ASSESSMENT OF ELECTROCHEMICAL TREATMENT EFFICIENCY FOR ARTIFICIALLY CONTAMINATED SOIL WITH PAHs AND PCBs

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Key words: soil remediation, PCBs, PAHs, electrochemical treatment.

Abstract: 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 results obtained during an experimental campaign that took place in the framework of a research project co-funded by the European Regional Development Fund. Based on 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 an organic contamination. The remediation of these contaminants is essential to promote public health, environmental quality, and the economy. In the present paper, the application of electrochemical treatment of polychlorinated biphenyls (PCBs) and polyaromatic hydrocarbon (PAHs) contaminated soils was investigated. For the present research, three tests have been analyzed. The conclusion showed that the electrochemical treatment could be a viable solution for the removal of different types of PCBs and PAHs. If an analysis is to be done by comparing the obtained results, it can be noticed that after each treatment we have lower concentrations of PCBs and PAHs; most of them are lower than the strictest legal limit according to Order 756/1997 (the intervention thresholds for sensitive use).

Generalities

The subject of the present research involves the treatment of contaminated soils by polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyl (PCBs). The PAHs are a group of organic molecules composed of fused benzene rings, classified among hydrophobic organic compounds (HOCs). PAHs are tightly bound to soil and sediment particles and have little mobility (Cairney et al, 1993, Istrate et al, 2012a). A PCB is any of the 209 configurations of

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organochlorides with 1 to 10 chlorine atoms attached to biphenyl, which is a molecule composed of two benzene rings. 130 of the 209 different PCB arrangements and orientations are used commercially. PCBs have been widely used as coolants and lubricants in transformers, capacitors and other electrical equipment because of their insulating and non-flammable properties (National Safety Council, 2004). PCBs are a family of aromatic compounds consisting of a biphenyl molecule that has been chlorinated to form a large number of possible congeners. In the 1970s, due to severe concerns regarding their human toxicity, suspected carcinogenicity, and environmental persistence, several countries limited the use of PCBs. Finally, in 1985, the use and placing on the market of PCBs in the European Community was strictly restricted or banned (European Commission, 2012).

1. Materials and methods

1.1. Electrochemical oxidation, or electrooxidation, is a branch of the Direct Current Technologies (DCTs), which are innovative techniques for contaminated soil remediation, in which electrical fields are created in the polluted media by applying low-voltage direct currents (DC) to electrodes placed in the ground (Cairney et al, 1993; Van Cauwenbergh et al, 1997; Istrate et al, 2012a). These treatments are emerging for the in situ or ex situ remediation of environmental matrices. At first, DCT were used mainly for the remediation of metals, radionuclides and polar inorganic pollutants from soil and groundwater, and the process was called electrokinetic Remediation (Cocarta et al, 2009; Cuypers et al, 1998; Reddy et al, 2001). In recent years, several researches have been developed about DCT and their effectiveness in the removal of organic pollutants from soils and sediments. These studies seem to suggest that DCT can be effectively used for the mineralization of many organics, with lower energy expenditure, if compared to traditional electrokinetic remediation methods (Henner et al, 1997; Watts et al, 2002; Wick et al, 2005; Istrate et al, 2012b).

1.2. Experimental setup. The pilot plant used to apply the electrochemical treatment was developed in the frame of a research project co-financed under the Sectoral Operational Programme “Increase of Economic Competitiveness” POSCCE-A2-O2.1.2.-2009-2, RECOLAND (ID519, SMIS-CSNR: 11982 (2010-2013)).

The experimental setup used for this research (IPER 2 – Pilot plant for electrochemical remediation) is presented in figure 1. The electrodes are represented by a network formed by stainless steel tubes. Each network is formed of four stainless steel tubes, of 30 cm height, having this way a non active area of only 10%. Sample extractions were carried out using Soxhlet equipment. Soxhlet
Assessment of electrochemical treatment efficiency for artificially contaminated soil

extraction has an advantage when analyzing solid waste and soil/waste mixtures that form emulsions with more rigorous solvent mixing extraction techniques (see Fig.1).

