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THE TREATMENT OF DIESEL CONTAMINATED SOIL BY DCTs METHODS

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In the present work, the results obtained after testing of two technologies that are based on the usage of an electric field to treat contaminated soil, are presented. The first technology is the electroremediation and the second one is the electro-flushing remediation. The tests were performed at laboratory scale during two different PhD researches. The treatment efficiency was up to 80% for the simple technology, while for the second one the recovery of the diesel contaminant was in proportion of 31.82%. The diesel that was not recovered and remained in soil will be removed by electrochemical processes.

Keywords: electro-flushing, electrochemical remediation, diesel, clay

1. Introduction

Soil contamination consists of many individual sites where the contamination occurred either in the past, or is still occurring. The number of such sites, and hence the area of contaminated land, should diminish with time as these sites are recognized, treated and returned to use. Also, it is possible that some land that has not yet been contaminated will become so at some time in the future [1, 2]. So, in terms of contamination we can speak about historical contamination and current contamination. A wide range of contaminated sites exists as historical contaminated sites [3]. This type of contamination of soils often occurs because of their use by industry and by processes and practices, which by current environmental standards would be judged inadequate. Although much of the contamination caused by these methods occurred since the beginning of the Industrial Revolution, some examples of much older contamination are known [1, 4, 5].

The present research is focused on the study of two types of treatments that are based on the application of electric field in a polluted soil. The two treatments are the electrochemical one based on the application of a constant

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voltage that corresponds to a specific voltage of 1 V/cm, and the electro-flushing that combines the first treatment with another one named flushing that involves the use of water (or other chemical substance) which has a movement direction from the anode towards the cathode.

2. Material and methods

This paper will present two type of research performed during two different PhD research. The first one was done at University POLITEHNICA of Bucharest and the second one was done in the frame of a co-supervised PhD between University POLITEHNICA of Bucharest, Romania and University of Trento, Italy. For the last research, the experimental part was done exclusively in the laboratories of University of Trento while for the first one the experiments were performed at University POLITEHNICA of Bucharest in the Laboratory of Renewable Energy and Environment from Power Engineering Faculty.

Taking into account the limitation of some of the treatments (including the flushing treatment), that is they are not applicable in a low permeable soil; we tried to use a method that could be efficient when it is used in a contaminated soil with a low permeability. The method is the electrochemical one, used also in combination with flushing treatment; the soil that was chosen is the clay because has a very low permeability.

For both experimental studies, the contamination was done artificially with diesel.

2.1.Electrochemical treatment – simple method

The electrochemical treatment is classified as a direct current treatment (DCTs) and it is based on the application of a constant voltage to two electrodes (anode and cathode) in order to induce an electric field in a polluted matrix (soil in our case). Electric fields as well as electron transfer processes have been used for the decontamination of soils and underground water containing unwanted organic or inorganic substances. The main phenomena involved in this process are: electrolysis, geochemical reactions, electrophoresis, electroosmosis, and electromigration.

Till nowadays, there are several examples of application of DCT to real cases of contamination across Europe [6] and America [7], but a deep knowledge of the phenomena ruling the remediation process has not been reached. Therefore, at the moment the calibration of the remediation action is mainly based on empirical data and on the results of field preliminary tests. Usually, for in situ DCT applications, the current density is of the order of milliamperes per square centimeter ($1 mA/cm^2$) and the electric potential difference is on the order of a few volts per centimeter across the electrodes placed in the ground (1V/cm) [7]. The electrodes can be made of different materials, as stainless steel or carbon, and they can be placed in the soil either in a vertical or horizontal array.

The electrochemical remediation depends on several important factors, as it will be presented in the following: soil chemistry or soil-contaminant interaction; water content; soil structure; positioning of the electrodes and electrode structure.

The electrode distribution when electrochemical remediation is applied can vary from the bench scale to commercial installations as it is presented in Fig 1.

