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ELECTRO-OXIDATION TREATMENT USED FOR THE REMEDIATION OF ORGANIC POLLUTED SOILS

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The objective of the experiment was to evaluate a combined treatment of contaminated soil remediation, to determine the main parameters which influence the technology, that can be considered as being applicable to petroleum contaminated soils. This type of soil has an expanded location in Romania.

In the case of the experiment it was chosen the electroremediation method as main tehnique to remediate the soil samples. In adition, to improve the removal percentages, the electroremediation method was combined with chemical oxidation, therefore resulting a combined method: electro-oxidation.

Keywords: soil decontamination, electro-remediation, chemical oxidation.

1. Introduction

So far, soils have not been the subject to specific protection measures at Community level. Soil protection is reflected in various directives related to either environmental or other policy areas such as agriculture and rural development. Industrial activities brought a great amount of polluting chemicals and/or toxic substances (persistent organic compounds, heavy metals) through accidental spills or improper handling or use, which led to the current situation that consists in many contaminated sites throughout the world. Soil, sediments and groundwater pollution are a real problem for those sites that require the application of remediation technologies, as soon as possible, for the restoration of natural balance, to protect the public health and the environment. Unfortunately, conventional remediation technologies prove to be ineffective and/or to expensive for application, mostly, on low permeability soils, in the case of heterogeneous subsoil conditions or contaminants mixtures. The development of a new technology or the improvement of an existing one is imperative to resolve these problems and limitations. Recently, electrochemical technologies have proven to be effective for the remediation of sites with such complex problems.

These remediation technologies used for soil and groundwater treatment is based on the application of an electric field directly in the polluted area. The effect of the electric field mobilizes ionic species that are removed from the soil and collected on the electrodes. At the same time, the electric field causes the

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mobilization of interstitial fluid (constituents) from the soil, generating an electro-osmotic flow through the cathode, allowing the removal of soluble contaminants. The success rate of the electroremediation processes relies on the efficiency of extraction and solubilization of the contaminants and their transport to the electrodes, where they can be collected, pumped and treated. A number of studies have been conducted to determine the influence of the operating conditions and the effect of contaminants in the soil (depending on their nature) to improve the effectiveness and applicability of electroremediation treatment.

The main purpose of this study was to evaluate the effectiveness of different treatments to find the best solution that can be applied for the remediation of petroleum contaminated sites. The main point from which we started was to find a solution for the treatment of hydrocarbon contaminated site. This particular chosen soil type can be found in large areas of Romania's surface.

Other objectives of the experiment were to attempt fixing the system parameters so as they won’t affect treatment effectiveness (applying an appropriate voltage and duration of treatment) and finding a link between contaminant removal efficiency and macroscopic electrochemical phenomena, such as electro-osmotic flow and changes in soil pH.

2. Electro-oxidation of polluted soil

In recent years, electrochemical applications used to reduce pollution have received much attention [1]. In general, the removal or destruction of pollutants species can be realized directly or indirectly by electrochemical oxidation or reduction process in an electrochemical cell, without continuous supply of chemicals. In addition, the selectivity of many electrochemical processes helps preventing the production of derivatives and/or waste, which in most cases must be appropriately treated before disposal. Jüttner, Galla and Schmieder [2] noted that the application of electrochemical technology for wastewater treatment generally offers the following advantages: versatility, energy efficiency, possibility of automation and economic efficiency. Despite these advantages, there are limitations such as the electrochemical processes are heterogeneous in nature, and long-term stability and activity of the electrode material and the cell components.

An electrochemical oxidation/disposal of certain pollutants can be subdivided into two categories: direct oxidation at the anode and indirect oxidation, using specific anodic formed oxidants [1, 3].

Indirect electrochemical oxidation of pollutants in aqueous solutions can be accomplished in many different ways, including the use of chlorine or hypochlorite anodic generated [4, 5]; by utilizing hydrogen peroxide electrochemically generated [6, 7]; throughout electric generated ozone [8].

Intermediary electro oxidation is a different type of electro oxidation proposed by Farmer, utilizing Ag^{2+}, Co^{3+}, Fe^{3+}, Ce^{4+} and Ni^{2+} as mediators [9, 10].

The second type of electro-oxidation, direct anodic oxidation, refers to the generation of active adsorbed oxygen (e.g., adsorbed) or chemisorbed active oxygen (for example, oxygen in the structure/ network oxide) directly to the anodes [10]. This type of active adsorbed oxygen will be able to achieve the complete combustion of organic compounds, while the active chemisorbed oxygen will take part in the formation of the selective oxidation products, with electrocatalitic transfer mechanisms [11, 12, 13]. Generally, it has higher efficiency for pollutants oxidation than Mnx^{+1} [12, 14,15, 16].

3. Experimental activity

The experimental activity was divided into two parts, each part involving the application of different technologies, namely electroremediation and electro - chemical oxidation. In both cases, treatments were applied to a plant identified as IPER 3. Plant capacity was 0.5 m^3 (approximately 550 kg of contaminated soil).

