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The Application of Fenton-Based Processes for Wastewater and Soil Treatment

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TALLINN 2008

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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 academic degree.

Niina Kulik

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Fentoni protsesside rakendamine reovete ja pinnaste töötlemiseks

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INTRODUCTION

A rapid increase in the variety of fields to meet the growing requirements of humankind have led to the presence of new compounds in the wastewater streams of processing plants, and subsequently in the environment. Some of those compounds are not readily degraded by the conventional methods applied for wastewater and soil treatment. It is of utmost importance to keep the concentration of chemicals in the effluent streams and soil to a certain minimum level in order to comply with the environmental laws, which are becoming nowadays more stringent. Thus, research into new and more efficient treatment technologies capable to degrade extensively organic contaminants in a variety of wastewater streams and soil is vital to combat the deteriorating environment quality.

The Fenton-based treatment is a part of advanced oxidation processes (AOP), which are defined as the processes that generate hydroxyl radicals in sufficient quantities to be able to oxidize majority of the complex chemicals present in water (Glaze et al., 1987). The oxidation system based on the Fenton's reagent, hydrogen peroxide catalyzed by ferrous salt, has been increasingly used in the treatment of contaminated wastewater and soil. The Fenton system has dual functions of free hydroxyl radicals' pre-oxidation as well as ferrous/ferric coagulation. The non-specific reactivity of hydroxyl radicals generated during hydrogen peroxide catalytic decomposition is feasible in degradation of a wide range of organic compounds. The coagulation process is notably dependent on pH of the wastewater; with the raise of pH value the yield of the polishing coagulation step increases. The optimized Fenton-based treatment can significantly reduce the COD value, increase biodegradability, and detoxify contaminated media. In order to obtain higher efficacy of the treatment process, the Fenton system can be implemented in tandem with other AOP techniques or treatment methods.

The present research is an attempt to enlarge the knowledge concerning application of Fenton-based processes for wastewater and soil treatment.

In the experiments of wastewater treatment, aqueous solutions of acidic dyes, surfactant stabilized oil-in-water emulsions, leachate from oil shale semicoke and pharmaceutical effluents from medical ointment production were treated with Fenton/Fenton-like systems. The combination of Fenton-based processes with lime coagulation was also investigated with the purpose of improving the overall treatment process efficacy.

The trials on soil treatability with Fenton-like processes were conducted with commercial creosote contaminated soil. Creosote has been widely used for wood preservation for over a century. It is manufactured by distillation of coal tar and may consist of up to 85% polycyclic aromatic hydrocarbons (PAH) by mass. Most PAH are known to be toxic to living organisms, and thus remediation of sites contaminated with creosote is a matter of concern because of the potential threat that PAH pose to the local ecosystem. The Fenton-like treatment and its combination with subsequent biological treatment were studied with the purpose of degrading PAH in creosote contaminated soil samples.

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I want to thank all the former and present colleagues for fruitful discussions and for all the help during this work. My special thanks belong to Viktor Ahelik and researcher Yelena Veressinina for their technical assistance with experimental set-ups and analyses. Senior researcher Anna Goi is thanked for providing me an excellent role model of a researcher in the early stage of my career. I would also like to thank M.A. Denis Trapido for his invaluable help in the language revision of research articles.

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My warmest thanks go to my family for encouragement and love throughout the years of this study.

Tallinn, March 2008

Niina Kulik

LIST OF ORIGINAL PAPERS

The present doctoral thesis is based on the following papers, which are referred to in the text by their Roman numerals I-V:

I **Kulik, N.**, Trapido, M., Veressinina, Y., Munter, R. 2007. Treatment of surfactant stabilized oil-in-water emulsions by means of chemical oxidation and coagulation. *Environmental Technology*, 28, 1345-1355.

II Trapido, M., Munter, R., Veressinina, Y., **Kulik, N.** 2006. Oil shale semicoke leachate treatment using ozonation and the Fenton oxidation. *Environmental Technology*, 27, 307-315.

III **Kulik, N.**, Panova, Y., Trapido, M. 2007. The Fenton chemistry and its combination with coagulation for treatment of dye solutions. *Separation Science and Technology*, 42, 1521-1534.

IV **Kulik, N.**, Trapido, M., Goi, A., Veressinina, Y., Munter, R. 2008. Combined treatment of pharmaceutical effluents from medical ointment production. *Chemosphere*, 70, 1525-1531.

V **Kulik, N.**, Goi, A., Trapido, M., Tuhkanen, T. 2006. Degradation of polycyclic aromatic hydrocarbons by combined chemical pre-oxidation and bioremediation in creosote contaminated soil. *Journal of Environmental Management*, 78, 382-391.

In the appendix A, copies of these publications are included.

Approbation

International Conferences

1. International Conference on Environmental Research and Technology, May 28-30, 2008, Penang, Malaysia.
2. World Congress on Ozone and Ultraviolet Technologies, August 27-29, 2007, Los Angeles, California, USA.
3. 1st European Conference on Environmental Applications of Advanced Oxidation Processes, September 7-9, 2006, Chania, Greece.
4. Wasser Berlin, International Conference Ozone and UV: Sustainable Solutions for Industry and the Environment, April 3, 2006, Berlin, Germany.
5. Conference on Knowledge-based Materials and Technologies for Sustainable Chemistry, June 1-5, 2005, Tallinn, Estonia.
6. International Conference Eco-Balt 2005, May 5-6, 2005, Riga, Latvia.

7. 9th FECS Conference and 2nd SFC meeting on Chemistry and the Environment: Behaviour of Chemicals in the Environment, 29 August – 1 September, 2004, Bordeaux, France.

Author's own contribution

The contribution by the author to the papers included in the thesis is as follows:

I Niina Kulik wrote the paper and is the corresponding author. She supervised the experimental work of a B.S. and M.Sc. student and interpreted the results.

II Niina Kulik participated in writing the paper. She supervised the experimental work of a B.S. student and interpreted the results.

III Niina Kulik wrote the paper and is the corresponding author. She planned and supervised the experimental work carried out together with a M.Sc. student, and interpreted the results.

IV Niina Kulik wrote the paper and is the corresponding author. She planned and supervised the experimental work carried out together with a M.Sc. student, and interpreted the results.

V Niina Kulik wrote the paper and is the corresponding author. She interpreted the results obtained by a M.Sc. student.

ABBREVIATIONS

AAS	atomic absorption spectroscopy
AOP	advanced oxidation processes
AB74	Acid Blue 74
AO10	Acid Orange 10
AV19	Acid Violet 19
BOD_7	7-day biochemical oxygen demand
COD	chemical oxygen demand
ddH_2O	double distilled water
HEIDA	hydroxyethyliminodiacetic acid
HPLC-FLD	high performance liquid chromatography with fluorescence detector
IC-SCD	ion chromatography with suppressed conductivity detector
NAPLs	non-aqueous phase liquids
NTA	nitrilotriacetic acid
O/W	oil-in-water
PAH	polycyclic aromatic hydrocarbons
B(a)A	benz(a)anthracene
B(k)Fl	benzo(k)fluoranthene
Chr	chrysene
Fl	fluoranthene
Flu	fluorene
P	pyrene
Ph	phenanthrene
TPh	triphenylene
US	ultrasound
UV	ultraviolet light
UV_{220}	ultraviolet absorbance at 220 nm
UV_{254}	ultraviolet absorbance at 254 nm
VIS	visible light
SVOC	semi-volatile organic compounds
VOC	volatile organic compounds
2,4-D	2,4-dichlorophenoxyacetic acid

1. LITERATURE REVIEW

1.1. Background

The oxidation processes utilising activation of hydrogen peroxide by iron salts is referred to as the Fenton's reagent. The history of Fenton chemistry (the term comprises both the oxidation and coagulation capabilities of the Fenton system) dates to 1894, when Henry J. Fenton reported that ferrous iron salts strongly promote the oxidation of tartaric acid by hydrogen peroxide (Fenton, 1894). The application of Fenton system for oxidation of hazardous organic pollutants began only seventy years later.

In 1934 Haber and Weiss (1934) proposed that the catalytic decomposition of hydrogen peroxide by Fe^{2+} is a chain reaction, where the active oxidant generated is the hydroxyl radical ($^{\bullet}OH$). The original mechanism of Haber and Weiss (1934) has been subsequently revised and modified by Barb et al. (1951a, 1951b). This expanded sequence of reactions is now referred to as the classical Fenton chain reaction and involves hydroxyl radical production as the key step.

In 1975, Walling published a comprehensive paper of his research group's study in Fenton oxidation of organic compounds that promoted the free radical pathway over existing challenges and served to renew interest in the Fenton's reagent among workers in several fields of chemistry.

It should be pointed that for many years an alternative interpretation of the Fenton system has existed (Bray and Gorin, 1932; Kremer, 1985, 1999). Thus, the ferryl ion (FeO^{2+}) was proposed as the key intermediate in the Fenton reaction, which is involved both in the oxidation of ferrous ions and in the evolution of oxygen. Conceptually, this theory stands in sharp contrast to the free radical mechanism. However, several researches have proved minor role of high-valent oxoiron species in the Fenton system (Lloyd et al., 1997; Mártire et al., 2002; Pignatello et al., 2006).

The Fenton and related reactions are viewed as potentially feasible and economical ways to generate oxidizing species for degradation of hazardous organic pollutants. The key Fenton reagents, hydrogen peroxide and iron salts, are relatively inexpensive and safe. Iron is highly abundant, may be naturally occurring in the system being treated and is non-toxic, environmentally friendly substance. Compared to other oxidants, hydrogen peroxide is easy to transport and handle, and it poses no lasting environmental threat as readily decomposes to water and oxygen. The application of Fenton chemistry to hazardous waste, wastewater and soil treatment began in academic laboratories only around 1990 and has increased exponentially over the years (Pignatello et al., 2006).

The Fenton-based processes (the Fenton process, in one or another of its modifications) are being increasingly used in the treatment of contaminated water and soil. The reactions produce a range of free radicals, which can react with virtually all organic compounds. Reactions involving the highly reactive hydroxyl radicals are the most important, and are characteristic of all advanced oxidation processes (Glaze et al., 1987). Thus, due to generally accepted the free radicals pathway of reaction the Fenton chemistry belongs to AOP.

Hydroxyl radical is one of the most reactive free radicals and one of the strongest oxidants (E^o=2.33 V). Hydroxyl radicals non-specifically oxidise target compounds at high reaction rates (Huang et al., 1993; Neyens and Baeyens, 2003).

Generally, the Fenton treatment is composed of four steps: pH adjustment, oxidation reaction, neutralization and coagulation/precipitation. Therefore, the organic compounds are removed at two phases: the oxidation and the coagulation. The problem of iron oxide sludge generation in the Fenton process, which is inherent in homogeneous catalyst system, and several other disadvantages of the classic Fenton's reagent can be particularly solved by application of modified Fenton systems. The most promising among those are Fenton-like processes with application of transition metal ions different from ferrous iron, modified Fenton with heterogeneous and chelated catalysts, and photo-Fenton and electro-Fenton with UV irradiation and electrochemical assistance, respectively.

1.2. Chemistry of the classical Fenton reaction

Haber and Weiss (1934) first established both radical and chain mechanism of the Fenton reaction. The main stages of the reactions are presented by the following four equations [1-4]. The values of the rate constants (k, M^{-1} s^{-1}) have been taken from Chen and Pignatello (1997) unless stated differently.

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH$ k_1=76 [1]

${}^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO_2^{\bullet}$ k_2=2.7 × 10^7 [2]

$HO_2^{\bullet} + H_2O_2 \rightarrow O_2 + H_2O + {}^{\bullet}OH$ k_3=3 (Koppenol et al., 1978) [3]

$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^-$ k_4=4.3 × 10^8 [4]

These equations mainly describe the reactions of hydrogen peroxide with ferrous salts at acidic conditions with continuous addition of dilute H_2O_2. Reaction [1] is the so-called Fenton's reaction, according to which the ferrous iron initiates the chain by generation of hydroxyl radicals. Reactions [2] and [3] propagate the chain; however reaction [3] is extremely slow and can be neglected (Koppenol et al., 1978). Termination of the chain is caused by reaction [4], in which ferrous iron is also consumed.

Barb et al. (1951a, 1951b) revised the original mechanism proposed by Haber and Weiss (1934) to provide the present accepted scheme for the classic Fenton's reagent. This sequence of reactions includes additional reactions, mainly iron cycles between +2 and +3 oxidation states, which are presented in Eqs. [5-8].

$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+$ k_5=0.01 [5]

$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + H^+ + O_2$ k_6=1 × 10^4 [6]

$Fe^{2+} + HO_2^{\bullet} + H^+ \rightarrow Fe^{3+} + H_2O_2$ k_7=1.2 × 10^6 [7]

$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2$ k_8=8.5 × 10^5 [8]

The newly formed ferric ions may catalyse hydrogen peroxide, causing its decomposition into water and oxygen. Ferrous ions and radicals are also formed in the reactions. The reaction of hydrogen peroxide with ferric ions Eq. [5] is referred to as a Fenton-like reaction (Walling and Goosen, 1973; De Laat and Gallard, 1999).

