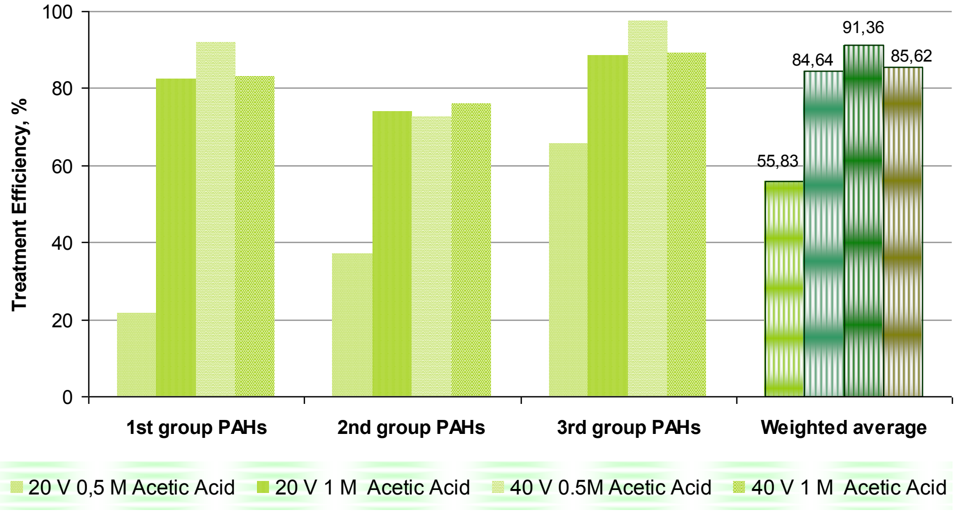


Figure 5.45 Treatment efficiencies of PAH groups with Acetic acid (AA) as electrolytic solution

The effect of different EtOH concentrations and DC voltages can only be seen on 1st group PAHs treatment, which could not influence the overall treatment efficiency because of their low initial concentration.

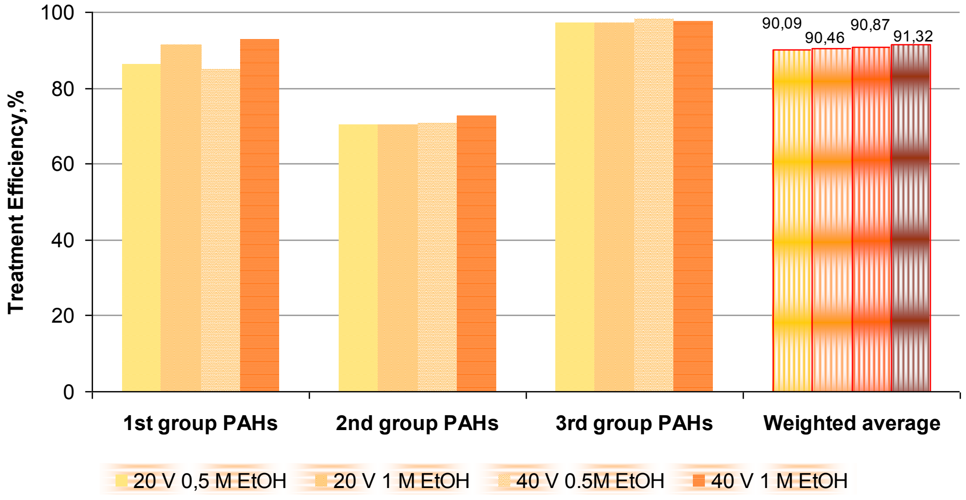


Figure 5.46 Treatment efficiencies of PAH groups with Ethanol (EtOH) as electrolytic solution

5.8 Discussion

In this part the findings will be discussed according to the electrolyte solutions used in the systems.

5.8.1 Treatment studies with NaOH as electrolyte solution

The removal of TPHs in electrokinetic treatment system by using NaOH solution resulted with the highest removal efficiency in the experiment conducted with 0.5 M NaOH in 20 V DC electric potential (85.25%). This is an expected result because of the constant increase in electroosmotic flow (EOF) observed during the experimental period, which gave a 151 mL of final cumulative score.

In the set with 0.5M NaOH in 40 V of DC, EOF has retained after the first 24 hours and the experiment resulted with 64.55% TPHs removal.

The EOF was negative in the first 144 hours of the experiment with 1 M NaOH under 20 V DC, but then EOF reversed to positive and it was expected that the set could give higher treatment efficiencies. However, the overall TPHs treatment efficiency in this set was 72.63%, which can be explained by the high pH levels observed in the soil that hindered the migration of contaminants and does not allow high removal efficiencies in front of the anode. When compared to hydrogen production in cathode, relatively low oxygen production in anode chamber can also be an indicator of the poor electrolysis occurred in the anode area which could not serve enough H^+ ions to the soil column to increase the zeta potential of the soil to allow higher EOF. The pH level observed in anode and the EOF occurred in the system during the experimental period showed that; the release of H^+ ions to the soil started after 72nd hour, the zeta potential in the soil became zero at 144th hour, and then the EOF moved backward to positive for the last 48 hours of the test.

