Electrokinetic remediation of a soil contaminated with anthracene by using different surfactants

A. R. Estabragh
Assistant Professor. Faculty of Soil and Water Engineering, University of Tehran, PO BOX 4411 Karaj 31587-77871, Iran
ORCID: 0000-0003-4545-2310
Tel: +98 261 2241119
Fax: +98 261 2226181
Email: raeesi@ut.ac.ir

M. Lahoori
Postgraduate Student, Faculty of Soil and Water Engineering, University of Tehran, PO BOX 4411 Karaj 31587-77871, Iran
Tel: +98 261 2241119
Fax: +98 261 2226181
Email: lahoori.m@ut.ac.ir

F.Ghaziani
Assistant Professor, Faculty of Agricultural, University of Tehran, PO BOX 4411 Karaj 31587-77871, Iran
Tel: +98 261 2248082
Fax: +98 261 2246752
Email: Ghaziani@ut.ac.ir

A. A. Javadi
Professor, Computational Geomechanics Group, College of Engineering, Mathematics and Physical Sciences, University of Exeter, Devon, EX4 4QF, UK
Tel: +44 1392 723640
Fax: +44 1392 217965
Email: a.a.javadi@exeter.ac.uk

Electrokinetic remediation of a soil contaminated with anthracene by using different surfactants

Abstract

Electrokinetic technique is one of the common methods that can be used for removal of organic contaminants in soil. There are some of organic contaminants with low solubility in water. In order to improve the efficiency of remediation it is possible to use appropriate surfactants as flushing solution. In this work non-ionic (Poloxamer 407 and Tween 80), anionic (sodium dodecyl sulfate, SDS) and humic acid (HA) with solution of 0.1 M NaOH were selected for improving the remediation of a soil contaminated with anthracene. The solution of NaOH and surfactants were used as anolyte but humic acid was mixed with contaminated soil. At the end of each test a number of soil samples were extracted from the middle of the soil at different distances from the anode and the removal of contaminant was measured by a HPLC (High Performance Liquid Chromatography) apparatus. The results show that the effectiveness of solution surfactants and NaOH in removal of anthracene was SDS>Tween 80> Poloxamer 407. In addition, the results indicate that effect of humic acid on remediation is less than SDS and more than non–ionic surfactants.

Key words: organic contaminants, electrokinetic technique, surfactant, humic acid

Introduction

In some areas of the developing world, rapid commercial and technological growth is increasing the extent of the problem of soil pollution. Often, industrial processes have led, accidentally or otherwise, to chemical spills or leaks. These chemicals would then escape into the ground, and from there could contaminate groundwater supplies or remain in the soil until disturbed at a later date. In recent years, more attention has been given to the remediation of contaminated land. Electrokinetic is one of the techniques that is used for remediation of soil and it involves the application of an electric field to soil. The applied current of electricity through the soil leads to a number of phenomena that are named electromigration, electrophoresis and electroosmotic flow. Electromigration is the term that describes the transport of ions in pore fluid. Electrophoresis includes the transport of the colloidal or charged materials through the soil and electroosmosis involves creation of a flow of water in mass of soil. One of the major effects of applying electric current through a soil mass is the electrolysis of water molecules at the electrodes. Hydrogen gas and hydroxyl ions are produced at the cathode and oxygen gas and hydrogen ions at the anode. These reactions lead to acidic and basic environment around anode and cathode. These productions cause the hydrogen and hydroxyl ions to migrate through soil due to the electric field and diffusion and create a pH gradient through the soil mass. Therefore one of the effects of electrokinetic phenomenon involves changes in the chemistry of soil such as development of pH gradient. Acar and Alshawabkeh (1993) explained many of the effects that occur in soil due to pH changes subjected to an electric field. They described removal of lead and calcium from kaolinite due to the gradient of pH in soil mass. Eykholt and Daniel (1994) examined the major influences of pH and changes to

2

pore water chemistry on efficiency of pollutant removal. They used copper contaminated soil to show that pH has a dominant effect on the overall processes with high pH leading to high electroosmotic flow but also leading to the precipitation of metal contaminants. It has been also shown that this method can be used for remediation of soil contaminated by organic matters. Bruell *et al*. (1992) demonstrated removal of a range of water soluble organic contaminants such as benzene, xylene and hexane by this method. Similar reports were also presented by Acar *et al*. (1992) and Kim *et al*. (2000).

Polycyclic aromatic hydrocarbons (PAHs) such as anthracene are common contaminating matters in environment. The source of these contaminants is industrial activities that are spread in environment such as soil and water. Masih and Taneja (2006) reported that these groups of chemical components are insoluble in water, persistent in soil and many of them can be carcinogenic. The remediation of soil from these kinds of organic components by methods such as electrokinetic is relatively difficult because of their insolubility in water and their behavior to remain attached to soil particles and organic substances in soil. Maturi *et al*. (2009) and Lu and Yuan (2009) suggested using suitable surfactants for solving this limitation during remediation by the electrokinetic technique. Surfactant can enhance the solubility of organic components when it is used as flushing solution in anode and/or cathode. Surfactants are surface active agents that are used to reduce interfacial tension and increase solubility of non-aqueous phase liquids through a process called micelles solubilization. They are classified based on their nature as anionic, cationic and non ionic. Therefore, the selection of the appropriate surfactant is important in removal of PAHs and hydrocarbons from soil. Saichek and Reddy (2003), Khodadoust *et al*. (2005) and Park *et al*. (2007) showed that this technique can remove PAHs and

hydrocarbon by 60-90% from a contaminated kaolin in the laboratory. Lancolet *et al*. (1990), Acar *et al*. (1993), and Kim and Lee (1999) used surfactants for removal of petroleum hydrocarbons, hexachlorobutadiene and diesel oil from the soil. Saichek and Reddy (2005) used a surfactant to enhance electrokinetic remediation of two kinds of soil contaminated with phenanthrene and found that the surfactant was sufficient for removal of the contaminant from the soil. Park *et al*. (2007) used a surfactant for removal of phenanthrene from kaolin. Boulakradeche *et al*. (2015), Mao *et al*. (2015), Hahladakis *et al*. (2016), Estabragh *et al*. (2016), Alden *et al*. (2016) and Wei *et al*. (2017) used surfactant for enhancing the electerokinetic remediation of soil contaminated with organic matter. They reported that some of the examined surfactants can improve the remediation of contaminated soil.

Surfactant agents have also been widely adopted for stabilization of clayey soils, which enhance the compatibility, induce the bearing capacity and reduce swelling (Park *et al*., 2006; Onyejekwe and Ghataora, 2015 and Soltani *et al*., 2017)

A review of the literature shows that investigation on the remediation of a soil contaminated with anthracene by the electrokinetic method is relatively rare, except the study that was done by Boulakradeche *et al*., (2015). In this work the solution of NaOH and surfactant was used as anolyte to lower the critical micelle concentration and to increase the electroosmotic flow. Therefore, the aim of this work is to study the effect of different kinds of surfactants (anionic and non ionic) along with NaOH on remediation of a soil contaminated by anthracene.

