

## COMPARASION BETWEEN CHEMICAL AND ELECTROCHEMICAL TECHNIQUES FOR THE REMEDIATION OF PAH CONTAMINATED SEDIMENTS

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*The aim of this experimental investigation was to assess the effectiveness and the feasibility of two different remediation techniques, chemical oxidation and electrochemical oxidation, for the remediation of fluvial sediments contaminated by polycyclic aromatic hydrocarbons (PAHs).*

*Chemical oxidation is a remediation technique that uses reactants to chemically degrade the organic pollutants, while in electrochemical oxidation an electrical field is created in the polluted medium by applying a low-voltage direct current to electrodes placed in the ground to induce electrochemical oxidation reactions. In the first phase of the research, the effectiveness of chemical oxidation was investigated. For this purpose several bench scale laboratory tests were performed, with the following reactants: hydrogen peroxide, modified Fenton's reagent, ozone, activated sodium persulfate, potassium permanganate, as well as some combination these oxidants. In the second phase, the applicability of electrochemical oxidation was studied. Some tests were performed in order to assess the effects of different voltages and exposure times. The voltages applied during this experimentation ranged from 1 V/cm to 2 V/cm.*

*Chemical oxidation proved to be an effective technology for PAH remediation, even though different reactants resulted in different removal efficiencies. The best remediation performances were achieved with the use of modified Fenton's reagent, hydrogen peroxide and potassium permanganate, with high oxidant doses (about 100 mmols per 30 g sediment samples) which resulted in about 95% removal of total PAHs. The research about electrochemical oxidation showed that a 90% PAH removal could be easily achieved with a four week treatment under a constant voltage of 1 V/cm.*

*Based on the results of this study, both chemical oxidation and electrochemical oxidation proved to be effective in the remediation of the sediments of concern. Because of the sediments heterogeneity and low permeability, chemical oxidation is thought to be applicable only in an ex situ remediation action, while the electrochemical treatment seems amenable both in situ and ex situ.*

**Keywords:** polycyclic aromatic hydrocarbons, chemical oxidation, electrochemical-oxidation, sediments, contamination.

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## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are a group of organic molecules composed of fused benzene rings, classified among hydrophobic organic compounds (HOCs). PAHs can derive from many industrial activities, as combustion of wastes 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; in particular, due to their hydrophobic nature, low water solubility and high  $K_{ow}$  they can become rapidly associated with sediments [1, 2, 3]. PAHs are regarded as 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 [1, 4].

Several remediation techniques have been applied for PAH removal from contaminated sites, including biological, chemical and physical methods. This study was undergone to investigate the feasibility of using chemical oxidation and electrochemical oxidation to degrade sorbed PAHs in river sediments, in case of old date contamination.

The contaminated sediments of concern were collected from a canal in Trento (Italy), which for several decades had received industrial effluents polluted by organic and inorganic compounds. The light PAH species considered in this study were naphthalene, acenaphthylene, acenaftene, fluorene, phenantrene, anthracene and fluoranthene. The heavy PAH species considered here were pyrene, chrysene, benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene. The initial total PAH concentration in sediment samples was about 2800 mg/kg<sub>SS</sub> (light PAHs about 1600 mg/kg<sub>SS</sub>, heavy PAHs about 1200 mg/kg<sub>SS</sub>) and a 90-95% degradation was required to meet the remediation goals. The initial TOC content was about 190 g/kg<sub>SS</sub> and the pH was about 7.7.

## 2. 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, like PAHs. The oxidants that are most commonly used for environmental purposes are ozone, hydrogen peroxide, permanganate and activated persulfate [5].

In order to investigate the effectiveness of this technique, two sets of experiments were conducted during this experimental investigation: batch tests and column tests.

The batch tests were conducted in conditions of soil slurry. Several laboratory tests were performed in order to estimate the removal efficiency under different conditions, with the following liquid reactants:

- hydrogen peroxide ( $H_2O_2$ ) (addressed as HP tests);
- modified Fenton's reagent (MF tests);
- potassium permanganate (PP tests);
- activated sodium persulphate (AP tests).

Also some combination of these chemicals were tested as remediation agents, e.g. potassium permanganate and hydrogen peroxide (PPHP test), or activated sodium persulphate and modified Fenton's reagent (APHP).

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 the catalysts), the soil slurries were brought to a normalized volume of 100 mL by adding deionized water. During the tests, a complete mixing was ensured by the use of magnetic or orbital shakers to allow a perfect contact between oxidants and contaminants. The reactions were allowed to continue until the complete consumption of all chemicals. 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 (MF100 tests) and to 1:50 (MF50 tests). For the activated sodium persulfate tests, a 1:25 catalyst:oxidant molar ratio was used.

Chemical oxidation column tests are very important since they allow evaluating the treatment effectiveness in conditions similar to in situ conditions, as for soil density, permeability and contact between pollutants and oxidants. Therefore, the removal efficiencies evaluated with these tests must be considered more representatives of real in situ remediation conditions. Nevertheless, 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 was 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.

