The assessment of chemical and electrochemical treatment for the remediation of diesel contaminated soils

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Abstract: Starting with the 1st of January 2007, when Romania become one of the European Union members, our country had to comply and apply all EU directives in all areas but especially in the field of the contaminated sites. Presently the Romanian regulations regarding the contaminated sites are not very developed and must be enriched. One of the most important environmental problems is the pollution that can be seen around refineries or gas stations. The aim of this experimental investigation was to evaluate the effectiveness of electrochemical and chemical technology for the remediation of diesel contaminated soil. The soils taken into account for this study were the sand and the kaolin in different configurations.

Key-Words: contaminated soil, sand, kaolin, electrochemical treatment, chemical treatment, diesel.

1 Introduction

Soil contamination is in Europe as a widespread problem of varying intensity and significance. Cleaning up all historically - contaminated sites, commonly of industrial origin, to background concentrations or levels suitable to all uses often is not viewed as technically or economically feasible [1]. As a result, clean-up strategies increasing are designed to employ sustainable, long-term solutions, often using a risk-based approach to land management aimed at achieving “fitness for use” appropriate to the location. In the absence of specific EU legislation to address the clean up of contaminated soil, Member States apply the “polluter pays” principle to varying degrees in clean-up programs. Soil contamination consists of many individual sites where the contamination occurred either in the past, or is still occurring. The number of such sites, and hence the area of contaminated land, should diminish with time as these sites are recognized, treated and returned to use. Also, it is possible that some land that has not yet been contaminated will become so at some time in the future [2]. Site contamination is an important environmental issue. It can result from such land uses as refuse disposal, timber preservation plants, service stations, petroleum storage areas, chemical manufacturing industries and gas works. In most of the countries for which data are available, these are specifically related to the disposal of waste, losses during industrial and commercial operations and the oil industry (extraction and transport) [3]. Environmental pollution is considered a serious problem in Europe, and it has been regulated by several directives and regulations, with the purpose to limit the amount of pollutants that reaches the environment. Even so, at the moment there is no directive dedicated exclusive to soil pollution and the problems that are involved. Cleanup methods are techniques to treat or contain pollution in order to make it less dangerous for human health or for the environment [4].

In this paper will be presented a part of a research developed during a co-supervised PhD between University Politehnica of Bucharest, Romania and University of Trento, Italy [5]. The research involved the application of chemical and electrochemical treatments on artificially contaminated sand and kaolin.

2 Material and methods

The two technologies chosen for the study can be applied both in situ and ex situ. Electrokinetic remediation, variably named as electrochemical soil processing, electromigration, electrokinetic decontamination or electroecloration uses electric currents to extract radionuclides, heavy metals, certain organic compounds, or mixed inorganic species and some organic wastes from soils and slurries [6]. The base method for the current research, the electro-oxidation, is a branch of Direct Current Technologies (DCTs), which are remediation techniques for contaminated soils, in which an electrical field is created in the polluted medium by applying a low-voltage direct current to electrodes placed in the ground. The degree of toxicity of a wide range of pollutants can be substantially decreased by oxidation or reduction processes [7]. Electric fields as well as electron transfer processes have been used for the decontamination of soils and underground water containing unwanted
organic or inorganic substances. The main phenomena involved here are: electrolysis, geochemical reactions, electrophoresis, electroosmosis, and electromigration. When suitable anodes and cathodes are strategically buried in the ground or placed in contact with slurry and an electric field from a DC source is applied, one or more of these phenomena occur and the resulting effect is used for the removal of polluting substances.

**Chemical Oxidation** is a patented technology to remediate hydrocarbon and/or halocarbon contamination in groundwater and soil, and it can be ex-situ or in situ. **Ex-situ** chemical oxidation involves mixing an oxidizing compound with contaminated groundwater or soil in a vessel. The oxidizing compound can be a solution (e.g., sodium hypochlorite in water) or a gas (e.g., ozone). The oxidizing agents most commonly used for the chemical treatment of organic contaminants are ozone, hydrogen peroxide, hypochlorites, chlorine, and chlorine dioxide. For a fast site clean-up, oxidants can be pumped in one well and out another well. This approach helps mix the oxidant solution with the harmful chemicals in the groundwater and soil. In the present research the oxidant that used was the hydrogen peroxide. During the basic experimental research the experimental setup presented in fig.1 were used and included the following elements: an electrochemical cell where the sample will be inserted; a pair of electrodes that have a shape as a square from stainless steel; a direct current power supply that is connected to the electrodes with copper cables of about 2.5 mm in diameter; two cylinders for the insertion of the oxidant (for the combined tests) and eventually can be introduced two bottles for collecting the interstitial water that can be transported with electroosmotic flux in electrodes compartments.

