THESIS ON CHEMISTRY AND CHEMICAL ENGINEERING

ADVANCED OXIDATION PROCESSES FOR WATER PURIFICATION AND SOIL REMEDIATION

ANNA GOI

Faculty of Chemical and Materials Technology
Department of Chemical Engineering
TALLINN UNIVERSITY OF TECHNOLOGY

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Supervisor: Prof. Rein Munter, Chair of Environmental and Chemical Technology, Tallinn University of Technology

Co-supervisor: Dr. Marina Trapido, senior research scientist, Chair of Environmental and Chemical Technology, Tallinn University of Technology

Opponents:

Prof. Vladislav V. Goncharuk, Academician of National Academy of Sciences of Ukraine, director of the A.V.Dumansky Institute of Colloid and Water Chemistry of the National Academy of Sciences of Ukraine, Kiev, Ukraine

Prof. Toomas Tenno, Chair of Colloid and Environmental Chemistry, Tartu University, Tartu, Estonia

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Declaration: Hereby I declare that this doctoral thesis, my original investigation and achievement, submitted for the doctoral degree at Tallinn University of Technology has not been submitted for any degree or examination. (Deklareerin, et käesolev doktoritöö, mis on minu iseseisva töö tulemus, on esitatud Tallinna Tehnikaülikooli doktorikraadi taotlemiseks ja selle alusel ei ole varem taotletud akadeemilist kraadi.)

Anna Goi

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ABSTRACT

The main goal of the present study was to enlarge the existing knowledge in advanced oxidation processes application for water and soil decontamination. Advanced oxidation processes, which involve the in situ generation highly potent chemical oxidants such as hydroxyl radical, have recently emerged as an important class of technologies for accelerating the oxidation and destruction of a wide range of organic contaminants in polluted water and soil.

The reaction rate constants of nitrophenols oxidation in different advanced oxidation processes systems (the Fenton, photo-Fenton, H_2O_2/UV, O_3, O_3/H_2O_2, O_3/UV, O_3/H_2O_2/UV) were determined for oxidation processes optimisation. Studies on ozonation by-products indicated that the quinone-type compounds were formed. The mineralization of organically bounded nitrogen to nitrate altered from about 50 up to 100% in these experiments. The biodegradability enhancement and toxicity reduction was observed as the result of advanced oxidation processes treatment that allows recommending advanced oxidation processes as pre-treatment for nitrophenols-contaminated water purification.

Ozonation and the Fenton treatment were able to remediate nitrophenols, polycyclic aromatic hydrocarbons, diesel, shale oil and transformer oil contaminated soil. Chemical treatment of contaminants adsorbed in peat resulted in lower contaminants’ removal and required higher addition of chemicals than chemical treatment of contaminants in sand matrix. Fenton-like treatment was found to be feasible for soil remediation at natural soil pH. Iron that is present in soil was able to catalyse hydrogen peroxide without addition of extra Fe^{2+} in the Fenton treatment. It was found that combined chemical and biological treatment (the Fenton treatment or ozonation with moderate doses of chemical oxidants and biodegradation) was more effective than either one alone and can be used as a successful treatment technology for contaminated soil remediation.

A cost calculation indicated that the Fenton treatment was found to be the cheapest chemical treatment method for contaminated water purification and soil remediation. The results obtained comprise a basis for introduction of chemical oxidation (ozonation and advanced oxidation processes) for water and soil purification providing with technically feasible, economically acceptable and environmentally sufficient methods.

KOKKUVÕTE

Töö eesmärgiks oli laiendada olemasolevaid teadmisi täiustatud oksüdatsiooniprotsesside rakendamisel vee ja pinnase puhastamiseks. Täiustatud oksüdatsiooniprotsessid, milles toimub nii kõrge potentsiaaliga keemilise oksüdandi, nagu hüdroksüülradikaal, in situ moodustumine, on hiljuti esile kerkinud kui tähtis tehnoloogiaharu suure hulga orgaaniliste saasteainete oksüdatsiooniks ja lagundamiseks saastatud vees ja pinnases.

Täiustatud oksüdatsiooniprotsesside optimeerimiseks määrati nitrofenoolide oksüdatsiooni reaktsioonide kiiruskonstandid erinevates süsteemides (Fenton, foto-Fenton, H_2O_2/UV, O_3, O_3/H_2O_2, O_3/UV, O_3/H_2O_2/UV). Aromaatsete ühendite nukleaarsel hüdroksüleerimisel osoonimise käigus tekkinud kõrvalproduktide hulgas identifitseeriti kinoon-tüüpi aineid. Lämmastiku mineralisatsiooni aste ulatus nitrofenoolide lagundamisel erinevate täiustatud oksüdatsiooniprotsesside puhul 50%-st kuni 100%-ni. Täiustatud oksüdatsiooniprotsessid võimaldasid kõrvaldada nitrofenoolide lagunemise käigus moodustunud kõrvalproduktide toksilisust ning tagasid nitrofenooli detoksifitseerimise vesilahuses. Täiustatud oksüdatsiooniprotsesside rakendamine võimaldas tõsta nitrofenoolide segu biodegradatsiooni astet. Järelikult võib täiustatud oksüdatsiooniprotsesside kombinatsiooni biopuhastusega edukalt rakendada nitrofenoole sisaldava reovee puhastamiseks.

Osoonimine ja Fentoni reaktiiviga töötlus võimaldasid taastada polütsükliliste aromaatsete süsivesinikega, nitrofenoolidega, diisliga, põlevkiviõliga ja trafoõliga saastatud pinnast (liiv, turvas), kusjuures protsessi efektiivsus sõltus suurel määral pinnase omadustest. Võrreldes turbaga toimus liivas saasteainete lagundamine kiiremini ja nõudis väiksemat reagentide kulu. Pinnases olev raud oli võimeline katalüüsima vesinikperoksiidi ilma eraldi katalüsaatori lisamiseta Fentoni reaktiiviga töötlusel. Fentonile sarnane töötlus võimaldas pinnase taastamist pinnase loodusliku pH puhul. Antud töö põhjal võib järeldada, et saastatud pinnase puhastamist on efektiivsem teostada kombineeritud meetoditega (Fentoni reaktiiv mõõdukatel oksüdeerimistingimustel ja järgnev biolagundamine ning osoonimine ja biolagundamine) võrreldes ainult biolagundamise või keemilise töötlemisega.

Töötlemisekulude (reaktiivid, energia) kalkulatsioon näitas, et Fentoniga töötlemine osutus odavaimaks töötlusprotsessiks saastatud vee puhastamiseks ja pinnase taastamiseks. Saadud tulemused on teoreetiliseks aluseks osooni ja täiustatud oksüdatsiooniprotsesside praktiliseks rakendamiseks vee ja pinnase puhastamiseks, mis kätkevad tehniliselt teostatavaid, majanduslikult vastuvõetavaid ja keskkonnahoiu seisukohalt piisavaid meetodeid.

LIST OF PUBLICATIONS

The present dissertation is base on the following papers, which are referred to in the text by their Roman numerals I-VII:

I **Goi, A.**, Trapido, M. 2001. Comparison of advanced oxidation processes for the destruction of 2,4-dinitrophenol. - Proceedings of the Estonian Academy of Sciences Chemistry, vol 50, no 1, p 5-17.

II **Goi, A.**, Trapido, M. 2002. Hydrogen peroxide photolysis, Fenton reagent and photo-Fenton for the degradation of nitrophenols: a comparative study. - Chemosphere, vol 46, no 6, p 913-922.

III **Goi, A.**, Trapido, M., Tuhkanen, T. 2004. A study of toxicity, biodegradability and some by-products of ozonised nitrophenols. - Advances in Environmental Research, vol 8, p 303-311.

IV **Goi, A.**, Trapido, M. 2004. Combined methods for the remediation of nitrophenol- contaminated soil. - Fresenius Environmental Bulletin, vol 13, no 11b, p 1191-1196.

V **Goi, A.**, Trapido, M. 2004. Degradation of polycyclic aromatic hydrocarbons in soil: the Fenton reagent versus ozonation. - Environmental Technology, vol 25, no 2, p 155-164.

VI **Goi, A.**, Trapido, M., Kulik, N., Palmroth, M.R.T., Tuhkanen, T. Ozonation and the Fenton treatment for remediation of soil – diesel fuel contaminated soil. - Ozone Science & Engineering. Accepted.

VII **Goi, A.**, Kulik, N., Trapido, M. Combined chemical and biological treatment of oil contaminated soil. - Environmental Science and Pollution Research - International. Submitted.

In the appendix of this thesis, copies of the papers I-VII have been included.
Papers I-VI were reproduced with permission from the publishers.

THE AUTHOR’S CONTRIBUTION TO PUBLICATIONS

Paper I:

The author supervised the experimental study, participated together with B.S. student, and interpreted the obtained data. Author performed all BOD and COD analyses, Fenton, UV/H_2O_2, photo-Fenton and partly ozone experiments. She wrote the paper and is the corresponding author.

Paper II:

Author performed all the experimental work and interpreted the results. She wrote the paper and is the corresponding author.

Paper III:

Author performed all the experimental work and interpreted the results. She wrote the paper and is the corresponding author.

Paper IV:

The author planned and supervised the experimental study, participated together with B.S. student, and interpreted the obtained data. She wrote the paper and is the corresponding author. The results were also presented at the 12th International Symposium on Environmental Pollution and its Impact on Life in the Mediterranean Region, 4-8 October 2003, Antalya, Turkey.

Paper V:

The author supervised the experimental study, participated together with B.S. student, and interpreted the obtained data. She wrote the paper and is the corresponding author.

Paper VI:

The author planned and supervised the experimental study, participated together with B.S. student. She performed all GC-MS analyses and interpreted the obtained data. She wrote the paper and is the corresponding author. The results were also presented at the IOA International Conference in Advances in Science and Engineering for Industrial Applications of Ozone and Related Oxidants, 10–12 March 2004, Barcelona, Spain.

Paper VII:

The author supervised the experimental study, participated together with B.S. students. She performed all GC-MS and UV-254 analyses and interpreted the obtained data. She wrote the paper and is the corresponding author. The results were also presented at the International 9th FECS Conference on Chemistry and Environment: Behaviour of Chemicals in the Environment, August 29th-September 1st 2004, Bordeaux, France.

TABLE OF CONTENTS

Appendix 1

Appendix 2

Appendix 3

ABBREVIATIONS

AOP	advanced oxidation processes
BOD	biochemical oxygen demand
CAT	catalyst
COD	chemical oxygen demand
DO	dissolved oxygen
di-NP, DNP	dinitrophenol
EC_{50}	median effective concentration
Ext	extinction
FLD	fluorescence detector
GAC	granulated activated carbon
GC-MS	gas chromatograph with a mass-selective detector
HPLC	high performance liquid chromatograph
$h\nu$	light quantum
LC_{50}	median lethal concentration
mono-NP	mononitrophenol
NPs	nitrophenols
4-NP	4-nitrophenol
2-NP	2-nitrophenol
2,4-DNP	2,4-dinitrophenol
2,5-DNP	2,5-dinitrophenol
2,6-DNP	2,6-dinitrophenol
4,6-DN-*o*-CR	2-methyl-4,6-dinitrophenol
2,6-DN-*p*-CR	4-methyl-2,6-dinitrophenol
PAH	polycyclic aromatic hydrocarbons
pKa	solution phase acidity
TDS	total dissolved solids
TOC	total organic carbon
TPH	total petroleum hydrocarbons
US	ultrasound
UV	ultraviolet irradiation
UV-254, UV_{254nm}	ultraviolet absorbance at 254 nm
VIS	visible light

INTRODUCTION

Many different chemicals are discharged into the aquatic environment. Some of them are not only toxic but also partly biodegradable; therefore they are not easily removed in biological wastewater treatment plants. That is why there is a need to develop effective methods for the degradation of organic pollutants, either to less harmful compounds or to their complete mineralization.

Advanced oxidation processes (AOP), which involve the in situ generation of highly potent chemical oxidants such as the hydroxyl radical ($OH^{\bullet}$), have recently emerged as an important class of technologies for accelerating the oxidation and destruction of a wide range of organic contaminants in polluted water and air (Glaze et al., 1987). AOP when applied on a right place, give a good opportunity to reduce the contaminant concentration from several hundreds ppm to less than 5 ppb. That is why they are called “the treatment processes of the 21st century”.

Nitrophenols (NPs) are among widely utilised industrial organic compounds. They are applied as pesticides, herbicides, insecticides, photochemicals, wood preservatives and explosives. NPs may enter the environment from industrial discharges, spills, or possibly as a breakdown product of certain pesticides containing NPs (EPA US, 1993). NPs have also been present in the degradation of pesticides like parathion and nitrofen (Kiwi et al., 1994). The generation of aqueous wastes during the formulation, distribution, and field application of pesticides is often unavoidable. As secondary pollution arising from aromatic hydrocarbon and nitrogen oxide emissions by photochemical reactions in the atmosphere, NPs have been identified in cloud- and fog water condensates as well as on airborne particulate matter (Herterich, 1991). EPA US has included four NPs (2-NP, 4-NP, 2,4-DNP and 4,6-DN-*o*-CR) to 129 priority pollutants list (Keith and Telliard, 1979). NPs are often detected in industrial effluents, in ambient freshwater, in marine environments, in the atmosphere and in soil.

NPs are very toxic compounds. They accumulate in the organism of warm-blooded. Towards animals and human, both the acute and chronic effects have been reported. Epidemiological studies of NPs have indicated that they damage central nervous system, liver, kidney and blood. They are highly toxic upon swallowing, inhalation and sorption through the skin (EPA US, 1986, 1993; ATSDR, 1992).

Only a few studies using AOP and ozonation for the degradation of NPs have been published. There is not earlier data available on reaction kinetics of 4,6-DN-*o*-CR, 2,6-DN-*p*-CR, and 2,5-DNP degradation. Reaction kinetics of 2-NP, 4-NP, 2,4-DNP, 2,6-DNP by Fenton’s reagent, hydrogen peroxide photolysis, photo-Fenton treatments (Kiwi et al., 1994; Lipzynska-Kochany, 1991; 1992;

Ma et al., 2000) and non-accompanied ozonation (Masschelein and Goossens, 1984; Beltran et al., 1992; Yu and Yu, 2001; Stover et al., 1982; Adams et al., 1997; Wang, 1990) has been studied to some extent. Among of the studies concerning AOP including ozone for the NPs degradation only O_3/UV treatment of 2-NP (Ku et al., 1996) was investigated. There is not any data concerning the NPs degradation by O_3/H_2O_2, O_3/H_2O_2/UV treatment processes. Only few studies assessed the effect of ozonation on the biodegradability of 2,4-DNP and 4-NP (Stover et al., 1982; Wang, 1990; Adams et al., 1997), Fenton on the biodegradability of 4-NP (Ma et al., 2000), and toxicity of NPs (4-NP and 2,4-DNP) ozonised solutions (Adams et al., 1997). These sparse data have demonstrated that the further studies on the application of ozonation and AOP for the degradation of NPs are required.

Besides the wastewater treatment, the problem of contaminated soil remediation comprises one of the important domains of environmental engineering. Conventional treatment methods, such as pump-and-treat technology, are often costly and less than effective (Technical/Regulatory Guidelines, 2001). Emerging ozone and AOP for soil treatment is the most recent, modern direction in this area, providing with technically feasible, economically acceptable and environmentally sufficient methods. This treatment technique can be applied both in situ and on site. In situ remediation of contaminated environments is more cost-effective than on site excavation and off site treatment (Cunningham, et al. 1995; Levin and Gealt, 1993). In situ chemical remediation of soil offers several advantages over conventional treatment technology such as pump-and-treat. For instance, the technology does not generate large volumes of wastes that must be disposed of and/or treated. It is also implemented over a much shorter time frame. Both of these advantages should result in savings on material, monitoring and maintenance (Technical/Regulatory Guidelines, 2001). Chemical oxidation may be used in applications where the effectiveness of bioremediation is limited by the range of contaminants and/or climate conditions. An improvement of the biodegradability during the chemical oxidation gives a presumption for implementation of consecutive chemical oxidation and biodegradation stages to make the purification process also cost-effective. Thus, the remediation of NPs, polycyclic aromatic hydrocarbons (PAH), diesel fuel, shale oil and transformer oil contaminated soils was carried out by combining chemical oxidation (ozonation and Fenton-like treatment) and biological treatment in the present study.

PAH are the products of thermal decomposition, formed during incomplete combustion of organic materials and geochemical formation of fossil fuels (Grimmer, 1983). PAH have been identified in many emission sources, such as vehicle exhausts, power plants, chemical-, coke- and oil-shale industries (Dabestani and Ivanov, 1999). Primary natural sources are forest fires and volcanic activity (Grimmer, 1983). Accumulation of PAH in soil is believed to result from atmospheric deposition after long-range transport (Dabestani and Ivanov, 1999). A very high PAH pollution level in soil is associated also with oil spills. There are more than 100 different PAH compounds known and 17 (acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, pyrene, fluoranthene, chrysene, benz(a)anthracene, benzo(a)pyrene, benzo(e)pyrene, benzo(b)fluoranthene, benzo(j)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, dibenz(a,h)anthracene, indeno(1,2,3-c,d)pyrene) have been classified by the US EPA as priority pollutants (Dabestani and Ivanov, 1999). In many circumstances the environmental occurrence of PAH has been associated with adverse effects on public health.

Diesel fuel, transformer oil and shale oil are dangerous environmental pollutants. They are toxic and can create a significant threat to public health and the environment. While the problem of shale oil pollution is important in Estonia, diesel and transformer oil pollution is widespread all over the world. Soil contamination with diesel is caused mainly by leakage of underground storage tanks and accidental spills during transportation and disposal (Richard and Vogel, 1999). Transformer oil may enter the environment during salvage operations, as it is dumped, spilled, or leaks from used transformers into the ground. The contamination of soil with shale oil (produced by liquefaction of solid oil shale) is a serious environmental problem in oil shale industry. Diesel, transformer oil and shale oil can migrate to deeper layers through leaching, and surface flow pose a substantial threat of release of aromatic (polychlorinated biphenyls, PAH and phenols) and aliphatic compounds. A considerable amount of these contaminants can be held in soil in the form of residual saturation and lead to long-term contamination of groundwater. Thus, due to the vast number of sources and environmentally hazardous chemical composition of these contaminants, implementation of innovative treatment technologies is a matter of pressing concern.

There are no any studies on the degradation of NPs, transformer oil and shale oil contaminants in soil by the Fenton/Fenton-like treatment or ozonation. Ozonation (Masten and Davies, 1997; Nam and Kukor, 2000; Stehr et al., 2001) and the Fenton/Fenton-like treatment (Gates-Anderson et al., 2001; Nam et al., 2001; Bogan and Trbovic et al., 2003; Kim and Choi, 2002; Watts et al., 2002) were applied for the degradation of PAH in soil. It was demonstrated that PAH chemical oxidation might enhance subsequent biodegradation (Nam and Kukor, 2000; Nam et al, 2001; Lee et al., 1998; Lee and Hosomi, 2001; Stehr et al., 2001). The Fenton/Fenton-like treatment and ozonation were used for the remediation of diesel-contaminated soil (Watts and Dilly, 1996; Kong et al., 1998; Ahn et al., 2005) with the following biotreatment (Ahn et al., 2005). In general, the prevalent part of existing studies on chemical remediation of contaminated soil (Nam and Kukor, 2000; Nam et al., 2001; Kong et al., 1998;

Ahn et al., 2005; Lee et al., 1998; Lee and Hosomi, 2001; Watts et al., 2002; Watts and Dilly, 1996) have been limited to soil with low content of natural organic matter. Moreover, effectiveness of combined chemical (the Fenton, ozonation) pre-treatment and biodegradation was generally studied (Nam and Kukor, 2000; Nam et al., 2001; Lee et al., 1998; Lee and Hosomi, 2001; Stehr et al., 2001) using microorganisms introduced into chemically pre-treated soil, while employing of indigenous microorganisms will be relatively ecologically sound.

