TALLINN UNIVERSITY OF TECHNOLOGY
SCHOOL OF ENGINEERING
Department of Materials and Environmental Technology

DEGRADATION OF HERBICIDE ALACHLOR USING PULSED CORONA DISCHARGE

ALAKLOOR HERBITSIIDI LAGUNDAMINE KOROONA IMPULSSLAHEDNUSE ABIL

MASTER THESIS

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AUTHOR’S DECLARATION

Hereby I declare, that I have written this thesis independently.
No academic degree has been applied for based on this material. All works, major viewpoints and data of the other authors used in this thesis have been referenced.

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Thesis is in accordance with terms and requirements

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THESIS TASK

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PREFACE

This master’s thesis was done at Tallinn University of Technology, School of Engineering, Department of Materials and Environmental Technology under the guidance of PhD Sergei Preis and PhD Juri Bolobajev.

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Pulsed corona discharge, non-thermal plasma, alachlor, AOP, oxidation by-products, master thesis

List of abbreviations and symbols

AOP	Advanced oxidation process
atm	Standard atmosphere, pressure unit
DBD	Dielectric barrier discharge
E	Energy efficiency of oxidation, g kW^{-1} h^{-1}
EE/O	Electric energy per order
g	Gram, mass unit
GAC	Granulated activated carbon
h	Hour, time unit
h*v*	Light photon energy
K	Kelvin, temperature unit
L	Littre, volume unit
M	Molarity, concentration unit
m	Meter, length unit
min	Minute, time unit
MW	Molecular weight
NTP	Non-thermal plasma
•OH	Hydroxyl radical
PCD	Pulsed corona discharge
pps	Pulses per second
PS	Persulfate
RT	Retention time
S	Siemens, derived unit of electric conductance
s	Second, time unit
TOC	Total organic carbon
US	Ultrasound
UV	Ultraviolet
V	Volt, electric potential unit
v	volume
W	Watt, power unit
w	weight
ZVI	Zero-valent iron

ZVI/PS	Zero-valent iron/Persulfate
ZVM	Zero-valent metal
λ	Wavelength
)))	Ultrasound waves

INTRODUCTION

Starting from the 20th century, human population experiences fast growth resulting in growing food production and consumption. Human race is concerned about increased productivity of existing food sources to available maximum to provide maintaining living standards. One of the crop-protecting solutions consists of usage of pesticides of various kinds [1]. Applying herbicides preventing growth of weeds results in the yield productivity [2]. The study concerns one of the herbicides widely used in near past, alachlor [3]. After its application on the agricultural fields, it ends up dissolved in groundwater changing from a useful chemical to a toxic pollutant [4, 5]. The toxicity of alachlor together with its entrance and distribution in aqueous environment are described in the first chapter. One should realize that the pesticide, once reaching underground anaerobic aqueous strata, may persist the environment for the time much longer than the official ban of the pesticide production and usage.

Conventional water treatment technologies including coagulation, filtration and disinfection cannot effectively eliminate alachlor from potable water, requiring new approaches developed and implemented [6]. Advanced oxidation processes (AOPs) are known as promising effective alternative or amendment for elimination of toxic and refractory substances, although their cost efficiency remains questionable making AOPs usage rather seldom [7]. Besides, degradation by-products sometimes appear to be more toxic than the parent pollutants for aquatic lifeforms and consumers requiring thorough analysis [6]. To make an appropriate choice of water treatment technologies, technological and safety factors including efficiency, estimated operating and capital costs, and possible effects on environment should be considered.

The objective of this work was to establish the dependence of the efficiency of treatment of aqueous solutions containing alachlor with pulsed corona discharge (PCD) on the process parameters. Available literature was reviewed for the ways alachlor reaching waterbodies, the treatment technologies applied for the herbicide removal and their drawbacks. Experimental study in PCD oxidation of aqueous alachlor was undertaken for the energy efficiency and the degradation products identification. The obtained experimental results were compared to other AOPs with calculated oxidation efficiencies.

1. LITERATURE REVIEW

1.1 General overview on micropollutants

Rapid development of technologies makes human life more comfortable, affecting, however, the environment by increased pollution and resource depletion. Anthropogenic pollutants include highly potent organic micropollutants detected in ground and surface waters worldwide [8].

The European Union Water Framework Directive is the main policy instrument to control and monitor pollutants in surface waters. This, however, is poorly developed for anthropogenic micropollutants reaching the aquatic environment via municipal and industrial wastewater discharges or with agricultural runoff, shipping, and storm water drainage. Micropollutants are described as persistent, non-biodegradable and bio-accumulative residues from daily used substances such as pharmaceuticals. It is important to note that micropollutants released to the environment do not necessarily remain in surface waters; they also enter groundwater and even drinking water possessing a threat to the whole ecosystem [9].

Organic micropollutants occur in water bodies world-wide attracting increased global attention due to the negative effects on aquatic ecosystems and human health. Persistent organic pollutants are able to accumulate in the living tissues thus causing disfunction of nervous, endocrine and immune systems. Due to the toxic effect of several micropollutants in aquatic systems, biodiversity is reduced thus resulting in loosing of some important natural services and functions. For instance, the amount of invertebrate families can be significantly reduced by pesticides even at legally accepted regulatory concentrations [10].

Micropollutants include a wide variety of chemical compounds, such as industrial chemicals, pharmaceuticals, pesticides and their degradation products. After entering the environment, a part of the contaminants is adsorbed or transformed via biotic and abiotic reactions. The remaining part can reach the aquifer, thus polluting potential drinking water source [8]. Figure 1.1 shows potential sources and distribution pathway of organic micropollutants.

