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Advanced Oxidation Processes for the Treatment of Water and Wastewater Contaminated with Refractory Organic Compounds

ALEKSANDR DULOV

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

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Supervisor: Professor Marina Trapido, Department of Chemical Engineering, Tallinn University of Technology, Estonia

Opponents: Professor Tuula Tuhkanen, Department of Chemistry and Bioengineering, Tampere University of Technology, Finland

Professor Toomas Tenno, Institute of Chemistry, University of Tartu, Estonia

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Tallinn University of Technology, Ehitajate tee 5,
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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.

Aleksandr Dulov

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Süvaoksüdatsiooni protsessid raskesti lagundatavate orgaaniliste ainetega saastatud vee ja heitvee töötlemiseks

ALEKSANDR DULOV

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LIST OF ORIGINAL PUBLICATIONS

The present doctoral thesis is based on the following original publications referred to by their Roman numerals I-IV in the text:

Paper I: **Dulov, A.,** Dulova, N., Trapido, M. 2011. Combined physicochemical treatment of textile and mixed industrial wastewater. Ozone: Science & Engineering, 33, 285-293.

Paper II: **Dulov, A.**, Dulova, N., Veressinina, Y., Trapido, M. 2011. Degradation of propoxycarbazone-sodium with advanced oxidation processes. Water Science and Technology: Water Supply, 11, 129-134.

Paper III: Dulova, N., Trapido, M., **Dulov, A.** 2011. Catalytic degradation of picric acid by heterogeneous Fenton-based processes. Environmental Technology, 32, 439-446.

Paper IV: **Dulov, A.,** Dulova, N., Trapido, M. 2012. Photochemical degradation of nonylphenol in aqueous solution: the impact of pH and hydroxyl radical promoters. Environmental Engineering Science, *Submitted*.

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

The author's contribution to the publications

Paper I: The author supervised the experimental work of M.Sc. students and performed DOC analyses, analysed the results and wrote the paper. The results were presented by the author at the International Conference IOA-EA3G "Ozone & Related Oxidants for Emerging Pollutants of Concern to the Water and the Environment", April 28-30, 2010, Geneva, Switzerland.

Paper II: The author supervised the experimental work of M.Sc. students, analysed the results and wrote the paper. The results were presented by the author at the 2011 World Congress "Ozone and UV: Leading-Edge Science and Technologies", May 23-27, 2011, Paris, France.

Paper III: The author analysed the results obtained by a M.Sc. student, participated in writing the paper.

Paper IV: The author supervised the experimental work of M.Sc. student, analysed the results and wrote the paper.

INTRODUCTION

In recent decades, environmental laws and regulations became more stringent that forced researchers to develop and evolve novel technologies for water and wastewater treatment which are capable to reach higher mineralization rate with lower amount of detectable pollutants than conventional methods.

The application of advanced oxidation processes (AOPs) is a promising and effective tool for oxidation, decolourisation, mineralization and degradation of most organic pollutants. Advanced oxidation processes belong to the group of technologies that lead to hydroxyl radical generation as the primary oxidant. These radicals are produced by means of oxidizing agents such as H_2O_2 and O_3, ultraviolet irradiation, ultrasound, and homogeneous or heterogeneous catalysts. Hydroxyl radicals are non-selective in nature and they can react without any other additives with a wide range of contaminants whose rate constants are usually in the order of 10^7-10^{10} L/mol·s.

Due to high oxidation rate of the chemical reactions caused by AOPs, the behavior of contaminants is significantly changed after the treatment. The majority of by-products formed during organic pollutants degradation are smaller and more biodegradable. At sufficient contact time and proper operation conditions, it is practically possible to mineralize the target pollutant to CO_2. The advantage of AOPs overall chemical and biological processes is that they do not transfer pollutants from one phase to the other (as in chemical precipitation, adsorption, and volatilization) and do not produce massive amounts of sludge (as in biological processes). However, the application of AOPs alone for wastewater treatment proved to have higher operating cost comparing to conventional treatment. Therefore, it is proposed to combine these technologies and use AOPs as pre- or post-treatment step. In other words, AOPs may prepare biologically persistent or toxic water and wastewater for subsequent biological degradation or be applied as a polishing step for biologically or physicochemically pre-treated effluents. The main purpose of integrating different treatment methods is to enhance the process efficiency as well as to reduce the overall operating cost.

The main objective of the current work was to study the efficiency of different AOPs and combined processes for the treatment of real and synthetic water/wastewater samples containing refractory organic contaminants and to assess the economical feasibility of applied processes. In the present research real industrial wastewater samples were presented as textile factory and industrial park effluents, and synthetic water/wastewater samples as propoxycarbazone-sodium (an active component of herbicide), picric acid and nonylphenol (endocrine disrupting compound) aqueous solutions.

The AOPs of concern were ozonation and related processes, direct and indirect photolysis, and Fenton-based processes. The aim of this work was to evaluate and compare different advanced oxidation technologies for the degradation of target compounds in aqueous matrices and overall improvement of wastewater quality.

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My personal deep thanks goes to my wife Senior Research Scientist Niina Dulova, to my children and parents for support during the years of the study.

ABBREVIATIONS

AOP	advanced oxidation process
AS	activated sludge
BOD_5	5-day biochemical oxygen demand
BOD_7	7-day biochemical oxygen demand
C	pre-coagulation
COD	chemical oxygen demand
DAF	dissolved air flotation
DCL	diclofenac
DOC	dissolved organic carbon
EC	electroconductivity
EDC	endocrine disrupting compound
E1	estrone
E2	estradiol
HPLC-UV	high performance liquid chromatography with ultraviolet detector
IC-CSC	ion chromatography with chemical suppression of eluent conductivity
LP	low pressure UV lamp
MP	medium pressure UV lamp
NDMA	n-nitrosodimethylamine
NP	nonylphenol
NPEO	nonylphenol ethoxylates
OPEO	octylphenol ethoxylates
PA	picric acid
PS	propoxycarbazone-sodium
RO	reverse osmosis
SMX	sulfamethoxazole
TOC	total organic carbon
TS	total solids
TSS	total suspended solids
$T_{90\%}$	90% conversion time
$T_{1/2}$	half-life time
US	ultrasound
UV	ultraviolet light
UV_{254}	ultraviolet absorbance at 254 nm
UVA	ultraviolet light A (long wave, 315-400 nm)
UVB	ultraviolet light B (medium wave, 280-315 nm)
UVC	ultraviolet light C (short wave, 100-280 nm)
VIS	visible light (over 400 nm)
VUV	vacuum ultraviolet light (100-200 nm)
WWTP	wastewater treatment plant

1. LITERATURE REVIEW

1.1. Principles of advanced oxidation processes

Advanced oxidation processes (AOPs) differ in their reacting systems (Table 1), meanwhile all are identified by the same chemical nature - production of hydroxyl radicals. Hydroxyl radicals are extremely reactive species and powerful oxidants (Table 2). They react with target molecules with rate constants in the order 10^7-10^{10} L/mol·s (Hoigné and Bader, 1983, Huang et al., 1993). These hydroxyl radicals are also characterized as non-selective oxidizing agents and can react with organic compounds by electrophilic addition of OH-group, by hydrogen atom abstraction, or by electron transfer (Legrini et al., 1993):

$$^{\bullet}OH + R \rightarrow ROH \qquad [1]$$

$$^{\bullet}OH + RH \rightarrow {}^{\bullet}R + H_2O \qquad [2]$$

$$^{\bullet}OH + RX \rightarrow RX^{\bullet +} + {}^{-}OH \qquad [3]$$

In general, reactions [1] and [2] are extremely fast and result in new oxidized intermediates with lower molecular weight or in case of complete mineralization in carbon dioxide and water. Electron transfer reactions Eq. [3] of hydroxyl radical with organics are uncommon (Pignatello et al., 2006).

Table 1. Types and classification of AOP systems

Non-photochemical	**Photochemical**
O_3/OH^- (ozonation in alkaline media)	H_2O_2/UV
O_3/H_2O_2	O_3/UV
O_3/Ultrasound (US)	O_3/H_2O_2/UV
O_3/AC (activated carbon)	H_2O_2/Fe^{2+}/UV (photo-Fenton)
H_2O_2/Fe^{2+} (Fenton system)	UV/TiO_2
electro-Fenton	H_2O_2/TiO_2/UV
pulsed plasma	O_2/TiO_2/UV
US	UV/US
H_2O_2/US	Vacuum UV (VUV)
O_3/Catalyst	
Microwave	
Wet air oxidation	
Supercritical water oxidation	

Table 2. Relative oxidation power of some oxidants

Oxidant	**Oxidation potential (V)**
$h^+(TiO_2)$	3.50
Fluorine	3.03
Hydroxyl radical	2.80
Atomic oxygen	2.42
Ozone	2.07
Hydrogen peroxide	1.78
Perhydroxyl radical	1.7
Potassium permanganate	1.68
Hypobromous acid	1.59
Chlorine dioxide	1.57
Hypochlorous acid	1.49
Hypoiodous acid	1.45
Chlorine	1.36
Bromine	1.09
Iodine	0.54

As it was above-mentioned, the hydroxyl radical is a non-selective oxidant, and thus can be consumed by organic or inorganic compounds other than the contaminants of concern. Carbonates, bicarbonates, and phosphates are well-known hydroxyl radicals scavengers, which reduce the efficiency of pollutant oxidation in direct proportion to their (carbonate, bicarbonate, and phosphate) concentrations:

$$^{\bullet}OH + HCO_3^- \rightarrow {}^{-}OH + HCO_3^{\bullet} \qquad [4]$$

$$^{\bullet}OH + CO_3^{2-} \rightarrow {}^{-}OH + {}^{\bullet}CO_3^- \qquad [5]$$

$$^{\bullet}OH + PO_4^{3-} \rightarrow {}^{-}OH + {}^{\bullet}PO_4^{2-} \qquad [6]$$

Also, it has been observed that hydroxyl radicals can be significantly consumed by excessive amounts of the primary oxidants (e.g. ozone and hydrogen peroxide) applied in treatment process as well as by reduced cations (e.g. iron) presented in water/wastewater naturally or artificially added (Hernandez et al., 2002).

1.1.1. Ozonation in alkaline media

Once the ozone is generated, the oxidation of the organics can occur through two different reaction pathways, i.e., direct and indirect (free radical) ozonation, leading to different oxidation products and different types of kinetics. The reaction pathways (direct and indirect) are dependent on the pH of the treated solution (Hoigné and Bader, 1983)

When the direct ozonation takes place (pH<4), ozone is the main oxidizing agent of the process. On the other hand, the indirect ozonation (pH>9) is based on the formation of hydroxyl radicals acting as main oxidizing agent. At this point, it has to be noted that ozonation can be considered as an AOP when the hydroxyl radicals are prevailing oxidants. At pH range 4-9 both (direct and indirect) reactions take place.

Decomposition of ozone to produce hydroxyl radicals passes through the following mechanism, where hydroxide ions initiate the reaction (Andreozzi et al., 1999):

$O_3 + OH^- \rightarrow O_2 + HO_2^-$ [7]

$O_3 + HO_2^- \rightarrow HO_2^{\bullet} + O_3^{\bullet -}$ [8]

$HO_2^{\bullet} \rightarrow H^+ + O_2^{\bullet -}$ [9]

$O_2^{\bullet -} + O_3 \rightarrow O_2 + O_3^{\bullet -}$ [10]

$O_3^{\bullet -} + H^+ \rightarrow {}^{\bullet}OH + O_2$ [11]

1.1.2. O_3/H_2O_2 process

Hydrogen peroxide can be combined with ozone to enhance its transformation to hydroxyl radicals. Hydrogen peroxide is a weak acid, which partially dissociates into the hydroperoxide ion in water. Hydrogen peroxide reacts slowly with ozone, whereas the hydroperoxide ion can react rapidly with ozone to form hydroxyl radicals. The reaction mechanism for the perozonation process is described by Hernandez et al. (2002):

$H_2O_2 + H_2O \leftrightarrow H_3O^+ + HO_2^-$ [12]

$O_3 + HO^- \rightarrow HO_2^- + O_2$ [13]

$O_3 + HO_2^- \rightarrow {}^{\bullet}OH + O_2^{\bullet -} + O_2$ [14]

$O_3 + O_2^{\bullet -} \rightarrow O_3^{\bullet -} + O_2$ [15]

$O_3^{\bullet -} + H_2O_2 \rightarrow {}^{\bullet}OH + OH^- + O_2$ [16]

1.1.3. UV photolysis and H_2O_2/UV process

The photolysis is the decomposition of organic compounds caused by natural or artificial light. Two photo-induced processes are commonly occurring in aqueous matrices: direct and indirect photolysis. In the former case, the organic compounds absorb UV light and may react with the constituents of the aqueous matrix or undergo self-decomposition. Indirect photolysis involves the photo-degradation by photo-sensitizers, e.g. hydroxyl or peroxyl radicals.

In H_2O_2/UV process hydroxyl radicals are produced from the photolytic dissociation of hydrogen peroxide in water by UV irradiation (Legrini et al., 1993):

$$H_2O_2 + h\nu \rightarrow {}^{\bullet}OH + {}^{\bullet}OH \qquad [17]$$

The rate of hydrogen peroxide photolysis is pH dependent and increases under alkaline conditions due to formation of peroxide anion which has higher molar absorption coefficient (240 L/mol·cm) at 253.7 nm comparing to hydrogen peroxide (18.6 L/mol·cm):

$$HO_2^- + h\nu \rightarrow {}^{\bullet}OH + O^- \qquad [18]$$

1.1.4. O_3/UV process

In ozone photolysis hydroxyl radicals are produced through different reaction pathways:

$$O_3 + H_2O + h\nu \rightarrow H_2O_2 \qquad [19]$$

$$H_2O_2 + h\nu \rightarrow {}^{\bullet}OH + {}^{\bullet}OH \qquad [20]$$

$$2O_3 + H_2O_2 \rightarrow 2{}^{\bullet}OH + 3O_2 \qquad [21]$$

As it is seen, the photolysis of ozone generates hydrogen peroxide and, thus, O_3/UV process involves all mechanisms present in O_3/H_2O_2 and H_2O_2/UV processes (Homem and Santos, 2011).

1.1.5. The classical Fenton reaction (H_2O_2/Fe^{2+})

The Fenton reaction is a catalytic process under acidic conditions, based on electron transfer between hydrogen peroxide and iron ion acting as catalyst. The main steps of the reaction mechanism are:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \qquad [22]$$

$${}^{\bullet}OH + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \qquad [23]$$

$$HO_2^{\bullet} + H_2O_2 \rightarrow O_2 + H_2O + {}^{\bullet}OH \qquad [24]$$

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + OH^- \qquad [25]$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \qquad [26]$$

$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + H^+ + O_2$ [27]

$Fe^{2+} + HO_2^{\bullet} + H^+ \rightarrow Fe^{3+} + H_2O_2$ [28]

$HO_2^{\bullet} + HO_2^{\bullet} \rightarrow H_2O_2 + O_2$ [29]

The overall Fenton reaction Eq. [22] can be simplified by accounting for the dissociation water (Walling, 1975):

$2Fe^{2+} + H_2O_2 + 2H^+ \rightarrow 2Fe^{3+} + 2H_2O$ [30]

This equation demonstrates that the Fenton reaction is strongly dependent on solution pH; in general only at acidic pH values near 3 the hydroxyl radical is the principal oxidant (Neyens and Baeyens, 2003).

The Fenton reagent (H_2O_2/Fe^{2+}) is known to have different treatment functions depending on the hydrogen peroxide/iron catalyst ratio. When the amount of hydrogen peroxide applied is higher than iron catalyst dosage, the treatment tends to have effect of chemical oxidation. When the two amounts are reversed, the treatment tends to have effect of chemical coagulation (Neyens and Baeyens, 2003).

In general, the Fenton treatment involves four steps: pH adjustment, oxidation reaction, neutralization and coagulation/sedimentation. Thus, the target compounds are removed in two phases: the oxidation and the coagulation/sedimentation.

1.1.6. Photo-Fenton process

The way to increase the Fenton reaction process efficiency is its combination with UV radiation (photo-Fenton process). The use of UV radiation can increase the efficiency of this process mainly due to the regeneration of ferrous ion and the extra production of hydroxyl radicals by the photolysis of ferric complexes. The newly generated ferrous ions react with hydrogen peroxide generating a second hydroxyl radical and ferric ion, and the cycle continues:

$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + H^+ + {}^{\bullet}OH$ [31]

Ferric iron can form complexes with many substances and undergo photo-reduction. The main compounds absorbing light in photo-Fenton system are ferric ion complexes $[Fe^{3+}(OH)^-]^{2+}$ and $[Fe^{3+}(RCO_2)^-]^{2+}$, which produce additional Fe^{2+} by photo induced ligand-to-metal charge-transfer reactions (Sagawe et al., 2001):

$[Fe^{3+}(OH)^-]^{2+} + h\nu \rightarrow Fe^{2+} + {}^{\bullet}OH$ [32]

$[Fe^{3+}(RCO_2)^-]^{2+} + h\nu \rightarrow Fe^{2+} + CO_2 + {}^{\bullet}R$ [33]

The pH plays an important role in the efficiency of the photo-Fenton reaction, because it strongly predetermines which iron complexes are formed.

1.1.7. Heterogeneous Fenton process

The main disadvantages associated with the homogeneous Fenton process are the formation of high amounts of metal-containing sludge at the end of the process, with high environmental impact and costs associated, and requirement for acidic conditions. Application of iron ions immobilized on a solid support is a strategy to avoid sludge formation and to expand the effective pH range of the Fenton reaction.

Available sources for catalytic ion include transition metal-exchanged zeolites, pillared interlayered clays, iron-oxide minerals, metallic iron, nanocatalysts, iron-oxide coated allophone nanocatalysts (Garrido-Ramirez et al., 2010). These minerals can operate over a wide range of pH and temperature, it is easy to separate and keep their activity during successive operation.

Heterogeneous Fenton-based reactions may follow different mechanisms of generation of hydroxyl radicals. The hydroxyl radicals may be formed by the reactions with Fe^{2+} dissolved from the mineral surface or, for example, the catalysis may occur at the surface of heterogeneous catalyst (Lin and Gurol, 1998; Lu, 2000). The reaction leading to the dissolution of Fe^{2+} from goethite surface:

$\alpha\text{-}FeOOH_{(s)} + 2H^+ + \frac{1}{2}H_2O_2 \rightarrow Fe^{2+} + \frac{1}{2}O_2 + 2H_2O$ [34]

Hydroxyl radicals are then produced by the Fenton's basic reaction Eq. [22]. Further, Fe^{3+} is precipitated according to following reaction:

$Fe^{3+} + H_2O + OH^- \rightarrow \alpha\text{-}FeOOH_{(s)} + 2H^+$ [35]

Lin and Gurol (1998) proposed a mechanism for the radical formation by catalyzed peroxide decomposition on mineral surface. The series of chain reactions are initiated by the production of a complex of H_2O_2 with the oxide surface ($\equiv Fe^{3+}\text{-}OH$) Eq. [36].

$\equiv Fe^{3+}OH + H_2O_2 \leftrightarrow (H_2O_2)_s$ [36]

$(H_2O_2)_s \rightarrow \equiv Fe^{2+} + H_2O + HO_2^{\bullet}$ [37]

$\equiv Fe^{2+} + H_2O_2 \rightarrow \equiv Fe^{3+}OH + {}^{\bullet}OH$ [38]

$HO_2^{\bullet} \leftrightarrow H^+ + O_2^{\bullet -}$ [39]

$$\equiv Fe^{3+}OH + HO_2^{\bullet}/O_2^{\bullet -} \rightarrow \equiv Fe^{2+} + H_2O/OH^{-} + O_2 \qquad [40]$$

1.2. AOPs for water and wastewater treatment – state of the art

Advances in analytical chemistry, hydrology, and engineering have greatly improved ability to identify and study new group of chemicals which are harmful to environment and human health. A plenty of new contaminants are not commonly monitored, however, had been recently detected in the environment. These chemicals are referred to as contaminants of emerging concern, because the risk to human health and the environment associated with their presence, frequency of occurrence or source may not be known yet and ability to detect them in the environment often may exceed ability to understand the risks. These contaminants of emerging concern are consisting of pharmaceuticals, personal care products, natural and synthetic estrogens, pesticides, surfactants and etc. Many of emerging contaminants are labeled as endocrine disrupting compounds (EDCs).

The conventional water and wastewater treatment technologies include biological, thermal and physicochemical treatments. Usually biological treatments may require a longer residence time for microorganisms to degrade the pollutant because they may be affected by pollutant toxicity. Secondary biological treatment of wastewater may also provide not satisfactory result, especially for industrial wastewater, consisting of recalcitrant compounds, or the water contaminated with emerging pollutants. Treatment efficiency of biological process may completely fail for the reason of low biodegradability of certain compounds. As these compounds are found in water bodies, it means they are not removed with conventional biological treatment at wastewater treatment plants (WWTP) and further they can pass to drinking water treatment facility that faces with the problem of their removal. Thermal treatment may pose considerable emissions of other hazardous compounds after their incineration. Such techniques as coagulation, flocculation, activated carbon adsorption, air stripping and reverse osmosis will require a post-treatment to remove the accumulated pollutants.

Therefore, one of feasible options for elimination of biologically persistent contaminants of emerging concern in water and wastewater processing is the use of alternative treatment technologies based on chemical oxidation, such as the AOPs. AOPs are characterized as efficient treatment methods for aqueous matrices containing refractory organic contaminants. A review concerning different types of AOPs implemented for removal of emerging pollutants from water and wastewater is presented in Table 3. Processes of concern are ozonation, O_3/H_2O_2, O_3/UV, $O_3/UV/H_2O_2$ process, UV photolysis and H_2O_2/UV process, homogeneous and heterogeneous Fenton-based systems, and photo-Fenton process. The efficacy of AOPs application is demonstrated both for treatment of synthetic aqueous solutions and real water/wastewater samples.

Table 3. Review of AOPs application for degradation of emerging pollutants in water and wastewater

Compound/ class	**Initial concentration**	**Matrix**	**Reaction conditions**	**Results and comments**	**References**
Ozonation (O_3)					
25 different pharmaceuticals and estrogens	0.5-5 µg/L	WWTP effluents spiked with pharmaceuticals and estrogens	O_3 dose 0.5-5 mg/L, pH 7	90-99% degradation for ozone doses above 2 mg/L. Suspended solids in water matrix has minor effect on removal efficiency.	Huber et al., 2005
17β-Estradiol (E2)/ estrogen	0.4 mM	Distilled water	O_3 dose 30-63 µM/min, pH 5.3-6.3	Complete degradation of E2 after 55, 75, and 90 minutes of ozonation for O_3 dosage rate of 15.78, 12.25, and 9.78 µM/min, respectively.	Irmak et al., 2005
Carbamazepine, Caffeine, Cotinine/ pharmaceuticals	0.3-3.8 ng/L, 2.3-24.0 ng/L 0.1-1.6 ng/L	Raw intake water from river	O_3 dose 1.5–2 mg/L, pH 7.5 as part of conventional treatment	66-100% degradation after 20 min of ozonation. Conventional treatment alone fails to remove target compounds.	Hua et al., 2006
Sulfamethoxazole/ pharmaceutical	200 mg/L	Distilled water	O_3 dose 2.4 g/h	95% compound and 18% TOC removal after 10 and 60 min, respectively.	Dantas et al., 2008
Ibuprofen/ pharmaceutical	10 µM	Distilled water	O_3 dose 0.4 mg/(L·min), pH 5-7	Complete degradation after 15 min at pH 7; 20% removal at pH 5. Low mineralization.	Oh et al., 2007
Erythromycin, Tylosin/ pharmaceuticals	40 mg/L	Spiked distilled water	O_3 dose 0.4 mg/(L·min), pH 3-11	97% removal after 10 min and complete degradation in 20 min for both compounds.	Lin et al., 2009

C.I. Acid Blue 193/ dye	10 µM	Distilled water	O_3 dose 1-2 g/(L·h), pH 4-12	Decolourisation of solution after 10 min. Dye removal was depended on pH value and the ozone dosage.	Bauman et al., 2011
Bleaching effluent from pulp and paper mill	COD 455-1145 mg/L	Real wastewater	O_3 dose 1224 mg/(L·h), pH 7 and 12	80% UV absorbance reduction and 50% COD removal at pH 12.	Balcıoğlu et al., 2006
Industrial wastewater	COD 743±14 mg/L	Real landfill leachate	O_3 dose 0.5 g/(L·h), pH 7-11	49% COD and 41% UV_{254} removal at pH 7	Cortez et al., 2011
Metropolol, Naproxen, Amoxicillin, Phenacetin/ pharmaceuticals	1 µM	Reservoir water, Groundwater, WWTP effluent	O_3 dose 14 mg/h, pH 3 and 7	The second-order rate constants were obtained for degradation of each compound.	Benitez et al., 2011
Industrial wastewater	COD 4650 mg/L	Real winery wastewater	O_3 dose 100 mg/min, pH 4	12% COD removal after 180 min of treatment	Lucas et al., 2010
5 different phenolic compounds	COD 970 mg/L	Spiked synthetic olive mill wastewater	O_3 dose 100 mg/min, pH 3.4	91% total phenols and 42% COD removal, respectively.	Martins and Quinta-Ferreira., 2011
Industrial wastewater	COD 14500 mg/L	Real detergent industry wastewater	O_3 dose 100 mg/min, pH 3, 5.5 and 9.5	6% COD removal was achieved.	Martins et al., 2011
N-Nitrosodimethylamine (NDMA)/ pesticide manufacturing by-product	2.5 µg/L	Spiked river water	O_3 dose 0.6-10 mg/L	12% NDMA removal was achieved.	Pisarenko et al., 2012

Table 3. (continued)

Compound/ class	**Initial concentration**	**Matrix**	**Reaction conditions**	**Results and comments**	**References**
O_3/H_2O_2 process					
Sulfadimethoxine, Sulfamethazine, Sulfamethoxazole/ pharmaceuticals	40 mg/L	Spiked distilled water	O_3/H_2O_2 m/m 0.5-18	Complete degradation of all antibiotics after 20 min of O_3. The addition of H_2O_2 accelerated the degradation (O_3/H_2O_2 optimum m/m 5).	Lin et al., 2009
Estrone (E1)/ estrogen	2.54-6.62 µM	Distilled water	O_3/H_2O_2 m/m 1:2, 2:1, and 4:1; pH 4, 7, and 8.5	The reaction rate was dependent on pH value and independent on O_3/H_2O_2 ratio.	Nakonechny et al., 2008
Metropolol, Naproxen, Amoxicillin, Phenacetin/ pharmaceuticals	1 µM	Reservoir water, Groundwater, WWTP effluent	O_3 dose 16 mg/h, H_2O_2 10 µM, pH 3	The first-order rate constants were obtained for degradation of each compound.	Benitez et al., 2011
Industrial wastewater	COD 743±14 mg/L	Real landfill leachate	O_3 dose 0.5 g/(L·h), H_2O_2 100-400 mg/L, pH 7-11	72% COD and 66% UV_{254} removal at pH 7 and 400 mg/L H_2O_2, respectively.	Cortez et al., 2011
Cyanide	0.5 mg/L	Distilled water	O_3 dose 0.12 g/(L·h), H_2O_2 2-15 mg/L, pH 9	Cyanide concentration reduced to drinking water level of 0.05 mg/L.	Kepa et al., 2008
NDMA/ pesticide manufacturing by-product	2.5 µg/L	Spiked river water	O_3 dose 0.6-10 mg/L, H_2O_2 0.5-3.5 mg/L	46% NDMA removal was achieved.	Pisarenko et al., 2012