OBJECTIVES OF THE STUDY

The main goal of the present study was to enlarge the existing knowledge in AOP application for water and soil decontamination.

The study on water purification was an attempt to find the benefits of using AOP such as ozone accompanied by hydrogen peroxide or/and by UV-radiation, the Fenton, photo-Fenton, and hydrogen peroxide photolysis for the degradation of NPs (2-NP, 4-NP, 2,4-DNP, 2,5-DNP, 2,6-DNP, 4,6-DN-*o*-CR, 2,6-DN-*p*-CR), as a group of bio-resistant toxic compounds. Ozonation, ozone including AOP and hydrogen peroxide photolysis of NPs at different pH values were investigated. The influence of the addition of different doses of hydrogen peroxide in AOP concomitantly used H_2O_2 and catalyst (Fe^{2+}) in the Fenton and photo-Fenton treatments was studied. The effect of ozonation and AOP on the biodegradability of NPs was studied with the purpose of assessing the potential of ozonation and AOP to enhance the capacity of conventional biological treatment to remove poorly biodegradable NPs. Among the factors that contribute to biodegradability improvement the degree of organically bounded nitrogen mineralization, total organic carbon mineralization, aromatic carbon reduction and detoxification were considered. The *Daphnia magna* toxicity test was utilised for following the changes in the toxicity of solutions during the treatment and evaluation of by-products toxicity. Some by-products formed during the ozonation of 4-NP and 2,4-DNP at initial pH 9.5 were identified. The comparison of the treatment efficiency and treatment costs of ozonation and AOP applied for NPs degradation was undertaken in order to find the most effective way for NPs-contaminated water purification.

The objective of the study on soil remediation was to investigate the degradation of NPs, PAH, diesel fuel, shale oil and transformer oil in contaminated soil in order to find the most effective chemical treatment (Fenton's reagent and ozonation) method. The assessment of ozonation and Fenton-like treatment ability for contaminated soil remediation was performed dependently on various process parameters. The efficiency of contaminants' removal depending on oxidant doses (the H_2O_2/contaminant/Fe^{2+} weight ratio, ozone consumed) in ozonation and the Fenton/Fenton-like chemical treatment methods was evaluated. The influence of treatment time, manner of hydrogen peroxide addition and pH in Fenton-like treatment on the removal of contaminants in soil was investigated. The effect of soil water content on the degradation of contaminants by ozonation was assessed by the comparison of three-phase (sand-water-ozone) and two-phase (sand-ozone) ozonation systems. The efficiency of ozonation was estimated on the basis of contaminant degradation and consumed ozone doses.

In order to increase the effectiveness of contaminated soil remediation and make the treatment more cost-effective the combined chemical + biological treatment was applied for soil remediation. Thus, the influence of chemical pre-treatment on the following biodegradability was evaluated. The optimal doses of chemical oxidants (ozone, hydrogen peroxide) were found in chemical pre-treatment, with the purpose of facilitating of the following bioremediation by the indigenous microorganisms.

The assessment of influence of natural organic matter content on the feasibility of chemical and combined chemical + biological treatment to degrade PAH, diesel, transformer oil and shale oil in different soil matrixes (sand and peat) was performed. Sand represented a mineral part of soil, while peat was chosen as a model of organic-rich soil.

In addition to contaminants' degradation, the removal of aliphatic hydrocarbons (alkanes) in diesel-contaminated soil and reduction of absorbency at 254 nm, indicating the aromatic carbon content, in diesel, transformer oil and shale oil contaminated soil were followed. A rough estimation and comparison of treatment cost of the Fenton, Fenton-like treatment and ozonation (with the moderate additions of chemical oxidants) for contaminated soil remediation was presented.

The results obtained comprise a basis for introduction of efficient and economical treatment processes of a great practical significance enabling to achieve a new quality in contaminated water and soil treatment.

1 LITERATURE REVIEW

1.1 Advanced oxidation processes for water purification

During the last few years a series of new methods for water and wastewater purification, called advanced oxidation processes (AOP), have received increasing attention.

The concept of “advanced oxidation processes” was established by Glaze et al. (1987). AOP were defined as the oxidation processes, which generate hydroxyl radicals in sufficient quantity to affect water treatment.

Many systems are qualified under this broad definition of AOP. Most of these systems use a combination of strong oxidants, e.g. O_3 and H_2O_2, catalysts, e.g. transition metal ions or photocatalyst, and irradiation, e.g. ultraviolet (UV), ultrasound (US), or electron beam. Table 1.1 lists typical AOP systems.

Table 1.1. List of typical AOP systems (Huang et al., 1993)

Non-photochemical	Photochemical
O_3/OH^-	H_2O_2/UV
O_3/H_2O_2	O_3/UV
O_3/US^a	$O_3/H_2O_2/UV$
O_3 /GAC[b]	H_2O_2/Fe^{2+} (photo-Fenton)
Fe^{2+}/H_2O_2 (Fenton system)	UV/TiO_2
electro-Fenton	$H_2O_2/TiO_2/UV$
electron beam irradiation	$O_2/TiO_2/UV$
ultrasound (US)	UV/US
H_2O_2/US	
O_3/CAT^c	

[a] Gogate and Pandit, 2003
[b] Jans and Hoigné, 1998
[c] Legube and Karpel Vel Leitner, 1999

The main advantages of these methods are high rates of pollutant oxidation, flexibility concerning water quality variations, and small dimension of the equipment. The main disadvantages are relatively high treatment costs and special safety requirements because of the use of very reactive chemicals (ozone, hydrogen peroxide), etc. and high-energy sources (UV lamps, electron beams, radioactive sources) (Kochany and Bolton, 1992).

Some of pilot plant or full-scale elaborations of AOPs are known already as a registered trademark like ULTROX, RAYOX, WEDECO, UVOX, ECOCLEAR and BioQuint.

The hydroxyl radical ($OH^\bullet$) is a powerful, non-selective chemical oxidant that acts very rapidly with most organic compounds. Only fluorine gas has a higher electronegative oxidation potential, but it is not used in water treatment (Table 1.2).

Table 1.2. Relative oxidation power of some oxidising species (Ullmann's 1991)

Oxidation species	Oxidation potential, eV
Fluorine	3.06
Hypochlorous Acid	1.49
Chlorine	1.36
Hydrogen peroxide	1.77
Ozone	2.07
Perhydroxyl radical	1.70
Hydroxyl radical	2.80
Nascent oxygen	2.42

In ozone including treatment methods various compounds can react with ozone in direct reactions with the dissolved molecular ozone (O_3) or in indirect reactions with the radical species ($OH^\bullet$, $HO_2^\bullet$) that are formed when ozone decomposes in water (Hoigné and Bader, 1975; 1976).

The reactions of radicals are unselective and instant (Langlais et al., 1991). The reaction rate constant for radical reactions are several order of magnitude higher than for molecular ozone, but due to the high reactivity of radicals, they are spent to undesirable reactions with matrix compounds, for example carbonate and bicarbonate ions (Haberl et al., 1993).

The reactions of molecular ozone are highly selective and limited to unsaturated aliphatic and aromatic compounds, and to specific functional groups. Initial molecular reaction sites are either multiple bonds (C=C, C=C-O-R, -C=C-X) or atoms carrying a negative charge like N, P, O, S, and nucleophilic carbon as reviewed by Langlais et al. (1991). The reaction rate constants of molecular ozone to different substrates vary over the range 10^{-5} - 10^{9} $M^{-1}s^{-1}$ (Hoigné and Bader, 1983a and 1983b; Hoigné et al., 1985). Because of the variation of reaction kinetics is even several orders of magnitude, it is possible to selectively oxidise particular harmful compounds over total matrix effect. Ozone is not consumed by removal of non-desirable, for example, carbonate and bicarbonate ions (Haberl et al., 1993).

All reaction mechanisms may occur simultaneously, but in practice one or another reaction pathway will predominate, depending on the reaction conditions and the chemical composition of the water being treated. The reaction conditions for ozonation can be chosen to favour one of the two very different oxidation mechanisms (Hoigné and Bader, 1976; Hoigné, 1988).

1.1.1 Typical reactors used for water treatment by chemical oxidation

1.1.1.1 Typical reactor used for the Fenton oxidation

A batch Fenton reactor essentially consists of a non-pressurised stirred reactor with metering pumps for the addition of acid, base, a ferrous sulphate catalyst solution and industrial strength (35-50%) hydrogen peroxide (Gogate and Pandit, 2004). It is recommended that the reactor vessel be coated with an acid-resistant material, because the Fenton reagent is very aggressive and corrosion can be a serious problem. Addition of reactants is done in the following sequence: wastewater followed by dilute sulphuric acid (for maintaining acidic conditions) catalyst in acidic solutions, base or acid for the adjustment of pH at a constant value (must be added slowly with proper maintenance of temperature). The discharge from the Fenton reactor is fed into a neutralising tank for adjusting the pH of stream followed by a flocculation tank and a solid-liquid separation tank for adjusting the TDS content of the effluent stream. A schematic representation of the Fenton oxidation treatment is presented in Figure 1.1.

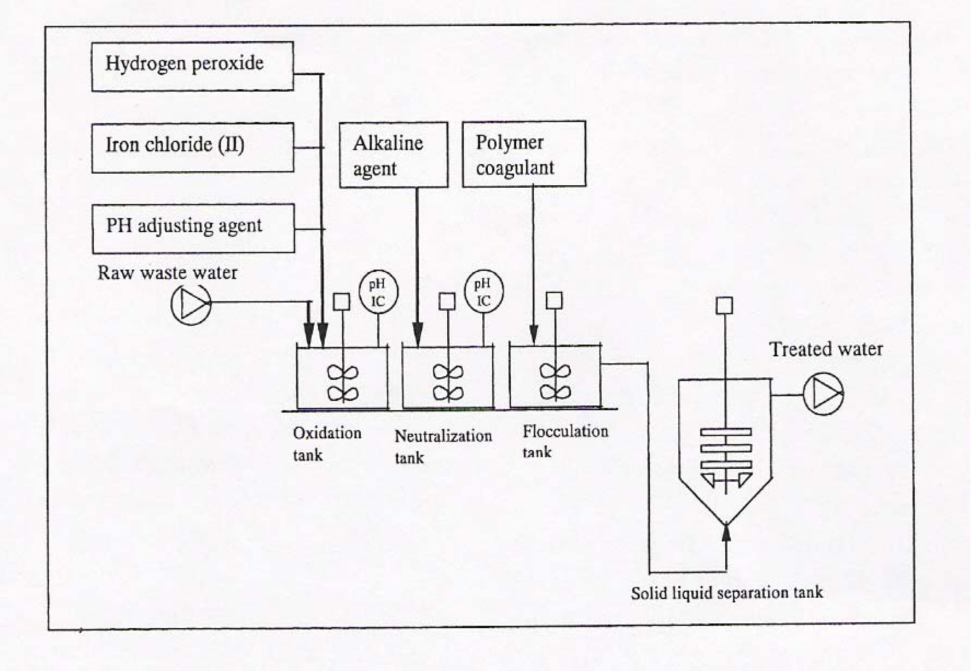
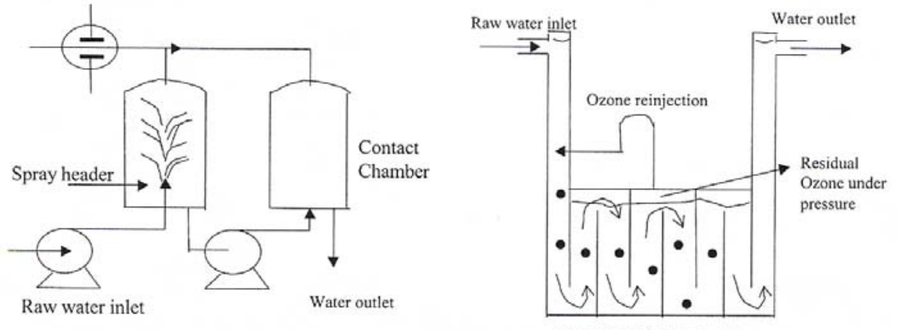


Figure 1.1. Scheme of the Fenton oxidation treatment (Gogate and Pandit, 2004)

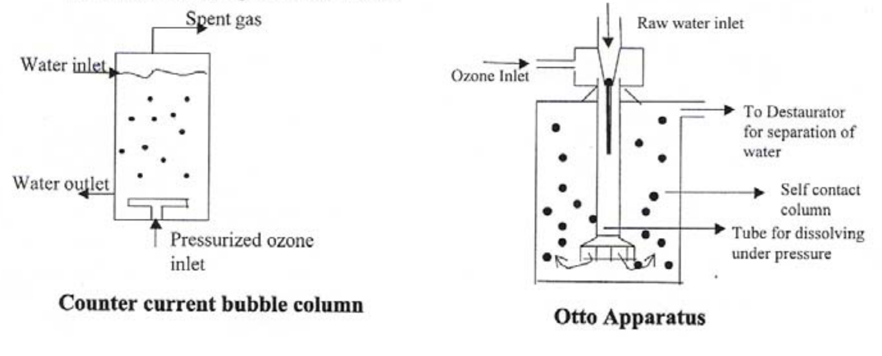
1.1.1.2 Reactors used for ozone transfer

A number of devices can be used to transfer the generated ozone into water such as countercurrent bubble column, packed and plate columns, static mixers, jet reactors and agitated vessels (Bowers et al., 1973; Glaze, 1987, Munter et al., 1993). Figure 1.2 shows some of the commonly used equipments for transferring ozone in water. Ozone transfer efficiency should be maximised by increasing the interfacial area of contact (reducing the bubble size by using small size ozone diffusers such as porous disks, porous glass diffusers (Ledakowicz et al., 2001), ceramic membranes (Janknecht et al., 2001; Ciardelli et al., 2001; Ciardelli and Ranieril, 2001), and increasing the contact time between the gas and the effluent (increase the depths in the contactor, optimum being 3.7 to 5.5 m). Side stream injectors can be used for avoiding plugging which also gives additional advantages of operation at higher ratio of gas flow rate to liquid flow rate and higher mixing efficiency without bubble channelling problems, but are also subject to lower contact times, bumping and corrosion. Static mixers offer bright potential for effectively dissolving ozone in water and can be used at larger scale also. They are usually used in water disinfection. The use of static mixers for actual wastewater treatment applications is increasing, despite of the fact that pressure drop will be higher due to the presence of solids and different physical properties of the effluent stream as compared to water containing only microorganisms.



Film Layer Purifying Chamber Process

Torricelli Apparatus



Counter current bubble column

Otto Apparatus

Figure 1.2. Schematic representation of equipments used for ozonation

1.1.1.3 Reactors for oxidation using hydrogen peroxide

Introduction of hydrogen peroxide into the waste stream is critical due to lower stability of hydrogen peroxide. The reaction rate between hydrogen peroxide and the pollutant usually dictates the point where H_2O_2 should be added. An additional point should give large residence time of H_2O_2 in the pollution stream, but due the practical constraints and poor mixing conditions, it is not always possible to inject H_2O_2 in line and additional holding tank may be required. The other optimising parameters can be the injection rate, catalyst and temperature of the reaction. The simplest, faster and cheapest method for injection of hydrogen peroxide is gravity feed system. Pump feed systems can also be used, but it requires regular attention. Multistage injection systems (reactors in series) are another recent invention (Furukawa et al., 1997; Shishida et al., 1999). Apart from using reactors in series, the addition of hydrogen peroxide can be adjusted in increasing steps depending on the concentration of the remaining pollutants as well as the oxidation products.

1.1.1.4 UV reactor design

Most conventional UV reactors are available in two types; namely, closed vessel and open channel. Figure 1.3 shows a conventional closed vessel UV reactor. The major elements that should be considered in the hydraulic design of a UV closed vessel reactor are: dispersion, turbulence, effective volume, residence time distribution, and flow rate (EPA US, 1996).

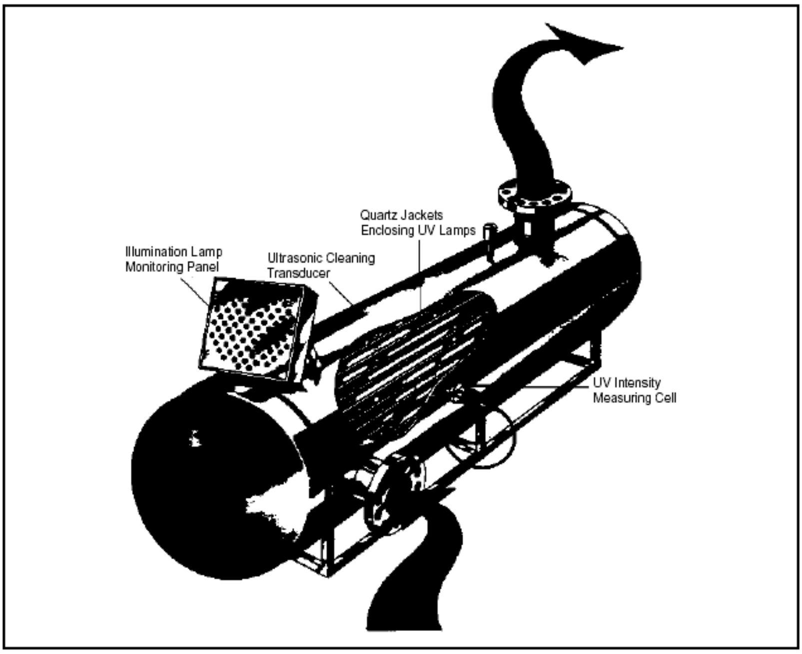


Figure 1.3. Closed vessel ultraviolet reactor (EPA US, 1996)

Dispersion is the characteristic of water elements to scatter spatially. The ideal UV reactor is plug flow, where water particles are assumed to discharge from the reactor in the same sequence they entered and each element of water passing through the reactor resides in the reactor for the same period of time. An ideal plug flow reactor has no dispersion and is approximated by a long tank with high length-to-width in which dispersion is minimal (EPA US, 1996). In addition, the ideal UV reactor has a flow that is turbulent radially from the direction of flow, to eliminate dead zones. A negative of having a radially turbulent flow pattern is that some axial dispersion results, thus disrupting the plug flow characteristics. Techniques such as misaligning the inlet and outlet, and using perforated stilling plates, have been used to accommodate the contradicting characteristics of plug flow and turbulence (EPA US, 1996).

Producing UV radiation requires electricity to power UV lamps. Both low-pressure and medium-pressure are available for water treatment. Low-pressure lamps emit heir maximum energy output at wavelength of 253.7 nm, while medium pressure lamps emit energy with wavelengths ranging from 180 to 1370 nm. The intensity of medium-pressure lamps is much higher than low-pressure lamps. Typically, low-pressure lamps are enclosed in a quartz sleeve to separate the water from the lamp surface. Although Teflon sleeves are an alternative to quartz sleeves, quartz sleeves absorb only 5% of the UV radiation, while Teflon sleeves absorb 35% (Combs and McGuire, 1989).

1.2 Chemical oxidation of contaminated soil

The most common method for remediation of contaminated soil is excavation followed by landfilling or incineration. However, excavation followed by landfilling cannot destroy contaminants and incineration can cause a secondary pollution such as formation of polychlorinated dibenzofurans or polychlorinated-*p*-dioxins (Fox, 1996). Using of chemical oxidation technologies for soil cleaning is the most recent, modern direction in this area, providing with technically feasible, economically acceptable and environmentally sufficient methods.