The samples were artificially contaminated with diesel fuel commercially available that was purchased from a gasoline pump at a typical refuel station. To prepare the diesel contaminated soil samples, the soil was at first dried and then spiked with diesel fuel. One kilogram of dry soil was mixed with about 100 mL of diesel fuel, and then the sample was stirred with stainless steel spoons in a glass backer, to ensure the contaminants to be evenly distributed through the soil. After mixing, the sample was allowed to evaporate for about two weeks. Before the test, the spiked samples were saturated with demineralized water and allowed to evaporate overnight at room temperature before being inserted in the experimental setup. Two parameters were used to consider the contaminant content in the soil samples: TPH (total petroleum hydrocarbons), which refers to a family of many petroleum-based hydrocarbons, and TOC (total organic carbon), which represents the whole content of organic substances in the soil samples. The experimental part was divided in four parts:

(i) electrochemical treatment applied on contaminated clay (kaolin);
(ii) electrochemical treatment applied on contaminated sand;
(iii) electrochemical treatment applied on contaminated mixed sample (sand and kaolin);
(iv) a combined treatment (chemical oxidation applied simultaneously with electrochemical oxidation) applied on a diesel contaminated sand.

### 3 Experimental part – tests and results

In the following paragraphs the different tests performed during this research, will be presented. During this experimental research, the tests were performed on three types of matrix: sand, kaolin and a mixed sample composed by sand and kaolin.

#### 2.1 Electrochemical oxidation applied on a diesel contaminated soil

The implementation of the electrochemical remediation system in the field is relatively simple, its design and operation for successful remediation is cumbersome due to complex dynamic electrochemical transport, transfer, and transformation processes that occur under applied electric potential [8].

##### 2.1.1 Test on artificially contaminated kaolin

Test EO_K, which aimed at investigating the variation of contaminant removal with test duration, was performed with a constant voltage of 10 V (1 V/cm) for 4 weeks. The initial current flowing across the soil specimen was 17 mA (the measurement was done at the beginning of the test, after 20 minutes). An initial current of 2 mA was measured at the beginning of the experiment, while 1 mA was encountered at the steady state. Although the measured current was not very high, the current trend was once more characterized by a rapid decrease, and by some fluctuations during the period.
from the 1st to the 3rd day of the treatment, when some temporal rebounds of the current flowing were encountered. TOC removal increased with the increase of the treatment time from 45% to 54%, and for TPH the removal percentages are higher from 50 to 80%. The results are presented in fig. 2.

The results obtained at the end of the test across the soil samples, it can be noticed that the pH decreases with the increase of distance from cathode on one hand and on the other hand the TOC and TPH increases with the increase of the distance.

2.1.2 Test on artificially contaminated sand
Another type of soil that wanted to be tested was the sand. That was because of two main reasons: one is the difficulty that was encountered when it was tried to treat this type of soil, and another reason was the fact that in Romania this type of soil can be found in large contaminated areas (by it self or combined with other types of soils). The main characteristics of the tests performed during this research are presented in table 1.

Table 1. The main characteristics of the tests performed on sand

<table>
<thead>
<tr>
<th>Test</th>
<th>Applied voltage [V]</th>
<th>Specific voltage [V/cm]</th>
<th>Treatment period [days]</th>
</tr>
</thead>
<tbody>
<tr>
<td>EO_S1</td>
<td>5</td>
<td>0.5</td>
<td>28</td>
</tr>
<tr>
<td>EO_S2</td>
<td>10</td>
<td>1</td>
<td>28</td>
</tr>
<tr>
<td>EO_S3</td>
<td>30</td>
<td>3</td>
<td>28</td>
</tr>
</tbody>
</table>

The results obtained after a treatment period of 28 days are presented in fig. 3.

The relative values for TPH, with the time passing increase to return to decrease after a period; the values for TOC after an initial decrease are starting to increase in day 21. For the test EO_S1 the removal percentages are increasing at the beginning, but after a while the values for TOC and TPH are a little bit strange and that is why it cannot be define a variation law of the removal percentages.

In test EO_S2, the removal percentages were modest (20% for the TOC and 27% for TPH) and lower than the results obtained in the previous test, were the applied voltage was lower. So it can be noticed that an increasing of voltage does not always produce increasing pollutant removal.

It was noticed a non uniformity in the removal along the sample; indeed, the biggest removal was obtained near the anode side and also near the cathode side, while in the center the removal is very low.