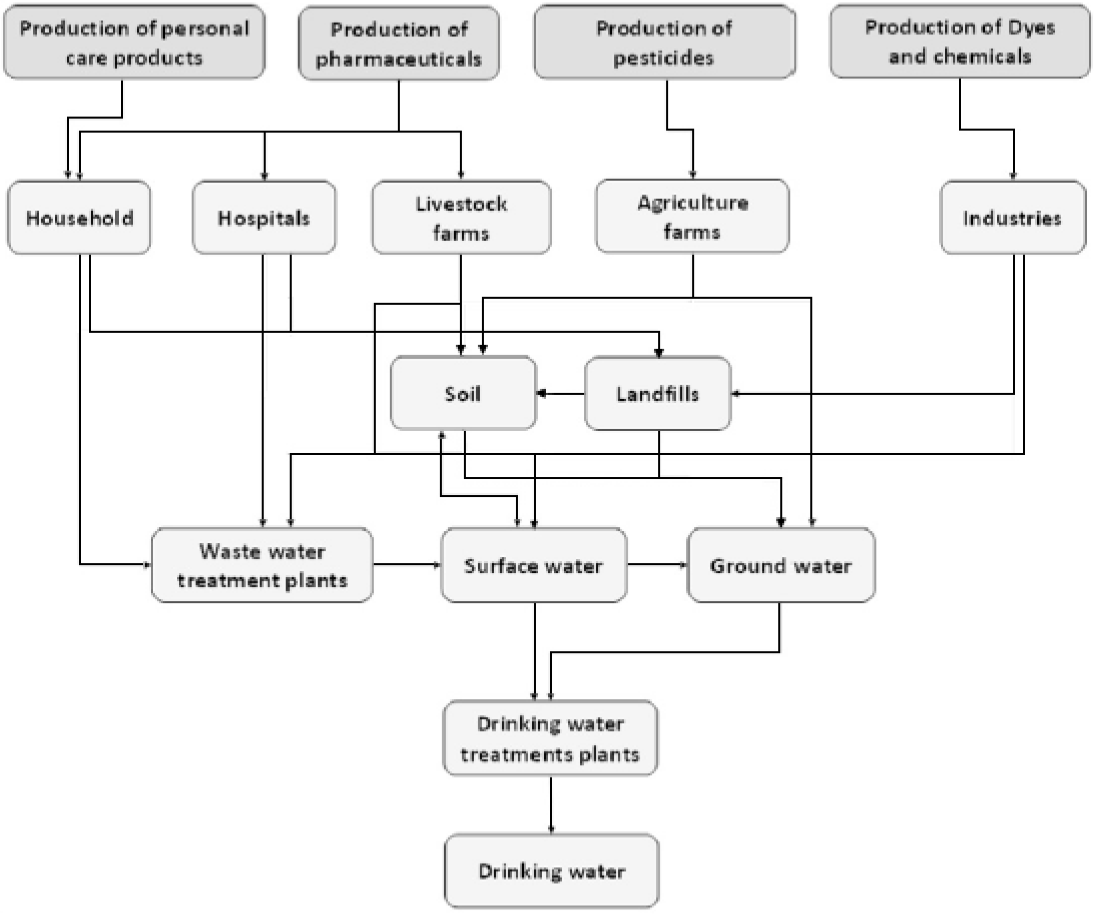


Figure 1.1. Potential sources and pathways of organic micropollutants [11] (modified)

Pesticides are considered as problematic organic micropollutants since the significant amount of those, about 4.6 million tons in 2002, is being continuously spread as a result of agricultural activity. Approximately 99% of applied pesticides are exposed to non-target media through agricultural runoffs and domestic effluents: a huge amount of pesticides reaches water bodies from crop fields serving as a non-point pollution source. Moreover, some of them contain poisonous substances like lead, mercury and arsenic. The World Health Organization reports approximately three million cases of pesticides poisoning and 220 thousand lethal cases annually [11].

1.2 Herbicide alachlor as a water pollutant

Weeds presenting the most undesirable problem of farmers in the world include around 200 species with nearly 80 of them interfering with crops. Weeds are unwanted plants lowering the yield of target crop by harboring pests. Besides, the competitive processes between weed and crops for necessary resources of sunlight, moisture, fertilizers and space result in reduced crop quality and quantity. In order to prevent the development of weeds and other parasite plants, and to increase the crop yield, modern agriculture applies herbicides in order to prevent selectively the development of undesirable plants [2].

Pesticides are classified into types dependent on their target pests: insecticides, herbicides, fungicides, and nematicides. In addition, pesticides may be divided into classes by their chemical structure or functional groups, like carbamates, chlorophenoxy compounds, organochlorines, organophosphates, triazines and others. Alachlor (2-chloro-N-(2,6-diethylphenyl)-N-(methoxymethyl)acetamide) belongs to a chloroacetanilide group [1, 2].

Alachlor (Fig. 1.2), also known by its tradename Lasso, was registered and introduced in 1967 [12, 13]. Monsanto Company (USA) has manufactured alachlor since 1968. From 1969 to 1987, alachlor was second most used herbicide applied on agricultural fields in the United States [14]. It was mainly used for control of broad-leaf weeds and annual grasses in soybean, corn and sorghum fields [5]. It is clear that the soil and groundwater pollution with alachlor is a direct consequence of its usage in agriculture. The contamination of groundwater occurs through the soil via infiltration and runoff processes [4]. The presence of alachlor in water sources is undesirable since it has possible impacts on human health and influences ecosystem in general [5].

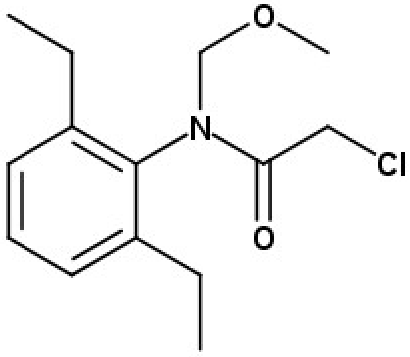


Figure 1.2. Alachlor molecular structure [6] (modified)

Several data sources indicate that short-term exposure to alachlor may lead to a minor eye and skin irritation [5]. However, the long-term exposure may be the reason of an organ damage or even cancer. It should be noted that USA Environmental Protection Agency (EPA) classified alachlor as a B2 carcinogen, even though collected data reflecting mutagenicity or genotoxicity *in vivo* are unconvincing, e.g. the relevance of nasal tumors observed in rats is not confirmed nor rejected in the human body [5]. In addition, alachlor is also an endocrine disruptor [15]. EPA established the maximum permissible concentration of alachlor in drinking water as 2 µg L^{-1} [16].

Alachlor had been widely applied on the crop fields of Europe and North America. In the early 2000s, roughly 37 thousand tons of this herbicide was used annually on the fields of the US alone. Alachlor was found present in raw, rain, treated and tap waters at concentrations from 1.0 to 270 μg L^{-1}. In other studies, concentrations of alachlor in groundwater were up to 3 mg L^{-1} [3]. Table 1.1 demonstrates some physical, chemical and toxicological properties of alachlor.

Table 1.1. Physical, chemical, and toxicological properties of alachlor [3] (modified)

Property	**Value**
Molecular formula	$C_{14}H_{20}ClNO_2$
Molecular weight, g mol^{-1}	269.8
Physical form	White solid
Aqueous solubility at 25 °C, mg L^{-1}	240 [17]
Melting point, °C	40-41
Mammalian toxicity, LD_{50}	
Oral (rat), g kg^{-1}	0.93
Dermal (rabbit), g kg^{-1}	13
Inhalation (rabbit), mg L^{-1}	>5.1

At present, alachlor is partly restricted: banned in Canada since 1985 because of its possible health risks and existent lower-risk alternative, metolachlor; sales of any products containing alachlor are prohibited since 2006 in European Union [12, 18]. Due to its non-biodegradable character and persistence in the environment, alachlor, nevertheless, presents a problem for safe aquatic flora and fauna and, ultimately, water supply, remaining a subject for the research in abatement technologies [19]. Nevertheless, it is still applied in the USA, although in much smaller amounts being replaced by another acetanilide herbicide acetochlor [14].

1.3 Treatment technologies

Alachlor may be removed from water using various technologies, almost all of them belonging to advanced oxidation processes (AOPs), such as direct ozonation [20] and its combination with other AOPs [6, 21], Fenton process [22] and sonochemistry [16, 17]. Biological [3] and electrochemical [5] treatment was also described. Qiang et al. [6] concluded that conventional drinking water treatment methods like coagulation, filtration and chlorination demonstrate rates of alachlor removal not exceeding 10%.