Some recent studies have demonstrated the efficiency of oxidation processes, such as ozonation and the Fenton treatment for contaminated soil remediation (Watts and Dilly, 1996; Masten and Davies, 1997; Lee et al., 1998; Kong et al., 1998; Watts et al., 1999a,b; Watts and Stanton, 1999; Watts et al., 2000; Nam and Kukor, 2000; Lee and Hosomi, 2001; Teel et al., 2001; Pierpoint et al., 2003; etc.). These studies have showed that such treatment technique can be applied both in situ and on site. In situ treatment technology can be used for hot spot treatment, when the emergency response actions must be taken within a few hours after pollution to remediate contaminated soil and prevent pollution of the groundwater. Consequently, the application of in situ chemical treatment can be a very effective and fast response for soil recovery minimising environmental impact.

In situ chemical treatment offers several advantages over conventional treatment technologies. The cost of reagents are relatively low, so application of in situ oxidation is generally far less costly than other active source removal technologies, such as in situ thermal treatment or flushing using surfactants or co-solvents (In Situ Oxidation, 1999). This technology does not generate large volumes of waste that must be disposed of and/or treated and is also implemented over a much shorter time frame (Technical/Regulatory Guidelines, 2001). Since the reaction is almost immediate, such treatment is far more rapid than biological techniques, and can be faster than thermal or vapour recovery technologies (In Situ Oxidation, 1999). This technology also has various limitations and should not be considered as a magic bullet for every site. For example, application of chemical treatment may actually disrupt other remedies. For example, application of chemical oxidation on a site that is benefiting from natural reductive dehalogenation may temporarily upset the geochemistry that facilitates the process (Technical/Regulatory Guidelines, 2001).

Implementation of oxidation technologies is aimed at transforming hardly biodegradable components into better biodegradable ones. There is no doubt that bioremediation remains the most widely used technology for cleaning of polluted soil. However bioremediation has limited application for biorefractory pollutants and slow response under cold climate conditions. In situ and on site oxidation processes have an advantage over bioremediation on these matters. A substantial improvement of the biodegradability during the chemical oxidation gives a presumption for implementation of chemical oxidation combined with biodegradation processes.

In situ chemical oxidation is useful for source area mass reduction and intercepting of plumes to remove mobile contaminants. Each chemical oxidant is effective for different contaminants. The appropriateness of in situ technologies at a site also depends on matching the oxidant and delivery system to the site contaminants and site conditions. This requires careful site characterization and screening. For instance, oxidation is dependent on achieving adequate contact between oxidants and contaminants. In addition, there may be limitations both on the delivery of the oxidant as well as its stability in the subsurface. For example, in clay strata the delivery of reagents may be very poor or not possible at all without some modifications to the subsurface. In other instances, the contaminant may be trapped or pooled in rock fissure or cracks or may be bound within the soil matrix. (In Situ Oxidation, 1999; Technical/Regulatory Guidelines, 2001; EPA US Chemical Oxidation, 1998).

Hydrogen peroxide and ozone are the chemical reagents most extensively used for in situ treatment of contaminated sites. The application of these oxidation technologies for remediation of contaminated soil is under consideration in the present study.

1.2.1 Hydrogen peroxide treatment

There are several patented and commercial approaches for applying Fenton's reagent. Among them are Geo-Cleanse®, ISOTEC™, Clean-Ox® (In Situ Oxidation, 1999; EPA US Chemical Oxidation, 1998) that were successfully applied for full-scale soil remediation using in situ chemical oxidation for the removal of dense non-aqueous phase liquids such as chlorinated solvents and hydrocarbons.

In commercial applications of Fenton's reagent, admixture of approximately 5-35% H_2O_2 (w/w) is applied. The initial weight (or equivalent volume) of H_2O_2 and ferrous ions is based on contaminants levels, subsurface characteristics, soil to be treated, and the specific stoichiometry of H_2O_2:Fe^{2+} determined during the laboratory study. Sometimes, additional reagent, stabilizers, may be applied to account for heterogeneity of the medium and unanticipated rate of decomposition of H_2O_2 to provide additional contact time for the contaminants (Baciocchi et al., 2003; Watts and Dilly, 1996; Watts et al., 1999b). Monobasic potassium phosphate (KH_2PO_4) is most commonly used in bioremediation formulations because it is not only organic stabilizer, but also a bacterial nutrient (Hinchee et al., 1990). If the natural pH of the contaminant zone is not low enough for efficient hydroxyl radical generation, acids may be added to adjust pH of the subsurface prior to the Fenton's reagent application (Technical/Regulatory Guidelines, 2001). It was found that the pH adjustment is far more efficient in reducing H_2O_2 decomposition rate (Baciocchi et al., 2003).

There are several advantages of applying H_2O_2 at lower concentrations below 35% (e.g. 10%). Low-concentration applications reduce the chance of excessive heat and gas generation and reduce the potential of simply stripping of contaminants from aqueous phase to the vapour phase without oxidising them (Technical/Regulatory Guidelines, 2001). In addition, excess application of H_2O_2 may not be economical due to undesirable reactions including those of hydroxyl radicals with H_2O_2 (Walling, 1975). However, bulk H_2O_2 is generally available in 35% or 50% concentrations and 10% application may mean additional chemical handling at the site (Technical/Regulatory Guidelines, 2001).

In one method, before the application, it is verified that the formation is capable of accepting a certain liquid flow rate. Once an acceptable liquid flow rate is established, a 35% H_2O_2 solution and ferrous ions are injected at the same location so that chemical mixing occurs once the chemicals have reached the zone of treatment. In this patented delivery device, the injector is designed to prevent mixing inside the injector tube (Technical/Regulatory Guidelines, 2001). In another patented method, an organically complexed and more mobile form of a ferrous ion catalyst is initially applied to the subsurface. The subsurface is allowed to equilibrate to ensure that conditions (pH, level of iron, etc.) are favoured for the Fenton's reaction. A 50% H_2O_2 is finally applied under pressure to mix with the iron in the subsurface to generate the hydroxyl radicals (Technical/Regulatory Guidelines, 2001). In a third Fenton's approach, a mixture up to 5% H_2O_2, an iron catalyst, and several proprietary compounds is injected in one step through a direct-push probe. The oxidant solution is injected while driving the probe, liquefying the soil around the probe tip and enabling the probe to be advanced by hand (Technical/Regulatory Guidelines, 2001).

Fig. 1.4 illustrates how a vertical injection well could be used to introduce hydrogen peroxide into vadose and the saturated zone.

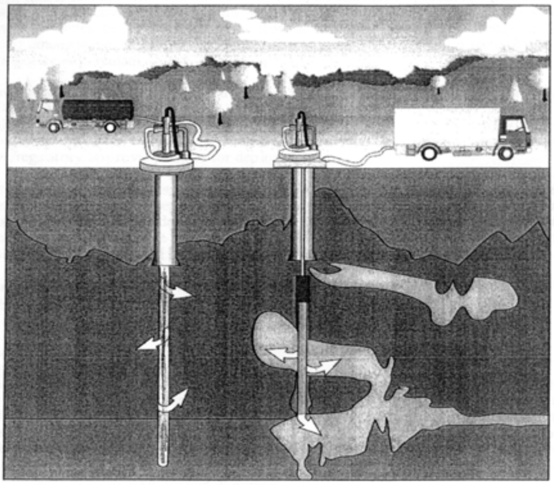


Figure 1.4. Schematic of in situ hydrogen peroxide oxidation of contaminated soil and groundwater (Technical/Regulatory Guidelines, 2001)

In general, single injection, several re-injections at intervals or continuous injection using re-circulation of amended waters can be used. For single or multiple injections, permanent or temporary injection points are established, and an aqueous solution containing the oxidant and any catalysts is injected under pressure. The oxidant (and catalyst) concentration, the target pH, the injection well spacing (i.e. radius of influence), the number of injections, and the injection pressure are all important design parameters that can affect cost and performance (In Situ Oxidation, 1999).

Fenton's reagent treatment has several advantages over other soil remediation methods. The Fenton process is relatively fast, taking only days or weeks. The contaminants are treated in situ, converted to innocuous and/or natural occurring compounds (e.g. H_2O, CO_2, O_2, halide ions). By acting/reacting up on the contaminant in place, the reagent serves to eliminate the possibility of vertical movement of the contaminant other than resulting from the act of vertical injection itself, which is often a concern in other remediation technologies (Technical/Regulatory Guidelines, 2001). As a side advantage, aerobic biodegradation of contaminants can benefit from the presence of oxygen released during H_2O_2 decomposition, if large quantities of reagent need to be applied. Hydrogen peroxide can be electrochemically generated on site, which may further increase the economic feasibility and effectiveness of this process for treated contaminated sites (Technical/Regulatory Guidelines, 2001). Recently, it has been shown (Watts et al., 1992; Watts et al., 1999a; Kong et al., 1998; etc.) that natural iron oxide minerals (hematite α-Fe_2O_3, goethite α-FeOOH, magnetite Fe_3O_4 and ferrihydrite) present in soil can catalyse hydrogen peroxide oxidation of organic compounds (Fenton-like treatment). Thus, in situ Fenton-like treatment of contaminated soils would require no addition of soluble iron catalyst because of the catalytic ability of naturally occurring iron minerals in soil or subsurface solids.

Disadvantages include the need for pH control in some cases and difficulties controlling in situ heat and gas production (In Situ Oxidation, 1999). The usefulness of Fenton's reagent may be limited by low soil permeability, incomplete site delineation, subsurface heterogeneities, and highly alkaline soils where carbonate ions are free radical scavengers (Technical/Regulatory Guidelines, 2001).

1.2.2 Ozone treatment

Ozone is one of the strongest oxidants available for in situ soil treatment. Similar to the water treatment ozone can oxidise organic compounds in two ways, either with direct oxidation by ozone or by the generation of free radicals intermediates. Ozone readily decomposes via catalytic reaction with reactive sites such as metal oxides on soil to form $OH^\bullet$, a powerful, effective, non-specific oxidising agents (Glaze and Kang, 1988). Metal oxides such as α-FeOOH, MnO, and Al_2O_3 on the surface of sand and soil are known to accelerate ozone decomposition to generate $OH^\bullet$ via heterogeneous catalytic reactions of ozone with the metal oxides (Masten, 1991; Choi et al., 2001). Hence, ozone and $OH^\bullet$ can react with most of the organic compounds in the subsurface. The use of gaseous ozone to remediate unsaturated contaminated soils has significant potential because of the strong reactivity of ozone and its primary decomposition product, $OH^{\bullet}$.

Ozone is a gas that is generated on site from either atmospheric or compressed oxygen. The ozone concentration and gas flow rate produced by ozone generated is fixed within fairly narrow ranges. The ozone concentrations are in the range of 5% (by weight) when generated from oxygen and about 1% when generated from atmospheric air (Langlais et al., 1991). Ozone generator capacities are typically expressed in terms of mass output. Since the ozone generators produce a continuous ozone stream, the in situ oxidation process using ozone is more of continuous process, compared to the batch injection approaches that are common with Fenton's reagent. The ozone generator capacity required is determined from the overall oxidant loading, the gas flow rates that the subsurface will accept, and the allowable time frame for treatment (Technical/Regulatory Guidelines, 2001).

Subsurface delivery and transport of ozone gas is substantially different from that involved with aqueous-phase oxidants. In situ ozonation involves mass transfer from the gas phase to the aqueous phase, where the oxidation reactions primarily occur. Ozone can be injected into the vadose zone or into the saturated zone. The concentration of ozone in the gas phase is orders of magnitude higher than that obtainable in aqueous solution. Ozone is more stable in the gas phase than in water. In water, $OH^{\bullet}$ catalyses the autodecomposition of ozone (Langlais et al., 1991). Also, higher flow velocities can be achieved in the vadose zone than is possible in aquifers. Both cases (injections into vadose or the saturated zone) involve consideration of flow under variable saturated conditions. The distribution of ozone gas injected in the vadose zone depends strongly on the existing moisture conditions and geological heterogeneity. Ozone injection into the saturated zone involves the gas flow mechanisms of in situ sparging, where injected gases displace groundwater to form an unsaturated region of gas flow. In this scenario, subsurface heterogeneity can lead to preferential gas flow, and ozone transport may be limited by mass transfer and aqueous-phase diffusion in regions that remain water-saturated (Technical/Regulatory Guidelines, 2001).

Patented and commercial approach for applying ozone for soil remediation C-Sparge^{TM} was effectively used to remediate soil contaminated with petroleum hydrocarbons and benzene, toluene, ethylbenzene, xylene (BTEX) and PAH (In Situ Oxidation, 1999; In Situ Remediation Technology; EPA US Chemical Oxidation, 1998).

For in situ ozonation vertical or horizontal injection wells can be used to inject ozone into the subsurface. Fig. 1.5 illustrates how a vertical injection well could be used to introduce ozone into unsaturated soils. Extraction wells may, if necessary, be used to control the direction of ozone flow in the subsurface. Horizontal wells could also be used to inject ozone (Masten and Davies, 1997). Nelson and Brown (1994) have claimed that the use of horizontal wells is more effective for the introduction of ozone into unsaturated soils than is the use of vertical wells. Horizontal wells are also advantageous when using ozone in combination with sparging technologies. However, while horizontal wells may have some advantages, it is not clear that these advantages warrant the additional cost necessary to install such wells.

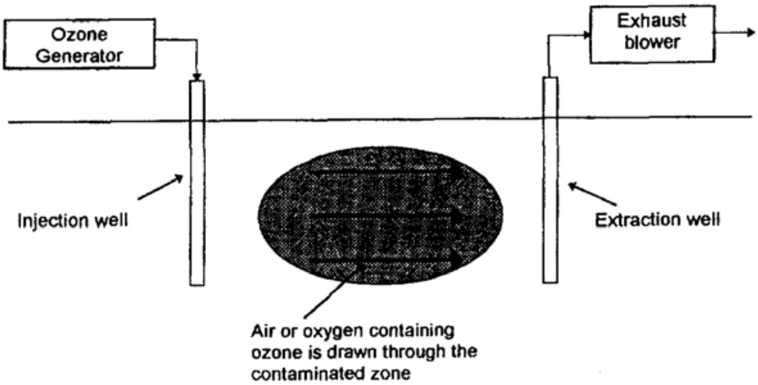


Figure 1.5. Schematic of in situ ozone treatment system (Masten and Davies, 1997)

Compared to the other technologies, in situ ozonation offers several advantages (Masten and Davies, 1997; Technical/Regulatory Guidelines, 2001): 1) it is much easier to deliver ozone to a contaminated zone than aqueous oxidants; 2) it can be generated on site, and this eliminates the storage and handling problems associated with other oxidants; 3) in situ ozonation often leads to an increase of hydrophilic substances, which are mostly better biodegradable and can be degraded faster by microorganisms; 4) it may also assist bioremediation by breaking down complex compounds into simpler compounds that are easier to degrade; 5) when ozone decomposes, it provides oxygen to the microbial community, which can improve bioremediation; however, ozone is also a sterilising agent in high concentrations or long residence times, so it must be carefully controlled before biotreatment is encouraged; 6) no volatilisation of target chemicals is required and, therefore, overcomes mass transfer limitations associated with soil venting; 7) in situ ozonation would likely be more rapid than biodegradation or soil venting processes, and thus reduce the remediation time and treatment costs.

2 MATERIALS AND METHODS

2.1 Water treatment

2.1.1 Model compounds in water treatment

The chemicals studied were 2-nitrophenol (2-NP), 4-nitrophenol (4-NP), 2,4-dinitrophenol (2,4-DNP), 2,5-dinitrophenol (2,5-DNP), 2,6-dinitrophenol (2,6-DNP), 2-methyl-4,6-dinitrophenol (4,6-DN-*o*-CR), 4-methyl-2,6-dinitrophenol (2,6-DN-*p*-CR). Nitrophenols (NPs) were purchased from Aldrich Co. (analytical grade). The mixture of NPs consisted of 2-NP, 4-NP, 2,4-DNP, 4,6-DN-*o*-CR. The samples were prepared dissolving NPs in twice-distilled water. The initial concentration of a single NP was 0.4 mM and concentration of NPs in mixture was 2 mM (0.5 mM of each NP). Some chemical-physical properties of NPs are presented in *paper II*, Table 1 and *paper IV*, Table 1.

2.1.2 AOP applied

2.1.2.1 The Fenton, photo-Fenton, photolysis

Papers I and II

The degradation rate of individual NPs in aqueous solution during the Fenton and photo-Fenton treatments was examined under batch conditions.

The standard procedure was that 0.7 L of fresh NP solution was treated in the cylindrical glass reactor with magnetic stirring. The reaction was stopped by adding 10% aqueous solution of Na_2SO_3 in these experiments. Photolysis in the presence of hydrogen peroxide was carried out under the same conditions with different H_2O_2 concentrations. A mercury low-pressure OSRAM lamp with an energy input of 10 W was used as a UV-source during photo-Fenton, direct UV-photolysis and hydrogen peroxide photolysis treatments. The UV-radiation intensity at 253.7 nm (I^I_0) measured by potassium ferrioxalate actinometry and calculated by Eq. 2.1 (Gordon and Ford, 1976) was 3.315 ± 0.104 μEinstein s^{-1}.

$$I^I{}_0 = \frac{(c_0 - c_n)V}{\varphi T} \qquad (2.1)$$

where c_0 - initial concentration of Fe^{2+} ions (mol L^{-1}), c_n - Fe^{2+} concentration at the moment T (mol L^{-1}), V – volume of irradiated solution (L), T – irradiation time (s), φ – quantum efficiency (φ = 1.25 at λ = 253.7 nm) (Gordon and Ford, 1976). Fig. 2.1 shows a schematic diagram of the system used in photo-Fenton, hydrogen peroxide photolysis and direct UV-photolysis. The reactor was maintained at desired temperature 20 ± 1 °C using cooling jacket.

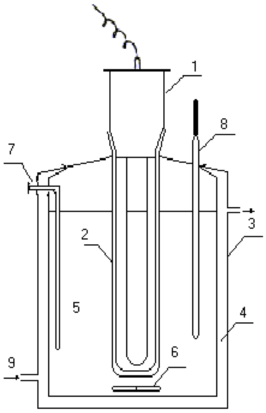


Figure 2.1. Scheme of experimental apparatus used in UV/H_2O_2, direct UV-photolysis, and photo-Fenton oxidation processes (1 – UV lamp; 2 – quartz sleeve; 3 – cooling jacket; 4 – reactor; 5 – irradiated solution; 6 – stirrer; 7 – sample intake; 8 – thermometer; 9 – thermostat)

2.1.2.2 Non-accompanied ozonation, and peroxone

Papers I and III

The ozonation of NPs was conducted on synthetic solutions in twice-distilled water. The experiments were carried out in semi-continuous bubble column with 0.8 L of volume (18 cm high and 8.0 cm in diameter). A scheme of the experimental set is presented in Fig. 2.2.

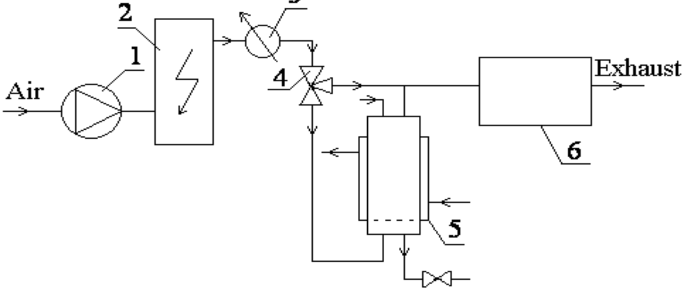


Figure 2.2. Scheme of the experimental set (1 – compressor; 2 – ozonator; 3 – flow meter; 4 – three-way cock; 5 – bubble column equipped with water jacket and UV-lamp; 6 – spectrophotometer)

The volume of fresh NP solution placed to the reactor was 0.6 L. In all experiments the ozone concentration in the feed-gas was kept at 0.50 ± 0.02 mg L^{-1} (*paper I*, 1.52 ± 0.02 mg L^{-1} in several experiments) and a gas flow rate at 1.0 L min^{-1}. O_3/H_2O_2 was carried out under the same conditions with different H_2O_2 concentrations. H_2O_2 was injected directly to the reactor right away before ozone was supplied. The experiments were carried out at room temperature (20 ± 1°C).