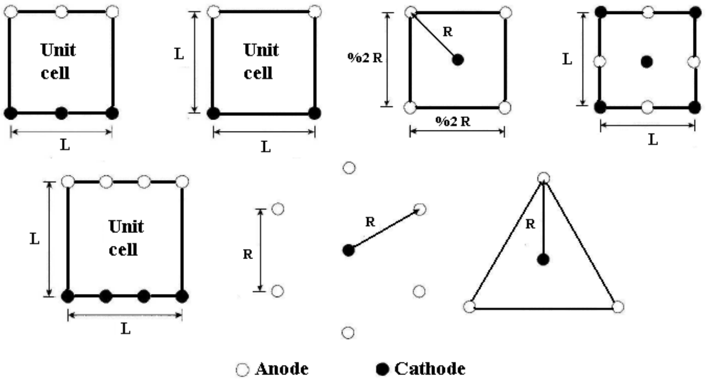

Fig. 1. Possible electrode distribution for the application of electrochemical remediation [6]

For our experimental studies we used two types of configurations, the rectangular one for the simple application of electrochemical treatment and the circular one for the combined treatment.

2.2.Electro – flushing treatment: combined method

Soil Flushing is a physico-chemical method, which is used for removing organic pollutants, inorganic soluble pollutants and heavy metals by using a natural pressure gradient or an artificial one created by the injection of different washing fluids with pumps.

"In situ" soil washing allows pollutants extraction from soil without excavating it. This method is applicable to permeable soils and is based on a water infiltration system into the soil washing which involves the mechanical movement of pollutants and also their solubilization. The resulted liquid is collected through the collection system located downstream and pumped at the surface in order to treat the washing liquid. The extract will be decontaminated, after which it can be reintroduced into the ground. One major disadvantage of this process is that the fluid volume is dispersed in all directions and cannot be directed in its entirety to the extraction points.

By combining the flushing method with the electrochemical one, it can be resolved two major disadvantages of the flushing method:

- the movement of the liquid inserted into soil, due to the electroosmotic process that appears as a consequences of using electric current could be better controlled;
- the combined technology can be applied also in low permeable soils, as clays.

2.3.Experimental setup

For the experimental part, two different setups were used. The first one is presented in Fig. 2 and is composed from:

- a rectangular reactor (10 x 60 x 10 cm) from a transparent PVC with a thickness of about 10 mm;
- a pair of electrodes (10x10 cm) from stainless steel with holes to permit the flow of interstitial water;
- a power supply;
- two bottles to collect the interstitial water from both compartments.

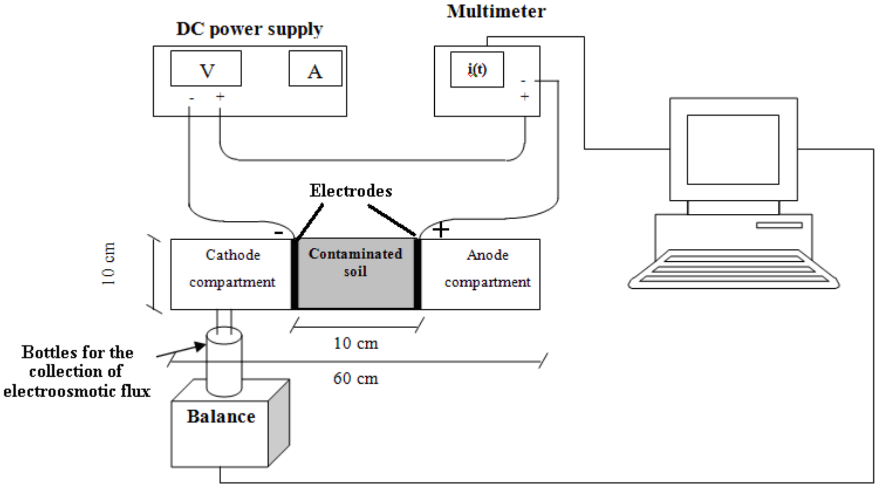

Fig. 2. General configuration of experimental setup 1

In this setup the soil samples has a length of 10 cm and a height of 10 cm but his length can vary from 2 cm to 50 cm just by changing the electrodes position. For this research the experimental setup was equipped also with:

- a digital multimeter (ISO-Tech IDM 207, with software for the registering of the data ISO-Tech 300 Virtual DMM) for the continuous monitoring of the current;

- a sale (Sartorius GW6206 Gold Scale) that allowed us to perform the monitoring of the electroosmotic flux;
- a computer for the stockage of the data;
- a manual multimeter (Mitek) for the manually monitoring of the current;
- a pH meter from Hannah Instruments for the pH monitoring;
- an instrument that measures the redox potential.