Advanced oxidation processes are the methods of water treatment aimed to generate hydroxyl or sulphate radicals in order to degrade organic pollutants existing in water matrix. AOPs based on •OH are most widely spread due to the hydroxyl radical's excellent oxidation potential, the value of which is close to that of fluorine. Sulphate radical based AOPs are also of interest due to their high efficiency and ability to degrade a variety of organic contaminants. This can be explained by the life-span difference of the radicals in water, 30-40 μs for sulphate radicals versus 20 ns for hydroxyl radicals. The presence of hydroxyl radicals may lead to non-selective complete mineralization of organic pollutants which degrade through different chemical reactions, like dehydrogenation, hydroxylation and redox reactions [7].

The most studied AOPs are briefly described in Table 1.2. It should be mentioned that AOPs showed great effectiveness in oxidation of the "dirty dozen" components including chlordane, DDT, polychlorinated biphenyls and others. These processes are also found to be effective in wastewater treatment from various industries, such as pharmaceutical, textile, petroleum refinery and tanning industries [7].

Table 1.2. Description of selected AOPs [7] (modified)

Process	**Description**	**Major reactions**	**Enhancements**
Fenton	Generation of •OH during reaction between Fe^{2+} and H_2O_2 at pH≈3	$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + \bullet OH$ Regeneration of Fe^{2+}: $Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + H^+ + HO_2^\bullet$	Heterogeneous Fenton process using solid catalysts effective in wide pH range Fenton-like process using heavy metals other than Fe^{2+} Fluidized Fenton process: ferric hydroxide sludge is attached to the carriers in fluidized bed acting as a heterogeneous Fenton catalyst
Anodic oxidation	Generation of •OH in aqueous oxidation at high O_2 evolution overvoltage anodes	Water oxidation at anode surfaces: $M + H_2O \longrightarrow M(\bullet OH) + H^+ + e^-$ M – anode	Efficiency improvement of anodes by: 1) adding suitable substrates; 2) using Pt and boron-doped diamond anodes
Electro-Fenton	Advanced Fenton: H_2O_2 generated in electrolytic media by supplying O_2 at cathode surfaces under acidic conditions	$O_2 + 2H^+ + 2e^- \longrightarrow H_2O_2$ Fe^{2+} regeneration by cathodic reduction of Fe^{3+}: $Fe^{3+} + e^- \longrightarrow Fe^{2+}$	Heterogeneous electro-Fenton Peroxicoagulation: iron or stainless steel anodes for *in situ* Fe^{2+} generation Anodic Fenton: H_2O_2 is added externally to the electrolytic system
Photo-catalysis	Generation of oxidants at irradiated semiconductors, mostly TiO_2	Photo-excitation reaction: $S + h\nu \longrightarrow e^- + h^+$ Water ionization: $h^+ + H_2O \longrightarrow H^+ + \bullet OH$	Use of supporting and doping materials for reducing electron-hole recombination

Process	**Description**	**Major reactions**	**Enhancements**
		Oxygen ionosorption: $e^- + O_2 \longrightarrow O_2^{\bullet -}$ Superoxide protonation: $O_2^{\bullet -} + H^+ \longrightarrow HO_2^{\bullet}$ $HO_2^{\bullet} + e^- + H^+ \longrightarrow H_2O_2$ $H_2O_2 + e^- \longrightarrow OH^- + \bullet OH$	
Photo-Fenton	Fenton with photolysis combination: •OH is generated in Fenton process and degradation of H_2O_2 in UV	Photolysis: $H_2O_2 + hv \longrightarrow 2HO\bullet$ (λ <300 nm) Fe^{2+} regeneration: $Fe(OH)^{2+} + hv \longrightarrow Fe^{2+} + \bullet OH$ (λ <450 nm)	Heterogeneous and solar photo-Fenton processes Use of ferrioxalate as mediator for acceleration
Ozonation and catalytic ozonation	Direct reaction with ozone (acidic pH) or •OH (alkaline pH). Catalysts decompose ozone at low pH levels	Catalytic ozonation: $Fe^{2+} + O_3 + H_2O \longrightarrow Fe^{3+} + OH^- + \bullet OH + O_2$	Heterogeneous catalytic ozonation, photocatalytic ozonation, peroxone i.e. ozone/H_2O_2 Electroperoxone: ozonation combined with electro-Fenton process
Sono-chemistry	Acoustic cavitation of micro-bubbles in water generates high pressure and temperature, eliminating contaminants by homolytic bond breaking and •OH attack from water dissociation	Water thermal dissociation in ultrasound: $H_2O +))) \longrightarrow \bullet OH + H\bullet$	Ultrasound combined with O_3, H_2O_2, photocatalysis and electrochemical oxidation
Sono-Fenton	Fenton combined with sonolysis	Water thermal dissociation Fenton reaction	Sono-photo-Fenton, sono-electro-Fenton
Persulfate/ peroxymono sulfate oxidation	Persulfate or peroxymonosulfate decompose to sulphate radicals accelerated by UV, heavy metals, ultrasound and heat	Persulfate activation with heavy metals: $S_2O_8^{2-} + Fe^{2+} \longrightarrow Fe^{3+} + SO_4^{2-} + SO_4^{\bullet -}$	Heterogeneous catalysis In-situ sulphate radicals generated electrolytically from sulphate ions with high oxygen over-voltage potential anodes, Pt and boron doped diamond
Zero-valent metal/H^+/O_2	In acidic media zero valent metals (ZVM) are exposed to corrosive oxidation generating H_2O_2. The latter decomposes generating •OH	$2Al^0 + 3O_2 + 6H^+ \longrightarrow 2Al^{3+} + 3H_2O_2$ $2Al^0 + 3H_2O_2 \longrightarrow Al^{3+} + 3OH^- + 3HO\bullet$	ZVM/H^+/O_2/EDTA enhances H_2O_2 formation ZVM/H^+/O_2/ultrasound ZVM/H^+/O_2/heavy metal ZVM/H^+/O_2/Polyoxometalate

One of the advantages of AOPs is enhancement of biodegradability useful for further treatment of refractory pollutants. Detoxification of treated water is also a feature of AOPs because of their ability to degrade toxic organic pollutants [7].

1.3.1 Direct ozonation and its combination with other AOPs

Ozone was discovered in 1840 by a German-Swiss chemist Christian Friedrich Schönbein. Since 1906, ozone was used in water treatment in Nice (France) for drinking water disinfection. Since then, ozonation has gained popularity throughout the world. For instance, by 1940, 119 drinking water treatment plants in the world used this technique and by 1977 their amount increased to at least 1039 [23].

