APPLICATION OF THE ELECTROCHEMICAL TREATMENT METHOD FOR THE REMEDIATION OF PETROLEUM HYDROCARBONS FROM CONTAMINATED SOILS

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Rezumat. *Solurile contaminate cu poluanți toxici și persistenți prezintă potențiale pericole semnificative pentru mediu și sănătatea umană. Problema solurilor poluate și alegerea celei mai adecvate strategii de remediere reprezintă o preocupare actuală în întreaga lume. Ca urmare a activităților industriale aferente sectorului energetic (în principal din industria extractivă), contaminanții de interes la nivel național și internațional în sensul remedierii siturilor contaminate sunt hidrocarburile petroliere. În acest context, scopul principal al prezentei cercetări a fost evaluarea gradului de remediere a acestor contaminanți în timpul aplicării metodei electrochimice de remediere. Solul contaminat cu țiței, supus remedierii, este din județul Teleorman, comuna Siliștea, zonă în care sunt amplasate sonde de extracție a petrolului și a gazelor naturale. În urma aplicării procesului electrochimic s-a observat scăderea nivelului concentrației de TPH de la o concentrație inițială de 5000 mg/kg s.u. la 2228 mg/kg s.u., obținându-se un procent de remediere de 55%, după o perioadă de 14 zile. În consecință, se poate aprecia că procesul electrochimic aplicat în vederea remedierii unui sol contaminat cu produse petroliere este avantajos prin prisma duratei scurte de timp, însă metoda prezintă și unele dezavantaje precum consumul de energie și implicit costuri semnificative aferente cu aceasta.*

Abstract. *Contaminated soils with toxic and persistent pollutants pose significant potential hazards to the environment and human health. The problem of polluted soils and choosing the most appropriate remediation strategy is a current concern throughout the world. As a result of the industrial activities related to the energy sector (mainly from the extractive industry), the contaminants of interest at the national and international level in terms of the remediation of contaminated sites are petroleum hydrocarbons. In this context, the main aim of the present research was to evaluate the degree of remediation of these contaminants during the application of the electrochemical remediation method. The soil contaminated with crude oil,*

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subject to remediation, is from Teleorman county, Siliștea commune, an area where oil and natural gas extraction wells are located. Following the application of the electrochemical process, a decrease in the TPH concentration level was observed from an initial concentration of 5000 mg/kg s.u. to 2228 mg/kg s.u., thus obtaining a 55% remediation percentage, after a period of 14 days. Consequently, it can be appreciated that the electrochemical process applied in order to remediate a soil contaminated with petroleum products is advantageous in terms of the short duration of time, but the method also presents some disadvantages such as energy consumption and implicitly significant related costs.

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

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1. Introduction

Petroleum hydrocarbons are common site contaminants that affect human health and alter both microbial community and ecosystem functionality when these are introduced into a clean environment [1]. At the same time, these types of hydrocarbons can come into contact with the soil, forming an impermeable coating on the surface that prevents the circulation of water in the soil and the exchange of gases between the air and the soil [2].

Industrialization and practices have left us a legacy of thousands of contaminated sites in Europe. Therefore, at the EU level, there are currently approximately 3.5 million potentially contaminated sites. Soils represent a non-renewable but essential source for achieving the key objectives of the European Green Pact. Thus, the EU soil strategy for 2030 aims to protect and restore soil health for the benefit of people, nature, and climate change by establishing a series of objectives and strategies [3].

Fig. 1. European Green Deal [4]

Over time, a series of physical, chemical or biochemical technologies have been developed and applied to treat polluted soils, including electrochemical treatment, bioremediation, thermal desorption, and many others [5], [6]. Electrochemical treatment is a method of remediation of soils contaminated with various inorganic, organic, and mixed compounds [7]. Unlike other methods, the electrochemical method has the following advantages:

- It can be applied both in situ (in the place where there is contamination) and ex-situ (outside the polluted areas).
- The ecosystem is not affected when applying the method [5].

Also, the disadvantage of this method is that it depends on variables such as the characteristics of the soil, the amount of moisture, the organic matter present [6]. In our study, the technology of electrochemical treatment of polluted soils was used. In the following chapters, the steps taken to carry out the experiment and the results obtained will be presented.