Hydroxyl radicals can oxidise organic compounds by addition of OH-group, or by hydrogen atom abstraction:

$^{\bullet}OH + RH \rightarrow H_2O + R^{\bullet}$ [9]

$^{\bullet}OH + R \rightarrow {}^{\bullet}ROH$ [10]

In both cases, the oxidation process is extremely fast. The rate constants are as high as 10^7–10^{10} (M^{-1} s^{-1}) (Huang et al., 1993). The reaction of $^{\bullet}OH$ with organic compounds leads to the formation of carbon-centred radicals. The hydroxyl radical abstracts H from C–H, N–H, or O–H bonds, attaches to the aromatic or heterocyclic rings as well as to the unsaturated bonds of alkenes or alkynes (Neyens and Baeyens, 2003). Hydroxyl radical hardly undergoes electron transfer reactions with organics (Pignatello et al., 2006).

The organic free radicals formed in reaction [9] may then be oxidised by Fe^{3+}, oxygen, hydrogen peroxide, hydroxyl radicals or other intermediates, reduced by Fe^{2+}, or dimerised. The following equations illustrate these processes:

$Fe^{3+} + {}^{\bullet}R \rightarrow Fe^{2+} + R^+$ (oxidation) [11]

$2{}^{\bullet}R \rightarrow R\text{-}R$ (dimerization) [12]

$Fe^{2+} + {}^{\bullet}R \rightarrow Fe^{3+} + R^-$ (reduction) [13]

If the concentration of reactants are not limiting, the organics can be completely mineralized by full conversion to CO_2, H_2O, and, in the case of substituted organics, inorganic salts if the treatment is continued.

As seen in reaction [2], hydrogen peroxide can act as a hydroxyl radical scavenger as well as an initiator Eq. [1]. Also ferrous iron can scavenge hydroxyl radical according Eq. [4]. In addition, certain anions can reduce the degradation rates of contaminants by Fenton or Fenton-like reactions. Anions can react with hydroxyl radical or form complexes with ferrous or ferric ions that are less reactive with hydrogen peroxide (Pignatello, 1992; Lu et al., 1997; Hug and Leupin, 2003). Bicarbonate ion has been found to scavenge hydroxyl radicals (Kanel et al., 2003). The reactions of chloride ion (Cl^-) with hydroxyl radical are presented in Eqs. [14]-[17] and the reaction of bisulphate (HSO_4^-) with hydroxyl radical is presented in Eq. [17].

$$^{\bullet}OH + Cl^- \rightarrow HOCl^{\bullet -} \quad [14]$$

$$HOCl^{\bullet -} + H^+ \rightarrow Cl^{\bullet} + H_2O \quad [15]$$

$$Cl^{\bullet} + Cl^- \rightarrow Cl_2^- \quad [16]$$

$$^{\bullet}OH + HSO_4^- \rightarrow H_2O + SO_4^- \quad [17]$$

Walling (1975) simplified the overall Fenton chemistry Eq. [1] by accounting for the dissociation water:

$$2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O \quad [18]$$

This equation indicates that the presence of H^+ is required in the radical decomposition of hydrogen peroxide. Thus, the Fenton reaction is strongly dependent on solution pH. In fact, only in acidic conditions the hydroxyl radical is the predominant oxidant (Neyens and Baeyens, 2003). Previous Fenton studies have shown that pH levels near 3 are usually optimum for the Fenton oxidation (Pignatello, 1992; Huang et al., 1993; Arnold et al., 1995). This is particularly due to the tendency for ferric oxyhydroxide precipitation to occur at pH>3-4, depending on the iron concentration. At neutral pH the predominant route of H_2O_2 decomposition is oxygen evolution (Barb et al., 1951a; Kremer, 2003):

$$2H_2O_2 \rightarrow O_2 + 2H_2O \quad [19]$$

The ferrous ions generated in the process react with hydroxide ions to form ferric hydroxycomplexes according to (Walling and Kato, 1971; Lin and Lo, 1997; Neyens and Baeyens, 2003):

$$[Fe(H_2O)_6]^{3+} + H_2O \leftrightarrow [Fe(H_2O)_5OH]^{2+} + H_3O^+ \quad [20]$$

$$[Fe(H_2O)_5OH]^{2+} + H_2O \leftrightarrow [Fe(H_2O)_4(OH)_2] + H_3O^+ \quad [21]$$

Within pH 3 and 7, the above complexes become:

$$2[Fe(H_2O)_5OH]^{2+} \leftrightarrow [Fe(H_2O)_8(OH)_2]^{4+} + 2H_2O \quad [22]$$

$$[Fe(H_2O)_8(OH)_2]^{4+} + H_2O \leftrightarrow [Fe_2(H_2O)_7(OH)_3]^{3+} + H_3O^+ \quad [23]$$

$[Fe_2(H_2O)_7(OH)_3]^{3+} + [Fe(H_2O)_5OH]^{2+} \leftrightarrow [Fe_2(H_2O)_7(OH)_4]^{5+} + 2H_2O$ [24]

which accounts for the coagulation capability of the Fenton's reagent. Dissolved suspended solids are captured and precipitated. It should be noted that large amounts of small flocs are consistently observed in the Fenton oxidation step. Thus, the chemical coagulation is an essential stage of the Fenton process.

The Fenton's reagent is known to have different treatment functions depending on the H_2O_2/Fe^{2+} ratio. When the amount of Fe^{2+} employed exceeds that of H_2O_2, the treatment tends to have the effect of chemical coagulation. When the two amounts are reversed, the treatment tends to have the effect of chemical oxidation (Neyens and Baeyens, 2003).

1.3. Modifications of the Fenton process

Although ferrous iron is the catalyst used in the classic Fenton's reagent, many other materials, both soluble and particulate, have been utilized to catalyse hydrogen peroxide decomposition. Three categories of catalyst modifications have been the subject of recent studies: soluble ferric iron, iron-chelate complexes, and iron minerals (naturally occurring iron oxides). Additionally, the improvement of Fenton process efficacy by means of light irradiation and electrochemical assistance has been evaluated.

1.3.1. Ferric iron and other transition metals as Fenton catalysts

As presented in Eq. [5], ferric iron has the ability to catalyse hydrogen peroxide decomposition. Reactions of dissolved Fe^{3+} or other transition metals with hydrogen peroxide are often called Fenton-like reactions. A schematic diagram of the Fe^{3+} initiated decomposition of hydrogen peroxide modified from Kwan and Voelker (2002) is presented in Figure 1.

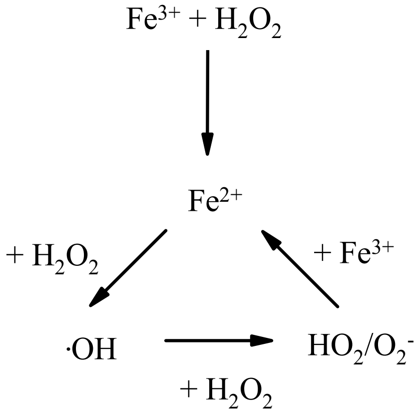

Figure 1. Fe^{3+} initiated decomposition of hydrogen peroxide.

The chain is initiated by the reduction of Fe^{3+} by hydrogen peroxide leading to the formation of soluble Fe^{2+}, which is quickly oxidized by hydrogen peroxide. The chain is propagated, leading to the regeneration of Fe^{2+}. The chain is terminated if Fe^{2+} reacts with hydroxyl radical or HO_2/O_2^- forming Fe^{3+}. Reactions of hydroxyl radical with organic molecules may propagate the chain if species capable of reducing Fe^{3+} are formed. Otherwise the chain is terminated in the reactions of hydroxyl radical with organic molecules.

Numerous transition metal ions (Cu^+, Cr^{2+}, Co^{2+}, Mn^{2+}, etc.) with hydrogen peroxide have the oxidative features of the Fenton reaction (Goldstein and Maeyerstein, 1999; Strlič et al., 2003). Transition metals are usually applied in the form of their complexes in their lower oxidation states, and thus can act as catalysts at near neutral pH values. However, many of those potentially suitable metallic catalysts are toxic to varying degree (Strlič et al., 2003).

1.3.2. Iron complexes as Fenton catalysts

To overcome limitations of the classic Fenton reaction, chelate-mediated Fenton reactions involving the participation of ferric iron chelate and hydrogen peroxide to produce hydroxyl radicals have been suggested during the last few years as an alternative oxidative process.

The use of organic compounds that can complex Fe^{3+} is an important modification of the Fenton process because the addition of large amounts of acid to achieve the optimum process efficiency, followed by base to neutralise the water after the oxidation is complete, makes the process unsuitable for many applications, due to the accompanying salinity increase. It has been found that addition of certain organic chelates that can complex Fe^{3+} enables the process to be carried out at higher pH (Balmer and Sultzberger, 1999). This takes place both because chelation limits the loss of Fe^{3+} by oxyhydroxide precipitation and, in the case of photo-Fenton, because organically chelated Fe^{3+} is more efficiently photolysed than hydrated or organically bound Fe^{3+} (Andreozzi et al., 1999). The organic ligands that can be used are usually at least partially consumed in the process and should be biodegradable. Suitable chelates should bind Fe^{3+} strongly, but allow transformation of Fe^{3+} to Fe^{2+}. Chelates that have been used for this purpose include oxalic and citric acids. It is advantageous if the compounds are naturally occurring in water or may be added from natural sources. However, since most organic compounds also react with radicals and other oxidants, increasing the concentration of chelating agents can also lead to a decrease in the rate of oxidation of the contaminant. Thus, to be useful, the Fe^{3+} chelate must also have catalytic activity for H_2O_2 decomposition, be resistant to oxidation in the medium and be environmentally safe (Sun and Pignatello, 1992).

The application of iron chelates and complexes has been studied extensively in recent years as a means of maintaining iron solubility at neutral pH in catalyzed hydrogen peroxide propagation reactions. Thus, Sun and Pignatello (1992) evaluated fifty ferric iron chelates for their ability to promote catalyzed hydrogen peroxide propagation oxidation. Twenty of the compounds were active catalysts; Fe^{3+}-nitrilotriacetic acid (NTA) and Fe^{3+}-hydroxyethyliminodiacetic acid (HEIDA) were the most effective ones. Later, those results were effectively applied to the Fenton-like oxidation of 2,4-dichlorophenoxyacetic acid (2,4-D) and metolachlor in soil (Pignatello and Baehr, 1994).

The primary advantage of using chelates as catalysts is that *in situ* groundwater remediation and *ex situ* soil treatment can be conducted at near neutral pH. In addition, iron chelates may migrate farther in subsurface than soluble iron improving transport of the catalyst downward. However, the chelate complexes are degraded by the matrix of oxygen species generated by the Fenton reaction, and their long-term potential for treatment should be evaluated.

The use of chelates does not solve the problem of iron remaining in solution after treatment, and their use may prevent iron precipitation by alkali or coagulant addition, if the ligands have not been degraded by Fenton-based process. Significant reduction in dissolved iron can be achieved by the use of heterogeneous Fenton processes, where the iron remains substantially in the solid phase, either as a mineral or as an adsorbed ion. Most of these heterogeneous processes have the additional advantage that they can be operated in close to neutral pH range.

1.3.3. Heterogeneous catalysts for the Fenton process

The main disadvantage of the classic Fenton process is the fact that the soluble iron, added as a catalyst, cannot be retained in the process as causes additional water pollution. The undesirable iron sludge is generated, which needs proper treatment and disposal. In order to avoid the need of removing iron after the treatment, which increases the treatment cost, heterogeneous catalysts can be used.

In the Fenton reaction, as well as many of its modifications, all the reactants are present in the dissolved phase, i.e., as a homogeneous process. At systems with pH above the optimum of about 3 and no iron complexing agent present, the low solubility of iron is believed to be limiting factor for the chain reaction (Sun and Pignatello, 1992). However, the Fenton reaction can also be carried out as a heterogeneous process, in which the catalyst is present as solid phase. The source of iron used as the catalyst can be a solid surface, including iron-containing minerals or iron-coated silica particles. Additionally, the iron can be adsorbed onto zeolites or iron exchangeable membranes (Parsons, 2004).

There are two basic possibilities for the mechanism of heterogeneous Fenton-like reactions forming hydroxyl radicals. The hydroxyl radicals may be formed by the reactions with Fe^{2+} dissolved from the mineral surface or the catalysis may occur at the surface itself (Lin and Gurol, 1998; Lu, 2000).

For the former possibility, the reaction leading to the dissolution of Fe^{2+} from goethite surface is presented in Eq. [25]. Hydroxyl radicals are then produced by the Fenton's reaction, presented in Eq. [1]. Further, Fe^{3+} is precipitated according to reaction [26].

$\alpha\text{-FeOOH}_{(s)} + 2H^+ + \frac{1}{2}H_2O_2 \rightarrow Fe^{2+} + \frac{1}{2}O_2 + 2H_2O$ [25]

$Fe^{3+} + H_2O + OH^- \rightarrow \alpha\text{-FeOOH}_{(s)} + 2H^+$ [26]

In general, Eqs. [25]-[26] represent a simplified approach and would probably require more ferrous ions to be present than could be formed by the dissolution of goethite in order to obtain the reaction rates required for practical application. The formation of the hydroxyl radicals is expected to occur by homogeneous catalysis.