Ozone is unstable partially soluble in water gas with a specific odor. In alkaline solutions, its redox potential is equal to 2.07 V. Water ozonation can proceed via two mechanisms: (1) direct oxidation where O_3 molecule reacts directly with pollutant and (2) indirect mechanism where pollutant reacts with •OH generated during O_3 decomposition [23]. Ozone decomposition can be described as a chain reactions including initiation sequence (Eqs. 1.1 and 1.2), propagation (Eqs. 1.3–1.7) and termination [24].

$$O_3 + OH^- \longrightarrow HO_2^- + O_2^{\bullet -} \tag{1.1}$$

$$HO_2^- + O_3 \longrightarrow HO_2^\bullet + O_3^{-\bullet} \tag{1.2}$$

$$O_3 + O_2^{\bullet -} \longrightarrow O_3^{\bullet -} + O_2 \tag{1.3}$$

$$O_3^{\bullet -} + H^+ \longrightarrow HO_3^\bullet \tag{1.4}$$

$$HO_3^\bullet \longrightarrow {}^\bullet OH + O_2 \tag{1.5}$$

$$O_3 + {}^\bullet OH \longrightarrow HO_4^\bullet \tag{1.6}$$

$$HO_4^\bullet \longrightarrow HO_2^\bullet + O_2 \tag{1.7}$$

Termination step consists of any recombination of •OH, O_2 and $HO_2^\bullet$.

Hydroxyl radicals are non-selective meaning they are capable of oxidizing almost all organic and even some inorganic pollutants. It makes indirect mechanism preferable in water treatment. However, under the acidic or neutral pH, formation of •OH is slow [23].

Ozonation, alone or in combination with other AOPs, presents one of the strategies in alachlor removal. Despite its wide-spread character, several studies [6] showed that ozonation alone does not provide sufficient alachlor removal rates (84% removal in 60 min of treatment with initial concentration of alachlor 5.5 μM or 1.5 mg L^{-1} and initial dissolved ozone concentration in the reactor of 15.0 mg L^{-1}). Complete alachlor degradation only occurred with the addition of H_2O_2 in order to produce hydroxyl radicals thus revealing the leading role of indirect oxidation with •OH. The authors of the referred paper noted that incomplete oxidation of some pesticides, e.g. dichlorvos, resulted in a number of degradation by-products with some of them being equally or even more toxic than the parent compound [6].

Better performance of ozonation was shown by Li et al. [20]: alachlor degradation for 93.4, 95.8 and 95.9% with its initial concentration of 120 mg L^{-1} was observed in 60, 120 and 180 min of treatment, respectively. The ozone flow rate was 30 mL min^{-1} with delivered ozone amount of 1.17 mg L^{-1} min $^{-1}$, providing delivered ozone doses of 70, 140 and 210 mg O_3 L^{-1}. Such treatment resulted in alachlor yield as high as 1.6 mg mg^{-1} O_3 for the first hour of treatment. The removal of TOC, however, was insignificant, only 24.5% was mineralized after 180 min of ozonation. Refractory character of TOC indicates ozonation by-products being sustainable towards the treatment.

Refractory character of alachlor ozonation products resulted in studying catalytic ozonation [21]. Metal-catalyzed ozonation appeared to eliminate toxic pollutants degrading recalcitrant by-products and increasing overall alachlor removal efficiency: ozonation with Cu/Al_2O_3-honeycomb catalyst removed 99% of alachlor in 30 min and 75.3% of TOC in 180 min of treatment. The initial concentration of alachlor was 100 mg L^{-1}, the delivery of gaseous ozone was 12.2 mg L^{-1} min^{-1} and its flow rate 40 mL min^{-1} providing the alachlor yield of 0.27 mg mg^{-1} O_3. However, application of catalytic ozonation has its major concerns about separation of the catalyst solids and partial dissolution of heavy metals in treated waters [21]. For this reason, further research aims the development of supported metal catalyst avoiding the separation and secondary contamination problems.

1.3.2 Fenton process

The generalized Fenton reaction given in Table 1.2 summarizes the sequence of reactions influenced by conditions of pH, concentrations of target pollutant, H_2O_2 and ferrous ions, and temperature. The reaction pathway is described by reactions, Eqs. 1.8–1.14 [22]:

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + \bullet OH \qquad (1.8)$$

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + HO_2^{\bullet} + H^+ \qquad (1.9)$$

$$\bullet OH + H_2O_2 \longrightarrow HO_2^{\bullet} + H_2O \qquad (1.10)$$

$$\bullet OH + Fe^{2+} \longrightarrow Fe^{3+} + OH^- \qquad (1.11)$$

$$Fe^{3+} + HO_2^{\bullet} \longrightarrow Fe^{2+} + O_2 + H^+ \qquad (1.12)$$

$$Fe^{2+} + HO_2^{\bullet} + H^+ \longrightarrow Fe^{3+} + H_2O_2 \qquad (1.13)$$

$$HO_2^{\bullet} + HO_2^{\bullet} \longrightarrow H_2O_2 + O_2 \tag{1.14}$$

Ferrous ion plays major role in these reactions activating Fenton process by generation of highly reactive species including •OH. In the presence of H_2O_2, ferrous ion is oxidized to ferric ion Fe^{3+}. Under strongly acidic conditions in absence of complexing agents and H_2O_2, Fe^{3+} exists in a solution as a hexa-aqua ion $Fe(H_2O)_6{}^{3+}$. With pH increase, extensive hydrolysis of Fe^{3+} takes place leading to precipitation of amorphous ferric oxyhydroxide (Eq. 1.15) [22]:

$$Fe^{3+} \leftrightarrow FeOH^{2+} \leftrightarrow Fe(OH)_2^{+} \leftrightarrow Fe_2(OH)_2^{4+} \leftrightarrow \text{other polynuclear species} \leftrightarrow$$
$$\leftrightarrow Fe_2O_3{\cdot}nH_2O\ (s) \tag{1.15}$$

Ferrous ions also co-precipitate with ferric oxyhydroxides if the two ions are present together at solution pH exceeding 3.0. This leads to a continuous accumulation of ferric oxyhydroxide sludge formed in clarifiers because of coagulation and precipitation in the final stage of wastewater treatment. Accumulating sludge is the main disadvantage of the Fenton process on an industrial scale. Modifications of Fenton process described in table 1.2 allow minimizing the amounts of iron necessary to complete the reaction. However, modified processes require, in turn, modifications for reactors and additional energy, limiting the application range of these methods [22].

Alternative solution, sludge recirculation and reuse, is implemented in three strategies: (1) sludge thermal treatment at 300-400 °C in order to remove organic residues and use it as an activator in Fenton process; (2) using sludge as an additive to improve coagulation efficiency; (3) electrochemical reduction of Fe^{3+} to Fe^{2+} in the sludge with its reuse as an activator [22].

Fenton process was found to be effective in degradation of alachlor [22]: more than 90% out of starting 100 μM was oxidized in just one minute of treatment. Besides, addition of L-ascorbic acid to Fe^{3+}/H_2O_2 system significantly improved alachlor oxidation since Fe^{3+} was reduced to Fe^{2+} with ascorbic acid deprotonation and dehydroascorbic acid formation [22].