2. Material and methods

In the framework of the current experimental work, soil samples were collected from Romania Teleorman county, Siliștea commune, an area where oil and natural gas extraction wells are located.

A homogeneous sample was obtained following the sanctification and quartering of five soil samples that were collected from an area of 1000 m^2, according to the regulations in force. To determine the concentration of TPH present in the soil, the homogeneous soil sample was analyzed gravimetrically, in compliance with the national standard SR EN ISO 16703:2011. The equipment used to determine the concentration of TPH (5000 mg/Kg d.w.) was the Soxhlet manual extraction system (Fig. 2), which includes the following components: flask, extractor, refrigerant. Along with this equipment, the rotavapor (Fig. 3) was also used to separate the solvent from the contaminated.

Fig. 2. The SOXHLET extraction system (Laboratory for Analysis, Control and Remediation of Contaminated Soils/CAMPUS)

Fig. 3. The rotavapor (Laboratory for Analysis, Control and Remediation of Contaminated Soils/CAMPUS)

2.1. The experimental framework

The contaminated soil was subjected to electrochemical treatment, the experiment being carried out in the Laboratory for Analysis, Control and Remediation of Contaminated Soils within the Research Center for Advanced Materials, Products and Processes (CAMPUS) of the National University of Science and Technology Politehnica Bucharest. The chemical cell (Fig. 4) used for soil treatment has the following dimensions: 750 mm x 220 mm x 220 mm (L x W x H).

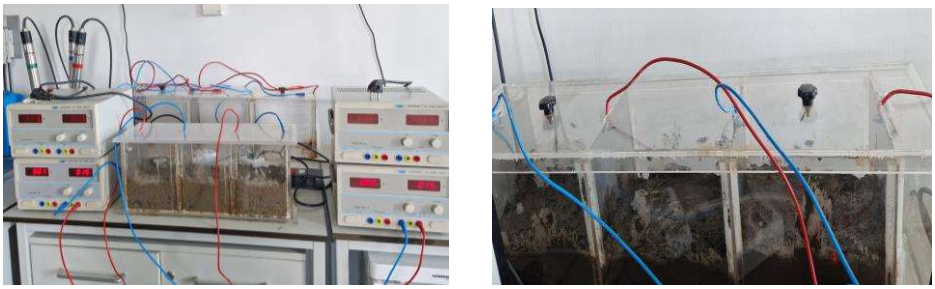

Fig. 4. Chemical cell used for soil treatment (Laboratory for Analysis, Control and Remediation of Contaminated Soils/CAMPUS)

The electro-remediation (ER) process, also called the electrokinetic electrochemical treatment, is a technique within physicochemical treatments [5]. The physical and chemical phenomena within the electroremediation method are evidenced in Fig. 5.

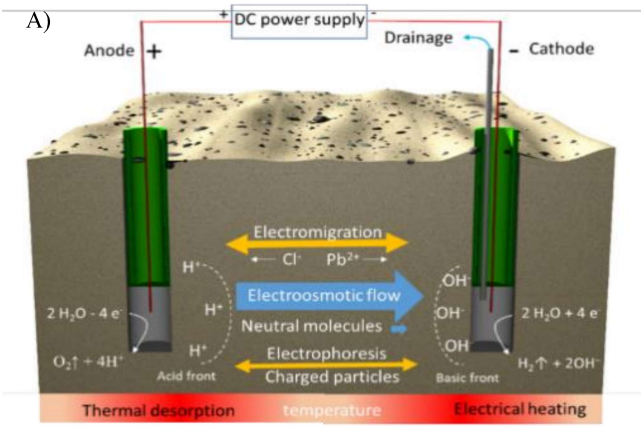

Fig. 5. Physical and chemical phenomena within the electroremediation method

3. Carrying out the experimental activity

The contaminated soil with hydrocarbons has been subjected to a pretreatment procedure. The sample was grinded, homogenised, and saturated. Water was further added to the pre-treated soil to increase the soil moisture, with humidity being an important factor in facilitating the electrochemical process. The contaminated soil was placed into the electrochemical cell, with a 25-cm distance being established between the electrodes (anode and cathode). Within the cell, the soil was compacted to avoid air voids. Also, the connections between the flat electrodes (Fig. 5) and the power source (Fig. 6) were made by using the electrical conductors.