2.1.2.3 $O_3/H_2O_2/UV$, O_3/UV

Paper I

The ozonation with UV-radiation was carried out under the same treatment conditions as non-accompanied ozonation experiments. The UV-radiation intensity of low-pressure mercury lamp (58.8 W, type DRB 8-1, USSR) located inside the bubble column in the quarts tube measured by potassium ferrioxalate actinometry and calculated by Eq. 2.1 (Gordon and Ford, 1976) was 0.749 ± 0.054 μEinstein s^{-1}. All experiments were carried out at 20 ± 1°C using cooling jacket.

2.1.3 Calculations of consumed ozone doses in water treatment

The concentration of ozone in (c_{O_3}, mg L^{-1}) feed-gas during ozonation was calculated according to Eq. 2.2:

$$c_{O_3} = 0.15Ext \tag{2.2}$$

where Ext - extinction (cm).

The inlet dose of ozone (d^{in}, mg L^{-1}) was calculated using Eq. 2.3:

$$d^{in} = \frac{GTc^{in}}{V} \tag{2.3}$$

where G – gas flow rate (L min^{-1}), T – time (min), V – volume of solution (L), c^{in} – inlet concentration of ozone (mg L^{-1}).

The consumed dose of ozone (d^c, mg L^{-1}) was calculated using Eq. 2.4:

$$d^c = \sum_{n=1}^{n} \left[\left(\frac{G \Delta T_n}{V} \right) \left(c^{in} - \frac{\left(c^{out}{}_{n-1} + c^{out}{}_n \right)}{2} \right) \right] \tag{2.4}$$

where G – gas flow rate (L min^{-1}), T – time (min), c^{out} - outlet concentration of ozone (mg L^{-1}), c^{in} – inlet concentration of ozone (mg L^{-1}), V – volume of solution (L), n – number of experimental points.

2.1.4 Kinetic studies

The degradation curves of NPs in different oxidation conditions were obtained in a semicontinuous bubble column with verification of the chemosorptions regime. It is well-known (Dankwerts, 1973) that the influence of mass-transfer on the velocity of chemical reaction is eliminated in the bubble column and the process proceeds in the kinetic regime, if following conditions is satisfied:

$$\frac{D_{O_3} \times k_1}{k_L{}^2} < 1 \tag{2.5}$$

where D_{O_3} – coefficient of ozone diffusion (m^2 s^{-1}), k_1 is the first order chemical reaction rate constant (s^{-1}) and k_L the individual liquid phase mass transfer coefficient for ozone physical absorption (m s^{-1}).

Assuming the average value of $k_L = 1 \times 10^{-5}$ m s^{-1} for bubble columns (Dankwerts, 1973) and taking the coefficient of ozone diffusion 1.26 x 10^{-9} m^2 s^{-1} (Munter, 1985) the following value for the ratio was obtained:

$$k_1 < \frac{k_L{}^2}{D_{O_3}} = \frac{\left(10^{-5}\right)^2}{1.26 \times 10^{-9}} = 0.079\,\mathrm{s}^{-1}$$

Thus, the necessary presumption for proceeding of the chemical reaction of ozonation mostly in the bulk of liquid (in the kinetic regime) is satisfied, if the first order rate constant of NPs decomposition follows the inequality $k_1 < 7.9 \times 10^{-2}$ s^{-1} and the curves of the NPs degradation in time can be correspondingly interpreted to compare the rate of chemical reactions under different conditions of oxidation. This was in force in all ozone including experiments conducted in the present study (*paper I*).

The regression analysis of the concentration curves versus reaction time indicated that the decomposition rate of NPs can be described by pseudo-first order kinetics with respect to NP concentration:

$$\frac{dc_{NP}}{dT} = -k_1 c_{NP} \tag{2.6}$$

Thus, the degradation rates of different NPs in aqueous solution were compared by pseudo-first order reaction rate constants with respect to NPs concentrations. Reaction rate constants were calculated using the NP concentrations at the moment T determined in HPLC-analysis, (C_{NP}), and known initial concentration of NP, (C_{NP0}). A plot of ln(C_{NP}/C_{NP0}) versus time (T) gave a straight line whose slope was -k_1 (according the Eq. 2.7); the negative value of pseudo-first order reaction rate constant.

$$\ln\left(\frac{c_{NP}}{c_{NP_0}}\right) = k_1 T \tag{2.7}$$

The half-life ($T_{1/2}$) is the time required for half of the amount of reactant (NP) to disappear. For the first-order reaction $T_{1/2}$ was calculated using Eq. 2.8:

$$\ln\left(\frac{c_{NP_0}}{0.5c_{NP_0}}\right) = k_1 T_{1/2} \qquad \text{and} \qquad T_{1/2} = \frac{0.693}{k_1} \tag{2.8}$$

The 90% conversion time ($T_{90\%}$) is the time when 90% reduction of initial concentration was achieved. Thus, $T_{90\%}$ was calculated using Eq. 2.9:

$$\ln\left(\frac{c_{NP_0}}{0.1c_{NP_0}}\right) = k_1 T_{90\%} \qquad \text{and} \qquad T_{90\%} = \frac{2.303}{k_1} \tag{2.9}$$

In the experiments where the solution of NPs was treated with photolysis in the presence of hydrogen peroxide, non-accompanied ozonation and ozone combinations with H_2O_2 or/and UV-radiation the reactions rates were compared calculating $T_{1/2}$ and $T_{90\%}$ using Eqs. 2.8 and 2.9 (*papers I, II, III*). In the experiments where Fenton's reagent and photo-Fenton were used for the decomposition of NPs the rates of the reactions were compared calculating $T_{1/2}$ and $T_{90\%}$ from the experimental curves (*papers I, II*).

2.1.5 Acute toxicity of NPs and the toxic effect after the AOP treatment

Papers I, II, III

Acute toxicity of NPs and the toxic effects after the AOP treatment were studied with *Daphnia magna* (Cladocera, Crustacea) test. The *Daphnia* clone used was of Finnish origin (*Daphnia magna EF*) from the North Savo Regional Environmental Centre in Kuopio, Finland. NPs were treated until at least 90% conversion of the initial compound to products was achieved. The initial concentration of single NPs was 0.4 mM and the concentration of NPs in mixture was 2 mM (0.5 mM of each studied NP). The *Daphnia* living conditions were kept optimal and a 24-hour toxicity test was carried out according to Finnish Standard SFS 5062 (1984). A special computer program PROBIT was used for the approximation of median effective concentration values (EC_{50}) and their 95% confidence limits.

2.1.6 Analyses used in water treatment

The analyses used in water treatment are summarised in Table 2.1.

Table 2.1. List of analyses and analytical methods used in water treatment

Analysis	Analytical instrument/Method	Reference	Paper
pH	pH-meter		I, II, III
UV_{254nm}	spectrophotometer	EPA method 0415.1	III,
NPs products	HPLC-UV		III
NPs	HPLC-UV	Trapido and Kallas, 2000	I, II, III
NO_3^-	ion chromatograph	Penchuk et al., 1986	I, II, III
H_2O_2	spectrophotometer	Eisenberg, 1943	I, II
Total iron	spectrophotometer	Standard Methods, 1994	I, II
TOC	TOC analyser	Standard Methods, 1994	III
COD	closed reflux titrimetric method	Standard Methods, 1994	I, III
BOD, DO	oxygen analyser	Standard Methods, 1994	I, III
O_3 inlet, outlet	spectrophotometer	IOA Revised Guideline Document, 1998	I, III

2.2 Soil treatment

2.2.1 Characterization of soil samples

Sand and peat were used as models to test the feasibility of chemical treatment in different soil matrixes.

Papers IV, V, VI, VII

Sand was sieved through a 0.16-1.0 mm sieve and dried at 50°C before the spiking. The pH of sand was 6.7. Sand contained 94.36% SiO_2, 4.81% Al_2O_3, 0.47% organic carbon, 4.52 g kg^{-1} total iron and 0.27 g kg^{-1} ion-exchangeable Fe(II).

Papers V, VI, VII

The pH of peat was 6.4. Peat contained 2.64 g kg^{-1} total iron and 0.23 g kg^{-1} ion-exchangeable Fe(II).

2.2.2 Model compounds in soil treatment

Dry soil was artificially spiked with contaminant by adding a contaminant-acetone solution. The acetone was evaporated to dryness under continuous mixing to ensure contaminant distribution homogeneity and, hence, a better reproducibility in repeated experiments. Initial concentrations of contaminants were verified by the analysis of at least four replicates.

Paper IV

The mixture of NPs consisted of 4-NP, 2,4-DNP and 4,6-DN-o-CR purchased from Aldrich Co. (analytical grade) was applied as soil contaminant. Total initial concentration of NPs in sand was 685.5 mg kg^{-1}. Some chemical-physical properties of NPs are presented in *paper II*, Table 1 and *paper IV*, Table 1.

Paper V

The mixture of PAH consisted of phenanthrene (Ph), anthracene (A), fluoranthene (Fl), pyrene (P), triphenylene (TPh), benz(a)anthracene (BaA), chrysene (Chr), benzo(e)pyrene (BeP), perylene (Per), benzo(a)pyrene (BaP) and benzo(ghi)perylene (BghiPer) purchased from Aldrich Co. (analytical grade). Sand with the total concentrations of PAH 52.46 (sand I), 66.64 mg kg^{-1} (sand II) and peat 357.8 (peat I), 121.83 (peat II), 40.21 mg kg^{-1} (peat III) were used for the treatment. Some chemical-physical properties of PAH are presented in *paper V*, Table 1.

Paper VI

Commercial diesel was used for the spiking. The initial concentrations of diesel were 12.5 ± 0.4 and 10.4 ± 0.3 g kg^{-1} in peat and sand, respectively. Some chemical-physical properties of diesel, determined in the present study are given in *paper VI*, Table I.

Paper VII

Shale oil or transformer oil were used as individual contaminants. The initial concentrations of shale oil were 5.6 ± 0.07 g kg^{-1} in sand and 5.5 ± 0.09 g kg^{-1} in peat. The initial concentrations of transformer oil were 17.4 ± 0.1 g kg^{-1} in sand and 19.0 ± 0.1 g kg^{-1} in peat. Some chemical-physical properties of shale oil and transformer oil, determined in the present study are given in *paper VII*, Table 1.

2.2.3 Chemical treatment applied

2.2.3.1 The Fenton treatment

Papers IV, V, VI, VII

The degradation of contaminants in slurry during the Fenton/Fenton-like treatment was examined under batch conditions. The standard procedure was that slurry of soil and liquid (bi-distilled water + H_2O_2 solution and/or without Fe^{2+} solution) were treated in the cylindrical glass reactor with 0.2 L of volume under vigorous magnetic-stirring during 24 h (*papers IV, V*) or 72 h (*papers V, VI, VII*). The contaminated soil was treated without pH adjustment (*paper VII*) and at pH 3.0 (*papers IV, V, VI, VII*). Various manner of hydrogen peroxide addition (the addition of H_2O_2 all at once or stepwise addition) was used in these experiments. The reaction was stopped by adding 10-20% aqueous solution of Na_2SO_3. All experiments were carried out at 20 ± 1°C.

2.2.3.2 Three-phase ozonation

Papers IV, V

The three-phase ozonation of NPs (*paper IV*) or PAH (*paper V*) contaminated soil was conducted in a semi-continuous bubble column with 0.3 L of volume (14.2 cm high and 5.2 cm in diameter). A mixture of ozone gas and air produced by laboratory ozone generator was transferred to slurry of soil (soil + water). Vigorous magnetic-stirring was performed to ensure a good contact between ozone and contaminants. Gas flow rate was kept at 1.0 L min^{-1} and the concentration of ozone in the feed-gas at 1.00 ± 0.02 mg L^{-1}.

2.2.3.3 Two-phase ozonation

Papers IV, V, VI, VII

The two-phase ozonation of dry sand or peat was carried out in semi-continuous bubble column with 0.05 L of volume (29 cm high and 1.5 cm in diameter). A mixture of ozone gas and air produced by laboratory ozone generator was transferred to dry soil. Soil was ozonated without pH adjustment. Gas flow rate was kept at 1.0 L min^{-1} and the concentration of ozone in the feed-gas at 1.00 ± 0.02 mg L^{-1} (*papers IV, V*) and 5.00 ± 0.02 mg L^{-1} (*papers VI, VII*). All experiments were carried out at 20 ± 1°C.

2.2.4 Calculations of consumed ozone doses in soil treatment

The concentration of ozone in (c_{O_3}, mg L^{-1}) feed-gas during ozonation was calculated according to Eq. 2.10:

$$c_{O_3} = 0.15Ext \tag{2.10}$$

where Ext - extinction (cm).

The inlet dose of ozone (d^{in}, mg kg^{-1}) was calculated using Eq. 2.11:

$$d^{in} = \frac{GTc^{in}}{m} \tag{2.11}$$

where G – gas flow rate (L min^{-1}), T – time (min), m – weight of sample (kg), c^{in} – inlet concentration of ozone (mg L^{-1}).

The consumed dose of ozone (d^c, mg kg^{-1}) was calculated using Eq. 2.12:

$$d^{c} = \sum\nolimits_{n=1}^{n} \left[\left(\frac{G\Delta T_n}{m} \right) \left(c^{in} - \frac{\left(c^{out}{}_{n-1} + c^{out}{}_{n} \right)}{2} \right) \right] \tag{2.12}$$

where G – gas flow rate (L min^{-1}), T – time (min), c^{out} - outlet concentration of ozone (mg L^{-1}), c^{in} – inlet concentration of ozone (mg L^{-1}), m – weight of sample (kg), n – number of experimental points.

2.2.5 Biodegradation of contaminants in soil

Papers IV, V, VI, VII

Biodegradation of contaminants (NPs, PAH, diesel, shale oil, transformer oil) in soil followed ozonation and Fenton-like treatment. Duplicates of treated samples as well as duplicates of untreated and control samples were aerobically incubated without shaking at 20ºC in dark. The residual hydrogen peroxide was not removed after Fenton-like pre-treatment. No pH adjustment was performed after the ozonation. The samples with initial pH 3.0 after the Fenton and Fenton-like pre-treatment were neutralised to pH 6.5 ÷ 7.0 (*papers IV, V, VI*). No pH adjustment followed Fenton-like pre-treatment of shale oil and transformer oil contaminated soil (*paper VII*). Sterile twice-distilled water was added to keep soil completely wet. No microbial inoculums were added.

2.2.6 Analyses used in soil treatment

The analyses used in soil treatment are summarised in Table 2.2.

Table 2.2. List of analyses and analytical methods used in soil treatment

Analysis	Analytical instrument/Method	Reference	Paper
pH of soil	pH-meter	EPA method 9045C	IV, V, VI, VII
total iron in soil	atomic absorption spectrophotometer	Slight modification from Heron et al., 1994; papers IV, V, VI, VII	IV, V, VI, VII
ion-exchangeable Fe(II) in soil	atomic absorption spectrophotometer	Slight modification from Tessier et al., 1979; papers IV, V, VI, VII	IV, V, VI, VII
UV-254	spectrophotometer	EPA method 0415.1	VI, VII
NPs	HPLC-UV	Trapido and Kallas, 2000	IV
PAH	HPLC-FLD	Trapido and Veldre, 1996	V
diesel	GC-MS	Palmroth et al., 2002	VI
alkanes	GC-MS	Palmroth et al., 2002	VI
shale oil	GC-MS	VII	VII
transformer oil	GC-MS	VII	VII
O_3 inlet, outlet	spectrophotometer	IOA Revised Guideline Document, 1998	IV, V, VI, VII

Typical chromatograms of NPs and PAH obtained by HPLC-UV and HPLC-FLD, respectively, are presented in Fig. 2.3. GC-MS chromatogram of multi-state hydrocarbon window defining standard DRX-008S including thirty-five alkanes from octane to tetracontane (Accustandard, New Haven, CT, USA) used for qualitative and quantitative analyses of alkanes (*paper VI*) is presented in Fig. 2.4. Typical chromatograms of transformer oil, shale oil and diesel fuel obtained by GC-MS analyses are presented in Fig. 2.5.

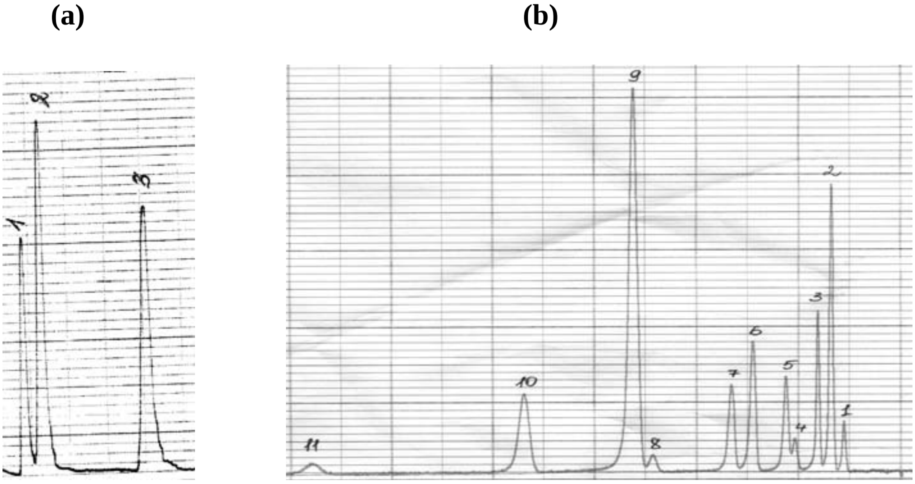


Figure 2.3. Typical (a) NPs chromatogram obtained by HPLC-UV (λ = 280 nm): 1 – 4-NP; 2 – 2,4-DNP; 3 - 4,6-DN-*o*-CR and (b) PAH chromatogram obtained by HPLC-FLD (λ = 254 nm): 1 – Ph, 2 – A, 3 – Fl, 4 – P, 5 – TPh, 6 – BaA, 7 – Chr, 8 – BeP, 9 – Per, 10 – BaP, 11 – BghiPer

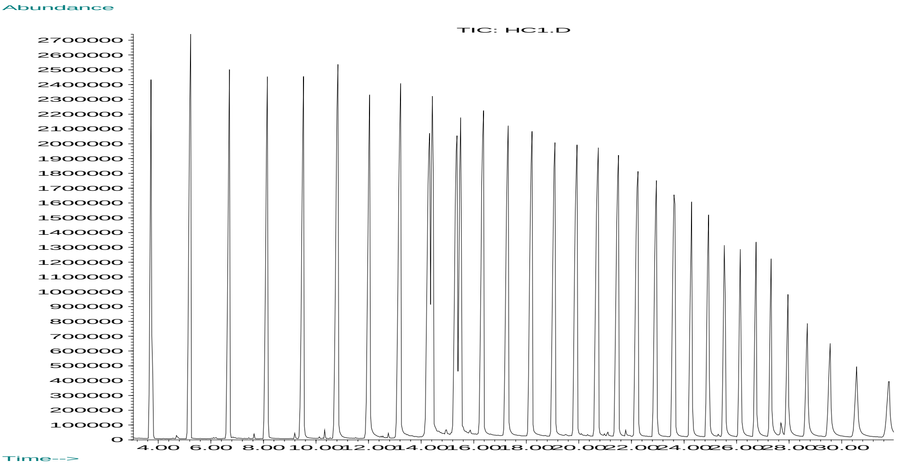


Figure 2.4. GC-MS chromatogram of multi-state hydrocarbon window defining standard DRX-008S including thirty five alkanes from octane to tetracontane, Accustandard, New Haven, CT, USA