1.3.3 Zero-valent iron activating oxidation with persulfate

Ferrous ion is recommended as an activator of persulfate (PS) generating sulphate radicals due to its high activity, environmental safety and cost efficiency. However, during activation Fe^{2+} converts to Fe^{3+}, the following regeneration of which is complicated. As a result, substantial amount of ferrous ion is used in the process. The excessive Fe^{2+} acts as a persulfate radical scavenger generating additional sludge. The treatment of latter is technically complex and requires additional expenses [15].

To avoid abovementioned problems, ZVI is used having several advantages such as low cost, harmlessness and availability. In addition to the ZVI being a source of Fe^{2+}, it is able to recycle Fe^{3+} on its surface, i.e. reduce the precipitation of iron hydroxides. Moreover, application of ZVI/PS helps avoiding the addition of anions into the water matrix as with ferrous salts. The production of Fe^{2+} by ZVI is described by the reactions, Eqs. 1.16–1.23 [15]:

$$Fe^0 \longrightarrow Fe^{2+} + 2e^{-1} \tag{1.16}$$

$$Fe^0 + H_2O + 0.5O_2 \longrightarrow Fe^{2+} + 2OH^- \tag{1.17}$$

$$Fe^0 + 2H_2O \longrightarrow Fe^{2+} + 2OH^- + H_2 \tag{1.18}$$

$$S_2O_8^{2-} + Fe^{2+} \longrightarrow SO_4^{2-} + SO_4^{\bullet-} + Fe^{3+} \tag{1.19}$$

$$SO_4^{\bullet-} + Fe^{2+} \longrightarrow SO_4^{2-} + Fe^{3+} \tag{1.20}$$

$$Fe^0 + Fe^{3+} \longrightarrow 2Fe^{2+} \tag{1.21}$$

$$Fe^0 + 2H^+ \longrightarrow Fe^{2+} + H_2 \tag{1.22}$$

$$Fe^0 + S_2O_8^{2-} \longrightarrow Fe^{2+} + 2SO_4^{2-} \tag{1.23}$$

ZVI/PS systems were applied in degradation of organic pollutants such as acid orange II and methyl orange dyes, p-nitrophenol and bisphenol A, as well as alachlor. The performance of the ZVI/PS treatment in alachlor removal was studied establishing key parameters influencing oxidation kinetics: ZVI and PS dosages, temperature and initial pH [15]. The best conditions for herbicide degradation include acidic pH range from 1.5 to 3.0, increased, up to 60 °C, temperature, and moderate amounts of ZVI and PS at their molar ratio of 2:1. Compared to Fe^{2+}, ZVI provides benefits minimizing sulphate radicals scavenging and improving the iron reuse efficiency [15].

1.3.4 Sonochemical processes

Cavitation induced by the application of ultrasonic field is one of the methods for degradation of complex organic pollutants. This approach is briefly described in Table 1.2. Cavitation may be used in water treatment since it produces highly reactive radicals, generates turbulence and creates high temperatures and pressures [16]. Equation 1.24 illustrates an ultimate reaction between hydroxyl radical and organic compound leading to the degradation and mineralization of pollutants. Organic contaminants may also be exposed to pyrolysis degradation (Eq. 1.25) in close proximity to collapsing microbubbles produced by ultrasonic waves. This process is caused by high local temperatures and pressures inside the bubbles (5000 K; 600 atm) [17].

$$\bullet OH + \text{Organic compounds} \overset{)))}{\rightarrow} CO_2 + H_2O \tag{1.24}$$

$$\text{Organic compounds} \overset{)))}{\rightarrow} \text{Products} \tag{1.25}$$

The performance of sonochemical alachlor oxidation was studied in [16]. The experiments were carried out with ultrasound alone at pH values from 2 to 11. The treatment parameters in the experiments comprised the frequency of 20 kHz with power of 100 W applied to the 100-mL sample containing initially 20 ppm of alachlor. The best oxidation result was reached at pH 3.0, comprising 86.4% of alachlor degradation in 120 min of treatment. In order to increase degradation, addition of H_2O_2 was tested, showing the best performance at the oxidant to herbicide ratio of 10:1 (H_2O_2 dose of 200 ppm) reaching 98.6% of alachlor removal under the same experiment conditions as before. Ultrasound treatment was also combined with Fenton process varying $FeSO_4$ addition at a fixed amount of H_2O_2 of 70 ppm. Experiment parameters were maintained as previously described with the sonication time was reduced to 60 min. The best results were obtained at $FeSO_4$ concentrations of 70 and 35 ppm with 100% herbicide degradation [16].

Wang et al. [17] also degraded alachlor with US alone and US/Fenton combination. In a 1-L sample containing 50 ppm of alachlor US alone degraded less than 6.5% of herbicide in 60 min. In the US/Fenton combination, maximum degradation was observed at 20 mg L^{-1} of Fe^{2+} and 2 mg min^{-1} H_2O_2 reaching almost total pollutant degradation, 99.7%, confirming predominant hydroxyl-radical role in oxidation.

1.3.5 Biological treatment

Badriyha et al. [3] referred to previous studies, which demonstrated aerobic and anaerobic biodegradation of alachlor in soil with half-life period ranging from 4 to 10 days. White rot fungi showed alachlor biodegradation for over 90% at, however, only 6-14% mineralization in 122 days. The reviewed studies brought the authors to the conclusions that alachlor cannot be extensively degraded, even less mineralized, by a pure culture showing actinomycetes and fungi being more effective than bacteria. Mixed fungi and bacteria populations provide deeper degradation. In experiments, bioactive granulated activated carbon (BGAC) adsorbers were used (Fig. 1.3) providing bioactive and non-bioactive conditions. The results showed that the biofilm on GAC particles significantly extends adsorbent useful lifetime. The fungal strain *C. globossum* was able to biodegrade alachlor for 40% during the first three weeks, having the first ten days most active in degradation. Bacterial populations of *C. testosteroni* and *C. acidovorans* showed minor efficiency in degradation of alachlor [3].