A mechanism for the radical production by mineral surface catalyzed hydrogen peroxide decomposition is proposed by Lin and Gurol (1998). The main reactions are presented in Eqs. [27]-[31]. The series of chain reactions is initiated by the formation of a complex of H_2O_2 with the oxide surface ($\equiv Fe^{3+}$-OH) [27].

$\equiv Fe^{3+}OH + H_2O_2 \leftrightarrow (H_2O_2)_s$ [27]

$(H_2O_2)_s \rightarrow \equiv Fe^{2+} + H_2O + HO_2^{\bullet}$ [28]

$\equiv Fe^{2+} + H_2O_2 \rightarrow \equiv Fe^{3+}OH + {}^{\bullet}OH$ [29]

$HO_2^{\bullet} \leftrightarrow H^+ + O_2^{\bullet -}$ [30]

$\equiv Fe^{3+}OH + HO_2^{\bullet}/O_2^{\bullet -} \rightarrow \equiv Fe^{2+} + H_2O/OH^- + O_2$ [31]

Lin and Gurol (1998) mechanism assumes that no dissolution of goethite occurs, and all reactions take place on the mineral surface. Hence the formation of hydroxyl radicals occurs by heterogeneous catalysis. However, most likely, the formation of hydroxyl radicals occurs simultaneously by both mechanisms.

Kwan and Voelker (2003) proposed that a chain mechanism may not significantly contribute to the production of hydroxyl radicals on the iron mineral surface. Furthermore, some of the hydrogen peroxide decomposes to oxygen and water at the surface without producing dissolved radicals (Kwan and Voelker, 2002).

Heterogeneous modified Fenton processes involving iron oxides can be used for either soil remediation or water treatment. Numerous studies documented that naturally occurring minerals (hematite $\alpha\text{-}Fe_2O_3$, goethite α-FeOOH, magnetite Fe_3O_4 and ferrihydrite) can effectively catalyse the oxidation of organic compounds by H_2O_2 at pH from 3 to 7 (Watts et al., 1990; Tyre et al., 1991; Ravikumar and Gurol, 1994; Watts and Dilly, 1996; Kong et al., 1998; Lin and Gurol, 1998; Valentine and Wang, 1998; Chou and Huang, 1999; Teel et al., 2001; Matta et al., 2007).

Experiments that evaluated different iron oxides under the same conditions exhibited differences in the degradation rates of hydrogen peroxide and contaminants. Magnetite (Fe_3O_4) was the most effective catalyst as compared to the other iron oxides (Tyre et al., 1991; Kong et al., 1998), possibly because it was the only one that had Fe^{2+} in its structure to enhance the production of hydroxyl radical. Goethite is the preferred mineral oxide catalyst mainly because it appears to have the fastest reaction with H_2O_2 (Valentine and Wang, 1998; Lu, 2000). Thus, the contaminants can be oxidized successfully both by the Fenton's or Fenton-like reagents with or without supplemental ferrous ions (and without pH adjustment).

The main advantages of iron minerals application in the Fenton chemistry are: extended periods of catalyst life without requiring regeneration or replacement; the catalyst may be removed from the treated water by sedimentation or filtration; pH of treated media may be in the range 5-9; it is almost insensitive to the inorganic carbonate concentration (Parsons, 2004).

Investigators have explored the use of iron ions immobilized on a solid support as a strategy to avoid sludge formation and to expand the effective pH range of the Fenton reaction. Thus, the Fenton and photo-Fenton processes using iron ions immobilised on Nafion perfluorinated membranes can be used to degrade organic compounds (Fernandez et al., 1999; Sabhi and Kiwi, 2001). The reactions of Fe^{2+} and Fe^{3+} ions on the membrane surface are equivalent to the reactions of dissolved Fe^{2+} and Fe^{3+} ions. The membrane could be reused through many cycles, without leaching out of a significant amount of Fe^{3+} ions from the membrane, which would cause loss of efficiency (Sabhi and Kiwi, 2001).

Other supported media for catalytic ion include zeolites (Bossmann et al., 2001), iron-modified clays (Feng et al., 2003), beads of cross-linked organic material (Fernandez et al., 2000), modified polyethylene films (Dhananjeyan et al., 2001), and silica/Fe-structured fabrics (Bozzi et al., 2003).

In recent years, metallic iron, Fe^0, a potential three electrons donor, has been also studied as a precursor of Fe^{2+} in the Fenton reaction (Arienzo et al., 2001b; Roy et al., 2003; Liao et al., 2007). Elemental iron is regarded as a suitable donor of electrons for the *in situ* remediation of contaminated groundwater and soil. The Fe^{2+} was found to dissolve from the Fe^0 surface, especially if the solution is in acidic condition (Liao et al., 2003). However, the direct electron transfer from Fe^0 to H_2O_2 in a chain mechanism during the Fenton reaction is a very slow process in a near neutral pH medium (Moura et al., 2005).

1.3.4. Photo-Fenton process

There are several photochemical processes involving iron compounds and hydrogen peroxide that provide alternative ways of generating hydroxyl radicals. Photo-Fenton reaction and its modifications lead to the considerable improvement of destruction of organic pollutants. The photo-Fenton reaction is based on the parallel applying of the Fe^{2+}/Fe^{3+} and H_2O_2 reagents with near-UV and visible light (Sun and Pignatello, 1993).

When irradiated with light of suitable wavelength (180-400 nm) Fe^{3+} can catalyse the formation of hydroxyl radicals:

$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + H^+ + {}^{\bullet}OH$ [32]

This is a wavelength dependent reaction and the quantum yield of formation of ${}^{\bullet}OH/Fe^{2+}$ ion decreases with increasing wavelength. For example, the quantum yield of hydroxyl radical formation is 0.14-0.19 at 313 nm and 0.017 at 360 nm (Faust and Hoigné, 1990). The reaction [32] is the so-called photo-Fenton reaction and is followed by reaction [1]. Hence, iron is cycled between +2 and +3 oxidation states. In theory, by combination of reaction [32] and [1], two moles of ${}^{\bullet}OH$ should be produced per mole of hydrogen peroxide consumed.

Ferric ion hydroxycomplexes present in mildly acidic solution, such as $Fe(OH)^{2+}$ and $Fe_2(OH)_2{}^{4+}$, absorb light appreciably in the UV and visible region. These complexes undergo photoreduction to give hydroxyl radicals and Fe^{2+}. The most important species is $Fe(OH)^{2+}$ due to a combination of its relatively high absorption coefficient and concentration compared with other Fe^{3+} species under typical conditions.

The enhancement of the Fenton process is also due to the photochemistry of Fe^{3+}. Ferric iron complexes undergo ligand-to-metal charge transfer excitation and dissociate to give Fe^{2+} and an oxidized ligand (Sima and Makanova, 1997). The photochemistry of Fe^{3+} is advantageous to the Fenton process because the reduced iron can then react with hydrogen peroxide to produce hydroxyl radicals and because oxidation of the ligand may lead to further degradation of the target pollutant (Sun and Pignatello, 1993). The photolysis of Fe^{2+} species is unimportant at wavelengths employed in photo-Fenton systems.

The main advantage of the photo-Fenton process is that ultraviolet (UV) radiation can enhance reduction of dissolved Fe^{3+} complexes to Fe^{2+}, and generate additional ${}^{\bullet}OH$ via photolysis. As a result, the production of iron sludge can be reduced. However, the mechanisms of action including the roles of Fe^{2+} and Fe^{3+}, as well as the equilibrium concentration of both species, are complex and not understood in details yet.

1.3.5. Electro-Fenton process

Electro-Fenton processes include electrochemical reactions that are used to generate *in situ* one or both of the reagents for the Fenton reaction. There are two main types of electro-Fenton methods, which differ mainly in the form of iron that enters the system. In cathodic Fenton process, the iron is added as Fe^{2+} or Fe^{3+} salt, whereas in anodic Fenton process the source of the iron is a sacrificial iron anode.

In the cathodic processes, there are several possibilities, in which one or both of the reagents Fe^{2+} and H_2O_2 are produced *in situ*. The source of Fe^{2+} may be direct Fe^{2+} addition or it may be produced by reduction of Fe^{3+} at the cathode reaction [33] (Brillas et al., 1998; Qiang et al., 2003).

$Fe^{3+} + e^- \rightarrow Fe^{2+}$ [33]

The source of hydrogen peroxide may be either direct hydrogen peroxide addition or it may be produced by reduction of dioxygen at the cathode [34] (Brillas et al., 1998; Casado et al., 2005).

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \qquad [34]$$

Simultaneous Fe^{3+} and O_2 reduction can take place at the cathode at comparable rates. Since ferrous ions and hydrogen peroxide are continuously produced at controlled rates, this leads to a more efficient and more complete degradation of the contaminant compared with the classic Fenton system, where all the reagents are typically added at the beginning of the reaction. This is because there are less competitive reactions, which consume the reagents without producing hydroxyl radicals (Ventura et al., 2002).

The electro-Fenton systems may also be exposed to irradiation by UV/visible light, leading to photoelectron-Fenton processes (Flox et al., 2006; Peralta-Hernández et al., 2006; Sirés et al., 2007).

In the anodic Fenton process, an iron electrode is used as the anode and becomes the source of Fe^{2+}. The system consists of two cells, with a salt bridge providing electrical connectivity between the cells and a graphite electrode used as a cathode. The anodic Fenton treatment has several advantages over the classic Fenton process (Wang and Lemley, 2001). Since Fe^{2+} is produced by controlled electrolysis using a sacrificial iron electrode, there is no need to handle Fe^{2+} and Fe^{3+} salts.

The electro-Fenton process design for detoxification of hazardous organic compounds in water has been proposed by several authors (Qiang et al., 2003; Chang et al., 2004).

1.4. Application of the Fenton chemistry and its combination with other methods for wastewater and soil treatment

The Fenton chemistry, in which the decomposition of hydrogen peroxide is catalyzed by iron to form hydroxyl radicals, has been applied for the treatment of wastewater and remediation of contaminated soil. Hydroxyl radicals are capable of oxidizing a range of contaminants because they react with almost all types of organics, such as ethylenic, lipid, aromatic, and aliphatic, and inorganics, such as anions and cations, in solution at near-diffusion controlled rates (Huang et al., 1993; Watts and Dilly, 1996).

In general, use of the Fenton process can lead to the complete mineralisation of some organic compounds, converting them to CO_2, H_2O, and inorganic ions. However, this would usually involve a large excess of chemicals, often preventing the process from being cost effective. Hence, a partial degradation of contaminants generally occurs and results in reduction of the contaminants' toxicity and increase of the residue's biodegradability. However, sometimes the generated products have the same or even higher toxicity than the parent compounds. These degradation products are probably not the same as those formed in the environment by the naturally occurring processes (Fernández-Alba et al., 2002).

It should be noted that the Fenton chemistry is not a universal solution as there are many chemicals, which are refractory towards the Fenton's reagent such as methylene chloride, oxalic acid, acetone, etc. Moreover, it may happen that a certain compound in the waste stream is oxidized to some of the above-mentioned toxic compound.

The Fenton chemistry was efficiently applied to treat waste streams from dyeing manufacture and dyeing operations (Kuo, 1992; Rodriguez et al., 2002; Lucas and Peres, 2006; Arantes et al., 2006), wood pulping effluent (Rodriguez et al., 1999; Perez et al., 2002), agricultural effluents (DeHeredia et al., 2001), landfill leachate (Lopez et al., 2004; Zhang et al., 2005), surfactant (Lin et al., 1999), and complex industrial wastewater (Oliveros et al., 1997; Moraes et al., 2004). The Fenton oxidation is also effective for removing trace levels of inorganic contaminants from water sources (Arienzo et al., 2001a).

The Fenton treatment is a potential alternative to incineration or landfilling of contaminated soil and represents a possible choice for *in situ* remediation of aquifers. However, the Fenton technologies applied to the cleanup of natural soils have serious difficulties: interference by organic soil components, the pH limitation, problems with effective dispersal of reagents, and potential alteration of the soil environment. It is clear, that at enough aggressive conditions degradation of almost any oxidizable compound in soil can take place.

In general, the amount of hydrogen peroxide needed to transform, and especially mineralize, a given concentration of contaminant in soil is often far greater than in aqueous system. The high oxidant demand is due to the presence of natural organic matter, non-productive catalyzed decomposition of hydrogen peroxide to oxygen and water, or the presence of inorganic reductants in soil that consume the hydrogen peroxide. It should be noted that high hydrogen peroxide concentrations and acidity render the soil "sterile", at least temporary (Miller et al., 1996).

In contrast to water-soluble compounds, contaminants in soil are usually sorbed or present as non-aqueous phase liquids (NAPLs), which can significantly effects on the Fenton process. Fenton-like oxidations in soil have focused on the processes that most effectively destroy and mineralize biorefractory contaminants. Watts et al. (1990) first reported application of the Fenton chemistry for soil remediation and showed that pentachlorophenol in silica sand was destroyed in a slurry at pH of 2-3.