O_3/UV process					
Industrial wastewater	COD 4650 mg/L	Real winery wastewater	O_3 dose 100 mg/min, pH 4, UV (LP, 254 nm)	21% COD removal after 180 min of treatment.	Lucas et al., 2010
p-chlorophenol/ intermediate in herbicide manufacturing	130 mg/L	Deionized water	O_3 dose 591 mg/h , UV (LP, 254 nm), pH 3-11	The pseudo-first-order rate constant was obtained. 95% compound and 46% TOC removal at pH 9, respectively.	Peternel et al., 2012
O_3/UV/H_2O_2 process					
Industrial wastewater	COD 4650 mg/L	Real winery wastewater	O_3 dose 100 mg/min, pH 4, UV (LP, 254 nm), COD/H_2O_2, w/w 4:1	35% COD removal after 180 min of treatment	Lucas et al., 2010
p-chlorophenol/ intermediate in herbicide manufacturing	130 mg/L	Deionized water	O_3 dose 591 mg/h, H_2O_2 10-30 mM, UV (LP, 254 nm), pH 3-11	The pseudo-first-order rate constant was obtained. 95% compound and 50% TOC removal at pH 9, respectively.	Peternel et al., 2012
UV photolysis and H_2O_2/UV process					
Metronidazole/ pharmaceutical	1 mg/L	Deionized water	UV (LP, 254 nm), UV (MP, 200-400 nm), H_2O_2 0-50 mg/L, pH 6	Degradation followed the first-order kinetics and reaction rate increased at higher H_2O_2 dose. MP irradiation more effective than LP	Shemer et al., 2006
Anatoxina/ cyanotoxin	0.6-1.8 mg/L	Deionized water	UV (LP, 254 nm), H_2O_2 20-60 mg/L	70% degradation after 45 min. The degradation rate improved with increasing H_2O_2 dose.	Afzal et al., 2010
Metropolol, Naproxen, Amoxicillin, Phenacetin/ pharmaceuticals	1 µM	Reservoir water, Groundwater, WWTP effluent	UV (LP, 254 nm), H_2O_2 10-50 µM, pH 3.6 and 7.85	The first-order rate constants were obtained for degradation of each compound	Benitez et al., 2011

Table 3. (continued)

Compound/ class	**Initial concentration**	**Matrix**	**Reaction conditions**	**Results and comments**	**References**
Sulfamethoxazole, Sulfamethazine, Sulfadiazine, Trimethoprim, Bisphenol A, Diclofenac/ pharmaceuticals	4±1 µM	Real lake water, WWTP effluent	UV (LP, 254 nm), H_2O_2 2-10 mg/L, pH 3.6 and 7.85	At H_2O_2dose of 10 mg/L, UV dose consumed to remove 90% SMX and DCL was <860 and<330 mJ/cm^2, respectively. For the remaining compounds UV>900 mJ/cm^2	Baeza and Knappe, 2011
Bromoxynil, Trifluralin/ herbicides	3 µM	Spiked real surface water samples	UV (LP, 254 nm), H_2O_2 0.4-1.8 mM, pH 2-9	90% removal of both compounds and toxicity decrease was observed.	Chelme-Ayala et al., 2010
Clofibric acid/ herbicide	10 mg/L	Distilled water, WWTP effluent	UV (LP, 254 nm), H_2O_2 100 mg/L, pH 4.5 and 7	Complete compound removal after 25 and 20 min at pH 4.5 and 7, respectively.	Li et al., 2011
Nonylphenol ethoxylates (NPEO), Octylphenol ethoxylates (OPEO)/ endocrine disruptors	5 µM	Ultrapure water, Aqueous environmental matrices	H_2O_2 600 mM, UV (LP, 254 nm)	More than 97% after 10 min in ultrapure water; in other matrices degradation is hindered.	Nagarnaik and Boulanger, 2011
Cytarabine/ pharmaceutical	1-20 mg/L	Ultrapure water, Groundwater, Wastewater	UV (MP, 238-334 nm), H_2O_2 100-1000 mM	98, 75, and 65% degradation after 1 h in ultrapure water, groundwater, and wastewater, respectively.	Ocampo-Pérez et al., 2010

Meprobamate, Dilantin, Carbamazepine, Primidone, Atenolol, Trimethoprim/ pharmaceuticals	Pre-determined concentrations	Spiked WWTP effluents	UV (LP, 254 nm), H_2O_2 0-20 mg/L, pH 7.1-8.2	The overall removals between 0 and >99% proved dependent on the scavenging rate.	Wert et al., 2009
Roxithromycin, Sulfamethoxazole, Trimethoprim/ pharmaceuticals	100 µg/L	Spiked membrane bioreactor permeate	UV (MP) 15W, H_2O_2 17 mg/L, pH 3	12, 100 and 7% removal of roxithromycin, sulfamethoxazole, trimethoprim, respectively	Tambosi et al., 2009
Dimethyl phthalate/ endocrine disruptor	0.35-8.04 mg/L	Distilled water	UV (LP, 254 nm), H_2O_2 2.5-40 mg/L, pH 2.5-11	The pseudo-first-order rate constant of compound degradation was obtained.	Xu et al., 2009
p-chlorophenol/ intermediate in herbicide manufacturing	130 mg/L	Deionized water	UV (LP, 254 nm), H_2O_2 0-100 mM, pH 3-11	The pseudo-first-order rate constant was obtained. 90% compound and 40.3% TOC removal, respectively.	Peternel et al., 2012
Homogeneous Fenton process					
Amoxicillin, Ampicillin, Cloxacillin/ pharmaceuticals	104 mg/L 105 mg/L 103 mg/L	Distilled water	H_2O_2/COD m/m 1.0-3.5, H_2O_2/Fe^{2+} m/m 2-150, pH 2-4	Complete degradation in 2 min at H_2O_2/Fe^{2+} m/m 10 and pH 3. 81% COD and 54% DOC removal in 60 min, respectively.	Elmolla and Chaudhuri, 2009
Metropolol, Naproxen, Amoxicillin, Phenacetin/ pharmaceuticals	1 µM	Reservoir water, Groundwater, WWTP effluent	H_2O_2 and Fe^{2+} 10 µM, pH 3	The first-order rate constants were obtained for degradation of each compound.	Benitez et al., 2011

Table 3. (continued)

Compound/ class	**Initial concentration**	**Matrix**	**Reaction conditions**	**Results and comments**	**References**
Metronidazole/ pharmaceutical	1 mg/L	Deionized water	H_2O_2 29.4 µM, Fe^{2+} 2.94-11.76 µM, pH 3.5	Degradation followed the second-order kinetics and reaction rate increased at higher Fe^{2+} dose. Max 76% drug removal was achieved.	Shemer et al., 2006
Industrial wastewater	COD 743±14 mg/L	Real landfill leachate	H_2O_2/Fe^{2+} m/m 1-3.5, pH 3	46% COD and 62% UV_{254} removal, respectively; BOD_5/COD ratio increased from 0.01 to 0.15.	Cortez et al., 2011
Phthalic acid esters, Bisphenol A/ endocrine disruptors	1.5 mg/L 0.08 mg/L	Spiked landfill leachate	H_2O_2/Fe^{2+} m/m 7:1, pH 3	90% removal of pollutants was observed.	He et al., 2009
Ampicillin/ pharmaceutical	20 mg/L	Distilled water	H_2O_2 230-570 µM, Fe^{2+} 53-87 µM, pH 2.3-5.7	Complete degradation was achieved under optimal conditions (H_2O_2 373 µM, Fe^{2+} 87 µM, pH 3.7).	Rozas et al., 2010
5 different phenolic compounds	COD 970 mg/L	Spike synthetic olive mill wastewater	H_2O_2 310 mM, Fe^{2+} 0.9 g/L, pH 2.3-5.7	60% COD removal was observed.	Martins and Quinta-Ferreira, 2011
p-chlorophenol/ intermediate in herbicide manufacturing	130 mg/L	Deionized water	H_2O_2 30-100 mM, Fe^{2+} 1 mM, pH 3	The pseudo-first-order rate constant was obtained. Complete compound and 56% TOC removal was observed.	Peternel et al., 2012

Industrial wastewater	COD 14500 mg/L	Detergent industry wastewater	H_2O_2 125 mM, Fe^{2+} 50 mM, pH 3	20% COD removal was observed.	Martins et al., 2011
p-nitroaniline/ intermediate in pharmaceutical synthesis	181 µM	Deionized water	H_2O_2 2.5-40 mM, Fe^{2+} 0.025-0.1 mM, pH 2-6	90% pollutant removal after 30 min of treatment.	Sun et al., 2008
Roxithromycin, Sulfamethoxazole, Trimethoprim/ pharmaceuticals	100 µg/L	Spiked membrane bioreactor permeate	H_2O_2 17 mg/L, Fe^{2+} 3.4 mg/L, pH 3	2, 0 and 10% removal of roxithromycin, sulfamethoxazole, trimethoprim, respectively.	Tambosi et al., 2009
NPEO, OPEO/ endocrine disruptors	5 µM	Ultrapure water, Aqueous environmental matrices	H_2O_2 100 mM, Fe^{2+} 25 mM, pH 3	More than 80% removal of pollutants after 10 min in ultrapure water; in other matrices degradation was hindered.	Nagarnaik and Boulanger, 2011
Heterogeneous Fenton process					
Chlorobenzene/ solvent in pesticide industry	18.3 mg/L	Distilled water, Spiked groundwater	H_2O_2/Fe^0 (Fe^{3+}, Cu^{2+}); H_2O_2 500-1500 mg/L, Fe^0 1000 mg/L, pH 2.8-3; Fe^{3+} 150-300 mg/L, Cu^{2+} 250-1000 mg/L, pH 4.3-4.7	The efficacy of H_2O_2/Fe^0 system was enhanced by the addition of $Fe^{3+}$and Cu^{2+}. The performances of the H_2O_2/Fe^0 system proved dependent on sample matrix	Pagano et al., 2011
Acid orange 2/ dye	100 mg/L	Distilled water, Real dying wastewater	H_2O_2 15 mM, $Fe_2V_4O_{13}$ 0.5 g/L, pH 6	The pseudo-first-order rate constant was obtained. 88% COD removal in real dying wastewater was achieved.	Zhang et al., 2010
Reactive black 5/ dye	0.061 mM	Distilled water	Thermally immobilized Fe^{3+} in fly ash; H_2O_2 4.56-5.5 mM, pH 2.8	80% COD removal was observed after 2 hours of treatment.	Flores, et al., 2008

Table 3. (continued)

Compound/ class	**Initial concentration**	**Matrix**	**Reaction conditions**	**Results and comments**	**References**
17β-estradiol/ estrogen	272 µg/L	Milli-Q water	H_2O_2 9.7 mM, α-FeOOH loaded resin (5 g/L, 0.5 g Fe/L), pH 7.47, UV (365 nm)	The pseudo-first-order rate constant was obtained. 99% compound removal was achieved.	Zhao et al., 2008
Photo-Fenton process					
Metronidazole/ pharmaceutical	1 mg/L	Deionized water	H_2O_2 29.4 µM, Fe^{2+} 2.94-11.76 µM, pH 3.5, UV (LP, 254 nm)	Degradation followed the second-order kinetics and reaction rate at higher Fe^{2+} dose. Max 94% compound removal was achieved.	Shemer et al., 2006
Amoxicillin, Ampicillin, Cloxacillin/ pharmaceuticals	104 mg/L 105 mg/L 103 mg/L	Distilled water	H_2O_2/COD m/m 1.0-2.5, H_2O_2/Fe^{2+} m/m 10-150, pH 2-4, UV (365 nm)	Complete pollutants removal in 2 min at H_2O_2/Fe^{2+} m/m 5 and pH 3. 81% COD and 58% DOC removal in 50 min, respectively.	Elmolla and Chaudhuri, 2009
Ampicillin/ pharmaceutical	20 mg/L	Distilled water	H_2O_2 230-570 µM, Fe^{2+} 53-87 µM, pH 2.3-5.7, UV (365 nm)	Complete drug degradation was achieved under optimal conditions (H_2O_2 454 µM, Fe^{2+} 87µM, pH 3.5).	Rozas et al., 2010
Lincomycin/ pharmaceutical	25 mg/L	Distilled water, Real wastewater	H_2O_2 1-10 mM, ferrioxalate 0.2 mM, $FeSO_4$ 0.2 mM, $Fe(NO_3)_3$ 0.2 mM, UV (365 nm) and solar radiation	Complete drug removal after 8 and 20 min of treatment with ferrioxalate and $Fe(NO_3)_3$ catalyst, respectively.	Bautitz and Nogueira, 2010

p-chlorophenol/ intermediate in herbicide manufacturing	130 mg/L	Deionized water	H_2O_2 30-100 mM, Fe^{2+} 1 mM, pH 3, UV (254 nm)	The pseudo-first-order rate constant was obtained. Complete compound and 92% TOC removal was achieved.	Peternel et al., 2012
p-nitroaniline/ intermediate in pharmaceutical synthesis	181 µM	Deionized water	H_2O_2 2.5-40 mM, Fe^{2+} 0.025-0.1 mM, pH 2-6, solar light	99% compound removal after 30 min of treatment.	Sun et al., 2008
Roxithromycin, Sulfamethoxazole, Trimethoprim/ pharmaceuticals	100 µg/L	Spiked membrane bioreactor permeate	H_2O_2 17 mg/L, Fe^{2+} 3.4 mg/L, pH 3, UV (MP) 15W	18, 100 and 20% removal of roxithromycin, sulfamethoxazole, trimethoprim, respectively.	Tambosi et al., 2009
Sulfamethazine/ pharmaceutical	50 mg/L	Deionized water	H_2O_2 176-1024 mg/L, Fe^{2+} 12-68 mg/L, pH 3, sunlight lamp (400-580 nm)	Complete drug removal after 2 min of treatment.	Perez-Moya et al., 2010
Sulfamethoxazole/ pharmaceutical	50 mg/L	Distilled water, Seawater	H_2O_2 30-210 mg/L, Fe^{2+} 2.6-10.4 mg/L, pH 2.5-9, UV (MP, 290 nm)	DOC removal was 80 and 50% for distilled water and seawater, respectively.	Trovo et al., 2009
Amoxicillin, Bezafibrate, Paracetamol/ pharmaceuticals	0.1 mM 0.055 mM 0.1 mM	Distilled water, WWTP effluent	H_2O_2 1-10 mM, Fe^{2+} 0.2 mM, pH 2.5, UV (365 nm)	98% removal of all compounds was achieved after 5 min of treatment in both matrices.	Trovo et al., 2008
NPEO, OPEO/ endocrine disruptors	5 µM	Ultrapure water, Aqueous environmental matrices	H_2O_2 100 mM, Fe^{2+} 25 mM, UV (254 nm)	More than 95% compounds removal after 10 min of treatment in ultrapure water; in other matrices degradation was hindered.	Nagarnaik and Boulanger, 2011

Studies on artificial matrix treatment give plenty information about intermediates' formation during the target compound degradation and mineralization extent. Moreover, such kind of experiments can be extended for a range of different concentrations for each compound. In the case of real water/wastewater solutions from a specific source, the main benefit of such studies is the opportunity to solve an original problem.

Ozonation is well studied process widely used in full-scale applications for drinking water purification and wastewater treatment. The main advantage of ozone oxidation is the applicability for effluents with fluctuating flow rate and/or composition. However, the high cost of equipment and maintenance, energy required to supply the process, as well as mass transfer limitations are relevant factors to be considered in evaluation of the ozonation process efficacy and operating cost. As can be seen in Table 3 several studies have been conducted on the applicability of ozonation to different emerging contaminants classes: pharmaceuticals (Huber et al., 2005; Hua et al., 2006; Oh et al., 2007; Dantas et al., 2008; Lin et al., 2009; Benitez et al., 2011), estrogens (Huber et al., 2005; Irmak et al., 2005), pesticides (Pisarenko et al., 2012), constituents of real industrial effluents (Balcioğlu et al. 2006; Lucas et al., 2010; Cortez et al., 2011; Martins et al., 2011), etc. It was found for majority of these compounds that although high removal efficacies were achieved (compounds degradation >90%, COD removal >40%), the degree of mineralisation was low, even for extended treatment times. The pH influence on the ozonation efficacy was extensively studied as well indicating increase in degradation rates with increase in pH value. It should be noticed that in some cases, mainly for real wastewater samples, ozonation proved ineffective or showed low treatment efficacy (Lucas et al., 2010; Cortez et al., 2011; Martins et al., 2011; Pisarenko et al., 2012). In order to improve the performance of ozonation treatment, it is possible to combine ozone with UV (Lucas et al., 2010), with hydrogen peroxide (Cortez et al., 2011; Pisarenko et al., 2012) or both (Lucas et al., 2010).

UV photolysis (and in particular UVC irradiation) has been traditionally used for the disinfection purposes of drinking water with the advantage, compared to chlorination, of reduction the formation of disinfection by-products. In water and wastewater treatment, UV photolysis has been effectively applied to samples containing photo-sensitive compounds and with low COD concentrations. From the studies summarized in Table 3, it seems that UV treatment is dependent on the chemical structure and absorption spectrum of the target compound (Tambosi et al., 2009; Wert et al., 2009; Baeza and Knappe, 2011; Benitez et al., 2011), radiation intensity and frequency (Shemer et al., 2006) and type of aqueous matrix (Ocampo-Pérez et al., 2010; Baeza and Knappe, 2011; Benitez et al., 2011; Li et al., 2011; Nagarnaik and Boulanger, 2011). The efficiency of UV treatment could be improved by combination with hydrogen peroxide or ozone. The positive impact of hydrogen peroxide on UV photolysis has been demonstrated in several studies reviewed in Table 3. For example, H_2O_2/UV process was efficiently applied for degradation of EDCs (Xu et al., 2009; Nagarnaik and Boulanger, 2011) and herbicides (Chelme-Ayala et al., 2010; Li et al., 2011; Peternel et al., 2012) both in deionized water and real aqueous matrices.

Fenton based processes may be effectively employed to treat wide range of micropollutants in different matrices: deionized water (Shemer et al., 2006; Sun et al., 2008; Zhao et al., 2008; Elmolla and Chaudhuri, 2009; Trovo et al., 2009; Perez-Moya et al., 2010; Rozas et al., 2010; Peternel et al., 2012), surface- and groundwater (Benitez et al., 2011; Nagarnaik and Boulanger, 2011; Pagano et al., 2011), and industrial effluents (Trovo et al., 2008; Bautitz and Nogueira, 2010; Benitez et al., 2011; Martins and Quinta-Ferreira, 2011) (Table 3). The efficiency of dark Fenton-based process may be enhanced in the presence of UVC (Shemer et al., 2006; Peternel et al., 2012; Nagarnaik and Boulanger, 2011), UVB (Tambosi et al., 2009; Trovo et al., 2009), UVA (Elmolla and Chaudhuri, 2009; Trovo et al., 2008) or solar light (Sun et al., 2008) irradiation, as more hydroxyl radicals are produced in the photo-Fenton reaction compared to the classical Fenton process. The performance of Fenton-based processes proved to be mainly affected by pH, temperature, catalyst, hydrogen peroxide and target compound concentration. The narrow pH range (between 2 and 4) of operation constitutes one disadvantage, as well as the common necessity to recover the dissolved catalyst. The use of heterogeneous system allows overcoming these problems, since the catalyst is immobilized in a heterogeneous matrix, giving the opportunity to work in all pH range and to recover the catalyst from the treated effluent (Zhao et al., 2008; Zhang et al., 2010).

The current literature review does not cover all the AOP's applied for removal of pollutants of emerging concern. Thus, very popular and widely used semiconductor photocatalytic process as well as new and very promising AOPs with ultrasound were left beyond the scope of the review presented in Table 3. Photocatalytic processes proved efficient tool for degradation of EDCs (Gültekin and Ince, 2007), antibiotics (Homem and Santos, 2011) and other pharmaceuticals (Klavarioti et al., 2009) in aqueous matrices. Application of sonolysis for removal of recalcitrant compounds is fast developing AOP. It was found efficient for degradation of pharmaceuticals (Emery et al., 2005; Hartmann et al., 2008; Memarian and Farhadi, 2008; Sancez-Prado et al., 2008), EDCs (Kitajima et al., 2006; Méndez-Arriaga et al., 2008; Chiha et al., 2011; He et al., 2011) and other persistent organic compounds (Kidak and Ince, 2006; Lesko et al., 2006; Sponza and Oztekin, 2011).

1.3. AOPs in combination with other treatment methods for water and wastewater treatment

Application of chemical oxidation for complete mineralization of organics may become significantly expensive because the oxidation intermediates formed during treatment tend to be more and more resistant to their complete chemical degradation. Furthermore, they all consume energy (radiation, ozone, etc.) and chemical reagents (catalysts and oxidizers) which increase with treatment time. Therefore, various combinations of AOPs with biological and physicochemical processes have been developed and applied in water and wastewater treatment. AOPs may be used as a pre-treatment step to convert the initially persistent organic compounds into more biodegradable and less toxic intermediates, preventing the death of microorganisms involved into the subsequent biological treatment. The rate of mineralization may be minimal during the pre-treatment step in order to avoid unnecessary expenditure of chemicals and energy, thus lowering the operating cost (Oller et al., 2011). Alternatively, AOPs can be applied in tandem with other treatment technologies as a polishing post-treatment step. A short review of application of AOPs in combination with other technologies in water and wastewater treatment is presented in Table 4.

The most common application of AOPs in combinations is chemical oxidation followed by biological treatment; in some cases reversed order is used as well. As can be seen in Table 4 combined chemical and biological treatment was effectively applied for degradation of pharmaceuticals (Badaway et al., 2009; Sirtori et al., 2009; Serra et al., 2011) and constituents of industrial wastewater (Tünay et al., 2008; Wang et al., 2008). The results of these combined schemes application indicated more than 90% removal of COD and/or TOC for all studied synthetic and real aqueous samples. Combination of coagulation/flocculation with subsequent advanced chemical oxidation proved effective in degradation of pharmaceuticals and EDCs (Rahman et al., 2010) as well as in treatment of real industrial wastewater (de Velasquez and Monje-Ramirez, 2006; Mizuno et al., 2008; Tünay et al., 2008; Martins et al., 2011). In general, a variety of technologies, e.g. reverse osmosis (Zhang et al., 2006), nanofiltration (Zhang and Pagilla, 2010), dissolved air flotation (de Sena et al., 2008), etc., may be used in tandem with AOPs to improve overall treatment efficacy of water/wastewater samples contaminated with refractory organic compounds.

The selection of processes to be combined depends on the quality standards to be met and the most effective treatment with the lowest reasonable cost. When preliminary chemical oxidation is used in combination, its efficacy is sometimes negligible or effect even harmful to the properties of the original water/wastewater. The reasons for that may be formation of stable intermediates which are less biodegradable or more toxic than the original compounds. Chemical pre-treatment may have low selectivity to the more bio-resistant fractions of the wastewater to be treated. Incorrect selection of treatment conditions may lead to generation of an effluent with low metabolic value for the microorganisms. Oxidants and metals used in AOPs in improper doses may become harmful for microorganisms. All these limitations underline the need to establish a step-by-step research methodology for application of combined methods, taking these effects into account, because operating conditions that impact on the original properties of the pretreatment step (contact time, oxidant and/or catalyst type, dose and toxicity, temperature, etc.) should be known.