Both tests had a specific voltage of 1 V/cm and a treatment period of 28 days. The main parameters that were monitored throughout the experiments were: pH, ORP, current, conductivity, TDS, RO and the most important parameter can be considered the pollutant concentration.

3.2. Application of electrochemical treatment

The initial current recorded at the beginning of the experiment was 5.16 A, and this value represented the maximum value of the experiment. It can be due to the high concentration of total hydrocarbons in the soil. After the peak was measured, the trend of the current was to decrease and reach a constant value until water was added to stimulate the electrochemical processes. In those moments we observed higher values in comparison with the others. Current variation is similar to that reported in the literature where different treatments based on the use of electricity were applied for soil remediation.

Regarding changes in pH variation it can be seen that the front is mainly basic rather than alkaline because pH value does not fall below the value of 8. Changes in pH values are within the range 8-10 exception of a measurement carried out after 576 hours of treatment, where the value is 11.7. For all the samples intermediately taken it was established a different sampling scheme, specifically from three different points of the anode zone, the same for the middle and the cathode.

Thus, tests were carried out at the beginning of the experiment in order to determine the initial concentration of hydrocarbons. In addition to that intermediate determinations have been made and final samples to observe the change in concentration of total hydrocarbons in time.

The sampling was also carried out in the three areas of interest, namely the anode, the middle and the cathode. Initial concentration of total hydrocarbons was 57889.48 mg / kg$_{dw}$. The concentrations of hydrocarbons before and after the electrochemical treatment are shown in the table below and in Figure 1. The efficiency of the treatment is shown in Figure 2.

Table 1

Variation of hydrocarbons concentrations before and after electrochemical treatment

Sample type	Hydrocarbon concentration [mg/kg$_{dw}$]
Initial	57889.4868
IPER3 A- 3 sapt	51465.3270
IPER3 M- 3 sapt	31103.0963
IPER3 C- 3 sapt	42842.6493
IPER3 A- 4 sapt	52474.1166
IPER3 M- 4 sapt	47552.0210
IPER3 C - 4 sapt	43237.8563

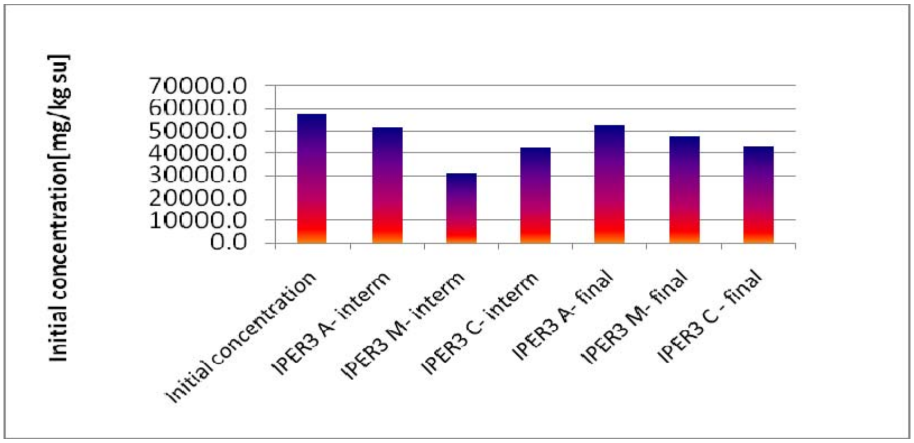

Fig.1. Changes in the concentration of total hydrocarbons

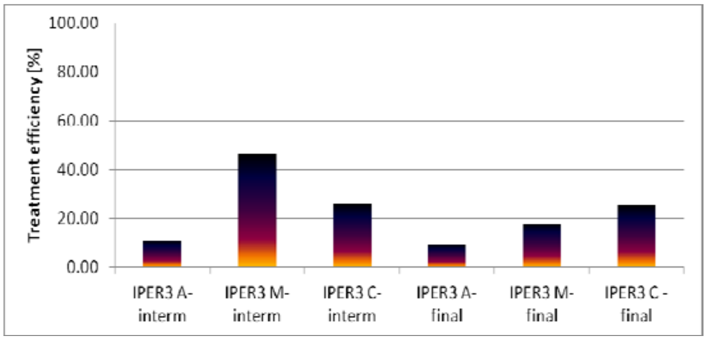

Fig. 2. Electrochemical treatment efficiency for the test applied on IPER 3 – electrochemical

Due to the fact that the soil used for the experimental activity was heavily contaminated, it is noted that for a relatively short period and a large quantity of soil we do not have very good results and it has been decided to do again the test, using the same amount of soil, but combining the electric treatment with another treatement based on the use of oxidants, namely chemical oxidation.

3.2. Application of combined treatment- electro-oxidation

In this experiment, samples were made to carry out intermediate monitoring of the three areas of concern as mixed samples, and not by three samples for each area. It was decided to make such sampling because it was observed that there is no high variation between the three samples from each area.

Since oxidant was added at the beginning of each week in the anode area and the rest in all the electrochemical cell (about 1 L for the anode and about 1 L for the rest of the cell), the pH clearly formed an acid front managing to descend to the value of 4.32 at the anode, and at the cathode increased until reached the value of 11.86. Corresponding with pH variation, there was an ORP variation, so that after 12 days of experiment, the ORP was below zero in the cathode, and thus it was decided to change polarity. After this episode, there was not any decrease in redox potential.