When PAHs removals were investigated; it was seen that the overall efficiencies of the systems are high and close to each other. The most efficient of PAHs has seen in the set conducted with 0.5 M NaOH by applying 40 V of DC (94.46%), since the removal efficiencies slightly higher in the soil at the cathode front of the reactor system. The removal efficiencies are almost equal in all the sets, especially in the middle sections of the reactor, but lower efficiencies has detected in the sections in front of the anode and cathode in the sets with 20 V DC.

5.8.2 Treatment studies with pure water as electrolyte solution

Two different electrical potential were tested in electrokinetic system by using pure water as electrolyte solution. The TPHs treatment obtained for 40 V DC (89.47%) application were better from the removal efficiencies with 20 V DC (74.7%).

The major reason for this difference between the treatment efficiencies is the EOF obtained in the systems. In the system operated under 40 V electrical potential, EOF occurred in the system increased linearly and were in the direction from cathode to anode (positive) as expected during the experimental period with a cumulative value of 16.8 mL, where it reversed to cathode (negative direction) between the 120th and

144th hours of operation with 20 V, and then forwarded to anode again and reached a cumulative value of 7.38 mL. Lower EOF is an expected result when pure water used as electrolytic solution, The reverse EOF seen in the system operated under 20 V can be explained by the higher soil pH (~ 8) appeared during operation than the pH observed in the system operated with 40 V DV (pH ~ 7.5). As it was mentioned before, zeta potential increases as the number of hydrogen ions in the soil increases. It was also seen that the pH levels in electrolyte chambers in the system under 20 V DC were more aggressive (in anode between 2.0-2.9, in cathode between 12.3-12.6) than the test with 40 V (in anode between 4.2-5.8, in cathode between 10-11.2), which indicates the H^+ and OH^- transfers from the electrolyte chambers to soil could not be achieved in this system. The gas production from the electrolytic chambers shows that, H_2 production under 40 V DC is higher than the O_2 production in anode and also higher than the gas productions in the set conducted with 20 V DC. The EOF levels obtained in the systems are compatible with the literature (Altin & Değirmenci, 2005).

In addition to the higher treatment efficiency in 40 V DC, the distribution of the remaining TPHs in the reactor sections were similar. This situation was not the same for the system operated with 20 V DC, where significant distinctions have seen between the sequential soil sections.

The results obtained with pure water were close for overall PAHs removal under 20 V and 40 V DC electrical potentials; 88.5% and 86.4%, respectively. But, lower treatment has seen in front of the anode with 40 V DC. Furthermore, the treatment efficiencies for 2nd Group and 3rd Group PAHs are higher in the set operated under 20 V electrical potential.

5.8.3 Treatment studies with acetic acid as electrolyte solution

Four different set of experiment were conducted by using Acetic acid (AA). The effect of EOF on the treatment efficiency of TPHs in soil has also seen in these sets.

In the set conducted with 1 M AA under 40 V DC, EOF retained during the experimental period which resulted with an average treatment efficiency of 44.51%.

The set operated under 20 V DC with 0.5 M AA, EOF moved backwards and forwards continuously, as a result; cumulative EOF was -36.36 mL. The average treatment efficiency in this set was 82.74 mL because of the negative movement of EOF towards the cathode that obtains higher treatment efficiencies in front of the anode. This movement also affected the pH levels in the electrolyte chambers, which increased above 11 after the 72nd hour in cathode, and decreased below 2 in anode at the end of first 96 hours.

When 40 V DC was applied with 0.5 M AA as electrolyte solution, EOF appeared in reverse direction and retained in first 72 hours, moved forward for the next 24 hours, and then retained until the end of the experiment by supplying 13.67 mL of EOF.

The highest TPHs removal efficiency was achieved in the set operated under 20 V of DC with 1 M AA. In this set, EOF was 52 mL at 24th hour, moved forward in first 72 hours, and then retained. But, the highest EOF yielded was this set (82,23 mL) among the ones completed with Acetic acid. Additionally, the final soil pH was more acidic (4.22 in anode front and 5.75 in cathode front) which is an evidence of an H^+ transport from anode to soil and raise in soil zeta potential that increases the EOF. This set was also the experiment that evenly distributed remaining contaminants in soil sections was detected.

PAHs are well treated in the sets, except the one conducted with 20 V DC with 0.5 M AA (55.83%). In the set the highest TPHs treatment yielded (20 V DC with 1 M AA), PAHs treatment efficiency was 84.64%. The electrokinetic remediation with 40 V DC resulted with better PAHs treatments; 85.62% for 1 M AA and 91.36 % for 0.5 M AA. The set with 1 M AA under 40 V DC, showed higher treatment efficiencies for PAHs in 2nd and 3rd Groups.