Table 4. Review of application of AOPs in combination with other treatment methods for degradation of emerging pollutants in water and wastewater

Compound/ class	**Initial concentration**	**Matrix**	**Combination; reaction conditions**	**Results and comments**	**References**
Municipal wastewater	COD 240-560 mg/L, TOC 85-168 mg/L, BOD_5 81-203 mg/L	Real municipal wastewater	Pre-coagulation/ozonation/ O_3/H_2O_2 process; O_3 dose 1.25-20 mg/min, H_2O_2 50 mg/L	COD, TOC and BOD_5 were lower than 7, 6 and 5 mg/L, respectively, after 79 min of total treatment.	Mizuno et al., 2008
Industrial wastewater	COD 2500-3520 mg/L	Real effluent from hardboard manufacturing plant	Pre-coagulation (C)/ activated sludge (AS)/O_3, C/AS/O_3/H_2O_2, C/AS/Fenton; $FeCl_3$ 50 mg/L, O_3 dose 40 mg/min, O_3/H_2O_2 m/m 2:1, H_2O_2/Fe^{2+} m/m 1:1, 2:1	Under studied conditions all combinations demonstrated similar efficacy.	Tünay et al., 2008
Industrial wastewater	COD 1720 mg/L	Real landfill leachate	Pre-coagulation/O_3; Al_2O_3 1250 mg/L, Fe_2SO_4 2400 mg/L, O_3 dose 2.3 g/(L·h)	The treated effluent met local discharge limits for lagoons.	de Velasquez and Monje-Ramirez, 2006
Amoxicillin/ pharmaceutical	TOC 18925 mg/L	Real effluent from production plant	Fenton/reverse osmosis (RO); H_2O_2 10 g/L, Fe^{2+} 0.74 g/L, RO polyamide membrane cell (155 cm^2)	99.7% TOC removal after combined treatment	Zhang et al., 2006
Nalidixic acid/ pharmaceutical	45 mg/L	Distilled water	Solar photo-Fenton/AS; H_2O_2 10 mg/L, Fe^{2+} 200-400 mg/L, AS operation flux 500 L/h	95% TOC removal after combined treatment	Sirtori et al., 2009

Table 4. (continued)

Compound/ class	**Initial concentration**	**Matrix**	**Combination; reaction conditions**	**Results and comments**	**References**
Industrial wastewater	COD 14500 mg/L	Detergent industry wastewater	Flocculation/Fenton; SNF 4190SH flocculant, H_2O_2 125 mM, Fe^{2+} 50 mM, pH 3	88% COD removal and BOD_5/COD increase from 0.32 to 0.8 was observed.	Martins et al., 2011
Atrazine, Bisphenol A, Diclofenac, Carbamazepine, Gemfibrozil, Naproxen, Fluoxetine, Atorvastatin, Ibuprofen/ pharmaceuticals and endocrine disruptors	Pre-determined concentrations	Spiked lake water	Pre-coagulation/O_3/H_2O_2 process; polyaluminium chloride 6 mg/L, O_3 dose 2-2.3 mg/L, H_2O_2 0.2 mg/L	22 and 41% removal of atrazine and ibuprofen, respectively. The others compounds reduced to concentrations below the detection limit.	Rahman et al., 2010
Industrial wastewater	COD 1500 mg/L	Real detergent plant effluent	Fenton/AS; H_2O_2 60-180 mg/L, Fe^{2+}/H_2O_2 w/w 1:5 and 1:10, pH 3-5, reaction time 40 min, AS dose 4 g/L, retention time 5-20 h	The Fenton pre-treatment improved biodegradability of wastewater. 94% COD removal was observed.	Wang et al., 2008
Industrial wastewater	COD 2800-3000 mg/L, BOD_5 1400-1600 mg/L	Real meat processing plant	Dissolved air flotation (DAF)/UV/H_2O_2 process, DAF/photo-Fenton; H_2O_2 150-525 mg/L, Fe^{3+} 80 mg/L, UV (254 nm)	More than 95% removal of COD and BOD_5 in DAF/photo-Fenton system. DAF/UV/H_2O_2 process combination demonstrated lower efficacy.	de Sena et al., 2008

Diclofenac, Chloramphenicol, Paracetamol, p-aminophenol, Phenol, Benzoic acid, Nitrobenzene, Salicylic acid/ Pharmaceuticals and by-products	Pre-determined concentrations of compounds, COD 4100-11987 mg/L, BOD_5 1050-3000 mg/L	Real pharmaceutical wastewater	Fenton/AS; Fe^{2+}/H_2O_2 m/m 1:50, COD/H_2O_2 w/w 1:2.2, pH 3, reaction time 1.5 h, AS dose 3-4 g/L, O_2 dose 2 mg/L, retention time 12 h	Complete removal of all pharmaceuticals in combined method. 92-99% COD and 81-98% BOD_5 removal, respectively, was observed.	Badawy et al., 2009
Malation/ pesticide	10 mg/L	Spiked synthetic wastewater	Nanofiltration/photo-Fenton; polyamide membranes (0.55-0.71 nm), Malation/H_2O_2 w/w 1:50 and 1:150, Fe^{2+}/H_2O_2 w/w 1:10 and 1:80, pH 3, UV (LP, 254 nm)	99% drug removal was achieved. The economic feasibility of combination was assessed on the basis of specific energy consumption.	Zhang and Pagilla, 2010
α-methylphenylglycine/ pharmaceutical	TOC 327 mg/L	Synthetic wastewater	Solar photo-Fenton/AS; H_2O_2 36.3-72.5 mM, Fe^{2+} 10 mg/L, pH 2.9, AS dose 0.6 gVSS/L, O_2 dose 4 mg/L, retention time 1-2 d	93-98% TOC removal was achieved. Life cycle assessment of combined treatment process was carried out.	Serra et al., 2011

As it was above-mentioned, the main purpose of integrating different treatment methods is to enhance the process efficiency as well as to reduce the operating cost. The important parameter to evaluate the effectiveness of the system in combined processes is the synergetic effect which shows the enhancement of pollutant degradation under combined method relative to the linear combination (sequential) method. The synergetic effect could be estimated as follow (Kang and Hoffmann, 1998):

$$\text{Synergetic effect} = \frac{\text{Combined reaction rate constant}}{\text{Linear summation of individual methods rate constant}}$$

The purpose of combination of advanced oxidation processes is to enhance the degradation rate that is not achievable by a single process alone under the same condition.

The design, construction, operation, and maintenance of combined treatment processes is more difficult than those of the individual methods, but by combining various technologies, lower capital and operating costs are achievable. Several factors are required to be considered simultaneously in evaluation of combined treatment technologies. These factors are as follows (Kang and Hoffmann, 1998):

- **Method**: The strength of different combined methods is useful to decide whether this hybrid system is beneficial. For those methods employed to degrade organic compounds or to enhance the biodegradability, the combined method which has the greatest removal rate would be the best choice. On the other hand, if the goal of the treatment is mineralization, it is better to select the combined system that has the highest TOC reduction rate.
- **Residence time**: The product of the synergetic effect and residence time is equal to the summation of individual processes' residence times.
- **Cost**: Fixed and operating costs of hybrid methods are less than those of the summation of different individual process. By increasing the synergetic effect, these costs can be even lower. Synergetic effects of less than one are almost always not practical due to the lower degradation rate and higher maintenance cost. It is also not reasonable to combine different methods with the synergetic effect slightly greater than one when the contribution of a method is lower in the degradation of organic compounds and synergetic effect.
- **Energy**: In combining different single processes, the amount of energy or power required for the degradation should be considered. Methods employing UV, ultrasonic irradiation, ozone generation, gas sparging, and mechanical mixing consume a higher amount of energy relative to others, but they may substantially enhance the degradation rate.

1.4. Aims of the present study

Although basic reaction steps of AOPs are widely described, it may become complicated to predict the transformation and mineralization rates of certain compounds without providing preliminary research experiments.

The main objective of the present study was to specify the potential of different AOPs in degradation of refractory organic compounds in water and wastewater matrices, and thus to enlarge the existing knowledge of AOPs application solely as well as in combination with other treatment techniques.

In the current research real industrial wastewater samples from textile factory and industrial park, and synthetic aqueous solutions of propoxycarbazone-sodium, picric acid and nonylphenol were subjected to AOPs treatment.

The objectives of the study were as follows:

- to evaluate the overall efficacy of combined physicochemical treatment schemes applied for purification of real industrial effluents;
- to study and compare the implementation of UV and hydrogen peroxide photolysis, the Fenton reagent, ozonation and related processes for degradation of herbicide active component;
- to study the use of different heterogeneous catalysts in Fenton-based processes and to compare their efficiencies for picric acid degradation;
- to study and compare the application of UV and hydrogen peroxide photolysis, and Fenton-based processes for degradation of endocrine disrupting compound;
- to estimate and compare the operating costs of different treatment schemes.

2. MATERIALS AND METHODS

The description of main experimental characteristics is briefly presented in this section. For more details see the complete experimental part in *Papers I-IV*.

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 twice-distilled water. Sodium hydroxide and sulphuric acid aqueous solutions were used for pH adjustment.

Real wastewater samples were obtained from textile factory with finishing technology (including bleaching, dyeing and printing processes) and industrial park with main industries: tannery (technology without tanning, the process starts with semi-finished product processing), textile factory with finishing technology (including bleaching, dyeing and printing processes), bus fleet and food-processing industry. The main properties of the investigated effluents are presented in *Paper I, Table 1*.

Synthetic propoxycarbazone-sodium (PS) aqueous solutions were prepared using commercial herbicide containing PS as an active ingredient at concentration of around 70%. Artificial solutions with initial ATTRIBUT™ concentration of 200 mg/L were freshly prepared in twice-distilled water. Molecular structure of PS is presented in *Paper II, Figure 1*.

Model picric acid (PA, 2,4,6-trinitrophenol) solutions were freshly prepared in twice-distilled water. The initial concentration of PA was 0.4 mM.

Stock nonylphenol (NP) solution of 4.54 mM was prepared in 100 mL methanol. Synthetic solutions with initial NP concentration of 20 μM were freshly prepared by dilution of the stock in twice-distilled water. The structure and main properties of studied pharmaceutical are presented in *Paper IV, Table 1*.

Goethite (α-FeOOH, 30-50 mesh), magnetite (Fe_3O_4, 98%, <5 μm) and iron powder (Fe^0, ≥99%, 200 μm) were used as heterogeneous catalysts. The results of specific surface area measurement of heterogeneous catalysts are presented in *Materials and reagents* section in *Paper III*.

The real wastewater samples and all stock solutions were stored in the dark at 2-4 ºC.

2.2. Experimental procedure

The ozonation experiments (*Papers I, II*) were carried out in semi-continuous bubble reactor (for details see *Experimental procedure* sections of *Paper I* and *II*). Ozone produced by laboratory ozone generator from oxygen was bubbled through 1 L of wastewater or model solution. The ozone concentration in the feed-gas was kept at 10.0 ± 0.5 mg/L (*Paper I*) or 5.0 ± 0.25 mg/L (*Paper II*) and the gas flow rate in all experiments was kept at 1.0 L/min. The duration of ozone treatment was 120 min. Samples were treated both with pH adjustment to 3 (*Papers I, II*) or 9 (*Paper II*) and without pH regulation at initial pH value (*Papers I, II*). The stripping experiments of wastewater samples at initial pH values were carried out in the same reactor and treatment conditions as the respective ozonation trials.

Mercury low-pressure OSRAM lamp with an energy input of 10 W located in a quartz tube inside the reactor was used as an UV source (*Papers II, IV*). The incident UV radiation photon flux at 254 nm measured by potassium ferrioxalate actinometry (Gordon and Ford, 1972) was 3.25 ± 0.3 μEinstein/s (*Paper II*) and 5.52 ± 0.38 μEinstein/s (*Paper IV*).

O_3/H_2O_2, O_3/UV and O_3/H_2O_2/UV experiments (*Paper II*) were carried out in the same reactor and treatment conditions as the ozonation experiments. For details see *Experimental procedure* section of *Paper II*.

All Fenton-based process trials were carried out in the batch mode and in non-buffered solutions. Wastewater and model aqueous solutions were treated in cylindrical glass reactor with permanent agitation at a speed to provide complete mixing for uniform distribution of reagents (*Papers I-IV*) and full suspension of iron catalyst particles (*Paper III*); samples were withdrawn at selected time intervals (*Papers II-IV*) and filtered through a Millipore filter (0.45 μm) (*Paper III*). The homogeneous Fenton reaction was initiated by adding an optimum amount of hydrogen peroxide stepwise (*Paper I*) and/or all at once (*Papers I-IV*) to solutions containing a known amount of Fe^{2+}. The molar ratio of H_2O_2/Fe^{2+} was kept invariable at 10:1, which is the optimal ratio of hydrogen peroxide to ferrous ions (Tang and Huang, 1997). The classic Fenton oxidation experiments (*Papers I-IV*) were carried with pH adjustment to 3. Fenton-like system trials (*Papers I, II*) were conducted without pH adjustment. Heterogeneous Fenton-based treatment experiments (*Paper III*) with goethite, magnetite and zero valent iron were carried out with known catalyst dosages at different pH values. The termination of Fenton reaction in synthetic aqueous solutions was done by adding aqueous solution or solid crystals of Na_2SO_3 (*Papers II, III*) or was omitted (*Paper IV*). The oxidation of real effluents (*Paper I*) was stopped by the adjustment of samples' pH to basic values by adding lime milk and/or NaOH aqueous solution. The wastewater samples were kept for 2 hours to allow the settling of solids, and then supernatant was decanted for analytical measurement.

The experiments on oxidation with non-catalyzed hydrogen peroxide and adsorption effect of heterogeneous catalysts (*Paper III*) were conducted in the same reactor and treatment conditions as the respective Fenton-based treatment trials.

The direct UV photolysis (*Papers II, IV*), H_2O_2/UV process (*Papers II, IV*) and photo-Fenton experiments (*Paper IV*) were carried out in the same reactor and treatment conditions as the respective Fenton-based process trials. For details see *Experimental procedure* section of *Paper II* and *IV*.

Ferric chloride pre-coagulation and lime post-coagulation were used in combined treatment of real wastewater samples (*Paper I*). All details concerning coagulation procedure can be found in *Experimental procedure* section of *Paper I.*

2.3. Analytical methods

An overview of the analytical methods applied for wastewater and synthetic water samples is presented in Table 5.

Table 5. Analytical methods used for aqueous samples treatment

Analysis/Parameter	**Analytical instrument/method**	**Paper**
COD	Closed reflux titrimetric method (APHA, 2005)	*I-III*
DOC	TOC analyzer (APHA, 2005)	*I, III*
BOD_7	Digital oxygen analyzer (APHA, 2005)	*I*
pH	Digital pH meter	*I-IV*
EC	Digital EC meter	*I*
TSS	Determined according to APHA (2005)	*I*
TS	Determined according to APHA (2005)	*I*
Total Fe	Phenanthroline method (APHA, 2005)	*I-IV*
H_2O_2 initial	Spectrophotometric method, λ=254 nm	*I-IV*
H_2O_2 residual	Spectrophotometric method (Eisenberg, 1943)	*I-IV*
O_3 initial, residual	Digital ozone monitor, λ=258 nm	*I, II*
NO_3^-	IC-CSC (APHA, 2005)	*I, III*
PO_4^{3-}	IC-CSC (APHA, 2005)	*I*
SO_4^{2-}	IC-CSC (APHA, 2005)	*I*
Cl^-	IC-CSC (APHA, 2005)	*I*
Acute toxicity (EC_{50}) to *Daphnia magna*	*Daphnia magna (Cladocera, Crustacea)* 24-hours toxicity test (ISO, 1996)	*I, II*
PS	HPLC-UV	*II*
PA	HPLC-UV	*III*
NP	HPLC-UV	*IV*

Dissolved organic carbon (DOC) was measured in samples filtered through a Millipore filter (0.45 μm). The correction of hydrogen peroxide interference on COD test was done by the correlation equation according to Kang et al. (1999).

The concentration of NO_3^-, PO_4^{3-}, SO_4^{2-} and Cl^- ions was measured by means of ion chromatography with chemical suppression of eluent conductivity (IC-CSC; 761 Compact IC, Metrohm) coupled with a METROSEP A Supp 5 analytical column (4 × 150 mm). PS, PA and NP concentrations were quantified using a high performance liquid chromatograph CLAS MPm (Labio Ltd.) equipped with a MAG 0 (1.5 × 50 mm) Biospher PSI 100 C18 (particle size, 5 μm) microcolumn and UV/VIS detector SAPHIRE. The concentration of target compound was determined by using the standard chemical to fit the retention time. All details concerning inorganic ions and studied organic compounds analysis are presented in *Analytical methods* section of *Papers I-IV*.

3. RESULTS AND DISCUSSION

AOPs and combined processes are efficient tools for the treatment of wide range of refractory organic contaminants found in water/wastewater and industrial effluents. In the present research real industrial wastewater samples, and synthetic aqueous samples as propoxycarbazone-sodium, picric acid and nonylphenol aqueous solutions were subjected to treatment with AOPs and combined processes.

3.1. Treatment of real industrial wastewater

Ozonation, Fenton-based process combined with lime post-coagulation and combined treatment schemes: ferric chloride pre-coagulation/Fenton-based process/lime post-coagulation and ferric chloride pre-coagulation/ozonation were applied for textile and mixed industrial wastewater treatment (*Paper I*). The effectiveness of treatment methods was mainly evaluated by COD, DOC and BOD_7 removal.

3.1.1. AOPs treatment

The application of ozonation as the only treatment process proved to have moderate efficacy in wastewater samples quality improvement. The highest COD removal achieved after ozonation was 28 and 32% for textile and industrial park samples, respectively (*Paper I, Figure 5*). DOC reduction in textile wastewater after ozonation step was negligible; in the case of mixed industrial wastewater only 16% of DOC was removed. Wastewater samples treated with ozone oxidation exceeded the discharge limits stated by regulations for wastewater directed to local sewerage.

Post-coagulation with lime in the Fenton treatment was used as it proved more effective technique than post-coagulation with sodium hydroxide for removal of COD and DOC and resulted in lower residual hydrogen peroxide and dissolved iron concentrations (Kulik et al., 2008). The characteristics of both wastewater samples treated by Fenton-based treatment schemes with H_2O_2/COD weight ratio 0.5:1 complied with the discharge limits stated by regulations for wastewater directed to local sewerage. The increase of H_2O_2/COD weight ratio to 2:1 in the Fenton-based process/lime post-coagulation treatment of textile wastewater resulted in 5, 10, and 7% of residual COD, DOC (*Paper I, Figures 2 and 3*) and BOD_7, respectively, and thus improved sample characteristics to the discharge limits stated by regulations for wastewater directed into water bodies. In the case of mixed industrial effluent analogous treatment resulted in 85, 91 and 72% removal of COD, DOC and BOD_7, respectively. The Fenton-based oxidation step proved dependent on pH value of wastewater samples. It was noticed, that treatment experiments performed at samples' initial pH in oxidation step were less effective comparing to those performed at pH 3 (*Paper I,*

Figure 4). The impact of hydrogen peroxide stepwise addition on the efficiency of the samples treatment was also investigated and turned out negligible.

3.1.2. Combined physicochemical treatment

The pre-coagulation was utilized in order to remove suspended organic and inorganic compounds from the wastewater before ozonation or Fenton-based treatment application, and reduce the amount of oxidant required. Ferric chloride pre-coagulation proved an effective pre-treatment step for the following chemical oxidation with COD removal ability more than 50% (*Paper I, Figure 1*). DOC reduction in coagulation trials was lower compared to COD elimination due to mainly dissolved carbon nature.

The results of COD and DOC removal by application of combined pre-coagulation with the following Fenton-based treatment are presented in *Paper I, Figures 2 and 3*. Fenton-based treatment of pre-coagulated samples demonstrated lower removal efficacy compared to chemical oxidation of untreated samples for both studied real effluents. It can be assumed, that compounds removed during the ferric chloride pre-coagulation step act as promoters in hydroxyl radical formation chain in the subsequent Fenton-based oxidation step. The maximum COD and BOD_7 removal for ferric chloride pre-coagulation/Fenton-based process/lime post-coagulation was ~80% for both wastewater samples. The decrease of DOC for this combined treatment scheme was slightly lower and resulted in 40 and 24% of residual value for textile and mixed industrial effluents, respectively.

In combined pre-coagulation and the subsequent ozone oxidation the total removal of COD and DOC was higher compared to single ozonation, but mainly due to applied $FeCl_3$ coagulation step (*Paper I, Figures 1, 5 and 6*). The highest total COD removal in combined scheme with ozonation was 56 and 62% for textile and mixed industrial wastewater, respectively (*Paper I, Figure 6*). The results of total DOC removal by combined $FeCl_3$/ozonation treatment of textile and mixed industrial effluents were 12 and 42%, respectively. Lower performance of ozonation schemes comparing to Fenton-based systems may be explained by low oxidative capacity of the ozonation process at studied treatment conditions. The increase in ozone concentration or treatment duration most likely will lead to higher treatment efficacy but also to doubtful cost efficiency of the ozonation process.

3.2. Treatment of synthetic aqueous solutions

Ozonation, the Fenton reagent, UV photolysis and related processes were applied for treatment of synthetic aqueous solutions spiked with recalcitrant organic contaminants (Table 6). The efficacy of studied processes was assessed on the basis of residual concentration of target compound (*Papers II-IV*) and by COD (*Papers II, III*) and DOC (*Paper III*) reduction.

Table 6. AOPs applied for synthetic aqueous solutions

Target compound	**Processes applied**	**Paper**
Propoxycarbazone-sodium (PS)	UV photolysis, H_2O_2/UV, O_3, O_3/UV, O_3/UV/H_2O_2, O_3/H_2O_2, H_2O_2/Fe^{2+}	*II*
Picric acid (PA)	H_2O_2/Fe^{2+}, H_2O_2/α-FeOOH, H_2O_2/Fe^0, H_2O_2/Fe_3O_4	*III*
Nonylphenol (NP)	UV photolysis, H_2O_2/UV, H_2O_2/Fe^{2+}, H_2O_2/Fe^{2+}/UV	*IV*

The degradation of PS, PA and NP mainly followed a pseudo-first order kinetic law and can be described with regard to the compound concentration:

$$\frac{\mathrm{d}C}{\mathrm{d}t} = -\mathrm{k}_1 \times C \qquad [41]$$

where k_1 is the pseudo-first order rate constant.

The $-k_1$ constants were calculated from the slopes of the straight lines by plotting $\ln(C/C_0)$ as a function of time t, through linear regression.

3.2.1. Ozone and related processes

Ozonation, O_3/UV, O_3/H_2O_2, and O_3/UV/H_2O_2 processes were used for degradation of propoxycarbazone-sodium in aqueous solution (*Paper II*). The data on half-life times ($T_{1/2}$), 90% conversion times ($T_{90\%}$) and the pseudo-first order rate constants (k_1) of propoxycarbazone-sodium degradation with ozone and related processes is presented in *Paper II, Table 1*. The influence of pH on the degradation of PS by studied ozone-based processes in most cases was minor. Propoxycarbazone-sodium 90% conversion was not achieved with ozonation alone at studied treatment conditions which are common for potable water treatment. The highest COD removal during ozonation reached 36%. The O_3/H_2O_2 process resulted in a twofold increase of k_1 relative to ozonation only. The COD removal by O_3/H_2O_2 treatment was in the range of 11-34%. The addition of UV radiation to ozonation substantially improved PS degradation efficacy and resulted in tenfold k_1 value increase from 10^{-4} to 10^{-3} 1/s. The COD removal by the O_3/UV process at different pH values was in the range of 30-44%. The addition of hydrogen peroxide to O_3/UV process did not improve the degradation of PS but increase COD reduction up to 60%.

3.2.2. UV and hydrogen peroxide photolysis

Direct UV and hydrogen peroxide photolysis were applied for degradation of propoxycarbazone-sodium (*Paper II*) and nonylphenol (*Paper IV*) in aqueous solutions. The efficacy of UV photolysis was dependent on pH value and was improved by addition of hydrogen peroxide.

Application of direct UV photolysis for degradation of PS resulted in a higher reaction rate constant than ozonation (*Paper II, Table 1*). Thus, k_1 was 1.76×10^{-4} and 5.72×10^{-4} 1/s for ozonation and UV process, respectively. The addition of H_2O_2 to UV photolysis improved the propoxycarbazone-sodium degradation substantially and resulted in the highest k_1 of 10.2×10^{-4} 1/s. The degradation rate of PS was to some extent dependent on H_2O_2 concentration and pH of solution. The COD elimination by the H_2O_2/UV process at different treatment conditions was in the range of 25-40%.

The results of NP degradation by UV and hydrogen peroxide photolysis presented in *Paper IV, Table 2*. It was observed that pH has significant influence on the degradation of nonylphenol during application of UV photolysis. Nonylphenol removal was faster in alkaline medium. This is probably due to the fact that in alkaline medium the molar absorption coefficients of the molecule are slightly higher than at acidic and basic pH values (Neamțu and Frimmel, 2006). Additionally, the fraction of deprotonated NP, which reacts faster than the protonated compound, increases at alkaline pH. The 90% conversion times ($T_{90\%}$) for UV photolysis at pH 7 and pH 11 were 110 and 30 min, respectively. The k_1 at pH 11 was 13.2×10^{-4} 1/s which was 3 times higher than rate constant for trial at pH 7.

The addition of H_2O_2 to UV treatment improved the NP degradation substantially comparing to single UV photolysis and was dependent on the added H_2O_2 concentration. The addition of 50, 100 and 500 μM of hydrogen peroxide (pH 7) resulted in $T_{90\%}$ of 80, 70 and 35 min, respectively. Similarly to direct photolysis NP degradation rate in H_2O_2/UV system was considerably dependent on solution pH. The pseudo-first order rate constants for H_2O_2/UV process at pH 11 were 19.4×10^{-4}; 23.7×10^{-4} and 31.7×10^{-4} 1/s after addition of 50, 100 and 250 μM of hydrogen peroxide, respectively.

3.2.3. Fenton-based processes

The application of Fenton-based processes was studied for propoxycarbazone-sodium (*Paper II*), picric acid (*Paper III*) and nonylphenol (*Paper IV*) degradation in aqueous solutions. Kinetic constants' values were not calculated for H_2O_2/Fe^{2+} (*Papers II, IV*) and H_2O_2/Fe^0 (*Paper III*) systems because the data did not properly fit any kinetic model. The efficacy of Fenton-based processes proved dependent on the catalyst, pH value and hydrogen peroxide concentration.

In the Fenton system, the degradation of propoxycarbazone-sodium proved dependent on the H_2O_2 concentration (*Paper II, Table 1*). The value of $T_{90\%}$ for the experiment with H_2O_2 concentration of 35 mM decreased by factor 100 (from 3200 s to 30 s) as compared with the trial where the H_2O_2 concentration was 3.5 mM. The efficacy of PS degradation was dependent on pH value and proceeded slower at the initial solution pH than at pH 3. The efficiency of COD removal improved with the increase of the H_2O_2 dosage, and thus 52 and 70% removal of COD was achieved at 3.5 and 14 mM H_2O_2 (pH 3), respectively. The

Fenton process proved the most efficient for propoxycarbazone-sodium degradation, resulting also in the highest COD removal.

The Fenton process (H_2O_2/Fe^{2+}, pH 3) turned out an effective tool for PA oxidation in aqueous solution. Thus, PA degradation was completed in 7 min and a pseudo-first order rate constant of $k_1=84.4 \times 10^{-4}$ 1/s was established for PA/H_2O_2 m/m of 1:10. In the case of two times smaller hydrogen peroxide dosage (PA/H_2O_2 m/m of 1:5), PA completely disappeared in 15 min and a pseudo-first order rate constant was equal to $k_1=32.7 \times 10^{-4}$ 1/s.

Heterogeneous Fenton-based oxidation of PA catalysed by goethite (α-FeOOH), magnetite (Fe_3O_4) and iron powder (Fe^0) was studied as well. The results demonstrated negligible degradation of target compound within 120 minutes of reaction in both goethite and magnetite catalysed Fenton-based processes independent of system pH, hydrogen peroxide concentration, and catalyst type and dosage. The PA adsorption effects of both iron oxides turned out to be insignificant at all studied pH values and catalyst dosages.

The zero valent iron catalysed Fenton-based oxidation proved efficient in PA degradation under acidic conditions (pH 3) (*Paper III, Figure 1*). Thus, for catalyst dosage of 0.5 g/L PA degradation was completed in 10 min. The measurement of the total dissolved iron ions in reaction solutions indicated that for 0.5 g/L Fe^0 dosage the concentration of total dissolved iron ions reached 0.4 mM in less than 1 min of reaction time. This amount of iron ions is comparable with Fe^{2+} concentration utilized in the classic Fenton system with PA/H_2O_2 molar ratio of 1:10 (*Paper III, Figure 1*). Therefore, the major PA degradation mechanism in H_2O_2/Fe^0 process at pH=3 proved oxidation throughout homogeneous Fenton reactions in the bulk. On the other hand, the adsorption of PA molecules onto the iron powder surface where oxidation reaction with hydroxyl radicals occurs may also contribute to the overall efficiency of PA degradation. The results of the experiments on zero valent iron adsorption effect at pH=3 demonstrated 7.5 and 12.5% PA removal for 0.1 and 0.5 g L^{-1} Fe^0, respectively. The application of H_2O_2/Fe^0 process at pH≥5 resulted in no obvious degradation of PA.

The overall efficacy of the of PA degradation by H_2O_2/Fe^0 and H_2O_2/Fe^{2+} systems at pH 3 was assessed on the basis of COD and DOC removal after 120 min of reaction *(Paper III, Figure 4)*. In general, the classic Fenton treatment proved more effective in decreasing COD and DOC values of PA aqueous solutions than the zero valent iron catalysed Fenton-based process.

