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THE REMEDIATION OF CONTAMINATED SEDIMENTS BY CHEMICAL OXIDATION

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La ora actuală, poluarea aerului, a apei şi a solului reprezintă o mare problemă pentru societatea umană. Scopul acestui articol este de a prezenta o evaluare a eficienţei oxidării chimice pentru înlaturarea hidrocarburilor policiclice aromatice din solurile poluate. Oxidarea chimică este o metodă de remediere ce presupune introducerea în sol a unui agent oxidant care reacţionează cu compuşii organici transformându-i în substanţe inofensive. Agenţii oxidanţi folosiţi au fost: H_2O_2*, agentul Fenton,* $KMnO_4$*,* $Na_2S_2O_8$*, şi combinaţii între aceştia.*

In our days the pollution of air, water and soil represents a serous problem for human society. The aim of this work is to present an evaluation of effectiveness of chemical oxidation for the remediation of PAHs from polluted sediments. Chemical oxidation is a technique that uses chemicals to mineralize organic contaminants by changing them to harmless substances. The use of the chemical oxidation processes has been investigated for the remediation of environmental matrices contaminated by polycyclic aromatic hydrocarbons (PAHs). Laboratory experiments were conducted to assess the effects of different oxidant agents: H_2O_2*, Fenton's Reagent,* $KMnO_4$*,* $Na_2S_2O_8$*, and combinations between them.*

Keywords: soil pollution, PAHs, chemical oxidation, batch.

1. Introduction

Land contamination: problems and issues

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While soils are as essential to human society as air and water, soil degradation has not received nearly as much attention as the threats to these other two elements. Still soils are the basis for 90% of all human food, livestock feed, fibre, and fuel. They support human settlements and provide raw materials and groundwater [1].

Land can become contaminated because of many human activities. In past times mining, quarrying, industrial activity and waste dumping were carried out with little regard to impact on the land. Agriculture and contaminants from the atmosphere can also impact on land and become a source of contamination. The depositing of industrial and domestic waste in landfill sites can result in the contamination of ground water as pollutants can become concentrated into liquid that leaches from the site. Also, methane gas from the decomposing waste can build up to potentially explosive levels if not properly managed [2,3,4,5].

2. The problem of contaminated sites in Europe

Several economic activities are still causing soil pollution in Europe, particularly those related to inadequate waste disposal and losses during industrial operations. It is expected that the implementation of preventive measures introduced by the legislation already in place would limit the inputs of contaminants into the soil in the coming years [4]. The range of polluting activities and their importance vary considerably in each country, according to different industrial and commercial structures, different classification systems or incomplete information available.

A broad range of industrial and commercial activities have had impacts on soil through the release of a broad variety of different pollutants. Heavy metals, mineral oil, polycyclic aromatic hydrocarbons (PAHs), chlorinated hydrocarbons and aromatic hydrocarbons are reported to be the main chemical compounds causing soil contamination from local sources at industrial and commercial sites (Fig. 1) [4].

Globally, these contaminants alone affect more than 90% of contaminated sites, while their relative contribution may vary greatly from country to country. The implementation of existing legislative and regulatory frameworks (such as the Integrated Pollution Prevention and Control Directive and the Landfill Directive, [4]) should result in less new contamination of Europe’s soils [4].

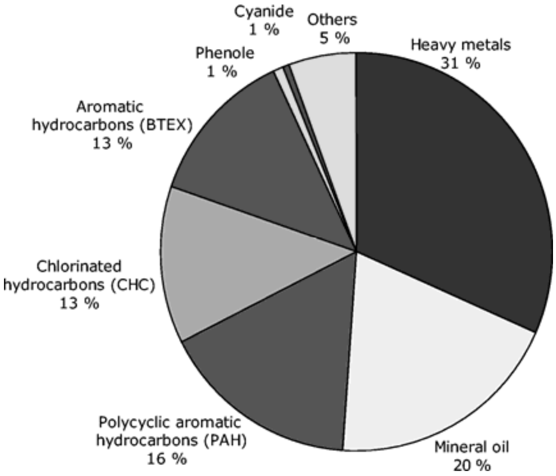

Fig. 1. Main contaminants at industrial and commercial sites affecting soil and groundwater in Europe as % of total [4]

Experience has shown that some industrial activities have a higher probability of contaminating a site, as oil production and storage, chemical manufacturing and formulation. Any commercial, mining, industrial or agricultural site has the potential to be contaminated; however some activities intrinsically give rise to contamination more frequently than others [5].