5.8.4 Treatment studies with ethanol as electrolyte solution

In the electrokinetic treatment of TPHs by using ethanol (EtOH) as electrolytic solution, it was observed that the applications with 1 M EtOH concentration give higher removal rates (91.87% - 94.22 %) than 0.5 M applications (82.27% - 89.3%). The electroosmotic flow in all the experiments with EtOH solution was quite low (between -5 and 5 mL) because of the lower dielectric constant of the ethyl alcohol (24.3 at 25°C) that decreases the dielectric constant of the solution when they are mixed with water that has a dielectric constant of 78.54 at 25°C (Saichek & Reddy, 2003). That means, ethanol solution may be loaded less number of ions than the pure water can carry. The soil pH levels after the treatment and the pH levels in the electrolytic chambers are around neutral levels in the tests conducted with EtOH.

Since the cumulative EOFs were such low, its effect on electrokinetic treatment was not very dominant. But there are two major requirements from organic contaminants removal from the soils; i) the sufficient soil-solution-contaminant interaction, and ii) the electrolyte solution should be capable of dissolving the contaminant (Saichek & Reddy, 2003). Ethanol is a good solvent for organic contaminants, and it is able to carry TPH and PAH compounds. That's why, in the experiments with 1 M EtOH yielded with higher removal efficiencies.

PAHs are effectively treated in all the sets conducted with ethanol. But, the set with 1 M EtOH under 40 V DC electrical potential resulted with the highest efficiency and the evenly distributed remaining contaminants were found in all of the soil sections. Furthermore, in this experiment, the 1st Group PAHs are also well treated.

5.8.5 Operational cost analysis of the systems used and their comparison with the systems reported in the literature

The electrokinetic systems in this study were operated for 192 hours (8 days), 20 V or 40 V DC electrical potential was applied, and 0.5 M or 1 M NaOH, Acetic acid, and ethanol were used as electrolytic solutions, as well as pure water. The liquid volume in the fixed soil bed was 0.375 L, and the operational costs were calculated according to the prices of electricity and chemicals used in the systems. The calculated operational costs for 1 m^3 dry soil are given in Table 5.2 as in Turkish Lira (TL) and USD ($).

According to the Table 5.2; the minimum and maximum operational costs are calculated for 20 V DC application with pure water (8.5 TL/5.7 $ for 1m^3 dry soil) and 40 V DC application with 1 M Acetic Acid (124 TL/82.7 $ for 1m^3 dry soil).

In the use of NaOH, total operational costs will be 24.7 – 49.3 $/$m^3$ dry soil, while it will be 38-76 $/$m^3$ dry soil (ds) for the use of ethyl alcohol.

The energy need of the systems are 34.8 kWh/ m^3 ds for 20 V DC and 69.6 kWh/ m^3 ds for 40 V DC, which are quite low compared with the energy needs of the electrokinetic study reported by Han et al. (2010) as high as 188-599 $/$m^3$ ds.

Gomez et al. (2009) also reported that, the unit energy cost for an electrokinetic treatment system to remove benzo[a]pyrene and reactive black from the soil was 80.6 kWh/m^3 ds.

Yuan & Weng (2004) compared the commercial electrokinetic systems of SAEK and Lasagna and the approximated operational costs are reported as 17-42 $ and 50-120 $, respectively, for a cubic meter of dry soil.

Table 5.2 Analysis of the Operational costs for the systems

Cost Item, unit	**Unit Price**	**20 V DC**		**40 V DC**	
		0.5 M	**1 M**	**0.5 M**	**1 M**
NaOH, t	6000 TL (4000$)	30 TL (20$)	60 TL (40$)	30 TL (20$)	60 TL (40$)
Pure Water, m^3	4 TL (3.3$)	1.5 TL (1$)		1.5 TL (1$)	
Acetic acid, m^3	5000TL (3333 $)	55 TL (36.7 $)	110 TL (73.4 $)	55 TL (36.7 $)	110 TL (73.4 $)
Ethyl Alcohol, m^3	6000 TL (4000$)	50 TL (33.3 $)	100 TL (66.6 $)	50 TL (33.3 $)	100 TL (66.6 $)
Electricty, kWh	0,2 TL (0.13$)	7 TL (4.7 $)	7 TL (4.7 $)	14 TL (79.3 $)	14 TL (9.3 $)

Same authors denoted that the operational costs for soil heating/vapor extraction systems are between 85.5 and 94 $/m^3 ds, while the unit operational costs for chemical oxidation is between 100 and 153 $/m^3 ds.

When the operational costs are considered, the investigated systems investigated express a low to medium level expenses, depending on the type of the electrolytic solution used. Since the applied electrical potentials are low and the treatment interval is as short as 192 h (8 days), the energy costs of the systems are very low.

CHAPTER SIX
CONCLUSIONS

In the content of this thesis, electrokinetic remediation of contaminated soils by petroleum hydrocarbons, which are frequently detected organic contaminants in polluted sites, was investigated.

A natural clean soil collected from an agricultural area was used to obtain veridical results and to complete the deficiency of data about the behavior of the natural soils under electrokinetic treatment conditions.