The results of NP degradation in the Fenton system indicated dependence of the treatment efficacy on the H_2O_2 concentration (*Paper IV, Table 2*). Thus, the increase in hydrogen peroxide dose from 100 to 200 μM intensified the degradation of the target compound. The Fenton process efficacy was lower than in the case of UV and hydrogen peroxide photolysis. The moderate NP removal can be explained at least by the following reasons: the small amounts of MeOH used for NP dissolution and present in the treated solutions scavenge the hydroxyl radicals and/or effective scavenging of the hydroxyl radicals by the elevated concentrations of hydrogen peroxide used.

The addition of UV radiation to the Fenton system resulted in improvement of NP removal (*Paper IV, Table 2*). The efficacy of photo-Fenton process proved dependent on H_2O_2 concentration. The 90% conversion times of photo-Fenton experiments at pH 3 after addition of 50 and 100 µM of hydrogen peroxide were 60 and 45 min, respectively. Further increase in hydrogen peroxide concentration up to 500 µM indicated decrease in NP degradation efficacy. The influence of pH on the degradation of target compound during photo-Fenton was more obvious at elevated H_2O_2 concentration, and consequently at higher iron concentration.

Although photo-Fenton process efficacy was higher than of the Fenton system, the result of NP degradation indicated no considerable improvement compared to H_2O_2 photolysis.

3.3. Biodegradability and toxicity

To assess the option of the subsequent biological treatment of studied water/wastewater samples an acute toxicity to *Daphnia magna* (*Papers I, II*) and biodegradability (*Paper I*) were evaluated. In most cases, treatment with AOPs proved effective as a pre-treatment technology for the following biological oxidation of studied water and wastewater samples.

The biodegradability of initial and treated wastewater samples was estimated by the BOD_7/COD ratio and presented in *Paper I, Figure 7*. The biodegradability of mixed industrial wastewater was increased up to 65% after application of Fenton-based process/lime post-coagulation system. All other studied treatment schemes resulted in negligible BOD_7/COD ratio changes. The increase of BOD_7/COD ratio in the range of 21-42% was achieved for textile effluents by all considered treatment methods except single ozonation, which showed no improvement of biodegradability. In general, combined Fenton-based process/lime post-coagulation treatment scheme proved the most effective for biodegradability improvement for both studied real wastewater samples.

An acute toxicity to *Daphnia magna* of the initial and treated wastewater samples was studied by 24-hours test (*Paper I, Table 2*). The results indicated general similarity in toxicity reduction behaviour of both wastewater samples after treatment with different processes and combined physicochemical schemes. All studied processes and combined physicochemical treatment schemes resulted in toxicity reduction in both wastewater samples. The application of Fenton-based process/lime post-coagulation and ozonation at pH 3 led to complete detoxification.

The results of 24-hours test on acute toxicity of the initial and treated PS aqueous solutions to *Daphnia magna* are listed in *Paper II, Table 2*. Although the initial stock solution was non-toxic, some increase in toxicity was observed after treatment with ozonation, H_2O_2/UV, and O_3/UV. The application of UV photolysis, O_3/UV/H_2O_2 and Fenton process resulted in non-toxic samples. The Fenton-based process performed at an elevated H_2O_2 concentration resulted in toxicity increase, probably due to hydrogen peroxide residue.

3.4. Treatment operational costs

To assess the economical feasibility of different treatment schemes for real wastewater samples and synthetic aqueous solutions purification, the operational costs were calculated. The cost estimation was done on the basis of methodology published by Munter et al. (2006).

The data obtained from the laboratory experiments allowed to make approximate calculation of operating costs comprising of energy required for ozonation, UV photolysis, and chemicals. Doses of ozone and hydrogen peroxide injected to studied samples were used in calculations without presumption of re-circulation of non-consumed chemicals. The specific energy requirement for ozone production from air was 20 kWh/kgO_3; the estimated unit energy cost was 0.1 EUR/kWh. In the Fenton-based process hydrogen peroxide cost was 0.9 EUR/kg calculated as 100%; $FeSO_4 \cdot 7H_2O$ and iron powder price was 0.13 and 4.2 EUR/kg, respectively. For sodium hydroxide and sulphuric acid used for pH adjustment average current prices of chemical on the Estonian market were taken as a basis.

3.4.1. Treatment cost of real industrial wastewater

Operational costs of selected treatment methods in EUR/m^3 are presented in Table 7. For details concerning costs of all studied treatment processes at optimal conditions see *Paper I, Table 3*.

The cost of ozonation turned out extremely high taking into account its poor treatment efficacy. Schemes with combination of ozone were also relatively expensive considering low purification efficacy. The application of Fenton-based treatment schemes was the most cost-effective considering their high treatment efficacy. Hence, treatment of textile and mixed industrial wastewater for meeting the discharge limits stated by regulations for wastewater directed to local sewerage costs were 1 and 1.22 EUR/m^3, respectively (Table 7). Although application of Fenton-based treatment scheme including pre-coagulation demonstrated lower removal efficiency, this method is less costly at higher H_2O_2/COD weight ratios comparing to Fenton-based process/lime post-coagulation method.

Table 7. Operational costs of selected wastewater treatment methods in EUR/m^3

Treatment	**pH***	**H_2O_2**	**$FeCl_3$**	**$FeSO_4·7H_2O$**	**O_3**	**H_2O_2**	**Total**
		mM	**EUR/m^3**				
$FeCl_3$**/Fenton/CaO	3	12.4	0.38	0.04	-	0.38	1.0
$FeCl_3$/Fenton/CaO	3	24.8	0.38	0.09	-	0.76	1.43
$FeCl_3$/Fenton/CaO	3	49.6	0.38	0.18	-	1.52	2.28
Fenton/CaO	3	24	-	0.08	-	0.72	1.0
Fenton/CaO	3	48	-	0.18	-	1.56	1.84
Fenton/CaO	3	96	-	0.35	-	3.03	3.48
$FeCl_3$/Ozone	9	-	0.38	-	2.76	-	3.24
$FeCl_3$/Ozone	3	-	0.48	-	2.76	-	3.34
Ozonation	3	-	-	-	2.84	-	2.94
Ozonation	initial	-	-	-	2.64	-	2.64
$FeCl_3$/Fenton/CaO	3	14.6	0.48	0.05	-	0.45	1.2
$FeCl_3$/Fenton/CaO	3	29.2	0.48	0.11	-	0.89	1.68
$FeCl_3$/Fenton/CaO	3	58.4	0.48	0.21	-	1.79	2.68
Fenton/CaO	3	29.7	-	0.11	-	0.91	1.22
Fenton/CaO	3	59.4	-	0.21	-	1.83	2.24
Fenton/CaO	3	118.8	-	0.44	-	3.65	4.28
$FeCl_3$/Ozone	9	-	0.38	-	2.79	-	3.17
$FeCl_3$/Ozone	3	-	0.48	-	3.46	-	3.94
Ozonation	3	-	-	-	3.11	-	3.11
Ozonation	initial	-	-	-	2.54	-	2.54

*pH regulation in average was 0.1 EUR/m^3

**$FeCl_3$ concentration in pre-coagulation was 3.7 mM

3.4.2. Treatment cost of synthetic aqueous solutions

Treatment cost calculations in EUR/m^3 for propoxycarbazone-sodium, picric acid and nonylphenol degradation in aqueous solutions are presented in Table 8.

The most efficient propoxycarbazone-sodium removal was achieved by Fenton and Fenton-based treatment which were also the cheapest among studied methods. At H_2O_2 concentration 7 mM treatment costs were 0.24 and 0.34 EUR/m^3 for Fenton-based and Fenton systems, respectively (Table 8). The cost of energy consuming processes such as ozone and UV oxidation was considerably higher than in Fenton and Fenton-based processes. Combination schemes with UV and ozone proved more efficient in propoxycarbazone-sodium removal than direct UV photolysis, but also became more expensive.

Picric acid degradation with the classic Fenton process became considerably cheaper comparing to heterogeneous H_2O_2/Fe^0 system mainly due to higher cost of powder iron. The operational cost of PA degradation by H_2O_2/Fe^{2+} (4 mM H_2O_2) and H_2O_2/Fe^0 system (4 mM H_2O_2, 0.1 g/L Fe^0) were 0.23 and 2.32 EUR/m^3, respectively (Table 8).

Table 8. Operational costs of synthetic aqueous solutions treatment methods in EUR/m^3 for $T_{90\%}$ of target compound

Treatment	**pH**[*]	**H_2O_2**	**$FeSO_4·7H_2O/Fe^0$**	**O_3**	**H_2O_2**	**UV**	**Total**
		mM	**EUR/m^3**				
Propoxycarbazone-sodium							
UV	initial	-	-	-	-	1.13	1.13
O_3/UV	initial	-	-	0.38	-	0.93	1.31
O_3/UV	3	-	-	0.38	-	0.93	1.41
O_3/UV	9	-	-	0.55	-	1.33	2.08
O_3/UV/H_2O_2	3	7	-	0.38	0.21	0.93	1.63
O_3/UV/H_2O_2	9	7	-	0.38	0.21	0.93	1.63
O_3/UV/H_2O_2	initial	3.5	-	0.38	0.11	0.93	1.42
O_3/UV/H_2O_2	initial	7	-	0.38	0.21	0.93	1.53
O_3/UV/H_2O_2	initial	14	-	0.28	0.43	0.71	1.42
H_2O_2/UV	3	3.5	-	-	0.11	1.04	1.25
H_2O_2/UV	3	7	-	-	0.21	0.83	1.15
H_2O_2/UV	3	14	-	-	0.43	0.75	1.28
H_2O_2/UV	initial	7	-	-	0.21	1.13	1.34
H_2O_2/UV	9	7	-	-	0.21	1.13	1.44
H_2O_2/Fe^{2+}	3	3.5	0.01	-	0.11	-	0.22
H_2O_2/Fe^{2+}	3	7	0.03	-	0.21	-	0.34
H_2O_2/Fe^{2+}	3	14	0.05	-	0.43	-	0.58
H_2O_2/Fe^{2+}	initial	7	0.03	-	0.21	-	0.24
H_2O_2/Fe^{2+}	initial	14	0.05	-	0.43	-	0.48
Picric acid							
H_2O_2/Fe^{2+}	3	4	0.014	-	0.12	-	0.23
H_2O_2/Fe^{2+}	3	2	0.007	-	0.06	-	0.17
H_2O_2/Fe^0	3	4	2.1	-	0.12	-	2.32
H_2O_2/Fe^0	3	4	0.42	-	0.12	-	0.64
Nonylphenol							
UV	7	-	-	-	-	2.66	2.66
UV	11	-	-	-	-	0.73	0.83
H_2O_2/UV	7	0.05	-	-	0.0015	1.93	1.93
H_2O_2/UV	7	0.1	-	-	0.0031	1.69	1.69
H_2O_2/UV	7	0.5	-	-	0.015	0.84	0.86
H_2O_2/UV	11	0.05	-	-	0.0015	0.41	0.51
H_2O_2/UV	11	0.1	-	-	0.0031	0.31	0.41
H_2O_2/UV	11	0.25	-	-	0.0077	0.17	0.28
H_2O_2/Fe^{2+}	3	0.2	0.0072	-	0.0061	-	0.11
H_2O_2/Fe^{2+}/UV	3	0.05	0.0018	-	0.0015	1.45	1.55
H_2O_2/Fe^{2+}/UV	3	0.1	0.00036	-	0.0031	1.09	1.19
H_2O_2/Fe^{2+}/UV	7	0.05	0.00018	-	0.0015	1.21	1.21
H_2O_2/Fe^{2+}/UV	7	0.1	0.00036	-	0.0031	1.45	1.45

[*] pH regulation in average was 0.1 EUR/m^3

The results of H_2O_2/Fe^0 system application at acidic pH indicated homogeneous mechanism of PA degradation, which proceeded through leaching iron ions from powder surface. Consequently, PA degradation was performed mainly by classic Fenton reaction process in the bulk solution. It can be assumed that after optimizing reaction conditions of H_2O_2/Fe^0 process, the operational cost of this system will be similar to cost of classic Fenton process.

Due to more effective nonylphenol degradation at basic pH values, the operational costs of experiments performed at pH 11 were lower than at acidic and neutral pH values (Table 8; *Paper IV, Table 3*). On the other hand, low concentration of chemicals used in the treatment processes under conditions studied resulted in low operational cost of processes with the fastest NP removal. The cost of UV radiation comprised a major part in overall operational costs of all photo-treatment processes. The cheapest treatment was the Fenton process (0.11 EUR/m^3 at 200 µM H_2O_2), but due to low efficacy it cannot be considered as the main NP degradation technique. The operational cost of photo-Fenton process was at least 10 times higher comparing to the cost of H_2O_2/Fe^{2+} system. In general, the optimal treatment method of NP regarding operational cost and treatment efficacy was H_2O_2/UV system (250 µM H_2O_2, pH 11) with respective cost of 0.28 EUR/m^3 (Table 8).

To sum up, the operational costs of degradation of refractory organic contaminants found in water and wastewater by AOPs and combined processes were calculated for real industrial wastewater samples (Table 7; *Paper I, Table 3*) and synthetic aqueous samples (Table 8; *Paper IV*, *Table 3*). It was ascertained that the operational cost of Fenton-based processes was the lowest among other studied processes. On the other hand, the application of Fenton-based processes demonstrated superior performance in treatment of wastewater (*Paper I*) and degradation of PS (*Paper II*) and PA (*Paper III*), and thus proved the most feasible and cost-effective treatment technique for these water/wastewater samples. The cost of ozonation turned out unreasonably high for wastewater treatment (Table 7) and PS degradation in aqueous solution (Table 8) taking into account its low treatment efficacy (*Paper I, Figure 5; Paper II, Table 1*). Combined treatment schemes with ozone oxidation were also comparatively expensive (Table 7) taking into consideration moderate wastewater purification efficacy (*Paper I, Figure 6*). The application of UV radiation required significant amounts of energy and led to increased operational cost of all photo-treatment processes (Table 8). However, treatment with hydrogen peroxide photolysis under optimized reaction conditions led to cost reduction (Table 8) and resulted in the best NP treatment efficacy (*Paper IV, Table 2*) and operational cost balance.

4. CONCLUSIONS

The efficacy of AOPs in degradation of refractory organic compounds in water and wastewater matrices was studied. Chemical oxidation was applied solely as well as in combination with other treatment techniques. The results of the present study indicated high potential of AOPs in target compounds removal from synthetic aqueous solutions and in wastewater overall quality improvement.

The application of combined physicochemical schemes proved efficient in industrial wastewater treatment. The characteristics of studied wastewater samples treated by Fenton-based treatment schemes complied with the discharge limits stated by regulations for wastewater directed to local sewerage. Moreover, use of elevated oxidant dosages in Fenton-based process/lime post-coagulation scheme proved feasible to improve wastewater characteristics up to the discharge limits stated by regulations for wastewater directed into water bodies. All studied AOPs as well as related combined treatment schemes resulted in wastewater toxicity reduction in some cases up to complete detoxification. Additionally, wastewater biodegradability improvement was observed in most cases after application of combined Fenton-based process treatment schemes.

The degradation of studied target compounds by AOPs mainly followed a pseudo-first order kinetic law. The performance of AOPs was essentially influenced by organic compounds properties and treatment conditions. The Fenton process was the most efficient for PS and PA removal from aqueous solutions. In the case of NP degradation hydrogen peroxide photolysis proved the most effective process. The efficacy of Fenton-based processes and UV photolysis turned out dependent on the pH value and hydrogen peroxide concentration. In heterogeneous Fenton-based processes removal efficacy was also dependent on catalyst type. Among studied catalysts the superior performance showed zero valent iron but only in acidic medium due to predominant oxidation mechanism of homogeneous catalysis. In general, AOPs with high target compound removal efficacy also resulted in non-toxic treated samples.

The results of treatment operational costs estimation indicated that Fenton-based processes were the most cost-effective technique for treatment of industrial wastewater and degradation of PS and PA in aqueous solutions. The cost of ozonation and combined treatment schemes with ozone turned out unreasonably high for wastewater treatment and PS removal from aqueous matrix taking into account its low treatment efficacy. The application of UV radiation led to increased operational cost of all photo-treatment processes. However, optimization of reaction conditions in hydrogen peroxide photolysis resulted in feasible balance between NP removal efficacy and treatment operational cost.

To conclude, the data obtained within the present study helps to enlarge the existing knowledge of AOPs application solely as well as in combination with other techniques for treatment of contaminated water and wastewater. The wastewater and synthetic aqueous solutions investigated in the current work were not previously subjected to treatment by studied AOPs and/or combined physicochemical processes. The results of this study are unique and could provide important information for practical purposes.

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ABSTRACT

The main objective of the current thesis was to specify the potential of different AOPs in degradation of refractory organic compounds in water and wastewater matrices, and thus to enlarge the existing knowledge of AOPs application solely as well as in combination with other treatment techniques.

In the present study real industrial wastewater samples from textile manufacture and industrial park, and synthetic aqueous samples of propoxycarbazone-sodium (PS), picric acid (PA) and nonylphenol (NP) were subjected to treatment with AOPs and combined processes to evaluate and compare purification efficacy of applied methods, to estimate and compare the operating costs of different treatment schemes.

The application of combined physicochemical schemes proved efficient in industrial wastewater treatment. The characteristics of studied wastewater samples treated by Fenton-based treatment schemes complied with the discharge limits stated by regulations for wastewater directed to local sewerage. All studied AOPs and combined treatment schemes resulted in wastewater toxicity reduction. Moreover, wastewater biodegradability improvement was observed in most cases after application of combined Fenton-based process treatment schemes.

The degradation of studied target compounds by AOPs mainly followed a pseudo-first order kinetic law. The performance of AOPs was essentially influenced by organic compound properties and implemented treatment conditions. The Fenton process proved the most efficient for PS and PA removal from aqueous solutions. In the case of NP degradation hydrogen peroxide photolysis was the most effective process. In heterogeneous Fenton-based processes the superior performance in PA removal showed zero valent iron but only in acidic medium due to predominant oxidation mechanism of homogeneous catalysis. In most cases, AOPs with high target compound removal efficacy also resulted in non-toxic treated samples.

The results of treatment operational costs estimation indicated that Fenton-based processes were the most cost-effective technique for treatment of industrial wastewater and degradation of PS and PA in aqueous solutions. The cost of ozonation and combined treatment schemes with ozone turned out unreasonably high for wastewater treatment and PS removal from aqueous matrix taking into account its low treatment efficacy. The application of UV radiation led to increased operational cost. However, optimization of reaction conditions in hydrogen peroxide photolysis resulted in feasible balance between NP removal efficacy and treatment operational cost.

KOKKUVÕTE

Käesoleva töö eesmärgiks oli erinevate süvaoksüdatsiooni protsesside potentsiaali määratlemine raskesti lagundatavate orgaaniliste ainete kõrvaldamisel veest ning reoveest. Selle tulemusena laienevad olemasolevad teadmised süvaoksüdatsiooni protsesside rakendamise võimalustest nii eraldi, kui ka kombinatsioonides teiste meetoditega.

Antud töös rakendati süvaoksüdatsiooni protsesse ning kombineeritud meetodeid tööstuslikele reoveeproovidele tekstiilivabrikust ja tööstuspargist ning sünteetilistele veeproovidele, mis sisaldasid propoksükarbasoon-naatriumi (PS), pükriinhapet (PA) ja nonüülfenooli (NP) selleks, et hinnata ja võrrelda kasutatud meetodite puhastamisefektiivsust ja ekspluatatsioonikulusid.

Kombineeritud füüsikokeemiliste skeemide rakendamine osutas efektiivseks tööstuslike reovete töötlemisel. Reoveeproovid, mis olid töödeldud Fentoni sarnase süsteemiga, vastasid ühiskanalisatsiooni juhitavate reovete piirnormidele. Kõik uuritud süvaoksüdatsiooni protsessid viisid reovete toksilisuse vähenemisele. Kombineeritud Fentoni sarnaste skeemide rakendamine viis enamikel juhtudel reovee biolagundatavuse parendamisele.

Uuritud sihtühendite lagundamine süvaoksüdatsiooni protsessidega vastas pseudo-esimest järku reaktsiooni kiiruse võrrandile. Süvaoksüdatsiooni protsesside efektiivsus sõltus uuritud aine omadustest ja kasutatud protsessi tingimustest. Fentoni protsess osutus kõige efektiivsemaks propoksükarbasoon-naatriumi ja pükriinhappe eemaldamisel vesilahusest. Vesinikperoksiidi fotolüüsi protsess oli kõige efektiivsem nonüülfenooli kõrvaldamiseks. Heterogeense Fentoni sarnase protsessi rakendamisel pükriinhape eemaldamiseks osutus kõige efektiivsemaks katalüsaatoriks null-valentne raud happelises keskkonnas. Protsessi mehhanism sarnaneb süsteemile homogeense katalüsaatoriga. Enamikel juhtudel kaasnesid kõrgema efektiivsusega süvaoksüdatsiooni protsessidega mittetoksilised proovid.

Puhastuse ekspluatatsioonikulude hinnang näitas, et Fentoni sarnased protsessid olid kõige ökonoomsemad tööstuslike reovee puhastamisel ning PS ja PA lagundamisel. Osoonimise ning osooniga skeemide maksumus oli põhjendamatult kõrge reovee puhastamisel ning PS lagundamisel, arvestades nende madalat puhastamisefektiivsust. UV rakendamine viis ekspluatatsioonikulude suurenemisele. Vesinikperoksiidi fotolüüsi protsessi tingimuste optimeerimise tulemuseks oli saavutatud tasakaal NP kõrvaldamisefektiivsuse ja ekspluatatsioonikulude vahel.

APPENDIX A

PAPER I

Dulov, A., Dulova, N., Trapido, M. 2011. Combined physicochemical treatment of textile and mixed industrial wastewater. Ozone: Science & Engineering, 33, 285-293.

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Combined Physicochemical Treatment of Textile and Mixed Industrial Wastewater

A. Dulov, N. Dulova, and M. Trapido

Department of Chemical Engineering, Tallinn University of Technology, Ehitajate tee 5, Tallinn 19086, Estonia

Wastewaters derived from a textile factory and an industrial park were subjected to treatment with ferric chloride coagulation; ozonation; ferric chloride pre-coagulation/Fenton-based process/lime post-coagulation; Fenton-based process/lime post-coagulation; and ferric chloride pre-coagulation/ozonation. Schemes with the Fenton-based process proved the most efficient for treatment of both wastewater samples. The characteristics of wastewater samples treated by a Fenton-based process at H_2O_2/COD *weight ratio 0.5:1 complied with the discharge limits stated by regulations for wastewater directed to local sewerage. The Fenton-based process/lime post-coagulation scheme proved more efficient than ferric chloride pre-coagulation/Fenton-based process/lime post-coagulation system. The increase of* H_2O_2/COD *weight ratio to 2:1 resulted in 5 and 10% of residual COD and DOC, respectively. All studied processes and combined physicochemical treatment schemes, except single ozonation, resulted in toxicity reduction and biodegradability improvement in both wastewater samples. The operational costs of applied treatment schemes were calculated and indicated the Fenton-based process schemes as the most feasible and cost-effective.*

Keywords Ozone, Advanced Oxidation Processes, Coagulation, Fenton-Based Treatment, Wastewater Treatment

INTRODUCTION

Development and growth of industries is often accompanied with the production of wastewaters containing different kinds of pollutants. Usually industrial wastewaters are mixtures of contaminants in a wide range of concentrations. The evolution of cost-beneficial technical solutions is needed to successfully overcome the increasingly complex problems arising in the field of industrial wastewaters (Bautista et al., 2008).

Chemical oxidation by advanced oxidation processes (AOP) is widely used for decomposing organic pollutants in industrial wastewater, and thus reducing the environmental discharge of hazardous substances from municipal STPs (Ikehata et al., 2006). Hydroxyl radicals are non-specific oxidizing agents which are capable to degrade a range of contaminants because they react with almost all types of organics.

In general, application of the AOP has the potential and can lead to the complete mineralization 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 (Fernández-Alba et al., 2002). It should be noted that the oxidation by AOP is not a universal solution as there are some chemicals, which are refractory towards the hydroxyl radicals 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 compounds. Thus, the use of combined processes has been suggested to overcome the disadvantages of individual unit processes. Addition of the AOP along with the components of other treatment process often leads to enhanced degradation degree or degradation rate.

Numerous researches proved that combined schemes are feasible and practical tools for treatment efficiency enhancement. The most common employment of the hydroxyl radicals' reaction in a sequential mode is the advanced oxidation followed by a biological process. Hence, the AOP pre-treatment improved in several cases the biodegradability of organic contaminants both under aerobic and anaerobic conditions (Martins et al., 2005). The application of combination of pre-coagulation and Fenton treatment for industrial wastewater treatment resulted in increased COD removal and reduced essentially the hydrogen peroxide amount compared to a conventional dosage (Bae et al., 2004). The study undertaken by Lim et al. (2004) demonstrated successful degradation of the recalcitrant organic matters remained in the effluent after biological treatment process to CO_2 by combined ozonation with and without hydrogen peroxide.

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Address correspondence to A. Dulov, Department of Chemical Engineering, Tallinn University of Technology, Ehitajate tee 5, Tallinn 19086, Estonia. E-mail: alexandr.dulov@gmail.com

The application of AOPs and its combinations to dyeing wastewater showed a better performance compared to conventional chemical treatment methods (Azbar et al., 2004). Barredo-Damas et al. (2005) reported that implementation of pre-ozonation improved the subsequent physical-chemical treatment (coagulation-flocculation process) by reducing the organic matter content and turbidity of the wastewater, and thus decreasing required coagulant dosage. The application of integrated ozone and GAC adsorption in pharmaceutical wastewater treatment improved deficiencies of separate processes by enhancement of COD removal and ozone utilization efficiency (Lecheng et al., 2007).

In the present study, special attention has been given to combination of advanced chemical oxidation, such as Fenton-based processes, ozonation, and traditional treatment methods, such as ferric chloride and lime coagulation. Ozone is known to oxidize organic compounds either by direct oxidation or through generation of hydroxyl radicals, or both, and thus can be included to AOP (Glaze et al., 1989). Ozonation and the Fenton chemistry, in which the decomposition of hydrogen peroxide is catalyzed by iron to form hydroxyl radicals, have been successfully applied for wastewater samples with different origin (Huang et al., 1993; Watts et al., 1996; Poznyak et al., 2008; Li-Bing et al., 2008; Ensar et al., 2008; Chang et al., 2008; Badawy et al., 2006; Papadopoulos et al., 2007).

