

ELECTROCHEMICAL TREATMENT OF PAH CONTAMINATED SEDIMENTS AND HUMAN HEALTH RISK ASSESSMENT

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Abstract. According to the European Environmental Agency, soil contamination requiring clean up is about 250,000 sites in the European Economic Area (EEA) and this number is expected to grow. The main aim of this paper is to present an approach that was taking into account in order to identify the optimal solution for the remediation of contaminated soils and to assess human health risk from exposure to polluted soils. The technologies used in the experimental work are based on chemical and electrochemical oxidation. The considered exposure pathway for the assessment of the individual risk is soil ingestion. PAHs and B(a)P are the pollutants considered for the identification of new concentration levels after soil remediation and the influence of different decontamination technologies in relation with effects on the exposure through the soil exposure pathway. Based on the results of the experimental part of this study, chemical oxidation proves to be an effective remediation technology for the contamination of concern. Different oxidants and different reagent dosages showed different removal efficiencies. The best removal percentages were achieved with: modified Fenton's reagent (100 mmols of H₂O₂ per 30 g - sample of sediments); hydrogen peroxide (25 mmols of H₂O₂ per 30 g - sample); potassium permanganate (50 mmols and 100 mmols of KMnO₄ per 30 g - sample). The electro-oxidation showed to be able to achieve a very good PAH removal (above 90%) after a four week treatment. The approach that will be illustrated in the following paper will demonstrate that the assessment of the human health effects must really become an important component of environmental assessment.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic molecules composed of fused benzene rings, classified among hydrophobic organic

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compounds (HOCs). PAHs are tightly bound to soil and sediment particles and have little mobility.

PAHs can derive from many industrial activities, as combustion of waste and fossil fuels, production of coke, asphalt or coal tar, fuel processing, as well as oil spills. Once they are released in the environment, PAHs tend to persist and occur in natural media such as soil, sediments, water and air, resulting in a widespread distribution (Cuypers et al, 1998; Harvey, 1997; Henner et al, 1997). PAHs are persistent organic pollutants (POPs), and the environmental persistence increases with ring number; it is also reported that the greater the number of benzene rings in the PAH molecule, the greater the resistance to degradation (Bossert, 1986; Henner et al, 1997).

It is believed that PAHs in soils are a result of local or long-range air transport and subsequent deposition. Background PAHs levels are generally the highest in urban soils and bordering near shore sediment due to the presence of large concentrations of anthropogenic activity in the urban corridors (Cairney, 1993). Other more direct sources of PAHs in soils include sludge disposal from public wastewater treatment plants, automotive exhaust, irrigation with coke oven effluent, leachate from bituminous coal storage sites, and use of contaminated soil compost and fertilizers (Watts et al, 2002).

The aim of the experimental investigation presented in this paper was to assess the effectiveness and the feasibility of two different remediation techniques, chemical and electrochemical oxidation, for the remediation of fluvial sediments contaminated by polycyclic aromatic hydrocarbons (PAHs). Additionally, it was evidenced the importance of using risk assessment as a tool for the decision-makers.

The present research was started across two PhD theses as a result of an international collaboration between University "POLITEHNICA" of Bucharest and University of Trent, Italy. As a consequence of the two remembered PhD researches, at this time, at the University "POLITEHNICA" of Bucharest is developing a new project co-financed under the Sectorial Operational Programme "Increase of Economic Competitiveness" POSCCE-A2-O2.1.2.-2009-2, RECOLAND (ID519, SMIS-CSNR: 11982 (2010-2013)). The main topic of the RECOLAND project is the remediation of persistent and toxic pollutants (PTPs) contaminated soils through different proposed technologies (electro-remediation, bioremediation and thermal treatments: pyrolysis and incineration) and the assessment of the risk coefficient before and after the soil decontamination through the proposed technologies. The present paper is illustrating the feasibility of using chemical and electrochemical oxidations to degrade PAHs from a natural contamination considering in the same time the human health individual risk. It must be underlined that RECOLAND will consider besides the electrochemical

oxidation also biological and thermal treatments and cost analysis. In this way, the multicriteria decisional system that will be developed will be able to decide which remediation technique is most appropriate to be applied in order to decontaminate soils.

1. Remediation treatments of soils

1.1. Chemical oxidation. Chemical oxidation is a remediation technique that uses chemicals (named oxidants) to mineralize organic pollutants by redox reactions. It is considered effective for the remediation of many types of hydrocarbons and organic pollutants, including halogenated compounds and recalcitrant contaminants, as PAHs. The oxidants that are most commonly used for environmental purposes are ozone, hydrogen peroxide, permanganate and activated persulfate (Bossert, 1986).