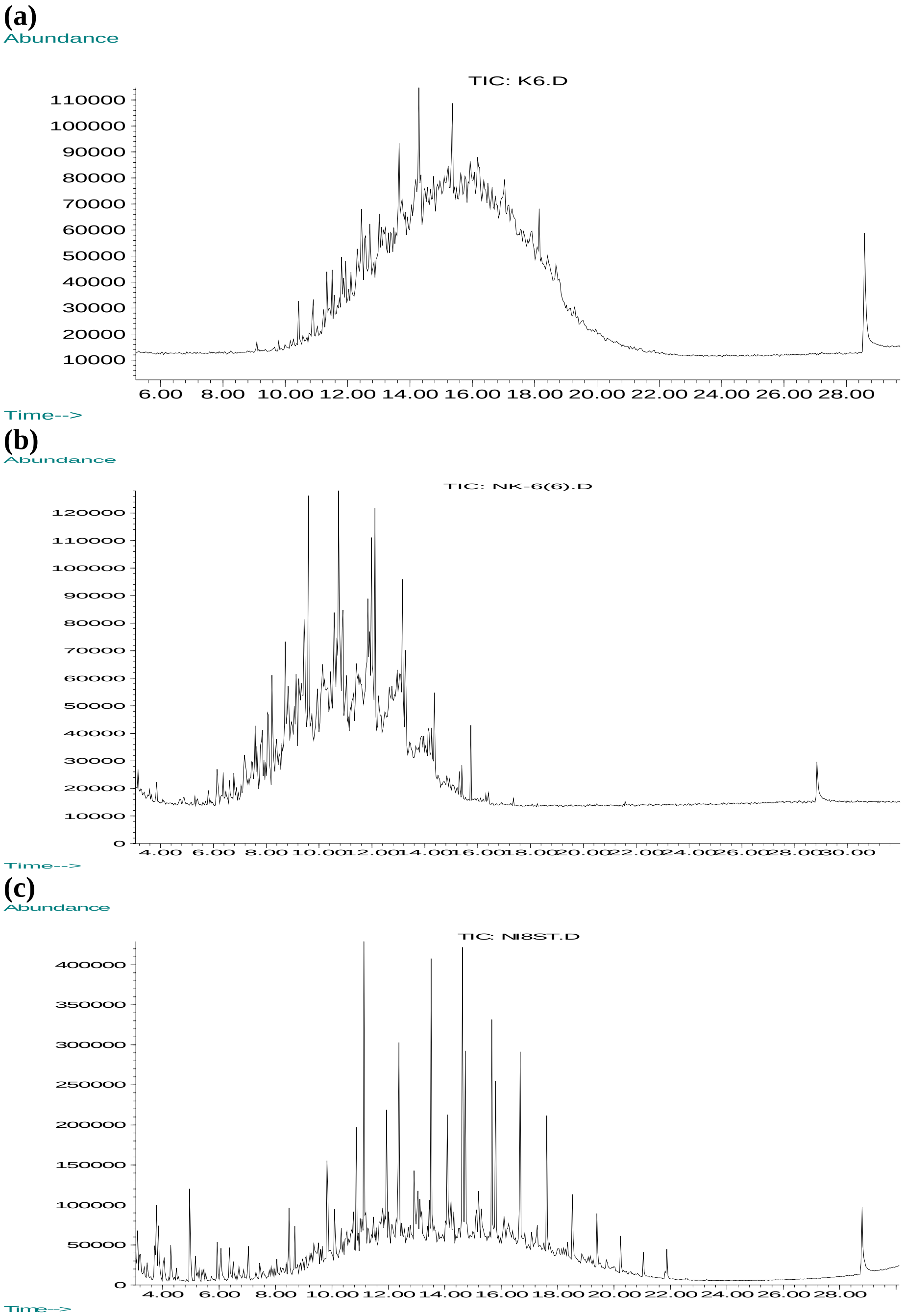


Figure 2.5. Typical (a) transformer oil (from retention time of tridecane to docosane), (b) shale oil (from retention time of decane to phytane), (c) diesel fuel (from retention time of octane to octacosane) chromatograms obtained by GC-MS (28,8 min – retention time of internal standard, hexatriacontane)

3 RESULTS AND DISCUSSION

3.1 NP-contaminated water purification

3.1.1 AOP for water purification

In the present study non-accompanied ozonation and various AOP (hydrogen peroxide photolysis, the Fenton, photo-Fenton, O_3/UV, O_3/H_2O_2 and $O_3/UV/H_2O_2$,) were applied for purification of NP-contaminated water in order to compare their ability to degrade the target compound.

3.1.1.1 Hydrogen peroxide photolysis

The stirring of NPs with hydrogen peroxide without UV-radiation did not lead to the degradation of NPs. Direct UV-photolysis resulted in quite slow degradation of NPs with a pseudo-first order reaction rate constant about 10^{-5} s^{-1} that is not acceptable for practical application (*paper II*, chapter 3.1). The degradation of NPs was notably accelerated by the addition of hydrogen peroxide to the UV treatment. The degradation time was considerably shortened with the increase of H_2O_2 concentration (*paper II*, Table 2). The enhancement of the degradation rate was more notable for mono-NPs than for di-NPs and methyl-dinitrophenols. The degradation rate in hydrogen peroxide photolysis treatment was linearly dependent (*paper II*, Figure 1) on hydrogen peroxide concentration (for H_2O_2 concentration range 0-10 mM). Similar influence of H_2O_2 concentration on the degradation rate of phenol was observed by Chen et al. (1997) who demonstrated that the increasing of hydrogen peroxide concentration enhances strongly the efficiency of phenol degradation. Thus, relatively high molar ratios of H_2O_2 to NPs in UV/H_2O_2 treatment were favourable (up to 10:1).

The influence of pH on the degradation of 4-NP and 4,6-DN-*o*-CR was also evaluated (*paper II*, chapter 3.1). Contrary to Trapido et al. (1997 and 1998) studies on hydrogen peroxide photolysis of some other phenols where definite dependence of the degradation rate on the pH in hydrogen peroxide photolysis was observed, it was found that the pH did not considerably influence the degradation of NPs.

According to the pseudo-first order rate constants the NPs degradation rate (*paper II*, Table 2 and Figure 2) by UV/H_2O_2 treatment followed the order:

4-NP > 2-NP >> 2,5-DNP ≈ 2,6-DN-*p*-CR > 2,6-DNP ≈ 4,6-DN-*o*-CR
> 2,4-DNP.

3.1.1.2 The Fenton, photo-Fenton treatments

Fenton's reagent and photo-Fenton treatments with different concentrations of hydrogen peroxide and the catalyst (Fe^{2+}) were applied for the degradation of NPs. The pH of initial solution (pH = 3.0) was low enough to keep the solution homogeneous. Half-lives and 90% conversion times for the degradation of NPs calculated from the degradation curves are presented in *paper II*, Table 3.

Both the concentration of hydrogen peroxide and the catalyst (Fe^{2+}) affected the degradation of NPs during the Fenton and photo-Fenton treatment. The effects observed in the treatment of 4,6-DN-*o*-CR are presented in *paper II*, Figure 3, as a typical example. The increasing of H_2O_2 and catalyst concentrations intensified 4,6-DN-*o*-CR degradation. Similar effects were observed for all other NPs investigated. These results coincide with the results reported by Benitez et al. (1999), Huang et al. (1993), Kwon et al. (1999), Barbeni et al. (1987), and Trapido et al. (1998), who observed positive effects of the increasing of Fe^{2+} and H_2O_2 concentrations in the Fenton and photo-Fenton treatments of various chlorophenols and substituted phenols. This was also confirmed by the results of Ma et al. (2000) for 4-NP degradation by the Fenton treatment.

The results of the present study demonstrated that UV-radiation improved the action of Fenton's reagent system, and at the same concentrations of hydrogen peroxide, photo-Fenton led to a more rapid decomposition of all NPs than the Fenton treatment. The enhancement factor for different NPs altered from 1.3 to 75 and was dependent on NP and concentration of Fenton's reagent applied (*paper II*, Table 3).

Complete degradation of all NPs under study was reached at hydrogen peroxide concentration ≥ 4 mM. Still, mono-NPs can be completely degraded with lower hydrogen peroxide concentration ($[H_2O_2]_0 = 2$ mM and $[Fe^{2+}]_0 = 0.1$ mM). Low concentration of H_2O_2 (< 1-2 mM) did not allow achieving complete degradation of NPs in the Fenton as well as in photo-Fenton treatment. Some examples of incomplete degradation of NPs are presented in *paper II*, Figure 4. The degradation rate was high at the initial stage of the process, then the reaction was definitely retarded, and further degradation took place at a slow rate. The residual concentration of hydrogen peroxide measured immediately after the treatment was zero in these cases. It can be assumed that the degradation of NPs in this case was limited by low ratio of NP to hydrogen peroxide concomitantly used in the Fenton and photo-Fenton treatments. These results can be confirmed by the results reported by Kwon et al. (1999) for the treatment of *p*-chlorophenol, who found out that not only low ratio of hydrogen peroxide to *p*-chlorophenol, but also catalyst (Fe^{2+}) to *p*-chlorophenol can retard its degradation.

The optimal ratio of chemicals in the Fenton treatment recommended from the results of the present study could be hydrogen peroxide:di-NP or methyl-dinitrophenols:catalyst (Fe^{2+}) 10:1:1 and hydrogen peroxide:mono-NP:Fe^{2+} 5:1:0.25. Due to the regeneration of the consumed Fe^{2+} through the irradiation (Eq. 3.1, Yang et al., 1998) the amount of catalyst (Fe^{2+}) to be added can be reduced in photo-Fenton treatment of di-NPs and methyl-dinitrophenols.

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + OH^{\bullet} \tag{3.1}$$

The optimal ratio of chemicals in photo-Fenton treatment could be hydrogen peroxide:di-NP or methyl-dinitrophenols:Fe^{2+} 10:1:0.25. They are closed to those recommended as optimal for the Fenton treatment of organics-contaminated water (Tang and Huang, 1997; Ruppert et al., 1994).

A comparison of the 90% conversion times of different NPs (*paper II*, Table 3 and Figure 5) revealed that mono-NPs were degraded more easily than di-NPs, and methyl-dinitrophenols were the most stable. According to the 90% conversion times NPs degradation followed the order:

2-NP > 4-NP > 2,5-DNP > 2,6-DNP > 2,4-DNP > 2,6-DN-*p*-CR ≈
≈ 4,6-DN-*o*-CR.

3.1.1.3 Ozonation and ozone combinations with UV and/or hydrogen peroxide

Ozonation of organics in water is a complex technology involving mass transfer process and a variety of possible chemical reactions, e.g. direct reactions between the ozone molecule and the organics, and radical reactions between hydroxyl radicals and organics. Because of the presence of the hydroxyl group attached to the aromatic ring, reactions with electrophilic reagents like ozone are markedly favoured. Therefore, at $pH < 12$, the radical route of degradation of phenolic compounds may be neglected and these substances are degraded exclusively by direct reaction with ozone (Beltran et al., 1992; Beltran et al., 1999a).

Ozonation of NPs mixture was studied at pH values 2.5 and 9.5 (*paper III*, Figures 1 and 2). The ozone consumption can be reduced by factor of 1.2 and the pseudo-first order reaction rate constant of NPs mixture degradation was enhanced by factor of 2 when the ozonation was carried out at pH 9.5 to compare with pH 2.5. The latter was expected, as it is known that an increase of pH enhances the degree of dissociation of phenols, and phenolates react with ozone with higher rate than non-dissociated phenols (see pKa values presented in *paper II*, Table 1) (Langlais et al., 1991). Thus, basic medium was favourable for the ozonation of the NPs mixture.

When NPs mixture was ozonated in the acidic medium (pH 2.5), the degradation rate of individual NPs decreased in the following order (*paper III,* Figure 1):

4,6-DN-*o*-CR > 2-NP > 4-NP > 2,4-DNP.

In the basic medium the order of NPs degradation in mixture was (*paper III,* Figure 2):

2-NP > 4-NP ≈ 4,6-DN-*o*-CR > 2,4-DNP.

Some experiments have been carried out with increased ozone concentration in the feed-gas (1.52 ± 0.05 mg L^{-1}). It was ascertained that the increasing of the ozone concentration in the feed-gas by factor 3 (from 0.5 to 1.5 mg L^{-1}) led to approximately to a three-fold acceleration of 2,4-DNP degradation rate, but did not influence the ozone consumption (*paper I*, Table 3).

The comparative assessment of ozonation and AOP based on ozone (such as O_3/UV, O_3/H_2O_2 and $O_3/UV/H_2O_2$) for NPs degradation was studied on example of 2,4-DNP. The chemical reaction of ozonation proceeded in the bulk of liquid (in the kinetic regime) as pseudo-first order rate constant of NPs decomposition (*paper I*, Table 2) followed the inequality $k_1 < 7.9 \times 10^{-2}$ s^{-1} (chapter 2.1.4). Thus, the curves of the NPs degradation in time were correspondingly interpreted (chapter 2.1.4) to compare the rate of chemical reactions under different conditions of ozone oxidation.

It is known that the impact of pH on the removal rate of phenols is dependent on the pKa value of the compound (Langlais et al., 1991). In general, at pH values higher pKa phenols present in the dissociated form and as a result the reaction rate is higher than at lower pH values (pH < pKa). At the intermediate pH values (pH < pKa < pH) the reaction rate increases with the increasing of pH, while in higher pH range (pH >> pKa) the degradation rate practically does not dependent on the pH. Therefore, the results on 2,4-DNP degradation with non-accompanied ozonation (*paper I*, Figure 3) indicated the slight enhancement of 2,4-DNP degradation rate in the intermediate pH range (2 < pH < 5 and pKa = 4.03). The further increase of the pH value did not practically influence the degradation rate of 2,4-DNP (*paper I*, Figure 3).

The general changes in the ozone concentration in the inlet and outlet feed-gas and pH values of the treated solution during 2,4-DNP ozonation in the initial basic medium are shown in *paper I*, Figure 2. The initial pH of the solution decreased by 5.9 units during ozonation due to the formation of the considerable amount of acidic by-products (*paper I,* Figure 2). Similar decrease (by 6.5 units) of initial pH of the solution during the NPs mixture ozonation at pH 9.5 was also observed (*paper III*, Figure 2).

The degradation rates of 2,4-DNP in O_3/UV treatment were quite similar to those observed in ozonation at pH 9.5 and somewhat higher at pH 2.5 (*paper I*, Table 2). The possible reason for this phenomenon is the considerable UV-absorptivity of di-NPs at $\lambda = 254$ nm, which diminishes the part of UV radiation absorbed by ozone for $OH^{\bullet}$ radical formation. Also there were no considerable differences in the ozone consumption observed in O_3/UV treatment and non-accompanied ozonation at both pH values. These results are in a good agreement with the results reported previously for 2,4-dichlorophenol (Trapido et al., 1998).

The addition of hydrogen peroxide to the ozonation enabled to achieve the reduction of ozone consumption and acceleration of 2,4-DNP degradation. It was found that beyond a certain hydrogen peroxide concentration there was no further enhancement of the treatment performance. In the acidic medium the degradation rate was higher than in non-accompanied ozonation at the same pH value with the admixture of H_2O_2 1-4 mM (*paper I*, Table 2 and Figure 4). At initial pH value 9.5 some acceleration of 2,4-DNP degradation was observed only with the H_2O_2 dose of 1 mM. The introduction of 2-4 mM H_2O_2 did not enhance degradation rate at pH 9.5 compared with ozonation, and even considerable deceleration was noticed (*paper I*, Table 2 and Figure 4). Thus, H_2O_2 admixture excess may decrease the reaction rate of the target compound acting as a radical scavenger. The application of O_3/H_2O_2 treatment enabled to achieve reduction in the ozone specific consumption to compare with non-accompanied ozonation by 40-50% in the acidic medium and 10% in the basic medium (*paper I*, Table 2).

2,4-DNP degradation can be accelerated by the application of O_3/H_2O_2/UV combination. The degradation of 2,4-DNP in O_3/H_2O_2/UV treatment dependent on hydrogen peroxide addition and initial pH of 2,4-DNP solution (*paper I*, Figure 4). Like to the previous case, the effects were definitely more noteworthy at low pH values (*paper I*, Table 2). The increasing of hydrogen peroxide concentration clearly intensified the degradation rate of 2,4-DNP in O_3/H_2O_2/UV treatment in both media. H_2O_2 admixture of 8 mM in O_3/H_2O_2/UV treatment in both media enabled to reduce ozone consumption to about 1 mM of ozone per 1 mM of 2,4-DNP degraded, which is the lowest value for all the processes under study (*paper I*, Table 2).

3.1.2 Biodegradability

The influence of the AOP treatment and ozonation on biodegradability (BOD_7/COD) of NPs was studied (*paper I*, Table 4; *paper III*, Table 1). The results of the study show that the products formed during the AOP treatment and ozonation are much more biodegradable than untreated NPs. Besides the fact that COD removal (24-80%) was lower than NPs removal (77-100%), it can be seen that an increase in biodegradability of NPs was achieved.

In ozonation experiments the pH had a profound effect on biodegradability of the reaction by-products (*paper III*, Table 1). It was found that biodegradability of 4,6-DN-*o*-CR ozonation by-products in acidic medium was miserably improved if compare with the initial compound. However, a considerable improvement of biodegradability was achieved during the ozonation of 4,6-DN-*o*-CR in basic medium. The by-products of 4-NP ozonation in acidic medium and 2,4-DNP ozonation in basic medium (initial pH 9.5) and initial neutral pH (7.0) (*paper* I, Table 4) were completely biodegradable. The former coincided with the results of Wang (1990) who found out that ozonation products of 2,4-DNP formed in the basic pH range were more biodegradable than those formed in the acidic pH range under the same concentration of ozone in the feed-gas. Biodegradability improvement was observed during the ozonation of NPs mixture as well (*paper III*, Table 1). The treatment of NPs with AOP combinations (UV/H_2O_2, Fenton, O_3/UV) also enabled to improve the biodegradability (typical example, 2,4-DNP; *paper I*, Table 4). The improvement of biodegradability after the Fenton treatment of 4-NP was also observed by Ma et al. (2000). The achieved biodegradability improvement of treated NPs supports the potential use of ozonation and the AOP to enhance the capacity of conventional biological treatment to remove poorly biodegradable NPs. Thus, it is apparent that by-products of treated NPs are less biorecalcitrant than the parent compounds. Among the factors that contribute to the biodegradability improvement the nitrogen mineralization, transformation of aromatics to aliphatics by ring opening reactions, ring hydroxylation (Dieckmann and Gray, 1996; Adams et al., 1997), and toxicity reduction can be mentioned. Therefore, these factors were under consideration in the present study.

3.1.3 Nitrogen mineralization

Cleavage of nitro-group from the aromatic ring and its conversion to nitrate took place during the degradation of NPs. Nitrite ion that was followed in the reaction medium only at the initial stage of the treatment in extremely small quantities was subsequently oxidised in nitrate ion, and among the inorganic nitrogen species nitrate was the predominant one. Almost in all the cases measured nitrate concentration was lower than theoretically calculated as nitrated aliphatic intermediates were probably formed during the treatment.