The general scheme of the second experimental setup is presented in Fig. 3, where in this case the electrochemical cell has a round shape with a diameter of 0.5 m and a height of 0.15 m. In the electrochemical cell, 10 electrodes (that were the anodes) were inserted on the exterior part of the cell and in the middle an electrode that had the role of the cathode. All electrodes have a cylindrical shape and the following dimensions: anode d_e/d_i = 0,02 m/0.018 m, h= 0,15 m; cathode - d_e/d_i = 0,09 m/0,089 m, h = 0,15 m.

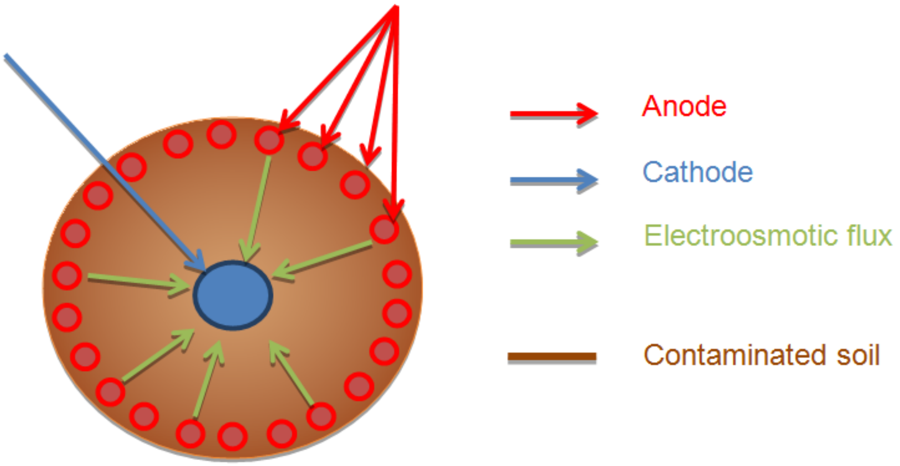

Fig.3. The general scheme of the second experimental setup

In order to perform the study about the diesel fuel-contaminated soils, the following parameters were measured: current, pH, temperature, redox potential, soil humidity, soil granulometry, TPH.

For the second research the pH, redox and temperature were taken in a soil/water suspension using sensors IQ SENSOR NET pH/ORP that was attached to a multiparameter instrument 2020XT. The TPH was determined accordingly with the procedure described in SR 13511. For this analysis a SOXHLET and a Heildolph Hei VAP Advantage were used. These instruments were purchased with the funds from a project co-financed under the Sectorial Operational Programme “Increase of Economic Competitiveness” POSCCE-A2-O2.1.2.-2009-2, RECOLAND ID519, SMIS-CSNR: 11982, Nb. 182/18.06.2010 (2010-2013).

3. Experimental research

The experimental research performed during this project foresees the application of electrooxidation (as a simple method and as a combined method with flushing treatment), on matrix of artificial contaminated soil with diesel. The diesel used was purchased from petrol station from Trento. The diesel, as almost all the hydrocarbons, is a product of distillation fractional of crude oil, or is produced by cracking (operation through which the hydrocarbons of high molecular weight are fragmented in the presence of a catalyst). In diesel, generally, there are several classes of hydrocarbons such as paraffin, naphthenic and aromatic, whose proportions vary from diesel to diesel: generally, is a mixture containing aliphatic hydrocarbons (including cyclical) from 13 to 18 carbon atoms and is composed of approximately 75% from saturated hydrocarbons (mainly paraffin) and 25% aromatic hydrocarbons. The choice of diesel as a contaminant of soil appeared from the need to represent environmental pollution caused by oil spills and various oil products; indeed the most frequent sources of contamination are made up of losses of oil, which may arise from industrial activities, refineries and oil spills fuel.