Materials and methods

The materials that were used in this work were soil, anthracene, ionic surfactant, non ionic surfactant, NaOH and humic acid. A summary of the characteristics of these materials is presented below:

1-Soil

A clay soil was used in this work. The physical and mechanical properties of this soil were determined according to ASTM standard and are summarized in **Table 1**. The soil can be classified as clay with low plasticity (CL) according to the Unified Soil Classification System (USCS). The maximum dry unit weight and optimum water content of the soil were determined (according to the ASTM standard compaction test) as 17.75 kN/m3 and 17.90% respectively. XRD (X-ray diffraction) tests were conducted on samples of this soil and the results are shown in **Fig.1**. As shown in **Fig.1a** the minerals of soil include quartz, calcite, clay minerals, feldspar (Na, Ca) and fledspar (K). The results also show that the clay minerals of kaolin are illite, chlorite and montmorillonite (**Fig.1b**). The chemical properties of the soil are summarized in **Table 2**.

2- Anthracene

Anthracene is a chemical substance from PAHs (Polycyclic aromatic hydrocarbons) group with chemical formula $C_{14}H_{10}$ and molecular weight and density equal to 178.23 g/mol and 0.7407 g/mL respectively. Its chemical structure is composed of three fused benzene rings. Its appearance may vary from a colorless to pale yellow crystal like solid. Its water solubility at 25^0C is 0.044g/L and its boiling and melting points are 340^0C and 218^0C respectively. The major application of it is in production of dyes, plastics and pesticides. PAHs components are relatively resistant to biodegradation and can remain in the environment for a long time (Maliszewska-Kordybach, 1999; Wild and Jones, 1995).

Jensen and Folker-Hansen (1995), Ren *et al*. (1996), Smreczak and Maliszewska-Kordybach (1999) and Maliszewska-Kordybach *et al*. (2000) indicated that existence of anthracene in soils may exhibit a toxic activity towards different biological elements of the environment such as plants, microorganisms and invertebrates.

3-Anionic and Non-ionic surfactants

Surfactants can increase the solubility of organic contaminants in the aqueous phase by solubilizing hydrophobic organic contaminants into micelles. However, the adsorption of surfactant onto soil or soil organic substances can decrease the efficiency of remediation. Anionic surfactants are less likely to be absorbed to the soil because of their negative charge but they interfere with electroosmotic flow (Mulligan *et al*., 2001 and Han *et al*., 2009). In this work SDS (sodium dodecyl sulfate) was chosen as anionic surfactant with HLB (Hydrophilic-Lipophilic Balance) equal to 22. Its chemical formula and molecular weight are $NaC_{12}H_{25}SO_4$ and 288.5 g respectively.

Non-ionic surfactants are appropriate for the electrokinetic process because their neutral charge does not affect electroosmotic flow and they are biodegradable (Han *et al*., 2009). Poloxamer 407 and Tween 80 were selected as non-ionic surfactant in this work. The HLB values of them were 20 and 13.4 respectively. Poloxamer 407 is a hydrophilic non-ionic surfactant. The majority of the common uses of it are related to its surfactant behaviors. It is widely used in cosmetics for dissolving oily gradients in water. This surfactant has never been applied before in electrokinetic remediation of contaminated soils/sediments or even used as extracting agents except by Hahladakis *et al*. (2014). It has been used by some authors with NaOH as anolyte. In this work the solution of 0.1 M

NaOH and the above surfactant or cosolvent were used to increase the electroosmotic flow.

4- Humic acid

Humic acid (HA) is a principal component of humic substances, which are the major organic constituents of soil. It is produced by biodegradation of dead organic matter. It is not a single acid; rather, it is a complex mixture of many different acids containing carboxyl and phenolate groups so that the mixture behaves functionally as a diabasic acid or, occasionally, as a tribasic. Humic acids can form complexes with ions that are commonly found in the environment creating humic colloids. A typical humic substance is a mixture of many molecules, some of which are based on a motif of aromatic nuclei with phenolic and carboxylic substituents, linked together. It is usually dark brown to black in colour, with high CEC (400 – 870 meq/100g).

Electrokinetic apparatus

The electrokinetic test setup that was used in this work is the apparatus that was designed and fabricated by Estabragh et al. (2016). It is similar to those used by Mohamedelhassan and Shang (2001) and Ritirong *et al*. (2008) for simulating contaminant transport. Fig.2 shows the schematic plan of the apparatus. As shown in the figure, this apparatus consist of main cell, a loading frame and a D.C. power supply. The main cell was made of Plexiglas with thickness of 1 cm and its length, width and height are 30, 10 and 25 cm respectively. At the two sides of the main cell two reservoirs, namely anode and cathode reservoirs, were added. They were connected to the main cell through perforated Plexiglas sheets. These reservoirs can be filled by desired fluid and the total hydraulic head in them can be controlled by adjusting two identical standing tubes through valves. Two electrodes were vertically placed at a distance of 5 cm from the soil in the main cell.

This kind of arrangement of electrodes was also used by Hahladakis *et al*. (2014). They were EVD material that were made of copper foil covered with conductive polymer. The front and back of the soil samples were covered by two pieces of saturated geotextile in order to inhibit the migration of colloidal particles of soil into the electrode components as used by Jeon *et al*. (2010) and Kim *et al*. (2009). For measuring the electrical potential along the soil during the test, a number of voltage probes were installed at the bottom of the main cell. The distance of them from anode was 2, 5, 8 and 11 cm. A loading system was made for applying load to the soil in the main cell. The loading system involved a plate that is placed at the top of the sample and is connected to another plate at the bottom of it by a bar that was covered with a foam material to isolate against electric current. The load was applied on the sample through the bottom plate. A dial gauge was mounted on the top plate for measuring the vertical deformation due to the settlement of soil. The power supply for D.C. current consisted of a generator to produce various ranges of voltage and connected to the EVD through special connection.

Sample preparation and test procedure

For preparing soil samples contaminated with anthracene, 500 mg anthracene per kg of soil was considered based on the recommendation of USEPA (2000). Saichek and Reddy (2003) used phenanthrene with concentration of 500 mg/kg for their work and Delgado-Balbuers *et al*. (2013) also used 500 mg/kg of anthracene in their research work. The solubility of anthracene in water is very low but it is completely dissolved in acetone (Eibes *et al*., 2005). Therefore, the mixture of acetone and anthracene (10 g anthracene per one liter acetone) was subsequently mixed as spray with the measured amount of soil. The soil-acetone-anthracene mixture was placed in a tray for nearly one week until the

acetone completely evaporated and the contaminated soil was dry. After that the dry contaminated soil was mixed with a measured amount of distilled water and mixed manually until the water content of it reached more than liquid limit (i.e., in saturation condition). The moist soil was kept in a sealed cover for 48 hours for uniform distribution of water in it. The prepared soil was then poured into the main cell of apparatus in several layers and each layer was tamped into the cell so that the entrapped air could go out and the space between the particles reached to minimum. After that the whole soil was placed in the main cell, the cell was assembled and other accessories were connected to it. After that the anode and cathode reservoirs were filled with desired solutions so that the level of fluid in them was the same as the level of soil in the main cell. A total of 5 tests were conducted on the contaminated soil samples with different anolyte fluids as shown in **Table 3**. Test 1 was considered as reference test and the anode and cathode reservoirs were filled with distilled water. In the rest of the Tests (2, 3 and 4 the anode was filled with mixture of solution of 0.1 molar NaOH and desired surfactant or cosolvent (Poloxamer 407, Tween 80 or SDS). The amount of cosolvent that was used in this work was 1% for Poloxamer or SDS and 3% for Tween 80. Test 5 was conducted on the contaminated soil that was mixed with humic acid with concentration of 250 mg/kg soil and during the test the anode reservoir was filled with solution of 0.1 molar NaOH. A constant voltage gradient of 1.5 V/cm was applied for duration of 7 days for all tests. During the tests, the pH, EC, and discharge volume of fluid flow out of the cathode were measured periodically. At the end of the tests, soil samples were extracted at the middle section of the main cell at constant distances from anode (7, 14, 21 and 28 cm). For chemical analysis of the extracted samples the procedures of sample preparation was

done according to the (EPA 1986-3540). In this method the extracted soil samples were dried, then 2 g of each sample was selected and mixed with 5 cm^3 of hexan and acetone mixture with ratio of 2:1. It was shacken for 2 minutes for uniform mixing, and then it was put in centrifuge for about 5 minutes with 3500 rpm for settlement of particles and separation of the liquid-solid phases. The liquid phase was passed through a filter with mesh size of 0.45 um and then this extracted liquid was injected to the HPLC (High Performance Liquid Chromatography) apparatus. Before performing the chemical analyses the HPLC was calibrated by using a standard pure compound. A standard pure compound was injected to the apparatus and the peak in the chromatogram was assigned based on the retention time of the standard. The peak areas or heights were used to determine the concentration of released contamination from the sample. Comparing the response of the unknown concentration to that of the known (standard) concentration is used to find the amount of concentration in the released leaching liquid.