The treatment chemicals typically mineralize most organic compounds to carbon dioxide, water, and salts. Chemical oxidation can be applied both: in situ and ex situ. The main advantage of ex situ treatment is that generally requires shorter time periods than in situ treatment, and there is more certainty about the uniformity of treatment. This is because of the ability to homogenize, screen, and continuously mix the soil. Ex situ treatment, however, requires excavation of soils, leading to increased costs and engineering for equipment, possible permitting, and material handling/worker exposure conditions (Van Cauwenberghe, 1997).

In the present research two types of test will be presented: batch tests and column tests. In order to assess the removal efficiency of the batch tests, several laboratory tests were performed under different conditions, with the following liquid reactants: a) hydrogen peroxide (H_2O_2) (addressed as T_{HP} tests); b) modified Fenton's reagent (addressed as T_{MF}); c) potassium permanganate (addressed as T_{PP} tests) and d) activated sodium persulfate (addressed as T_{AP} tests). Also some combinations of these chemicals were tested as remediation agents, e.g. potassium permanganate and hydrogen peroxide (addressed as T_{PPHP} test), or activated sodium persulfate and modified Fenton's reagent (addressed as T_{APHP}).

1.2. Electrochemical oxidation. Direct Current Technologies (DCTs), are techniques for contaminated soil remediation, in which an electrical field is created in the polluted medium by applying a low-voltage direct current (DC) to electrodes placed in the ground (Van Cauwenberghe, 1997). The application of an electrical field to a soil has several complex physical and chemical effects, which include water electrolysis, electroosmosis, electromigration, electrophoresis, changes of pH

in soil and geochemical reactions. During the electrochemical treatment of a contaminated soil, the soil-pore water system can be considered as an electrochemical cell, in which oxidation and reduction reactions occur, water electrolysis providing the partners for the redox reactions.

In soils, the presence of microconductors (ITRC, 2005), mainly composed by particles of iron and other metals, allow the redox reactions to occur not only near the electrodes, but within the entire treated medium, simultaneously at any interfaces between soils and pore water. This way, hydrogen peroxide (H_2O_2) can be produced as a result of redox reactions. Since soils commonly contain significant amounts of iron, once H_2O_2 has been created, hydroxyl radicals ($\bullet OH$) can be produced, according to the Fenton's catalytic reaction.

Generally, the DCTs include two types of processes (Rahner et al, 2002): 1) the electrokinetic transport, including electroosmosis, electromigration and electrophoresis, which lead to the mobilization and removal of metals, radionuclides and polar organic pollutants, and 2) the electro-oxidation, based on the electrochemically induced redox reactions, responsible of the mineralization of immobile organic contaminants.

During this experimental investigation, three laboratory tests were performed in order to investigate the effectiveness of electrooxidation on the PAH contaminated sediments.

2. Experimental tests

2.1. Chemical oxidation. This first part of the research was performed on a historical contamination, PAHs polluted sediments. The contaminated sediments of concern were collected in a canal, located in the town of Trento (Italy), which for several decades had received industrial effluents polluted by organic and inorganic compounds, deriving from a coal tar production site. Several samples (total weight about 10 kg) of fine-grain silty sediments were collected from the first layer (30-40 cm) at the bottom of the canal; these samples were then mixed together and mechanically stirred to produce a final, homogeneous sample.

In order to investigate the effectiveness of chemical oxidation, several laboratory batch tests were carried out at bench scale. Some preliminary column tests showed that the permeability of the sediments of concern was very low. For this reason, an in situ chemical treatment could not be considered easily feasible. The investigation continued in order to assess the feasibility of an ex-situ treatment of chemical oxidation with liquid reactants.

Each batch test was conducted on a 30g sample of contaminated soil placed in a 100 mL reaction bottle. After adding chemical agents (oxidants, and where

necessary, catalysts), the soil slurries were brought to a normalized volume of 100 mL by adding deionized water. For each reactant the tested dosages ranged from 25 mmols to 200 mmols. For the tests with modified Fenton's reagent and activated persulfate, which required the use of a catalyst, a solution of chelated ferrous ions was added to the samples soon after the oxidant agent. Ferrous ions were obtained from ferrous chloride salts (FeCl_2), while catechol was used as chelating agent. Two molar ratios catalyst:oxidant were considered for modified Fenton's reagent, equal to 1:100 (T_{MF100} tests) and to 1:50 (T_{MF50} tests). For the activated sodium persulfate tests, a 1:25 catalyst:oxidant molar ratio was used.