After 77-100% conversion of single NPs by ozonation the degree of nitrogen mineralization was 66-100% at pH 2.5 and 38-87% at pH 9.5 (*paper III*, Table 1). Nitrate formation was quite slow at the initial stage of ozonation until 35-40% of NPs was degraded and accelerated at the final stage of ozonation. The degree of nitrogen mineralization during the NPs mixture ozonation at pH 2.5 was higher than at pH 9.5 (*paper III*, Figure 4). After 90% conversion of NPs with H_2O_2/UV, the degree of nitrogen mineralization was 50-60% (at pH 3.0) (*paper II*, chapter 3.1). This is much higher than those of organically bounded chlorine to chloride (30-39%) in Trapido et al. (1997) studies on hydrogen peroxide photolysis of chlorophenols at pH 2.5. Similar to ozonation experiments nitrogen mineralization was very slow till 60-70% conversion of NPs with the Fenton treatment was achieved and then it was accelerated (*paper II*, Figure 6). The degree of organically bounded nitrogen conversion to nitrate after 90% degradation of NPs with the Fenton treatment was 51-67%. In photo-Fenton treatment organically bounded nitrogen mineralization was 85-90% (*paper II*, chapter 3.2).

The formation of nitrate ions followed the destruction of NPs with non-accompanied ozonation, O_3/H_2O_2, O_3/H_2O_2, O_3/UV/H_2O_2, UV/H_2O_2, the Fenton and photo-Fenton oxidation processes was compared on example of 2,4-DNP degradation. In different AOP nitrogen mineralization took place at different stages of the treatment (*paper I*, Figure 5). In the Fenton, photo-Fenton treatment and hydrogen peroxide photolysis nitrogen mineralization was very slow at the initial stage and accelerated at the final stage of 2,4-DNP destruction. In some processes, for example, O_3 (pH 12.5), O_3/H_2O_2 (pH 9.5), and O_3/UV/H_2O_2 (pH 2.5) nitrate ion was formed quite evenly during 2,4-DNP destruction. In ozonation and O_3/H_2O_2 at pH 2.5 the formation of NO_3^- practically coincided with the theoretical maximum value (*paper I*, Figure 5). The degree of nitrogen mineralization also varied in a large range. Complete mineralization (97-100%) was achieved in O_3/H_2O_2 (pH 2.5), O_3 (pH 2.5) and O_3/UV (pH 9.5) treatments (*paper I*). In all the other processes value was 70-90%, except the Fenton, O_3/UV (pH 2.5), and UV/H_2O_2 processes where it achieved only 50-60% (*paper I*). Therefore, prolonged treatment time was needed to achieve more complete mineralization of 2,4-DNP in these treatment processes.

3.1.4 Total organic carbon mineralization and aromatic carbon reduction

Absorbance at 254 nm (UV_{254nm}) reduction and TOC removal were followed during the ozonation of NPs. Carbon mineralizaton was very slow during the degradation of NPs by ozonation at the present conditions (*paper III*, Figure 5). The degree of carbon mineralization (*paper III*, Figure 5) was much lower than the degree of nitrogen mineralization (*paper III*, Table 1). UV_{254nm} was monitored as a parameter, which is indicated the aromatic carbon content reduction during the ozonation. Some UV_{254nm} absorbance reduction was observed during the ozonation (*paper III*). This reduction was mainly achieved by NPs degradation and transformation of aromatics by-products to aliphatics by ring opening reactions. These aliphatic by-products are more resistant to mineralization than NPs and their aromatic by-products, but susceptible to biodegradation (Langlais et al., 1991). Such reaction pathway can also account for the biodegradability enhancement.

3.1.5 By-products

GC-MS chromatograms of acetylated fractions showed the formation of a variety of hydroxylated intermediates during oxidation of NPs (4-NP and 2,4-DNP). According to Beltran et al. (1992, 1999a) direct reaction of molecular ozone with phenols was predominant during the ozonation at pH values lower than 12. In a benzoic ring with electron donor groups (-OH) the electrophilic attack of ozone molecule was preferentially marked in *orto* and *para* positions. For the NPs with electron-withdrawing groups ($-NO_2$) the initial attack of the ozone molecule takes place mainly on the *meta* position (Langlais et al., 1991). This can explain a variety of degradation by-products, which were formed by the electrophilic attack of the ozone molecule. 4-Nitrocatechol was identified as the reaction product of electrophilic ozonation of 4-NP and 2,4-DNP (*paper III*, Table 3). Among the by-products resulting from aromatic nuclear hydroxylation hydroquinone formation with a simultaneous cleavage of nitro-group was also observed. Then hydroquinone was very easily oxidised into *p*-quinone. Some reaction pathways were proposed for the degradation of 4-NP by ozonation at pH 9.5 (*paper III*, Figure 7).

After the electrophilic attack of ozone, a 1,3-dipolar cyclo addition of ozone proceeded to open the aromatic ring and ozonation intermediates with carbon-carbon double bonds could be formed (Yu and Yu, 2001; Beltran et al., 1999b). The products of the ring opening reaction might be alcohols, aldehydes or ketones (from quinone) and carboxylic acids. The formation of acids was confirmed by the substantial decrease of pH value during the ozonation (*paper I*, Figure 2; *paper III*, Figure 2). Unfortunately, it was not possible to identify the major carboxylic acids formed from oxidative cleavage of hydroxylated aromatic compounds. The formation of such low-weight intermediates can probably account for biodegradability improvement.

3.1.6 Toxicity

The acute toxicity of initial and treated single NPs (*paper I*, Figure 6; *paper II*, Table 5; *paper III*, Table 2, Figure 6) and their mixture (*paper III*, Table 2) was studied with *Daphnia magna* test. Initial single NPs (except 2-NP) and their mixture were extremely toxic to *Daphnia Magna* and resulted in quite low EC_{50} values (*paper II*, Table 5; *paper III*, Table 2). Among the NPs studied 2,4-DNP and 4,6-DN-*o*-CR were the most toxic. These results coincide with the toxicological data (LC_{50}) for white rats and white mice presented by Sax, 1984.

All treatment processes, namely the Fenton, hydrogen peroxide photolysis and ozonation enabled to remove the toxicity. Total detoxification of the solutions was achieved when 90% of the initial NP was degraded. Ozonation enabled to eliminate the toxicity of by-products formed during the degradation of single NPs and their mixture. After > 90% degradation of the target compound detoxification of NP/NPs aqueous solution was achieved, independent of the pH of the initial solution (*paper III*, Table 2). The reduction of the toxicity took place with the progress of ozonation of single NPs (*paper I*, Figure 6) or their mixtures (*paper III*, Figure 6). A similar result was observed after the Fenton treatment of various single NPs (*paper II*, Table 5). Other AOP applied, such as hydrogen peroxide photolysis and ozone combinations with UV and/or hydrogen peroxide, were also able to detoxify 2,4-DNP solution (*paper I*). Thus, AOP can be used not only for the destruction of NPs but also, which is extremely important, for detoxification of their aqueous solutions.

Destruction of the aromatic structures, hydroxylation and nitrogen mineralization was involved in the detoxification of the contaminants. For instance, it was ascertained that quinones that are formed during the ozonation of NPs (*paper III*, Table 3 and Figure 7) are very toxic compounds. The EC_{50} obtained by *Daphnia magna* test for *p*-quinone was 0.181 mg L^{-1} (95% confidence limit 0.15-0.21 mg L^{-1}). However, quinones were very easily oxidised during the further ozonation and were not identified in the solution at the prolonged stages of the treatment (*paper III*).

3.1.7 Comparison of efficiency of studied processes for NPs degradation

The efficiency of NPs degradation with non-accompanied ozonation, ozone combinations with UV and/or hydrogen peroxide, hydrogen peroxide photolysis, the Fenton, and photo-Fenton was compared on example of 2,4-DNP (Fig. 3.1). The degradation of NPs in all the processes involving hydrogen peroxide, namely Fenton, photo-Fenton, UV/H_2O_2, O_3/H_2O_2, and $O_3/H_2O_2/UV$ was definitely dependent on hydrogen peroxide additions. Therefore, treatment processes with the additions of H_2O_2 resulted in most effective removal of 2,4-DNP (*paper I*) were chosen for the comparison.

As can be seen from Fig. 3.1, photo-Fenton process led to a more rapid decomposition of 2,4-DNP than the other treatment methods. Due to the regeneration of the consumed Fe^{2+} ions through the irradiation, the amount of catalyst can be reduced in photo-Fenton treatment. Still, the application of more complicated and therefore costly method is not reasonable, because more than 90% degradation of NPs in the Fenton's reagent treatment was achieved in time that is quite acceptable for practical application (*paper II*, Table 3).

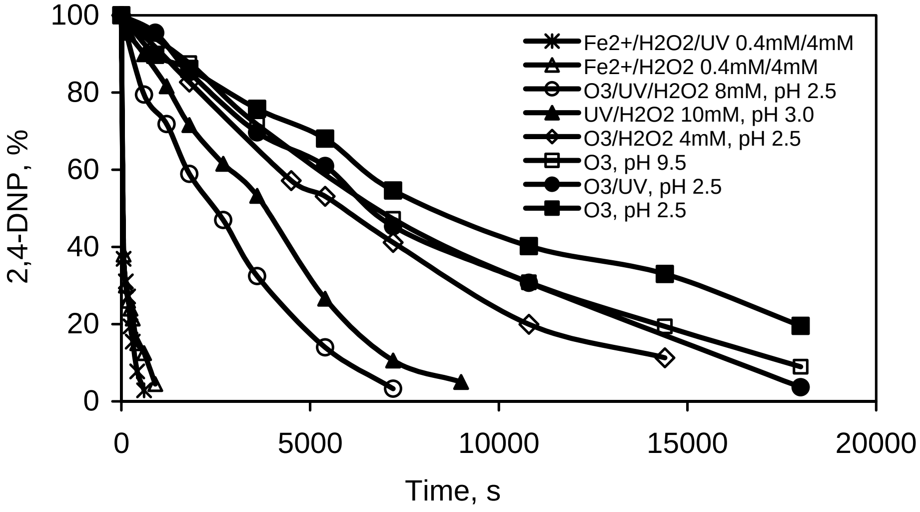


Figure 3.1. Degradation of 2,4-DNP with studied treatment processes

After the Fenton treatment, the residual iron can be removed by alkalisation of the solution. Iron was precipitated at pH ≥ 9.0 in the form of $Fe(OH)_3$ and removed as a sludge. The residual concentration of total iron after alkalisation and consequent filtration remained mainly at 0.3-3.2% of the initial value (*paper II*, chapter 3.2), when the 90% degradation of NP was achieved. The residual concentration of hydrogen peroxide was 4-12% (*paper II*, chapter 3.2) of the initial value after Fenton's reagent treatment. On the other hand, the residual concentration of hydrogen peroxide, in spite of its relatively high toxicity (Trapido and Kallas, 2000), does not cause any problems, as hydrogen peroxide concomitantly used in this processes is an ecologically friendly oxidant giving only oxygen and water as degradation by-products.

Therefore, although all the processes led to the degradation of NPs, Fenton's reagent was found to be the most promising method for NP-contaminated water purification.

3.1.8 Treatment costs of AOP for NP-contaminated water purification

The data derived from the experiments on the degradation of NPs allowed carrying out a rough estimation of treatment costs (energy and chemicals) taking into account the costs of chemicals (H_2O_2, $FeSO_4$ x 7 H_2O), and cost of energy for UV-radiation and O_3 generation. These calculations were performed on example of 2,4-DNP and presented in Table 3.1. The cost of energy for UV and ozone generation was 0.07 \$ kWh^{-1} (at the moment of 2001), $FeSO_4 \times 7H_2O$ cost 0.12 \$ kg^{-1}, hydrogen peroxide cost 0.86 \$ kg^{-1} calculated as 100% Ozonation treatment costs were calculated taking into consideration that for the production of 1 kg ozone required 28 kWh of energy.

As can be seen from Table 3.1, direct UV-photolysis was the most expensive way of 2,4-DNP degradation. Treatment costs could be considerably lowered through the hydrogen peroxide addition. Higher hydrogen peroxide concentrations were more cost-effective for 2,4-DNP degradations by UV/H_2O_2 treatment. The addition of Fe^{2+} to UV/H_2O_2 system (photo-Fenton) allowed substantially reducing treatment cost if compare with UV/H_2O_2 treatment. Nevertheless, the Fenton treatment gave the lowest treatment cost among the above mention studies. The treatment costs for direct UV-photolysis, UV/H_2O_2, the Fenton and photo-Fenton treatments for 90% degradation of 4,6-DN-*o*-CR, 2,6-DNP and 4-NP were also evaluated and compared (*paper II*, Table 4). The Fenton treatment costs of NPs degradation were calculated for the recommended ratios of chemicals. As in case of 2,4-DNP treatment, treatment cost of the Fenton was found to be the lowest among the treatment costs of AOP studied.

2,4-DNP treatment cost by O_3/H_2O_2 with 1 and 2 mM admixture of H_2O_2 was very close to the treatment cost of non-accompanied ozonation (Table 3.1). Higher additions of H_2O_2 (4 mM and 10 mM) resulted in somewhat higher treatment costs of O_3/H_2O_2 treatment. O_3/UV was quite expensive treatment process if compared with other treatment processes except direct UV-photolysis. The addition of hydrogen peroxide to O_3/UV enabled to achieve some reduction in treatment costs (Table 3.1). The treatment cost of 2,4-DNP treatment by $O_3/UV/H_2O_2$ reduced with the increasing of H_2O_2 concentration. The 8 mM addition of H_2O_2 to O_3/UV treatment allowed reducing 2,4-DNP treatment cost by factor 2.8 (from 5.79 \$ m^{-3} to 2.10 \$ m^{-3}) and 2.7 (from 6.09 \$ m^{-3} to 2.28 \$ m^{-3}) at pH 2.5 and 9.5, respectively. Lower additions of H_2O_2 (2 mM and 4 mM) resulted even in higher 2,4-DNP treatment cost by $O_3/UV/H_2O_2$, if compare with high additions of H_2O_2 (Table 3.1). In these cases 90% degradation of 2,4-DNP needed pro-longer treatment time leading to higher energy consumption required for UV generation.

Table 3.1. Treatment costs for 90% reduction of 2,4-DNP initial concentration (0.4 mM)

Treatment process	$[H_2O_2]_0$, mM	$[Fe^{2+}]_0$, mM	Energy required for O_3, kWh m^{-3}	Energy required for UV, kWh m^{-3}	Cost of energy for UV, \$ m^{-3}	Cost of energy for O_3, \$ m^{-3}	Chemicals (H_2O_2 + $FeSO_4 \times 7H_2O$) cost, \$ m^{-3}	Total cost, \$ m^{-3}
UV, pH 3.0	0	0	0	809	56.7	0	0	56.7
UV/H_2O_2, pH 3.0	10	0	0	28.6	2.0	0	0.29	2.29
UV/H_2O_2, pH 3.0	4	0	0	72.9	5.1	0	0.12	5.22
Fenton, pH 3.0	4	0.4	0	0	0	0	0.13	0.13
photo-Fenton, pH 3.0	4	0.4	0	1.5	0.11	0	0.13	0.24
O_3, pH 2.5	0	0	1.96	0	0	0.14	0	0.14
O_3, pH 9.5	0	0	1.57	0	0	0.11	0	0.11
O_3/UV, pH 2.5	0	0	1.81	81.0	5.67	0.13	0	5.80
O_3/UV, pH 9.5	0	0	1.55	85.5	5.98	0.11	0	6.09
O_3/H_2O_2, pH 2.5	1	0	1.09	0	0	0.08	0.03	0.11
O_3/H_2O_2, pH 9.5	1	0	1.36	0	0	0.09	0.03	0.12
O_3/H_2O_2, pH 2.5	2	0	1.24	0	0	0.09	0.06	0.15
O_3/H_2O_2, pH 9.5	2	0	1.41	0	0	0.10	0.06	0.16
O_3/H_2O_2, pH 2.5	4	0	0.90	0	0	0.06	0.12	0.18
O_3/H_2O_2, pH 9.5	4	0	1.40	0	0	0.10	0.12	0.22
O_3/H_2O_2, pH 2.5	10	0	1.01	0	0	0.07	0.29	0.36
$O_3/UV/H_2O_2$, pH 2.5	2	0	0.76	51.4	3.60	0.05	0.06	3.71
$O_3/UV/H_2O_2$, pH 9.5	2	0	1.10	60.2	4.21	0.08	0.06	4.35
$O_3/UV/H_2O_2$, pH 2.5	4	0	0.72	40.5	2.83	0.05	0.12	3.00
$O_3/UV/H_2O_2$, pH 9.5	4	0	1.11	45.5	3.19	0.08	0.12	3.39
$O_3/UV/H_2O_2$, pH 2.5	8	0	0.53	26.0	1.82	0.04	0.24	2.10
$O_3/UV/H_2O_2$, pH 9.5	8	0	0.78	28.4	1.99	0.05	0.24	2.28

The treatment costs of non-accompanied ozonation and O_3/H_2O_2 were quite close to the Fenton treatment cost, but taking into account the high capital costs required for ozone production, ozone including treatments could not be competitive with the Fenton one. Thus, the Fenton treatment was found to be not only the most effective in terms of NPs degradation, but also the most cost-effective treatment process to purify NP-contaminated water.

3.2 Soil treatment

3.2.1 Ozone treatment of soil

3.2.1.1 The effect of soil matrix in ozone treatment

The efficiency of the ozone treatment was strongly dependent on the matrix of soil (sand or peat). Sand represented a mineral part of soil, while peat was chosen as a model of organic-rich soil. Two-phase ozonation of contaminants (PAH, diesel, shale oil, transformer oil) adsorbed in peat resulted in lower contaminant removal and required higher ozone doses than ozonation of contaminant in sand matrix (*paper V*, Figure 2; *paper VI*, Figure 1; *paper VII*, Figures 3 and 4). Similar effect of soil matrix was observed for three-phase ozonation of PAH-contaminated sand and peat (*paper V*, Figures 1 and 2). Ozonation of peat may be limited by the rate of contaminant desorption and by the high content of organic matter, which may consume considerable amount of ozone.

Ozone consumption during the ozonation of non-contaminated soil was also higher for peat than for sand (1.29 and 0.26 g of ozone per one kg of soil, respectively).

3.2.1.2 The effect of soil water content in ozone treatment

The effect of water content on the degradation of contaminants in soil by ozonation was investigated on example of NPs (*paper IV*) and PAH (*paper V*).

In case of PAH the decrease in their removal was observed when water was added (*paper V*, Table 2). Having compared two ozonation systems, it can be concluded, that two-phase ozonation was more effective in terms of PAH degradation and ozone consumption for both PAH contaminated sand and peat than three-phase one. This decrease in efficiency is thought to be due to the fact that the majority of PAH are in the sorbed state, which is a function of their high octanol-water partition coefficients (Mackay et al., 1992) and low water solubility (*paper V*, Table I). In addition, in the three-phase ozonation system, the competing reactions (dissolution of ozone into soil pore water and ozone self-decomposition) consume ozone that would otherwise react with PAH.

Contrary to PAH ozonation, high solubility of NPs in water (*paper IV*, Table 1), which can lead to desorption of the trapped organic phase from small pores making it more available to the ozone reaction is favoured for three-phase ozonation of NPs. Thus, three-phase ozonation was found to be more effective in terms of NPs removal and ozone consumed doses than two-phase one (*paper IV*, Figures 1 and 2).

3.2.2 The Fenton/Fenton-like treatment of soil

3.2.2.1 The effect of soil matrix in the Fenton treatment

As in ozonation experiments, the efficiency of the Fenton treatment was dependent on the soil matrix. Fenton-like reaction in peat required higher hydrogen peroxide dose for the effective degradation of contaminants, if compared with the treatment of sand. As can be seen from Fig. 3.2, under the same treatment conditions and the same weight ratios of H_2O_2/contaminant (transformer oil, shale oil, diesel) contaminant removal in sand was higher than in peat.