Engine oil was used as the contaminant, which is a mixture of hydrocarbons, to simulate the actual circumstances met in a polluted site, where many hazardous organic compounds can be detected.

The electrokinetic system was operated under different conditions. NaOH, Acetic acid, and ethyl alcohol were used as electrolytic solutions in two different concentrations; 0.5 M and 1 M, as well as pure water.

Additionally, the effect of applied electrical potential was investigated by conducting the systems under 20 V or 40 V DC.

The performance of the electrokinetic treatment was tested by following the TPHs and PAHs in soil.

For the understanding the effects of the electrokinetic phenomenon on contaminated natural soils, the parameters of extent and behavior of electroosmotic flow during treatment, pH changes in electrolyte reservoirs during the treatment period and in the soil sections after the treatment, and gas productions from the system are followed.

Furthermore, cost analysis of the systems is completed and the results are compared with the previous works on electrokinetic treatment and with the unit costs reported about the other treatment methods.

The findings of the study are reported and discussed in the previous chapters. Here, the concluded points are presented as follows:

- The treatment of TPHs are realized in applied electrokinetic conditions and the highest treatment efficiency was seen in the set conducted with 1 M ethyl alcohol as electrolyte solution under the electrical potential of 20 V.

- Except in the use of pure water, higher TPH removal efficiencies has seen in the sets operated under 20 V DC.

- The achievement of the electrolytic solution on the treatment TPHs can be given as decreasing order as follows according to the average data of the sets studied: Ethyl alcohol> Acetic acid>pure water> NaOH

- It was observed that the treatment efficiency increases as the electroosmotic flow (EOF) increases in the sets operated with NaOH, Acetic acid, and pure water.

- It was also recognized that, continuous changes in the direction of EOF adversely effects the treatment of the contaminants, since they move between anode and cathode and could not be removed.

- It was detected that the direction of EOF is less important than its stability in one direction (towards anode or cathode), because in the cases with dominant reverse EOFs treatment of TPHs could be achieved.

- The extent of the electrolysis in the electrolyte chambers are important for treatment when the soil medium receives higher pH values, since H^+ ions produced at anode could migrate to the soil and increase the zeta potential of the soil that controls the electroosmotic flow.

- Electrolysis (electromigration) and electroosmosis are the major phenonmenon affecting the treatment efficiency, which are controlling each other. In the systems operated, any evidence on the effects of electrophoresis could not be detected.

- PAHs are the compounds which have low solubility, and their response to applied treatment conditions is partially different from TPHs.

- The highest PAH treatment efficiency was detected in set operated under 40 V of DC with 0.5 M of NaOH as high as 94.46%.

- In contrast with the TPHs, PAHs are well treated in the sets conducted under 40 V of DC electric potential, except the set with pure water, which is a poor solvent because of its high polarity. It should be indicated that, in the sets with pure water, PAH groups are treated evenly.

- Acetic acid and NaOH solutions resulted with better PAHs removal than the pure water when the achieved maximum treatments are considered, since they contain extra H^+ and OH^- ions, respectively, for stimulating the electroosmotic flow.

- 0.5 M of NaOH and Acetic acid obtained high PAHs removal under 40 V DC, which is in contrast with ethanol solution that gave the higher treatment efficiency with 1 M concentration.

- The consistent removal of PAHs in soil sections are detected in the sets with ethanol. As ethanol is a good solvent for the organic compounds, even EOF was low; the removal of both TPHs and PAHs could be achieved in all the sets.

- The 3rd Group PAHs, which has a high concentration, are treated up to 98% in the sets with NaOH, Acetic acid, and ethanol. The 2nd Group PAHs, which has the highest solubility, is the group with lowest removal rate, especially with ethanol.

- The achievement of the electrolytic solution on the treatment PAHs can be given as decreasing order as follows according to the average data of the sets studied: NaOH> Ethyl alcohol>pure water> Acetic acid

- The maximum and minimum operational costs of the systems are determined as 82.7 \$/m^3 of dry soil and 5.7 \$/m^3 dry soil, for 40 V DC application with 1 M Acetic acid and 20 V DC application with pure water, respectively.

- The interval given for the operational costs are representing a system with low to medium level expenses relative to the other systems.

- The energy need of the system was quite low (34.8 kWh/ m^3 dry soil), due to the short treatment interval and moderate electrical potential application.

When the systems are analyzed according to the TPHs and PAHs treatment efficiencies and the operational costs, the use of 0.5 M Acetic acid under 40 V of DC electrical potential results with 89.99% TPHs and 91.36% PAHs treatment efficiency with a operational cost of 46 \$/m^3 dry soil, which can strongly compete with the systems reported previously.