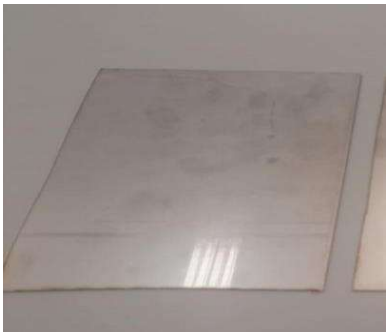

Fig. 6. Flat electrode

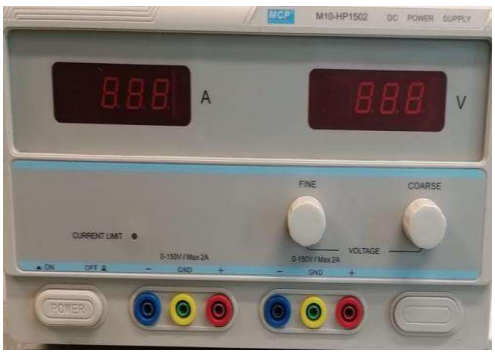

Fig. 7. Power source

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	25	V
Specific voltage	1	V/cm
Remediation time	7	days
	14	

The electrotrochemical process took place over a period of 14 days. Samples were taken to assess their degree of remediation (Table 2) after 7 days and 14 days, respectively. Different parameters such as redox potential (ORP) and pH. The parameters monitored during the experiment were redox potential (ORP) and pH (Table 2). The redox potential is a parameter measured in mV, the size of which indicates whether a solution is reducing or oxidizing. In 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, an acid front is formed. The acid front moves twice as fast as the basic front that forms at the cathode. This leads to a tendency towards soil acidification. If the objective is to return the remedied soil to its natural cycle, it is necessary to create a favorable environment. This is done by equalizing the pH around a neutral value. On the twelfth day of the process, to maintain optimal humidity for the electrochemical process, water was added to the electrochemical cell. The obtained results are illustrated in the next chapter.

Table 2. Determination of TPH content at different time intervals, and evaluation of the degree of remediation

	TPH concentration in soil	Concentration of TPH removed from contaminated soil	The degree of remediation
U.M.	[mg/Kg d.w.]	[mg]	[%]
Contaminated soil	5000	-	-
EC7	2228	2772	55.44
EC14	2871	2129	42.56

4. Results and discussion

After the soil was subjected to the electrochemical remediation process, the concentration of TPH in the soil decreased as follows:

• At the end of the first stage of the process, EC7 (after 7 days), the concentration of TPH in the soil was 2871 mg/kg d.w.

• At the end of the process, EC14 (after 14 days), the concentration of TPH in the soil decreased until it reached the value of 2228 mg/kg d.w.

The decrease in TPH concentration during the application of the electrochemical treatment is highlighted in Figure 8.