3. Physical-chemical characteristics of the most involved soil contaminants.

Soil contaminants can have various chemical and physical characteristics [6]:

- Volatile organic compounds (VOCs): compounds whose pressure vapor, measured at a standard temperature of 250 C, is lower than 5,28 atmosphere (53500 Pa) (e.g.:1,1,1,2-Tetrachloroethane, Bromomethane, Hexachloroethane).
- Semivolatil organic compounds (SVOCs): compounds whose pressure vapor, measured at a standard temperature of 25°C, is larger than 5,35 bar. These compounds can be classified in two categories: halogenated SVOCs (PCBs - polychlorinated biphenyl, PCO - pentachlorophenol) and non halogenated SVOCs (PAHs – polycyclic aromatic).
- Fuels: are generally nonhalogenated (1,2,3,4-Tetramethylbenzene, 3-Ethylpentane, Toluene, etc.).
- Inorganic (Antimony, Magnesium, Molybdenum, Zirconium, etc.);

Exposure to contaminants can be caused by inhalation of dust or vapours, contact with and ingestion of soil, or through food grown on the land. Leachates (pollutants draining from the site in liquid form or dissolved in water) can pollute groundwater and rivers or ponds. Some contaminants may be corrosive, and some can pose a risk of explosion or fire. It is used a risk assessment bases on a conceptual model using a Source-Pathway-Receptor methodology, which takes into account all the possible and plausible pathways through which contaminants can reach receptors [2,7,8,9,10,11].

4. Remediation technologies

Cleanup methods are techniques to treat or contain pollution in order to make it less dangerous for human health or for the environment [6,7,12,13].
Common remediation technologies are:

- soil excavation;
- chemical and physical treatments, including pump and treat; soil vapour extraction and air sparging; soil flushing and soil washing; chemical oxidation; chemical dehalogenation; solvent extraction; permeable reactive barriers; solidification/stabilization; electrokinetic’s techniques;
- thermal treatments, including incineration; vitrification; thermal desorption
- biological treatments, including: bioremediation; phytoremediation; monitored natural attenuation;
- containment measures, including: capping, lateral containment, bottom containment, hydraulic barrier.

5. Lab scale comparison of different oxidation technologies

Chemical Oxidation is a method widely used for the cleanup of both saturated and unsaturated soil [14,15,16,17].

The objective of this project was to evaluate the effectiveness of different chemical oxidants for the remediation of freshwater sediments polluted by PAHs.

The contaminated sediments of concern were collected in a canal which for several decades had received industrial effluents polluted by organic and inorganic compounds. This canal is located in the northern part of the city of Trento, Italy.

Several sediment samples (total weight about 10 kg) were collected from the first 30-40 cm layer at the bottom of the canal; these samples were then mixed together and mechanically stirred to produce a final, homogeneous sample.

Both organic pollutants and natural organic matter occurred in the sediment samples, which proved to be contaminated by PAHs, but not by BTEX, whose presence was detected just in traces. Both light and heavy PAHs were detected. The characteristics of these sediments are summarized in table 1.

The average PAHs concentration in sediment samples surpassed the Italian limit both for residential land use (10 mg/kg, as summation of heavy PAHs) and for industrial-commercial land use (100 mg/kg, as summation of heavy PAHs).