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APPENDIX

Table 1. PAHs treatment efficiency, % (20 V 0.5 M NaOH)

Distance from anode, cm	**Acenaphthylene**	**Acenaphthene**	**Fluorene**	**Phenanthrene**	**Anthracene**	**Carbazole**	**Fluoranthene**	**Pyrene**	**Benz(a)anthracene**	**Chrysene**	**Benzo(b)fluoranthene**	**Benzo(k)fluoranthene**	**Benzo(a)pyrene**	**Indeno(1,2,3-cd)pyrene**	**Dibenz(a,h)anthracene**	**Benzo(g,h,i)perylene**
4	74.40	81.16	88.43	88.34	83.93	78.34	89.71	84.85	87.90	74.59	76.81	85.72	83.80	97.18	99.58	81.22
8	60.27	84.05	85.47	86.85	86.97	91.98	89.00	83.34	94.41	74.12	83.66	95.09	69.16	93.41	99.92	89.45
12	76.25	81.29	89.42	91.29	92.87	87.14	91.66	88.07	92.39	74.99	72.77	80.96	80.03	94.53	99.83	87.19
16	40.94	82.35	88.86	82.63	87.87	89.53	86.17	73.89	88.03	75.25	87.88	82.19	65.17	95.56	99.57	93.96
20	84.35	85.55	93.48	89.93	92.94	76.96	94.07	91.50	88.71	85.78	92.97	54.87	85.14	97.49	99.85	90.24
24	74.90	78.56	89.51	80.62	93.00	80.43	87.79	81.87	69.99	72.67	82.25	16.95	85.36	93.32	99.77	86.46

Table 2.PAHs treatment efficiency, % (20 V 1 M NaOH)

Distance from anode, cm	**Acenaphthylene**	**Acenaphthene**	**Fluorene**	**Phenanthrene**	**Anthracene**	**Carbazole**	**Fluoranthene**	**Pyrene**	**Benz(a)anthracene**	**Chrysene**	**Benzo(b)fluoranthene**	**Benzo(k)fluoranthene**	**Benzo(a)pyrene**	**Indeno(1,2,3-cd)pyrene**	**Dibenz(a,h)anthracene**	**Benzo(g,h,i)perylene**
4	60.58	56.42	86.10	64.94	85.04	60.63	84.06	55.13	29.73	33.51	47.03	41.51	46.20	81.75	99.44	38.75
8	66.71	82.02	89.01	90.54	91.35	78.16	91.92	86.70	93.87	78.23	88.40	80.50	83.14	95.07	99.75	85.13
12	71.53	79.94	85.54	88.46	90.65	80.31	91.14	87.24	92.11	68.10	84.80	75.44	70.27	91.08	99.59	90.97
16	85.99	86.30	94.22	94.82	93.44	79.30	95.05	93.46	91.72	83.93	86.47	90.48	80.37	97.35	99.84	96.22
20	30.76	69.69	84.71	78.21	77.74	51.48	85.34	75.95	85.71	53.48	76.37	77.43	73.38	93.41	99.70	69.80
24	42.30	67.67	79.45	76.19	85.41	54.89	86.35	77.37	80.46	64.70	70.75	45.20	51.74	91.35	99.55	77.50

Table 3.PAHs treatment efficiency, % (40 V 0.5 M NaOH)

Distance from anode, cm	**Acenaphthylene**	**Acenaphthene**	**Fluorene**	**Phenanthrene**	**Anthracene**	**Carbazole**	**Fluoranthene**	**Pyrene**	**Benz(a)anthracene**	**Chrysene**	**Benzo(b)fluoranthene**	**Benzo(k)fluoranthene**	**Benzo(a)pyrene**	**Indeno(1,2,3-cd)pyrene**	**Dibenz(a,h)anthracene**	**Benzo(g,h,i)perylene**
4	92.83	76.19	97.13	41.77	96.02	93.86	71.60	40.20	90.36	92.51	94.01	87.90	90.01	95.89	99.91	63.59
8	91.47	68.26	97.19	41.01	95.67	87.42	74.39	35.53	89.58	93.04	93.65	87.44	88.90	95.22	99.90	62.47
12	92.64	75.64	97.26	58.56	97.73	89.97	92.72	65.11	92.25	93.89	94.99	84.53	94.01	97.68	99.87	91.41
16	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
20	93.48	66.55	97.40	43.04	94.38	93.50	74.61	35.85	93.05	91.92	94.37	91.88	88.34	96.42	99.85	72.64
24	95.21	82.58	97.92	65.35	94.14	98.18	91.32	60.03	90.73	95.44	97.77	94.79	83.57	96.92	99.95	92.07

Table 4. PAHs treatment efficiency, % (20 V Pure water)

