APPLICATION OF THE ELECTROCHEMICAL TREATMENT METHOD FOR THE REMEDIATION OF HYDROCARBON-CONTAMINATED SOILS

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Remediation of the existing contaminated sites assumes the application of different remediation approaches that are closely related to site-specific characteristics. Along the time, different decontamination methods and approaches have been tested with direct and indirect costs and benefits. In the framework of the current experimental study, a historically contaminated soil with high levels of petroleum hydrocarbons (TPH concentration in soil 15.967,4 mg/kg$_{d.w.}$) was the subject of the electrochemical treatment. The main aim of the applied experimental research was to evaluate the remediation potential of the electrochemical process when high levels of TPH in contaminated soils are identified.

Keywords: Total Petroleum Hydrocarbons, TPHs, contaminated soil, remediation, electro-kinetic remediation

1. Introduction

Over the years, different actions have been conducted for soil remediation and thus to environmental protection. This environmental issue is present worldwide, and environmental decision makers are using different strategies for managing the contaminated sites. Over the years, different treatment methods were studied and tested to identify suitable solutions. At national, European, and global level, increased attention is paid to soil protection, sustainable use, and to conservation and restoration of soil. In the sustainable development context, the remediation of contaminated sites is a main component. The necessity of contaminated soils restoration and their further sustainable use is continuously growing worldwide.

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In 2015, in Romania, there was a total number of 1393 contaminated or potentially contaminated sites based on the results of the national inventory conducted at the end of 2013 [1, 2, 3].

In Romania, "*Law no. 74/2019 regarding the management of potentially contaminated and contaminated sites*" has as declared objective the protection of the humans' health and of the environment from the effects of soil contamination by regulating measures to improve the quality of environmental factors affected by the confirmed presence of pollutants at levels that pose a significant risk to human health and to the environment [4]. This law is also defining the objectives for the remediation of the contaminated sites that should consider the present and future use of the contaminated site and costs of the treatment process [4]. Another goal of the present law is to improve the collaboration with the European Union's Member States by having a common objective, namely the reduction of the soil contamination [4].

The National plan and strategy for management of contaminated sites in Romania has as main objective to protect the environment, humans and animal's health from the effects of toxic substances. Decreasing of the number of the contaminated sites, followed by the quality improving of environmental factors are some of the specific environmental objectives. Ensure food security, together with promoting the further use of remediated sites, can be remembered within the socio-economic objectives in the processes of decontamination [2]. Important objectives are those that ensure that development and implementation of legal frameworks for remediation of contaminated sites. Other objective is represented by the development and implementation of the best cost-efficient soil decontamination techniques [2].

Soil contamination can arise because of different factors and circumstances, such as abandoned and inactive mine lands, leaking underground storage tanks, accidental spills of petroleum hydrocarbons, crude oil processing and use, and others. All these factors that are conducting to soil contamination will further affect the environment and both human and animal's health [4, 5].

Total petroleum hydrocarbons (TPH) are represented by different chemical compounds which have the origin in crude oil [6]. Examples of chemicals that belong to petroleum hydrocarbons (PH) are benzene, toluene, hexane, mineral oils, gasoline components and others [6]. The presence of the petroleum hydrocarbons affects soil's chemical, biochemical and physical properties [7].

Different treatment methods were applied along the time with the aim of soil remediation. Among these methods it can be mentioned the electrochemical treatment, thermal treatment, solvent extraction, bioremediation, and others [8, 9, 10]. Applying these methods and others good results can be achieved, specifically the reduction of the contaminants in soils below the thresholds established by the regulation in force in different countries. On the other hand, in choosing the appropriate treatment method or strategy, some important factors should be considered. Some examples in this regard are the age and degree of contamination, the remediation time, costs and if the proposed remediation strategy is a sustainable one. Some of the advantages of the electrochemical treatment, compared to other methods, include the following:

- the method can be applied both in-situ and ex-situ
- the ecosystem is not affected when the electrochemical method is applied
- the electrochemical method can be easily integrated with other methods for an optimization of the result.