Results and discussion

In what follows, the results obtained from the test program are presented and discussed.

pH

The electrokinetic remediation was conducted with pH control in both electrode reservoirs. It is seen from **Fig.3** for Test 1 that a rapid acidification occurred at the anode to pH of 3.5 and alklinaztion of catholyte up to pH of 12 due to the electrolysis of water. The acid and alkaline fronts penetrate in the soil from anode and cathode respectively and change the properties of soil. As the results the soil close to anode becomes acidified and close to cathode alkalinized. For Test 2 in which the anolyte liquid is solution of 0.1 m NaOH and Poloxmer 407, the final values of pH at anode and cathode are 5.45 and 12

respectively. The final values of pH for Tests 3 and 4 are 7.35 and 6.11 at anode and nearly 12 at cathode for both tests (**Fig.3).** Figure 3 also shows the variations of pH with time in the anode and cathode reservoirs during the tests. As shown in this figure, when the reservoirs are initially filled with distilled water, the initial pH for both reservoirs is 7. However, during the test a reduction and increase in the values of pH are observed in the anode and cathode respectively; at the end of test the values of pH at anode and cathode reach to 3.5 and nearly 12 respectively. For Test 5 in which humic acid was mixed with contaminated soil and both reservoirs were filled of distilled water, the final value of pH at anode was 5.5. Comparison of the results shows that using NaOH with cosolvent prevents from reduction in the value of pH and formation of acidic front at anode.

EC (Electrical Conductivity)

EC was measured during the tests in both electrode reservoirs (**Fig.4)**. The results of these tests provide information about the concentrations of ions in the reservoirs. As shown in this figure, the values of EC are increased from the initial value at both electrode reservoirs for all tests but the amount of increase at the cathode reservoir is more than the anode. **Fig.4** shows that the final values of EC at anode for different anolyte fluids are more than 4 ds/m except for the solution of NaOH and Tween 80 for which it reaches to 3.85 ds/m (Test 3). The values of EC at the end of the tests for the different catholyte fluids are not the same and depend on the anolyte liquid that was used. For the solution of Poloxmer 407 and SDS (Tests 2 and 4) at anode, the final values of EC at cathode are nearly 8.5 ds/m but when distilled water or solution of Tween 80 is used in the anode reservoir, they are 6.4 and 5.8 ds/m respectively. For Test 5 in which

humic acid was mixed with the contaminated soil, value of EC in cathode reservoir was 10.3 ds/m at the end of the test.

Discharge water

The cumulative volumes of flow out from cathode reservoir are shown in **Fig.5** for different tests. As shown in this figure for Test 1 the cumulative volume of flow out fluid at the end of Test is 685 cm^3. When the anolyte fluid is solution of NaOH with Tween 80 or Poloxmer 407 the final volume of flow out fluids are 1316 and 1270 cm^3 but for the case of solution of NaOH and SDS the flow out volume of fluid is reached to the 1915 cm^3. It is resulted that the outflow of fluid is dependent on the type of surfactant. When comparing with the results of Test 1 it is seen that the solution of NaOH and surfactant causes increase in the volume of outflow from the cathode reservoir. Fig.5 shows that for the case of humic acid mixed with contaminated soil, the volume of the outflow water is 2910 cm^3 more than the other tests.

Remediation

The removal of organic contaminants from the soil with an enhanced electrokinetic treatment depends on the ability of the surfactants to extract or desorbe the contaminant from the soil particle surface and maintain the contaminant in the solution forming micells. Then these micells are usually removed from the soil by electroosmosis. Therefore, two features can be considered in the removal of anthracene: the electroosmotic flow and solubility of contaminants with surfactants. **Fig.6** shows the percent of removal of anthracene from the soil at different distances (7, 14, 21 and 28 cm) from anode. As shown in Fig.6 when the anolyte reservoir is filled with distilled water the amounts of removal of anthracene at distances of 7, 14, 21 and 28 cm are 3.47, 3.03,

1.61 and 0.0 % respectively. It is seen that the removal of anthracene is not considerable. It can be said that, in this case the remediation is not effective using the electrokinetic technique because water cannot desorb or extract the anthracene from the soil particles. The results show that when NaOH with cosolvent is used as the anolyte fluid, the percent of removal of contamination is increased in comparison with Test 1. In all cases the percent of remediation is decreased with increasing the distance from the anode. It is found from the results that solution of NaOH and SDS as anolyte is more effective in remediation than the other solutions. For example at distance of 7 cm from anode the percent of removal of contaminating substance is nearly 38.2% for solution of SDS; this value is changed to 25 and 34% when the anolyte fluid is solution of Poxome or Tween 80. The results show that the mixture of humic acid is also effective in remediation of soil (Fig. 6) and its effect on remediation is similar to the effect of the SDS solution.

Discussion

When an electrical current under a potential is applied to a system of soil and fluid across the electrodes, it causes the electrolysis of fluid at the electrodes according to the following reactions:

$2H_2O \longrightarrow O_2(g) + 4H^+ + 4e^-$ at anode

$4H_2O + 4e^- \longrightarrow 2H_2(g) + 4OH^-$ at cathode
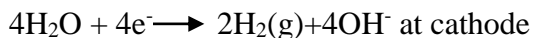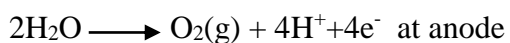
The above equations indicate that the electrolysis reactions produce acidic and alkali solutions at anode and cathode respectively. The mechanism of contaminant transport during electrokintic consists of electromigration, electroosmosis and electrophoresis. Electromigration includes the transport of present ion species in the pore fluid. This process includes the migration of $4H^+$ and OH^- towards the electrode with opposite

charge. However, the accumulation of gas at the electrode/soil interface increases the electrical resistance of the system against electrical current and hence decreases the efficiency the remediation.