While naturally occurring iron minerals (goethite, magnetite, hematite) can catalyze the Fenton reaction, they are much less reactive than soluble iron, especially when the pH in not lowered (Kong et al., 1998; Teel et al., 2001).

Successful Fenton treatment of soil on a laboratory scale has been demonstrated for chlorinated solvents (Ravikumar and Gurol, 1994), polycyclic aromatic hydrocarbons (Lee et al., 1998; Lee and Hosomi, 2001; Nam et al., 2001), polychlorinated biphenyls (Aronstein and Rice, 1995; Manzano et al., 2004; Riaza-

Frutos et al., 2007), pesticides (Tyre et al., 1991; Ravikumar and Gurol, 1994; Bier et al., 1999), explosives (Li et al., 1997, Arienzo et al., 1998), oil products (Tyre et al., 1991; Chen et al., 1998; Kong et al., 1998; Goi et al., 2006). Commonly such reactions are carried out in soil slurry, but column studies have also been performed (Ravikumar and Gurol, 1994).

The application of Fenton-like treatment for organically contaminated soil may use iron oxides naturally occurring in the soil or may require addition of dissolved iron salts or solid iron oxide particles. The efficiency of the process tends to be lower than in aqueous systems due to the effect of the components of the soil matrix. The concentration of the added hydrogen peroxide depends on the amount of water present, the amount of organic contaminant and the degree of treatment required.

During soil remediation by application of the Fenton-based process, precipitation of the mineral goethite can occur at near neutral pH, which leads to the acceleration of surface catalysed hydrogen peroxide decomposition as well as blocking of the entry of the reagents into the target zone. Chelating agents, such as citric acid, can be used to control precipitate formation, and hence decrease the amount of hydrogen peroxide required (Kakarla et al., 2002).

The Fenton treatment can be implemented not only alone, but also in tandem with other technologies. Addition of the Fenton's reagent along with the components of other treatment process often leads to enhanced degradation degree or degradation rate. The most common employment of the Fenton reaction in a sequential mode is the Fenton treatment followed by a biological process. Thus, the Fenton pre-treatment improved in several cases the biodegradability of organic contaminants both under aerobic and anaerobic conditions. The combination of pre-coagulation and Fenton treatment increased COD removal efficacy from industrial wastewater (Martins et al., 2005).

The right balance between treatment time in the Fenton process and the biological process should be determined to optimise the process (Pulgarin et al., 1999). Thus, the Fenton treatment step should proceed far enough to transform toxic compounds to biodegradable ones and to leave no residual hydrogen peroxide in the pre-treated water.

In the Fenton treatment of wastewater, the oxidation and coagulation by generated iron sludge both contribute to removal of organic compounds. The relative importance of oxidation and coagulation depends primarily of the H_2O_2/Fe^{2+} ratio (Neyens and Bayens, 2003). The iron used in the Fenton process may be used to replace some of the ferric iron that is dosed during coagulation (Yoo et al., 2001). Lower sludge production than in traditional treatment process presumes that the Fenton-based processes may be feasible in organically contaminated wastewater treatment.

There are several full-scale plants in South Africa that use the Fenton's reagent to treat wastewater form textile industry. Commercial scale photo-Fenton installations exist in the USA for treatment of water contaminated with VOC and SVOC (Parsons, 2004). A variety of patented technologies involving the Fenton reaction, such as Geo-Cleanse® Process, CleanOx® Process, ISOTEC℠, BIOX®, are available and used by companies in remediation of contaminated soil and groundwater. One of the disadvantages of *in situ* chemical oxidation is the violent exothermic reaction that may occur on injection of reagents. In addition, since the Fenton reaction performance is optimal at around pH 3, many applications are precluded due to presence of alkaline rock, which would neutralise the added acid. In most cases these problems can be overcome, to some extent, by utilization of iron chelating agents that allow operation in the near to neutral pH range and with minimal temperature change.

1.5. Aims of the present study

In homogeneous aqueous solution the fundamental reaction steps of the Fenton-based chemistry are fairly well understood and multistep kinetic models assuming the conventional mechanisms do a good job of predicting trends. However, it is still difficult to predict the transformation and mineralization rates of particular compounds without conducting treatability studies. The non-selectivity of the hydroxyl radical leads to a variety of products whose formation is sensitive to reaction conditions.

The main objective of the present doctoral study was to clarify the Fenton chemistry potential in treatment of certain recalcitrant compounds, original industrial wastewater effluents and creosote contaminated soil, and consequently to enlarge the existing knowledge in Fenton-based processes application as a treatment technique.

The study on wastewater purification was an attempt to find benefits of using the Fenton chemistry for treatment of different wastewater samples with specific origin. Thus, aqueous solutions of acidic dyes, surfactant stabilized oil-in-water emulsions, oil shale semicoke leachate and pharmaceutical effluents from medical ointment production were subjected to Fenton/Fenton-like treatment.

The influence of catalyst, hydrogen peroxide dosage, pH, oxidation duration on the efficacy of the treatment processes was analyzed. The overall efficiency of applied treatment was ascertained by COD, UV absorbance, and colour removal from wastewater samples.

The chemical pre-treatment of wastewater by means of Fenton-based processes aimed at reducing of organics' content, increasing the biodegradability, and removing toxicity. The improvement of biodegradability and toxicity reduction of investigated wastewater samples were observed by measuring BOD_7 and acute toxicity to *Daphnia magna*, respectively.

It is ascertained that the Fenton system does not only lead to oxidation but also to coagulation by formation of ferric hydroxycomplexes. The coagulation acts as a polishing step after the Fenton oxidation. The combination of Fenton chemistry with lime coagulation was also investigated with the purpose of improving the overall treatment process efficacy.

The efficacy of Fenton-based treatment was compared with coagulation (surfactant stabilized O/W emulsions) and ozonation (oil shale semicoke leachates) efficiencies.

The study on soil remediation was conducted to investigate the degradation of PAH originated from commercial creosote by means of Fenton-like treatment. The ability of combined chemical pre-oxidation and biological treatment to overcome the inherent bacterial bioavailability limitation and, hence, bioremediation limitation of PAH in creosote contaminated soil was also investigated. The influence of soil matrix, catalyst, hydrogen peroxide dosage, and treatment duration was studied. The comparison of Fenton-like treatment efficacy with ozonation was done.

Notably, the wastewater and soil samples, investigated in the present work, were not previously subjected to treatment by the Fenton chemistry and/or its combinations/modifications.

The data obtained within the study enlarged the knowledge of the treatability of organically contaminated wastewater and soil. The results of this study are unique and could provide important information for practical purposes.

2. MATERIALS AND METHODS

The main experimental characteristics are briefly presented in this section. For more details see the experimental part in *Papers I-V*.

2.1. Samples and chemicals

All chemicals used were of reagent or analytical grade, and were used without further purification. Stock solutions were prepared in ddH_2O. Adjustment of pH was performed by using H_2SO_4 and NaOH aqueous solutions.

The simulated O/W wastewater samples were prepared by mixing surfactant solution with petroleum products in laboratory conditions according to procedure presented in *Paper I*. Main properties of the wastewater samples prepared are presented in *Paper I*, *Table 2*. Some characteristics of oil products and detergents used in the present work can be found in *Paper I*, *Table 1* and in *Materials and Chemicals* section, *Paper I*, respectively.

Leachate samples were collected from the landfill area of the oil shale thermal treatment plant in Kohtla-Järve. The characteristics of these samples are presented in *Paper II*, *Table 1*.

Stock solutions of acidic dyes were freshly prepared in ddH_2O. Molecular structures and main properties of synthetic dyes in a non-hydrolyzed form are presented in *Paper III*, *Table 1*.

Pharmaceutical effluents were obtained from a plant formulating medical ointments. The untreated and plant pre-treated wastewater samples characteristics are presented in *Paper IV*, *Table 1*. The main active agents and formulation additives of the investigated effluents can be found in *Materials and Chemicals* section, *Paper IV*.

Soil (peat, sand) samples were artificially contaminated with creosote. The process of contaminated soil samples preparation in details is presented in *Soil Samples and Chemicals* section, *Paper V*. The mixture of PAH in creosote included seven compounds – Flu, Ph, Flu, P, TPh and trace amounts of B(a)A and Chr. The initial concentrations of PAH in creosote contaminated sand and peat are given in *Paper V*, *Table 1*. Sand and peat chemical and physical properties can be found in *Soil Samples and Chemicals* section, *Paper V*.

The initial wastewater (*Paper I, II, IV*) and soil (*Paper V*) samples were stored at 2-4 ºC.

2.2. Experimental procedure

2.2.1. Wastewater treatment

Batch experiments, for the Fenton (*Paper I-III*) and Fenton-like (*Paper II-IV*) oxidation, were performed in a cylindrical glass reactor. 0.2 L samples of wastewater were treated with (*Paper II, IV*) and without (*Paper I, III*) permanent agitation for a period of 1-6 hours (*Paper IV*) or 24 hours (*Paper I-III*). The catalyst ($FeSO_4 \cdot 7H_2O$ (*Paper I-IV*) or Fe^{3+} solution prepared by dissolving $Fe_2(SO_4)_3 \cdot xH_2O$ (*Paper III*) in ddH_2O) was added first and the reaction was subsequently initiated by adding H_2O_2 stepwise (*Paper II*) and/or all at once (*Paper I-IV*). The weight ratio of H_2O_2/Fe^{2+} was kept invariable at 6:1, which is the optimal ratio for hydrogen peroxide and ferrous ions (Tang and Huang, 1997). The same weight ratio was used for Fenton-like experiments with Fe^{3+} catalyst. In the Fenton oxidation experiments pH of wastewater samples was adjusted to 3. Fenton-like experiments with Fe^{2+} ions were carried out without pH regulation and with Fe^{3+} both with and without pH adjustment. Termination of the oxidation process was done by adjustment of samples' pH to basic values by adding NaOH aqueous solution (*Paper I-IV*) and/or lime milk (*Paper III, IV*). The samples were kept for a period of 1-2 hours to allow the settling of solids and then filtered (paper, pore size 2 μm). Na_2SO_3 aqueous solution (20%) was used to quench the oxidation by residual hydrogen peroxide, if any occurred, before the spectrophotometric analysis (*Paper I, III*).

The experiments of wastewater oxidation with non-catalyzed hydrogen peroxide were conducted in the same reactor and treatment conditions as the corresponding Fenton/Fenton-like treatment trials. Coagulation efficiency (*Paper III, IV*) with $Fe_2(SO_4)_3 \cdot xH_2O$ and CaO was controlled by jar test (blank test). For details see experimental section of *Paper III and IV*.

Coagulation with aluminium sulphate, ferric chloride solutions and lime milk and ozonation were applied as a separate treatment technique for O/W wastewater (*Paper I*) and landfill leachate (*Paper II*) samples, respectively. All details concerning coagulation and ozonation trials procedure can be found in experimental section of *Paper I* and *Paper II*, respectively.

2.2.2. Soil treatment

Fenton-like treatment of creosote contaminated soil samples was done in slurry under batch conditions. Sand and peat were treated for 24 hours in a cylindrical glass reactor under permanent agitation. No pH adjustment of soil samples was done. First, catalyst was added and then reactions were initiated by H_2O_2 stepwise addition. The weight ratio of H_2O_2/Fe^{2+} was kept constant at 6:1 (Goi and Trapido, 2004). Soil samples were also treated by hydrogen peroxide only. The oxidation was stopped by adding 20% aqueous solution of Na_2SO_3, except in samples that underwent further biodegradation. After that liquid phase was separated from solid one and filtered (paper, pore size 2 μm).

Two- and three-phase ozonation was carried out as a comparative treatment method for creosote contaminated soil samples. Also biodegradation of organic contaminants was investigated in chemically untreated, two-phase pre-ozonated and Fenton-like pre-treated creosote contaminated soil samples. For more information concerning ozonation and biodegradation procedure see experimental section of *Paper V*.

2.3. Analytical methods

A concise overview of the analytical methods applied for wastewater and soil samples are summarized in Table 1 and Table 2, respectively.

Table 1. Analytical methods used for wastewater samples

Analysis/Parameter	Analytical instrument/method	Paper
COD	Closed reflux titrimetric method (AHPA, 2005)	*I-IV*
BOD_7	Oxygen analyzer (AHPA, 2005)	*I-IV*
pH	pH-meter	*I-IV*
UV_{220}, UV_{254}	UV-VIS spectrophotometer (APHA, 2005)	*I-III*
VIS absorbance	UV-VIS spectrophotometer	*III*
Total Fe	Phenanthroline method (APHA, 2005)	*I, III, IV*
H_2O_2	Spectrophotometric method (Eisenberg, 1943)	*I-IV*
SO_4^{2-}	IC-SCD (Penchuk et al., 1986)	*II*
Cl^-	IC-SCD (Penchuk et al., 1986)	*II*
Toxicity to *Daphnia magna*	*Daphnia magna (Cladocera, Crustacea)* acute toxicity test (ISO, 1996)	*I-III*
O_3 inlet, outlet	Spectrophotometric method (IOA, 1998)	*II*
Al^{3+}	Colorimetric method (APHA, 2005)	*I*

Prior to PAH analysis soil samples were dried with anhydrous Na_2SO_4 and extracted twice (hexane/acetone mixture, US). The liquid phase was also extracted twice with hexane. All details concerning extraction procedure are presented in *Extraction and Analysis of PAH* section of *Paper V*. Joined soil extracts and liquid phase extracts were evaporated dry at room temperature and the residue was dissolved in 1 mL of acetone with internal standard (B(k)Fl). A mixture of PAH (Fl, Ph, Flu, P, TPh, B(a)A, and Chr) in hexane was used as an external standard.