At the same time, the method has disadvantages, and one of the main disadvantages is that the application of the electrochemical treatment depends on different variables such as:

- soil characteristics
- humidity amount
- the organic matter content.

2. Material and methods

In the framework of the current experimental work, soil samples were collected from a concrete platform, generally used for applying bioremediation treatment, located in southeastern Romania. The contamination of the forementioned soil resulted because of oil extraction activities [11], [12].

One homogenous sample was obtained after coning and quartering 5 soil samples which were collected from a 1000 m^2 area, according to the regulation in force. To determine the TPHs concentration in soil, the homogenous soil sample was chemically analyzed in the laboratory. The Standard method that was used for the identification of TPHs concentration in soil was SR EN ISO 16703:2011 [11]. The achieved results that are presented in the "Results and discussion" paragraph showed a high degree of contamination with TPHs in the investigated soil. The remediation approach proposed in the framework of the current study is the chemical oxidation that is generally used as a remediation solution for the oil contaminated soils.

2.1 Experimental setup

The contaminated soil was subjected to electrochemical experiments which were carried out in the *Laboratory for Analysis, Control and Remediation of Contaminated Soils* from the Research Centre for Advanced Materials, Products and Processes (CAMPUS) of University POLITEHNICA of Bucharest. Dimensions of the experimental setup (Fig. 1) are as following: 450 mm x 150 mm x 200 mm (L x W x H) [13]. The installation has 3 cells, each of them having a length of 150 mm. For the current experiments, only one electrochemical cell was used with the following dimensions L x W x H: 150 mm x 150 mm x 200 mm. The design of the experimental framework is evidenced in Fig. 2.

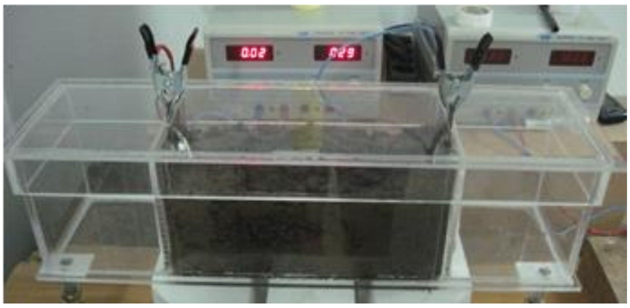

Fig. 1. The experimental setup used for the electrochemical treatment of the oil contaminated soil

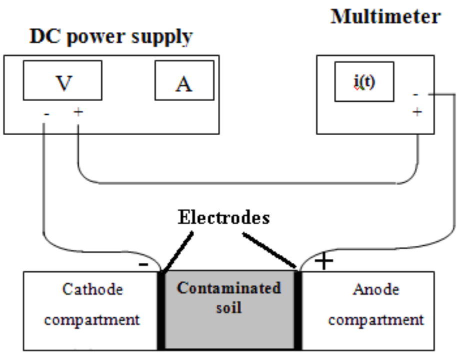

Fig. 2. The experimental framework

2.2 Experimental development

The contaminated soil with hydrocarbons has been subjected of a pre-treatment procedure. The sample was grinded, homogenized, and saturated. Water was further added on the pre-treated soil to increase the soil moisture, humidity being an important factor for facilitating the electrochemical process. The contaminated soil was placed into the electrochemical cell, 15 cm distance being established between the electrodes (anode and cathode). Within the cell, the soil was compacted in to avoid the air voids. Further, the connections between the flat electrodes (Fig. 3) and the power source (Fig. 4) were made by using the electrical conductors.

Fig. 3. Flat electrode

Fig. 4. Power source

Characteristics of the electrochemical process applied within the experimental work are presented in Table 1:

Table 1

Characteristics of the applied electrochemical process

Process parameter	**Value**	**UM**
Applied voltage	15	V
Specific voltage	1	V / cm
Remediation time	10	days
	20	

For the current research, the electrochemical process was applied for 20 days, with intermediary sampling (after 10 days) in order to evaluate the remediation degree of the contaminated soil after 10 days (EC 10) and at the end of the applied remediation process (EC 20). The achieved are illustrated in the next paragraph. Different parameters, such as Redox Potential (ORP) and pH, were monitored during the experiments. Redox Potential is an important parameter in the context of the electrochemical treatment and provides important information regarding the soil conditions.

