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THE ASSESSMENT OF A NEW TECHNOLOGY USED FOR THE TREATMENT OF PETROLEUM CONTAMINATED SOILS – LABORATORY STUDY

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Soil is an extremely complex medium and different soil fractions and constituents have very variable degrees of reactivity to any introduced compounds. Thus the simplicity of the "cause and effect" situations that can be obvious in air and water pollution incidents is usually unattainable. The objective of the present paper is to present the results obtained during an experimental campaign that took place in the frame of a post PhD study which had as a main subject the treatment of petroleum contaminated soils by using innovative technologies as electrochemical remediation From the preliminary results it can be said that the electrochemical treatment can be considered a viable solution that can be applied in the case of a petroleum contamination.

Keywords: soil contamination, petroleum products, hydrocarbons, electrochemical remediation.

1. Introduction

In the last decades, the contamination of soils becomes more evident, and that was because of the interest manifested by the public authorities regarding the ecological state of soils. It can be said that the soil can be classified on a third place after water and air [1, 2]. The European Environmental Agency has underlined in several documents the fact that the problem of contaminated soils is very big and until now were discovered over 300 000 sites [1, 3]. The majority of these sites are characterized by an historical contamination that resulted from different industrial activities. One of the most polluting industries after waste management is the industry of oil production, processing and transport [2].

The present paper will present an experimental activity that was developed during a post PhD done at University POLITEHNICA of Bucharest, Romania. This research activity continues a doctoral research on the same theme with the differences that in the second one the contamination was artificial and in the first case the contamination is natural.

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2. DCT technology

The treatment method used for this study is included in the DCT treatments, and it is known also under the name of electrochemical treatment. The method involves the use of a power supply in order to apply a constant voltage to a pair of electrodes inserted in the polluted soil [3, 4, 5]. The current applied will flow from the anode to the cathode, opposite to electron flow in the electrodes [6, 7]. In the electrolytic cell the power supply acts as an electron pump pushing electrons through the cathode and removing them at the anode. This movement of ions in an electric field is called electromigration [4, 6, 7]. The current is carried by ions in the soil as it was in a pure electrolyte solution.

One of the consequences is the formation of a basic front near the cathode and an acid front near the anode [4, 7, 8]. The acid front is formed because of the transportation of H^+ ions from the anode area by electromigration to the cathode area [8, 9]. Also it was noticed that the acid front moves twice faster than the basic front [4, 5, 10].

3. Laboratory tests

3.1. Sample preparation

The soil used for the experimental study was excavated from an ex industrial area, where for several years the oil industry processed different product. The contaminated area is situated near a main road on one side and near a industrial road on the other side. For the initial characterization was decided to take samples from 9 different points at two different depths, 0.2 m and 0.4 m. The initial characterization of the soil showed the following data: the density of the soil was 1.5 g/cm^3, the humidity was around 20% and from the granulometry point of view it could be noticed more than 55% was composed by particle with a diameter smaller than 0.08 mm. The contamination could be observed at the first look. The soil for the laboratory tests had been taken from different parts of the selected area in order to better represent the studied area.

Because the humidity of the soil was quite high it was decided not to add water before starting the experiment. The tests were performed using experimental setup from figure 1 and from figure 2. The second experimental setup (IPER 2 - Fig.2) has been done 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).

Fig.1. The experimental setup IPER 1 – electrochemical cell and the multimeter

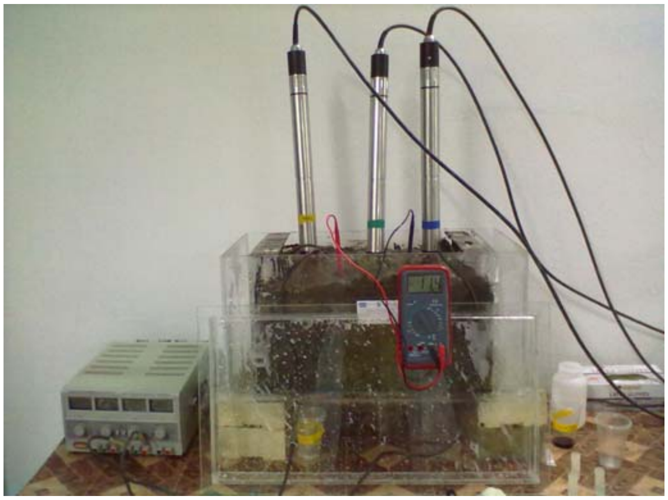

Fig.2. The experimental setup IPER 2 – electrochemical cell, power supply and the sensors used for pH and redox measurements