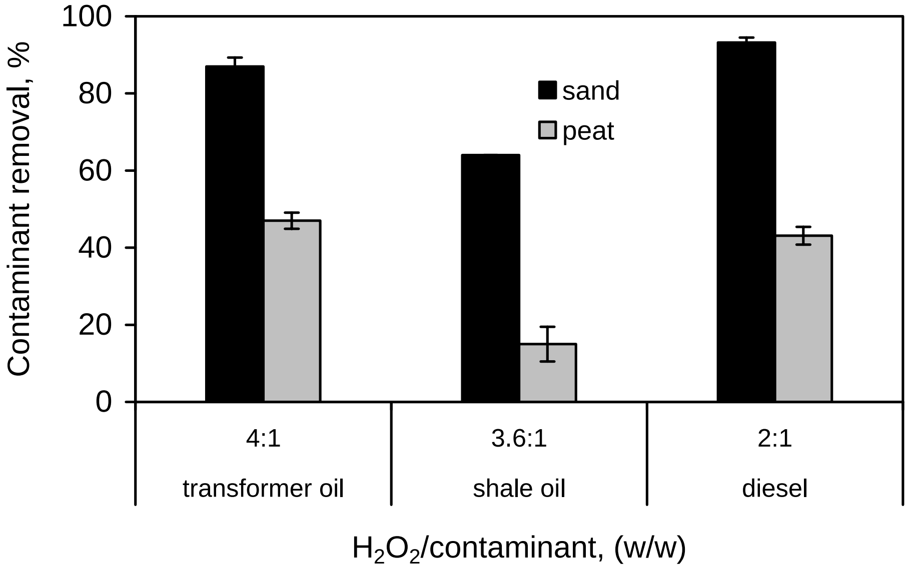


Figure 3.2. Comparison of contaminants (transformer oil, shale oil and diesel) removal by 72-hours Fenton-like treatment (once per day addition of H_2O_2: 0, 24, 48 h) in sand and peat matrix (*papers VI, VII*)

In case of PAH, the Fenton treatment was more effective for PAH degradation in sand (80% PAH removal) than in peat (61% PAH removal only) when 3-step addition of H_2O_2 per day (1d/3) was applied (*paper V*, Figure 1). H_2O_2 addition all at once resulted in 60% of PAH removal for both sand and peat. The degradation could be limited by the quenching of $OH^{\bullet}$ by hydrogen peroxide and hydroperoxyl radicals in the presence of hydrogen peroxide excess.

Organic matter content can be one of the factors that control the rate of hydrogen peroxide decomposition and hydroxyl radical formation that are responsible for contaminant desorption and oxidation. Petigara et al. (2002), who measured the $OH^{\bullet}$ formation rates in four different soil suspensions, have also shown, that $OH^{\bullet}$ were a major product of H_2O_2 decomposition in soils with low organic matter but they were a minor product in soils containing high amounts of organic matter. This can contribute to higher removal of contaminant in sand than in peat when moderate H_2O_2 additions were applied.

3.2.2.2 The effect of hydrogen peroxide and catalyst addition and treatment time in the Fenton/Fenton-like treatment

The contaminant removal in soil with Fenton/Fenton-like treatment was found to be dependent on H_2O_2/soil/Fe^{2+} or H_2O_2/soil weight ratios, treatment time and manner of hydrogen peroxide addition. The influence of these treatment conditions was quite different for various types of contaminants (NPs, PAH, diesel, transformer oil, shale oil) in both soil matrixes (sand or peat).

Paper V

PAH removal from soil with the Fenton treatment in slurry was found to be dependent on the ratio of H_2O_2/soil/Fe^{2+}, the manner of hydrogen peroxide addition, and the treatment time (*paper V*, Figures 3 and 4). The stepwise addition of H_2O_2 in the Fenton treatment was more effective for the removal of PAH from sand than the addition of H_2O_2 all at once. A slow addition of H_2O_2 to the system with excess iron provides conditions that minimise quenching of $OH^{\bullet}$ (Teel et al., 2001). Thus, 3-step addition of hydrogen peroxide during 24-hours treatment (1d/3) may be recommended for the Fenton treatment of PAH contaminated sand (*paper V*, Figure 3).

The increasing of H_2O_2/peat/Fe^{2+} weight ratio with 3-step addition of H_2O_2 during 24-hours did not enhance PAH degradation in peat (*paper V*, Figure 4). The increasing of treatment time from 1 day (24-hours 3-step addition, 1d/3) to 3 days (72-hours 1 addition per day, 3d) did not improve the degradation and resulted practically in the same removal of PAH from peat (*paper V*, Figure 4). Thus, the Fenton treatment manner (1-step addition or 3-step addition) and prolonged treatment time did not influence PAH removal in peat.

PAH could degrade in peat with the addition of H_2O_2 only and resulted practically in the same PAH removal as with the addition of catalyst (*paper V*, Figure 4). Thus, the addition of iron did not improve the degradation of PAH in peat. The possible reason can be that the excess iron can provide the conditions that increase quenching of $OH^{\bullet}$. Some chemical reactions could also decrease the catalytic activity of iron species in soil. These reactions could include the precipitation of soluble iron due to the oxidation of more soluble Fe^{2+} to Fe^{3+}.

Paper IV

NPs degradation with the 3-step injection of hydrogen peroxide during 24-hours Fenton treatment strongly depended on the addition of hydrogen peroxide and the catalyst (Fe^{2+}). A five-fold increase of Fe^{2+}/NPs/H_2O_2 molar ratio (from 1:1:10 to 5:1:50) enhanced the degradation and resulted in a complete (100%) removal of NPs in sand (*paper IV*, Figure 3). The ratio of hydrogen peroxide to the catalyst (Fe^{2+}) affected the degradation of NPs in sand (*paper IV*, Figure 3). Thus, the optimal molar ratio of hydrogen peroxide to catalyst in the Fenton treatment found in the present study was 10:1 (*paper IV*, Figure 3). Higher molar ratio of hydrogen peroxide to the catalyst (15:1) did not show any improvement and even reduced the degradation of NPs.

NPs degraded with the addition of hydrogen peroxide only (*paper IV*, Figure 3). The reason is that some of available iron from the total iron and some other transition metals that are present in soil (such as Mn, Cu, Co, Zn) can catalyse hydrogen peroxide without addition of extra Fe^{2+}. Moreover the addition of H_2O_2 only aimed to increase iron availability leading to alternative pathways of Fe^{2+} production.

Paper VI

The removal of diesel in sand increased with the increasing of H_2O_2/diesel/Fe^{2+} weight ratio until it reached the optimal removal of contaminant (*paper VI*, Figure 2). Further increasing of H_2O_2/diesel/Fe^{2+} weight ratio did not improve diesel degradation in sand and resulted even in lower diesel removal (*paper VI*, Figure 2). Thus, the optimal weight ratio of H_2O_2/diesel/Fe^{2+} in 72-hours Fenton treatment (with 1-step addition of H_2O_2 per day) applied for diesel removal in sand was found to be 0.3:1:0.05.

In several experiments with diesel-contaminated sand and peat only hydrogen peroxide was added (*paper VI*, Figure 2). The effects of Fenton-like treatment obtained for peat differ somewhat from those for sand. The increasing of H_2O_2/diesel ratio did not enhance diesel degradation and resulted in practically the same degree of diesel removal, while the increasing of H_2O_2/diesel in sand definitely improved diesel degradation (*paper VI*, Figure 2).

Paper VII

Increasing the H_2O_2/transformer oil ratio did not substantially influence the transformer oil degradation in sand with the Fenton-like treatment (*paper* VII, Figure 1). Even a hundred fold increase in H_2O_2/transformer oil weight ratio (from 0.04:1 to 4:1) did not improve transformer oil degradation and resulted in approximately the same removal of the contaminant. Comparable effects were observed for shale oil degradation (*paper* VII, Figure 2). Increasing the H_2O_2/shale oil weight ratio did not affect the degradation and even led to lower removal of shale oil from sand. Thus, the application of high H_2O_2/transformer oil or shale oil weight ratios may be not reasonable as similar transformer oil or even higher shale oil degradation (H_2O_2/shale oil varied between 0.06:1 and 0.24:1) in Fenton-like treatment was achieved with moderate addition of H_2O_2 (*paper VII*, Figures 1 and 2).

Contrary to the result obtained for Fenton-like treatment of sand raising the H_2O_2/transformer oil weight ratio increased the transformer oil removal in peat until it reached the optimum (*paper* VII, Figure 1). It was hypothesized by Walling (1975) that at high concentrations, hydrogen peroxide could compete with organics for hydroxyl radicals, reducing the efficiency of OH radical oxidation of organic compounds. This is also in concordance with the data of Petigara et al. (2002), who indicated that OH radicals were produced efficiently at lower concentrations of H_2O_2 in soil. Thus, the competition between H_2O_2 and organics for the OH radicals suggest that there is an optimum H_2O_2/contaminant ratio for efficient oxidation of organics that will vary with the reactivity of organic molecules toward OH radicals. The optimal ratio of H_2O_2/transformer oil obtained from the results of the present study on transformer oil degradation in peat by 72-hours Fenton-like treatment (with 1 addition of H_2O_2 per day) was 4:1 (*paper VII*, Figure 1). Rather similar results were obtained for shale oil degradation in peat (*paper VII*, Figure 2). Shale oil degradation in peat was the most effective at low hydrogen peroxide levels (H_2O_2/shale oil = 0.24:1, w/w). Further increase of the H_2O_2/shale oil ratio did not improve the degradation, and resulted even in a decrease of shale oil removal.

Thus, moderate doses and step-wise addition of hydrogen peroxide were found to be more effective for remediation of contaminated soil by Fenton/Fenton-like treatment. Among the benefits of using low hydrogen peroxide doses is the reduction of treatment costs and a chance to avoid excessive heat and gas generation that hinders contaminant stripping.

3.2.2.3 The effect of soil pH on the Fenton treatment

The influence of pH on the effectiveness of the Fenton/Fenton-like treatment of soil was also investigated. NPs, PAH and diesel were effectively degraded in soil with the Fenton/Fenton-like treatment at pH 3.0 (*papers IV, V, VI*). As a rule, the acidic pH conditions 2.0-4.0 favoured the oxidation of organic compounds, as it is known that the decomposition rate of hydrogen peroxide reaches the maximum in this pH range (Huang et al., 1993). This phenomenon is attributed to the progressive hydrolysis of the ferric ion, which provides a relatively large catalytically active surface for contact with H_2O_2. The accelerator Fe^{2+} ion in H_2O_2 decomposition will yield more hydroxyl radicals. The experiments without pH adjustment were also conducted in order to test the feasibility of the Fenton/Fenton-like treatment to remediate transformer oil and shale oil contaminated soil at natural soil pH (*paper VII*). In spite of Fenton-like treatment of contaminated soil under the same H_2O_2/contaminant weight ratio and at pH 3.0 led to a somewhat higher removal of the contaminant than at the natural soil pH, both pH conditions were found to be effective for studied soil remediation (*paper VII,* Figures 1 and 2).

In general, if the natural pH of the contaminated zone is not low enough for efficient hydroxyl radical generation, acids may be added to adjust the pH of the subsurface prior to Fenton's reagent application. Decreasing the pH will be very useful when emergency response actions must be taken within a few hours after pollution and for ex situ remediation of soil. However, pH adjustment of soil for in situ application will be complicated by the technological restrictions in remediation of the deeper layers and the difficulty of mixing big portions of soil. This makes the treatment less cost-effective. Also, sudden variation in soil pH can have a harmful effect on the soil microbial community and thereby retard subsequent biodegradation of residual contaminants or their oxidation by-products. As a result, the application of the Fenton technology for in situ remediation of contaminated soil needs a very careful investigation and its optimisation will be dependent on the specific case.

3.2.3 Biodegradation of contaminants in soil before and after the chemical pre-treatment

Effectiveness of combined chemical (the Fenton, ozonation) pre-treatment and biodegradation was previously studied using microorganisms introduced into chemically pre-treated soil (Nam and Kukor, 2000; Nam et al., 2001; Lee et al., 1998; Lee and Hosomi, 2001; Stehr et al., 2001). Different from the remediation strategy using introduced microorganisms, chemical pre-treatment and biodegradation employing indigenous microorganisms, required optimal dosage of chemical (ozone, hydrogen peroxide) to achieve removal of contaminants by chemical pre-treatment and maintain microbial activity for subsequent biodegradation. Such remediation strategy as combined chemical treatment and biodegradation by indigenous microorganisms is relatively ecologically sound, compared to soil remediation employing chemical treatment alone.

Thus, although chemical oxidation alone was found to be quite effective for studied contaminants degradation in soil, it was decided to carry out experiments with the combination of chemical and biological treatment *(papers IV, V, VI, VII)*. Moderate doses of chemical oxidants (hydrogen peroxide, ozone) should be applied in combinations of chemical treatment (both, Fenton-like or ozonation) and biodegradation for soil remediation. Therefore, the most effective and moderate doses of chemicals found in the present studies *(papers IV, V, VI, VII)* for the improvement of the subsequent biodegradation were selected. The results of combined chemical and biological treatment presented in Figs. 3.3, 3.4, 3.5, 3.6.

Biodegradation of contaminants in soil without chemical pre-oxidation was quite slow. In spite of biodegradation resulted in somewhat higher removal of contaminants in some cases than chemical treatment alone (Figs. 3.3 and 3.4) the biotreatment time cannot be competitive. Moreover, combined chemical and biotreatment led to more effective removal of contaminants in soil than either one alone (diesel degradation in peat is the only case). The results also indicated that PAH, diesel fuel, shale oil and transformer oil removal by combined chemical + biological treatment was substantially affected by the soil matrix.

The application of combined ozonation + biodegradation led to higher total removal of PAH and shale oil in sand, while the removal of diesel fuel was more effective in peat (Figs. 3.3 and 3.4). In spite of ozone pre-treatment alone led to higher removal of transformer oil in sand combined ozonation + biodegradation resulted in quite similar removal of transformer oil in both soil matrixes (Figs. 3.3 and 3.4). In addition, for the comparison of contaminants removal in deferent soil matrixes by combined ozonation + biodegradation ozone consumed doses, that were somewhat higher for peat than for sand remediation (Figs. 3.3 and 3.4), should be taken into account.

The influence of the soil matrix on the degradation of studied contaminants with Fenton/Fenton-like treatment was also noteworthy (Figs. 3.5 and 3.6). In case of PAH, transformer oil and shale oil contaminated peat the combined Fenton-like + biological treatment resulted in higher contaminant removal than biodegradation alone, but was not as successful as in case of contaminated sand. The same weight ratios of H_2O_2/contaminant for sand and peat remediation were applied in these cases. The removal of diesel by Fenton-like treatment in peat was also less effective than in sand in spite of higher addition of hydrogen peroxide (Figs. 3.5 and 3.6).

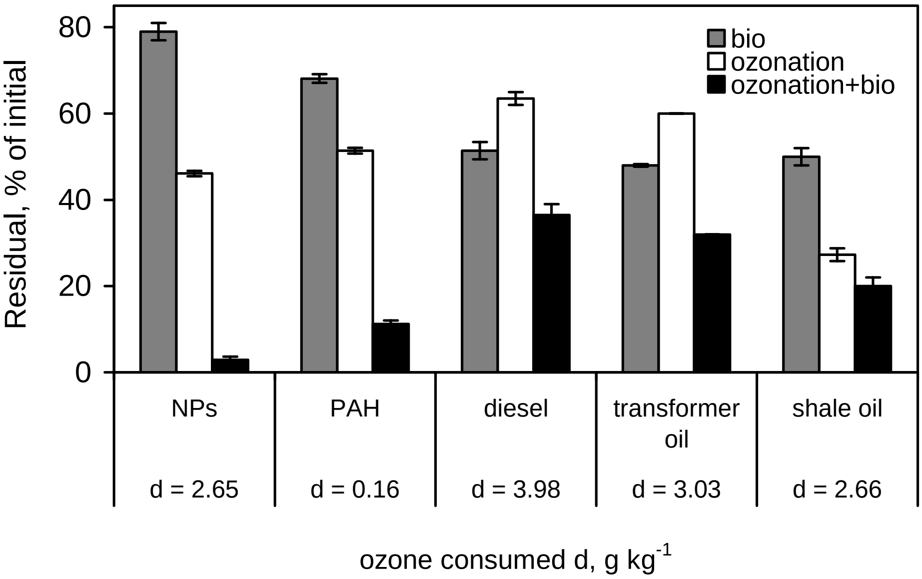


Figure 3.3. Residual concentrations of NPs, PAH, diesel, transformer and shale oils (%) in sand after 30 days biodegradation (diesel, transformer and shale oils), 28 days biodegradation (NPs) and 56 days biodegradation (PAH), ozonation and combined ozonation + biotreatment (*papers IV, V, VI, VII*)

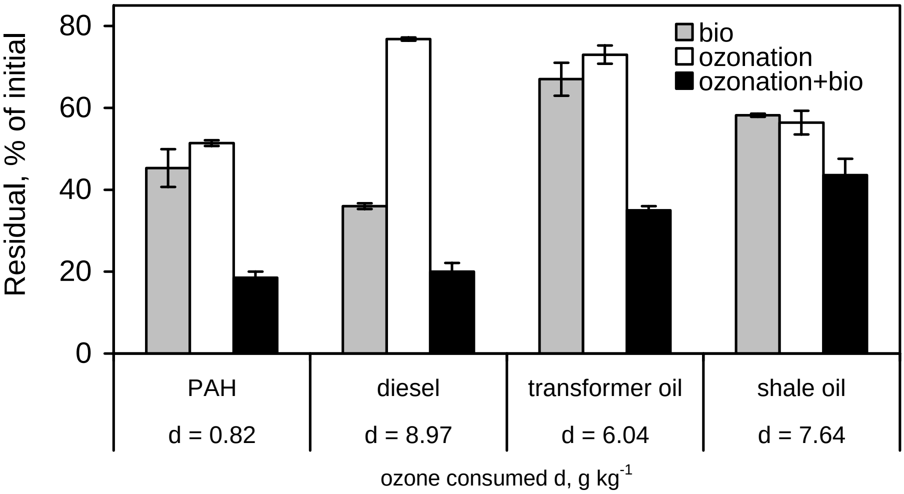


Figure 3.4. Residual concentrations of PAH, diesel, transformer and shale oils (%) in peat after 30 days biodegradation (diesel fuel, transformer and shale oils), 28 days biodegradation (NPs), 63 days biodegradation (PAH), ozonation and combined ozonation + biotreatment (in case of PAH 56 days biodegradation after the ozone pre-treatment) (*papers V, VI, VII*)

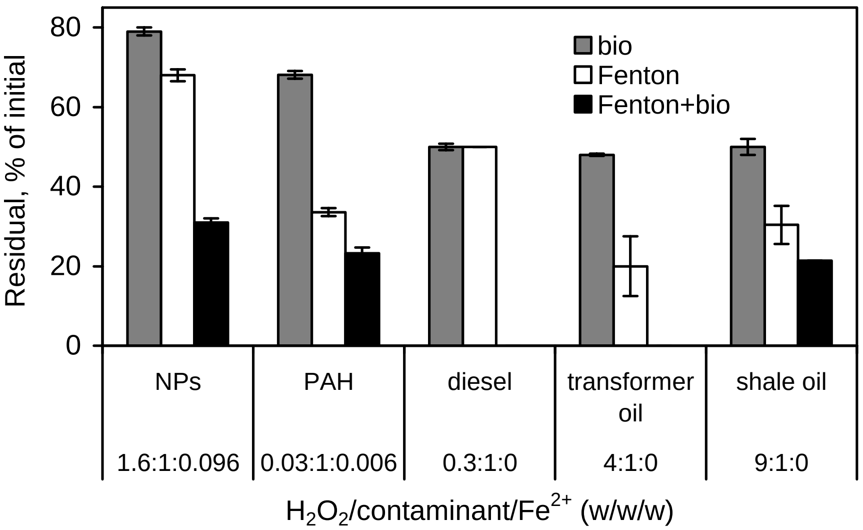


Figure 3.5. Residual concentrations of NPs, PAH, diesel, transformer oil and shale oil (%) in sand after 30 days biodegradation (diesel, transformer oil, shale oil), 28 days biodegradation (NPs) and 56 days biodegradation (PAH), Fenton/Fenton-like treatment, and combined Fenton/Fenton-like + biotreatment (*papers IV, V, VI, VII*)

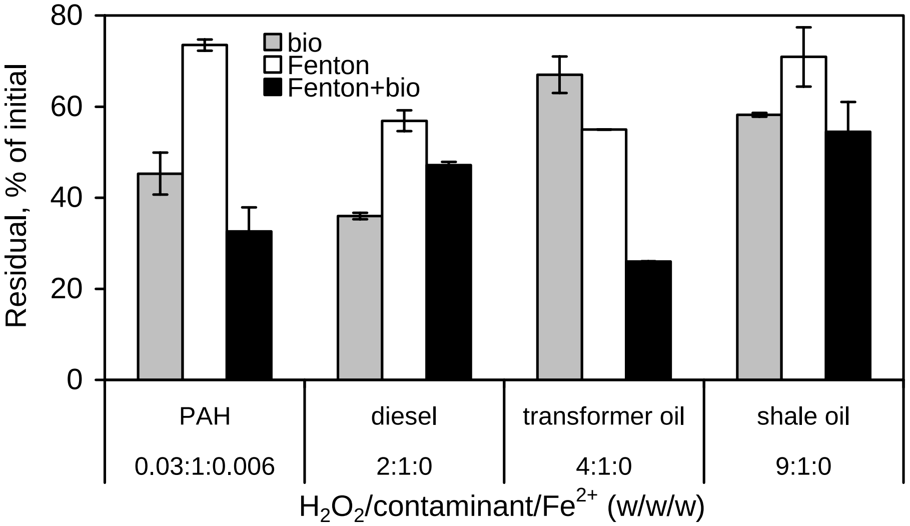


Figure 3.6. Residual concentrations of PAH, diesel fuel, transformer oil and shale oil (%) in peat after 30 days biodegradation (diesel, transformer oil, shale oil), 28 days biodegradation (NPs) and 63 days biodegradation (PAH), Fenton/Fenton-like treatment, and combined Fenton/Fenton-like + biotreatment (*papers V, VI, VII*)

Having compared different treatment methods, it was obtained that combined application of Fenton-like treatment and biodegradation is an effective technology for diesel-contaminated sand remediation, while biodegradation with pre-ozonation may be preferable for diesel-contaminated peat remediation. For remediation of transformer oil contaminated soil Fenton-like pre-treatment followed by biodegradation was found to be the most effective. Taking into account the stripping of shale oil during ozone pre-treatment (*paper VII*), the combination of Fenton-like and biotreatment may be also favourable for shale oil contaminated soil remediation.