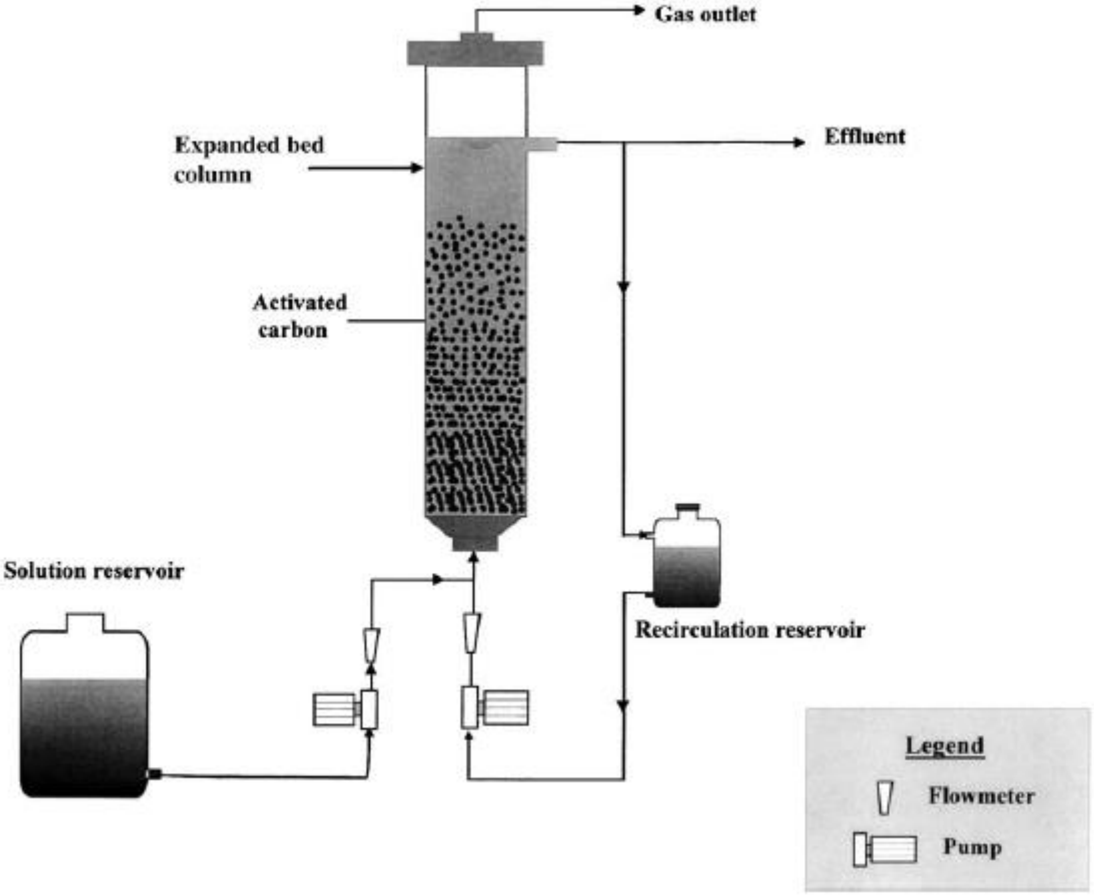


Figure 1.3. Expanded bed adsorber schematic diagram [3]

1.3.6 Electrochemical treatment

The most effective electrochemical AOPs are based on electro-Fenton processes and electro-oxidation. It is believed that electro-Fenton processes are more environmentally-friendly than their non-electrochemical analogues, since the necessary components of Fenton reaction (Fe^{2+} and H_2O_2) can be constantly electrogenerated *in situ* from compressed air and an initial catalytic amount of iron ions. Carbonaceous cathode reducing oxygen is the critical component in such systems. The key element in electro-oxidation, also known as electrochemical incineration/combustion or anodic oxidation, is anode able to produce •OH from water oxidation [5].

Degradation of alachlor using electrochemical techniques was studied with two anode-cathode systems, Pt and boron-doped diamond anodes with air-diffusion cathodes. The best performance was shown by using boron-doped diamond/air-diffusion electrode system. Alachlor solution with concentration of 0.6 mM (161.9 mg L^{-1}) was completely degraded in 360, 120 and 60 min with electro-oxidation in the presence of cathodically electrogenerated H_2O_2, electro-Fenton and photoelectro-Fenton processes, respectively [5].

1.4 Pulsed corona discharge oxidation

The AOPs described in Table 1.2 have several disadvantages: (1) O_3 and UV combinations demand substantial amounts of energy making them less cost-effective in treatment of large volumes of water; (2) peroxone O_3/H_2O_2 demands excessive H_2O_2 dosage for •OH generation; (3) photocatalytic AOPs show low quantum yield, i.e. are slow requiring increased operating costs when artificial light sources are used; (4) Fenton reaction generates substantial amounts of sludge and suffers excessive H_2O_2 expense due to oxidant scavenging; (5) sonochemical oxidation is applicable only to laboratory-scale experiments due to tremendous energy requirements; (6) during electrochemical treatment, halogenated by-products including halogenated oxy-anions are produced, possessing adverse health risks [25–27].

The mentioned drawbacks require an approach able to purify water effectively and simply, being free from disadvantages of other AOPs. Non-thermal plasma (NTP) of electric discharges is known to be capable of direct •OH generation with instant utilization. Moreover, H_2O_2, O_3 and UV – necessary components of AOPs – are also produced from the plasma [25].

Non-thermal plasma is one of the new directions in AOPs which receives special attention thanks to its environmental compatibility and ability to rapidly degrade organic pollutants. During NTP, active radicals, e.g. •OH, •N, •O and •O_2, active molecules, e.g. H_2O_2 and O_3, and abundant energetic electrons are produced making water treatment chemically similar to conventional ozonation. These reactive species are able to react with organic pollutants breaking their molecular bonds. The most commonly used plasma treatment systems in laboratory studies are dielectric barrier discharge and pulsed corona discharge [28, 29].

The use of electric discharges generated in aqueous or gaseous phase close to the gas-liquid interface has shown high efficiency in producing reactive oxygen species (ROS). Application of the gas-phase plasma in contact with treated water surface presents a new advancement in water purification industry. Radical species are mainly generated by electron-impact dissociation and following reactions between these species with each other and water surface. Radicals do not diffuse deep through the interface due to their high reactivity realized at the interface. Significant value of this phenomenon is that the oxidation efficiency depends on the interface area and mass transfer rate dependent on the reactor design and treatment conditions. Useful utilization of short-living ROS makes such gas-phase pulsed corona discharge (PCD) NTP the most energy-efficient AOP known nowadays. The high voltage pulses generating the discharge are ultra-short, around 100 ns in duration, are applied to uneven geometry electrodes [30, 31].

Oxidation efficiency of gas-phase PCD reactors with water droplets and jets in the discharge zone surpasses the one of corona above water reactors described by [32] due to more efficient mass transfer [33]. In addition, applying water showering rather than aerosol avoids the problem of energy expenses for aerosol generation and provides significantly higher flow-through capacities. However, water showering between electrodes may lead to the changes of the electric field pattern in the inter-electrode gap, which changes the routes of streamer propagation and may destabilize corona to a high-temperature spark discharge. The latter has a destructive effect on the electrodes. Moreover, the energy loss in conductive treated solutions takes place [34]. To avoid the described complications, the patented pulse shape is applied [31].

The energy efficiency of PCD application exceeds that of conventional ozonation a few times making it a promising alternative. The PCD equipment also simplifies the process: (1) the pulsed discharge is insensitive towards gas humidity, unlike in ozone synthesis where air must be dry, and (2) the gas transport is excluded, the water treatment takes place in a closed reactor chamber requiring only oxygen replenishment; if air is used for oxygen delivery, only minor residual ozone destruction in outlet gas flow is required [35].

The objective of the study was determining alachlor degradation efficiency in PCD treatment dependent on operation conditions including electrical conductivity caused by the presence of salts. Using data available in literature, oxidation energy efficiencies were derived for other AOPs in order to compare those in respect to alachlor degradation. Also, alachlor degradation kinetics and degradation products were the subjects of research. Identified degradation products were used to propose alachlor degradation mechanism.