![Experimental apparatus](image)

**Fig. 1 - Experimental apparatus used for this research:** a) general view of experimental setup; b) multimeter for current and voltage measurement; c) sensors for pH, ORP and temperature measurements; d) electrochemical cell; e) the SOXHLET used for the extraction of the solid samples; f) Heiolph Hei VAP Advantage

### 2. Experimental tests

The effectiveness of electrochemical treatment has been tested on three types of organic contamination.

In this research, three types of tests were performed. One soil sample was polluted with PAHs (test E1), another one with PCBs (test E2) and the third one with both types of contaminants (test E3). All tests were performed for a treatment period of 21 days with intermediary monitoring for the current, pH, ORP and pollutant concentration.

**2.1. Test on the PAHs contaminated soils.** The parameters that were monitored during this test were the same as for all the tests; that is the current, pH, ORP and pollutant concentration. For the first three parameters, the monitoring was done almost every two days, while for the pollutant concentrations, the analyses were performed at the beginning of the tests, after 10 days from the start of the test and at the end of the treatment.

The current trend is the same as the one mentioned in the literature (Istrate et al, 2012a, 2012b), that is an increasing in the first two days of treatment, followed
by a decreasing in the next 3 days and at the end, the steady state value for the current is reached (Fig.2).

![Fig.2. – Current variation during test E1](image)

During the 21 days of test, the soil sample did not become acid or basic, the maximum pH value measured during test E1 was 8.27 and the minimum was 7.3 (Fig.3). The highest value for the pH was registered before applying the electrochemical treatment and that was about 8.56.

![Fig.3. – pH variation during test E1 for all three areas of interest: a) anode; b) middle; c) cathode](image)

In the case of ORP (Fig.4), the values measured suggest that the predominant reactions are de oxidation ones. The values vary between 178 mV and 224 mV.

After 21 days of electrochemical treatment, a decreasing of PAHs concentrations at the end of the tests was observed compared to the ones analyzed at the beginning of E1. The treatment efficiency reached up to 90% - 100%, but the naphthalene was the only PAH that had very small efficiency, up to 20 % in the middle and cathode areas, while in the anode areas, it reached up to 55%.
Assessment of electrochemical treatment efficiency for artificially contaminated soil

Due to the results obtained at the end of test E1, the electric based treatment is an option for the PAHs polluted soils. The problem that occurred with the naphthalene can be solved by increasing the treatment period.

2.2. Test on PCBs contaminated soil. The second type of test, identified as E2, involves the application of electrochemical treatment on PCBs contaminated soil. PCBs mainly result from capacitors, transformers, batteries and other electrical equipment. In the 1970s, several countries limited the use of PCBs. So, the present test tries to offer a solution for the historical contamination of soils that already exists.

The parameters of this test were the same as the ones of the previous test, E1 that is a treatment period of 21 days and a specific voltage of 1 V/cm. The experimental setup that was used was again the same, IPER 2 (Fig.1).
The current variation (Fig. 6) is the same as for test E1, but the maximum value reached in test E2 is almost three times smaller compared to the one of the previous test (1400 mA for E1 and 550 mA for E2).

Regarding the pH, we noticed again that the soil sample was not acidified or basified, because the pH values ranged between 7 and 8. Also for the PCBs, the predominant reactions for all three areas of interest are the oxidation ones due to the fact that the ORP values ranged between 160 mV and 330 mV. A comparison between the variations of these two parameters is presented in Fig. 7.

After 21 days of electrochemical treatment, we noticed that the treatment efficiency is above 50% for individual PCBs and reaches up to 100% for PCB 156.
Assessment of electrochemical treatment efficiency for artificially contaminated soil and PCB 126. Taking into account that PCB 126 is considered to be toxic from the human health risk assessment point of view, the efficiency of the electrochemical treatment for this PCB is very good (around 95% as an average for the entire sample). Regarding the PCBs that had removal percentages smaller than 70%, the problem can be solved (as in the case of test E1) by increasing the treatment period.

