The Influence of *p*H and ORP for the Efficiency of Electrochemical Treatment Applied for Organic Polluted Soils

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The feasibility of the electrochemical treatment for a historical contamination was tested through laboratory-scale experiments. The chemical parameters like pH and ORP were carefully monitored considering that previous related research has established a close connection between these two and treatment efficiency. Based on results from the experimental study, electrochemical treatments proved to be effective for historical contamination with petroleum products. After only 21 days of treatments the removal percentages reached an average of 41% and after 28 days about 50%.

Keywords: electrochemical remediation, historical contamination, petroleum products, hydrocarbons, pilot-scale plant

The use of organics worldwide has soared since Second World War II. Improper use and accidents implying organics increased concern [1, 2]. Many of these compounds, for instance the gasoline, from improper use and storage, led to soil and water contamination. On the other hand, it is also common the spillage of motor oil onto soil due to improper handling. Contamination on land and in water has generally occurred as a consequence of accidents during petroleum transport (pipelines, ships, trucks) [2].

Certain petroleum hydrocarbons are severely toxic contaminants to public health, either via explosion hazard, defatting of biological tissue, direct toxicity, or simple asphyxiation. Long-term exposure to hydrocarbon compounds such as benzene (a common gasoline additive) or benzo[a] pyrene (a component of diesel exhaust fumes, tobacco smoke, and charbroiled food) is known to increase cancer risk [2]. The contamination that originates from introduction of xenobiotic chemicals to the environment or from naturally occurring sources; one of the most common chemical contaminants found in the environment is petroleum hydrocarbons [3, 4].

The natural processes of the self-cleaning of the geological environment cannot any longer cope with the pollution, which results in the degradation of ecosystems and sometimes leads to local environmental crises. In such situations, ecosystem rehabilitation is possible only by means of large-scale application of remediation technology for geological environment reclamation [5]. One of the most popular methods of soil decontamination is the electrochemical one based on passing a direct current flow through a contaminated soil. The resulting processes (electrolysis, electroosmosis, electrophoresis, electromigration, etc.) remove toxic components from the soil [1, 5]. This type of treatment, the electrochemical remediation, can be applied on different types of wastes from polluted soils to medical wastes [6].

This work presents the application of electrochemical treatment on historical contaminated soil with petroleum products. The main objective of the research is to underline the influence of chemical parameters on treatment efficiency.

Experimental part

Electrochemical treatment

The term "electrokinetic remediation" or "electrochemical remediation" embodies many different approaches. Broadly, these approaches have followed two separate paths each based on a different electrokinetic phenomenon [1]. The first approach is the removal of ionic (and polar) species using classical electromigration techniques where ions move under an applied direct current (DC) field [1,5,7-9]. The second approach relies on the movement of water through the electrical double layer created on porous media [1, 8-11]. Pollutants are carried along in this moving layer of water towards an implanted cathode or adsorption media placed in the way of this moving front. This approach was initiated, apparently simultaneously at Massachusetts Institute of Technology (MIT) [12, 13] and at Louisiana State [14, 15]. Empirical evidences indicated that the reaction rates are inversely proportional to grain size, such that this remediation technique is particularly effective in saturated low permeability soils (like clays and silts), which are often more difficult to treat with conventional chemical methods (such as chemical oxidation or soil flushing), because of their low permeability and their high sorption capacity [16].

Under the influence of the electrical field, electrolysis reactions take place at the electrodes, also resulting in *p*H changes: oxidation of water occurs at the anode and generates hydrogen ions (H^+); contrary, reduction of water occurs at the cathode and generates hydroxyls ions (OH^-). Hydrogen ions H^+ generated at the anode create an acid front which moves towards the cathode, while hydroxyls ions OH^- generated at the cathode create a base front which moves towards the anode [17, 18]. Since the transport of H^+ is faster than the transport of OH^- the acid front moves faster (approximately two times faster) than the base front; unless the H^+ transport is not retarded by the soil buffering capacity, this difference in fronts moving rate leads to an acidification of the soil between the electrodes [17, 19]. This acidification can also results in contaminants solubilization, especially metals, due to desorption and dissolution of polar species from soil [16].