In the current study, two real wastewater samples were obtained from 1) a textile factory with finishing technology and 2) an industrial park. The plants are situated in the north-eastern part of Estonia, in Narva. Annual produced wastewater amount in 2009 was the following: textile factory – 600,000 m^3/year, industrial park – 50,000 m^3/year. Both factories have a separate sewage header going to a sewage treatment plant where wastewaters are mixed together and undergo biological aerobic treatment separately from municipal wastewater. The plants have equalizing tanks and neutralizing units with sulfuric acid. After the equalization and neutralization, the characteristics of the effluents do not satisfy the discharge limits stated by regulations for wastewater directed to local sewerage. Hence, to improve effluent characteristics and comply with the regulations combined physicochemical treatment schemes: 1) ferric chloride pre-coagulation/Fenton-based process/lime post-coagulation, 2) Fenton-based process/lime post-coagulation, and 3) ferric chloride pre-coagulation/ozonation were applied.

MATERIALS AND METHODS

Materials and Chemicals

All chemicals used were of reagent grade, or analytical grade when available, and were used without further purification. Stock solutions were prepared in twice-distilled water. Sodium hydroxide and sulfuric acid aqueous solutions were applied for pH adjustment.

Wastewater samples were derived from 1) Sample A - textile factory with finishing technology (including bleaching, dyeing and printing processes) and 2) Sample B - industrial park with main industries: tannery (technology without tanning; the process starts with semi-finished product processing), textile factory with finishing technology (including bleaching, dyeing and printing processes), bus fleet and food-processing industry. The main properties of wastewater investigated are presented in Table 1. The collected wastewater samples were stored at 2–4 °C.

TABLE 1. General Chemical Properties of Wastewater Samples

Parameter	Sample A	Sample B
COD (mg/L)	1634	2020
BOD_7 (mg/L)	547	687
BOD_7/COD	0.33	0.34
DOC (mg/L)	322	561
pH	8.2	11.4
Ec (μS/cm)	4380	3652
N total (mg/L)	50.4	45.6
P total (mg/L)	2.54	9.42
SO_4^{2-} (mg/L)	1070	184
Cl^- (mg/L)	136	69
Fe total (mg/L)	4	6
TSS (mg/L)	306	442
TS (mg/L)	3920	3450

Experimental Procedure

In coagulation trials, ferric chloride aqueous solution used as a coagulant was added to initial wastewater samples with a volume of 0.7 L. The coagulation experiments were carried out at pH values of 4 and 9 with coagulant dosage 0.1–1 g/L. The jar test was conducted with a 2 min rapid mixing at 400 rpm, followed by 30 min slow mixing at 40 rpm. Then the mixed samples were allowed to settle without any agitation for 120 min and subsequently the supernatant was decanted for analytical measurement.

Batch experiments for Fenton-based oxidation were performed in a cylindrical glass reactor. 0.1 L of pre-treated (after coagulation) or initial wastewater samples were treated with permanent agitation speed (200–300 rpm) for a period of 2 h. The catalyst ($FeSO_4 \cdot 7H_2O$) was added first and the reaction was subsequently initiated by adding H_2O_2 all at once or in 2/3 steps (after 0, 30 and 60 min of treatment). The weight ratio of H_2O_2/Fe^{2+} was kept invariable at 6:1, which is the optimal ratio of hydrogen peroxide to ferrous ions (Tang et al., 1997). The classic Fenton treatment experiments were carried with pH adjustment to 3. Fenton-like system trials were conducted without pH adjustment.

The oxidation was terminated by the adjustment of samples' pH to 8–9 by adding 10% aqueous solution of lime (prepared by dissolving CaO in twice-distilled water) and 1 or 5 N of NaOH (if it was needed). The lime, whose consumption was 1 g/L, was utilized in order to carry out combined ferric/lime post-coagulation. The samples were kept for a period of 2 h to allow the settling of solids. After precipitation of iron hydroxycomplexes and slaked lime, the supernatant was decanted for analytical measurement. The experiments of wastewater oxidation with non-catalyzed hydrogen peroxide were conducted in the same reactor and treatment conditions as the respective Fenton-based treatment trials.

The ozonation experiments were carried out in semi-continuous bubble column 50 cm high and 9.0 cm in diameter with ozone diffuser (Ø 9 cm; porous size 0.1 mm) located in the center of the column's bottom. Ozone produced by laboratory ozone generator from oxygen was bubbled through 1 L of the wastewater sample. In all trials the ozone concentration in the feed-gas was kept at 10.0 ± 0.5 mg/L and the gas flow rate at 1.0 L/min. The initial and residual concentrations of ozone in the gas phase measured at $\lambda = 258$ nm with PCI-Wedeco ozone monitor (WEDECO Environmental Technologies Inc., USA) were used for calculation of ozone inlet and consumed doses. The duration of ozone treatment was 2 hours. Samples were treated both with pH adjustment to 3 and without pH regulation at initial pH value The stripping experiments of wastewater samples at initial pH values were carried out in the same reactor and treatment conditions as the respective ozonation trials.

All experiments were duplicated and the data on the initial wastewater samples was verified with at least 3 replicates. Results are presented including ± standard deviation of the mean ($n = 2$). In general, standard deviation in all trials was less than 4%. The experiments were performed at ambient room temperature (20 ± 1 °C).

Analytical Methods

The COD was determined by the closed reflux titrimetric method (APHA, 2005). The correction of hydrogen peroxide interference on COD test was done by the correlation equation according to Kang et al. (1999). The dissolved organic carbon (DOC) was measured in filtered (0.45 μm membrane) wastewater samples with total organic carbon analyzer (Shimadzu, Model TOC-5000, Kyoto, Japan). The total suspended solids (TSS) and total solids (TS) were determined according APHA (2005). Additionally, the BOD_7 for the treated and initial wastewater samples was determined (APHA, 2005). Acute toxicity of the initial and treated samples to *Daphnia magna* (*Cladocera, Crustacea*) was studied and a 24-h toxicity test was carried out. The medium effective concentration values (EC_{50}) and their 95% confidence limits were determined for the samples.

The pH measurements were performed using a digital pH meter (Model CG-840, Schot, Mainz, Germany). The electrical conductivity (EC) measurements were performed using a digital EC meter (Model HI9032, HANNA Instruments, Woonsocket, RI, USA). The total iron concentration in the solution was quantified by means of the phenanthroline method (APHA, 2005). The initial hydrogen peroxide concentration in stock solutions was determined spectrophotometrically by measurement of the absorption of hydrogen peroxide in the ultraviolet region at $\lambda = 254$ nm, using Heλion-β UV/VIS (Thermo Electron Corporation). The residual hydrogen peroxide concentration was measured by the spectrophotometric method with Ti^{4+} (Heλion-β UV/VIS, Thermo Electron Corporation, Waltham, MA, USA) (Eisenberg, 1943). The concentration of NO_3^-, PO_4^{3-}, SO_4^{2-} and Cl^- ions was measured by means of ion chromatography with chemical suppression of eluent conductivity (761 Compact IC, Metrohm).

RESULTS AND DISCUSSION

Characteristics of the wastewater samples (see Table 1) indicated excess of discharge limits required for local sewerage (i.e., BOD_7-350 mg/L and COD-770 mg/L). Thus, to improve effluents characteristics and comply with the regulations, combined physicochemical treatment schemes were implemented.

Ferric chloride coagulation, ozonation and three combined physicochemical treatment schemes: 1) ferric chloride pre-coagulation/Fenton-based process/lime post-coagulation, 2) Fenton-based process/lime post-coagulation, and 3) ferric chloride pre-coagulation/ozonation were applied for textile and mixed industrial wastewater treatment. To determine the most feasible and reasonable technique for real industrial wastewaters processing each treatment scheme was optimized separately. The effectiveness of treatment methods was mainly evaluated by COD, DOC and BOD_7 removal. The treated wastewater biodegradability improvement and toxicity changes were also assessed.

The results of the present study indicated general similarity in improvement of textile and mixed industrial wastewater quality by treatment with different processes and combined physicochemical schemes.

Coagulation

The coagulation process was utilized in order to remove suspended organic and inorganic compounds from the initial wastewater as well as a pre-treatment step before subsequent chemical oxidation (Fenton-based treatment and ozonation). In the coagulation experiments $FeCl_3$ was applied as the most common coagulant for wastewater treatment. The results of COD removal from Sample A and B after treatment with different doses of $FeCl_3$ at pH 4 and pH 9 are presented in Figure 1.

More than 50% reduction of COD was achieved for both wastewater samples principally due to TSS (partly including dispersed dye) decrease. The similar results for COD removal from textile wastewater by coagulation were obtained by Bae et al. (2004) and Selcuk (2005). Impact of pH on the coagulation proved to have a minor importance. DOC reduction in coagulation trials for Sample A was low due to mainly dissolved carbon nature with maximum removal efficiency of 13% for 1.0 g/L of $FeCl_3$ dosage. Application of $FeCl_3$

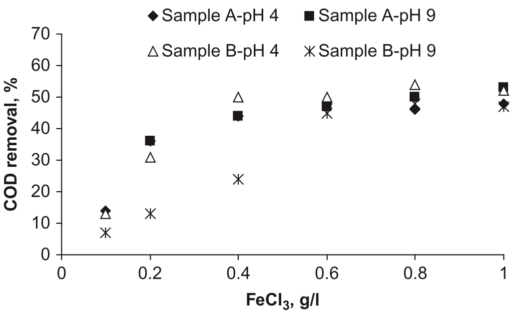

FIGURE 1. COD removal by coagulation with $FeCl_3$ at different pH values.

coagulation for wastewater Sample B showed better DOC removal efficiency up to 42% at 0.8 g/L of $FeCl_3$ dosage. In general coagulation removed larger molecules, and thus low molecular weight fraction of DOC is usually removed by this process with quite moderate efficacy. According to the results of the present study, the most feasible and reasonable $FeCl_3$ dosage for the highest wastewater quality improvement in the coagulation experiments was estimated at value of 0.6 g/L. Summarizing all above-mentioned results, coagulation proved effective pre-treatment step for the following chemical oxidation for both studied wastewater samples.

Treatment Schemes with Fenton-Based Process

After pre-coagulation step the partly treated wastewater was subjected to the following Fenton-based treatment combined with lime post-coagulation. The pre-coagulation was utilized in order to remove suspended organic and inorganic compounds from the wastewater before the Fenton process application and thus reduce the amount of oxidant required. Post-coagulation with lime was applied as it proved more effective technique than post-coagulation with sodium hydroxide for removal of main parameters such as COD and DOC as well as for removal of auxiliary parameters such as residual hydrogen peroxide and dissolved iron concentration (Kulik et al., 2008). In all trials with Fenton-based process the residual Fe^{2+} concentrations didn't exceed 1 mg/L.

Both the pre-treated and initial wastewater samples were subjected to Fenton-based treatment at different conditions: hydrogen peroxide concentration and way of its addition. All experiments presented in the current chapter were carried out at H_2O_2/Fe^{2+} w/w ratio of 6:1. The results of COD and DOC removal by application of treatment schemes with Fenton-based process are presented in Figures 2 and 3, respectively.

Treatment of Sample A demonstrated less than 5 and 10% of residual COD and DOC, respectively, for Fenton-based process/lime post-coagulation scheme. In the case of Sample B analogous treatment resulted in more than 85 and

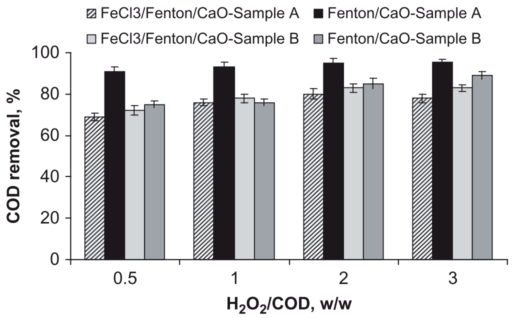

FIGURE 2. Total COD removal by treatment schemes with Fenton-based process.

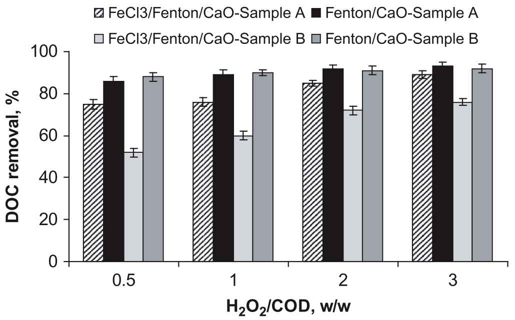

FIGURE 3. Total DOC removal by treatment schemes with Fenton-based process.

90% removal of COD and DOC, respectively. The maximum COD removal for ferric chloride pre-coagulation/Fenton-based process/lime post-coagulation was 80 and 83% for Sample A and Sample B, respectively. The decrease of DOC for this process was slightly lower and resulted in 40 and 24% of residual value for Sample A and Sample B, respectively.

Application of the Fenton-based process for pre-coagulated samples demonstrated lower removal efficiency for both studied wastewater samples. It can be assumed that compounds and its derivatives removed during the ferric chloride pre-coagulation step act as promoters in hydroxyl radical formation chain in the subsequent Fenton-based oxidation step. One more presumption is that elevated chloride ions concentration after $FeCl_3$ coagulation may inhibit Fenton reactions due to scavenging of hydroxyl radicals (Pignatello et al., 2006).

Both studied wastewater samples showed similar COD and DOC removal depending on the hydrogen peroxide dosage. H_2O_2/COD weight ratio of 2:1 proved optimal for both Fenton-based treatment schemes. It should be noticed that for achievement of compliance of discharge limits stated by regulations for wastewater directed to local sewerage it was sufficient to apply a H_2O_2/COD weight ratio of 0.5:1 for wastewater samples to fulfill needed requirements. The aim of further optimization of H_2O_2/COD weight ratio was the verification of assumption that Fenton-based treated wastewater effluents can comply with the requirements for discharge into water bodies.

According to Estonian environmental legislation conforming with EU Directive 91/271/EEC, treated industrial wastewaters can be discharged into water bodies in case of COD and BOD_7 reduction by 75 and 90%, respectively. In the current study Sample A treatment enabled COD and BOD_7 reduction by 95 and 93%, respectively, at H_2O_2/COD weight ratio of 2:1 for Fenton-based process/lime post-coagulation scheme and by 80 and 78%, respectively, at H_2O_2/COD weight ratio of 2:1 for ferric chloride pre-coagulation/Fenton-based process/lime post-coagulation method.

In the case of Sample B analogous treatment resulted in 85 and 72% removal of COD and BOD_7, respectively at H_2O_2/COD weight ratio of 2:1 for Fenton-based process/lime post-coagulation scheme and by 83 and 80%, respectively, at H_2O_2/COD weight ratio of 2:1 for ferric chloride pre-coagulation/Fenton-based process/lime post-coagulation method. Further increase of H_2O_2/COD weight ratio for Sample B treatment by Fenton-based process schemes to achieve needed BOD_7 could be unreasonable in economical point of view.

The influence of hydrogen peroxide stepwise addition on COD and DOC removal was also investigated. 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 et al., 2003; Teel et al., 2001). Thus, the two-step and three-step addition of hydrogen peroxide to samples at different H_2O_2/COD weight ratios was evaluated. In the current study the influence of the manner of hydrogen peroxide addition on the efficacy of the samples treatment by schemes with Fenton-based process was negligible. For example the three-step addition of hydrogen peroxide (H_2O_2/COD ratio 2:1, Fenton-based process/lime post-coagulation system) resulted in the final COD values 59 mg/L (Sample A, pH 3) and 276 mg/L (Sample B, pH 3), whereas the addition of hydrogen peroxide all at once led to COD residual values 79 and 296 mg/L, respectively. The difference in removal efficiencies was only 1–2%, and thus it can be concluded that hydrogen peroxide may be added all at once.

The influence of pH value of wastewater samples in Fenton-based oxidation step was investigated and results are presented in Figure 4. It was noticed, that experiments performed with samples with initial pH in Fenton-based process step were less effective comparing to those performed at pH 3. Thus, it is reasonable to adjust pH of effluents to above-mentioned value prior Fenton-based oxidation step for achievement of better wastewater quality improvement.

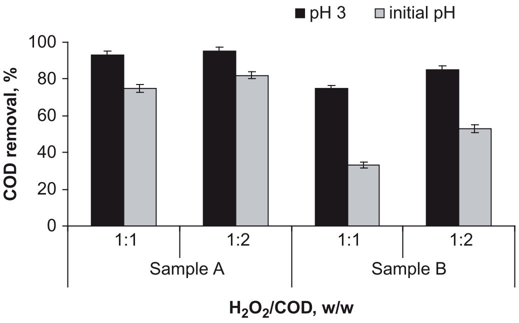

FIGURE 4. COD removal at different pH values by treatment with Fenton-based process/lime post-coagulation scheme.

The treatment of wastewater with hydrogen peroxide/lime post-coagulation, without Fe^{2+} catalyst addition, was also studied. The results demonstrated that application of H_2O_2 oxidation with subsequent lime post-coagulation for initial real wastewater samples was effective and reached 40–50% and up to 10% of COD and DOC removal, respectively. In general, these data are similar to those obtained in the pre-coagulation treatment scheme indicating the main impact of lime coagulation on wastewater samples' quality improvement.

Oxidation with H_2O_2 of pre-coagulated sample with following lime post-coagulation resulted in essentially lower COD and DOC reduction comparing to Fenton-based treatment schemes. The hydrogen peroxide applied without catalyst addition was not utilized entirely during the reaction time and its residual concentration was more than 1500 mg/L. As it is known, the by-products of H_2O_2 decomposition (oxygen and water) are natural components of the environment and not harmful, but entire H_2O_2 is a quite toxic to aquatic biota.

Treatment Schemes with Ozone

Four schemes with ozone were applied for treatment of wastewater samples: ozonation of original samples at initial and pH 3 values, and ozonation of pre-coagulated samples at pH 4 and 9.

The results of wastewater samples treatment by schemes with ozone are shown in Figures 5 and 6. In general, treatment schemes with ozone application were less effective comparing to systems utilizing Fenton-based process. The application of ozonation as the only treatment process proved to have quite moderate efficacy in wastewater samples quality improvement. In the case of combined pre-coagulation and subsequent ozone oxidation scheme the total removal of COD was more efficient, but mainly due to applied $FeCl_3$ coagulation step. Thus, the highest COD removal achieved after ozonation comprised only 28% and 32% for Sample A and Sample B, respectively. Combined $FeCl_3$/ozonation treatment of Sample A and Sample B resulted in 56 and 62% of total COD removal.

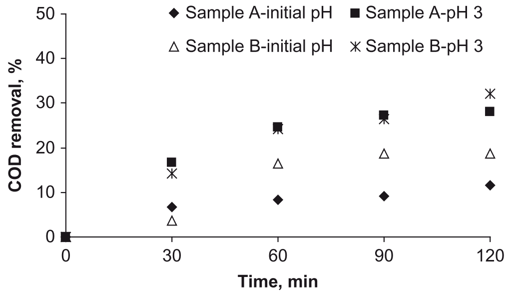

FIGURE 5. COD removal by ozonation at different pH values.

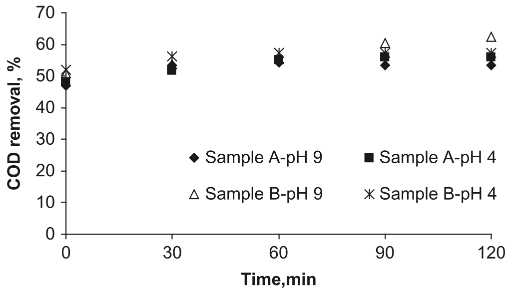

FIGURE 6. Total COD removal by $FeCl_3$/ozonation treatment scheme at different pH values.

In the case of DOC reduction ozone-based systems showed also lower efficiency compared to schemes with Fenton-based process. The results of total DOC removal by single ozonation and combined $FeCl_3$/ozonation treatment of Sample B were 16 and 42%, respectively. The total DOC reduction in Sample A after single ozonation step was negligible; after pre-coagulation/ozonation scheme only 12% of DOC was removed.

The ozonation process duration was two hours for every experiment and the pH drop after ozonation step was negligible for both samples. Thus, relatively low COD and DOC removal efficacy was confirmed by no formation of acidic intermediates during oxidation process. The similar results of moderate efficacy of textile wastewater treatment by the ozonation process were reported by Selcuk (2005). Lower performance of ozonation schemes comparing to Fenton-based systems may be explained by low oxidative capacity of the ozonation process at studied treatment conditions. Probably, the increase in ozone concentration will lead to higher treatment level. However, due to doubtful cost efficiency of the ozonation process at elevated ozone dosage, additional research was not done.

The experiments of initial wastewater samples stripping were also performed and demonstrated 13 and 10% of COD removal for Sample A and B, respectively. DOC removal during stripping was negligible (less than 5%) for both wastewater samples. Wastewater samples treated by schemes with ozonation exceed the discharge limits stated by regulations for wastewater directed to local sewerage.

Biodegradability and Toxicity

To assess the option of biological treatment of real wastewater samples after the every treatment schemes, the acute toxicity to *Daphnia magna* and biodegradability were evaluated. The biodegradability of initial and treated wastewater samples was estimated by the BOD_7/COD ratio and presented in Figure 7.

The results of Sample B treatment demonstrated effective biodegradability improvement up to 65% after application of Fenton-based process/lime post-coagulation system. All other studied treatment schemes showed negligible BOD_7/COD ratio changes. The increase of Sample A BOD_7/COD ratio in the range of 21–42% was achieved by all considered treatment methods except single ozonation, which showed no improvement of biodegradability for both wastewater samples. In general, combined Fenton-based process/lime post-coagulation treatment scheme proved the most effective for biodegradability improvement for both studied wastewater samples.

An acute toxicity to *Daphnia magna* of the initial and treated wastewater samples was studied by the 24-hours test. The results presented in Table 2 indicated general similarity in toxicity reduction behavior of both wastewater samples after treatment with different processes and combined physicochemical schemes.

All studied processes and combined physicochemical treatment schemes resulted in toxicity reduction in both wastewater samples. The application of Fenton-based process/lime post-coagulation and ozonation at pH 3 for Sample A and Sample B treatment showed complete detoxification.

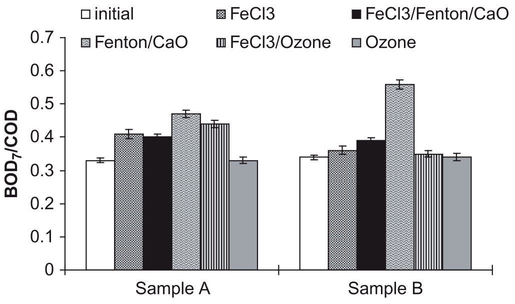

FIGURE 7. BOD_7/COD ratio of initial and treated wastewater samples at optimal conditions.

TABLE 2. Acute Toxicity (EC_{50}, %) of the Initial and Treated Wastewater Samples

		Coagulation					Ozonation	
Wastewater	Initial	pH 4	pH 9	$FeCl_3$/Fenton/CaO	Fenton/CaO	$FeCl_3$/Ozone	pH 3	Initial pH
Sample A	9.03	37.5	79.8	68.9	Non-toxic	Non-toxic	Non-toxic	39.1
Sample B	7.2	44	41.7	–	Non-toxic	80.3	Non-toxic	13.5

–no data.

Treatment Operational Costs

To assess the economical feasibility of different treatment schemes for wastewater samples purification the operational costs were calculated. The cost estimation and methodology was done on the basis of calculation undertaken by Munter et al. (2006).

The data obtained from the laboratory experiments in batch conditions were used to make an approximate calculation of operating costs comprising of energy required for ozonation and chemicals. Doses of ozone and hydrogen peroxide injected to wastewater samples were used in calculations without presumption of re-circulation of non-consumed chemicals. The specific energy requirement for ozone production from air was 20 kWh/kgO_3 with the estimated unit energy cost of 0.1 EUR/kWh. In the Fenton-based process hydrogen peroxide cost was 0.9 EUR/kg calculated as 100%, catalyst $FeSO_4 \cdot 7H_2O$ price was 0.13 EUR/kg. The cost for lime was taken 0.1 EUR/kg and coagulant ferric chloride 0.64 EUR/kg calculated as 100%. For sodium hydroxide and sulfuric acid used for pH adjustment average current prices of chemical on the Estonian market were taken as a basis. Treatment cost calculations in EUR/m^3 are presented in Table 3.

TABLE 3. Operational Costs of Treatment Methods at Optimal Conditions in EUR/m^3

	Chemical dosage		Treatment cost, EUR/m^3	
Treatment	$FeCl_3$, g/L	H_2O_2/COD, w/w	Sample A	Sample B
Coagulation at pH 4	0.6	–	0.48	0.48
Coagulation at pH 9	0.6	–	0.38	0.38
$FeCl_3$/Fenton/CaO	0.6	0.5:1	1.0	1.2
$FeCl_3$/Fenton/CaO	0.6	1:1	1.43	1.69
$FeCl_3$/Fenton/CaO	0.6	2:1	2.28	2.68
$FeCl_3$/Fenton/CaO	0.6	3:1	3.13	3.66
Fenton/CaO	–	0.5:1	1.0	1.22
Fenton/CaO	–	1:1	1.84	2.24
Fenton/CaO	–	2:1	3.48	4.28
Fenton/CaO	–	3:1	5.12	6.32
$FeCl_3$/Ozone at pH 9	0.6	–	3.24	3.17
$FeCl_3$/Ozone at pH 3	0.6	–	3.34	3.94
Ozonation at pH 3	–	–	2.94	3.11
Ozonation at initial pH	–	–	2.64	2.54

The cheapest method was the proven coagulation process that was efficient pre-treatment step for the following chemical oxidation. Fine wastewater purification was reached by Fenton-based treatment schemes, which was more expensive for studied wastewater samples. However, one should remember that a disadvantage of the using Fenton system either with a single coagulation process or coagulation pre-treatment step leads to chemical sludge formation, which requires the corresponding sedimentation basin installation and management of the produced waste sludge. The cost of ozonation turned out extremely high taking into account its poor treatment efficacy. Schemes with combination of ozone were also relatively expensive considering low purification efficacy.

The results of the current study indicated sufficiency of Fenton-based treatment schemes with H_2O_2/COD weight ratio 0.5:1 application for meeting the discharge limits stated by regulations for wastewater directed to local sewerage. The corresponding treatment costs were 1 and 1.22 EUR/m^3 for Samples A and B, respectively, by Fenton-based process/lime post-coagulation method. The costs of Fenton-based treatment scheme at H_2O_2/COD weight ratio 0.5:1 including pre-coagulation were comparable to above-mentioned prices for Sample A and B, respectively. If the aim of wastewater treatment was the discharge into water bodies, treatment cost would be higher. The related operational cost was 3.48 EUR/m^3 for Sample A at H_2O_2/COD weight ratio 2:1 by Fenton-based process/lime post-coagulation method. Although application of Fenton-based treatment scheme including pre-coagulation demonstrated lower removal efficiency, this method is less costly at higher H_2O_2/COD weight ratios comparing to Fenton-based process/lime post-coagulation method.