In IPER 1 the electrodes had a square form of 10 cm x 10 cm, but in IPER 2 the electrodes where conceived as a network formed by several cylindrical electrodes. The number of electrodes that composed the network was calculated according to “Basic and application of electrokinetic remediation” written by Akram N. Alshawabkeh in 2001. This paper presents the method to calculate the inactive areas, figure 3, and according to this can be taken a decision related to the number of electrodes that shoul compose a network.

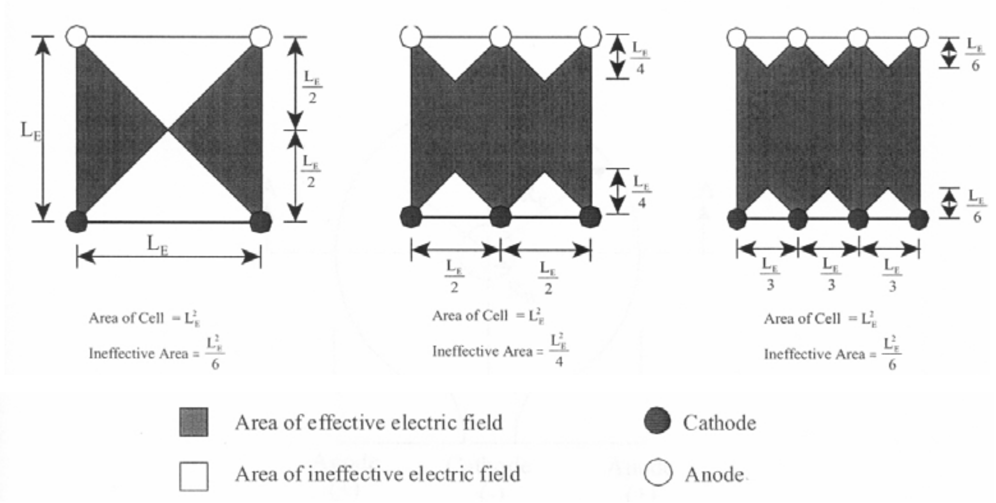

Fig. 3 – The method for the calculation of inactive areas (Alshawabkeh, 2001)

After the calculation and after it was taking into account the economic aspect, it was decided to do a network that includes for an electrode, for cylindrical stainless steel united on the upper and lower side by a stainless steel band. For this configuration the inactive areas were around 10% of the total area.

3.2. Experimental activity

The experimental activity to which it will be referred in the present paper involves two tests, each one developed at different scale in order to observe if there is or not any scale effect. First test was performed in IPER 1 and the second one in IPER2. The main characteristics of these tests are presented in table 1.

Table 1

The main characteristics of tests performed on IPER 1 and IPER 2

	IPER 1	IPER 2
pH	7.72	
Humidity [%	24	
Soil mass [kg]	3.27	50
Density [g/cm^3]	1.477	
Treated volume [m^3]	1539 cm^3=0.001 m^3	33840 cm^3=0.034 m^3
Specific voltage [v/cm]	1	0.5
Treatment period	21 days	

The parameters that were monitored during the experiments were: current, pH, redox potential and at the end the TPH was determined in order to characterize the content of petroleum hydrocarbons.

3.3. Results and discussions

During the experimental runs the current had the same tendency in the both experiments, to increase up to a maxim point after which started to decrease until reached a steady state. The trends of the currents for the two tests are presented in figure 4 and figure 5.