Another parameter that was measured was the ecotoxicity. At the end of the test it can be noticed a decreasing of the value for the ecotoxicity for all three tests. This means that the environment at the end is more toxic than at the beginning of the test. Indeed, the treatment could have been provoked the appearance of secondary products of diesel, products that are more hazardous for the bacteria than the initial ones.

2.1.3 Test on artificially contaminated mixed sample
The test EO_M applied electrooxidation on a heterogeneous matrix of soil composed of a layer of sand and one of kaolin, arranged horizontally, for the duration of 4 weeks, using a specific voltage of 1 V/cm.

The layers of soil were placed horizontal in the electrochemical reactor, precisely on the bottom of the reactor we have sand and on the top kaolin. The test EO_M have been performed on a sample of sand Vaga 12 and white kaolin with a total weight of 3 kg, both artificially contaminated by diesel fuel. The initial sample of soil had a pH of 8 in the layer of sand and a pH of 6 in kaolin. Instead, the initial humidity of kaolin was 48.7% and that of sand of 27.1%. It have been measured a final pH value of kaolin of about 4.52, while in sand the pH at the end of the treatment was 9.82. It can be said that while the kaolin had the tendency to get acidified (past from a pH of 6 to one of 4.52), the sand has increased its pH. Regarding the
humidity, even for this parameter, it was measured only the initial and final value. So, in sand the humidity passed from the initial value of 27.1% to a final value to 21.3%, while in the kaolin the humidity at the beginning of the test was 48.7, while at the end of treatment presented a value of 39.7%. For test EO_M have been analyzed the initial and final samples of sand and kaolin. In fig. 4 are presented the data for concentration (in terms of TOC and TPH) and removal efficiency obtained at the end of treatment.

The kaolin shows a modest decline in TOC and TPH at the end of treatment, while the sand shows a good removal. This fact leads us to believe that, again, has witnessed the phenomenon of exchange of pore water between sand and kaolin. During this test, the kaolin had a final humidity of about 8 percentage points lower compared to its initial humidity. Even the sand presents a decreasing in humidity at the end of the process. The fact that the kaolin has failed to recover all the quantity of water lost through electro-osmosis underlines the fact that the clay is able to take the water from the sand, because the kaolin is located above the sandy layer and have to defeat the gravitation in order to move the water from one layer to another.

2.2 Combined treatment applied on diesel contaminated sand
Some recent studies have demonstrated that the simultaneous application of two techniques had encouraging results. Indeed, applying in the same time electrooxidation and chemical oxidation, it is assumed that the electrokinetic treatment can facilitate the distribution of the oxidant and promote the production of radicals. It is thought; moreover, that the movement of the oxidant, which in generally is difficult to obtain in soils with low values for hydraulic conductivity, can be encouraged by the electrokinetic transport, such as electromigration and electro-osmosis. In this paragraph two types of methods will be presented: first one involves the application of the combined method on a stratified sample and the second one on a diesel contaminated sand.

2.2.1 Test on a stratified sample
The test ECO_M (electrochemical and chemical oxidation applied on a stratified sample) has been performed with the main purpose to observe the behavior of the integrated system and the effectiveness in terms of contaminant removal that can be obtained with hydrogen peroxide. The oxidizing agent chosen has a high potential for oxidation that can be applied to a wide range of organic contaminants. In the literature several studies that are related to the application of hydrogen peroxide for soil remediation, can be found. The test ECO_M has been conducted on a stratified sample with a total weight of 2.1 kg, previously artificially contaminated by diesel fuel. The test was performed using the experimental setup 2, had a duration of 4 weeks with a specific voltage of 1 V/cm.

The oxidant was inserted directly into the anode compartment and in this way, the flow that has been obtained has been a nearly saturated stream (unlike in the previous test where, as the basis of the two cylinders were above of the reactor extremities, the flow was saturated and forced). Regarding the oxidant quantity that had to be inserted into the soil sample it was decided to inject the hydrogen peroxide into the anode compartment until it was full and it was maintain at this level during the treatment so that the oxidant can penetrate throughout all the height of the sample.

While in sand it is noted a general increase of pH compared with the initial value, in kaolin the pH is decreased, with only 1-3 points respect to the initial value. Hence, unlike other oxidants, hydrogen peroxide probably did not succeed to create an oxidizing environment.