Table 2. Analytical methods used for soil samples (*Paper V*)

Analysis/Parameter	Analytical instrument/method	Reference
pH	pH-meter	EPA, 2004
Moisture content	Oven-drying at 105 ºC	Slight modification from ASTM, 2005
PAH	HPLC-FLD	Trapido and Veldre, 1996
Total Fe	AAS	Slight modification from Heron et al., 1994
Ion-exchangeable Fe(II)	AAS	Slight modification from Tessier et al., 1979
O_3 inlet, outlet	Spectrophotometric method	IOA, 1998

3. RESULTS AND DISCUSSION

3.1. Wastewater treatment

The Fenton treatment is known to be effective for elimination of a wide range of contaminants presented in wastewater and industrial effluents. In the present study an endeavour was undertaken to enlarge the area of the Fenton-based chemistry application for treatment of wastewater with various specific origins. Thus, previously not studied real and simulated wastewater samples were subjected to Fenton/Fenton-like treatment and to its combination with lime coagulation.

3.1.1. Fenton/Fenton-like treatment

The classic Fenton and Fenton-like processes were applied for simulated and real wastewater samples (Table 3).

Table 3. The Fenton-based processes applied for treatment of various wastewater samples

Wastewater samples	Processes applied	Paper
Simulated O/W emulsions with small diesel fuel and high surfactants content	H_2O_2/Fe^{2+}, pH adjusted to 3	*I*
Oil shale semicoke leachate samples from plant in Kohtla-Järve.	H_2O_2/Fe^{2+}, pH adjusted to 3 H_2O_2/Fe^{2+}, without pH adjustment	*II*
Aqueous solutions of Acid Blue 74 (AB74), Acid Orange 10 (AO10) and Acid Violet 19 (AV19) dyes	H_2O_2/Fe^{2+}, pH adjusted to 3 H_2O_2/Fe^{2+}, without pH adjustment H_2O_2/Fe^{3+}, pH adjusted to 3 H_2O_2/Fe^{3+}, without pH adjustment	*III*
Pharmaceutical effluents from medical ointments formulating plant	H_2O_2/Fe^{2+}, without pH adjustment	*IV*

The efficacy of the Fenton chemistry application for organic contaminants degradation and wastewater quality improvement proved dependent on hydrogen peroxide concentration, catalyst addition and its type, pH and treatment time. The influence of these treatment conditions was quite different for various types of contaminants and wastewater.

The Fenton-based treatment was applied in all studies as a system with a dual function of hydroxyl radicals' pre-oxidation as well as ferric coagulation. The coagulation with polymer hydroxycomplexes of Fe^{3+}, which are formed with the increase of pH, was applied after the oxidation step.

The COD is one of the most widely used indicators to determine wastewater characteristics. It was adopted as a main parameter to assess treatment efficacy in the current study. Hydrogen peroxide applied in the oxidation step of the Fenton-based processes can partly remain in oxidized wastewater samples, and thus interferes with the COD analysis by reduction of potassium dichromate used as an oxidant in the standard COD test (Talinli and Anderson, 1992; Kang et al., 1999). It is known that hydrogen peroxide is unstable and easily decomposes at pH basic values (Kuo, 1992). Thus, the adjustment of pH to 9-11 could reasonably reduce the amount of any residual H_2O_2 in treated solutions. For that reason, the COD measurements in all studies were performed only after the coagulation stage of Fenton/Fenton-like process.

Paper I

Two samples of O/W surfactant stabilized emulsion with diesel fuel contamination and various commercial detergents (Anrol/Decon90) were subjected to the classical Fenton treatment. 24 hours has been chosen as the experiment duration in the Fenton oxidation in order to insure the complete utilization of hydrogen peroxide.

A blank experiment with non-catalyzed hydrogen peroxide H_2O_2 demonstrated no removal of COD or UV absorbance. The absorbance of samples at 254 and 220 nm was used to characterise the aromatic carbon and general organic content, respectively.

The application of Fenton chemistry showed a different treatment tendency but similar final efficacy for both wastewater samples, as shown in *Paper I*, *Figure 4*. Thus, wastewater quality improvement by Fenton treatment was mainly dependent on surfactant type. The maximum COD and UV absorbance reduction and diesel removal for both wastewater samples was above 90%. The optimal H_2O_2/COD weight ratio, which comprises both efficacy of COD and UV absorbance removal and economical rationality, was 2 and 5 for Anrol and Decon90 stabilized O/W emulsions, respectively (*Paper I*, *Figure 4*). In both wastewater samples, UV_{254} absorbance elimination was somewhat lower than for UV_{220}, apparently due to higher aromatic ring recalcitrance to degradation by chemical oxidation.

In general, the Fenton treatment proved an effective technique for O/W emulsion breaking, oil products and surfactants degradation. Similar results of efficient oil product removal from simulated O/W emulsions by the Fenton chemistry were demonstrated by Tiburtius et al. (2005) and Galvão et al. (2006); however in those cases the Fenton treatment was UV-light assisted. Thus, the results of the present study demonstrated that hydrogen peroxide catalyzed by ferrous ions can effectively remediate complex wastewater samples containing commercial surfactants and diesel without the application of UV irradiation.

Paper II

Four samples of oil shale semicoke leachate were subjected to the Fenton-based treatment. In order to insure the complete utilization of hydrogen peroxide the assessment of the efficiency was done on the basis of a 24-hours treatment test.

However, it was ascertained that the reaction proceeded rapidly at the initial stage of the treatment and was mainly completed during first 2 hours of the Fenton oxidation.

Hydrogen peroxide oxidation solely (3:1 H_2O_2/COD weight ratio) resulted in 10-15% COD removal from leachate samples. The addition of ferrous catalyst led to a significant increase of the process efficiency. The COD removal was strongly dependent of the H_2O_2/COD ratio (*Paper II*, *Figures 4 and 5*) and increased with increase of the Fenton's reagent dosage.

The application of Fenton-like system without pH adjustment also proved efficient in oil shale semicoke leachate treatment (*Paper II*, *Figure 4*). It was ascertained that in the trials without pH adjustment the pH rapidly dropped to values favourable for the classic Fenton oxidation. The fast decrease in pH at the beginning of oxidation is probably due to a slight acidity of the both reagents in Fenton-like system and subsequently due to the formation of some acidic intermediates.

The highest 72-86% COD reduction was achieved with H_2O_2/COD weight ratio of 3:1 (*Paper II*, *Table 3*). Additionally, higher than 90% reduction of the samples' UV absorbance, indicating substantial degradation of organics, was observed.

The Fenton process with stepwise addition of hydrogen peroxide was also tested. Stepwise addition of hydrogen peroxide is recommended by several authors for improvement of the Fenton treatment performance, as slow addition of hydrogen peroxide to the system provides conditions that minimize quenching of hydroxyl radicals (Neyens and Baeyens, 2003; Teel et al., 2001). In the present study the manner of hydrogen peroxide addition did not affect considerably the efficiency of the leachate treatment. Therefore it can be concluded that hydrogen peroxide may be added all at once.

The results of this study suggest that under some circumstances the Fenton-based treatment could be used as the main treatment process for oil shale semicoke leachate.

Paper III

The classic and modified Fenton processes were applied to AB74, AO10 and AV19 aqueous solutions. Complete decolourization (or near to complete for low oxidant dosages) of dye solutions took place during the Fenton-based oxidation. The colour removal was easier than COD elimination, indicating that the chromophoric groups were first destroyed during the degradation of dyes. Accordingly, in order to demonstrate the highest available COD removal of studied dye solutions, the duration of oxidation trials was 24 hours.

The classic Fenton treatment of dyes showed similar COD removal dependence on hydrogen peroxide dosage (*Paper III*, *Figure 1*). Dye/H_2O_2 weight ratio of 1:2 proved optimal and resulted in 37, 27 and 40 percent of COD residual for AB74, AO10 and AV19, respectively. The same effect of hydrogen peroxide dose in the Fenton oxidation was observed for the aromatic carbon (UV_{254}) and general organic content (UV_{max}) removal in dye solutions (*Paper III*, *Figure 2*). Similar optimal conditions were established by Dutta et al. (2001) for thiazine dye oxidation by the Fenton's reagent.

Further increase of hydrogen peroxide amount did not markedly increase dye degradation. At higher hydrogen peroxide concentration, there is a competition between the substrate and H_2O_2 to react with hydroxyl radicals. Therefore, H_2O_2 in high concentrations acts as a scavenger of the hydroxyl radicals and produces hyperoxyl radicals, which have substantially lower oxidation capacity than hydroxyl radicals.

In trials with hydrogen peroxide oxidation, complete colour and moderate UV absorbance removal in AB74 and AV19 aqueous solutions was observed. In the case of AO10, hydrogen peroxide oxidation was absolutely ineffective, that is in accordance with data obtained by Solozhenko et al. (1995) for another azo dye.

Hydrogen peroxide oxidation with Fe^{2+} addition without pH adjustment resulted in the same COD and UV absorbance removal as the Fenton treatment trials. The reason to this is a rapid drop of solutions' pH from the initial level to 3 within seconds and subsequent decrease to 2.7-2.9 during the next 1-2 minutes. Consequently, the difference of process pH between H_2O_2/Fe^{2+} systems with and without pH adjustment was negligible.

In the case of hydrogen peroxide catalyzed by Fe^{3+} ions without pH adjustment, no rapid pH decrease was observed. However, after 24 hours of oxidation, pH values of dye solutions decreased to 2.8, 2.9 and 3.4 for AB74, AO10 and AV19, respectively. Thus, the mechanism of H_2O_2/Fe^{3+} oxidation principally differs from the classic Fenton reaction pathway, but intermediates in both cases are acidic compounds.

The moderate doses of hydrogen peroxide catalyzed by Fe^{3+} at initial dye solutions' pH values showed a degradation effectiveness of AB74 and AO10 comparable with efficacy of the classic Fenton treatment (*Paper III*, *Figure 4*). In the case of AV19, the removal of COD and UV absorbance was lower than for the H_2O_2/Fe^{2+} system. Subsequent increase in oxidant dose in the H_2O_2/Fe^{3+} system resulted in higher degradation of all dyes than for the Fenton treatment.

The adjustment of pH to 3 in H_2O_2/Fe^{3+} system improved the oxidation efficacy of all investigated dyes (*Paper III*, *Figure 4*). Furthermore, in the case of reasonable doses of hydrogen peroxide, the use of Fe^{3+} catalyst and regulation of reaction solution pH to 3 turned out to be the most feasible among the investigated methods in COD, aromatic carbon and general organic content removal from indigoid, azo and triarylmethane dye solutions.

Paper IV

Modification of the H_2O_2/Fe^{2+} system applied for pharmaceutical wastewater represented the treatment process without pH adjustment. During the very beginning of the oxidation, a fast decrease of reaction mixture's pH was observed even at 0.8:1 H_2O_2/COD weight ratio. In the case of small oxidant amount, such as

0.1:1 H_2O_2/COD weight ratio, the pH decrease in pharmaceutical wastewater samples was time-consuming, but finally 2 h of oxidation resulted in pH value of 3.5, 3.2 and 2.6 for Effluent I, II and III, respectively.

The relationship between the oxidative reaction time and COD removal indicated considerable improvement in total treatment efficacy during the first 2 h of Fenton-like oxidation (*Paper IV*, *Figure 1*). Further increase in oxidation time to 4-6 h resulted in 1-3% additional COD removal, and thus proved economically unjustified.

The Fenton-based treatment efficacy proved dependent on wastewater composition, and thus irrespective of reaction duration, Effluent I was more recalcitrant to oxidation than Effluent II and Effluent III.

The increase in H_2O_2/COD ratio led to quality improvement of pharmaceutical wastewater samples (*Paper IV*, *Figure 2*). The most efficient H_2O_2/COD weight ratio for Effluent I and II was 2:1 with residual COD of 13 and 6%, respectively, and 1:1 for Effluent III with residual COD of 5%.

In order to evaluate the possibility of ferrous iron dosage reduction, and subsequent decrease in the amount of sludge produced during Fenton-like treatment, influence of different H_2O_2/Fe^{2+} ratios on pharmaceutical effluents' treatment efficacy was investigated (*Paper IV*, *Figure 3*). The results indicated a reduction in treatment efficacy with decrease in ferrous ions amount in the reaction mixture. The H_2O_2/Fe^{2+} molar ratio of 10:1 was proved preferable and was applied in all Fenton-like oxidation trials.