Fig.3 shows the variations of pH at anode and cathode reservoirs during the tests. As shown in this figure, by adding 0.1 M NaOH with surfactant the value of pH is increased at anode reservoir in comparison with the results of Tests 1 (distilled water as anolyte and catholyte). It can be said that adding NaOH can change the values of pH at anode reservoir because the increase in the value of pH at anode causes reduction in the number of H^+ ions at the anode reservoir by reaction with OH^- that is resulted from NaOH. The results (Fig.6) show that using distilled water as anolyte and catholyte is not very effective in removing anthracene from the contaminated soil. This can be attributed to the low solubility of anthracene in water. Therefore, it can be concluded that electrokinetic remediation of soil contaminated with hydrophobic organic matter is not possible by using water during the remediation process (Maturi *et al*., 2009). By using surfactant for remediation the percent of removal of contaminant is increased (Fig. 6). The use of surfactant increases the extraction and solution of hydropholic organic matter and leads to formation of micells (as indicated by Reddy and Saichek 2003) and transportation by electroosmotic flow. The results show that the percent of remediation by using Tween 80 and Poloxamer 407 at the distance of 7 cm from anode is 34 and 25 % respectively. It is concluded that Tween 80 is more effective than Poloxamer 407 in remediation of anthracene-contaminated soil. The results (Fig.5) show at the end of the test the volume of fluid discharge is 1316 and 1270 cm^3 for the sample with Tween 80 and Poloxamer 407. This indicates that Tween 80 is more effective than Poloxamer 407 in discharge of

fluid from the sample. It is resulted that both the type of surfactant and the volume of fluid discharge from sample are important in remediation of soil. Tween 80 and Poloxamer 407 are non-ionic surfactants that penetrate into soil mass by electroosmosis from anode. The fact that Tween 80 is more effective than Poloxamer can be attributed to the lower critical micelle concentration (CMC) and higher hydrophile-hipophile balance (HLB) of Tween 80 in comparison with Poloxamer. Surfactants with high HLB number are more soluble in water and a low HLB indicates that the surfactant is more soluble in an organic solvent. The results show that the solution of SDS is considerably more effective than the Tween 80 and Poloxamer 407 surfactants in remediation of the contaminated soil. Fig. 5 shows that when using SDS, Tween 80 and Poloxamer solutions the volume of fluid discharge from the soil is 1915, 1270 and 1316 cm^3 respectively. It is resulted that the SDS solution is more effective than the other solutions in fluid discharge from the soil. SDS is an anionic surfactant and in this work it was used as anolyte as used by Yang *et al*. (2005) and Park *et al*. (2007). Ko *et al*. (1998) indicated that when using SDS as anolyte, it is possible that the charge density of it may be decreased at lower pH at anode and it may enter in the contaminated soil mass. The SDS in the soil forms micelles that enclose the contaminants and they are transported to the cathode by electroosmotic flow. These results are agreement with the results that were reported by Yang *et al*. (2005) and Park *et al*. (2007) for remediation a contaminated soil from phenanthrene.

Fig.6 shows that at distance of 7 cm from anode, the percent of remediation is 39.2, 25 and 34% for the solutions of humic acid (HA), Poloxamer 407 and Tween 80 respectively. It is seen that HA is more effective in remediation than the other solutions. On the other

hand, the volumes of discharge fluid for solutions of HA, Poloxamer 407 and Tween are 2910, 1316 and 1270 cm^3 respectively. It shows that the discharge of fluid for HA solution is more than the other solutions. HA is a natural polyelectrolyte that is formed by enzymatic degradation of plant polymers. In this process carboxylic acid groups are formed at one or more ends of polymer segment (Wershaw, 1993). Conte *et al*. (2005) reported that the unaltered segments of polymer will be relatively more hydrophobic than carboxylated segments. Therefore, the resulting polymer has both hydrophilic and hydrophobic moieties in its structure. In addition, HA has the function of surfactant in reducing sorption of organic contaminants on soil particles and enabling desorption-remediation of PAH (Conte *et al*., 2001 and Kim and Lee, 2002). Therefore, HA exhibits surface activity in aqueous solution and forms micelles that are transported to the cathode by electroosmotic flow.

The zeta potential is an indicator of the surface charge properties of the soil solids suspended in a fluid-electrolyte system. It is dependent on several factors including the charge on the surface of particles and conductivity of the pore solution (Saichek and Reddy; 2003). The zero point of charge (ZPC) is referred to the pH at which the net charge on the surface of particles is zero. When the value of pH is above the ZPC the zeta potential of soil is negative and electroosmotic flow occurs toward the cathode. Conversely, when the pH is less than ZPC the zeta potential is positive and the osmotic flow occurs to the anode. Therefore, the amount of cumulative water that flows out of the sample is dependent on the zeta potential. So, the decrease in the volume of water is resulted from the increase of zeta potential due to decrease in pH in the soil. Kaya and Yukselen (2005) studied the effect of ionic and non-ionic surfactants on the zeta potential

of clay particles. Their results showed that the surfactants produce negative zeta potential and the amount of fluid discharge is increased because the zeta potential.

It was observed from Fig.5 that the volumes of discharge fluid are 685, 1316, 1270, 1915 and 2910 cm^3 for distilled water, Poloxamer 407, Tween 80 and HA respectively. From comparison of the results it is concluded that discharge of fluid is increased by using solution of surfactant as anolyte. This can be attributed to the interaction that occurs between surfactant and soil particles and leads to the modification of zeta potential. The eletroosmosis flow is directly dependent on the value of zeta potential. Fig.5 shows that SDS causes higher volume of discharge flow out of contaminated soil in comparison the other surfactants. It is concluded that SDS produced negative zeta potentials and caused enhance the osmosis flow of fluid.

Soil remediation can be performed by this method in both in-situ and ex-situ conditions for saturated and unsaturated soils (De Battisti and Ferro, 2007). In this technique an electric field is created in the contaminated soil by inserting electrodes and passing low density direct current electricity. The contaminants are transported towards the electrodes and are pumped out. The area where the remediation occurs is only between the electrodes. This technique is applicable for a wide range of organic and inorganic contaminants. The in-situ method is preferred since it would be less expensive because the soil need not be removed; the amount of energy needed in situ would be comparatively lower than ex-situ procedures. This method also has some disadvantages. For example the pH around anode and cathode could remain acidic and basic for a duration after remediation (Kim *et al*., 2009) which affects the microbial activities in the soil after remediation

Conclusion

Electrokinetic treatment was used for removal of anthracene from a contaminated soil. Anthracene is hydrophobic and does not show electric charge, therefore its removal can be achieved by electrokinetic process using surfactants in the processing fluid to enhance the solubility of contaminants.

Two non-ionic surfactants (Poloxamer 407 and Tween 80) with combination of 0.1 M NaOH were used as anolyte. The results showed that both Poloxamer 407 and Tween 80 improved the efficiency of remediation of contaminated soil in comparison with distilled water as anolyte. Comparison of the non-ionic surfactants with ionic one (SDS) showed that the use of ionic surfactant results in a higher degree of remediation than non-ionic surfactants. The effect of humic acid is similar to the surfactants in improving the remediation of contaminated soils.

References

Acar, Y.B., and Alshawabkeh, A.N. (1993). Principles of electrokinetic remediation. Environ. Sci. Technol. 27, 1231.

Acar, Y.B., Li, H.-Y., and Gale, R.J. (1992). Phenol removal from kaolinite by electrokinetics. J. Geotech. Eng. 118, 1837.

Alden, A., David, R.S., Jun, N., Damian, S. and Michael, D.A. (2016). Improving Polycyclic Aromatic Hydrocarbon Biodegradation in Contaminated Soil Through Low-Level Surfactant Addition After Conventional Bioremediation. Environ. Eng. Sci., 33, 659.

Bruell, C.J., Segall, B.A., and Walsh, M.T. (1992). Electroosmotic removal of gasoline hydrocarbons and TCE from clay. J. Environ. Eng. 118, 68.

Boulakradeche, M.O., Akretche, D.E., Cameselle, C., and Hamidi, N. (2015). Enhanced electrokinetic remediation of hydrophobic organics contaminated soils by the combination of non-ionic and ionic surfactants. Electrochimica Acta, 174, 1057.