CONCLUSIONS

Ferric chloride coagulation, ozonation and three combined physicochemical treatment schemes: 1) ferric chloride pre-coagulation/Fenton-based process/lime post-coagulation, 2) Fenton-based process/lime post-coagulation, and 3) ferric chloride pre-coagulation/ozonation were used for textile and mixed industrial real wastewater treatment in order to improve effluents characteristics and comply with the regulations for wastewater directed to local sewerage. The results of the present study indicated general similarity in improvement of textile and mixed industrial wastewater quality by treatment with different processes and combined physicochemical schemes.

Ferric chloride pre-coagulation proved to be an effective pre-treatment step for the following chemical oxidation with COD removal ability more than 50%. The application of coagulation also improved biodegradability and reduced toxicity of the treated samples.

The characteristics of both wastewater samples treated by Fenton-based treatment schemes with H_2O_2/COD weight ratio 0.5:1 complied with the discharge limits stated by regulations for wastewater directed to local sewerage. In general, Fenton-based process/lime post-coagulation scheme proved more efficient than ferric chloride pre-coagulation/Fenton-based process/lime post-coagulation system. The increase of H_2O_2/COD weight ratio to 2:1 in the Fenton-based process/lime post-coagulation scheme resulted in 5 and 10% of residual COD and DOC, respectively, and thus improved textile wastewater characteristics up to the discharge limits stated by regulations for wastewater directed into water bodies. The influence of hydrogen peroxide stepwise addition on the efficiency of the samples treatment was negligible. Fenton-based treatment notably improved biodegradability of treated wastewater samples as well as reduced their toxicity. The complete detoxification was achieved after Fenton-based process/lime post-coagulation scheme.

The application of ozonation as the only treatment process proved to have moderate efficacy in wastewater samples quality improvement. In the case of combined pre-coagulation and subsequent ozone oxidation scheme the total removal of COD was more efficient, but mainly due to applied $FeCl_3$ coagulation step. Wastewater samples treated by schemes with ozone exceeded the discharge limits stated by regulations for wastewater directed to local sewerage. Single ozonation demonstrated no improvement of BOD_7/COD ratio for both studied wastewater samples.

The operational costs calculation showed that application of Fenton-based treatment schemes was the most reasonable considering their high treatment efficacy. Thus, treatment of textile and mixed industrial wastewater for meeting the discharge limits stated by regulations for wastewater directed to local sewerage costs were 1 and 1.22 EUR/m^3, respectively.

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PAPER II

Dulov, A., Dulova, N., Veressinina, Y., Trapido, M. 2011. Degradation of propoxycarbazone-sodium with advanced oxidation processes. Water Science and Technology: Water Supply, 11, 129-134.

Degradation of propoxycarbazone-sodium with advanced oxidation processes

A. Dulov, N. Dulova, Y. Veressinina and M. Trapido

ABSTRACT

The degradation of propoxycarbazone-sodium, an active component of commercial herbicide, in aqueous solution with ozone, UV photolysis and advanced oxidation processes: O_3/UV, O_3/UV/H_2O_2, H_2O_2/UV, and the Fenton process was studied. All these methods of degradation proved feasible. The kinetics of propoxycarbazone-sodium degradation in water followed the pseudo-first order equation for all studied processes except the Fenton treatment. The application of schemes with ozone demonstrated low pseudo-first order rate constants within the range of 10^{-4} s^{-1}. Addition of UV radiation to the processes improved the removal of propoxycarbazone-sodium and increased the pseudo-first order rate constants to 10^{-3} s^{-1}. The Fenton process was the most efficient and resulted in 5 and 60 s of half-life and 90% conversion time of propoxycarbazone-sodium, respectively, at 14 mM H_2O_2 concentration. UV treatment and the Fenton process may be recommended for practical application in decontamination of water or wastewater.

Key words | advanced oxidation processes (AOPs), propoxycarbazone-sodium, pseudo-first order rate constant, toxicity

A. Dulov (corresponding author)
N. Dulova
Y. Veressinina
M. Trapido
Department of Chemical Engineering,
Tallinn University of Technology,
Ehitajate tee 5,
Tallinn 19086,
Estonia
E-mail: *alexandr.dulov@gmail.com*;
niina.dulova@ttu.ee;
veressinina@staff.ttu.ee;
mtrapido@staff.ttu.ee

INTRODUCTION

In recent years, much research has assessed the possible adverse effects of herbicides on human health and ecosystems (Kundu 2005; Chu *et al.* 2006; Chen *et al.* 2008; Djebbar *et al.* 2008; Kaichouh *et al.* 2008; Qiang *et al.* 2010). Herbicides may cause contamination and greatly threaten the quality of groundwater overlaid by permeable soil (Gao & Deng 2009).

The herbicide contamination of water resources has led to an increasing interest in reliable technologies for their removal and degradation. The decontamination can be achieved by either appropriate physico-chemical methods, such as activated carbon adsorption and membrane filtration, or chemicals methods (Benitez 2006). Herbicides can be degraded with single oxidants such as UV radiation, ozone, hydrogen peroxide or their combinations in advanced oxidation processes (AOPs) (Meunier *et al.* 2006; Pignatello *et al.* 2006).

The AOPs consist of oxidant combinations such as O_3/H_2O_2, O_3/UV, etc., as well as the Fenton-based processes including the photo-Fenton system (Huston & Pignatello 1999). In general, they employ high oxidation-potential sources to produce hydroxyl radicals, which react with most organic compounds with rate constants in the range 10^7–10^{10} M^{-1} s^{-1} (Buxton *et al.* 1988). Once these radicals are generated, they can simultaneously oxidize organic compounds and produce additional organic radicals (Pignatello *et al.* 2006). Ozone is also known as an efficient oxidant for purification of drinking water, certain types of industrial wastewater, and as a source of hydroxyl radicals in the ozone-based AOPs (especially in the O_3/H_2O_2 system), which are feasible to eliminate refractory micropollutants, including pesticides. Chemical oxidation using the combination of UV radiation with hydrogen peroxide proved a very

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promising technique for oxidative degradation of persistent organic pollutants. Mercury lamps emitting at 254 nm are the UV sources most commonly used for cleavage of hydrogen peroxide into hydroxyl radicals (Benitez 2007).

Propoxycarbazone-sodium (Figure 1), which chemically belongs to sulfonylaminocarbonyltriazolinones, is an active ingredient of commercial herbicides developed by Bayer CropScience and marketed in Europe under the name of ATTRIBUT™ and in the USA/Mexico under the name of OLYMPUS™. In Estonia, it constitutes 19% of herbicides used for cultivation of cereal crops. Propoxycarbazone-sodium is used to control bromes, couch, and certain broad-leaved weeds in wheat and rye. Propoxycarbazone-sodium biochemical action results in inhibiting acetolactate synthase (ALS), which is a key enzyme in the biosynthesis of branched amino-acids (valine, leucine, and isoleucine) in the plant. The chemical is water soluble (42 g L^{-1}) and in the case of herbicide misuse, spillage and/or inappropriate storage, handling and disposal may present a hazard to the environment, including toxicity to aquatic organisms.

In the present study an aqueous solution of propoxycarbazone-sodium, an active component of commercial herbicide ATTRIBUT™, was treated with UV photolysis, H_2O_2/UV, the Fenton reagent, ozonation, O_3/UV, O_3/H_2O_2, and $O_3/UV/H_2O_2$ processes. To our knowledge, the degradation of propoxycarbazone-sodium with AOPs has never been studied yet. The main goal of the current research was to find methods for effective treatment of propoxycarbazone-sodium containing water.

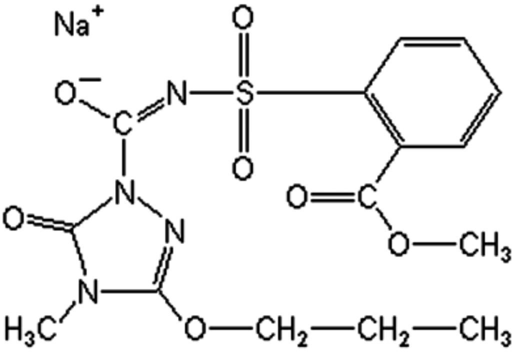

Figure 1 | Structure of propoxycarbazone-sodium.

EXPERIMENTAL

Materials and chemicals

All chemicals used were of reagent grade, or analytical grade when available, and were used without further purification. A commercial product ATTRIBUT™ containing active ingredient propoxycarbazone-sodium at concentration of around 70% was used as the model herbicide. Stock solutions with initial ATTRIBUT™ concentration of 200 mg L^{-1} were prepared in twice-distilled water. The initial pH of stock solution was in the range of 5.8–6.0. Sodium hydroxide and sulphuric acid aqueous solutions were used for pH adjustment.

Experimental procedure

All Fenton-based process trials were carried out in the batch mode and in non-buffered solutions. A standard procedure consisted of treating 1 L of stock solution in cylindrical glass reactor with a permanent agitation speed (200–300 rpm) for a period of 120 min; samples were withdrawn at selected time intervals (0, 60, 300, 900, 1800, 2700, 3600, 5400, and 7200 s). The reaction was stopped by adding 15% aqueous solution or solid crystals of Na_2SO_3 (Satoh *et al.* 2007). The classic Fenton reaction (H_2O_2/Fe^{2+}) was initiated by adding hydrogen peroxide (3.5–70 mM, the stoichiometric H_2O_2 concentration 11.2 mM) to the acidified stock solution ($pH = 3$) containing a known amount of Fe^{2+} ion. The molar ratio of H_2O_2/Fe^{2+} was kept at 10:1, which is optimal (Tang & Huang 1997). Fenton-based system trials were conducted without pH adjustment.

The hydrogen peroxide photolysis (H_2O_2/UV) experiments were carried out in the same reactor and treatment conditions as the respective Fenton-based process trials. The stock solution was treated both with pH adjustment to 3 or 9 and without pH regulation. The concentration of hydrogen peroxide was in the range of 3.5–14 mM.

A mercury low-pressure Osram lamp with an energy input of 10 W located inside the reactor in a quartz tube was used as an UV source in direct UV photolysis, H_2O_2/UV, O_3/UV and O_3/H_2O_2/UV processes. The UV radiation intensity at 254 nm measured by potassium ferrioxalate actinometry (Gordon & Ford 1972) was 3.25 ± 0.3 μEinstein s^{-1}. The lamp was turned on at least 10 min before the trial to insure constant output. The constant temperature in the reactor was maintained using a cooling jacket; the temperature was controlled by a thermometer immersed in the solution.

The ozonation, O_3/H_2O_2, O_3/UV and O_3/H_2O_2/UV experiments were carried out in 1.5 L Ace European-style three-neck flask with an ozone diffuser (Ø 3.5 cm; porous size 0.1 mm) located in the centre of the column and 1.5 cm from the column's bottom. Ozone produced by laboratory ozone generator from oxygen was bubbled through 1 L of stock solution. In all trials the ozone concentration in the feed-gas was kept at 5 ± 0.25 mg L^{-1} and the gas flow rate at 1.0 L min^{-1}. The initial and residual concentrations of ozone in the gas phase, measured at $\lambda = 258$ nm with a PCI-Wedeco ozone monitor (WEDECO Environmental Technologies Inc., USA), were used for the calculation of ozone inlet and consumed doses. The duration of ozone treatment was 120 min. The samples were treated both with pH adjustment to 3 or 9 and without pH regulation. The concentration of hydrogen peroxide in the O_3/H_2O_2 process was 7 mM; in the O_3/H_2O_2/UV system it was in the range of 3.5–14 mM.

All experiments were duplicated and the data on the initial solution was verified with at least three replicates. The results of the analysis are presented as means, with the standard deviation below 3% in all cases. The experiments were performed at 22 ± 1°C.

Analytical methods

Propoxycarbazone-sodium concentrations were quantified using a high performance liquid chromatograph CLAS MPm (Labio Ltd.) equipped with a MAG 0 (1.5×50 mm) Biospher PSI 100 C18 (particle size, 5 m) microcolumn and UV/VIS detector SAPHIRE. The isocratic method with a mobile phase containing 30% acetonitrile and 0.2% of acetic acid in water was applied. Samples were analyzed at a flow rate of 70 L min^{-1} and absorbance wavelength of 230 nm. The concentration of propoxycarbazone-sodium was determined by using the standard chemical to fit the retention time.

The COD was determined by the closed reflux titrimetric method (APHA 2005). The correction of hydrogen peroxide interference on the COD test was done by the correlation equation according to Kang & Chang (1997). The residual hydrogen peroxide concentration was measured by the spectrophotometric method with Ti^{4+} (Eisenberg 1943). Acute toxicity of the initial and treated samples to *Daphnia magna* (*Cladocera, Crustacea*) was evaluated with a 24-hours toxicity test (ISO 6341). The medium effective concentration values (EC_{50}) and their 95% confidence limits were determined for the samples.

RESULTS AND DISCUSSION

Degradation schemes with ozone

The efficiency of herbicide removal was monitored by residual concentration of propoxycarbazone-sodium and COD reduction. The propoxycarbazone-sodium (PS) degradation followed a pseudo-first order kinetic law and can be described with regard to the compound concentration:

$$dC_{ps}/dt = -k_1 C_{ps}$$

where k_1 is the pseudo-first order rate constant.

When ozonation alone was used, the reaction rate was lower than in other studied processes (Table 1). The 90% conversion times ($T_{90\%}$) of propoxycarbazone-sodium in the ozonation exceeded 7200 seconds (duration of the experiment). It was ascertained that the influence of pH on the degradation of propoxycarbazone-sodium during ozonation was minor. For example, the pseudo-first order rate constants for the ozonation process were 1.15×10^{-4}; 1.76×10^{-4} and 1.43×10^{-4} s^{-1} at pH 3.0, initial pH, and pH 9.0, respectively. The highest COD removal during ozonation reached 36% at pH 9. The air stripping trials demonstrated less than 2% removal of propoxycarbazone-sodium.

Combination of ozone with hydrogen peroxide is a possible way to produce hydroxyl radicals and, therefore, to increase the oxidation rate of propoxycarbazone-sodium. Indeed, the O_3/H_2O_2 process resulted in a twofold increase of k_1 relative to ozonation only. The highest value of k_1 2.87×10^{-4} s^{-1} was observed at pH 9 (Table 1). The COD removal by O_3/H_2O_2 treatment was in the range of 11–34%.

The UV-only treatment resulted in a higher reaction rate constant than ozonation. In the combined O_3/UV scheme, k_1 increased by a factor 2 and 10 as compared with UV photolysis and ozonation, respectively. The variation in the degradation rate among different pH values was minor.

Table 1 | Half-life times ($T_{1/2}$), 90% conversion times ($T_{90\%}$) and the pseudo-first order rate constants (k_1) of propoxycarbazone-sodium degradation with different treatment methods

Treatment method	pH	H_2O_2 (mM)	$T_{1/2}$ (s)	$T_{90\%}$ (s)	k_1 (s^{-1}) × 10^{-4}, $r^2 > 0.985$
Ozonation	initial	-	3600	>7200	1.76
Ozonation	3	-	6300	>7200	1.15
Ozonation	9	-	4400	>7200	1.43
O_3/UV	initial	-	900	2300	11.3
O_3/UV	3	-	800	2300	11.2
O_3/UV	9	-	900	3300	9.35
UV photolysis	initial	-	900	2700	5.72
O_3/H_2O_2	initial	7	3600	>7200	2.14
O_3/H_2O_2	3	7	7200	>7200	1.03
O_3/H_2O_2	9	7	2300	7200	2.87
$O_3/UV/H_2O_2$	3	7	900	2300	12.8
$O_3/UV/H_2O_2$	9	7	900	2300	11.0
$O_3/UV/H_2O_2$	initial	3.5	900	2300	10.7
$O_3/UV/H_2O_2$	initial	7	900	2300	8.7
$O_3/UV/H_2O_2$	initial	14	700	1700	14.1
H_2O_2/UV	3	3.5	800	2500	9.02
H_2O_2/UV	3	7	800	2000	9.31
H_2O_2/UV	3	14	700	1800	10.2
H_2O_2/UV	initial	7	800	2700	7.49
H_2O_2/UV	9	7	900	2700	7.64
Fenton	3	3.5	600	3200	-
Fenton	3	7	5	400	-
Fenton	3	14	5	60	-
Fenton	3	35	0	30	-
Fenton-based	initial	3.5	1800	>7200	-
Fenton-based	initial	7	20	1100	-
Fenton-based	initial	14	5	80	-

The COD removal by the O_3/UV process at different pH values was in the range of 30–44%.

Addition of hydrogen peroxide to O_3/UV process did not improve the degradation of propoxycarbazone-sodium (Table 1). However, COD removal by $O_3/UV/H_2O_2$ treatment was higher (up to 60%). The experiments with different H_2O_2 concentrations indicated a minor improvement of propoxycarbazone-sodium degradation with H_2O_2 dosage increase.

In general, the application of ozonation schemes with supplementary UV radiation was more effective for propoxycarbazone-sodium degradation and COD reduction.

Degradation with hydrogen peroxide photolysis

No degradation of propoxycarbazone-sodium was observed in the H_2O_2 oxidation test. The UV photolysis degraded propoxycarbazone-sodium with a constant $5.72 \times 10^{-4}\ s^{-1}$ reaction rate (Table 1). The addition of H_2O_2 to UV treatment improved the propoxycarbazone-sodium degradation substantially and resulted in the highest k_1 of $10.2 \times 10^{-4}\ s^{-1}$. As the degradation rate was slightly dependent on H_2O_2 concentration in the range of 3.5–14 mM, a lower H_2O_2 admixture may be recommended. A minor dependence of propoxycarbazone-sodium degradation rate on the pH was observed. For example, the pseudo-first order rate constants for H_2O_2/UV process were $9.31-10^{-4}$; 7.49×10^{-4} and 7.64×10^{-4} s^{-1} at pH 3, initial pH, pH 9, respectively. The COD elimination by the H_2O_2/UV process at different treatment conditions was in the range of 25–40%.

Degradation with the Fenton reagent

Kinetic constants' values were not calculated for the Fenton-based processes because the data did not fit any kinetic model. $T_{1/2}$ and $T_{90\%}$ for the degradation of propoxycarbazone-sodium calculated from the degradation curves are presented in Table 1.

In the Fenton system, the degradation of propoxycarbazone-sodium proved dependent on the H_2O_2 concentration. Thus, the increase in hydrogen peroxide dose from 3.5 to 35 mM clearly intensified the degradation of the target compound (Table 1.). The value of $T_{90\%}$ for the experiment with H_2O_2 concentration of 35 mM was decreased by factor 100 (from 3200 s to 30 s) as compared with the trial where the H_2O_2 concentration was 3.5 mM. It was noticed that degradation proceeded slower at the initial solution pH than at pH 3. Hence, to accelerate propoxycarbazone-sodium degradation, it is reasonable to adjust the pH of the solution to 3 prior the Fenton treatment step. The efficiency of COD removal improved with the increase of the H_2O_2 dosage (52 and 70% removal of COD at 3.5 and 14 mM H_2O_2 doses, respectively) and was higher than in other treatment methods.

In general, judging by $T_{1/2}$ and $T_{90\%}$ values and COD removal, the Fenton reagent proved the most efficient of the studied processes for the degradation of propoxycarbazone-sodium.

Toxicity

Acute toxicity of the initial and treated samples to *Daphnia magna* was studied in a 24-hours test. The toxic effects are listed in Table 2. Although the initial stock solution was non-toxic, some increase in toxicity was observed after treatment by several methods. The application of UV photolysis as well as the Fenton process resulted in non-toxic samples. Treatment with O_3/UV/H_2O_2 also produced a non-toxic solution at all studied conditions. The Fenton-based process performed at an elevated H_2O_2 concentration resulted in toxicity increase, probably due to hydrogen peroxide residue. Propoxycarbazone-sodium solutions treated with ozonation, H_2O_2/UV, and O_3/UV were mainly toxic. To eliminate acute toxicity, the treatment conditions should be carefully studied and controlled.

Table 2 | Acute toxicity of the initial and treated ATTRIBUT™ solutions

Treatment method	pH	H_2O_2 (mM)	Toxic effect
Stock solution	initial	-	Non-toxic*
Ozonation	initial	-	Toxic**
Ozonation	3	-	Slightly toxic***
Ozonation	9	-	Toxic
O_3/UV	initial	-	Slightly toxic
O_3/UV	3	-	Non-toxic
O_3/UV	9	-	Toxic
O_3/H_2O_2	initial	7	Non-toxic
O_3/H_2O_2	3	7	Non-toxic
O_3/H_2O_2	9	7	Toxic
O_3/UV/H_2O_2	initial	3.5	Non-toxic
O_3/UV/H_2O_2	initial	7	Non-toxic
O_3/UV/H_2O_2	initial	14	Non-toxic
O_3/UV/H_2O_2	3	7	Non-toxic
O_3/UV/H_2O_2	9	7	Non-toxic
Fenton	3	7	Non-toxic
Fenton-based	initial	7	Non-toxic
Fenton-based	initial	14	Toxic
UV photolysis	initial	-	Non-toxic
H_2O_2/UV	3	7	Toxic
H_2O_2/UV	initial	7	Toxic
H_2O_2/UV	9	7	Toxic

*$EC_{50} > 100\%$
**$EC_{50} < 60\%$
***$EC_{50} > 80\%$

CONCLUSION

This study was the first to evaluate the efficacy of AOPs for propoxycarbazone-sodium degradation. Propoxycarbazone-sodium was not degraded with ozonation alone at dosages and time common for potable water treatment. Moreover, ozonation led to toxicity increase. The Fenton process proved the most efficient for propoxycarbazone-sodium degradation, resulting also in the highest COD removal among the studied processes and non-toxic samples at moderate H_2O_2 admixture (7 mM). The UV radiation was quite effective as an only treatment: it substantially improved the degradation in combined schemes. However, the samples after H_2O_2/UV and O_3/UV implementation were mostly toxic irrespective of the treatment conditions. On the basis of this study, the UV treatment and the Fenton process may be recommended for practical application in decontamination of water or wastewater. Any mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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PAPER III

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Catalytic degradation of picric acid by heterogeneous Fenton-based processes

Niina Dulova*, Marina Trapido and Aleksandr Dulov

Department of Chemical Engineering, Tallinn University of Technology, Tallinn, Estonia

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The efficiency of goethite, magnetite and iron powder (Fe^0) in catalysing the Fenton-based oxidation of picric acid (PA) in aqueous solution was studied. The effect of pH, hydrogen peroxide concentration, and catalyst type and dosage on treatment efficacy was investigated. The adsorption of PA from aqueous solution by heterogeneous catalysts was also examined. The results demonstrated negligible PA removal in H_2O_2/α-FeOOH and H_2O_2/Fe_3O_4 systems independent of process pH, and hydrogen peroxide and catalyst dosage. The PA adsorption effects of both iron oxides turned out to be insignificant for all studied pH values and catalyst dosages. The H_2O_2/Fe^0 system proved efficient at degrading PA, but only under acidic conditions (pH 3). The results indicated that, due to rather fast leaching of ferrous ions from the iron powder surface, PA degradation was carried out mainly by the classic Fenton oxidation mechanism in the bulk solution. The adsorption of PA onto the iron powder surface may also contribute to the overall efficiency of PA degradation.

Keywords: AOPs; chemical oxidation; iron oxides; zero valent iron; 2,4,6-trinitrophenol

1. Introduction

The Fenton chemistry, in which the decomposition of hydrogen peroxide is catalysed by iron to form hydroxyl radicals, has recently been applied to the degradation of various persistent and refractory organic pollutants in water and wastewater [1–7].

The main disadvantage of the classic Fenton process (H_2O_2/Fe^{2+}) is the fact that soluble iron, added as a catalyst, cannot be retained in the process as it causes additional water pollution. An undesirable iron sludge is generated, which requires proper treatment and disposal. To avoid the need to remove iron after the treatment, heterogeneous catalysts can be used. The source of iron used as the catalyst can be a solid surface, including iron-containing minerals or iron-coated silica particles. In addition, metallic iron, Fe^0, a zero valent iron, has been recently studied as a precursor of Fe^{2+} in the Fenton reaction. The Fe^{2+} was found to dissolve from the Fe^0 surface, especially if the solution was acidic.

There are two 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 solid surface or the catalysis may occur at the surface itself. For the former possibility, the reaction leading to the dissolution of Fe^{2+} from the surface of goethite is presented in Equation (1). Hydroxyl radicals are then produced by the Fenton reaction, presented in Equation (2). Furthermore, Fe^{3+} is precipitated according to reaction (3).

$$\alpha\text{-FeOOH}_{(s)} + 2H^+ + \tfrac{1}{2}H_2O_2 \rightarrow Fe^{2+} + \tfrac{1}{2}O_2 + 2H_2O \qquad (1)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + {}^{\bullet}OH \qquad (2)$$

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

In general, Equations (1)–(3) 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 catalysed hydrogen peroxide decomposition is proposed by Lin and Gurol [8]. The main reactions are presented in Equations (4)–(8). 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) [Equation (4)].

$$\equiv Fe^{3+}OH + H_2O_2 \leftrightarrow (H_2O_2)_s \qquad (4)$$

$$(H_2O_2)_s \rightarrow \equiv Fe^{2+} + H_2O + HO_2^{\bullet} \qquad (5$$

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*Corresponding author. Email: niina.dulova@ttu.ee

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$$\equiv \mathrm{Fe}^{2+} + \mathrm{H_2O_2} \rightarrow \equiv \mathrm{Fe}^{3+}\mathrm{OH} + {}^{\bullet}\mathrm{OH} \qquad (6)$$

$$\mathrm{HO_2}^{\bullet} \leftrightarrow \mathrm{H}^{+} + \mathrm{O_2}^{\bullet -} \qquad (7)$$

$$\equiv \mathrm{Fe}^{3+}\mathrm{OH} + \mathrm{HO_2}^{\bullet} / \mathrm{O_2}^{\bullet -} \rightarrow \equiv \mathrm{Fe}^{2+} + \mathrm{H_2O} / \mathrm{OH}^{-} + \mathrm{O_2} \qquad (8)$$

The Lin and Gurol [8] mechanism assumes that no dissolution of goethite occurs and that all reactions take place on the mineral surface. Hence the formation of hydroxyl radicals occurs by heterogeneous catalysis. However, it is most likely that the formation of hydroxyl radicals occurs simultaneously by both mechanisms.

The main advantages of the application of iron minerals in Fenton chemistry are [9]:

- extended periods of catalyst life without the need for regeneration or replacement;
- the catalyst may be removed from the treated water by sedimentation or filtration;
- the pH of treated media may be in the range 5–9;
- the reaction is almost insensitive to the concentration of inorganic carbonate.