Since some preliminary tests showed that the sediment permeability was too low to allow a regular flux of liquid reactants across, only gaseous ozone was tested in the column tests. The column tests were conducted on 100 g sediment samples with a transparent PVC column (internal diameter 2.5 cm, length 30 cm), the ozone being produced by an ozonator from pure oxygen, provided by an oxygen cylinder. During tests the oxidant dose was regulated by changing the exposure time: two tests were performed with durations of 3 and 6 hours respectively, corresponding to a total ozone dose of 0.25 mols and 0.5 mols. The main results obtained across the presented remediation technique are presented in the next paragraphs.

2.2. Electrochemical oxidation. In the second part of the research, the matrix (silty clay mainly composed of kaolin) used for the experiments was artificially contaminated with diesel fuel commercially available that was purchased from a gasoline pump from 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, in order to ensure the even distribution of the contaminants through the soil sample. After mixing, the sample was allowed to evaporate for about two weeks. Before tests, the spiked samples were saturated with demineralized water and allowed to evaporate overnight at room temperature before being inserted in the experimental setup.

The experiments were performed with a one-dimensional experimental setup for bench scale testing. The setup consisted in a PVC reactor, including a reaction cell (10 cm by 10 cm by 10 cm), a pair of stainless steel plate electrodes and a stabilized DC generator, providing up to 60 V and up to 5 A. During each experiment, a contaminated sediment specimen, having a mass of about 2 kg, was at first saturated with demineralized water and inserted in the test setup. A direct electric current was generated across the specimen by applying a steady voltage

between the electrodes. Testing was continued for a fixed period of time, after which the soil specimen was removed from the cell and analyzed. All the tests were performed at room temperature and were unenhanced. Moreover, no hydraulic gradient was applied across the electrodes. The investigated parameters were voltage, current, soil pH, humidity, TOC and PAH contents. The following tests were performed during this study:

- test T_{EO1} : duration of 2 weeks, applied voltage 5 V (0.5 V/cm);
- test T_{EO2} : duration of 2 weeks, applied voltage 10 V (1 V/cm);
- test T_{EO3} : duration of 4 weeks, applied voltage 10 V (1 V/cm);
- test T_{EO4} : duration of 4 weeks, applied voltage 20 V (2 V/cm).

The main results obtained across the presented remediation technique are shown in the next paragraph.

3. Results obtained through the developed tests

Based on the results of the experimental part of the study, chemical oxidation proves to be an effective remediation technology for the contamination of concern. Different oxidants and different reagent dosages showed different removal efficiencies. The best removal percentages were achieved with: modified Fenton's reagent (100 mmols of H_2O_2 per 30 g - sample of sediments); hydrogen peroxide (25 mmols of H_2O_2 per 30 g - sample); potassium permanganate (50 mmols and 100 mmols of $KMnO_4$ per 30 g - sample).

Tab. 1. PAH concentrations in sediments after applying different treatment techniques [mg/kg_{dw}]

	Benzo(a)pyrene _{min} (T_{PP2})	0,7
Chemical oxidation	Total PAHs_{min} ($T_{MF50.1}$)	69,06
	Benzo(a)pyrene _{max} (T_{HP1})	105,40
	Total PAHs_{max} (T_{HP1})	1.586,41
	Benzo(a)pyrene (T_{EO1})	0
	Total PAHs (T_{EO1})	135,843
Electrochemical oxidation	Benzo(a)pyrene (T_{EO2})	19
	Total PAHs (T_{EO2})	327,143
	Benzo(a)pyrene (T_{EO3})	3,9
	Total PAHs (T_{EO3})	96,9
	Benzo(a)pyrene (T_{EO4})	6,0
	Total PAHs (T_{EO4})	64,5

The electro-oxidation showed to be able to achieve a very good PAH removal (above 90%) after a four week treatment. The applied voltage seems to have a limited influence on the efficiency of the remediation action, good results being

achieved with specific voltages as low as 1 V/cm, with low energy expenditures. On the other hand, the remediation efficiency proved to increase significantly with process duration. According to the results achieved, both techniques proved to be effective for the remediation of PAH contaminated sediments and to be able to meet the remediation goals. Chemical oxidation seems amenable only in ex situ remediation actions, because the low permeability of the sediments of concern, constrains its in situ applicability; on the opposite electro-oxidation is thought to be easily applicable for both in situ and ex situ remediation actions. The main results considering both technologies for the treatment of PAH contaminated sediments are presented in Table 1 (for chemical oxidation only the highest and lowest values of final concentrations are reported). Must be taken into consideration the fact that the initial concentrations for benzo(a)pyrene and total PAHs were 142.70 mg/kg_{dw}, respectively 2816.40 mg/kg_{dw}.