The type of fine grain soil that was used for the first experimental research to carry out the experimental investigation on diesel fuel remediation was speswhite kaolin. This type of soil could be classified as a silty clay, being mainly composed by particles having dimensions ranging between 2 μm and 75 μm (40%) or lower than 2 μm (60%). From a chemical point of view, it was manly composed by SiO_2 (47%) and Al_2O_3 (38%), its Cation Exchange Capacity (CEC) was 8.3 m_{eq}/100g and its pH was about 6. In order to assess any influence of the metal content on the system efficiency, the iron and manganese contents of the addressed soils were determined. The kaolin proved to be characterized by an iron content about 2794 mg/kg_{dw}. Before being mixed with diesel fuel, the TOC of the soil was negligible (about 0.01 mg/kg_{dw}).

The application of electric based treatments on diesel contaminated clay will be presented through two tests that will be described in this paragraph. These types of treatments proved to be effective on fine grain soils like clay. The first test will be identified with the acronym ER (electroremediation) and the second one with the acronym EFR (electro-flushing remediation).

3.1.Electrochemical treatment – simple approach

For the first test performed on an artificial contaminated soil where only the electro remediation, as a simple treatment, was applied, the following steps were performed prior to the treatment:

- it was establish the distance between the electrodes and after that the electrodes, covered in wet filter paper were put in place (to avoid the corrosion), and the free space between the electrodes is filled with contaminated soil;
- the soil was be compacted by hand in order to reach the same density as the natural soils (for example 2 kg/L), trying to avoid the free space that can be formed in the sample.

Test ER, which aimed at investigating the variation of contaminant removal with test duration, was performed with a constant voltage of 10 V (1 V/cm) for 4 weeks. The initial current flowing across the soil specimen was 17 mA (the measurement was done at the beginning of the test, after 20 minutes). An initial current of 2 mA was measured at the beginning of the experiment, while 1 mA was encountered at the steady stat. Although the measured current was not very high, the current trend was once more characterized by a rapid decrease, and by some fluctuations during the period from the 1st to the 3rd day of the treatment, when some temporal rebounds of the current flowing were encountered.

pH variation (Fig.4) is similar with the one encountered in literature [2, 3, 8, 9] were it is mentioned that at anode we have an acid front that moves towards the cathode and at cathode a basic front that moves towards the anode. The first one moves two time faster than the second one.

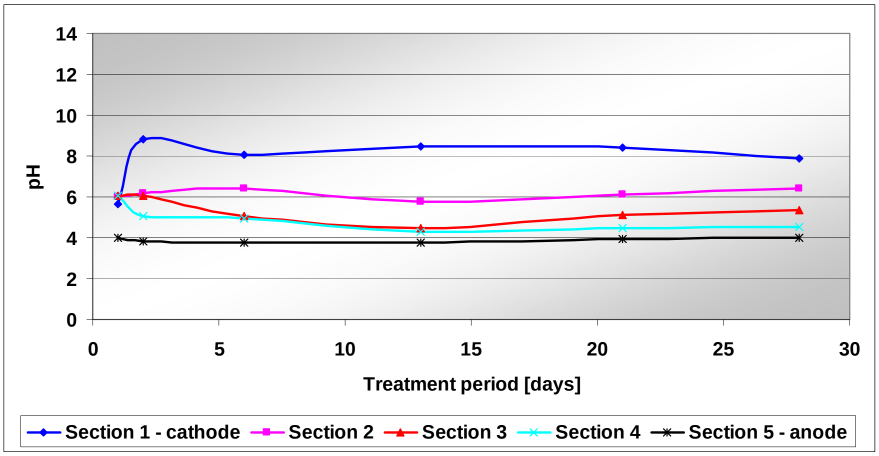

Fig.4. Trend of pH during 28 days of electrochemical treatment

TPH removal increased with treatment time from 50% to 80%. The results are presented in table 1 (for the concentrations variation) and Fig. 5 (for removal percentages of the treatment).