3.1.2. Combination with lime milk coagulation

In the Fenton treatment of wastewater, oxidation and coagulation by generated iron sludge both contribute to removal of organic constituents, though the effect of coagulation has not been well recognized. The improvement of coagulation step of the Fenton system by means of lime milk addition was first applied for simulated dyes contaminated water (*Paper III*) and subsequently utilized for real effluents from pharmaceutical plant (*Paper IV*)

Paper III

In all trials with application of combined Fenton chemistry and lime coagulation, the CaO dosage was kept between 200-400 mg L^{-1}. However, less than 200 mg of CaO per litre was enough to remove the solutions' colour completely. Preliminary blank experiments in coagulation with lime milk indicated no decolourization of AO10 and AV19 solutions. In the case of indigoid dye, 75% of colour was removed by 400 mg of CaO per litre of dye solution coagulation (CaO/dye weight ratio of 1:2.5).

The post-coagulation with lime milk resulted in similar removal efficacy for both the Fenton and Fenton-like pre-treatment methods with the same hydrogen peroxide dosage applied (*Paper III*, *Figure 5*). Moreover, combined treatment proved the most feasible COD and UV absorbance removal method: UV absorbance of AB74, AO10 and AV19 was almost entirely removed even in trials with low hydrogen peroxide doses. Dye/H_2O_2 weight ratio of 1:1 was sufficient to achieve the maximum possible treatment efficacy of AB74 and AV19 solutions and resulted in more than 30, 50 and 35% of additional COD, UV_{254} and UV_{max} absorbance removal, respectively, in comparison with the Fenton oxidation solely. As for AO10, the most effective pre-oxidation dye/H_2O_2 weight ratio was 1:2, and additional COD, UV_{254} and UV_{max} absorbance removal comprised 32, 65 and 48%, respectively.

Paper IV

A simple ferric iron coagulation and improved one by addition of CaO with subsequent combined ferric/lime precipitation were used for pre-oxidized wastewater samples (*Paper IV*, *Figure 1*). Both coagulation techniques resulted in lower than 2 mg L^{-1} residual iron concentration for all treated wastewater samples. Additionally, no traces of hydrogen peroxide in effluents were observed. In the case of COD removal, the results of different coagulation procedures were not similar and in general indicated higher efficacy of the combined ferric/lime precipitation. Thus, 3-14% additional COD removal was achieved for pharmaceutical effluents by application of combined coagulation step.

The CaO dosages in the range 250-750 mg L^{-1} were applied to find the preferable one for effective COD removal in all investigated effluents. The lime dose of 500 mg L^{-1} proved the most feasible from the quality improvement and the economic points of view.

The blank trials on coagulation with lime and ferric iron indicated ineffectiveness of both coagulants in improving the quality of pharmaceutical effluents.

Combined Fenton chemistry and subsequent lime coagulation proved more effective for acidic dyes degradation and pharmaceutical wastewater quality improvement than the Fenton-based treatment alone.

3.1.3. Biodegradability

To evaluate the option of the subsequent biological post-treatment of the studied wastewater samples, BOD_7 and BOD_7/COD were analyzed after Fenton/Fenton-like treatment.

The application of Fenton treatment showed significant COD and BOD_7 removal, but no improvement in O/W wastewater samples biodegradability (*Paper I*, *Figure 5*). The results indicated lower biodegradability of the Fenton pre-treated than untreated wastewater samples. In general, the enhancement in degradation of contaminants by increasing H_2O_2/COD ratio demonstrated identical increase in biodegradability of the samples. The highest BOD_7/COD ratio achieved for both wastewater samples was somewhat higher than 0.5, representing moderate final biodegradability.

It was ascertained that the Fenton treatment led to significant improvement of oil shale semicoke leachate biodegradability (*Paper II*, *Tables 1 and 3*). Even 0.96 BOD_7/COD ratio value was achieved, indicating virtually complete biodegradability of the Fenton pre-treated leachate.

The application of Fenton oxidation improved the biodegradability of all studied dye solutions (*Paper III*, *Figure 3*). Thus, the Fenton pre-oxidation of AB74 and AV19 even at dye/H_2O_2 weight ratio of 1:0.5 resulted in a twofold increase of the BOD_7/COD ratio in comparison with the initial samples. In the case of AO10, low hydrogen peroxide doses were ineffective in enhancing subsequent biodegradation. However, further increase of the oxidant dosage in the pre-treatment step to dye/H_2O_2 weight ratio of 1:1 raised the value of BOD_7/COD ratio from 0.18 to 0.46. A possible explanation to this is the breakdown of the azo bonds during azo dye decolourization, which leads to the formation of aromatic amines that are only partially degraded by low doses of hydrogen peroxide. The formed intermediates are not biodegradable and are more toxic than dye itself.

The biodegradability of pharmaceutical effluents was substantially improved by combined Fenton-based treatment (*Paper IV*, *Figure 4*). The highest BOD_7/COD ratios for Effluent I and II were achieved after oxidation at H_2O_2/COD weight ratio of 2:1 and resulted in 60 and 33% biodegradability increase, respectively, if compared with the initial values. In the case of Effluent III, the highest BOD_7/COD increase of 11% was observed after the application of hydrogen peroxide to COD weight ratio of 1:2.

The Fenton-based treatment proved efficient tool to eliminate recalcitrant organic compounds from wastewater. The degradation of toxic and biorefractory organic compounds increases content of hydrophilic substances, saturates water with oxygen via hydrogen peroxide decomposition, and breaks down complex compounds into simpler ones that are easier to degrade. Thus, the application of Fenton/Fenton-like pre-treatment facilitates subsequent biological processing of the studied wastewater samples.

3.1.4. Toxicity

The acute toxicity to *Daphnia magna* was evaluated by 24-hours test for surfactant stabilized O/W emulsions, oil shale semicoke leachate and acidic dyes solutions after the Fenton pre-treatment.

The application of such techniques as ozonation or photocatalytic oxidation was found to enhance the biodegradability of refractory surfactants, yet some by-products are more toxic than the initial compounds. In the case of the Fenton treatment, reduction of O/W wastewater samples toxicity was achieved, as demonstrated in *Paper I*, *Table 3*. Both commercial detergents' contaminated wastewater samples were found to be detoxified even with moderate hydrogen peroxide dosages in the pre-oxidation step.

The toxicity reduction after the Fenton oxidation of oil shale semicoke leachate was of great significance (*Paper II*, *Table 3*). Even application of low H_2O_2/COD weight ratios in the Fenton pre-treatment step resulted in substantial detoxification of leachate samples. Further increase in H_2O_2/COD weight ratio to 3:1 demonstrated 2.3-fold to 5.5-fold reduction of the toxicity after the Fenton treatment.

The acute toxicity of the initial and treated dye aqueous solutions to *Daphnia magna* was also studied. The initial dye solutions and pre-treated with moderate hydrogen peroxide doses AO10 and AV19 samples proved to be non-toxic. In the case of AB74, a moderate dosage of hydrogen peroxide led to the formation of toxic compounds, which retarded BOD_7/COD ratio increase (*Paper III*, *Figure 3*) and resulted in a slight toxicity of pre-treated dye solution.

Thus, the Fenton treatment could be effectively applied both for biodegradability improvement and detoxification of the studied wastewater samples.

3.1.5. Comparison of Fenton/Fenton-like treatment with other methods

Alternative treatment techniques to compare with the Fenton-based processes were applied for surfactant stabilized O/W emulsions (*Paper I)* and oil shale semicoke leachates (*Paper II)*.

Coagulation (*Paper I*)

The oil product content removal, and consequently O/W emulsion breaking was more effective than COD diminution by coagulation with different inorganic agents (*Paper I*, *Figures 1 and 3*). The highest COD removal of 36% was achieved by lime milk application. For all investigated wastewater samples, UV_{220} absorbance reduction was comparable to UV_{254} absorbance reduction due to oil product elimination.

The coagulation trials with all studied wastewater samples demonstrated no improvement or even lower BOD_7/COD ratio. Only in the case of lime milk as a coagulating agent, the biodegradability of the treated wastewater sample was the same or somewhat higher than for the untreated sample. No detoxification of wastewater samples during coagulation by different agents was found (*Paper I*, *Table 3*). Moreover, the toxicity of wastewater increased after coagulation. The sensible explanation of the presented finding is a partial removal of compounds that mitigates a very strong toxic effect of others substances remaining in the sample after coagulation.

Therefore, it was concluded that coagulation is ineffective treatment technique for surfactant stabilized O/W wastewater samples as well as pre-treatment step to facilitate subsequent biological degradation of residual contaminants.

Ozonation (*Paper II*)

Three-hour ozonation of oil shale semicoke leachate enabled to remove from 40 to 63% of COD (*Paper II*, *Figure 1*) and was linearly related to ozone consumption. The degradation of organics was reflected in the UV absorbance decrease at wavelength of 220 and 254 nm (*Paper II*, *Figure 2*).

The initial leachate was partly biodegradable. The ozonation led not only to the considerable reduction of COD but also enabled to enhance the biodegradability. However, 40-45% of the residual organics proved not biodegradable (*Paper II*, *Table 2*). Ozonation did not lead to the detoxification of leachate (*Paper II*, *Table 2*). In the best case, the toxicity of the pre-ozonated sample was the same as for untreated leachate, whereas in the rest of the experiments the toxicity of the pre-ozonated samples increased with respect to the initial one. The observed toxicity increase in the present study may be at least partly explained with the formation of the same ozone-resistant toxic by-products during ozonation of the phenols present in the leachate.

To summarize the results of oil shale semicoke leachate treatment, the application of Fenton chemistry proved more feasible than ozonation for leachate quality improvement.

3.2. Soil treatment

The Fenton-based treatment proved effective not only for wastewater quality improvement but also for soil remediation. In the present work the degradation of PAH originated from commercial creosote by Fenton-like treatment was studied. The combination of chemical oxidation and subsequent biological treatment to overcome bioremediation limitation of PAH in creosote contaminated soil was also investigated.

3.2.1. Fenton-like treatment

Fenton-like reactions at neutral pH were found to promote greater PAH mineralization than the same reactions conducted at acidic pH regimes (Watts et al., 2002). Thus, in the present study Fenton-like processes were conducted without pH adjustment at soil's natural pH.

The removal of PAH in creosote contaminated sand and peat during 24-hours Fenton-like treatment is presented in *Paper V*, *Figure 3*. The degradation of PAH proved dependent on applied H_2O_2/soil weight ratio, catalyst addition and the soil matrix of treated samples.

The efficiency of Fenton-like treatment depended on the soil matrix; higher PAH removal was achieved in sand than in peat. Degradation of PAH in peat during oxidation may be limited by the rate of desorption and by elevated content of soil naturally occurring organic matter, which may consume significant amount of hydroxyl radicals.

The application of the same hydrogen peroxide doses resulted in a higher PAH degradation in creosote contaminated sand in case of oxidation by hydrogen peroxide with ferrous ions addition than for oxidation by hydrogen peroxide without a supplementary catalyst. Thus, the 0.172:1 H_2O_2/sand weight ratio resulted in 88.5 and 55% PAH removal for hydrogen peroxide treatment with and without Fe^{2+} addition, respectively. The same effect was observed by Ravikumar and Gurol (1994), who ascertained that organic contaminants could be oxidized by hydrogen peroxide with or without extra ferrous ions, although addition of ferrous ions resulted in a greater oxidation and more extensive reaction.

The use of 0.133:1 H_2O_2/peat weight ratio was more effective in case of treatment by hydrogen peroxide only and resulted in 45 and 51% PAH degradation with and without ferrous ions addition, respectively. Nevertheless, doubling of H_2O_2/peat weight ratio (from 0.133:1 to 0.266:1) led to 26% higher removal of PAH by hydrogen peroxide oxidation with catalyst supplement than without it (*Paper V*, *Figure 3*).

Increasing the H_2O_2/soil/Fe^{2+} weight ratio enhanced PAH removal in creosote contaminated sand and peat. PAH degradation with the addition of hydrogen peroxide only was also depended on H_2O_2/soil weight ratio, but results obtained for hydrogen peroxide treatment without ferrous ions supplement differed from those for treatment by hydrogen peroxide with Fe^{2+} addition. Thus, increase of the H_2O_2/soil weight ratio did not improve the degradation and even resulted in a decrease of PAH removal. A possible explanation for these could be the scavenging of hydroxyl radicals by hydrogen peroxide in the presence of excess of hydrogen peroxide. At high concentrations hydrogen peroxide could compete with organic contaminants for hydroxyl radicals, reducing the efficacy of hydroxyl radical oxidation of organic compounds.

In general, the oxidation of creosote contaminated soil by hydrogen peroxide with and without supplementary ferrous ions resulted in a more complete 3-ring PAH removal compared to 4-ring PAH (*Paper V*, *Figure 3*).

The Fenton-based treatment proved a promising method of removing PAH from both creosote contaminated sand and peat, although it was more feasible for organic-poor sand matrix.