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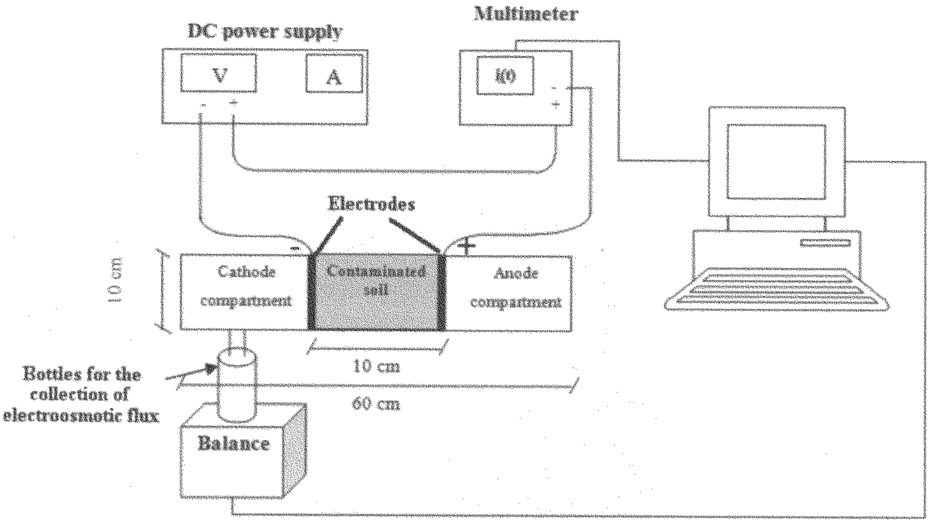

Fig. 1. General scheme of electrochemical treatment

Experimental setup

The experimental setup is identified as IPER 2, which means pilot installation used for electrochemical remediation, and number 2 is used for the second scale. In laboratory there were three types of installations, each one corresponds to one scale. For the present paper the research has been performed only on IPER 2.

IPER 2 (fig. 1) is composed by a rectangular electrochemical cell made from PVC (6 mm thickness) having the following dimensions: 600 mm x 300 mm x 300 mm. Inside the electrochemical cell, the two electrodes were inserted. These elements represent a network (for each electrode type) composed by 4 stainless steel bars that are coupled at the ends with a plat bar. The numbers of stainless steel bars were calculated according to „Basics and applications of electrokinetic remediation” written by Akram N. Alshawabkeh, in 2001. The idea was that when an electric current is applied, if the electrodes are bars and not plats, some inactive areas remaining. So, as a function of the bars number, a larger or smaller area risk to remain untreated. With the network formed from 4 bars, we had an inactive area of 10%. It remained this solution because for 5 or 6 bars for each network, the percentages did not decreased significnatly (7.6% respect to 6%) in order to justify the economical effort for bars purchase.

Results and discussions

The research has been performed on a contaminated soil with petroleum products. Soil samples were excavated from an ex industrial area, where for several years the oil industry processed different products. For the initial characterization was decided to take samples from 9 different points at two different depths, 0.2 m and 0.4 m. After the initial analyses were performed, the main characteristics of the soil were: apparent density 1.2 g/cm^3, soil humidity 20% (was determined with the gravimetric method, using un oven for 24 h at 105^{0}C); from the granulometry analysis it could be noticed that more than 55% was composed by particle with a diameter smaller than 0.08 mm. Soil samples for the laboratory tests had been taken from different parts of the selected area in order to better represent the studied area.

Tests have been performed for a treatment period of 21 days and 28 days, respectively. The main characteristic of the tests is the specific voltage that was maintained at 1V/cm. The soil sample weight was about 60 kg. The chemical parameters that were monitored during the treatment period were *p*H and ORP. Furthermore, the current, temperature and the total hydrocarbons (TH) were monitored.

Both experiments registered high values for the current: 3.3 A for test 1 (T1) and 3 A for test 2 (T2). From figure 2a and figure 2b it can be noticed that the current trends are similar. The maximum current intensity is reached in the first three days since the experiments started, after which in the next four days a continuous decreased was observed until the steady state is reached. For test T2 which lasted 28 days, the steady state value was about 0.28 A, while for test T1 was 0.55 A. If the first test would have lasted for other 7 days, it is possible that the steady value to be similar with the one from T2. This will be studied in future research.

The high electric current intensities observed in run T1 and T2 were caused by ion migration related to the soluble salt content (it was noticed after a visual contact), as confirmed by the drastic reduction in electric conductivity with time as soon as such species were depleted from the material.