At the end of the treatment, after 28 days, it was noticed an improvement in the results (Fig. 3), in a reduction of pollutant concentration with approximately 42.5% (Fig. 4).

Following the interimediate analysis it was observed that:

- at the first intermediate sampling there is an initial migration of hydrocarbons from the anode and the middle towards the anode
- at the second intermediate sampling there was a hydrocarbon migration in the cathode area due to electroosmotic flow and a remediation in the other two zones.

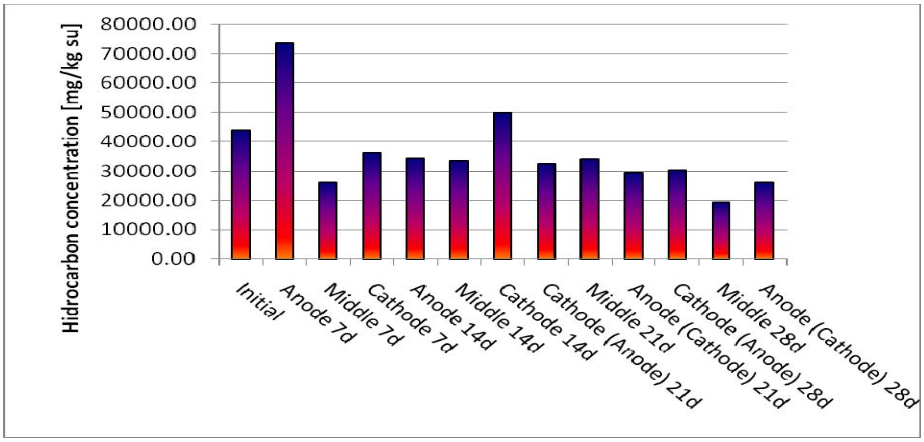

Fig. 3. Variation of hydrocarbon concentration during combined test

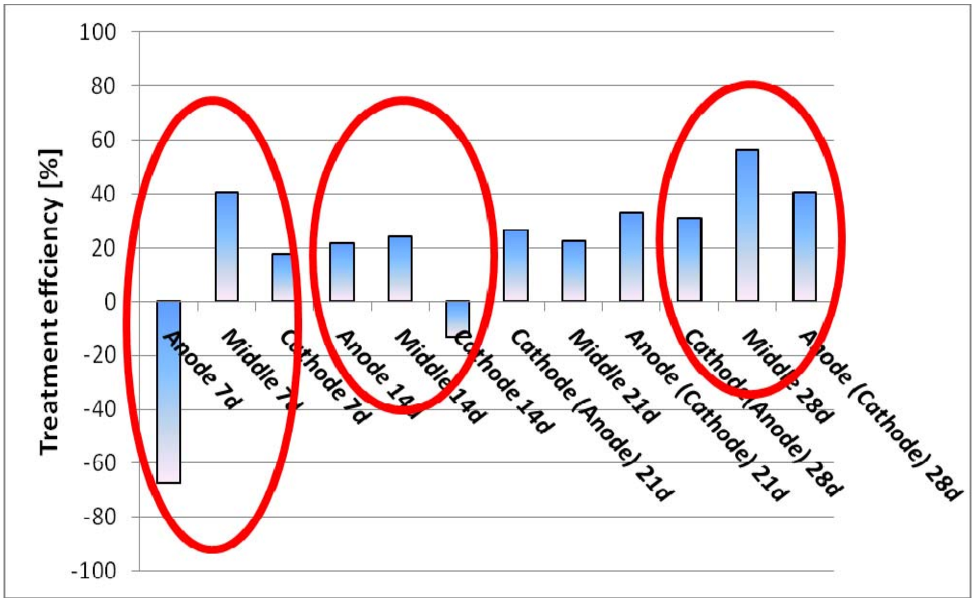

Fig. 4. Treatement efficiency for the combined test on IPER3

4. Conclusions

Experimental activity performed in this research used a natural polluted soil that comes from a petroleum processing area.

It is noted that for the electrochemical treatment should be a correlation between the amount of soil being treated and the application time of the treatment.

There were obtained similar results to those in the literature, the fact that the efficiency of electrochemical treatment increases with the increase of application of the treatment period, and no specific voltage increases.

For the electroremediation treatment it was noticed a uniform distribution of the contaminant on vertical, and a relative uniform one on horizontal.

Regarding the combined treatment it was observed that when we are dealing with excessive pollution, the first trend of the pollutant is being transported to an electrode or another due to electroosmotic flow, after which oxidation and reduction reactions occur.

Soil behavior under the influence of the electric field is totally different from what is found in the literature, probably because the initial concentration of hydrocarbons that is very high.

The type of experimental activity in this paper could be pursued by: identifying necessary factors for the correlation between the amount of soil treated and time needed for treatment; achieving a combined treatment using other stronger oxidants; testing the methods on smaller pollutions, and eventually determining a correlation between the initial quantity of pollutant and the necessary time for treatement application.

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