4. Human health risk assessment from decontaminated sediments

Based on the results illustrated below, both chemical oxidation and electrochemical oxidation proved to be effective in the remediation of the sediments of concern. In order to illustrate how individual human health risk is changing in relation with the proposed decontamination methodologies, the human health risk assessment as a tool in decisional criteria was applied. For now, the individual risk was assessed considering the HR_{AIRC} software developed through an international PhD (Cocârță 2009). During the research developed through the RECOLAND project, a multicriteria decision support system will be developed. The multicriteria system will help the decision-makers to decide with regard to most appropriate remediation technique to be applied in order to remediate PTPs contaminated soils. At this point, tools as risk assessment could play an important role for peoples who make the final choice among the alternatives for soil decontamination.

The present work is illustrating the main results of the assessed human health risk from contaminated sediments, before and after applying the decontamination techniques. The human health risk from contaminated sediments was estimated applying the methodology proposed by the United States Environmental Protection Agency (US EPA) (US EPA, 1998). The methodology includes four steps: 1. *hazard identification* (review key research to identify any potential health problem that a chemical can cause), 2. *exposure assessment* (assessment of the amount, lasting, and pattern of exposure to a chemical), 3. *dose-response assessment* (estimation of the relationship between dose, or level of exposure to a substance, and the incidence and severity of an effect) and 4. *risk characterization* (assessment of the risk from a chemical in term of cancer or other illnesses in the population). The main supposition in order to be able to assess the individual risk is

that the treated soil is from an area dedicated to a residential use. Considering that the residential area is developed after the soil remediation, no deposition from the contamination source exists. As a result, the main exposure pathway is soil ingestion.

5. Discussions

With the aim of assessing how the individual risk through the soil ingestion pathway in a residential area is changing, the HRA_{IRC} software based on MATLAB[®] was applied. The HRA_{IRC} software was developed along a PhD thesis. PAH concentrations in sediments before and after applying remediation techniques were applied. The associated individual risks to every single concentration are illustrated in Figures 1 and 2.

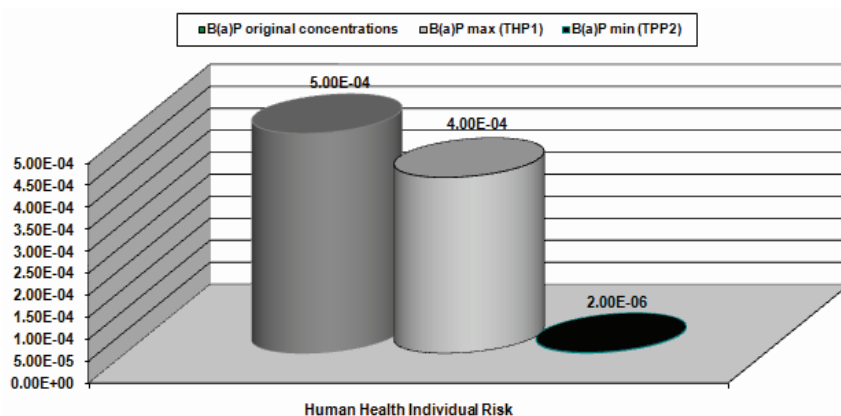


Fig. 1 – Human Health Individual Risk (IR) trend before and after applying chemical oxidation treatment of B(a)P contaminated sediments

It is known that an acceptable individual risk is 10^{-6} , which means one case of cancer over one million of exposed people (World Health Organization). B(a)P oral cancer potency (or slope factor) considered for assessing the risk through the soil ingestion pathway was 1.2×10^1 (US EPA, 2005). Concerning human health risk, in order to evaluate the worst scenario as well as to avoid a risk underestimation, the highest values of their range were chosen for some parameters; it was the same related to PAH cancer potency for which B(a)P oral cancer potency was chosen. The obtained results showed the importance of using risk assessment as a tool in choosing the most appropriate techniques for sediments (soil) remediation. Figure 3 is illustrating the tendency of Human Health Individual Risks from sediments contaminated with B(a)P before and after the electrochemical oxidation (T_{EO1})

proposed as a decontamination technology. What it can be observed in the following figure is that electrochemical oxidation (T_{EO1}) could be a solution for decreasing human health risk till an acceptable one, as a consequence of decreasing the concentration level of B(a)P in sediments. On the other way, an important decreasing of risk was noticed also for PAHs in case of applying electrochemical oxidation (T_{EO1}) (fig. 4).