Table 1

Characteristics of sediment samples of concern

	Elements	**Values [mg/kg$_{SS}$]**
BTEX	Benzene	<0.01
	Etilbenzene	<0.01
	Styrene	<0.01
	Toluene	0.001
	Xylene	0.002
	Total BTEX	**0.003**
PAHs	Naphthalene	59.22
	Acenaphtylene	5.58
	Acenaphtene	211.38
	Fluorene	119.06
	Phenanthrene	660.06
	Anthracene	56.67
	Fluoranthene	481.73
	Pyrene	368.80
	Crysene	157.00
	Benzo(a)anthracene	118.80
	Benzo(b)fluoranthene	194.60
	Benzo(k)fluoranthene	72.00
	Benzo(a)pyrene	142.70
	Dibenzo(a,h)anthracene	17.40
	Benzo(g,h,i)perylene	72.40
	Indeno(1,2,3-cd)pyrene	79.00
	Total Heavy PAHs	**2816.40**

6. Materials and Methods

In order to investigate the effectiveness of chemical oxidation of the contaminated soils of concern, a set of batch tests were carried on at bench scale.

Batch tests are very important because they allow to compare the effectiveness of different reactants, of different reaction modalities (e.g. single-step or multi-step reaction) and of different dosages, as well as to evaluate reaction kinetics. Therefore, bench tests represent an important screening tool in evaluating the best remediation conditions and the most effective oxidants in site-specific condition. For this reason, they are always performed during the preliminary studies for the optimization of a chemical oxidation remediation treatment.

In this study, four liquid oxidants were used:

- hydrogen peroxide (H_2O_2);

- modified Fenton's reagent
- permanganate
- activated persulphate

Some combinations of these chemicals were also tested: potassium permanganate and hydrogen peroxide activated sodium persulphate and modified Fenton's reagent.

The reactants used for the tests were sodium persulfate, potassium permanganate, ferric chloride, cathecol and hydrogen peroxide. All chemicals used for the tests were purchased from Sigma-Aldrich and were reagent grade. Deionised water was produced with a Milli-Q system from Millipore.

For the production of modified Fenton's Reagent, hydrogen peroxide is dosed together with a solution of chelated ions of a transition metal, typically, iron. In this case, ferric chloride $FeCl_3$ was used to provide iron ions, while cathecol was used as chelating agent. The ferric salt and catechol were dosed at a molar ratio equal to 1:1.

In order to produce an activated persulfate oxidant, the persulfate solution was added to the reaction vessel together with a 0.5M solution of chelated ferric ion (the same solution used for modified Fenton's reagent), with a molar ration catalyst: oxidant equal to 1:25.

During the experiments, to avoid cross-contamination, before use all vessels were rinsed with acetone, and then rinsed several times with deionised milli-Q water.

A solid matrix suspension (soil slurry) was prepared by adding deionised water to 30g-sediment sample. The amount of water to be added was determined in order to have a final solution volume (including the oxidant volume to be added) of about 100mL. The sediment-water system was magnetically stirred for a few minutes in order to obtain an homogeneous soil slurry. After stirring the suspension for a few minutes, the liquid oxidant was slowly added, with great care to avoid excessive temperature increase, especially in the case of tests with modified Fenton's reagent.

All tests were conducted at room temperature. During the tests, the sediment–oxidant slurries were stirred in order to obtain a complete mixing system during all the oxidation reactions and to allow a good contact between oxidant and soil matrix. During the first minutes of reaction, a magnetic stirring was used, and then the reaction vessels were periodically shaken to avoid the excessive formation of foam caused by magnetic or mechanical stirring.

All tests were repeated twice or three times in order to reduce uncertainty deriving from sample variability and instrumental errors.

Prior to starting the experiments, some preliminary tests were conducted in order to verify that the amount of oxidant solutions dosed did not cause excessive heating (especially in the case of modified Fenton's reagent) and to assess the compatibility of the volume of the dosed solution with sediment porosity and permeability. Based on the feedback from this pilot study, the experimental dosages described in Table 2 were chosen.

During the first phase of the experimental activity, the reactions were allowed to continue till the complete consumption of all chemicals, in order to evaluate the total removal efficiency of different reactants. For this purpose, even all chemical reactions appeared to be concluded within a few hours, the sediment slurries in the reactions vessels were allowed to rest for a period of 24 hours, in order to ensure the completion of all chemical reaction.