Distance from anode, cm	**Acenaphthylene**	**Acenaphthene**	**Fluorene**	**Phenanthrene**	**Anthracene**	**Carbazole**	**Fluoranthene**	**Pyrene**	**Benz(a)anthracene**	**Chrysene**	**Benzo(b)fluoranthene**	**Benzo(k)fluoranthene**	**Benzo(a)pyrene**	**Indeno(1,2,3-cd)pyrene**	**Dibenz(a,h)anthracene**	**Benzo(g,h,i)perylene**
4	41.23	84.63	75.38	79.49	89.59	80.85	90.87	84.85	88.56	75.65	77.77	80.81	79.26	93.99	99.80	90.18
8	73.81	84.21	88.11	79.07	87.39	79.54	88.46	81.57	83.08	65.01	80.85	67.46	66.17	94.35	99.53	87.59
12	59.91	81.86	77.76	76.72	83.45	68.17	84.82	76.07	86.72	66.15	77.07	92.02	55.07	89.69	99.49	93.63
16	64.83	82.50	84.59	77.36	85.57	65.72	86.32	79.40	74.42	71.11	81.82	62.54	81.25	94.62	99.78	87.06
20	73.69	89.16	89.51	84.02	94.24	83.13	92.76	89.91	82.80	75.57	87.53	70.07	81.25	97.71	99.81	94.29
24	64.88	90.39	85.92	85.25	91.97	94.20	92.26	88.32	82.59	80.95	86.21	86.64	85.02	97.09	99.90	93.56

Table 5. PAHs treatment efficiency, % (40 V Pure water)

Distance from anode, cm	**Acenaphthylene**	**Acenaphthene**	**Fluorene**	**Phenanthrene**	**Anthracene**	**Carbazole**	**Fluoranthene**	**Pyrene**	**Benz(a)anthracene**	**Chrysene**	**Benzo(b)Fluoranthene**	**Benzo(k)fluoranthene**	**Benzo(a)pyrene**	**Indeno(1,2,3-cd)pyrene**	**Dibenz(a,h)anthracene**	**Benzo(g,h,i)perylene**
4	34.03	71.31	58.96	76.45	76.13	50.04	81.32	73.15	87.68	59.50	75.23	82.81	71.49	92.42	99.69	91.84
8	72.99	82.73	83.58	87.87	87.61	85.04	87.84	83.09	88.93	67.57	84.01	90.94	78.37	94.58	99.82	89.78
12	70.11	82.36	83.53	87.50	87.24	84.86	88.97	85.20	69.78	73.38	84.89	82.19	85.36	98.57	99.85	95.09
16	59.02	81.37	81.12	86.51	84.03	88.33	86.62	80.45	87.15	70.95	84.45	83.11	81.92	97.58	99.78	90.71
20	56.31	80.15	82.45	85.29	83.91	75.83	87.59	81.53	86.78	75.81	87.17	72.37	81.03	97.49	99.66	90.18
24	67.10	83.35	86.04	88.49	88.39	77.20	88.75	84.42	84.87	73.85	84.28	90.94	86.47	96.64	99.65	94.23

Table 6. PAHs treatment efficiency, % (20 V 0.5 M Acetic acid)

Distance from anode, cm	**Acenaphthylene**	**Acenaphthene**	**Fluorene**	**Phenanthrene**	**Anthracene**	**Carbazole**	**Fluoranthene**	**Pyrene**	**Benz(a)anthracene**	**Chrysene**	**Benzo(b)fluoranthene**	**Benzo(k)fluoranthene**	**Benzo(a)pyrene**	**Indeno(1,2,3-cd)pyrene**	**Dibenz(a,h)anthracene**	**Benzo(g,h,i)perylene**
4	12.29	26.52	17.02	19.40	8.42	21.02	32.45	23.78	56.79	6.59	54.39	6.65	33.18	20.83	21.02	9.95
8	21.54	35.10	49.12	27.97	39.39	29.76	49.60	43.24	30.70	19.85	30.22	13.80	34.95	11.97	29.76	40.30
12	46.76	50.21	83.70	42.97	84.37	46.59	60.79	55.08	23.94	14.61	63.17	18.95	37.88	28.09	46.59	41.69
16	40.38	35.95	81.34	28.78	64.27	31.23	21.93	14.71	28.90	14.28	13.36	26.21	30.23	8.77	31.23	48.00
20	43.89	39.76	83.26	32.52	71.58	36.14	40.07	33.52	21.39	10.55	29.87	30.11	31.54	31.43	36.14	6.47
24	35.52	26.49	78.75	19.55	61.38	18.15	0.25	1.78	18.08	1.92	42.59	23.28	8.55	5.95	18.15	15.30

Table 7. AHs treatment efficiency, % (20 V 1 M Acetic acid)

Distance from anode, cm	**Acenaphthylene**	**Acenaphthene**	**Fluorene**	**Phenanthrene**	**Anthracene**	**Carbazole**	**Fluoranthene**	**Pyrene**	**Benz(a)anthracene**	**Chrysene**	**Benzo(b)fluoranthene**	**Benzo(k)fluoranthene**	**Benzo(a)pyrene**	**Indeno(1,2,3-cd)pyrene**	**Dibenz(a,h)anthracene**	**Benzo(g,h,i)perylene**
4	25.87	78.45	74.61	70.03	86.79	81.27	83.31	80.24	68.81	60.05	64.42	85.42	63.17	92.42	99.50	73.45
8	52.08	85.30	82.58	76.88	86.65	90.49	86.64	82.73	74.98	70.37	76.19	69.60	79.59	97.27	99.67	86.46
12	49.09	88.08	79.19	79.66	89.50	93.96	88.29	83.70	85.47	68.97	83.05	80.20	80.92	98.43	99.73	93.63
16	48.73	86.69	81.58	78.27	88.37	81.39	87.61	83.43	88.31	71.27	80.15	77.74	80.92	93.90	99.61	91.70
20	45.89	88.41	78.03	79.99	88.21	87.38	89.64	85.98	92.39	69.34	86.82	88.79	75.82	96.10	99.71	94.69
24	7.67	84.17	67.92	75.75	84.96	87.97	86.45	82.22	91.79	69.39	84.98	91.86	79.37	97.35	99.86	87.66