All the chemical oxidation tests performed are summarized in Table 1.

Table 1

**Chemical oxidation laboratory tests performed: reactants, dosages and main results**

| Test    | Reagent   | Oxidant dose [mmols] | Sample mass [g] | Test type |
|---------|---|----------------------|-----------------|-----------|
| HP 1    | Hydrogen Peroxide   | 25                   | 30              | batch     |
| HP 2    | Hydrogen Peroxide   | 50                   | 30              | batch     |
| HP 3    | Hydrogen Peroxide   | 100                  | 30              | batch     |
| HP 4    | Hydrogen Peroxide   | 200                  | 30              | batch     |
| MF100.1 | Modified Fenton's Reagent (molar ratio catalyst:oxidant=1:100)  | 50                   | 30              | batch     |
| MF100.2 | Modified Fenton's Reagent (molar ratio catalyst:oxidant=1:100)  | 100                  | 30              | batch     |
| MF100.3 | Modified Fenton's Reagent (molar ratio catalyst:oxidant=1:100)  | 200                  | 30              | batch     |
| MF50.1  | Modified Fenton's Reagent (molar ratio catalyst:oxidant=1:50)   | 50                   | 30              | batch     |
| MF50.2  | Modified Fenton's Reagent (molar ratio catalyst:oxidant=1:50)   | 100                  | 30              | batch     |
| AP1     | Activated Sodium Persulfate (molar ratio catalyst:oxidant=1:25) | 50                   | 30              | batch     |
| AP2     | Activated Sodium Persulfate (molar ratio catalyst:oxidant=1:25) | 100                  | 30              | batch     |
| AP3     | Activated Sodium Persulfate (molar ratio catalyst:oxidant=1:25) | 200                  | 30              | batch     |
| PP1     | Potassium Permanganate  | 50                   | 30              | batch     |
| PP2     | Potassium Permanganate  | 100                  | 30              | batch     |
| APHP    | Activated Sodium Persulfate + Hydrogen Peroxide                 | 50 + 50              | 30              | batch     |
| PPHP    | Potassium Permanganate + Hydrogen Peroxide                      | 50 + 50              | 30              | batch     |
| OZ.3h   | Ozone   | 250                  | 100             | column    |
| OZ.6h   | Ozone   | 500                  | 100             | column    |

Figure 1 presents the results achieved during these experiments. As can be seen from the data shown, hydrogen peroxide resulted in good PAH removal efficiencies (above 90% total PAH removal), but only with high dosages (as 100-200 mmols per 30 g-sediment sample), Modified Fenton's reagent lead to even better results (above 95% total PAH removal), especially when the 1:50 molar ratio catalyst:oxidant was used. Also the use of potassium permanganate lead to very good results, with a total PAH removal above 90%; in contrast, the combined used of permanganate and hydrogen peroxide led to poorer removal efficiencies, with very strong, rapid exothermic and difficult to control reactions. The PAH removal achieved with the use of activated persulfate was limited (always below 90%). Even if the combined use of activated persulfate and hydrogen peroxide led to a better PAH removal, these results were not as good as those achieved with hydrogen peroxide, modified Fenton's reagent and permanganate.

In all the tests performed, the removal efficiency for light PAHs was found to be higher than for the heavy PAHs. This can be considered as a typical

behavior of PAHs, whose lighter species are generally more available to reactants than heavy species, which are more hydrophobic and more sorbed onto sediments.

On the whole, the best removal percentages were achieved with the use of modified Fenton's reagent, hydrogen peroxide, and potassium permanganate, when oxidant dosages about 100 mmols per 30 g sediment sample were used. In all these cases, the total PAH removal was above 95% and the residual heavy PAH concentrations in the treated samples were below 100 mg/kg<sub>SS</sub>. The optimal dosages determined are quite high, since the mineralization of sorbed PAHs requires very vigorous oxidation conditions.

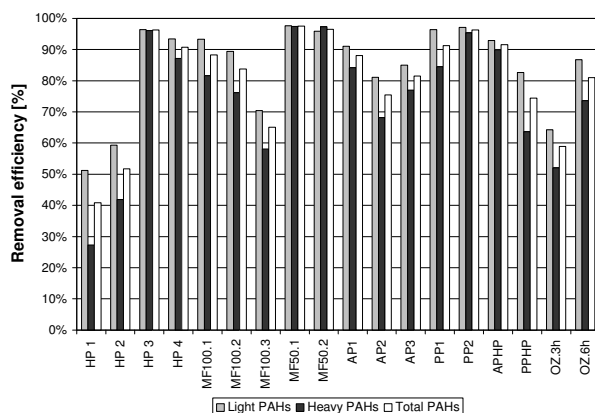
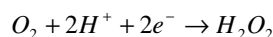


Fig. 1. Contaminant removal efficiencies achieved during the chemical oxidation tests.