Conte, P., Agretto, A., Spaccini, R., and Piccolo, A. (2005). Soil remediation: humic acids as natural surfactants in the washings of highly contaminated soils. Environ. Pollut. 135, 515.

Conte, P., Zena, A., Pilidis, G., and Piccolo, A. (2001). Increased retention of polycyclic aromatic hydrocarbons in soils induced by soil treatment with humic substances. Enviro. Poll. 112, 27.

De Battlisti, De. And Ferro, S. (2007). Electrokinetic remediation methods of remediation of soils and ground waters (ERE 2005). Electrochimica Acta, 52, 3345.

Delgado-Balbuers, L., Aquilar-Chàvez, A.R., Luna-Guido, M.L., and Dendooven, L. (2013). Mixing of an anthracene-contaminated soil: a simple but efficient remediation technique? Ecotoxicol. Environ. Saf. 96, 238.

Estabragh, A.R., Bordbar, A.T., Ghaziani, F. and Javadi, A.A. (2016). Removal of MTBE from a clay soil using electrokinetic technique. Environ. Technol. 37, 1745.

Eykholt, G.R., and Daniel, D.E. (1994). Impact of system chemistry on electroosmosis in contaminated soil. J. Geotech. Eng. 120, 797.

Eibes, G., Cajthaml, T., Moreira, M.T., Feijoo, G., and Lema, J.M. (2005). Enzymatic degradation of anthracene, dibenzothiophene and pyrene by manganese peroxidase in media containing acetone. Chemosphere 64, 408.

Jensen, J. and Folker-Hansen. (1995) . Soil quality criteria for selected organic compounds. Working report no.47, Danish Environmental Protection Agency.

Jeon, C.-S., Yany, J.-S., Kim, K.-J. and Baek, K. (2010). Electrokinetic removal of petroleum hydrocarbon from residual clayey soil following wasing process. Clean, 38, 189.

Hahladakis, J.N., Lekkas, N., Smponias, A., and Gidarakos, E. (2014). Sequential application of chelating agents and innovative surfactants for the enhanced electroremediation of real sediments from toxic metals and PAHS. Chemosphere. 105, 44.

Hahladakis, J.N., Latsos, N. and Gidavakos, E. (2016).Performance of electroremediation in real contaminated sediments using a big cell, periodic voltage and innovative surfactants. J. Hazard. Mater., 320, 376.

Han, H.M., Lee, Y.J., Kim. S.-H., and Yang, J.W. (2009). Electrokinetic remediation of soil contaminated with diesel oil using EDTA-cosolvent solutions. Separ. Sci. Technol. 44, 2437.

Kaya, A. and Yukselen, Y. (2005). Zeta potential of soils with surfactants and its relevance to electrokinetic remediation. J. Hazard. Mater., B120, 119.

Kim, S.-O., Moor, S.-H., and Kim, K.-W. (2000). Enhanced electrokinetic soil remediation for removal of organic contaminants. Environ. Technol. 21, 417.

Kim, J., and Lee, K. (1999). Effects of electric field directions on surfactant enhanced electrokinetic remediation of diesel-contaminated sand column. J. Environ. Sci. Health, A. 34, 863.

Kim, Y. and Lee, D. (2002). Solubility enhancement of PCDD/F in the presence of dissolved humic matter. J. Hazard. Mater. B91, 113.

Kim, J.-H., Kim, J.-Y., and Kim, S.-S. (2009). Effect of H_2SO_4 and HCl in the anode purging solution for the electrokinetic-fenton remediation of soil contaminated with phenanthrene. J. Environ. Sci. Heahth. A. 44, 1111.

Khodadoust, A.P., Reddy, K., and Maturi, K. (2005). Effect of different extraction agents on metal and organic contaminant removal from a field soil. J. Hazard. Mater. B117, 15.

Ko, S., Schlautman, M.A., and Carraway, E.R. (1998). Effect of solution chemistry on the partitioning of phenanthrene to sorbed surfactants. Environ. Sci. Technol. 32, 3542.

Lancelot, F., Londiche, H., De Marsily, G. (1990). Experimental results on the influence of electric fields on the migration of oil, ionic species and water in prous media. J. Pet. Sci. Eng. 4, 67.

Lu, X., and Yuan, S. (2009). Electrokinetic removal of chlorinated organic compounds, Electrochem. Remediat. Technol Polluted Soils Sediments Ground, 219.

Maliszewska-Kordybach, B. (1999). Sources, Concentrations, Fate and Effects of Polycyclic Aromatic Hydrocarbons (PAHs) in the Environment Part A: PAHs in Air. Pol. J. Environ. Stud. 8, 131.

Maliszewska-Kordybach B, Smreczak B, Martyniuk S, (2000). The effect of polycyclic aromatic hydrocarbons (PAHs) on microbial properties of soils of different acidity and organic matter content. Roczniki Gleboznawstwo, (3-4), 5.

Mao, X., Jiang, R., Xia, W. and Yu, J. (2015). Use of surfactants for the remediation of contaminated soils: A review. J. Hazad. Mater., 285, 419.

Masih, A., and Taneja, A. (2006). Polycyclic aromatic hydrocarbons (PAHs) concentrations and related carcinogenic potencies in soil at a semi arid region of India. Chemosphere 65, 449.

Maturi, K., Reddy, K.R. and Camselle, C. (2009). Surfactant-enhanced Electrokinetic Remediation of Mixed Contamination in Low Permeability Soil. Sep. Sci. Technol., 44, 2385.

Mohamedelhassan, E., Shang, J.Q. (2001). Effect of electrode materials and current intermittence in electro-osmosis. Pro.Civ.Eng. Groun. Improv. 5, 3.

Mulligan, C.N., Yong, R.N., and Gibbs, B.F. (2001). Surfactant-enhanced remediation of contaminated soil: a review. Eng. Geol. 60, 371.

Onyejekwe, S. and Ghataora, G.S. (2015). Soil stabilization using proprietary liquid chemical stabilizers: sulphonated oil and a polymer. Bull. Eng. Geol. Environ., 74, 651.

Park, J.-Y., Lee, H.-H., Kim, S.J., Lee, Y.-J., and Yang, J.-W. (2007). Surfactant enhanced electrokinetic removal of phenanthrene from kaolinite. J. Hazard. Mater. 140, 230.

Park, J., Vipulanandan, C., Kim, J.W. and Oh, M.H. (2006). Effects of surfactants and electrolyte on properties of soil. Environ. Geol., 49,977.

Reddy, K.R., and Saichek, R.E. (2003). Effect of soil type on electrokinetic removal of phenanthrene using surfactants as cosolvents. J. Environ. Eng. 129, 336.

Ren, L., Zieler, L.F., Dixon, D.G., and Greenberg, B.M. (1996). Photoinduced effects of polycyclic aromatic hydrocarbons on Brassica napus (Canola) during germination and early seedling development. Ecotox. Environ. Safety 33, 73.

Ritirong, A., Douglas, R.S., Shang, J.Q., and Lee, E.C. (2008). Electrokinetic improvement soft clay using electrical vertical draind. Geosynth. Int. 15, 369-381.

Saichek, R.E., and Reddy, K.R. (2003). Effect of pH control at the anode for the electrokinetic removal og phenanthrene from kaolin soil. Chemosphere 51, 273.

Saichek, R.E., and Reddy, K.R. (2005). Electrokinetically enhanced remediation of hydrophobic organic compounds in soils. A review , Crit. Rev. Environ. Sci. Technol. 35, 115.