Table 8. PAHs treatment efficiency, % (40 V 0.5 M Acetic acid)

Distance from anode, cm	**Acenaphthylene**	**Acenaphthene**	**Fluorene**	**Phenanthrene**	**Anthracene**	**Carbazole**	**Fluoranthene**	**Pyrene**	**Benz(a)anthracene**	**Chrysene**	**Benzo(b)fluoranthene**	**Benzo(k)fluoranthene**	**Benzo(a)pyrene**	**Indeno(1,2,3-cd)pyrene**	**Dibenz(a,h)anthracene**	**Benzo(g,h,i)perylene**
4	86.99	50.56	95.22	21.47	92.32	86.50	92.63	85.67	95.31	83.58	95.44	86.21	70.69	96.20	99.22	94.65
8	80.57	56.57	95.87	25.44	94.26	92.95	93.88	86.03	98.39	96.80	97.14	94.64	91.01	95.26	99.60	90.42
12	91.78	36.91	95.88	33.84	94.38	79.45	95.25	91.73	97.16	97.36	96.16	89.28	97.22	98.48	99.82	91.67
16	80.82	78.85	96.83	52.75	88.34	92.22	95.56	93.09	98.22	94.51	97.23	96.17	96.11	98.57	99.94	92.93
20	68.53	5.27	93.09	53.11	86.97	70.70	90.73	77.72	95.77	83.04	97.05	79.16	89.01	91.19	98.97	90.15
24	88.78	79.69	97.62	54.31	95.99	90.76	96.48	94.03	93.73	94.19	97.77	93.26	68.69	96.65	99.94	98.02

Table 9. PAHs treatment efficiency, % (40 V 1 M Acetic acid)

Distance from anode, cm	**Acenaphthylene**	**Acenaphthene**	**Fluorene**	**Phenanthrene**	**Anthracene**	**Carbazole**	**Fluoranthene**	**Pyrene**	**Benz(a)anthracene**	**Chrysene**	**Benzo(b)fluoranthene**	**Benzo(k)fluoranthene**	**Benzo(a)pyrene**	**Indeno(1,2,3-cd)pyrene**	**Dibenz(a,h)anthracene**	**Benzo(g,h,i)perylene**
4	1.62	75.97	60.08	78.49	85.96	83.49	89.08	84.35	91.70	72.06	81.46	68.84	77.92	96.59	99.87	88.19
8	37.55	81.10	76.74	83.62	88.91	81.15	89.81	86.59	92.58	70.21	81.11	82.04	80.70	95.16	99.81	90.64
12	64.71	81.74	83.16	84.26	87.34	72.30	87.43	76.41	94.60	70.66	73.12	86.03	84.58	95.43	99.86	86.40
16	52.24	79.82	81.14	82.34	85.28	71.76	86.00	80.34	94.80	65.75	82.96	73.60	77.48	94.49	99.84	89.45
20	76.18	85.32	88.00	87.84	90.87	87.79	91.26	88.37	93.06	70.16	75.84	81.89	82.03	96.86	99.94	89.91
24	60.81	80.48	81.08	83.00	78.58	86.66	84.98	71.76	89.72	59.68	80.76	83.42	79.59	92.96	99.68	94.62

Table 10. PAHs treatment efficiency, % (20 V 0.5 M EtOH)

Distance from anode, cm	**Acenaphthylene**	**Acenaphthene**	**Fluorene**	**Phenanthrene**	**Anthracene**	**Carbazole**	**Fluoranthene**	**Pyrene**	**Benz(a)anthracene**	**Chrysene**	**Benzo(b)fluoranthene**	**Benzo(k)fluoranthene**	**Benzo(a)pyrene**	**Indeno(1,2,3-cd)pyrene**	**Dibenz(a,h)anthracene**	**Benzo(g,h,i)perylene**
4	84.84	50.28	94.76	14.70	95.27	14.38	92.51	87.91	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
8	79.64	58.87	95.46	17.86	94.69	90.70	92.27	88.33	69.17	96.00	89.18	90.65	98.56	97.54	99.81	96.17
12	93.73	66.67	96.01	26.83	93.25	83.16	93.47	89.75	97.13	95.76	95.08	94.94	84.68	95.04	99.20	94.58
16	80.96	34.66	92.07	29.37	92.54	61.16	89.20	81.56	94.68	66.49	94.81	90.96	89.68	94.10	99.83	96.76
20	91.50	61.21	94.87	18.91	93.90	78.91	92.95	88.77	92.53	89.81	92.13	95.56	87.01	96.92	99.74	95.90
24	85.46	48.25	94.63	8.11	94.39	91.79	91.18	88.99	93.12	87.63	94.10	88.20	73.14	91.24	99.60	92.07