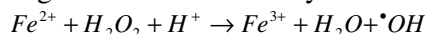
### 3. Electrochemical oxidation

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 [6,7].

The application of an electrical field to a soil has several complex physical and chemical effects, which include water electrolysis, electroosmosis, electromigration, electrophoresis, changes in soil pH 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 an electrochemical cell, hydrogen peroxide can be produced as a result of redox reactions and in particular by the reduction of O<sub>2</sub>, according to the following reaction:



In soils, the presence of microconductors [8], mainly composed by particles of iron and other metals, allows 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:



Hydroxyl radicals are strong non-selective oxidant agents, able to react with most of organic pollutants.

On the whole, the DCTs include two types of processes [8,9]:

- the electrokinetic transport, including electroosmosis, electromigration and electrophoresis, which lead to the mobilization and removal of metals, radionuclides and polar organic pollutants;
- 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 to investigate the effectiveness of electrooxidation on the PAH contaminated sediments. The trials 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 constant 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, i.e. no conditioning fluid was dosed at the electrode compartments to improve the soil conductivity, to adjust the soil pH or to promote contaminant migration. Moreover, no hydraulic gradient was applied across the electrodes. The investigated parameters were voltage, current, soil pH, humidity, TOC and PAH content. The following tests were performed during this study:

- test EO1: duration of 2 weeks, applied voltage 15 V (1.5 V/cm);
- test EO2: duration of 4 weeks, applied voltage 10 V (1 V/cm);
- test EO3: duration of 4 weeks, applied voltage 20 V (2 V/cm).

The first electro-oxidation test (EO1) was performed to assess the effectiveness of electro-oxidation in removing the addressed contaminants. During this trial, a sample of sediments was tested under a constant specific voltage of 1.5 V/cm for 14 days. At the end of the test, 85% PAH removal was observed and total PAH concentrations in the treated sample were 163 mg/kg<sub>SS</sub>.

Despite some variability due to sample heterogeneity, final PAH concentrations were found to be uniformly distributed across the treated sample. The other two laboratory tests (EO2 and EO3) were performed to assess influence of the applied voltage (1-2 V/cm) and treatment duration on PAH removal efficiency. During these tests samples were collected from the specimen every week to measure the PAH content. As shown in Figure 2, the contaminant removal significantly increased with time. During test EO2 (1 V/cm) 72% total PAH removal was found after 7 days. The total PAH removal gradually increased to 74% after 14 days, to 81% (21 days) and 91% (28 days). Higher removal efficiencies were encountered during test EO3, when a higher specific voltage (2 V/cm) was applied. In this case the total PAH removal efficiency was only 33% after 7 days, but it rapidly increased to 85% (14 days), 93% (21 days) and 96% (28 days). As already observed for traditional chemical oxidation, light PAH were removed more efficiently than heavy PAH. During the electro-oxidation tests the pH tended to increase at the cathode and to decrease at the anode, however these changes did not seem to influence the mineralization process

On the whole, the electro-oxidation proved to be an effective remediation technology, effectively applicable both for the in situ and for the ex situ remediation of the sediments of concern.

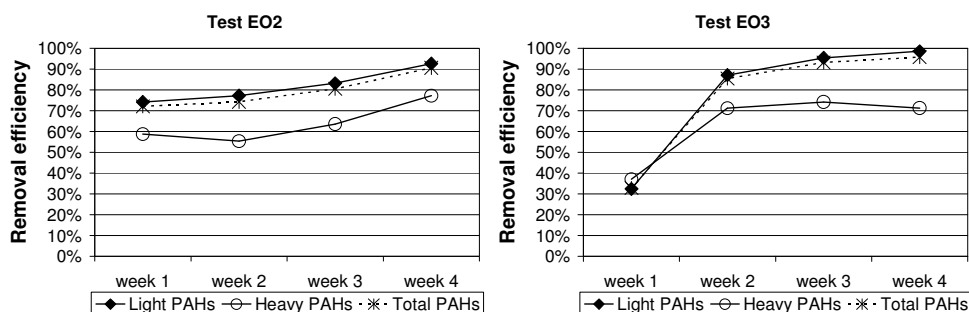


Fig. 2. PAH removal efficiencies against time during the electro-oxidation tests EO2 and EO3.

#### 4. Conclusions

The aim of this research was to assess the applicability and to evaluate the effectiveness of chemical and electrochemical techniques for the remediation of sediments contaminated with PAHs. For this purpose several laboratory tests were performed. During chemical oxidation tests, different reactants were tested; including hydrogen peroxide, modified Fenton's reagent, activated sodium persulfate, potassium permanganate, ozone and combinations of these oxidants. The best removal percentages (more than 95% PAH removal) were achieved with the use of hydrogen peroxide, modified Fenton's reagent and potassium

permanganate at a dose of about 100 mmols per 30 g of sediments. As for electro-oxidation, tests were performed with specific voltages ranging from 1 V/cm to 2 V/cm, in unenhanced conditions. 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, while 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.

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