In the framework of the current study, when the Redox Potential values were negative, the electrode polarity was reversed. In this way, the oxidation and reduction reactions were stimulated in the cathode area. In the first phase, in the anode area, it is formed an acid front. The acid front moves twice as fast as the basic one which forms at the cathode. This leads to the tendency to acidify the soil. If the objective is to return the remedied soil to the natural circuit, a favorable environment it is necessary to be created. This is done by uniformizing the pH around a neutral value. On the 9th day of the process, to maintain an optimal humidity for the development of the electrochemical process, water was added to the electrochemical cell.

3. Results and discussion

The pH variation during the electrochemical treatment is illustrated in Fig. 5.

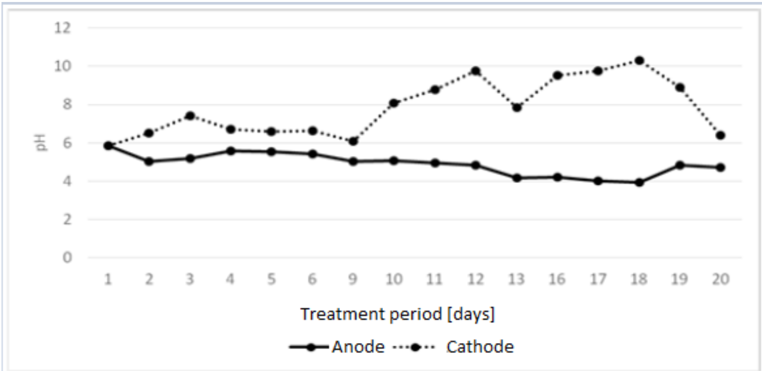

Fig. 5. pH variation during the electrochemical treatment

From the Fig. 5, it can be observed that the pH trend in the cathode area has a decrease only after the polarity is reversed. At the anode, the value increases after the 18th day, when the role of the electrodes is changed. Redox Potential variation during the experiment can be seen in the figure below:

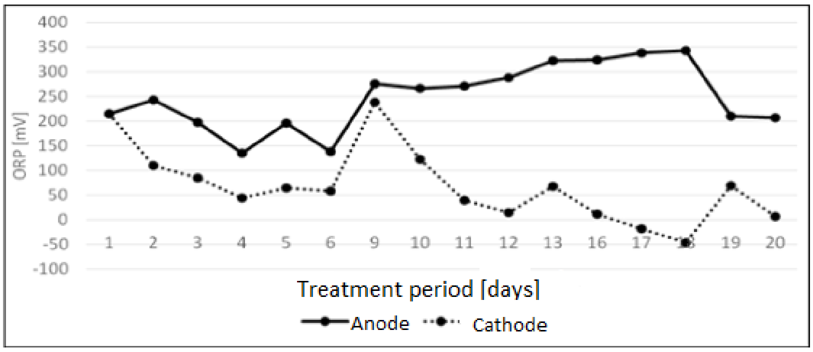

Fig. 6. Redox Potential variation during the electrochemical treatment

The chemical analysis of the contaminated soil before of applying the remediation treatment revealed the following concentration of TPHs in soil (Table 2):

Table 2

Total petroleum hydrocarbons/C_{10} - C_{40} concentration in the analyzed soil

Parameter	**U.M.**	**Concentration in soil**
Total petroleum hydrocarbons/C10 - C40	mg/kg d.w.	15967,4

The identified concentration of TPHs in soil was compared with the Romanian regulation in force [14]. As the current experimental research was developed in the framework of a collaborative research with University of Tuscia, Italy, the concentrations of TPHs in the contaminated soil were compared also with thresholds defined by the Italian regulation in force regarding environmental protection, specifically soil pollution [14]. Comparative evaluations on different other chemicals identified in the investigated soil considering the regulation in force in both countries (Romania and Italy) is detailed in a previous research paper of the authors of the current research [11].