Table 1

The TPH concentrations before, during and after the treatment was applied

Treatment time [days]	**TPH [mg/kg$_{dw}$]**
0	130.977
7	64.966
14	60.338
21	30.873
28	26.566

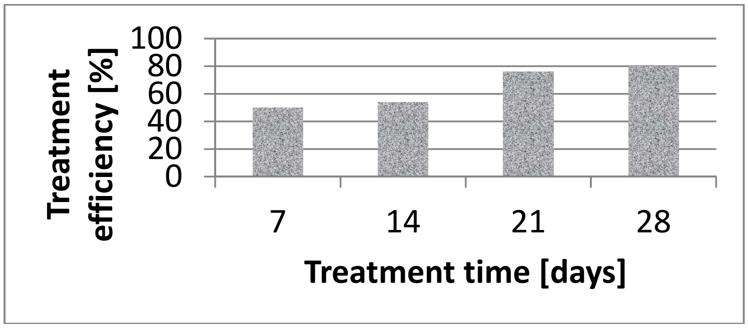

Fig.5. Removal percentages for the TPH after different periods of time

From the results obtained at the end of the test across the soil samples, it can be noticed that the pH decreases with the increasing of the distance from cathode on one hand and on the other hand, the TPH increases with the increasing of the distance.

3.2.Electro-flushing treatment – combined approach

This experiment, identified as EFR, involved the artificial contamination of 30 kg of clean soil with 3.61 L of diesel. The experimental setup had a circular shape with anodes on the exterior part and a cathode in the middle. The electrodes had holes along their length and circumference in order to facilitate the passage of the washing liquid. During the experiment the supply of the electrodes (anodes) was made as follows: 5 consecutive days were supplied with 0.25 L of distilled water, and then two days pause. The effluent was collected in a surge tank located in the lower part of the experimental setup. An initial voltage of 3 V was applied which resulted in a current value of 0.13 A. In this way the conditions for the electrochemical processes were developed, the two main processes that are helping this treatment are the electroosmosis and electromigration.

Comparing with the other test, in this one, the idea was to maintain constant the value of the current (and not the voltage as in the other). The established value was of about 0.13 A which corresponds to a current density of 0.1 mA/cm^2.

For this test a series of parameters where measured: total dissolved solids (TDS), pH, current, voltage, and the liquid volume that was recovered in the cathode area (demineralized water and diesel). The monitoring was done in three areas of interest: the anode area, the middle one and the cathode area.

Regarding TDS (Fig. 6) it was observed that after a treatment of 21 days, the measured value in all three areas, decreased significantly due to the effluent collection in the cathode area, which resulted in an impoverishment of the soil sample regarding the organic and inorganic substances that dissolved in the washing liquid. The TDS values are lower in the middle area (is the area located at a equal distance between anode and cathode) due to ions migration towards the anode and cathode creating this way an impoverishment of this parameter.

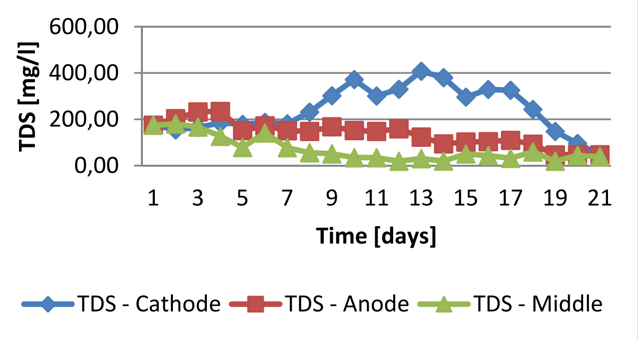

Fig.6. TDS variation during EFR test

Also for this test, pH variation is similar with the one encountered in literature [3, 5], which is acid at anode and basic at cathode. The minimum value did not go below 4 and the maximum value did not exceeded 12.

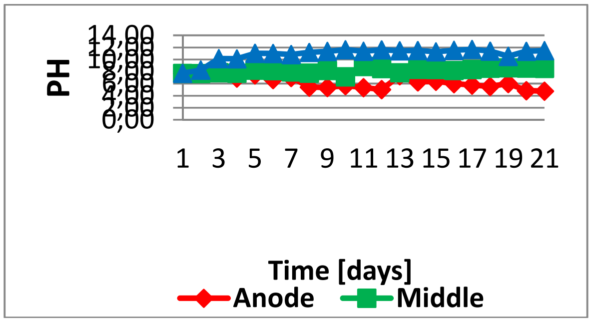

Fig. 7. pH variation during the application of the combined method

After a treatment of 21 days, 4.049 l of demineralized water and 1.15 L of diesel were extracted, which correspond to a recovery percentage for diesel of about 31.82%. From Fig. 8, could be observed three picks which represents effluent variation that was extracted in time and these high values are due to the fact that the effluent was collected after each 2 days pause.