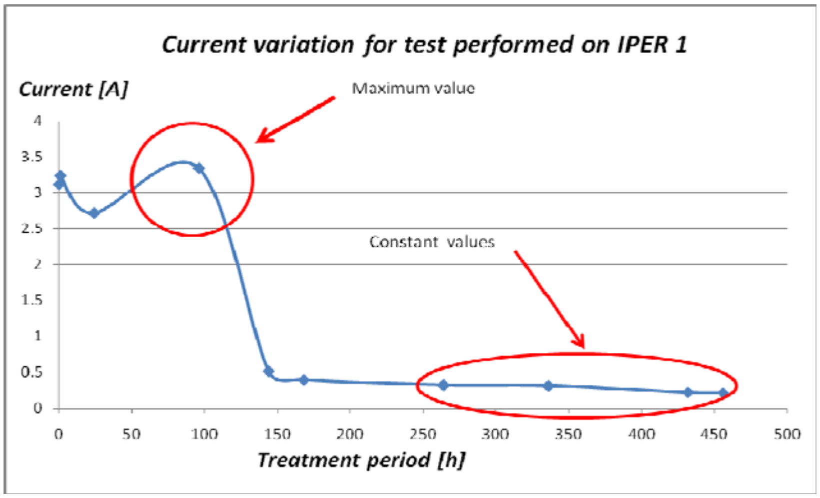

Fig.4. Current variation during 21 days of treatment on IPER 1

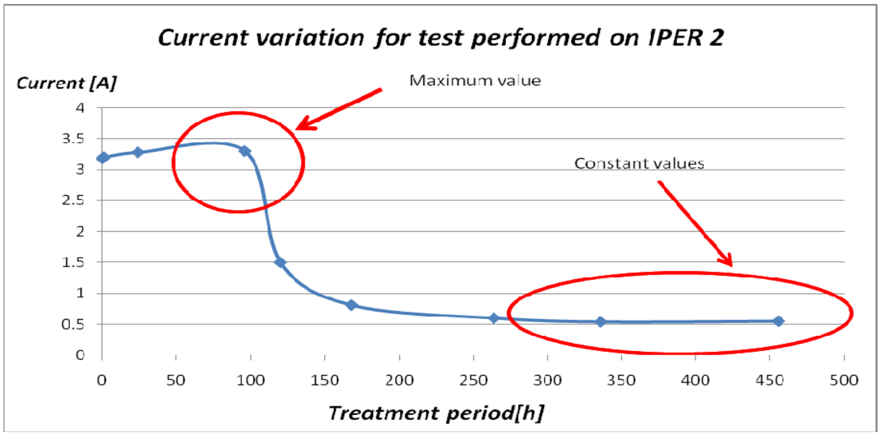

Fig.5. Current variation during 21 days of treatment on IPER 2

The trend of the two tests was similar with the difference that for the first case the drop was more evident.

Instead for pH it was noticed a strong profile in the test performed on IPER 1 maybe also because the distance between the electrodes was of only 20 cm compared with IPER 2 where the distance was of about 50 cm. So, if for IPER 1 the pH was strong acidified in the anode area (3.1) and with a basic character in the cathode area (12.3), for IPER 2 the pH along the sample ranged between 6.7 and 9.9. This is due also to the fact that the acid profile is two times faster than the basic one.

The efficiency of the treatment was assessed by analyzing total hydrocarbons according to the Romanian standard SR 13511. Even though in the treatments presented in this paper we have two different scales, the main objective was to demonstrate if there is any scale effect between these two types of treatment taking into account only a horizontal distribution. As illustrated in figure 6 for the smaller scale treatment the results were poorer than the ones for the larger scale.