The tests performed are summarized in table 2.

Table 2

Bench scale oxidation tests: dosages and reactants.

Tests		Oxidant	Oxidant Dose [mmols/ sample]	Oxidant Concentration [M]	Oxidant Solution Volume [ml]	Deionised Water Volume [ml]
H_2O_2	HP_1	H_2O_2	25	5	5	95
	HP_2		50		10	90
	HP_3		100		20	80
	HP_4		200		40	60
Fenton (1:100)	$MF_{100.1}$	H_2O_2	50	5	10	89
		Fe-chelated	1	0.5	1	
	$MF_{100.2}$	H_2O_2	100	5	20	78
		Fe-chelated	1	0.5	2	
	$MF_{100.3}$	H_2O_2	200	5	40	56
		Fe-chelated	2	0.5	4	
Fenton (1:50)	$MF_{50.1}$	H_2O_2	50	5	10	88
		Fe-chelated	1	0.5	2	
	$MF_{50.2}$	H_2O_2	100	5	20	76
		Fe-chelated	2	0.5	4	
$Na_2S_2O_8$ (1:25)	AP_1	$Na_2S_2O_8$	50	2	25	71
		Fe-chelated	2	0.5	4	
	AP_2	$Na_2S_2O_8$	100	2	50	42
		Fe-chelated	4	0.5	8	
	AP_3	$Na_2S_2O_8$	200	2	100	0^*
		Fe-chelated	8	0.5	16	
$KMnO_4$	PP_1	$KMnO_4$	50	0.4	125	0^+
	PP_2	$KMnO_4$	100	1	100	0
$Na_2S_2O_8 + H_2O_2$		$Na_2S_2O_8$	50	5	25	61
		Fe-chelated	2	0.5	4	
		H_2O_2	50	5	10	
$KMnO_4 + H_2O_2$		$KMnO_4$	25	0.4	62.5	27.5
		H_2O_2	50	5	10	

* total volume of resulting solution was 116mL.

$^+$ total volume of resulting solution was 125mL.

PAHs concentrations in sediments samples were determined with analysis by high pressure liquid chromatography (HPLC), after acetonitrile solvent extraction of the sorbed PAHs

7. Results and discussion

The sediments samples of concern showed a concentration of total PAHs of about 2816mg/kg (light PAHs 1593mg/kg, heavy PAHs 1222mg/kg).
In order to assess the efficiency of the tested treatments, the removal efficiencies of single PAH specie and of PAH summation were calculated; the results were also correlated with PAH solubility and with the partition coefficient Kow (data not shown)

The main results of the experiments performed are presented in fig. 3 and fig. 4. As can be seen from the pictures, different reactants and different oxidant dosages led to different removal efficiencies.