3.2.2. Biodegradation and combined Fenton-like and biological treatment

The elimination of PAH from the Fenton-like pre-treated soil by bioremediation was found to be dependent on the pre-treatment conditions and the matrix of soil samples (*Paper V*, *Figures 4 and 5*).

The results of the present study indicate that 3-ring PAH removal was higher than 4-ring PAH removal for the period of biodegradation. This is in agreement with Wilson and Jones (1993) and Nam et al. (2001), who determined that biodegradation of low molecular weight (2- and 3-ring) PAH occurred much more rapidly and extensively than of high molecular weight (4-, 5- and 6-ring) hydrocarbons.

The bioremediation of the chemically untreated soil resulted in a higher removal of PAH in peat compared to sand. Thus, 30 and 56% of PAH were degraded in sand and peat, respectively, by four-week incubation. Most likely, the natural organic matter presented in peat could be a nutrient for the microorganisms and, hence, could facilitate PAH biodegradation in creosote contaminated peat. However, doubling of biotreatment duration resulted in 18 and only 3% of additional PAH removal in sand and peat, respectively.

The treatment of the Fenton's control patterns of sand and peat by twice-distilled water for 24-hours did not heighten the bioavailability of PAH and resulted in the same removal of contaminants during the incubation as in chemically untreated soil samples.

The application of combined Fenton-like pre-treatment and biodegradation for the remediation of creosote contaminated sand demonstrated a remarkable overall PAH removal (*Paper V*, *Figure 4*). The oxidation by hydrogen peroxide with and without supplementary ferrous ions and the subsequent 8 weeks of incubation resulted in 94 and 85.5% PAH degradation, respectively. The additional PAH degradation for the period of 8-week bioremediation was 20.5 and 16.5% for hydrogen peroxide pre-treated sand with and without catalyst supplement, respectively. Thus, the release of oxygen during the decomposition of hydrogen peroxide in soil could stimulate aerobic biological activity. Moreover, the pre-oxidation of the PAH could lead to oxidation products that are more soluble in water and more easily available to microorganisms.

The results obtained for peat noticeably differed from those for sand (*Paper V*, *Figure 5*). There was only slight improvement of PAH biodegradability after hydrogen peroxide pre-treatment of creosote contaminated peat with/without ferrous ions addition. This could be explained by the inhibition of biodegradation caused by residual hydrogen peroxide that possibly will remain in soil after the application of high doses of hydrogen peroxide.

The results of the present study indicated that combined Fenton-based and biological treatment led to a more effective removal of PAH in creosote contaminated soil than either one alone. The combination of Fenton-like pre-treatment and the following biodegradation was more efficient technology for PAH removal in sand than in peat.

3.2.3. Comparison of Fenton-like pre-treatment/treatment with ozonation

As an alternative treatment technique a two-phase and three-phase ozonation was applied for the degradation of PAH in creosote contaminated sand and peat. Ozonation was found to be an effective technology for PAH removal in creosote contaminated soil. However, similar to the Fenton-based treatment the efficiency of the process depended strongly on the soil matrix and water content of the treated soil samples (*Paper V*, *Figure 1*). Three-phase and two-phase ozonation of PAH adsorbed on sand resulted in a higher PAH degradation and required lower ozone doses than ozonation of PAH adsorbed on peat. The removal of PAH and doses of ozone consumed during the ozonation of creosote contaminated soil in different systems are presented in *Paper V*, *Table 2*.

Having compared the two ozonation systems, it was concluded that two-phase ozonation was more efficient both in terms of PAH degradation and doses of ozone consumed.

It was found that during oxidation processes in both ozonation systems 4-ring PAH degraded in creosote contaminated sand and peat at approximately the same or higher rate than 3-ring PAH (*Paper V*, *Figure 2*). The results are similar to those obtained by other authors, who determined that low-molecular weight PAH (3-ring) degraded with ozone slower than higher-molecular weight (4-ring) PAH in aqueous medium (Trapido et al., 1995).

Considering all this evidence, it could be concluded that ozonation is effective in removing PAH from creosote contaminated soil, especially in case of PAH adsorbed on a sand matrix, but less feasible than the Fenton-based treatment.

The two-phase pre-ozonation of creosote contaminated soil was found to be an effective technology for the enhancement of PAH bioavailability. Although PAH elimination during the oxidation by ozone was higher in sand (53%) than in peat (35%), combining ozonation with subsequent biodegradation resulted in approximately the same (75%) removal of PAH in both soil matrixes (*Paper V*, *Figures 4 and 5*). The improvement of PAH biodegradability could be explained by the fact that ozonation generates more water-soluble and oxygenated metabolites, which are also more bioavailable.

It was ascertained that biodegradation with pre-ozonation could be applied as a feasible alternative to Fenton-like pre-treatment and subsequent biological degradation of PAH in creosote contaminated peat.

3.3. Final remarks

In the century since the discovery, the Fenton and related processes have become of a great interest for their relevance to the treatment of wastewater and soil remediation. As a result, the number of scientific publications on applications of the Fenton-based treatment has increased exponentially over the last years.

Nowadays it is known that the Fenton-based processes are capable of degrading organic compounds in a variety of contaminated media. In general, comparison of the Fenton-based processes with other AOP is quite favorable for the Fenton treatment. The latter can be performed at ambient temperature, without regulation of pH and without any irradiation, although the Fenton reaction could be frequently accelerated by light or by electron beam. For example, the photo-Fenton system typically gives faster rates and a higher degree of mineralization than the classic reaction and can take advantage of light in the solar spectral region.

The Fenton treatment can be implemented both alone and together with other technologies for wastewater and soil treatment. Generally, the most promising application of the Fenton chemistry involves coupling of the Fenton process with other treatment process or integrating the process into an existing treatment scheme. Similarly, in the present study the combination of Fenton-based system with subsequent lime milk coagulation proved feasible to improve total wastewater treatment process efficacy. Wastewater and soil biological treatment may be also improved with the addition of Fenton/Fenton-like pre-treatment step and as demonstrated in the current study.

The areas of the Fenton chemistry application can be enlarged by introducing novel variations of the Fenton system. For instance, the heterogeneous reactions and the preparation of supported iron catalysts are extensively studied in order to facilitate the reactions in soil and to avoid the problem of iron oxide sludge generation and disposal, which is inherent in the homogeneous Fenton treatment of wastewater. Further research on many other aspects of the Fenton chemistry is still needed to achieve breakthrough into a full-scale application. Thus, studies designed to limit the process side reactions, to increase use of heterogeneous catalysts and solid sources of iron, such as minerals and zero valent iron, and to use advances of electro-Fenton and photo-Fenton systems have to be continued. For successful application of the Fenton-based treatment processes for soil remediation, the ways to overcome mass transfer limitations associated with reagent delivery, which are particularly limiting in the case of Fenton due to the instability of the reagent mixture and decomposition of the bulk oxidant by the matrix, must to be found.

4. CONCLUSIONS

The results of the study can be summarized as follows:

1. The Fenton chemistry could be efficiently applied for surfactant stabilized O/W emulsions, oil shale semicoke leachate, acidic dyes solutions and pharmaceutical effluents treatment and quality improvement. The efficacy of wastewater treatment was dependent on the catalyst, pH, hydrogen peroxide concentration and oxidation duration. It was ascertained that the Fenton-based treatment of wastewater samples may be applied without pH adjustment. In the case of acidic dyes degradation, the H_2O_2/Fe^{3+} system with pH adjusted to 3 was the most efficient treatment technique. In general, the application of Fenton chemistry resulted in substantial COD, BOD_7, colour and UV absorbance removal. For all wastewater samples investigated the Fenton oxidation was mainly complete during the first 2 hours of treatment.

2. The combination of Fenton chemistry and subsequent combined ferric/lime coagulation proved very promising treatment process in the removal of COD, UV absorbance and improving overall wastewater quality.

3. The Fenton-based treatment was found capable of complete or near to complete detoxification of surfactant stabilized O/W emulsions and oil shale semicoke leachate and resulted in no or negligible formation of toxic intermediates during acidic dyes degradation. The reduction of the toxicity favours the subsequent biodegradation and, in most cases, considerable COD reduction and BOD_7/COD ratio increase was observed. Thus, the Fenton chemistry proved attractive as a pre-treatment technology for subsequent biological treatment of wastewater samples.

4. The Fenton-based treatment without pH adjustment proved feasible tool for the elimination of PAH in creosote contaminated soil. The efficiency of treatment was dependent on the soil matrix, and thus degradation of PAH in sand by chemical treatment required lower hydrogen peroxide doses and resulted in a higher removal of contaminants compared to peat. The extent of PAH removal by Fenton-like treatment depended on applied H_2O_2/soil weight ratio and catalyst addition. The application of oxidation by hydrogen peroxide with supplementary ferrous ions indicated a higher removal of PAH in both soil matrixes if compared with oxidation by hydrogen peroxide only. Increasing the $H_2O_2/soil/Fe^{2+}$ weight ratio enhanced PAH degradation in creosote contaminated soil.

5. The application of Fenton-like pre-oxidation enabled to overcome effectively the PAH recalcitrance to biodegradation in creosote contaminated sand. In the case of creosote contaminated peat, the PAH bioavailability improvement by Fenton-based pre-treatment was negligible; alternatively, pre-ozonation of peat samples to facilitate the subsequent bioremediation could be used.

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ABSTRACT

The Application of Fenton-based Processes for Wastewater and Soil Treatment

The present study was aimed at enlarging the area of the Fenton chemistry application for wastewater treatment and soil remediation. The Fenton chemistry is a part of advanced oxidation processes (AOP), which involve the generation of highly reactive oxidants such as hydroxyl radicals, has been increasingly used for degradation of the variety of organic contaminants.

Wastewater samples of surfactant stabilized oil-in-water emulsions, oil shale semicoke leachate, solutions of acidic dyes, and pharmaceutical effluents from medical ointment production and soil samples of commercial creosote contaminated sand and peat were subjected to Fenton/Fenton-like treatment. The combination of Fenton-based treatment with lime coagulation for wastewater samples and with biological post-treatment for soil samples was also studied.

The application of Fenton chemistry proved effective to improve the quality of all studied wastewater samples. The efficacy of wastewater treatment was dependent on the catalyst, pH, hydrogen peroxide concentration and oxidation duration. The Fenton-based treatment was found to be feasible for wastewater treatment without pH adjustment. The combination of Fenton chemistry and subsequent combined ferric/lime coagulation improved the overall efficacy of wastewater treatment. Additionally, the Fenton-based wastewater treatment resulted in complete or near to complete detoxification and biodegradability improvement, and thus proved attractive as a pre-treatment technology for subsequent biological processing of wastewater.

The Fenton-like treatment was found to be feasible to degrade substantially PAH in creosote contaminated soil. The efficiency of treatment was dependent on the soil matrix; degradation of PAH in sand by chemical treatment required lower hydrogen peroxide doses and resulted in a higher removal of contaminants compared to peat. The removal of PAH by Fenton-like treatment depended on applied hydrogen peroxide dosage and catalyst addition. The Fenton-based treatment of soil was efficiently catalysed by naturally occurring iron without addition of supplementary ferrous ions. The application of Fenton-like pre-treatment enabled to overcome effectively the PAH recalcitrance to biodegradation. Combined chemical and subsequent biological treatment proved more effective than either one alone for remediation of creosote contaminated soil.

The results of this study are unique and could provide important information for practical purposes.

KOKKUVÕTE

Fentoni protsesside rakendamine reovete ja pinnaste töötlemiseks

Antud töö eesmärgiks oli laiendada Fentoni protsessi kasutamist reovete ja pinnaste töötlemiseks. Fentoni protsess on osa süvaoksüdatsiooni protsessidest, milles toimub kõrge potentsiaaliga keemiliste oksüdantide, nagu hüdroksüülradikaal, genereerimine. Viimasel ajal kasutatakse Fenton-töötlust laialdaselt erinevate orgaaniliste saasteainete lagundamiseks.

Pesuvahendiga stabiliseeritud õli/vee emulsioone, põlevkivi poolkoksi nõrgvett, värvainetega saastatud reovett, farmaatsiatööstuse reovett ning kaubandusliku kreosoodiga saastatud liiva ja turvast töödeldi Fentoni/Fentonile sarnase süsteemiga. Samuti uuriti Fenton-töötluse kombinatsiooni lubja järelkoagulatsiooniga reovete puhul ning järgneva bioloogilise töötlemisega pinnase proovide puhul.

Fentoni protsessid osutusid efektiivseks töötlemismeetodiks ning parandasid uuritud vete kvaliteeti. Reovete töötlemise efektiivsus sõltus katalüsaatorist, pH-st, vesinikperoksiidi kontsentratsioonist ning oksüdeerimise kestvusest. Reovete töötlemine Fentoni protsessiga oli efektiivne ka pH reguleerimiseta. Fenton-töötlus koos järgneva raud(III)/lubja koagulatsiooniga oli kõige tõhusam meetod. Reovete töötlemine Fentoni protsessidega vähendas tunduvalt või isegi elimineeris täielikult toksilisuse ning suurendas märgatavalt proovide biolagundatavust. Seega, Fentoni/Fentonile sarnast süsteemi võib edukalt kasutada nii reovete põhipuhastusmeetodina kui ka eeltöötlusmeetodina enne biopuhastamist.