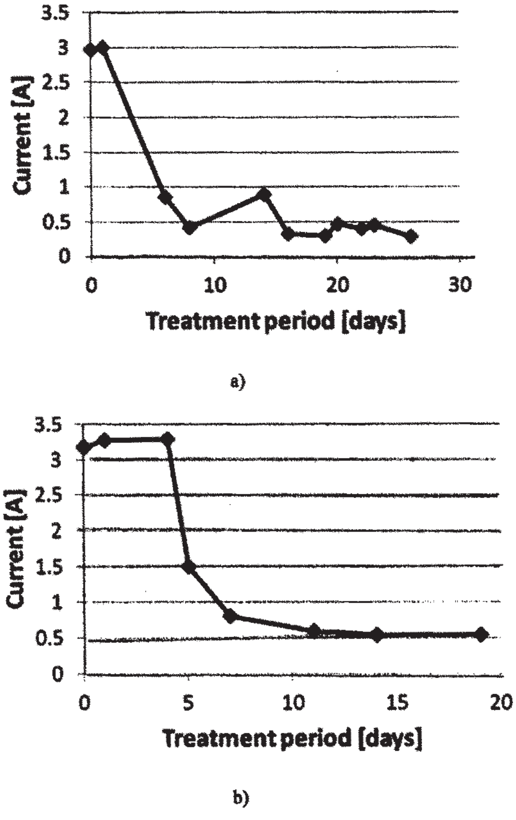

Fig. 2.Curent trend for the performed tests: a) test T1 performed for a treatment period of 21 days; b) test T2 performed for a treatment period of 28 days

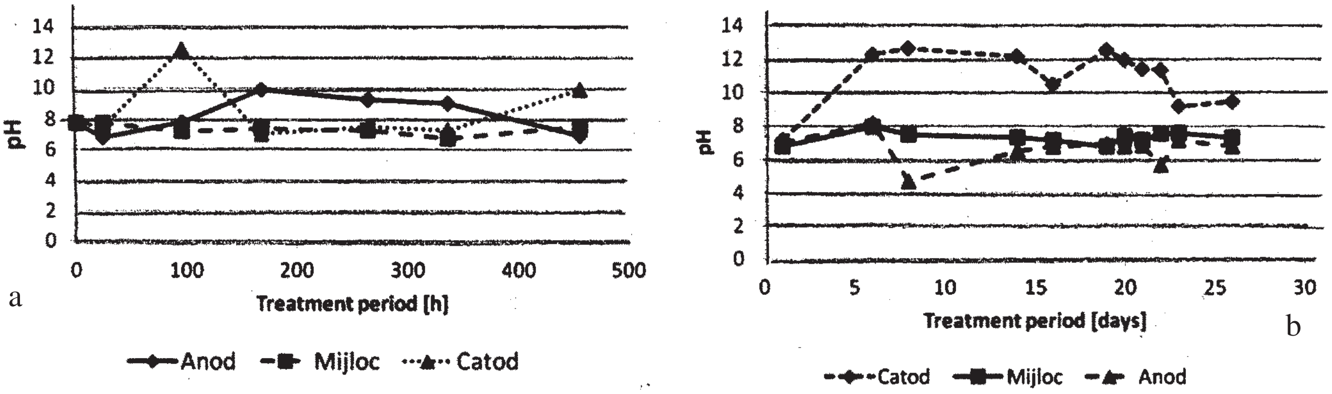

Fig. 3. pH variation during the electrochemical treatment: a) for a treatment period of 21 days, test T1; b) for a treatment period of 28 days test T2

In order to determine the soil-*p*H values, a mixture formed by 5 g of soil with 20 mL deionized water, was used. The *p*H variation for the two tests, T1 and T2, is presented in figure 3a and figure 3b where the values are presented for the three areas of interest (anode, middle and cathode). The soil *p*H represents a measure of the acidity which plays an important role in determining the solubility of important elements and processes from soils [20].

According to Krishna et al, in 2009, a slow drift of hydroxyl ions moves from the cathode displacing anions adsorbed onto the soil particles. Free anions in the water electrolyte will be in equilibrium with available sites on the soil. These sites compete with OH^- created at the cathode, and so there will be a net drift of displaced anions to the anode due to electromigration [21]. As a result, the soil acidifies from the anode into the direction of the cathode and if no measures are taken, practically all the energy will be used for the transport of H^+ ions [21]. From the previous research it was noticed that treatment efficiency is better at anode area [2, 15] while Rohr et al, in 2002 mentioned the fact that the pollutant degradation is faster and more obvious in the areas where the *p*H is higher [20,22]. So, during the experimental research presented in this paper, the *p*H was an important parameter that was monitored continuously in the two tests. The idea was to try to have a neutral *p*H in the treated soil sample in order o avoid an obvious acidification of soil. A treatment can be considered efficient not only by the obtained removal percentages of the pollutants but also through the soil quality after the applied treatment (this involves the *p*H value).