Smreczak, B., and Maliszewska-Kordybach, B. (2000). Effects of PAHs and Heavy Metals on Activity of Soil Microflora. in J. C. Block, V. V. Goncharuk and Ph.

Baveye (eds), Bioavailability of Organic Xenobiotics in the Environment, NATO ASI Series, Kluwer Academic Publishers, Dordrecht, Boston, London, 377.

Soltani, A., Deng, An, Taheri, A. and Mirzababaei, M. (2017). A sulphonated oil for stabilization of expansive soils. Int. J. Pavement Eng., Punlished online.

Wei, D., Hua, Z., Chao, S.Y., Rong, Z. and Sheng, Z.G. (2017). Surfactant-Enhanced Electrokinetic Remediation of Chromium and Phenanthrene Cross-Polluted Soils. Environ. Eng. Sci., 34, published online.

Wershaw, R.L. (1993). Model for humus in soils and sediments. Environ.Sci. Technol. 27, 814.

Wild, S.R., and Jones, K.C. (1995). Polynuclear aromatic hydrocarbons in the United Kingdom environment: A preliminary source inventory and budget. Environ. Pollut. 88, 91.

Yang, J.W., Lee, Y.-J., Park, J.-Y., Kim, S.-J., and Lee, J.-Y. (2005). Application of APG and Calfax 161-35 on surfactant enhanced electrokinetic removal of phenanthrene from kaolinite. Eng. Geol. 77, 243.

Table 1. Physical and mechanical properties of soil

Property	Standard Designation	Value
Specific gravity, G_s	ASTM D 854-10	2.71
Particle distribution		
Gravel (%)		0.0
Sand (%)		23.0
Silt (%)		52.0
Clay (%)		25.0
Consistency limits		
Liquid limit, LL (%)	ASTM D 4318-10	48.0
Plastic limit, PL (%)	ASTM D 4318-10	26.0
Plastic index, PI (%)	ASTM D 4318-10	22.0
Shrinkage limit, SL (%)	ASTM D 427-04	13.0
USCS classification	ASTM D 2487-11	CL
Compaction characteristics		
Optimum water content, w (%)	ASTM D 698-07e	17.9
Maximum dry unit weight, γ_{dmax} (kN/m^3)		17.75

Table 2. Chemical composition of soil

Chemical component	Amount	Chemical component	Amount
pH	7.8	Mg^{2+} (meq/L)	11.25
EC[a] (dS/m)	13.2	Cl^- (meq/L)	62.5
Na^+ (meq/L)	108.69	CO_3^{2-} (meq/L)	0.6
K^+ (meq/L)	0.20	HCO_3^- (meq/L)	5.0
Ca^{2+} (meq/L)	35.0	SO_4^{2-} (meq/L)	72.91
Ca CO_3 (%)	10.2	O.C.[b] (%)	0.11
		C.E.C.[c] (meq/100g)	8.42

a- Electric Conductivity
b- Organic Content
c- Cation Exchange Capacity

Table .3. Experimental plan

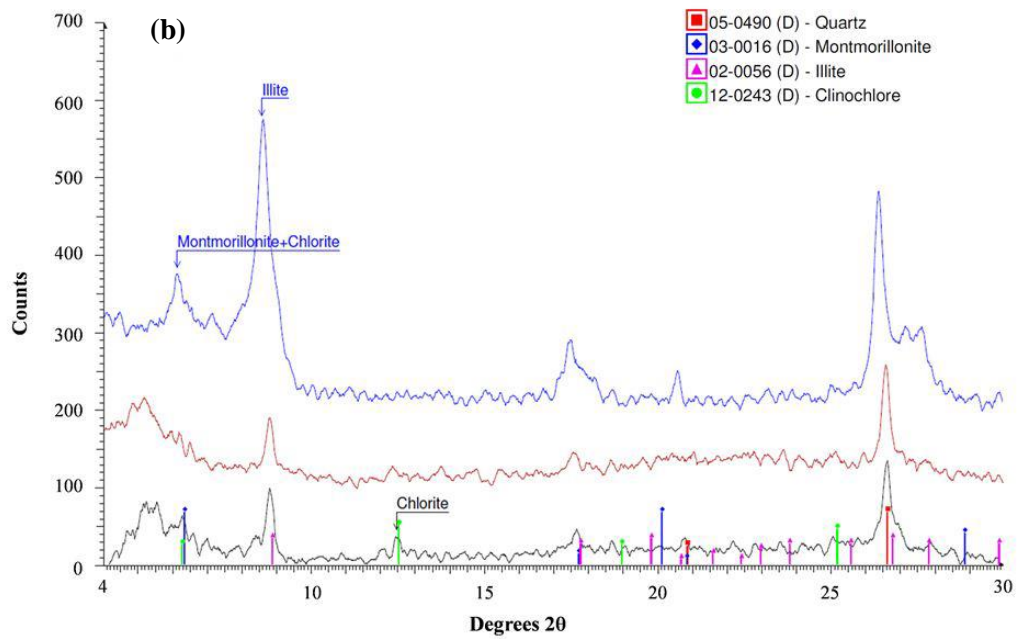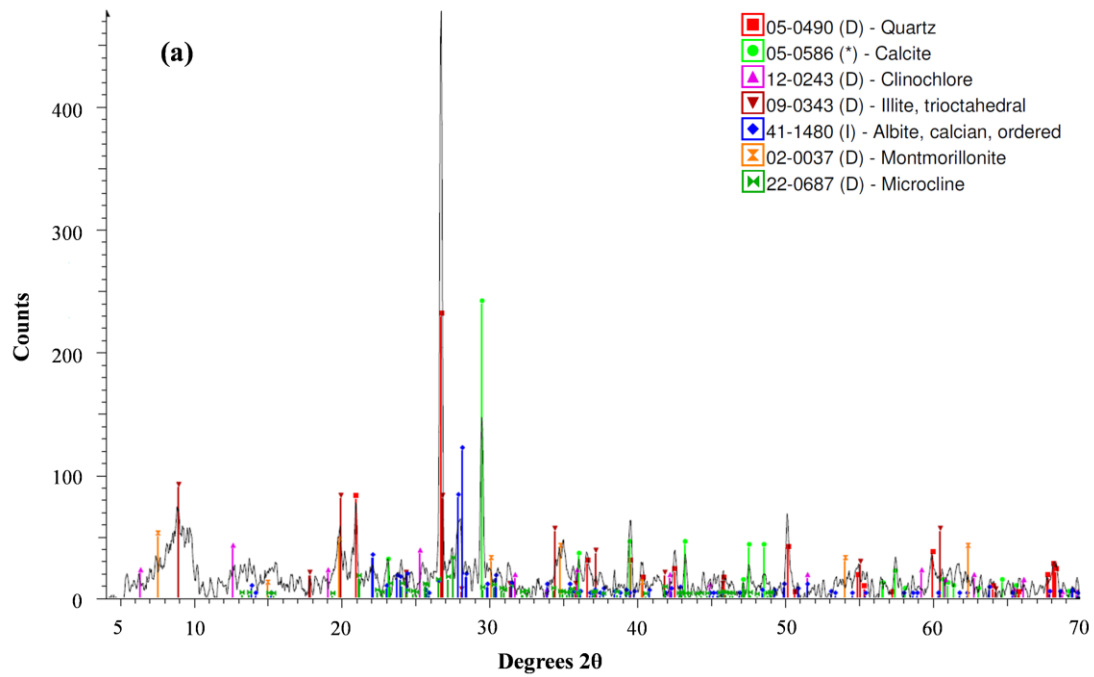| Test	Anolyte	Soil sample	Catholyte	Voltage gradient (v/cm)	Time (day)
1	Distilled water	Soil+anthracene	Distilled water	1.5	7
2	Poloxamer+0.1M NaOH	Soil+anthracene	Distilled water	1.5	7
3	Tween 80+0.1M NaOH	Soil+anthracene	Distilled water	1.5	7
4	SDS+0.1M NaOH	Soil+anthracene	Distilled water	1.5	7
5	Distilled water+0.1M NaOH	Soil+anthracene+ Humic acid	Distilled water	1.5	7