Picric acid (PA), more formally called 2,4,6-trinitrophenol (TNP), is used in the manufacture of explosives, rocket fuels, fireworks, coloured glass, matches, electric batteries and disinfectant. It is also used in the pharmaceutical and leather industries, and in dyes, copper and steel etching, histology and textile printing. However, environmental contamination by picric acid is associated principally with the explosives industry. In general, aromatic nitro compounds are resistant to chemical or biological oxidation because of their high stability due to the electron-withdrawing nitro groups and their solubility in water. Thus, the treatment of groundwater and soil contaminated with picric acid is a critical and vital issue.

In the present study, the application of heterogeneous catalytic reactions of hydrogen peroxide with goethite (α-FeOOH), magnetite (Fe_3O_4) and iron powder (Fe^0) particles to the degradation of PA in aqueous solution was investigated. The effect of pH, hydrogen peroxide concentration, and catalyst type and dosage on treatment efficacy was examined. In order to consider the adsorption effect in heterogeneous Fenton-based systems, the sorption of the PA at various pH values was also studied.

2. Materials and methods

2.1. Materials and reagents

All chemicals used were of reagent grade, or analytical grade when available, and were utilized without further purification. Goethite (30–50 mesh), magnetite (98%, <5 μm) and iron powder (≥99%, 200 μm) were used as heterogeneous catalysts. The specific surface area was measured by multipoint N_2-BET analysis using a sorptometer KELVIN 1042 (COSTECH Instruments) as 112.5, 7.5 and 0.08 $m^2\ g^{-1}$ for goethite, magnetite and iron powder, respectively. Stock solutions were prepared in twice-distilled water. The initial concentration of PA during all the experimental runs was 0.4 mM. NaOH and H_2SO_4 solutions were applied for pH adjustment.

2.2. Experimental procedure

All trials were carried out in batch mode and in non-buffered solutions. PA solutions were treated in a 0.6 L cylindrical glass reactor with permanent agitation at a speed sufficient to provide complete mixing for uniform distribution and full suspension of iron catalyst particles for a period of 120 minutes; samples were withdrawn at selected time intervals and filtered through a Millipore filter (0.45 μm). The reaction was stopped by adding 15% aqueous solution or solid crystals of Na_2SO_3.

The classic Fenton reaction (H_2O_2/Fe^{2+}) was initiated by adding an optimum amount of H_2O_2 to a PA solution (pH 3) containing a known amount of Fe^{2+} ion. The molar ratio of H_2O_2/Fe^{2+} was kept invariable at 10:1. Heterogeneous Fenton-based treatment trials (H_2O_2/α-FeOOH, H_2O_2/Fe_3O_4 and H_2O_2/Fe^0) were carried out with different catalyst dosages at pH values in the range 3–9. The suspensions were continuously stirred for ca. 30 minutes prior to H_2O_2 addition to establish the adsorption/desorption equilibrium between PA and the catalyst particles. The experiments on the adsorption effect of heterogeneous catalysts dosages and PA oxidation with non-catalysed hydrogen peroxide were conducted in the same reactor and under the same treatment conditions as the respective Fenton-based treatment trials.

All experiments were duplicated and the data on the untreated (initial) samples were verified with at least three replicates. The results of the analysis of initial and treated samples are presented as the mean, with the standard deviation below 3.0% in all cases. The experiments were performed at ambient room temperature (20 ± 1°C).

2.3. Analytical methods

PA concentrations were quantified by means of a CLAS MPm (Labio Ltd) high performance liquid chromatograph equipped with a MAG 0 ($1.5 \times 50\ mm^2$) Biospher PSI 100 C18 (particle size, 5 μm) microcolumn and UV/VIS detector SAPHIRE. The isocratic method with a solvent mixture of 30% acetonitrile and 0.2% acetic acid in water was applied. Samples were analysed at a flow rate of 70 µL min^{-1} and absorbance wavelength of 355 nm. The concentration of PA was determined using standard chemicals to fit the retention time.

The concentrations of NO_3^- ions formed as a result of organically bounded nitrogen mineralization were measured by means of ion chromatography with chemical suppression of eluent conductivity (761 Compact IC, Metrohm) coupled with a METROSEP A Supp 5 analytical column (4 × 150 mm^2). An eluent solution containing 3.2 mM Na_2CO_3 and 1.0 mM $NaHCO_3$ was pumped at flow rate of 0.7 mL min^{-1}.

Dissolved organic carbon (DOC) was measured in samples filtered through a 0.45 µm membrane by a TOC analyser (TOC-5000, Shimadzu) [10]. Chemical oxygen demand (COD) was determined by the closed reflux titrimetric method [10]. The correction of hydrogen peroxide interference on the COD test was performed using the correlation equation according to Kang *et al.* [11]. The pH measurements were performed using a digital pH meter (Model CG-840, Schott). The concentration of total dissolved iron in bulk solution was measured photometrically by the phenanthroline method (Heλion-β UV/VIS spectrophotometer, Thermo Electron Corporation) [10]. The residual hydrogen peroxide concentration was determined by the colorimetric method at 410 nm as a complex with Ti^{4+} (Heλion-β UV/VIS spectrophotometer, Thermo Electron Corporation) [12].

3. Results and discussion

3.1. The classic Fenton process

The effectiveness of the application of the classic Fenton process (H_2O_2/Fe^{2+}, pH 3) for the degradation of PA in aqueous solution was studied first. The influence of the initial molar ratio of PA/H_2O_2 on the process efficiency was investigated. In the present study, all experiments were conducted under normal laboratory lighting as Lin and Gurol [8] had proved that illumination had no effect on hydrogen peroxide decomposition.

The degradation of organic compounds by hydroxyl radicals (${}^{\bullet}OH$) is typically described as a second-order reaction. By assuming the hydroxyl radical's instantaneous concentration is constant, the kinetics of PA degradation in water can be described according to the pseudo-first order equation as given below:

$$\frac{dC_{PA}}{dt} = -k_1 \times C_{PA} \qquad (9)$$

where k_1 is the pseudo-first order rate constant.

The $-k_1$ constants were obtained from the slopes of the straight lines by plotting $\ln(C_t)$ as a function of time (t) through linear regression, which produced correlation coefficients >0.985. PA degradation was completed in seven minutes and a pseudo-first order rate constant of k_1=0.5064 min^{-1} was established for PA/H_2O_2 of 1:10. In the case of half smaller hydrogen peroxide dosage (PA/H_2O_2 of 1:5), PA completely disappeared in 15 minutes and a pseudo-first order rate constant was equal to k_1=0.1959 min^{-1}.

Blank non-catalysed hydrogen peroxide oxidation of PA in aqueous solution was also studied. H_2O_2 alone proved not effective for PA degradation due to the low rates of reaction at reasonable H_2O_2 concentrations.

Thus, Fenton treatment turned out to be an effective tool for PA degradation in aqueous solution. However, the classic Fenton process (H_2O_2/Fe^{2+}) has several disadvantages, including the problem of the generation of large volumes of iron-containing sludge, which is inherent in the homogeneous catalyst system. To solve all those drawbacks, modified Fenton processes can be applied. Heterogeneous Fenton-based processes are of particular interest, since most of the iron remains in the solid phase and can be reused.

3.2. Goethite and magnetite catalysed Fenton-based process

Numerous studies on the evaluation of different iron oxides under the same conditions exhibited differences in the degradation rates of hydrogen peroxide and organic contaminants. For example, Matta *et al.* [13] reported that the oxidation state of the iron catalyst and the iron dissolution rate are key parameters for effective performance of mineral-catalysed Fenton-based reactions. Thus, ferrous-bearing minerals (such as magnetite) proved more effective than ferric oxides (such as goethite) for degradation of nitroaromatics at acidic and neutral pH. On the other hand, goethite is generally the preferred mineral oxide catalyst mainly because it appears to have the fastest reaction with H_2O_2 [14]. Therefore, in the current study both goethite and magnetite were examined as heterogeneous catalysts for Fenton-based oxidation of PA in aqueous solution.

The mineral-catalysed Fenton-based reaction is a surface-controlled reaction that depends on H_2O_2 concentration, the iron mineral surface area and other system parameters (pH, etc.). According to Kwan and Voelker [15], the dominant reaction in the mineral-catalysed system is a chain of reactions occurring on the mineral surface. Secondly, and at pH below 4, a propagation reaction by dissolved iron ions may take place in solution due to proton-promoted dissolution of iron from the oxide surface. The overall heterogeneous reaction will include various steps such as diffusion of chemicals to the surface, surface complex formation (specific adsorption on the reactive sites), actual electron transfer, dissociation of the successor complex (desorption of products) and regeneration of the reactive sites [8].

The influence of catalyst load and the pH value of the reaction solution on PA degradation efficiency was investigated. The effect of goethite and magnetite dosages in the range 0.1–3 g L^{-1} at pH values of 3, 5, 7 and 9 on adsorption and overall treatment efficacy was studied. Adding excess catalyst could provide more surface areas for reaction interface. On the other hand, more PA adhered to the iron oxide surface increasing the adsorption effects. As a result, the dense covering of PA on iron oxides could reduce the area available for the dissolution of ferrous ions into the bulk solution and block the active sites that participate in the catalysis of the Fenton-based reaction.

A maximum sorption of PA was expected to be at pH 5–7 which is much higher than the pK_a of PA (0.38), implying electrostatic interactions between partial negative charges on the oxygen atom of the PA molecule and partially protonated surface of the iron oxides [13]. However, the PA sorption test showed that the adsorption effects were of very minor significance (less than 5%) for all studied pH values for both goethite and magnetite.

Lin and Gurol [8] demonstrated that H_2O_2 at low concentrations does not affect the dissolution kinetics of iron oxide and the surface reactivity. However, Liou and Lu [16] proved the dissolution kinetics and degradation interact as the molar ratio of PA/H_2O_2 is increased by over 1:1000. In order to understand whether the iron ion leached from iron oxides would contribute significantly to the decomposition of H_2O_2, control experiments of goethite and magnetite dissolution were conducted. Thus, 1 g L^{-1} of goethite was treated at pH 3 with H_2O_2 concentrations in the range 4–40 mM. The results showed less than 0.003 mM of the total dissolved iron ions in the solution after 120 minutes of reaction. Similar results were obtained for H_2O_2/Fe_3O_4 systems. The amount of the total dissolved iron ions for both $H_2O_2/\alpha\text{-FeOOH}$ and H_2O_2/Fe_3O_4 systems was negligible at pH values above 3.

The experiment of iron oxide catalysed Fenton-based oxidation of PA was conducted at different catalyst dosages (0.1–3 g L^{-1}), hydrogen peroxide concentrations (PA/H_2O_2 m/m 1:10, 1:50 and 1:100) and pH values (3, 5, 7 and 9). The results of the present study demonstrated scarcely any degradation of PA in 120 minutes of reaction in both $H_2O_2/\alpha\text{-FeOOH}$ and H_2O_2/Fe_3O_4 systems for all treatment conditions. Additionally, during 120 minutes of the iron oxide catalysed Fenton-based oxidation, some decrease in hydrogen peroxide concentration and negligible increase in the total dissolved iron ions in the solution were observed. Kwan and Voelker [15] proposed that some of the hydrogen peroxide decomposes to oxygen and water at the surface of the heterogeneous catalysts without producing dissolved radicals. In general, it seems that degradation of PA in iron oxide catalysed Fenton-based systems is a time-consuming process, as has been found for 4-chlorphenol degradation in the H_2O_2/Fe_3O_4 system by Zhou *et al.* [17].

3.3. Zero valent iron catalysed Fenton-based process

In recent years, metallic iron, Fe^0, a potential donor of three electrons, has been considered as a precursor of Fe^{2+} in the Fenton reaction. Elemental iron is regarded as a suitable donor of electrons for water and wastewater treatment as well as for the *in situ* remediation of contaminated groundwater and soil. Therefore, in the present study, the effectiveness of iron powder as a source of iron catalyst in the Fenton system was also examined.

The Fe^{2+} was found to dissolve from the Fe^0 surface, and thus zero valent iron acts as a catalyst in place of ferrous salts [18]. Initially, iron metal pieces produce ferrous ions and hydrogen gas when subjected to acidic conditions:

$$Fe^0 + 2H^+ \rightarrow Fe^{2+} + H_2 \qquad (10)$$

The ferrous ions then produce hydroxyl radicals in a similar way to the classic Fenton reaction [Equation (2)]. Finally, the ferric iron is reduced to ferrous by interaction with zero valent iron and the cycle continues as long as there is hydrogen peroxide present:

$$Fe^0 + 2Fe^{3+} \rightarrow 3Fe^{2+} \qquad (11)$$

The results of PA degradation by H_2O_2/Fe^0 system at pH 3 (PA/H_2O_2 molar ratio of 1:10) are presented in Figure 1. At a catalyst dosage of 0.5 g L^{-1}, PA degradation was complete in 10 minutes. The application of five times less zero valent iron under the same treatment conditions resulted in PA degradation that took three times longer. Kinetic constant values were not calculated in the latter cases because data did not fit properly with any kinetic model.

The measurement of the total dissolved iron ions in reaction solutions indicated that, for 0.5 g L^{-1} Fe^0 dosage, the concentration of total dissolved iron ions reached 0.4 mM in less than one minute of reaction time. This amount of iron ions is comparable with Fe^{2+} concentration utilized in the classic Fenton system with a PA/H_2O_2 molar ratio of 1:10 (Figure 1). In the case of the H_2O_2/Fe^0 system with a catalyst dosage of 0.1 g L^{-1}, the concentration of total dissolved iron ions was around 0.2 mM after 30 minutes of reaction time; thus, in 30 minutes, the concentration of iron ions was similar with the Fe^{2+}

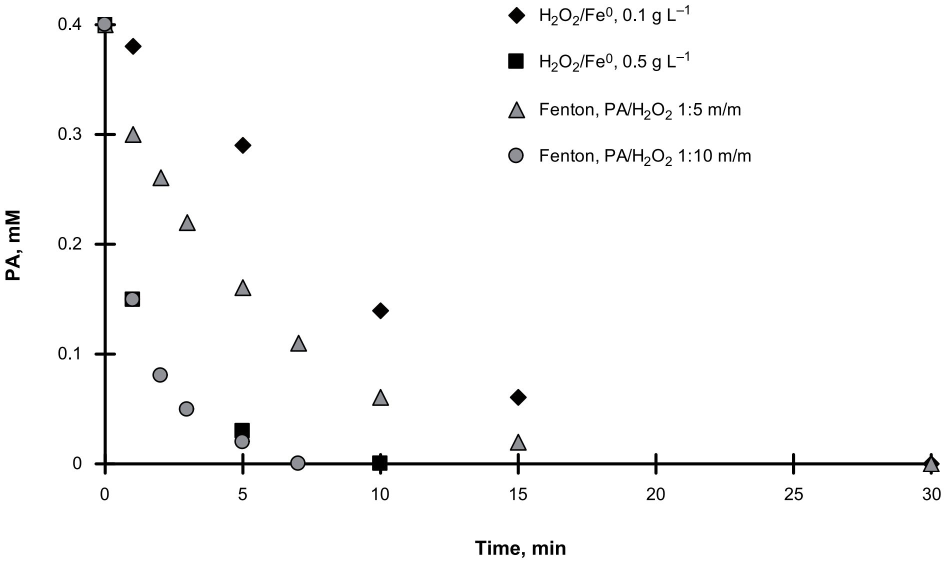

Figure 1. PA degradation by H_2O_2/Fe^0 systems at pH 3 (PA/H_2O_2 molar ratio of 1:10) and the classic Fenton systems.

concentration utilized in the classic Fenton system with a PA/H_2O_2 molar ratio of 1:5 (Figure 1). These results indicate that, after the initial leaching of ferrous ions from the iron powder surface, PA degradation is mainly carried out throughout by the classic Fenton oxidation mechanism in the bulk solution. The increase in dissolved iron concentration in the bulk solution ceased after 15 and 50 minutes of reaction in H_2O_2/Fe^0 system with 0.5 and 0.1 g L^{-1} Fe^0, respectively. Notably, at the same time, the amount of added H_2O_2 was completely used up in both systems as demonstrated in Figure 2.

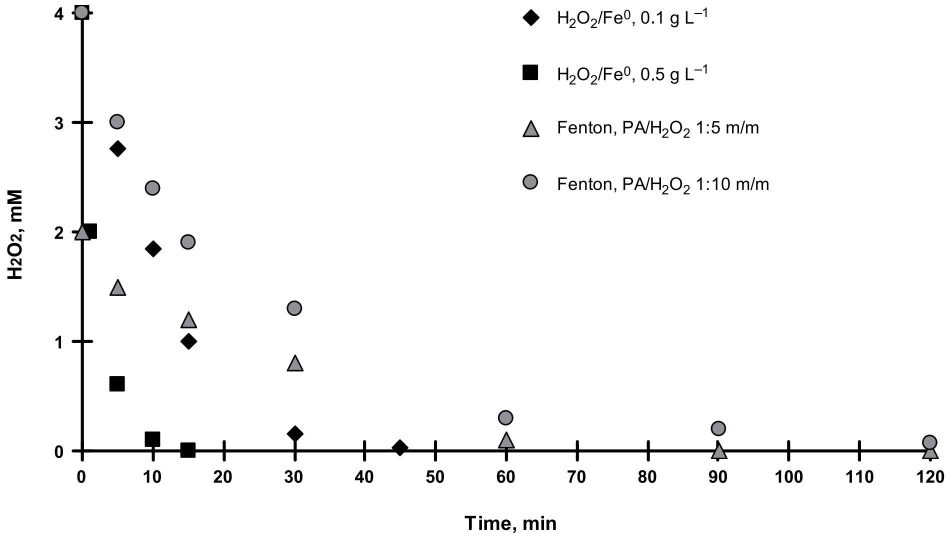

Figure 2. H_2O_2 degradation during PA degradation by H_2O_2/Fe^0 systems at pH 3 (PA/H_2O_2 molar ratio 1:10) and the classic Fenton systems.

Although the major PA degradation mechanism in H_2O_2/Fe^0 process at pH 3 proved to be oxidation throughout Fenton reactions in the bulk solution, the adsorption of PA molecules onto the iron powder surface where oxidation reaction with hydroxyl radicals occurs may also contribute to the overall efficiency of PA degradation. The results of the experiments on the zero valent iron adsorption effect at pH 3 demonstrated 7.5% and 12.5% PA removal for 0.1 and 0.5 g L^{-1} Fe^0, respectively. The removal of PA occurs for 30 and 10 minutes of adsorption for 0.1 and 0.5 g L^{-1} Fe^0, respectively; the process duration is equal with the time for complete PA degradation in the H_2O_2/Fe^0 system (Figure 2). Thus, highly oxidative media promote the oxidation reaction of organic molecules adsorbed onto surface of solid particles. Besides the gradual leaching of iron powder provides continuous ferrous ion input to the Fenton reaction system, which also contributes positively to the efficiency of H_2O_2/Fe^0 process for the degradation of PA and H_2O_2 utilization (Figure 2).

Similar to the classic Fenton system during the zero valent iron catalysed Fenton-based oxidation of PA at acidic conditions, a decrease in pH value from 3 to 2.65 was observed – most likely due to the formation of organic acidic intermediates.

Cleavage of the nitro group from the aromatic ring and its conversion to nitrate occurred during the degradation of PA. The formation of nitrate as a result of mineralization of organically bounded nitrogen during the PA aqueous solution treatment by H_2O_2/Fe^0 systems at pH 3 is presented in Figure 3. The results of NO_3^- formation in the classic Fenton systems with PA/H_2O_2 molar ratios of 1:5 and 1:10 are also demonstrated in Figure 3. Thus, the measured nitrate concentration achieved the theoretically calculated value only in the case of H_2O_2/Fe^{2+} process with a PA/H_2O_2 molar ratio of 1:10. For zero valent iron catalysed Fenton-based systems, the nitrate ion concentration reached 74–83% of the theoretical value. Nitrated aliphatic intermediates were probably formed during the oxidation process or, in the case of iron powder, some nitrogen-containing species remained adsorbed on the catalyst surface.

The overall efficacy of PA degradation by H_2O_2/Fe^0 and H_2O_2/Fe^{2+} systems at pH 3 was assessed on the basis of COD and DOC removal after 120 minutes of reaction (Figure 4). The application of the H_2O_2/Fe^0 system with 0.1 g L^{-1} Fe^0 showed 60 and 22% removal of COD and DOC, respectively. The five-fold increase in the amount of zero valent iron from 0.1 to 0.5 g L^{-1} resulted only in 6 and 10% of additional COD and DOC removal, respectively.

In general, the classic Fenton treatment proved more effective in reducing the COD and DOC values of PA aqueous solutions than the zero valent iron catalysed Fenton-based process. However, the results of the H_2O_2 concentration measurement indicated much faster utilization of hydrogen peroxide in H_2O_2/Fe^0 systems compared with the classic Fenton process. Thus, improvement of COD and DOC removal in zero valent iron catalysed Fenton-based system appears to be a question of process optimization.

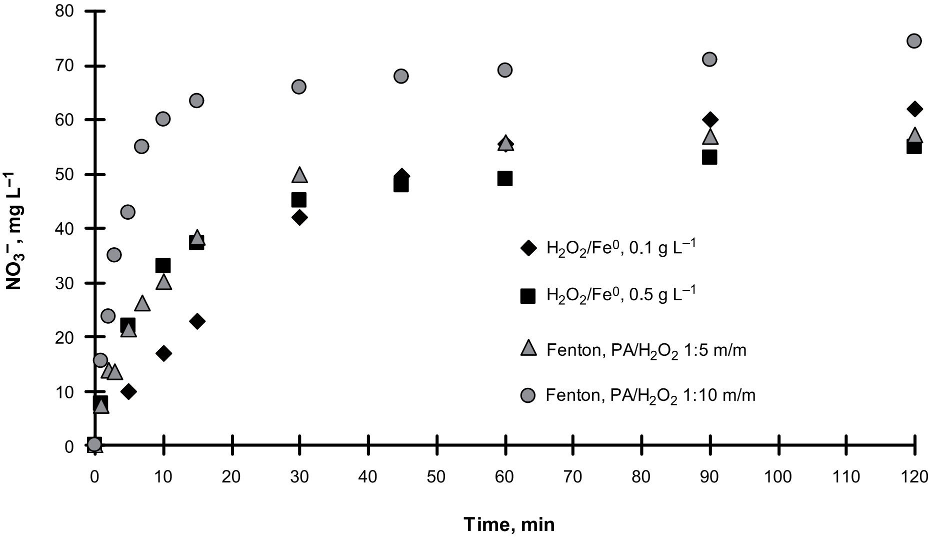

Figure 3. Nitrate ions formation during PA degradation by H_2O_2/Fe^0 systems at pH 3 (PA/H_2O_2 molar ratio of 1:10) and the classic Fenton systems.

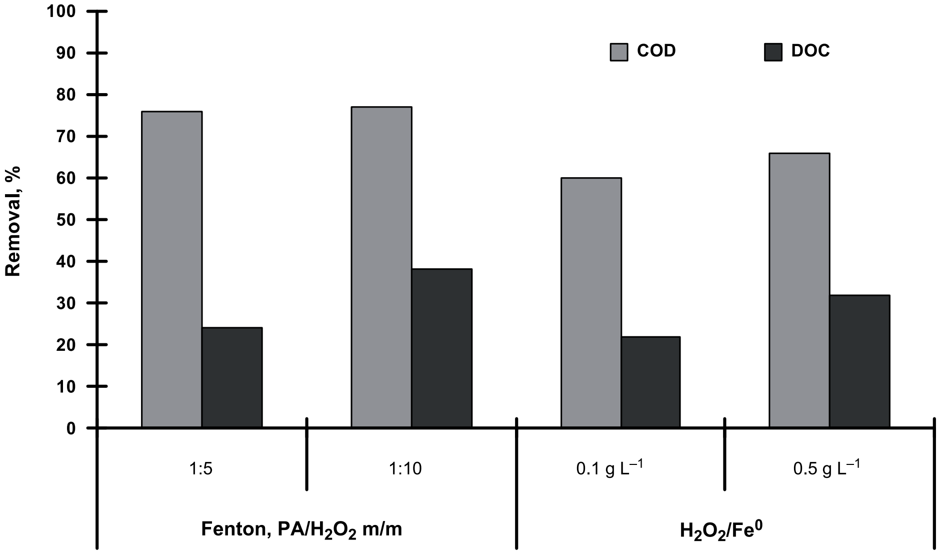

Figure 4. COD and DOC removal after 120 miutes of PA aqueous solution treatment by H_2O_2/Fe^0 systems at pH 3 (PA/H_2O_2 molar ratio of 1:10) and the classic Fenton system with different PA/H_2O_2 molar ratios.

The effectiveness of H_2O_2/Fe^0 process as well as Fe^0 adsorption effect to remove PA from aqueous solution was also studied at pH values of 5, 7 and 9. The results indicated negligible removal of PA for both treatment processes, and thus the zero valent iron catalysed Fenton-based process proved inefficient for PA degradation at neutral and slightly acidic/alkali conditions. Moura *et al.* [19] also reported that 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 or alkaline pH medium.

One of the major advantages of zero valent iron application in Fenton-based processes instead of iron salts is that, in the case of the optimized system, the concentration of iron in wastewater after the treatment can be reduced. According to Lücking *et al.* [20], the amount of iron ions can be reduced up to 50%. Moreover, the utilization of the Fe^0/H_2O_2 process avoids additional loading of treated wastewater with other anions, while a relatively small amount of remaining iron powder can be easily removed from the treated wastewater after treatment.

4. Conclusions

The present study investigated the application of heterogeneous H_2O_2/α-FeOOH, H_2O_2/Fe_3O_4 and H_2O_2/Fe^0 systems for PA degradation in aqueous solution. The results demonstrated negligible degradation of PA within 120 minutes of reaction in both goethite and magnetite catalysed Fenton-based processes independent of system pH, hydrogen peroxide concentration, and catalyst type and dosage. In addition, the PA adsorption effects of both iron oxides turned out to be insignificant at all studied pH values and catalyst dosages. The zero valent iron catalysed Fenton-based process proved efficient in PA degradation under acidic conditions (pH 3). At pH ≥5, no obvious degradation of PA was observed.

The Fe^0/H_2O_2 system is heterogeneous, but the results of the present study have indicated that the dissolution of zero valent iron is a relatively fast process and that the mechanism of homogeneous catalysis by soluble ferrous ions is predominant. The adsorption of PA onto the iron powder surface may also contribute to the overall efficiency of PA degradation. In general, the efficacy of the zero valent iron catalysed Fenton-based system under acidic conditions was comparable with the efficacy of classic Fenton treatment.

Acknowledgements

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PAPER IV

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Photochemical degradation of nonylphenol in aqueous solution: the impact of pH and hydroxyl radical promoters

Aleksandr Dulov*, Niina Dulova, Marina Trapido

*Corresponding author.