The second parameter that was monitored in a continuous manner for the two tests, T1 and T2, is the redox potential, measured in [mV]. When a direct electric current flows through an active electrochemical system, the products of electrolysis depend on the redox or electrode potentials of the chemicals in the system and the chemical properties of the electrodes [22]. In our case the electrodes are made of stainless steel.

ORP is a measure of the system ability to oxidize (accept electrons) or to reduce (donate electrons) in the system and subsequently to oxidize or to reduce other components in the system. In soil and sediment remediation, if the ORP is positive, less oxidant will be required to oxidize a component [17, 22, 23]. If it is positive and the objective is to reduce a component, more reducing agent will be required. In most soils and sediments, the ORP is generally found to be more positive in systems exposed to the air and to be more negative in systems such as sediments not exposed to air [1, 3, 21, 23, 24]. Oxidation – reduction reactions or redox reactions are defined as a family of reactions in which electrons are transferred between species. The species that receives electrons is reduced and that donates electrons is oxidized. Similar to acid – base reactions, redox reactions are always a matched pair of half - reactions. An oxidation reaction cannot occur without a reduction reaction occurring simultaneously.

Similar to the concept of *p*H on the overall acidity/alkalinity of a system, reduction potential (also known as redox potential, oxidation/reduction potential or ORP) is an intensity parameter of the overall redox reaction potential of a system. A system with a lower (more negative) reduction potential will have a tendency to lose electrons to the new species, that is, to be oxidized by reducing the new species.

Similar to the fact that transfer of hydrogen ions between chemical species determines the *p*H of a system, the transfer of electrons between chemical species determines the reduction potential of a system. However, it does not characterize the capacity of the system for oxidation or reduction; similar to the fact that *p*H does not characterize the buffer capacity of a system [21, 22].

So, in addition to the ORP, the *p*H of the system will play a part in the range that oxidation and reduction can take place. Secondly, the constant change of the polarization causes every time a change of the double layer and consumes a relatively high capacitive part of the current due to the double layer discharging or recharging.

The main objective of monitoring the ORP was not only to see where the oxidation/reduction reactions take place but also to control the treatment efficiency along the soil sample. In literature, there are papers [25] were it is underlined the fact that if we apply a constant voltage to an organic polluted soil and if the ORP variation is very pronounced (that is at anode we have oxidation and at cathode reduction), at the end of the treatment can be noticed a non uniformity in removal of organic pollutant (higher removal at anode where the oxidation reaction occurred and smaller at the cathode). So, in order to avoid this non-uniformity, it was decided to favour the oxidation reactions along the soil sample. In order to do this, each time the ORP values where below 0, the electric potential was changed. This means that the anode becomes cathode and the cathode becomes anode. This way the oxidation occurs in the whole sample and the removal percentages of this treatment could be uniform along the soil sample.

The ORP variation during the experimental research is presented in figure 4 and figure 5 where the moments when the electric potential was changed are revealed. As electrons migrate and reduction – oxidation (redox) reactions take place, the equilibrium potential is restored.

It can be also noted that, the contaminant removal increases significantly with the duration of the process, or better said, longer last the treatment, and better are the results. Concentration profile along the sample is not always uniformly distributed; sometimes some areas present a