List of figures

Fig.1 X-ray diffraction (XRD) plots of (a) minerals of soil, (b) clay minerals

Fig.2. Schematic plan of the test set-up (dimensions in mm)

Fig.3. Variations of pH at anode and cathode reservoirs with time

Fig.4. Variations of EC (Electrical conductivity) at anode and cathode reservoirs with time

Fig.5. Cumulative volume of discharge fluid from cathode reservoir with time

Fig.6. Percent of remediation of soil by different flushing liquids at different distances from anode

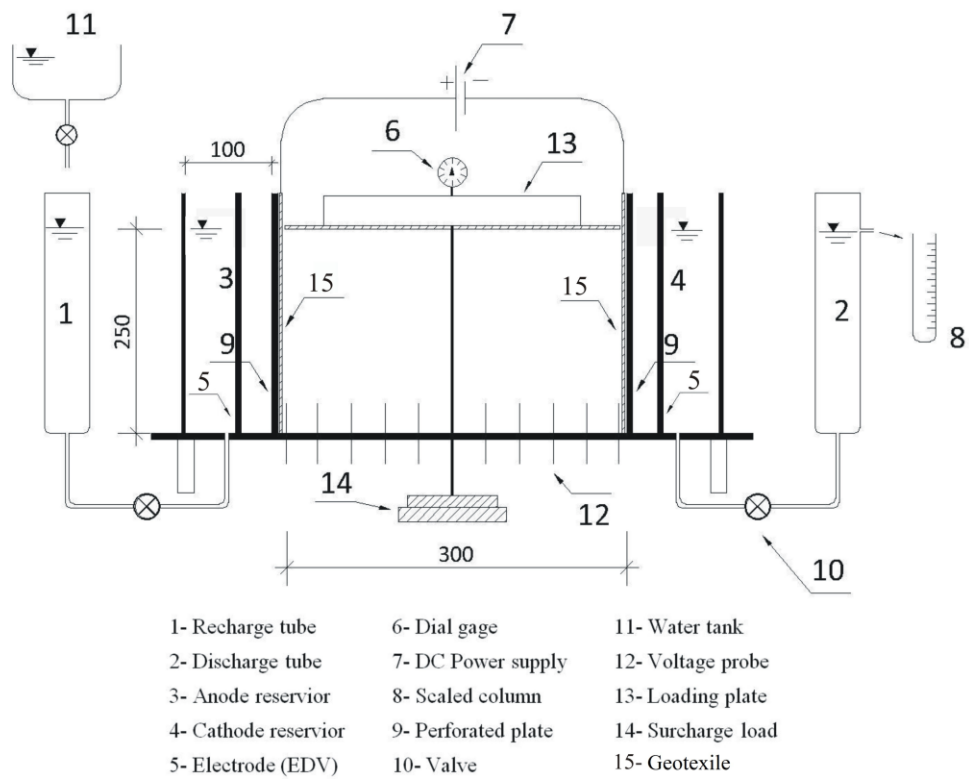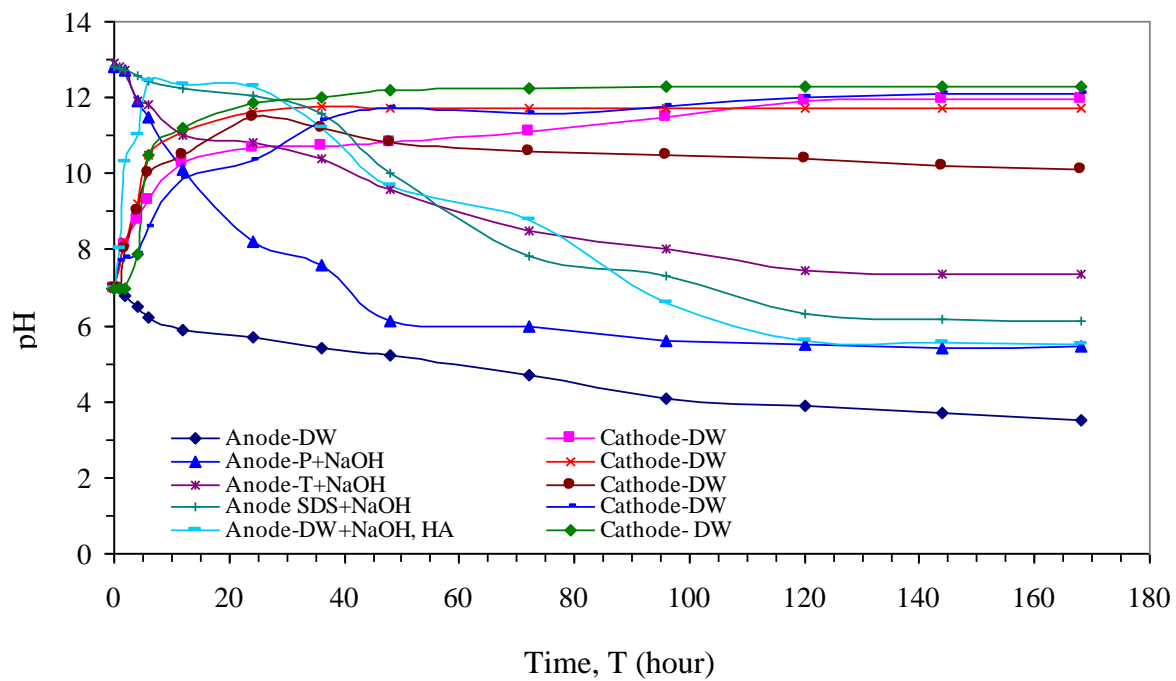**Fig.1** X-ray diffraction (XRD) plots of (a) minerals of soil, (b) clay minerals

1- Recharge tube   6- Dial gage   11- Water tank
2- Discharge tube   7- DC Power supply   12- Voltage probe
3- Anode reservior   8- Scaled column   13- Loading plate
4- Cathode reservior   9- Perforated plate   14- Surcharge load
5- Electrode (EDV)   10- Valve   15- Geotexile