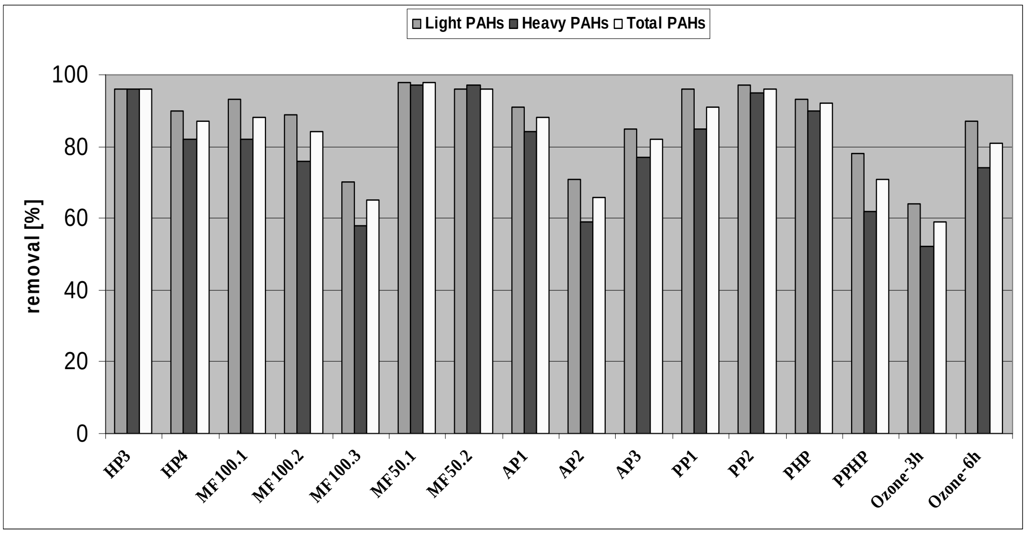

Fig. 3 – Comparison between all removal percentages obtained for all tests.

In the tests performed with hydrogen peroxide, the PAH removal efficiency increases with the oxidant dose, varying from about 50% to about 90%. The best removal efficiencies were reached in tests HP3 and HP4, and therefore with a dosage of hydrogen peroxide equal to 100-200mmols for a 30g-sediment sample. It can be concluded that dosages of hydrogen peroxide of this order of magnitude can ensure a good oxidation both of heavy and of light PAHs, with a total PAHs removal about 90-95%.

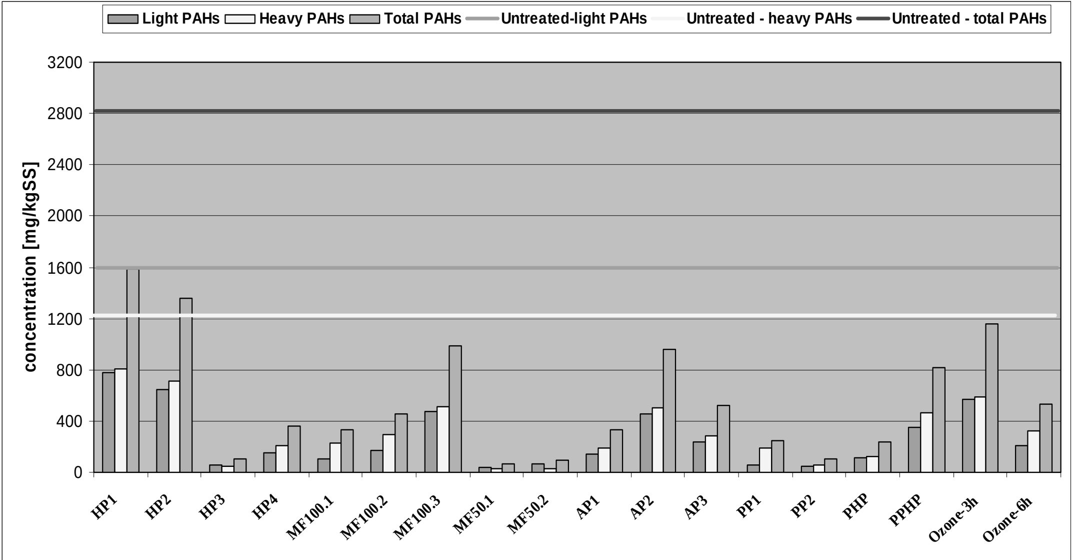

Fig. 4 – Contaminant concentration for all tests performed.

On the whole, hydrogen peroxide resulted in good removal efficiencies, but only with high dosages, and on the whole the performances were worse than for modified Fenton’s reagent.

It must be point out that in all tests, the removal efficiency for light PAHs is higher than for the heavy PAHs. This is 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. However, while the removal of light and heavy PAHs is significantly different in the tests with lower oxidant dosage (as in test HP1 and, to a smaller extent, in test HP2), this difference in removal efficiencies becomes smaller as the oxidant dose increases. In fact, in tests HP4, the removals of light and heavy PAHs reach very similar or equal values. This can due to the fact that a higher oxidant dose can enhance the oxidation of pollutants, by moving the equilibrium of the chemical reactions, and therefore can react even with the most recalcitrant substances, or, more likely, to the fact that a higher dosage of hydrogen peroxide causes an increase in the slurry temperature, thus enhancing the desorption of PAHs, and, consequently making them more available for oxidation reactions, which mainly take place in the aqueous phase.