The removal percentages registered after 10 days and after 21 days from the beginning of test E2, for individual PCBs are presented in Fig. 8 and for the sum of PCBs in Fig. 9.

Fig. 8. Treatment efficiencies for individual PCBs - intermediary and final monitoring for test E2

Fig. 9. Treatment efficiencies for the sum of PCBs - intermediary and final monitoring for test E2
2.3. Test on PCBs and PAHs contaminated soil. For the last type of experiment, we decided to assess the efficiency of electrochemical treatment on a mixed contamination, that is on PCBs and PAHs contaminated soil. The test, identified as E3, was developed in exactly the same conditions as the other two tests: a treatment period of 21 days and a specific voltage of 1 V/cm. The current variation (Fig. 10) is the same as for the other two tests and the maximum value that was reached was comparable to the one of test E2 (around 400 mA).

![Fig. 10. Current variation during test E3](image1.png)

Also, the pH and ORP have the same tendency as the ones encountered in tests E1 and E2. A comparison between these two parameter variations is presented in figure 11.

![Fig. 11. Comparison between pH and ORP variation for test E3](image2.png)

For this test, the removal efficiencies are smaller compared to the ones obtained when the two pollutants were treated separately. The PCBs are removed
Assessment of electrochemical treatment efficiency for artificially contaminated soil

by 50% to 90% (for only three types of PCBs: PCB 156, PCB 126 and PCB 128) and the PAHs are removed by 20% to 85% (Fig.12 and Fig.13). The difference that can be observed is that, in this case, the naphthalene is removed more easily than in test E1.

Anyway, the increase of the removal percentages can be achieved by increasing the treatment period. This idea is sustained also by the results obtained at the intermediary sampling that are smaller than the ones obtained at the end of the treatment.

Fig.12. Treatment efficiencies for individual PCBs - intermediary and final monitoring for test E3

Fig.13. Treatment efficiencies for individual PAHs - intermediary and final monitoring for test E3
Conclusions
A series of tests were performed in order to assess the efficiency of electrochemical treatment in the case of an organic contamination with petroleum products and oil capacitor.

During the tests, a continuous monitoring was done for current, pH and redox potential. At the end of experiments, in order to assess the efficiency of the treatment, we decided to analyze the 16 types of PAHs, the sum of PAH and 16 types of PCBs and the sum of PCB.

For the present research, three tests were analyzed. The conclusion showed that the electrochemical treatment could be a viable solution for the removal of different types of PCBs and PAHs.

If an analysis is to be done by comparing the obtained results, it can be noticed that after each treatment, we have lower concentrations of PCBs and PAHs; most of them are lower than the strictest legal limit according to Order 756/1997 (the intervention thresholds for sensitive use). Those that still have concentrations above this limit can be subjected to further treatment. When the initial concentrations are much higher compared to the other components, the electrochemical treatment efficiency would be much smaller, but the solution can be the protraction of the treatment period. Electrokinetic soil remediation is an emerging in situ technology which demonstrated efficiency in the remediation of fine-grained soils, and especially in the removal of organic contaminants.

The current variation for the experimental runs had the same tendency in all experiments and that was to increase up to a maximum point (1400 mA for E1, 550 mA for E2 and 400 mA for E3) after which it decreased until it reached a steady state that remained until the end of the experiment.

The illustrated approach demonstrates that the electrochemical treatment is a feasible solution for this type of organic contamination. The results can exceed 50% of removal for each type of individual pollutant that was studied. The increasing of the removal percentage can be achieved by increasing the treatment period as it was demonstrated several times in the literature by different authors.

Acknowledgements:
This work was supported 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).

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Assessment of electrochemical treatment efficiency for artificially contaminated soil