2. MATERIALS AND METHODS

2.1 Reagents and chemicals

Alachlor (PESTANAL™, analytical standard 99.3%) for degradation kinetics experiments and metazachlor (PESTANAL™, analytical standard 99.6%) used in alachlor quantification were purchased from Sigma-Aldrich (USA). Alachlor (99.9%) for reaction products determination was purchased from Dr. Ehrenstorfer GmbH (Germany). Sodium dodecyl sulphate (SDS, $C_{12}H_{25}NaO_4S$, ≥99%), analytical grade anhydrous sodium sulphate (Na_2SO_4, ≥99.3%) and sodium bicarbonate ($NaHCO_3$, ≥99%) were purchased from Lach-Ner, Ltd. (Czech Republic). Sodium chloride (NaCl, ≥99.7%) used in experiments was of technical grade. All solutions were prepared using distilled water produced on site.

2.2 Alachlor-contaminated water treatment

2.2.1 Preparation of working solutions

Aqueous solutions of alachlor were prepared by diluting 20 mg of herbicide in a 1-L volumetric flask. Thereafter obtained solutions were diluted in PCD reactor storage tank into final volume of 10 L, i.e., the concentration of treated solutions was 2 mg L^{-1}. For determination of degradation products, concentration of alachlor in the treated solution was ten times higher, 20 mg L^{-1}.

2.2.2 Experimental setup

Treatment of alachlor-containing solution was performed using equipment developed by Flowrox Oy (Finland) shown in Figure 2.1. It consists of PCD reactor with storage tank of 40 L, pulse generator and circulation pump providing the flow rate of 1.0 m^3 h^{-1}. The multiple string electrodes (0.55 mm in diameter and 20 m of total length) are installed horizontally between vertical parallel plates. The distance between the grounded plate and wire electrodes is 18 mm. Treated solutions were sprayed through the perforated plate with 51 perforations of 1.0 mm in diameter positioned right above the high voltage string electrodes in a vertical plane. Pulses of voltage amplitude of 18 kV, current of 380 A, and 100 ns duration with power delivered to the reactor of 9 W and 32 W at 50 and 200 pulses per second (pps), respectively, were provided by the generator. The pulse characteristics were quantified with a Rigol DS1102E Mixed Signal Oscilloscope, a Tektronix P6015 high voltage probe (Tektronix Inc., USA) and a current monitor PT-

7802 (PinTek, China). The energy efficiency of oxidation was calculated using Equation 2.1:

$$E = \frac{\Delta C \cdot V}{W} \tag{2.1}$$

where E – energy efficiency of oxidation, g kW^{-1} h^{-1},

ΔC – decrease in alachlor concentration, g L^{-1},

V – volume of treated solution, L,

W – energy consumption, kWh.

The electric output-input ratio of pulse generator is 65%.

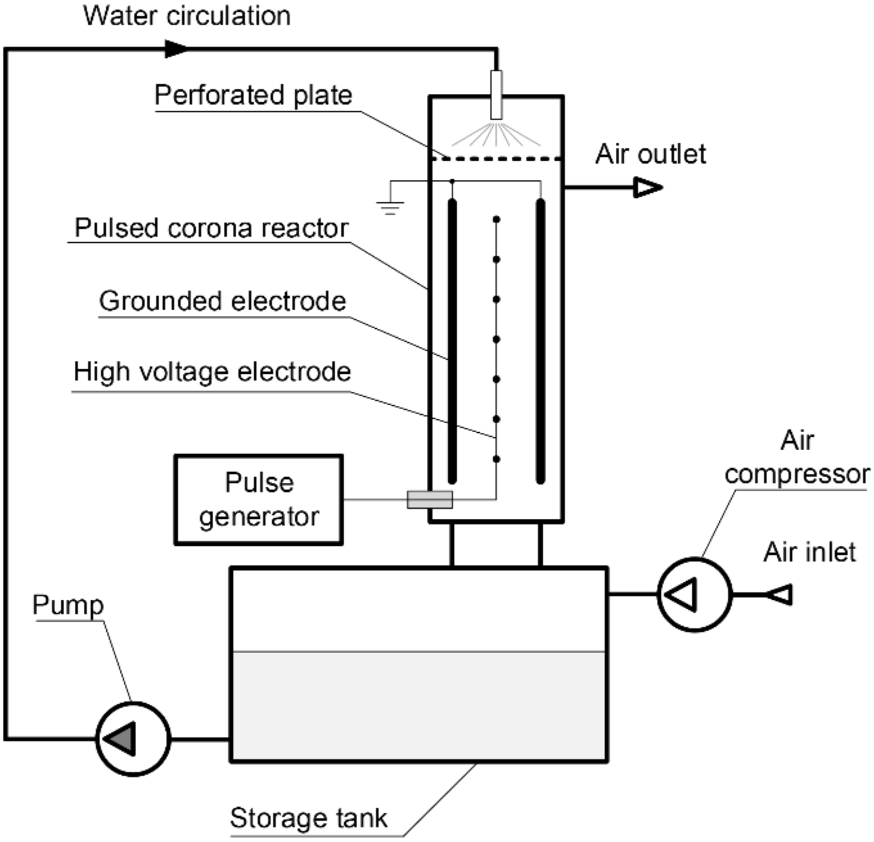


Figure 2.1. Outline of PCD equipment [30]

Before sample collection, pulse generator was turned off, samples were taken in three-minute mixing for uniform composition of the treated solution. During experiments with 50 pps, samples were taken every 0.5-2.5 min of treatment, making the total treatment time 20 min. Experiments at 200 pps were conducted for 5.0 min in total with samples collected at 0.5-1.0 min. Experiments for the products identification were performed at 200 pps frequency with 1.0-min sampling interval for 10 min in total; two more samples were collected at 15 and 20 min. All zero samples were taken after at least 3-minute mixing in reactor. Immediately after the sampling, sample flasks were capped. Unreacted ozone leaved the system through a polytetrafluoroethylene hose to a vent.

2.3 Analytical methods

2.3.1 GC-MS analyzer

Alachlor concentration in samples was quantified by means of liquid-liquid extraction with the three-step dichloromethane addition to the sample (1/1, v/v). Before extraction, 0.5 mL solution containing 25 mg L^{-1} of metazachlor was added to the test tube as an internal standard. All zero samples were analyzed twice for higher accuracy of the initial concentrations. The extract was dried with sodium sulphate with subsequent centrifugation of suspended particles. For products identification, the extract was concentrated by evaporation (1/10, v/v). The analysis was performed by gas chromatograph - mass spectrometer (GC–MS, Shimadzu QP2010, Japan). Samples of 2 µL were injected splitless into a ZB-5MS capillary column (30 m × 0.32 mm inner diameter with a film thickness of 0.25 µm). The temperature at the injection port was 260 °C. Helium was used as a carrier gas with a flow rate of 5.0 mL min^{-1}. Total program time was 23 min. The GC column oven was set to hold 80 °C for 1 min, then the temperature increased from 80 °C to 250 °C at 10 °C min^{-1}, final temperature was hold for 5 min.