Two sets of experiments were performed with the use of modified Fenton’s reagent: in the first set, hydrogen peroxide was dosed together with a solution of chelated ferrous ion (obtained from ferric chloride and catechol) with a molar ratio iron: peroxide equal to 1:100. In the following discussion, these tests are characterized by the code MF100.

During the second set of experiments, hydrogen peroxide was dosed together with a solution of chelated ferrous ion with a molar ratio iron: peroxide equal to 1:50. These tests are characterized by the code HP50.

In both sets of experiments the removal efficiency was dependent on the oxidants dosage. The results obtained suggest that if the oxidant dose increases above a certain level, the removal efficiency may decrease. This can be due to very strong and rapid reactions accused by higher reactant dosages, which prevent a good contact between oxidant and pollutants (too strong and rapid reactions); another possible explanation is connected to errors due to strong sample heterogeneity, which is a typical feature of PAH contamination and of sediment contamination. However, this phenomenon must be further on investigated and needs for further research.

On the whole, these results achieved with the use of modified Fenton's reagent can be considered very satisfying, the registered remediation efficiencies being very good in tests MF100.1 and MF100.2, and even excellent, above 95%, in the tests with a molar ratio catalyst: oxidant equal to 1:50. In conclusion, modified Fenton's reagent can be an effective chemical for the remediation of sediments contaminated by PAHs; for better results, a molar ratio iron: peroxide equal to 1:50 can be used rather than 1:100. The oxidant dosage of 50mmols of hydrogen peroxide for a 30g-sediment sample is recommended, and anyway the dose should not exceed 100mmols per 30g-sample, in order not to reduce the remediation efficiency because of too strong and rapid reactions.

Both tests performed with potassium permanganate showed very good removal efficiencies, with removal percentages above 90% for total PAHs. Moreover, both tests showed very high remediation not only of light PAHs and also of heavy PAHs. The removal efficiency increased slightly with the amount of oxidant dosage.

While permanganate led to good results when it was used alone, when it was used in combination with hydrogen peroxide, the results were below the expectations, being lower than the ones obtained only for permanganate. This was probably due to the excessive strength of the reactions achieved, which were very exothermic and led to a strong foam formation.

With activated sodium persulphate, the contaminant removal increased with the dose and reached high levels with higher doses (e.g. 200mmols per 30g of sediments); the total removal was of the order of magnitude of 80%.

When activate sodium persulphate was combined with hydrogen peroxide, the results were very good, even with low oxidant dosages, the reactions being not too strong or exothermic. The removal efficiency (92% for total PAHs, 93% for llight PAHs and 90% for heavy PAHs) achieved during this test can be considered excellent.

8. Conclusions

The aim of this project was to evaluate the effectiveness of chemical oxidation for the remediation of sediments contaminated by PAHs. For this purpose several laboratory tests were performed, with the following liquid reactants: hydrogen peroxide, modified Fenton's reagent (catechol and ferric chloride as catalyst agents, with molar ratios catalyst: oxidant equal to 1:100 and 1:50), activated sodium persulphate (catechol and ferric chloride as catalyst agents, with molar ratio catalyst: oxidant equal to 1:25), potassium permanganate, as well as a combination of potassium permanganate and hydrogen peroxide, and a combination of activated sodium persulphate and hydrogen peroxide. All tests performed are summarized in table 36.

Based on the results of this study, chemical oxidation proved 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 (100mmols of H_2O_2 per 30g-sample of sediments); hydrogen peroxide (25mmols of H_2O_2 per 30g-sample); potassium permanganate (50mmols and 100mmols of $KMnO_4$ per 30g-sample).

Besides the removal efficiencies obtained with laboratory tests, several factors must be taken into account for a real-scale application of this technology, including the cost of reactants, the availability of reactants and the ability of the chosen method to reach target levels (i.e. residual contaminant concentration). For in situ application, also the delivery of the reactants plays an important role, as strongest oxidants (like modified Fenton's reagent) can reach only a small area around the injection, as the delivery also depends on sediment permeability);

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