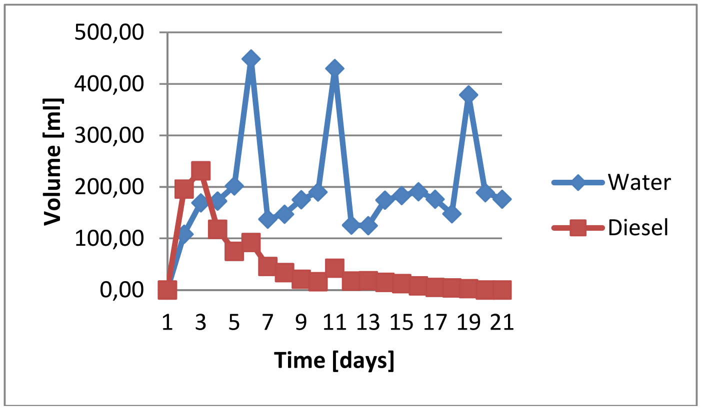

Fig. 8. The recovered volume of effluent in the cathode area

4. Energy consumption and costs

Bench-scale studies suggested energy expenditures of about 10-220 kWh/m^3 [8, 9], while more reliable pilot-scale tests indicated that the energy expenditures may rise up to 500 kWh/m^3 or more [10, 11]. Nevertheless, a few authors reported much higher energy expenditures (e.g. about 2000-9000 kWh/m^3) for the removal of HOCs by surfactant-enhanced electrokinesis [12].

The resulting cost may range from about 10 €/m^3 to 100 €/m^3 [10]. However, based on the site-specific conditions, the overall cost can arrive to 1200€/m^3 [6], mainly depending on [10, 11, 12]: soil properties (e.g. moisture, texture); depth of contamination; the cost of chemical enhancement (including the cost of conditioning fluids, if necessary, and the cost for the treatment of the process fluid, if necessary); the cost of system implementation (including electrodes, electrode accommodation, power supply system, etc); clean-up time; cost of labor; energy expenses cost.

A possible distribution of the overall remediation expenses can be the following [11, 13, 14, 15]: 40% for electrode construction; 10-15% for electricity; 17% for labor; 17% for materials; up to 16% for the licenses and other fixed costs.

Taking into account the values measured for the current and voltage, it was possible to approximate the energy consumption necessary for the remediation. Energy consumption per unit volume of soil is calculated using the following equation [13, 16, 17, 18, 19]:

$$E_{\mu} = \frac{1}{V_s} \int VI \, dt$$

where, Vs is volume of soil processed; V is voltage difference between the electrodes (applied voltage); and I is electric current. Eμ is calculated as kWh m^{-3}. The energy consumption obtained during all the test that have been performed in this research is 4.45 kWh $m^{-3}$for the first test and for the second one 549 kWh/m^3. The differences are due to the current values registered during the experiments: 2 mA and 1 mA for the first test and 130 mA for the second test.

5. Conclusions

Every year, millions of tons of hazardous waste are generated in the world. Due to inefficient waste handling techniques and hazardous waste leakage in the past, thousands of sites were contaminated by heavy metals, organic compounds and other hazardous materials, which made an enormous impact on the quality of groundwater, soil and associated ecosystems. One of these major problems is related to the oil spills are a frequent source of contamination that may derive from underground fuel leaks, industrial activities, or oil refinery.

In order to assess the influence of the soil mineralogy on the effectiveness of the electrochemical processes, two types of test were performed both having at the base the usage of electric field. The first test involved the application of a constant voltage for 28 days and reached an efficiency of about 80% for TPH removing, while the second one had the purpose to see what happens when we combine the electro remediation with the flushing method for 21 days. The results were promising if we take into account that after 21 days, using the washing liquid the demineralized water we recovered 31.82 % of the diesel that was initially introduced in soil (artificially contamination).

The combined technique is useful when we have a high contamination with diesel because helps removing a good part of the contaminant after which we can use the first technology or other types of technologies. The two technologies described in the current paper can be used with success especially when we want to recover also diesel from the contaminated soil.

Acknowledgments

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