Department of Chemical Engineering, Tallinn University of Technology, Ehitajate tee 5, Tallinn 19086, Estonia

E-mail: alexandr.dulov@gmail.com, niina.dulova@ttu.ee, marina.trapido@ttu.ee; phone: +372 6202855; fax: +372 6202856

Running title: Photochemical degradation of nonylphenol

Abstract

The degradation of nonylphenol in aqueous solution with UV, H_2O_2/UV, and Fenton/photo-Fenton processes was studied. The efficacy of direct and hydrogen peroxide photolysis proved dependent on the pH value. The addition of H_2O_2 to UV treatment improved NP degradation. The application of UV photolysis and the H_2O_2/UV system at pH 7 resulted in low pseudo-first order rate constants within the range of 10^{-4} s^{-1}. In the experiments at elevated pH values the pseudo-first order rate constants increased to 10^{-3} s^{-1}. The efficacy of the Fenton process was lower in comparison with UV and hydrogen peroxide photolysis. The addition of UV irradiation to the H_2O_2/Fe^{2+} system substantially improved NP degradation efficacy. In terms of performance, the photo-Fenton process was similar to the H_2O_2/UV process. The most favourable process for nonylphenol degradation considering both operational cost and treatment efficacy was H_2O_2/UV at pH 11 and 250 μM H_2O_2.

Keywords: AOPs; endocrine disrupting compound; photo-Fenton process; photolysis; UVC radiation

Introduction

The presence of compounds with estrogenic properties in the environment has become a subject of major concern throughout the world. Among the various endocrine disrupting compounds (EDCs), nonylphenol (NP) has been classified as a significant endocrine disruptor capable of interfering with the hormonal system of numerous organisms and acting as an estrogen mimic. NP is produced in large volumes, and it is mainly used as a chemical intermediate for the production of nonylphenol ethoxylates (NPEs). NPEs are efficient non-ionic surfactants used in a wide variety of industrial applications and consumer products, such as domestic liquid laundry detergents, industrial liquid soaps and cleaners, cosmetics, paints, and as dispersing agents in pesticides and herbicides. Most of the extensively used NPEs are discharged to the sewer system and directed into the wastewater treatment plants (WWTPs).

Although NPEs are highly treatable in conventional biological treatment facilities, effluent from wastewater treatment plants is one of the major sources of NPs, which are primary NPEs biodegradation products, due to incomplete removal and degradation of these pollutants (Ahel *et al.*, 1994; Soares *et al.*, 2008). NP is known to be persistent in the aquatic environment, moderately bioaccumulative, and extremely toxic to aquatic organisms (Soares *et al.*, 2008). Due to harmful effects of NP, its production and use is restricted in the EU since 2003 and the limits for NP in water bodies are set at 2 μg L^{-1} (Bertanza *et al.*, 2011).

The advanced oxidation processes (AOPs) involving ozone, hydrogen peroxide, UV photolysis, the Fenton process, etc. have been widely studied for the treatment of persistent organic pollutants (such as EDCs) and proved to have potential for complete degradation of the target compound as well as its degradation products (Lee *et al*., 2003; Irmak *et al*., 2005; Ning *et al*., 2007; Bertanza *et al*., 2011). The degradation of NP in aqueous medium by AOPs, such as photocatalytic processes with TiO_2 and ZnO (Ike *et al*., 2002; Babaei *et al*., 2011), sonolysis (Yim *et al*., 2003), and ozonation (Ning *et al*., 2007) has been reported. The effective removal of NP was demonstrated for adsorption on activated carbon (Choi *et al*., 2005). Additionally, combined biological and chemical (ozonation) treatment has been studied for real WWTP effluents contaminated with NP and resulted in estrogenic activity abatement and reduction of target compound concentration (Bertanza *et al*., 2011). However, no previous works have been found in the literature on the removal of NP by UVC photolysis, the H_2O_2/UVC system and Fenton-based processes with/without UVC radiation.

In the present study the degradation of NP using UVC photolysis, hydrogen peroxide photolysis, and Fenton/photo-Fenton processes was investigated. The efficacies of various oxidation processes on NP removal from aqueous solution were compared.

Experimental

Chemicals and Materials

Nonylphenol was purchased from Sigma-Aldrich; acetonitrile (99.8%, isocratic grade for HPLC) was obtained from Baker. The structure and the basic data concerning NP are presented in Table 1. All the other chemicals of analytical grade were used without further purification.

A stock NP solution of 4.54 mM was prepared in 100 mL methanol and stored in the dark at 4ºC. Test solutions with initial NP concentration of 20 μM were prepared by dilution of the stock in twice-distilled water. The solution was stirred for several hours to ensure complete NP dissolution. Sodium hydroxide and sulphuric acid aqueous solutions were used for pH adjustment.

Experimental procedure

A mercury low-pressure OSRAM lamp with an energy input of 10 W located in a quartz tube inside the reactor was used as an UVC (thereinafter UV) source. The incident UV radiation photon flux at 254 nm measured by potassium ferrioxalate actinometry was 5.52 ± 0.38 μEinstein s^{-1}. The constant temperature (22±1°C) in the reactor was maintained using a cooling jacket.

All Fenton-based process trials were carried out in batch mode and in non-buffered solutions. NP solutions were treated in a 1 L cylindrical glass reactor with permanent agitation for a period of 120-180 min; samples were withdrawn at pre-selected time intervals. The classic Fenton reaction (H_2O_2/Fe^{2+}) was initiated by adding H_2O_2 (100-500 μM) to NP solution (pH 3) containing a known amount of Fe^{2+} ion. The molar ratio of H_2O_2/Fe^{2+} was kept invariable at 10:1. The H_2O_2 concentration in the photo-Fenton experiments was in the range of 50-500 μM; the pH value of the stock solution was adjusted to 3 or 7.

The direct UV photolysis and H_2O_2/UV experiments were carried out in the same reactor (1 L of stock NP solution in a glass reactor with a permanent agitation speed for a period of 30-180 min). The pH value of the stock solution was 7 or 11. The H_2O_2 concentration varied from 50 to 500 μM.

Additionally, the experiments on NP oxidation with non-catalyzed H_2O_2 were conducted in the same reactor and treatment conditions as the respective Fenton-based treatment trials.

All the experiments were duplicated and the data on the concentration of NP was verified with at least three replicates. The results of the analysis of initial and treated samples are presented as the mean, with the standard deviation below 4% in all cases.

Analytical methods

NP concentrations were quantified by means of a CLAS MPm (Labio Ltd.) high performance liquid chromatograph equipped with a MAG 0 (1.5 × 50 mm) Biospher PSI 100 C18 (particle size, 5 µm) microcolumn and UV/VIS detector SAPHIRE. The isocratic method with a solvent mixture of 80% acetonitrile and 0.3% of acetic acid in water was applied. Samples were analyzed at a flow rate of 70 µL min^{-1} and an absorbance wavelength of 210 nm. The concentration of NP was determined by using the standard chemical to fit the retention time.

The total iron concentration in the solution was quantified with the phenanthroline method (APHA, 2005). The initial H_2O_2 concentration in stock solutions was determined spectrophotometrically by measuring the absorption of H_2O_2 at 254 nm using Heλion-β UV/VIS (Thermo Electron Corporation). The residual H_2O_2 concentration was measured by the spectrophotometric method with Ti^{4+} (Eisenberg, 1943).

Results and discussion

UV photolysis and H_2O_2/UV process

Nonylphenol absorbs mainly at lower wavelengths (in the range of 200-210 nm); its absorbance almost ceases at approximately 250 nm. Therefore, degradation of NP by the UV photolysis with the application of a low pressure lamp was expected to be slow.

The efficacy of NP removal was controlled by measuring the residual concentration of the target compound. The nonylphenol degradation followed a pseudo-first order kinetic law and may be described with regard to the compound concentration:

$$dC_{NP}/dt = -k_1 C_{NP}$$

where k_1 is the pseudo-first order rate constant.

The $-k_1$ constants were calculated from the slopes of the straight lines by plotting $\ln(C/C_0)$ as a function of time t, through linear regression.

Similarly to some other phenols, it was presumed that deprotonated NP reacts about an order of magnitude faster than the protonated compound. The fraction of the dissociated species depends on the dissociation constant and on the pH of the aqueous media. Therefore, the impact of pH on the nonylphenol degradation by the UV photolysis was studied.

It was observed that pH has significant influence on the degradation of nonylphenol during the application of the UV photolysis (Table 2). Nonylphenol removal was faster in alkaline medium. This is probably due to the fact that in alkaline medium the molar absorption coefficients of the molecule are slightly higher than at acidic and basic pH values (Neamțu and Frimmel, 2006). Differences in the quantum yields at the two pH values would lead to different rate constants as well. The 90% conversion times ($T_{90\%}$) for the UV photolysis at pH 7 and pH 11 were 110 and 30 min, respectively. The pseudo-first order rate constant for the experiment at pH 11 was 13.2×10^{-4} s^{-1}, which was three times higher than the rate constant for trial at pH 3.

Photo-degradation can occur by the direct absorption of radiation (direct photolysis) or by reaction with reactive intermediates (e.g. hydroxyl radicals) that are intensively generated when irradiation is combined with a strong oxidant, e.g. hydrogen peroxide (hydrogen peroxide photolysis). In general, addition of free radical promoters enhances the efficiency of the UV photolysis when irradiated substances have relatively low values of quantum yield and the molar absorption coefficient, as in the case of nonylphenol. In the present study, different concentrations of H_2O_2 were tested to increase the efficacy of the UV photolysis.

As compared to single UV photolysis, the addition of H_2O_2 to UV treatment improved NP degradation substantially and was dependent on the added H_2O_2 concentration (Table 2). The addition of 50, 100 and 500 μM of H_2O_2 (pH 7) resulted in $T_{90\%}$ of 80, 70 and 35 min, respectively. Similarly to the direct photolysis, NP degradation rate in the H_2O_2/UV system was considerably dependent on the pH of the solution. The pseudo-first order rate constants for the H_2O_2/UV process at pH 11 were 19.4×10^{-4}; 23.7×10^{-4} and 31.7×10^{-4} s^{-1} after the addition of 50, 100 and 250 μM of H_2O_2, respectively.

The results of blank H_2O_2 oxidation trials indicated no degradation of NP at all studied concentrations.

The Fenton and photo-Fenton process

Kinetic constants' values were not calculated for the Fenton-based processes because the data did not fit any kinetic model. $T_{90\%}$ values for the degradation of NP calculated from the degradation curves are presented in Table 2.

The experiments of the Fenton treatment (H_2O_2/Fe^{2+}) of NP were performed as preliminary trials for subsequent assessment of the efficacy of the photo-Fenton treatment. The results of NP degradation in the Fenton system indicated dependence of the treatment efficacy on the H_2O_2 concentration. Thus, the increase in H_2O_2 dose from 100 to 200 μM intensified the degradation of the target compound (Table 2). In general, the Fenton system efficacy was lower than in the case of UV and hydrogen peroxide photolysis. The moderate NP removal by the Fenton reagent under the conditions used in this study can be explained at least by the following reasons: the small amounts of MeOH used for NP dissolution and present in the treated solutions scavenge the hydroxyl radicals and/or effective scavenging of the hydroxyl radicals by the elevated concentrations of H_2O_2 used.

The addition of UV radiation to the Fenton system resulted in the improvement of NP removal (Table 2). Similarly to hydrogen peroxide photolysis, the efficacy of the photo-Fenton process proved dependent on H_2O_2 concentrations. The 90% conversion times of photo-Fenton experiments at pH 3 after addition of 50 and 100 μM of H_2O_2 were 60 and 45 min, respectively. Further increase in the H_2O_2 concentration up to 500 μM indicated a decrease in the NP degradation efficacy. This fact can be explained by the scavenging effect of H_2O_2 at the high concentration used. The influence of pH on the degradation of the target compound during photo-Fenton was more obvious at the elevated H_2O_2 concentration, and consequently at higher iron concentrations. Thus, the results of 500 μM H_2O_2 application at pH 3 and pH 7 demonstrated similarity of the efficacy of the photo-Fenton process oxidation with the Fenton system and hydrogen peroxide photolysis, respectively, indicating difference in NP oxidation at acidic and neutral pH values.

Although the efficacy of the photo-Fenton process was higher than that of the Fenton system, the result of NP degradation indicated no considerable improvement compared to the hydrogen peroxide photolysis. Therefore, H_2O_2/UV process without iron admixture may be recommended for NP removal, as it does not improve the overall degradation efficacy.

Operational costs of treatment

In order to assess the economical feasibility of different treatment schemes for nonylphenol 90% conversion time, the operational costs were calculated. The cost estimation and methodology were based on the calculation made by Munter *et al.* (2006).

The data obtained from the laboratory experiments allowed us to make approximate calculations of operating costs comprising the energy required for ozonation, UV photolysis, and chemicals. Doses of ozone and H_2O_2 injected to the studied samples were used in calculations without presumption of re-circulation of non-consumed chemicals. The specific energy requirement for ozone production from air was 20 kWh/kgO_3; the estimated unit energy cost was 0.1 EUR/kWh. In the Fenton-based process, the cost of H_2O_2 was 0.9 EUR/kg, calculated as 100%; $FeSO_4 \cdot 7H_2O$ price was 0.13 EUR/kg. For sodium hydroxide and sulphuric acid used for pH adjustment, average current prices of chemicals on the Estonian market were taken as a basis. Treatment cost calculations in EUR/m^3 are presented in Table 3.

Due to more effective NP degradation at basic pH values, the operational costs of experiments performed at pH 11 were lower than at acidic and neutral pH values. For example, the treatment cost of UV photolysis at pH 11 and pH 7 were 0.83 and 2.66 EUR/m^3, respectively, and the cost of H_2O_2/UV (50 µM H_2O_2) treatment at pH 11 and 7 was 0.51 and 1.93 EUR/m^3, respectively. On the other hand, low concentration of chemicals used in the treatment processes under the conditions studied resulted in a low operational cost of the processes with the fastest NP removal. In general, the cost of UV radiation constituted a major part in the overall operational costs of all photo-treatment processes.

The cost of the most efficient process H_2O_2/UV at pH 11 and 250 µM H_2O_2 ($T_{90\%}$ 7 min) was 0.28 EUR/m^3. The cheapest treatment was the Fenton process, but due to low efficacy it cannot be considered as the main NP degradation technique. The operational cost of the photo-Fenton process (that was also more efficient than the classical Fenton process) was at least 10 times higher than the cost of H_2O_2/Fe^{2+} system. For example, NP degradation by the photo-Fenton and the Fenton process at 100 µM H_2O_2 resulted in 1.19 and 0.10 EUR/m^3, respectively. Taking into consideration all above-mentioned facts, the optimal treatment method of NP regarding the operational cost and treatment efficacy was H_2O_2/UV at pH 11 and 250 µM H_2O_2.

Conclusions

In the current study the efficacy of photo-AOPs for NP degradation was evaluated. NP removal by the direct and hydrogen peroxide photolysis proved pH dependent. The addition of H_2O_2 to the UV system substantially improved the degradation of NP. The increase in the H_2O_2 dose from 50 to 500 µM intensified the degradation of the target compound in the H_2O_2/UV process. The application of the hydrogen peroxide photolysis at pH 11 and at H_2O_2 dose 250 µM demonstrated the highest NP removal rate (31.7×10^{-4} s^{-1}). The results of NP degradation by the photo-Fenton process revealed similarity in terms of performance with the hydrogen peroxide photolysis. The optimal treatment method of NP regarding operational costs and treatment efficacy was H_2O_2/UV (250 µM H_2O_2) treatment at pH 11 with the respective cost of 0.28 EUR/m^3.

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Author Disclosure Statement

No competing financial interests exist.

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Table 1. The structure and main properties of studied endocrine disrupting compound.

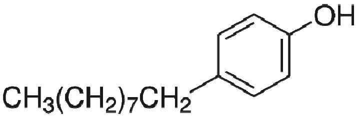
Compound	**Nonylphenol**
Abbreviation in text	NP
Empirical formula	$C_{15}H_{24}O$
Molecular formula	
CAS Nr.	104-40-5
Molecular weight, g/mol	220.4
pK_a	10.7 (Ince *et al.*, 2009)

Table 2. 90% conversion times ($T_{90\%}$) and the pseudo-first order rate constants (k_1) of NP degradation with different treatment methods.

Treatment method	pH	H_2O_2 (μM)	$T_{90\%}$ (min)	k_1 (s^{-1}) × 10^{-4}, r^2>0.985
UV photolysis	7	-	110	3.96
UV photolysis	11	-	30	13.2
H_2O_2/UV	7	50	80	4.77
H_2O_2/UV	7	100	70	6.41
H_2O_2/UV	7	500	35	10.2
H_2O_2/UV	11	50	17	19.4
H_2O_2/UV	11	100	13	23.7
H_2O_2/UV	11	250	7	31.7
H_2O_2/Fe^{2+}	3	100	>180	-
H_2O_2/Fe^{2+}	3	200	120	-
H_2O_2/Fe^{2+}	3	500	>180	-
H_2O_2/Fe^{2+}/UV	3	50	60	-
H_2O_2/Fe^{2+}/UV	3	100	45	-
H_2O_2/Fe^{2+}/UV	3	500	>180	-
H_2O_2/Fe^{2+}/UV	7	50	60	-
H_2O_2/Fe^{2+}/UV	7	100	50	-
H_2O_2/Fe^{2+}/UV	7	500	40	-

Table 3. Operational costs of treatment schemes in EUR/m^3 for $T_{90\%}$ of NP.

Treatment method	pH*	H_2O_2 (µM)	$FeSO_4 \cdot 7H_2O$, EUR/m^3	H_2O_2, EUR/m^3	UV, EUR/m^3	Total, EUR/m^3
UV photolysis	7	-	-	-	2.66	2.66
UV photolysis	11	-	-	-	0.73	0.83
H_2O_2/UV	7	50	-	0.0015	1.93	1.93
H_2O_2/UV	7	100	-	0.0031	1.69	1.69
H_2O_2/UV	7	500	-	0.015	0.84	0.86
H_2O_2/UV	11	50	-	0.0015	0.41	0.51
H_2O_2/UV	11	100	-	0.0031	0.31	0.41
H_2O_2/UV	11	250	-	0.0077	0.17	0.28
H_2O_2/Fe^{2+}	3	100	0.00036	0.0031	-	0.10
H_2O_2/Fe^{2+}	3	200	0.0072	0.0061	-	0.11
H_2O_2/Fe^{2+}	3	500	0.0018	0.015	-	0.12
H_2O_2/Fe^{2+}/UV	3	50	0.0018	0.0015	1.45	1.55
H_2O_2/Fe^{2+}/UV	3	100	0.00036	0.0031	1.09	1.19
H_2O_2/Fe^{2+}/UV	7	50	0.00018	0.0015	1.21	1.21
H_2O_2/Fe^{2+}/UV	7	100	0.00036	0.0031	1.45	1.45
H_2O_2/Fe^{2+}/UV	7	500	0.0018	0.015	0.97	0.99

*pH regulation in average 0.1 EUR/m^3

APPENDIX B

ELULOOKIRJELDUS

1. Isikuandmed

Ees- ja perekonnanimi: Aleksandr Dulov
Sünniaeg ja -koht: 09.04.1980, Narva
Kodakondsus: Eesti

2. Kontaktandmed

Aadress: TTÜ, Ehitajate tee 5, Tallinn, 19086, Eesti
Telefon: +3726202850
E-posti aadress: alexandr.dulov@gmail.com

3. Hariduskäik

Õppeasutus (nimetus lõpetamise ajal)	Lõpetamise aeg	Haridus (eriala/kraad)
Tallinna Tehnikaülikool	2006	Tehnikateaduste magistrikraad
Tallinna Tehnikaülikool	2003	Tehnikateaduste bakalaureusekraad
Narva Pähklimäe Gümnaasium	1998	Keskharidus

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

Keel	Tase
Eesti keel	Kõrgtase
Vene keel	Kõrgtase
Inglise keel	Kõrgtase

5. Teenistuskäik

Töötamise aeg	Tööandja nimetus	Ametikoht
10.2010 - 02.2012	AS Tallinna Vesi	heitveepuhastusjaama tehnoloog
08.2004 - 10.2010	AS Narva Vesi	laboratooriumi juhataja, keskkonnaspetsialist, heitveepuhastusjaama tehnoloog
11.2003 - 07.2004	AS EcoPro	ohtlike jäätmete kätluskeskuse operaator
08.2003 - 10.2003	AS SGS Eesti	keemik
06.2002 - 10.2002	Ida-Virumaa keskkonnateenistus	jäätmete spetsialist

6. Kaitstud lõputööd

Tehnikateaduste magistritöö: Võimaluste uurimine ammoniumühendite kõrvaldamiseks AS VKG Oil defenoleeritud veest. Tallinna Tehnikaülikool, 2006. Juhendaja: Jüri Soone
Tehnikateaduste bakalaureusetöö: Tahke soojuskandjaga põlevkivi utteprotsessi optimeerimine. Tallinna Tehnikaülikool, 2003. Juhendaja: Jüri Soone

7. Teadustöö põhisuunad

SF0142719s06 Tehnoloogiliste protsesside intensiivistamine aktuaalsete keskkonnaprobleemide lahendamiseks
ETF6564 Modifitseeritud Fenton-protsessi kasutamise uurimine orgaaniliste saasteainete kõrvaldamiseks kombineeritud heitvee töötlusskeemides
ETF8186 Esiletulevate orgaaniliste mikrosaasteainete eemaldamine veest/reoveest täiustatud Fenton-protsessidega

CURRICULUM VITAE

1. Personal data

Name: Aleksandr Dulov
Date and place of birth: 09.04.1980, Narva
Citizenship: Estonian

2. Contact information

Address: TUT, Ehitajate tee 5, Tallinn, 19086, Estonia
Phone: +3726202850
E-mail: alexandr.dulov@gmail.com

3. Education

Educational institution	Graduation year	Education (field of study/degree)
Tallinn University of Technology	2006	M.Sc. in Engineering
Tallinn University of Technology	2003	B.Sc. in Engineering
Narva Pähklimäe Gymnasium	1998	High school education

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

Language	Level
Estonian	Fluent
Russian	Fluent
English	Fluent

5. Professional employment

Period	Organisation	Position
10.2010 - 02.2012	AS Tallinna Vesi	technologist at wastewater treatment plant
08.2004 - 10.2010	AS Narva Vesi	laboratory manager, environmental specialist, technologist at wastewater treatment plant
11.2003 - 07.2004	AS EcoPro	operator of hazardous waste treatment plant
08.2003 - 10.2003	AS SGS Eesti	chemist
06.2002 - 10.2002	Ida-Virumaa county environmental department	specialist on waste

6. Defended theses

M.Sc. in Engineering: The research of possibilities of removal ammonium compounds from dephenolic water of VKG OIL AS. Tallinn University of Technology, 2006. Supervisor: Jüri Soone

B.Sc. in Engineering: Optimization of oil shale processing with solid heat carrier. Tallinn University of Technology, 2003. Supervisor: Jüri Soone

7. 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

ETF8186 Removal of emerging organic micropollutants from water and wastewater by application of advanced Fenton-based processes

DISSERTATIONS DEFENDED AT TALLINN UNIVERSITY OF TECHNOLOGY ON *CHEMISTRY AND CHEMICAL ENGINEERING*

1. **Endel Piiroja**. Oxidation and Destruction of Polyethylene. 1993.

2. **Meili Rei**. Lihatehnoloogia teaduslikud alused. Fundamentals of Food Technology. 1995.

3. **Meeme Põldme**. Phase Transformations in Hydrothermal Sintering Processing of Phosphate Rock. 1995.

4. **Kaia Tõnsuaadu**. Thermophosphates from Kovdor and Siilinjärvi Apatites. 1995.

5. **Anu Hamburg**. The Influence of Food Processing and Storage on the N-Nitrosamines Formation and Content in Some Estonian Foodstuffs. 1995.

6. **Ruth Kuldvee**. Computerized Sampling in Ion Chromatography and in Capillary Electrophoresis. 1999.

7. **Külliki Varvas**. Enzymatic Oxidation of Arachidonic Acid in the Coral *Gersemia fruticosa*. 1999.

8. **Marina Kudrjašova**. Application of Factor Analysis to Thermochromatography and Promotion Studies. 2000.

9. **Viia Lepane**. Characterization of Aquatic Humic Substances by Size Exclusion Chromatography and Capillary Electrophoresis. 2001.

10. **Andres Trikkel**. Estonian Calcareous Rocks and Oil Shale Ash as Sorbents for SO_2. 2001.

11. **Marina Kritševskaja**. Photocatalytic Oxidation of Organic Pollutants in Aqueous and Gaseous Phases. 2003.

12. **Inna Kamenev**. Aerobic Bio-Oxidation with Ozonation in Recalcitrant Wastewater Treatment. 2003.

13. **Janek Reinik**. Methods for Purification of Xylidine-Polluted Water. 2003.

14. **Andres Krumme**. Crystallisation Behaviour of High Density Polyethylene Blends with Bimodal Molar Mass Distribution. 2003.

15. **Anna Goi**. Advanced Oxidation Processes for Water Purification and Soil Remediation. 2005.

16. **Pille Meier**. Influence of Aqueous Solutions of Organic Substances on Structure and Properties of Pinewood (*Pinus sylvestris*). 2007.

17. **Kristjan Kruusement**. Water Conversion of Oil Shales and Biomass. 2007.

18. **Niina Kulik**. The Application of Fenton-Based Processes for Wastewater and Soil Treatment. 2008.

19. **Raul Järviste**. The Study of the Changes of Diesel Fuel Properties a its Long Term Storage. 2008.

20. **Mai Uibu**. Abatement of CO_2 Emissions in Estonian Oil Shale-Based Power Production. 2008.

21. **Valeri Gorkunov**. Calcium-Aluminothermal Production of Niobium and Utilization of Wastes. 2008.

22. **Elina Portjanskaja**. Photocatalytic Oxidation of Natural Polymers in Aqueous Solutions. 2009.

23. **Karin Reinhold**. Workplace Assessment: Determination of Hazards Profile using a Flexible Risk Assessment Method. 2009.

24. **Natalja Savest**. Solvent Swelling of Estonian Oil Shales: Low Temperature Thermochemical Conversion Caused Changes in Swelling. 2010.

25. **Triin Märtson**. Methodology and Equipment for Optical Studies of Fast Crystallizing Polymers. 2010.

26. **Deniss Klauson**. Aqueous Photocatalytic Oxidation of Non-Biodegradable Pollutants. 2010.

27. **Oliver Järvik**. Intensification of Activated Sludge Process – the Impact of Ozone and Activated Carbon. 2011.

28. **Triinu Poltimäe**. Thermal Analysis of Crystallization Behaviour of Polyethylene Copolymers and Their Blends. 2011.

29. **Mariliis Sihtmäe**. (Eco)toxicological Information on REACH-Relevant Chemicals: Contribution of Alternative Methods to *in vivo* Approaches. 2011.

30. **Olga Velts**. Oil Shale Ash as a Source of Calcium for Calcium Carbonate: Process Feasibility, Mechanism and Modeling. 2011.

31. **Svetlana Jõks**. Gas-Phase Photocatalytic Oxidation of Organic Air Pollutants. 2012.