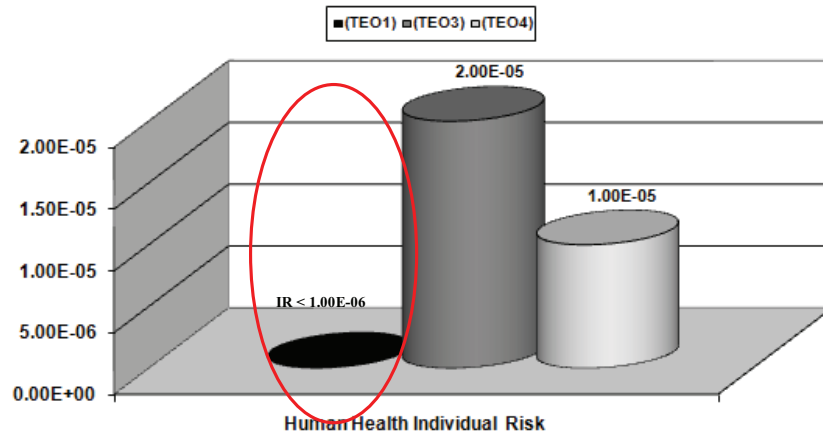


Fig. 2 - Human Health Individual Risks (IR) trend – decontamination applied technology for B(a)P contaminated sediments: electrochemical oxidation

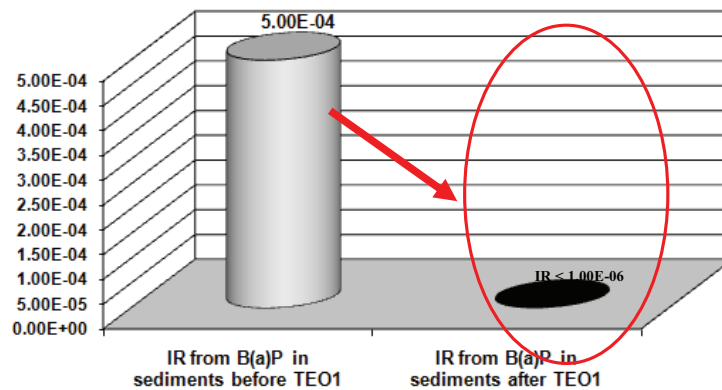


Fig. 3 - Trend of Human Health Individual Risks form sediments contaminated with B(a)P - decontamination applied technology: electrochemical oxidation (EO1)

Using appropriate tools in order to assess the individual human health risk from contaminated soils, as the one that we intend to develop through the RECOLAND project, it becomes possible not only to decide which remediation technology to adopt, but also what kind of destination could have the decontaminated soils.

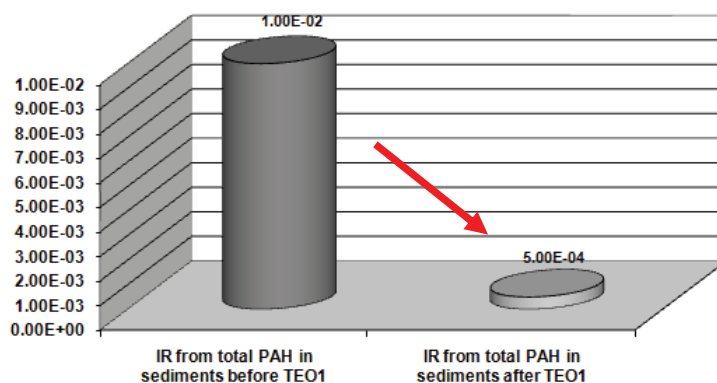


Fig. 4 - Trend of the Individual Human Health Risk from sediments contaminated with PAH - decontamination applied technology: electrochemical oxidation (EO1)

Conclusions

The illustrated approach demonstrates that the assessment of the human health effects must really become an important component of environmental assessment. This kind of approach will be facilitated through the RECOLAND project, and the main results will be published in the next papers. In this way, decision-makers will be able to develop appropriate mitigation measures and to reduce or even to eliminate the negative impact from human activities. The developed multicriteria system will allow managing the areas from the historical polluted surfaces belonging to big industries. The exemplified approach could be also adopted for optimizing waste management alternatives, and not only for evaluation of soil remediation solutions.

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