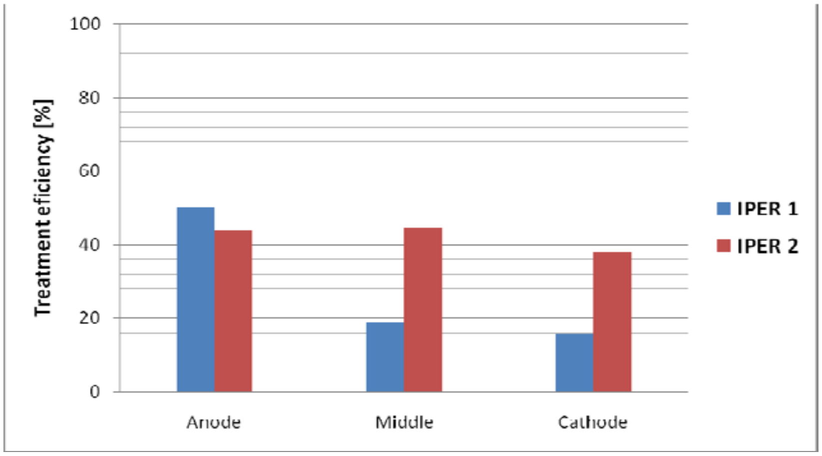

Fig.6. Comparison between the efficiency of the two tests

It was noticed after some intermediary analysis that the efficiency of the treatment increases with the increase of treatment period, the experiments having the same trend in the case of natural contamination as in the case of artificial contamination. Another aspect very important that was observed is that for the larger scale it was obtained a uniformity of the removal efficiency along the sample.

4. Conclusions

The electrochemical treatment, as it was shown before in the literature, is an efficient treatment when it is applied to a hydrocarbon contamination. The objective of the present paper is to see if in the case of a real contamination the treatment still works, and if there is any scale effect of the treatment when is applied at different scales. The removal percentages obtained after 21 days of treatment of about an average of 40% (for the larger scale) is quite promising, following that in the next papers to present other experiments that had a treatment period higher than 21 days. Also a high importance will be given to a more detail analysis for a vertical distribution of the contaminant and not only horizontal.

7. Acknowledgements

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REFERENCES

[1]. *Environmental European Agency*, "Europe's environment the fourth assessment executive summary – state of the environment", 2007, www.eea.eu

[2]. *Environmental European Agency*, "Suolo – la risorsa", 2010, www.eea.eu

[3]. *Y.B.Acar, R.J. Gale, A.N.Alshawabkeh, R.E.Marks, S.Puppala, M.Bricka, R.Parker*, "Electrokinetic remediation: basics and technology status", J. Hazardous Materials, **vol.40**, 1995, pp. 117-137.

[4]. *A.N. Alshawabkeh, T.C. Sheahan, X. Wu*, "Coupling of electrochemical and mechanical processes in soils under DC fields", Mech. Mater., **vol.36**, 2004, pp. 453-465.

[5]. *G. Andreottola, E. Ferrarese, E. Lorenzoni, I.A. Oprea*, "Remediation of hydrocarbon-contaminated soil by electrochemical methods",SIDISA 2008 "Simposio Internazionale di Ingegneria Sanitaria e Ambientale", 24-27 Giugno 2008, Firenze.

[6]. *E.Lorenzoni, I.A. Istrate, G. Andreottola, G. Ziglio, A. Badea, E. Ferrarese, T. Apostol*, "Applicazione dell'elettroossidazione su differenti matrici di terreno contaminate da diesel", rivista Riufiuti Solidi, n.1, anno XXIV, ISSN: 0394-5391, 2010, pp. 42-51;

[7]. *D. Rahner, G. Ludwig, J. Röhrs*, "Electrochemically induced reactions in soils - a new approach to the in-situ remediation of contaminated soils? Part 1: The microconductor principle", Electrochim. Acta, 47, 2002, pp.1395-1403.

[8]. *S.-S. Kim, J.-H. Kim, S-.J. Han*, "Application of the electrokinetic-Fenton process for the remediation of kaolinite contaminated with phenanthrene", J. Hazard. Mater., B118, 2005, pp.121-131.

[9]. *S. Mazzullo*, “Bonifica dei siti inquinati da attività storiche: volano della ripresa economica”, Centro Ricerche per la Chimica “Giulio Natta”, Basell Poliolefine, Ferrara, Italia, 2009.

[10]. *S. Meinero, O. Zerbinati*, “Oxidative and energetic efficiency of different electrochemical oxidation processes for chloroanilines abatement in aqueous medium”, Chemosphere, 64, 2006, pp.386-392.