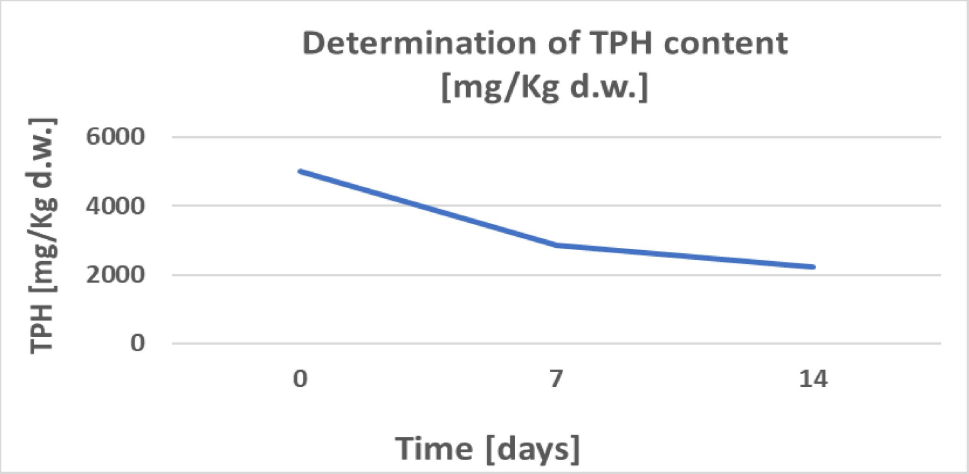

Fig. 8. TPH concentration determined after 7 and 14 days respectively

The TPH concentrations identified were compared with the reference values for traces of chemical elements present in the soil. The Romanian Regulation (Order No. 756) defines thresholds for certain chemical substances in soil for specific land uses (sensitive or less sensitive) [8].

Considering the specific land use, two different threshold categories are further defined: alert and intervention thresholds. The differences between the two thresholds are the level of contamination and the actions to be taken if they are exceeded. If the alert threshold is exceeded, additional monitoring should be carried out. If the intervention threshold is exceeded, a reduction in the contaminant concentration in the soil is required by the competent authorities.

As illustrated in Fig. 9, the soil TPH concentration was above both thresholds, and therefore a remedial strategy to reduce the soil TPH concentration was mandatory. Taking into account the level of TPH concentrations identified in the investigated

soil, which are higher than the intervention threshold in the Romanian regulation, the electrochemical treatment was considered a solution to reduce the existing contamination.

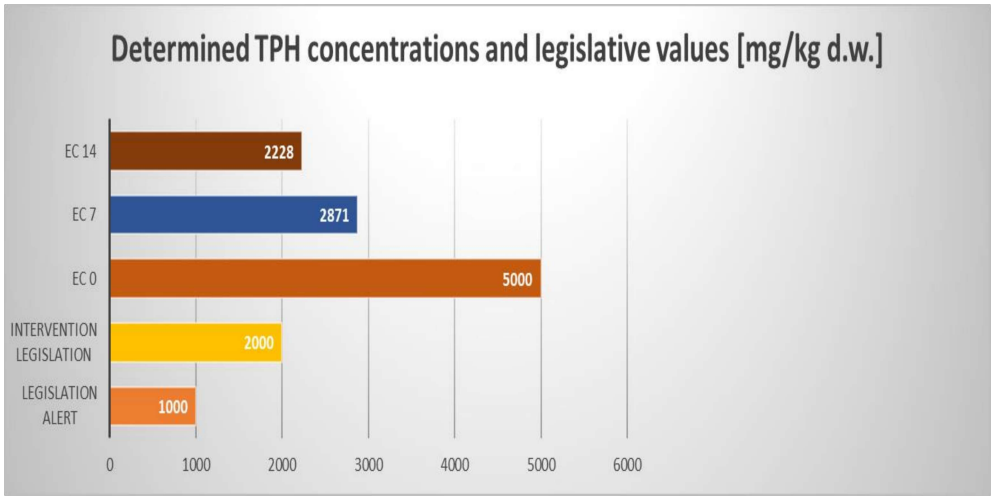

Figure 9. The evolution of the TPH concentration level in soil EC7 and EC14 compared to the legislative values according to Order 756/1997

5. Conclusions

In the current research study, a soil contaminated with petroleum hydrocarbons (soil TPH concentration 5000 mg/Kg d.w.) was subjected to electrochemical treatment and it was found that after the first 7 days, the remediation level was 42.56%, while what after 14 days the degree of remediation was 55.44%. Thus, the proposed remedial approach allowed to reach a lower concentration of petroleum hydrocarbons in the soil, but the level of concentrations did not fall below the thresholds of national legislation and regulations due to the short time interval.

6. Future research directions

In the future, the following points will be followed in the research activity:

- Evaluation of the impact of the electrochemical method of remediation of soils contaminated with petroleum products (VOCs)

- A comparative evaluation of the electrochemical method of remediation of soils contaminated with petroleum products with bioremediation

- Evaluation of a hybrid method of remediation of soils contaminated with petroleum products (bioremediation + electroremediation).

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