Ozonation combined with biodegradation resulted in a higher total removal of PAH in soil than the Fenton pre-treatment followed by biodegradation (*paper V*, Figures 5 and 6). Thus, ozonation followed by biodegradation may be preferable for PAH-contaminated soil remediation. Moreover, in sand and peat, 3-ring PAH biodegraded faster than 4-, 5- and more ring PAH, in both chemically treated and untreated soil (*paper V*). This is in concordance with the data of Nam et al. (2001) and Nam and Kukor (2000), who also found out that biodegradation of low-molecular weight PAH was faster and more extensive than that of high-molecular weight hydrocarbons.

The Fenton and ozonation pre-treatment allowed improving the subsequent biodegradation of NPs in sand. Ozonation followed by biodegradation resulted in a higher degree of NPs removal in sand than the Fenton pre-treatment combined with biodegradation (Figs. 3.3, 3.5). In addition, it was found that 4-NP was more susceptible to biodegradation if compared with higher-molecular weight NPs as 2,4-DNP and 4,6-DN-*o*-CR (*paper IV*, Figures 3 and 4).

Thus, integrated chemical (ozonation, the Fenton treatment) and biological processes were found more effective than either one alone and their applications can be recommended in order to increase the effectiveness of contaminated soil remediation and make the treatment more cost-effective.

3.2.3.1 Biodegradation of alkanes in diesel-contaminated soil

In situ biodegradation is quite complex. The extent of biodegradation is dependent on many factors including the type of microorganisms, environmental conditions (temperature, oxygen levels, moisture, etc.), predominant hydrocarbon types and bioavailability of hydrocarbon contaminants. One of the primary factors controlling the extent of biodegradation is the molecular composition of the soil contaminant. Diesel fuel, transformer oil and shale oil have complex chemical composition represented by different molecular constitutes. Thus, in order to evaluate the progress of bioremediation effort the degradation of some molecular constitutes by chemical pre-treatment and combined chemical + biological treatment was studied and compared on example of diesel fuel.

In general, petroleum hydrocarbons are organic compounds comprised of carbon and hydrogen atoms arranged in varying structural configurations. In the broadest sense, they are divided into two families, aliphatics (fatty) and aromatics (fragrant). Diesel fuel can include up to 30-40% of aromatics fraction (alkyl-aromatics, monoaromatics, diaromatics and polynuclear aromatics) (Composition of Petroleum Mixtures, 1998). The reduction of aromatic fraction followed by UV-254 absorbance removal during the chemical pre-treatment was observed. This reduction was probably achieved by degradation of aromatics with ring cleavage reactions (*paper VI*, Figures 1 and 3). Aliphatics are divided into three main classes, alkanes, alkenes and cycloalkanes. The majority of the fuels contains 60-90% normal, branched, and cyclic alkanes (Composition of Petroleum Mixtures, 1998). Applied diesel contained 20% of alkanes which consisted of 66.5% C_{11}-C_{18}, 16% C_{19}-C_{26} linear alkanes and 17.5% branched alkanes (pristane + phytane). In the present study the degradation of alkanes was studied and compared (*paper VI*, Figures 4 and 5).

Similar to biodegradation of alkanes in untreated sand and peat, the chemical treatment followed by 30-days biodegradation led to more effective removal of short-chained n-alkanes (C_{11}-C_{18}) than long-chained n-alkanes (C_{19}-C_{26}) in both diesel-contaminated sand and peat (*paper VI*, Figures 4 and 5). Moreover, short-chained alkanes were degraded more readily than alkanes with branched structure (pristane + phytane). This branched structure can greatly reduced the rate at which biodegradation occur.

The combined chemical + biological treatment resulted in higher alkanes removal in both diesel-contaminated sand and peat than chemical treatment alone (*paper VI*, Figures 4 and 5). Having compared different treatment methods, it was observed that application of combined Fenton-like treatment and biodegradation resulted in higher alkanes removal, than the application of combined ozonation and biodegradation for diesel-contaminated sand remediation. Biodegradation with pre-ozonation led to higher alkanes removal than the combined Fenton-like + biological treatment in diesel-contaminated peat.

3.2.4 Treatment costs of soil chemical remediation

The data derived from the experiments on studied contaminants degradation allowed a rough estimation of treatment costs taking into account the costs of chemicals ($FeSO_4 \times 7H_2O$, H_2O_2) and energy required for the ozone generation. In these calculations the cost of energy was 0.10 \$ kWh^{-1} (at the moment of

2005), $FeSO_4 \times 7H_2O$ cost $ 0.12 kg^{-1}, where ferrous sulphate heptahydrate is comprised of 20% ferrous iron, and hydrogen peroxide cost $0.86 kg^{-1} calculated as 100%. Ozonation treatment costs were calculated taking into consideration that for the production of 1 kg ozone required 28 kWh of energy. Doses of ozone and hydrogen peroxide injected to soil were used in calculations, as re-circulation of non-consumed chemicals is unlikely to be successful in situ.

To reduce the additions of chemicals and subsequently increase the economic feasibility of chemical treatment, the application of combined chemical + biological treatment for contaminated soil remediation can be recommended. Thus, treatment costs of the Fenton, Fenton-like and ozonation with moderate doses of chemicals (Figs. 3.4, 3.5, 3.6 and 3.7) applied as pre-treatment steps in combined chemical + biological treatment of NPs, PAH, transformer oil and shale oil contaminated soil were estimated and presented in Table 3.2.

Treatment costs of ozonation and the Fenton/Fenton-like treatment with moderate additions of chemicals applied for remediation of diesel-contaminated soil are presented in *paper VI*, Table 2. It was found that low hydrogen peroxide additions were found more cost-effective in the Fenton and Fenton-like treatment of diesel-contaminated soil (*paper VI*, Table 2). Treatment costs could be considerably lowered through the catalyst (Fe^{2+}) addition, which allowed reducing hydrogen peroxide doses. The treatment costs of ozonation were substantially higher than the Fenton and Fenton-like treatment costs (*paper VI*, Table 2).

As the remediation of contaminated peat with ozonation, the Fenton and Fenton-like treatments required higher addition of chemicals, it was found to be more costly than contaminated sand remediation (Table 3.2; *paper VI*, Table 2). If to compare treatment costs of the Fenton/Fenton-like treatment and ozonation, it was found that treatment costs of ozonation were considerably higher than of the Fenton/Fenton-like treatment. Moreover, in using the data on treatment costs, one must keep in mind that the chemical costs typically constitute between 15 to 30% of the total remediation life-cycle costs (Technical/Regulatory Guidelines, 2001). Ozone is generated on site from ambient air using an electrical discharge or similar means. Therefore, the costs associated with its use include the purchase of the generating equipment and the electricity required to operate it. Taking into account high capital costs required for ozone production, ozonation becomes even more expensive technology for contaminated soil remediation. This is confirmed by some cost estimates from actual in situ implementations presented in literature (Technical/Regulatory Guidelines, 2001; EPA US Chemical Oxidation, 1998; In Situ Oxidation, 1999). Thus, the Fenton/Fenton-like treatment was found to be less costly chemical treatment method for soil remediation than ozonation.

Table 3.2. Treatment costs of NPs-, PAH-, transformer oil- and shale oil-contaminated soil chemical treatment

Contaminant	Treatment process	H_2O_2/contaminant/ Fe^{2+} (w/w/w), *O_3/contaminant (w/w)	Contaminant removed, %	Energy required for O_3, kWh t^{-1}	Cost of H_2O_2, \$ t^{-1}	Cost of $FeSO_4 \times 7H_2O$, \$ t^{-1}	Total cost, \$ t^{-1}
sand							
NP	Fenton	1.6:1:0.096	32	0	0.94	0.04	0.98
	ozonation	*7.5:1	54	560	0	0	56
PAH	Fenton	0.3:1:0.06	66	0	0.02	0.0002	0.02
	ozonation	*60:1	49	112	0	0	11.2
transformer oil	Fenton-like	4:1:0	80	0	59.9	0	59.9
	ozonation	*2.3:1	22	1120	0	0	112
shale oil	Fenton-like	9:1:0	50	0	43.3	0	43.3
	ozonation	*7.1:1	73	1120	0	0	112
peat							
PAH	Fenton	0.03:1:0.006	26	0	0.03	0.0004	0.03
	ozonation	*493:1	22	1680	0	0	168
transformer oil	Fenton-like	4:1:0	45	0	65.4	0	65.4
	ozonation	*6.3:1	33	3360	0	0	336
shale oil	Fenton-like	9:1:0	29	0	42.6	0	42.6
	ozonation	*22:1	42	3360	0	0	336

CONCLUSIONS

The current study demonstrated that advanced oxidation enables a large choice of possibilities for the degradation of aqueous NPs. The degradation rate of NPs differed in such processes by several orders of magnitude from several minutes (the Fenton treatment) to many hours (UV-photolysis) required for a 10-fold reduction of the initial concentration of NPs.

Non-accompanied ozonation and AOP can be applied not only for the effective degradation of NPs, but also for detoxification and biodegradability improvement of NPs containing wastewater. Among the factors that contribute to the biodegradability improvement ring hydroxylation, the transformation of aromatics to aliphatics by ring opening reactions, nitrogen mineralization and toxicity reduction were considered. The achieved biodegradability improvement and detoxification of treated NPs supports the potential use of AOP and ozonation to improve the capacity of conventional biological treatment to remove toxic and poorly biodegradable NPs.

In spite of the fact that ozone treatment combined with hydrogen peroxide and/or UV-radiation led to some acceleration of NPs degradation and to reduction of ozone consumption, such AOP were found to be not competitive to non-accompanied ozonation when substantial increase in treatment cost is considered. In spite of the treatment cost of the Fenton and ozonation were found to be competitive, the Fenton treatment is preferable when capital costs for carrying out the treatment are taken into account. The installation of ozone equipment requires considerable capital expenditures, whereas the Fenton treatment does not. Therefore, Fenton’s reagent seems to be the most preferable treatment method among all AOP under study.

The remediation of NPs, PAH, diesel, transformer oil and shale oil contaminated soil by chemical (ozonation, the Fenton treatment) and combined chemical + biological treatment was quite effective. The results indicated that treatment efficiency was strongly dependent on the soil matrix. Chemical treatment of contaminants adsorbed in peat - used as a model of organic-rich soil - resulted in lower contaminants removal and required higher addition of chemicals than the chemical treatment of contaminants in sand matrix representing the mineral part of the soil. The applicability of two-phase or three-phase ozonation was dependent on specific contaminant and as a result affected on the choice of remediation technology (ex situ or in situ).

Contaminants can be degraded with the addition of hydrogen peroxide only indicating the ability of natural iron presented in soil to catalyse the reaction (Fenton-like treatment). Moderate doses and step-wise addition of hydrogen peroxide were found to be more effective for remediation of contaminated soil with the Fenton/Fenton-like treatment. Both pH conditions, pH 3.0 and natural soil pH, favoured soil remediation with the Fenton/Fenton-like treatment.

Application of chemical oxidation for contaminated soil remediation (ozonation or the Fenton treatment) made possible a more rapid reduction of contaminant's concentration than biodegradation did. Therefore, the chemical oxidation is indispensable for fast reduction of contaminants concentration in contaminated soil when it is necessary to avoid their penetration to deeper layers of soil or to the aquifer. Integrated chemical and biological processes were more effective than either one alone and can be used as a successful treatment technology for the remediation of contaminated soil. Moderate doses of chemical oxidants (hydrogen peroxide, ozone) should be applied in combination of chemical treatment (both, Fenton-like or ozonation) and biodegradation in order to facilitate bioremediation by the indigenous microorganisms survived after the chemical oxidation.

A cost calculation indicated that the Fenton/Fenton-like treatment was found to be the cheapest chemical treatment method for contaminated soil remediation. Although chemical treatment alone led to the degradation of studied contaminants (NPs, PAH, diesel, transformer oil and shale oil), the chemical (with the moderate doses of chemicals) and subsequent biological treatment would provide a more efficient and cost-effective way of site remediation than either single treatment methodologies.

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ARTICLE VII

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APPENDIX 2

ELULOOKIRJELDUS

Ees- ja perekonnanimi	Anna Goi
Sünniaeg	18.08.1977
Kodakondsus	eesti
Kontaktandmed	keemiatehnika instituut, Tallinna Tehnikaülikool, Ehitajate tee 5, Tallinn 19086, Eesti Tel. 6 204341, e-post: goi@staff.ttu.ee
Hariduskäik	Tallinna 48. Keskkool, 1995, keskharidus Tallinna Tehnikaülikool, keemia- ja keskkonnakaitse tehnoloogia õppesuund/B.S., 1995-1999 Tallinna Tehnikaülikool, keemia- ja keskkonnakaitse tehnoloogia õppesuund/M.Sc., 1999-2001 Tallinna Tehnikaülikool, keemia- ja keskkonnakaitse tehnoloogia õppesuund/doktorand 2001-2005
Täiendõpe	Toksikoloogia, ekotoksikoloogia ja kemikaalide riski analüüsi koolitus. Uppsala Ülikool, Karolinska Instituut (Rootsi-Eesti-Läti-Leedu), 08.03.2004–12.03.2004, 19.04.2004–23.04.2004, 07.06.2004–11.06.2004 Tampere Tehnikaülikool, biotehnoloogia ja keskkonnakaitsetehnika instituut, 03.01.2004–31.01.2004, 01.02.2003–01.04.2003, 01.02.2002–31.04.2002, 07.01.2001–01.05.2001 Kursused “Waste Management in Baltic Sea Ports“, Swedish Maritime Administration, SSPA Maritime Consulting, 03.11.1998–12.11.1998
Teenistuskäik	Eesti Keskkonnauuringute Keskus OÜ, laborant, 20.07.1997–30.08.1997 Leopold-Franzens Ülikool, Austria, laborant, 29.06.1998–10.08.1998 Veeteede Amet, ohtliku lasti talituse inspektor, 01.09.1998–01.02.2000 Tallinna Tehnikaülikool, inseneer, 01.09.1999–01.10.2001 Tallinna Tehnikaülikool, teadur, 01.10.2001 käesoleva ajani
Teadustegevus	Eesti Toksikoloogia Seltsi Liige
Kaitstud lõputööd	magistritöö “Täiustatud oksüdatsioon nitrofenoolide kõrvaldamiseks vesilahusest” bakalaureusetöö “Nitrofenoolide lagundamine Fentoni reaktiiviga”
Uurimisprojektid	Sihtfinantseerimise teadusteema 0141755Bs01 “Gaasiliste, vedelate ja tahkete jäätmete kombineeritud töötlusprotsesside uurimine” ETF grant 4974 “Täiustatud oksüdatsiooniprotsesside kasutusvõimaluste uurimine nafta- ja põlevkivitööstuse tootmisproduktidega saastatud pinnaste taastamiseks ja tahkete jäätmete töötlemiseks”

APPENDIX 2

CURRICULUM VITAE

Fist name and surname	Anna Goi
Date of birth	18.08.1977
Citizenship	estonian
Contact data	Department of Chemical Engineering, Tallinn University of Technology, Ehitajate tee 5, Tallinn 19086, Estonia Tel. 6 204341, e-mail: goi@staff.ttu.ee
Education	Tallinn 48 Secondary School, secondary education, 1995 Tallinn Technical University, programme of Chemical and Environmental Protection Technology/B.S., 1995-1999 Tallinn Technical University, programme of Chemical and Environmental Protection Technology/M.Sc., 1999-2001 Tallinn University of Technology, Ph.D. degree programm of Chemical and Environmental Protection Technology, 2001-2005
Additional studies	Advanced Course on Toxicology, Ecotoxicology and Risk Assessment of Chemicals, Uppsala University, Karolinska Institute (Sweden-Estonia-Latvia-Lithuania), 08.03.2004–12.03.2004, 19.04.2004–23.04.2004, 07.06.2004–11.06.2004 Tampere University of Technology, Institute of Environmental Engineering and Biotechnology, 03.01.2004–31.01.2004, 01.02.2003–01.04.2003, 01.02.2002–31.04.2002, 07.01.2001–01.05.2001, research visit Advanced Training Course “Waste Management in Baltic Sea Ports“, Swedish Maritime Administration, SSPA Maritime Consulting, 03.11.1998–12.11.1998
Professional Experience	Estonian Environmental Research Centre, Laboratory Assistant, 20.07.1997–30.08.1997 Leopold-Franzens University, Austria, Laboratory Assistant, 29.06.1998–10.08.1998 Estonian National Maritime Board, Surveyor on Dangerous Goods, 01.09.1998–01.02.2000 Tallinn Technical University, Engineer, 01.09.1999–01.10.2001 Tallinn Technical University, Researcher, 01.10.2001 to date
Scientific activities	Member of Estonian Society of Toxicology
Defended thesises	Master Degree thesis “Advanced Oxidation for Degradation of Aqueous Nitrophenols” Bachelor Degree thesis “Degradation of Nitrophenols by Fenton Reagent”
Research programmes	The basic joint research project 0141755Bs01 “Studies on combined treatment processes for gaseous, liquid and solid wastes” ESF grant 4974 “A study of possibilities for application of advanced oxidation processes for remediation of soils contaminated with oil-processing products and the treatment of solid wastes”

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