The Romania regulation (Order No. 756) is defining thresholds for specific chemicals in soil for specific land use (sensible/less sensible) [14]. Considering the specific land use there are further defined two different limit categories: alert and intervention thresholds. The differences between the two thresholds it's represented by the level of contamination and actions that must be followed if they are exceeded. In case of exceeding the alert threshold, supplementary monitoring must be done. In case of exceeding the intervention threshold, the reduction of the contaminants' concentration in soil is required by the competent authorities [14]. From the Italian regulation in force (Legislative Decree 152/2006) [15], no differences are made between thresholds, but specific land use and thresholds for each contaminant are defined. If the threshold of any contaminant of concern is exceeded, it's concentration in soil must be reduced [15]. For the interpretation of the achieved results, the TPHs concentration in soil identified after the chemical analysis was compared with thresholds from both regulations in Romanian and Italy. As illustrated in Fig. 6, the TPHs concentration in soil was above both thresholds and thus, a remediation strategy to reduce TPHs concentration in soil was mandatory. Taking into consideration the high-level concentration of TPHs identified in the investigated soil (8 times higher than intervention threshold from the Romanian regulation and 21 times higher than indicated in the Italian regulation (C>12)), the electrochemical treatment was taken into account as a solution for decreasing of the existing contamination.

After the soil was subjected of the electrochemical process, the TPHs concentration in soil decreased as following:

- At the end of the first part of the process, EC10 (after 10 days), the TPHs concentration in soil was 11933 mg/kg d.w.), with 4034,4 mg/kg d.w. less than the TPHs concentration in soil before of applying the electrochemical treatment.
- At the end of the process, EC20 (after 20 days), the TPHs concentration in soil decreased even more, until it reached the value of 8104,25 mg/kg d.w., that mean a reduction with 7863.15 mg/kg d.w. respect to the concentration in the contaminated soil.