From what is revealed by the data from the graphs (fig. 5 and fig. 6), it is seen that the removal of pollutant, in terms of TOC and TPH, obtained after 4 weeks of integrated treatment, proved to be somewhat modest (16% removal of TPH for the sand and 12% for TPH of kaolin).
The fact that in sand was noticed different distribution of treatment efficiency, in terms of TPH, equal to 68 at anode, while in the middle and at cathode has been seen an increase of the contaminant concentration if it is compared to the initial value. One of the reasons can be the fact that created conditions in soil because of the integration of the two remediation processes, have somehow blocked the oxidation from center to the cathode. Indeed, noting that the pH created at the end of treatment, resulted in sand in the formation of basic pH in the central area and at the cathode, while at anode the pH remained neutral having a value of 7.

### 2.2.2 Test on a diesel contaminated sand

This test has been performed with the main purpose to observe the behavior of the integrated system and the effectiveness in terms of contaminant removal that can be obtained after a periodical change of polarity. This trial been conducted on a simple sample of sand with a total weight of 2.4 kg, previously artificially contaminated by diesel fuel. The test ISECOPC (in situ electrochemical and chemical oxidation with polarity changing) has been performed on diesel contaminated sand, in the experimental setup 2 for a treatment period of 28 days with a specific voltage of 1 V/cm. The oxidant used for this test was hydrogen peroxide with a concentration of 10%. The quantity of oxidant that must be inserted into the contaminated sample was calculated at about 810 ml.

The trend of the current is decreasing and is characterized by small intensity peaks that are localized after a short period from the oxidant injection.

Regarding the evolution of soil pH, it is noted that the changes made during this test are very similar to those in the previous tests, where at anode the pH tends to decrease and at the cathode to increase. The difference consists in the fact that the variation is very small, almost undetectable.

Another parameter that has been monitored during the test ISECOPC is the redox potential. Redox potential (also known as oxidation / reduction potential or ORP) is the tendency of a chemical species to acquire electrons and thereby be reduced. Each species has its own intrinsic reduction potential; the more positive the potential, the greater the species affinity for electrons and tendency to be reduced. High redox potential near the anode indicates highly oxidizing conditions, while low redox potential near the cathode indicates reducing conditions. It was noticed that after the first day of treatment the redox potential decreased linearly from the anode to the cathode to a value closed to zero.

The removal percentages obtained at the end of the test were very good. For TOC it was registered almost 50% removal and for TPH around 70% (fig. 7). The TPH distribution was evaluated at the end of the experiment (fig. 8) to assess any influence of the electrode distance or of the transport phenomena on the pollutant removal. The TPH concentration in the soil sample ranged from 2.26 g/kg<sub>DW</sub> at the anode of the specimen to 2.77 g/kg<sub>DW</sub> in the section closest to the cathode and in the middle. Despite this small variability, that can be considered due to analytical errors and to a quite heterogeneous distribution of the hydrophobic pollutants of concern, as expected, no significant influence of the electrode distance or of the transport phenomena was detected for sand. For TOC it can be noticed also the uniformity in removal percentages along the soil sample.
4 Conclusion
This study was conducted to assess the effectiveness of electrochemical oxidation as a single treatment, or combined with chemical oxidation for the remediation of different organic pollutants from fine-grain (kaolin) soils and sand.

In the case of only electrochemical treatment applied on a diesel contaminated sand, it was noted that an increase in the applied voltage, results in higher removal percentages of diesel in terms of TPH (from a removal equal to 39% with a voltage of 0.5 V/cm – test EO_S1 and arrive at a removal of 46% with a voltage of 3 V/cm EO_S3). The removal percentages in terms of TOC did not suffer an increasing with increase of the applied electric gradient at times, the percentages decreased with increasing voltage (removal of 31% with a voltage of 1 V/cm and a removal of 23% with a voltage of 3V/cm). This leads us to believe that it is not convenient to use a high potential difference, as it does not always lead to a significant increase in terms of removal. It is sufficient to apply a low voltage, which in terms of specific voltage translates into an electric gradient of 1 V/cm (or lower than 0.5 V/cm).

Only electrooxidation, applied on a stratified sample of sand and kaolin, is not effective for removing the contaminant in the whole sample of soil, because it was created a strong non uniformity in contaminant degradation favoring the remediation in sand and limiting the removal in kaolin.

In the integrated tests where electrooxidation and chemical oxidation were applied, the simultaneous application of chemical oxidation and electrooxidation assures that in kaolin, thanks to the formation of electroosmotic flux, the oxidant succeeds to pass through the soil sample, while in sand, the contaminant that has not been degraded by the electrooxidation will be attacked by the oxidant.

The application of the test ISECOPC seems to have encouraging results. The results obtained with this techniques are the best compared to all the tests performed on sand (70% removal for TPH).

In conclusion, for the sand matrix the best solution could be the application of the test ISECOPC, while for the kaolin matrix the test EO_K seems to have the highest results.

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