Fentonile sarnane süsteem võimaldas tõhusalt vähendada polütsükliliste aromaatsete süsivesinike (PAH-de) sisaldust kreosoodiga saastatud pinnastes. Saadud tulemustest selgus, et töötlemise efektiivsus sõltus suurel määral pinnase maatriksist. Liivasse sorbeerunud PAH-d lagunesid keemilise töötlemise toimel kergemini ning nõudsid väiksemat oksüdeerija kogust, võrreldes turbasse sorbeerunud PAH-dega. Kreosoodiga saastatud pinnaste töötlemise efektiivsus sõltus katalüsaatorist ning vesinikperoksiidi kontsentratsioonist. Pinnases olev raud katalüüsis efektiivselt vesinikperoksiidi katalüsaatori lisamiseta. Fentonile sarnase protsessiga eeltöötlemine suurendas PAH-de biolagundatavust ning seega oli kreosoodiga saastatud pinnase taastamist efektiivsem teostada kombineeritud meetodiga, võrreldes ainult biolagundamise või keemilise töötlemisega.

Käesoleva uurimistöö tulemused on unikaalsed ning annavad väga olulist informatsiooni praktiliseks kasutamiseks.

APPENDIX A

PAPER I

Kulik, N., Trapido, M., Veressinina, Y., Munter, R.
Treatment of surfactant stabilized oil-in-water emulsions by means of chemical oxidation and coagulation.

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Environmental Technology, 2007, 28, 1345-1355.

PAPER II

Trapido, M., Munter, R., Veressinina, Y., Kulik, N.
Oil shale semicoke leachate treatment using ozonation and the Fenton oxidation.

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Environmental Technology, 2006, 27, 307-315.

PAPER III

Kulik, N., Panova, Y., Trapido, M.
The Fenton chemistry and its combination with coagulation for treatment of dye solutions.

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Separation Science and Technology, 2007, 42, 1521-1534.

PAPER IV

Kulik, N., Trapido, M., Goi, A., Veressinina, Y., Munter, R.
Combined treatment of pharmaceutical effluents from medical ointment production.

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Chemosphere, 2008, 70, 1525-1531.

PAPER V

Kulik, N., Goi, A., Trapido, M., Tuhkanen, T.
Degradation of polycyclic aromatic hydrocarbons by combined chemical pre-oxidation and bioremediation in creosote contaminated soil.

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Journal of Environmental Management, 2006, 78, 382-391.

APPENDIX B

ELULOOKIRJELDUS

1. Isikuandmed

Ees- ja perekonnanimi: Niina Kulik
Sünniaeg ja -koht: 18.08.1981, Tallinn
Kodakondsus: Eesti

2. Kontaktandmed

Aadress: TTÜ, Ehitajate tee 5, Tallinn, 19086, Eesti
Telefon: +3726204341
E-posti aadress: niina.kulik@ttu.ee

3. Hariduskäik

Õppeasutus (nimetus lõpetamise ajal)	Lõpetamise aeg	Haridus (eriala/kraad)
Tallinna Tehnikaülikool	2004	Tehnikateaduste magistrikraad
Tallinna Tehnikaülikool	2003	Tehnikateaduste bakalaureusekraad ***Cum laude***
Tallinna Tõnismäe Reaalkool	1999	Keskharidus

4. Keelteoskus (alg-, kesk- või kõrgtase)

Keel	Tase
Eesti keel	Kõrgtase
Vene keel	Kõrgtase
Inglise keel	Kõrgtase

5. Täiendusõpe

Õppimise aeg	Täiendusõppe läbiviija nimetus
September - Detsember, 2006	Adam Mickiewicz University, Department of Water Treatment Technology, Poznań, Poola. Teadur
Mai - Juuli, 2007	Tampere University of Technology, Department of Environmental Engineering and Biotechnology, Tampere, Soome. Teadur

6. Teenistuskäik

Töötamise aeg	Tööandja nimetus	Ametikoht
2007 - …	Tallinna Tehnikaülikool, UTTP doktorikool	Erakorraline teadur
2006 - …	Tallinna Tehnikaülikool, Keemiatehnika instituut	Insener

7. Kaitstud lõputööd

Tehnikateaduste magistritöö: Nafta- ja põlevkivitööstuse tootmisproduktidega saastatud pinnaste taastamine kombineeritud oksüdatsiooni protsessidega. Tallinna Tehnikaülikool, 2004. Juhendaja: Marina Trapido

Tehnikateaduste bakalaureusetöö: Diislikütusega saastatud pinnaste taastamine kombineeritud täiustatud oksüdatsiooni protsessidega. Tallinna Tehnikaülikool, 2003. Juhendaja: Marina Trapido

8. Teadustöö põhisuunad

SF0142719s06 Tehnoloogiliste protsesside intensiivistamine aktuaalsete keskkonnaprobleemide lahendamiseks

ETF6564 Modifitseeritud Fenton-protsessi kasutamise uurimine orgaaniliste saasteainete kõrvaldamiseks kombineeritud heitvee töötlusskeemides

G4974 Täiustatud oksüdatsiooniprotsesside kasutusvõimaluste uurimine nafta- ja põlevkivitööstuse tootmisproduktidega saastatud pinnaste taastamiseks ja tahkete jäätmete töötlemiseks

9. Teised uurimisprojektid

482L Pesemisvahendi ANROL kasutamisel tekkiva emulsioonse jääkvee lahutamise ja utiliseerimise võimaluste uurimine

529L Roostevabast materjalist detailide keemilise passiveerimise jääklahuste neutraliseerimine

654L Salvivalmistamise seadmete pesuvee töötlemine

CURRICULUM VITAE

1. Personal data

Name: Niina Kulik
Date and place of birth: 18.08.1981, Tallinn
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2. Contact information

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3. Education

Educational institution	Graduation year	Education (field of study/degree)
Tallinn University of Technology	2004	M.Sc. in Engineering
Tallinn University of Technology	2003	B.Sc. in Engineering ***Cum laude***
TTRK High School	1999	High school education

4. Language competence/skills (fluent, average, basic skills)

Language	Level
Estonian	Fluent
Russian	Fluent
English	Fluent

5. Special courses

Period	Educational or other organisation
September - December, 2006	Adam Mickiewicz University, Department of Water Treatment Technology, Poznań, Poland. Researcher
May - July, 2007	Tampere University of Technology, Department of Environmental Engineering and Biotechnology, Tampere, Finland. Researcher

6. Professional employment

Period	Organisation	Position
2007 - …	Tallinn University of Technology, UTTP Doctoral School	Extraordinary Researcher
2006 - …	Tallinn University of Technology, Department of Chemical Engineering	Engineer

7. Defended theses
    - M.Sc. in Engineering: Application of combined advanced oxidation processes for remediation of oil and oil-shale industry products contaminated soils. Tallinn University of Technology, 2004. Supervisor: Marina Trapido
    - B.Sc. in Engineering: Application of combined advanced oxidation processes for remediation of diesel fuel contaminated soils. Tallinn University of Technology, 2003. Supervisor: Marina Trapido

8. Main areas of scientific work/Current research topics
    - SF0142719s06 Intensification of technological processes for the solution of actual environmental problems
    - ETF6564 A study on the applicability of modified Fenton oxidation in combined schemes for elimination of organics in wastewater treatment
    - G4974 Application of advanced oxidation processes for oil and oil shale products contaminated soils treatment and solid wastes processing

9. Other research projects
    - 482L Study on separation and utilisation of the emulsified wastewater from the application of the ANROL
    - 529L Neutralization of the waste solutions from the stainless steel components chemical passivation
    - 654L Treatment of wastewater from ointment production

PUBLICATIONS RELATED TO THE TOPIC

1. Goi, A., Trapido, M., **Kulik, N.**, Palmroth, M.R.T., Tuhkanen, T. 2006. Ozonation and the Fenton treatment for remediation of diesel fuel contaminated soil. *Ozone Science & Engineering*, 28, 37-46.
2. Goi, A., **Kulik, N.**, Trapido, M. 2006. Combined chemical and biological treatment of oil contaminated soil. *Chemosphere*, 63, 1754-1763.
3. Andrzejewski, P., **Kulik, N.** 2007. The Hazard of N-nitrosamine Formation during Short Chain Secondary Amines Reactions with Catalyzed and Non-catalyzed Hydrogen Peroxide. *In*: e-Proceedings of 10th Conference on Environmental Science and Technology, September 5-7, Kos Island, Greece, A45-A54.
4. **Kulik, N.**, Trapido, M., Goi, A., Veressinina, Y., Munter, R. 2007. Combined Treatment of Pharmaceutical Effluents from Medical Ointment Production. *In*: e-Proceedings of World Congress on Ozone and Ultraviolet Technologies, August 27-29, Los Angeles, CA, USA, 795-808.
5. Munter, R., Trapido, M., Veressinina, Y., Goi, A., **Kulik, N.** 2007. Which Process to Prefer: Ozonation Versus Typical AOPs. *In*: e-Proceedings of World Congress on Ozone and Ultraviolet Technologies, August 27-29, Los Angeles, CA, USA, 2310-2321.
6. **Kulik, N.**, Panova, Y., Trapido, M. 2006. The Fenton Chemistry and its Combination with Coagulation for Treatment of Dye Solutions. *In*: e-Proceedings of 1st European Conference on Environmental Applications of Advanced Oxidation Processes, September 7-9, Chania, Greece, P 164.
7. Trapido, M., Goi, A., **Kulik, N.** 2006. Advanced Oxidation Processes – A Study on the Application for Soil Remediation. *In*: e-Proceedings of 1st European Conference on Environmental Applications of Advanced Oxidation Processes, September 7-9, Chania, Greece, P 252.
8. **Kulik, N.**, Trapido, M., Veressinina, Y., Munter, R. 2006. Oil Shale Semicoke Leachate Pre-treatment by means of Advanced Oxidation. *In*: Proceedings of International Conference on Ozone and UV: Sustainable Solutions for Industry and the Environment, April 3, Berlin, Germany, 41-46.
9. Veressinina, Y., Trapido, M., **Kulik, N.**, Munter, R. 2005. Detoxification of Oil-Shale Wastes by Advance Oxidation. *In*: Programme and Abstracts of ETS & SSCT Joint Conference: Chemicals, Human and Environment, October 20-23, Toila, Estonia, 84.
10. Trapido, M., Goi, A., **Kulik, N.** 2005. Application of Chemical Oxidation for Improvement of Subsequent Bioremediation in Soil Treatment. *In*: Abstracts of Scientific Conference 29th Estonian Chemistry Days, October 20-21, Tallinn, Estonia, 115-116.
11. Trapido, M., Goi, A., **Kulik, N.** 2005. Application of Chemical Oxidation for Improvement of Subsequent Biodegradation in Soil Treatment. *In*: Proceedings of 17th World Congress: Ozone & Relative Oxidants. Innovative & Current Technologies, August 22-25, Strasbourg, France, VII.3.1-1–VII.3.1-9.

12. **Kulik, N.**, Goi, A., Trapido, M., Veressinina, Y., Munter, R. 2005. Fenton Treatment as an Environmental Friendly Technique for Decontamination of Soil and Wastewater. *In*: Abstract book of Conference on Knowledge-based Materials and Technologies for Sustainable Chemistry, June 1-5, Tallinn, Estonia, 96.
13. Trapido, M., Goi, A., **Kulik, N.**, Tuhkanen, T. 2005. Advanced oxidation processes – a study on the application for soil remediation. *In*: Proceedings of Seventh Finnish Conference of Environmental Sciences: Science for Sustainability, May 12-13, Jyväskylä, Finland, 15-18.
14. Trapido, M., Goi, A., **Kulik, N.** 2005. Chemical Oxidation in Oil Contaminated Soil Remediation. *In*: Andrzejewski P., ed. Soil and Ground Water Contamination by Oil Products and Other Anthropogenic Organic Compounds: Analytics, Monitoring and Remediation, 35-40.
15. **Kulik, N.**, Trapido, M., Goi, A., Munter, R. 2005. Ozone – an efficient oxidant for water purification, wastewater and soil treatment. *In*: Proceedings of International Conference: Eco-Balt 2005, May 5-6, Riga, Latvia, 68-69.
16. Goi, A., **Kulik, N.**, Trapido, M. 2004. Combined methods for remediation of fuel and transformer oil contaminated soil. *In*: Proceedings of International Conference: Eco-Balt 2004, May 6-7, Riga, Latvia, 11-12.
17. Goi, A., **Kulik, N.**, Palmroth, M.R.T., Trapido, M. 2004. Ozonation and the Fenton treatment as a means for remediation of soil - diesel fuel contaminated soil. *In*: Proceedings of International Conference: Advances in Science and Engineering for Industrial applications of Ozone and Related Oxidants, March 10-12, Barcelona, Spain, I.2.10-1-I.2.10-6.