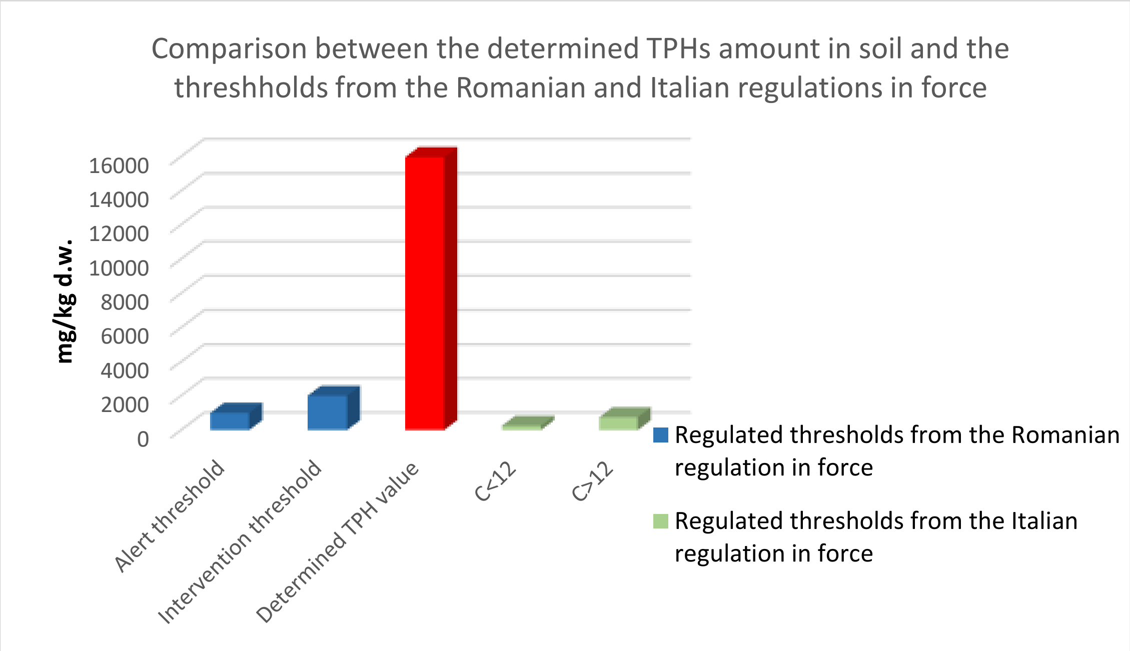

Fig. 6. The TPHs concentration in the contaminated soil and the thresholds from the Romanian and Italian regulation

Trends of the TPHs concentration in soil along the application of the electrochemical treatment are evidenced in Fig. 7.

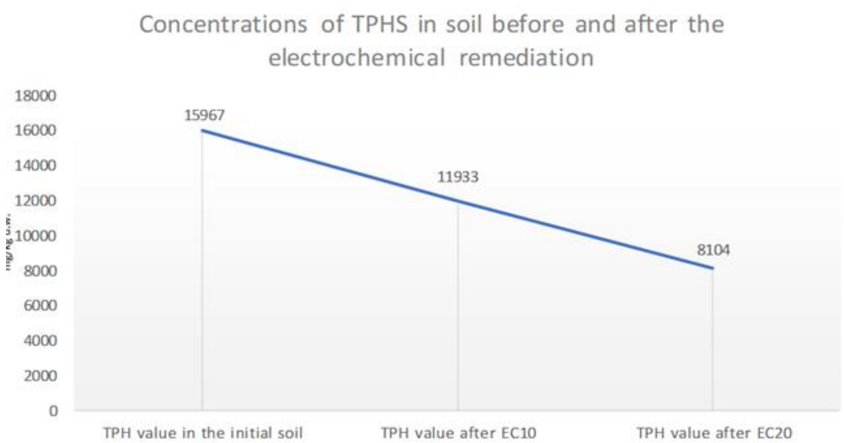

Fig. 7. The TPH concentration’s values before and after the application of the electrochemical treatment

Fig. 8 is evidencing a comparison between the concentration of TPHs in soil before and after (EC10 and EC20) the remediation, the amount of identified concentrations being compared also with thresholds from the Romanian and Italian regulation.

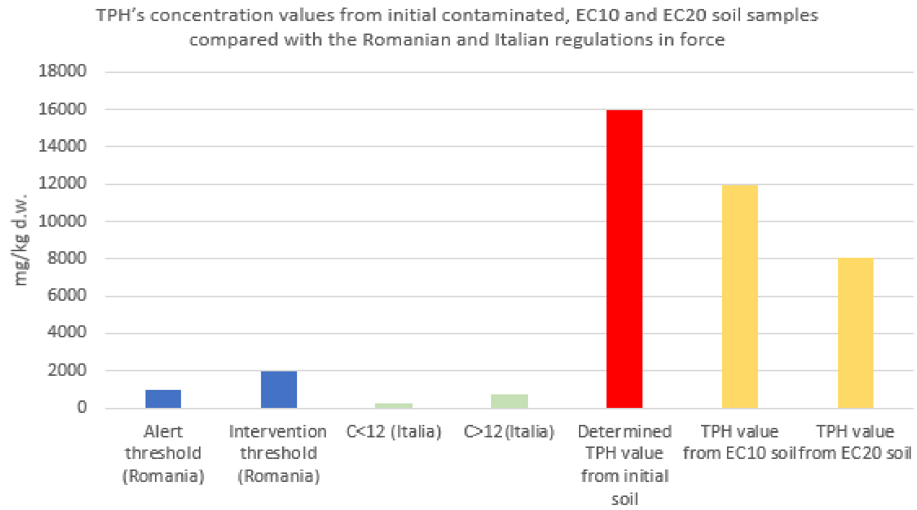

Fig. 8. TPHs concentration in the contaminated soil and after the remediation (EC10 and EC20) compared with thresholds from the Romanian and Italian regulation

The obtained results along the electrochemical treatment applied to the investigated hydrocarbon-contaminated soil are presented in Table 3.