Table 11. PAHs treatment efficiency, % (20 V 1 M EtOH)

Distance from anode, cm	**Acenaphthylene**	**Acenaphthene**	**Fluorene**	**Phenanthrene**	**Anthracene**	**Carbazole**	**Fluoranthene**	**Pyrene**	**Benz(a)anthracene**	**Chrysene**	**Benzo(b)fluoranthene**	**Benzo(k)fluoranthene**	**Benzo(a)pyrene**	**Indeno(1,2,3-cd)pyrene**	**Dibenz(a,h)anthracene**	**Benzo(g,h,i)perylene**
4	92.22	64.40	94.95	20.50	87.51	91.55	92.70	89.25	96.98	93.41	97.05	93.57	87.01	95.57	99.86	96.37
8	83.14	33.69	94.03	1.92	87.46	87.36	91.65	85.38	98.44	87.52	93.21	87.13	43.94	97.05	99.75	90.55
12	87.38	50.04	94.47	8.79	91.84	90.27	91.30	86.99	93.86	95.39	95.71	86.67	93.34	93.07	99.59	96.96
16	72.60	56.42	95.01	19.51	93.39	92.40	93.02	88.52	97.37	94.99	95.80	93.87	94.12	96.25	99.81	91.61
20	86.86	63.01	95.25	24.54	95.38	82.19	93.49	89.00	96.77	83.44	93.74	82.69	78.57	95.98	99.87	94.45
24	82.69	43.62	94.89	15.59	89.23	75.26	92.43	88.14	97.29	94.32	96.69	85.29	94.12	96.92	99.79	97.29

Table 12. PAHs treatment efficiency, % (40 V 0.5 M EtOH)

Distance from anode, cm	**Acenaphthylene**	**Acenaphthene**	**Fluorene**	**Phenanthrene**	**Anthracene**	**Carbazole**	**Fluoranthene**	**Pyrene**	**Benz(a)anthracene**	**Chrysene**	**Benzo(b)fluoranthene**	**Benzo(k)fluoranthene**	**Benzo(a)pyrene**	**Indeno(1,2,3-cd)pyrene**	**Dibenz(a,h)anthracene**	**Benzo(g,h,i)perylene**
4	87.92	68.24	96.40	22.12	93.80	90.27	59.45	4.40	90.51	93.73	84.89	83.15	83.46	92.18	99.65	33.99
8	88.69	61.36	96.66	41.37	95.60	91.00	77.51	5.41	92.36	91.20	89.27	79.32	82.57	94.55	99.79	66.63
12	91.54	74.62	97.28	40.17	96.46	96.90	68.80	6.10	92.38	95.55	92.67	90.65	87.57	95.84	99.92	61.61
16	91.59	71.91	97.12	38.10	96.64	96.23	69.76	4.89	95.77	87.36	94.10	89.89	87.23	95.04	99.96	59.89
20	91.21	72.61	97.26	50.18	96.43	95.02	82.30	11.50	95.14	93.81	95.35	88.05	89.90	96.16	99.92	73.11
24	88.35	65.26	96.52	4.41	93.66	87.42	40.15	10.11	90.56	89.15	87.48	85.14	67.92	88.96	99.69	3.11

Table 13. PAHs treatment efficiency,% (40 V 1 M EtOH)

Distance from anode, cm	**Acenaphthylene**	**Acenaphthene**	**Fluorene**	**Phenanthrene**	**Anthracene**	**Carbazole**	**Fluoranthene**	**Pyrene**	**Benz(a)anthracene**	**Chrysene**	**Benzo(b)fluoranthene**	**Benzo(k)fluoranthene**	**Benzo(a)pyrene**	**Indeno(1,2,3-cd)pyrene**	**Dibenz(a,h)anthracene**	**Benzo(g,h,i)perylene**
4	92.04	51.18	95.86	25.12	78.34	82.19	93.68	89.52	97.03	83.50	96.69	94.03	91.01	97.54	99.65	94.52
8	88.96	68.24	96.95	41.98	93.44	88.75	94.84	92.25	98.02	92.99	98.21	94.64	97.89	98.26	99.94	97.49
12	87.38	50.04	94.47	8.79	91.84	90.27	91.30	86.99	93.86	95.39	95.71	86.67	93.34	93.07	99.59	96.96
16	72.60	56.42	95.01	19.51	93.39	92.40	93.02	88.52	97.37	94.99	95.80	93.87	94.12	96.25	99.81	91.61
20	86.86	63.01	95.25	24.54	95.38	82.19	93.49	89.00	96.77	83.44	93.74	82.69	78.57	95.98	99.87	94.45
24	82.69	43.62	94.89	15.59	89.23	75.26	92.43	88.14	97.29	94.32	96.69	85.29	94.12	96.92	99.79	97.29