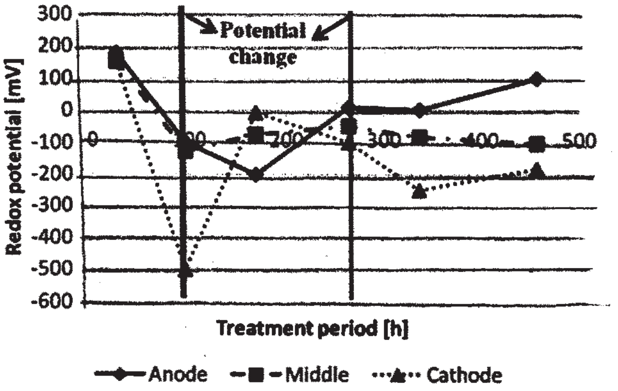

Fig.4. ORP variation during test T1 for a tratment period of 21 days

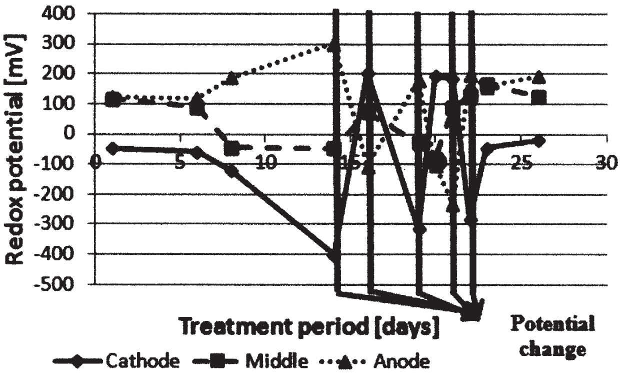

Fig. 5. ORP variation test T2, for a tratment period of 28 days

higher remediation than others. This probably is also due to the fact that the contaminant (petroleum product) is characterized by a quite high hydraulic conductibility and because of that tends to migrate at the top of the sample.

The initial concentrations of TH were about 33.108,00 mg/kg$_{dw,}$ respectively 42.000,00 mg/kg$_{dw}$. The initial values are significant higher with respect to the national regulation thresholds mentioned in Order 756/1997 for intervention point, less sensitive use (17 to 21 times higher than the legal limits).

In the literature [3, 17, 18, 24] was underlined the fact that the treatment efficiency increases with treatment period. After the experimental tests, the obtained removal efficiencies ranged between 40 up to 64%. The percentages for each area (anode, middle and cathode) can be observed in figure 6.

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Related literature [5, 26] mentioned the fact that in the case of petroleum products contamination the de-contamination efficiency ranges from 25 to 75% and higher depending on various internal and external factors. The results obtained in the present research confirm the previous suggestion, but also it can be concluded that the maximum range can be overlap if the treatment period is extended.

Conclusions

A series of trials have been performed in order to assess the efficiency of the electrochemical treatment on natural contaminated soils with petroleum products.

Experiments were carried out in a reaction cell with a rectangular body in order to investigate the influence of current on a petroleum product contaminated soil. Beside the current, a special attention was given also to pH and redox potential variation during the test. The technique is generally able to treat fine and low - permeability materials, and treatment costs can be limited by a proper selection of a low current/voltage application.

According to the data presented in the literature [14, 15, 17] was underlined the fact that generally, the removal and destruction of pollutant species can be carried out directly or indirectly by electrochemical oxidation/reduction processes in an electrochemical cell without a continuous feed of redox chemicals. Besides, the high selectivity of many electrochemical processes helps to prevent the production of unwanted by - products, which in many cases have to be properly treated before disposal.

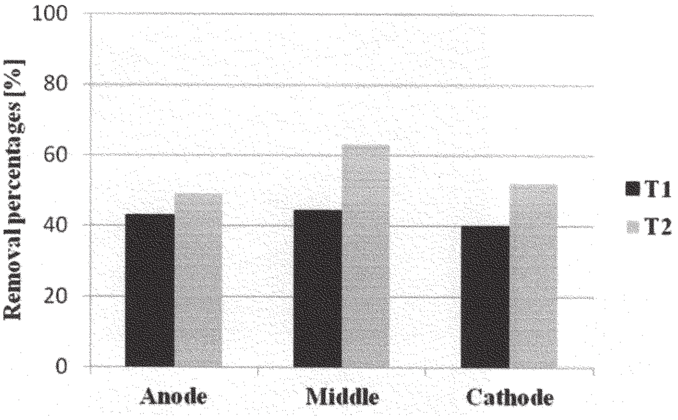

Fig. 6. Treatment efficiency for test T1 and T2

The described experiments have shown that the use of direct current is favorable for inducing a degradation reaction inside the soil matrix.

Based on the results of this study, electrochemical treatments proved to be effective for natural contamination with petroleum products. After only 21 days of treatments the removal percentages reached an average of 41%, while after 28 days the average was about 50%.

Some studies are still in progress in order to assess the optimum treatment period and also to evaluate if the same parameters are working to a larger scale (more than half a ton of contaminated soil will be treated in the next future).

Acknowledgements: This work was supported under FSE – European Structural Funds POSDRU with the Financing Contract POSDRU/89/1.5/S/62557 (EXCEL) and FSE – European Structural Funds POSCCE-A2-O2.1.2.-2009-2, RECOLAND ID519, SMIS-CSNR: 11982, Nb. 182/18.06.2010 (2010-2013).

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Manuscrit received: 12.03.2013