Table 3

Total petroleum hydrocarbons in soil before, along and after the electrochemical remediation

	Concentration of TPHs in soil	**Amount of TPHs removed from the contaminated soil**	**Degree of remediation**
U.M.	[mg/kg d.w.]	[mg]	[%]
Contaminated soil	15967	-	-
EC10	11933	**4034**	**25,26**
EC20	8104	**7863**	**49,25**
EC10 – EC20	-	**3829**	**32,08**

In the next table is evidenced a comparison between results achieved in the current research and results from the literature where the electrochemical process was applied to decrease the concentration of TPHs in soil [15] [16] [17] [18] [19] [20] [21]. On the paper from the literature, the same applied voltage was used (1 V / cm) for the decontamination of diesel-contaminated kaolin soil [16].

As it can be noticed in table 4, the electrochemical method shown good results for TPH decontamination in case of complex contamination existing in both study cases. It can be observed the fact that, the longer the treatment period is, a higher the degree of decontamination is achieved.

Table 4

Total petroleum hydrocarbons level of remediation from the current research along with other results from the literature

		Initial concentration of TPHs in soil	**Amount of TPHs removed from the contaminated soil**	**Degree of remediation**
	U.M.	[mg/kg d.w.]	[mg]	[%]
Current research	**Contaminated soil**	15967	**-**	**-**
	EC10	11933	**40 34**	**25,26**
	EC20	8104	**7863**	**49,25**
According Adreottola et al., 2010 [15]	**Contaminated soil**	131000	**-**	**-**
	Results after 7 days	65000	**66000**	**50**
	Results after 14 days	60300	**70700**	**54**
	Results after 21 days	30900	**100100**	**76**
	Results after 28 days	26600	**104400**	**80**

If only the electrochemical method is used to decrease the TPH contaminant’s level, a longer period is needed and consequently, higher costs might be involved. Moreover, the electrochemical treatment led to an important remediation removal of TPH from soil even in case of high degree of soil contamination.

4. Conclusions

In the framework of the current research study, a historically contaminated soil with high levels of petroleum hydrocarbons (TPH concentration in soil 15.967,4 mg/kg d.w.) was subjected to the electrochemical treatment. Along the electroremediation process, after 10 days (EC10), the remediation level is 25,26%., while at the end of the experiment (EC20) is 49.25%. In the first 10 days of the electrochemical treatment 4034 mg of TPHs from soil were eliminated, while after 20 days other 3.829 mg of TPHs. Even if the proposed remediation approach allowed to arrive to a concentration of TPHs in soil equal with 8104 mg/kg d.w., the achieved concentration didn’t decrease below the thresholds from the Romanian or Italian regulation. On the other hand, taking into consideration the high level of concentration of TPHs at the beginning of the experiment, it is appreciated the level of remediation of almost 50% after only 20 days of experiment. The current research supports the environmental decision factors facing with important oil contaminated sites management in Romania considering the fact the main topic of the current research is covering the treatment of contaminated soils with TPH by using the electrochemical method. In was evidenced that, when applying the electrochemical method for soil remediation in the context of complex pollution, the desired results cannot be obtained in a short period of time and consequently, higher costs are needed. Thus, a hybrid method as the one that is coupling the electrochemical method with the bioremediation processes could be a good option for achieving better results. Over the years, diverse methods were applied worldwide for the remediation of the contaminated soils, but, in case of a complex pollution, the best solutions are still under research. Consequently, the present research work is a precursor of future experimental research that could use the same remediation technique but extending the remediation time (for instance to 30 days), or keeping the same remediation time and integrating this remediation strategy with another one, as the bioremediation.

Acknowledgments

The authors acknowledge funding support from the Erasmus+ Programme, SafeEngine project, contract no 2020-1-RO01-KA203-080085 and from PROVED project ID P_40_301, SMIS-CSNR: 105707, ctr. 78/08.09.2016.

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