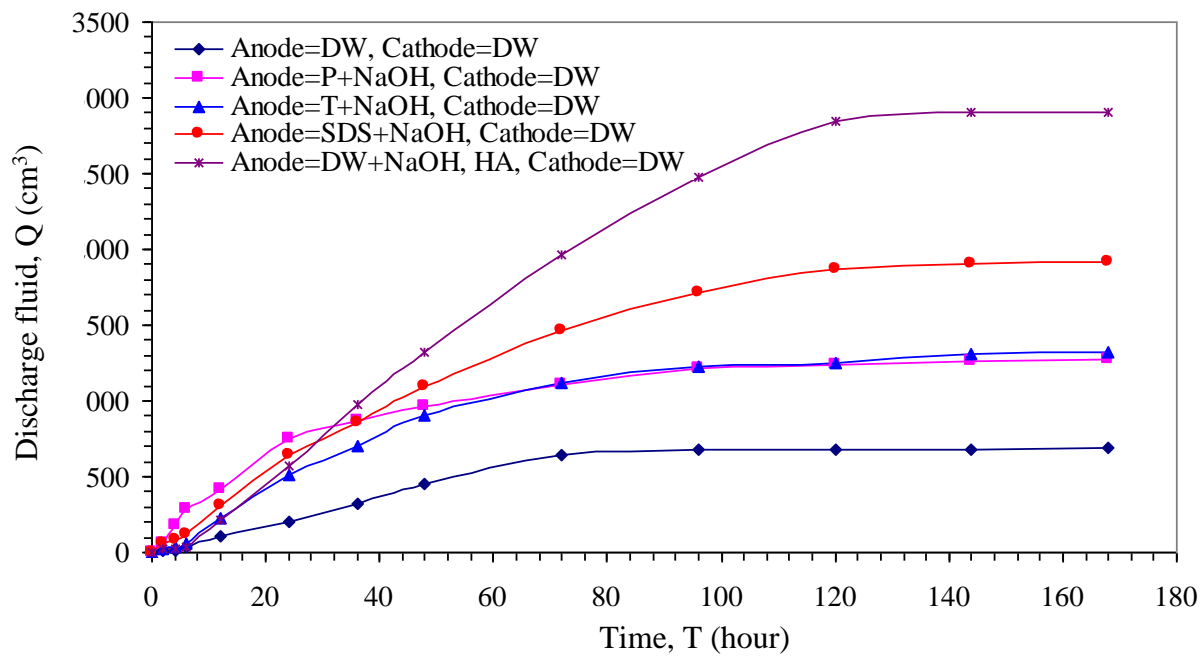**Fig.2.** Schematic plan of the test set-up (dimensions in mm)

DW= Distilled water, P= Poloxamer 470
T=Tween 80, HA= Humic acid

Fig.3. Variations of pH at anode and cathode reservoirs with time
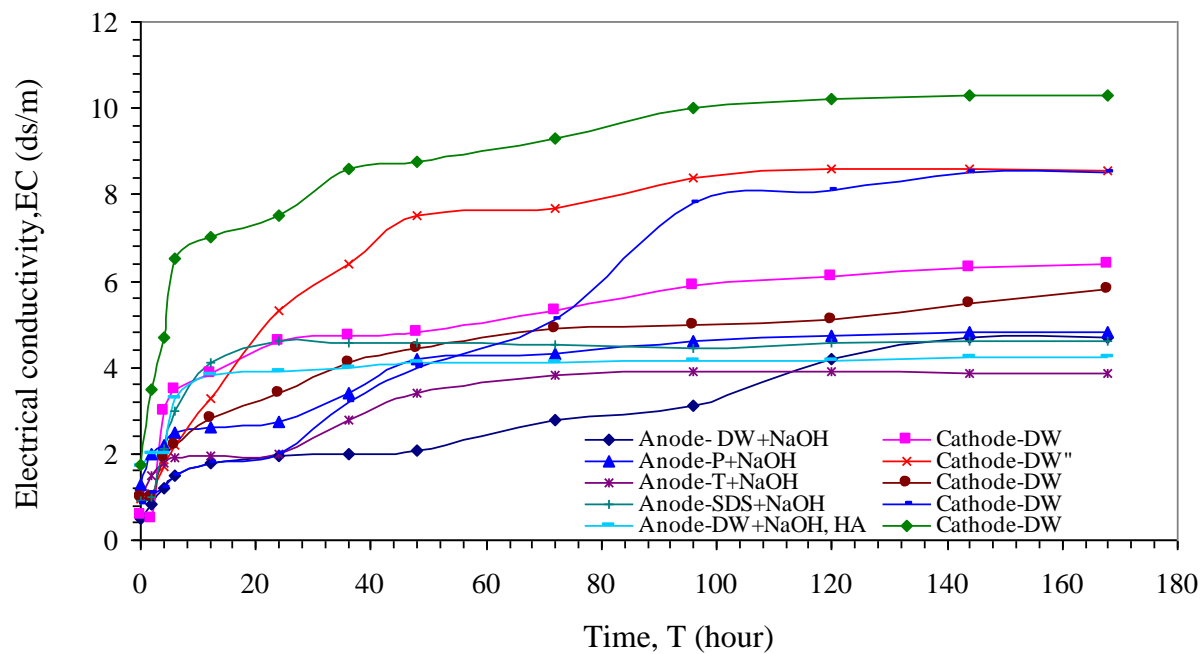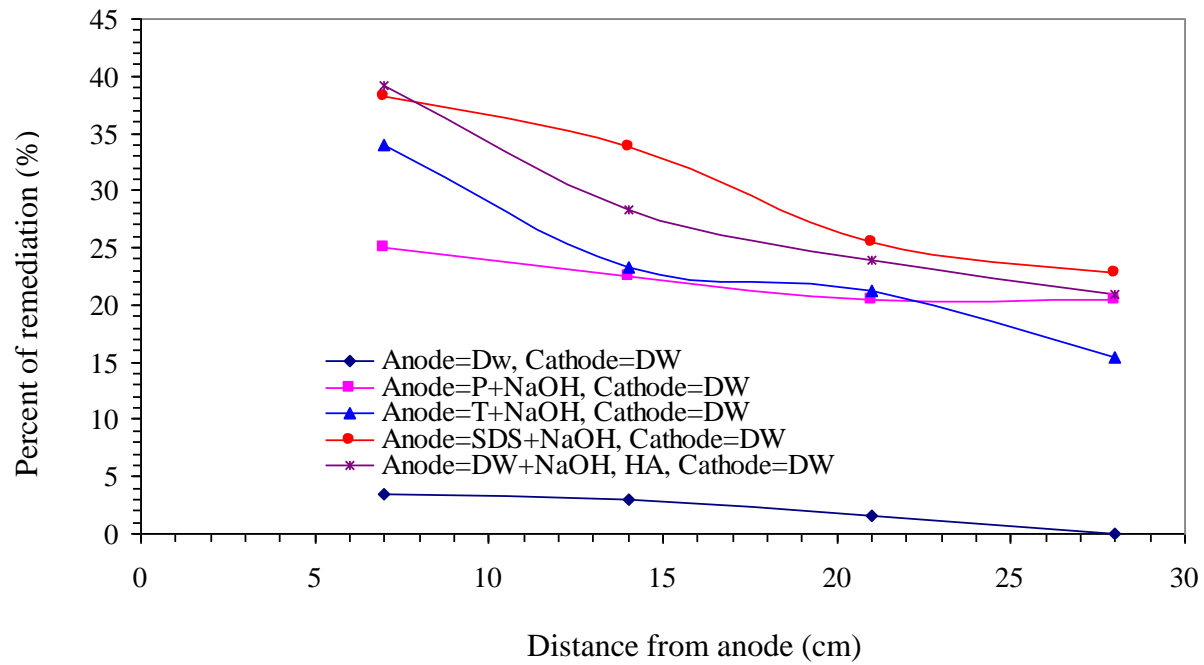
DW= Distilled water, P= Poloxamer 470
T=Tween 80, HA= Humic acid

Fig.4. Variations of EC (Electrical conductivity) at anode and cathode reservoirs with time

DW= Distilled water, P= Poloxamer 470
T=Tween 80, HA= Humic acid

Fig.5. Cumulative volume of discharge fluid from cathode reservoir with time

DW= Distilled water, P= Poloxamer 470
T=Tween 80, HA= Humic acid

Fig.6. Percent of remediation of soil by different flushing liquids at different distances
      from anode