Mass spectra were obtained using standard electron impact ionization mode coupled with quadrupole mass analyzer. Scanning was performed over m/z range of 35-350 with a scan speed 1111 amu s^{-1}. An interface temperature of 280 °C and an anion source temperature of 230 °C were applied. Since samples contained the solvent, data recording started from the third minute after injection.

2.3.2 Conductivity and pH determination

Electrical conductivity was measured with Multi-parameter meter HQ430d (Hach Company, USA). The pH value of samples was measured using S220 digital pH-meter (Mettler Toledo, Switzerland). Magnet stirrers provided homogeneity of the samples. The pH value of PCD-treated samples always decreased due to nitric acid formation [36] except for the experiments with solutions containing bicarbonates, where it remained unchanged due to the buffering capacity.

3. RESULTS AND DISCUSSION

3.1 Effect of pulse repetition frequency

To determine optimal parameters of PCD treatment, the first experiments were conducted with aqueous solutions containing 2.0 mg L^{-1} of alachlor under minimal pulse repetition frequencies of 50 and 200 pps with treatment time of 20 and 5 min, respectively. Treatment of alachlor-spiked water at 50 pps for 20 min resulted in the target compound concentration reduced for 94.1%. The energy efficiency of the herbicide removal comprised 7.4 g kW^{-1} h^{-1} at 50% reduction achieved in about 7 min of treatment (Fig. 3.1). Increased frequency of 200 pps resulted in 86.5% of alachlor degradation in 5 min of treatment. Oxidation efficiency at 50% of alachlor removal observed in about 3 min comprised 5.6 g kW^{-1} h^{-1}. The dependence of alachlor residual concentration on the energy delivered to PCD reactor is shown in Fig. 3.2.

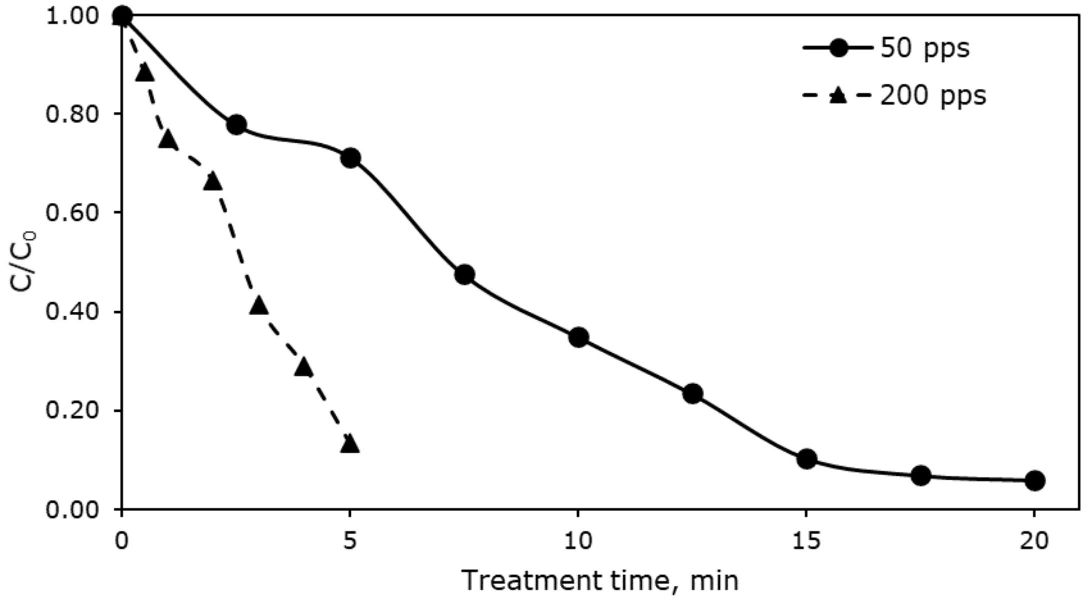


Figure 3.1. Dependence of relative alachlor concentration on treatment time: alachlor initial concentration 2.0 mg L^{-1}, treated solution flow rate 1 m^3 h^{-1}, reactor atmosphere air, temperature 22 °C

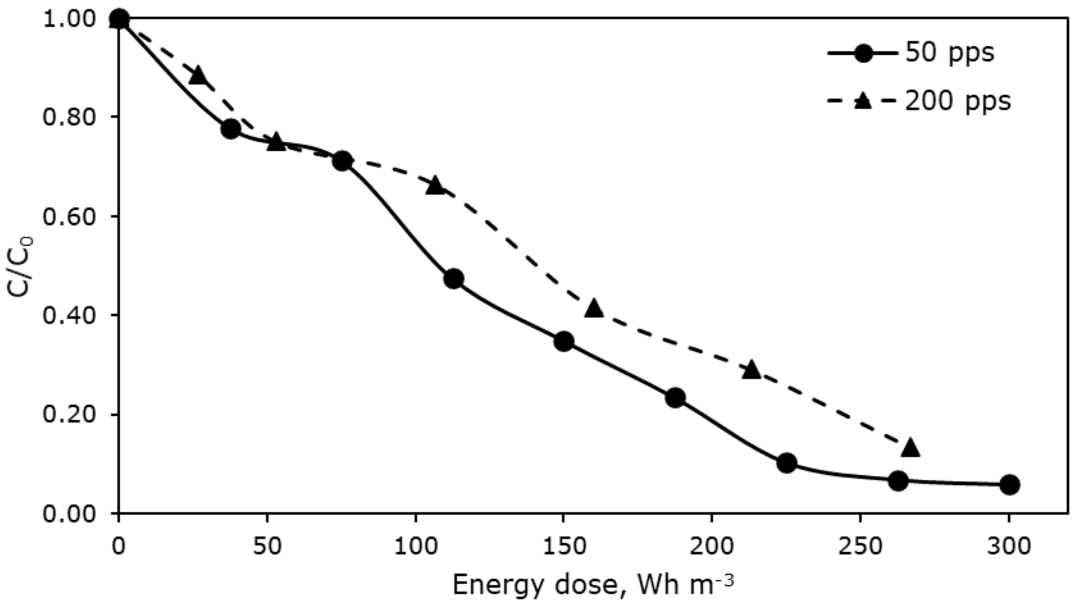


Figure 3.2. Dependence of relative alachlor concentration on delivered energy dose: for conditions see Fig. 3.1

Moderate difference in oxidation efficiencies expressed in g kW^{-1} h^{-1} at two different frequencies at relatively small efficiency numbers confirm the predominant role of OH-radicals in alachlor degradation as described in previously published works [6, 17]. The difference, although modest, indicate certain role of ozone in oxidation, direct or via forming OH-radicals, realized at longer treatment times [29, 30, 35].

Since 20 min of treatment under 50 pps showed almost the same concentration reduction as 200 pps in 5 min, further experiments were conducted at 200 pps for the experimental time saving.

3.2 Effect of bicarbonate

Beyond any doubt, polluted waters originated from contaminated ground sources are complex water matrices containing various dissolved and suspended organic and inorganic substances. Groundwater often contains bicarbonate anion, which is known OH-radical scavenger [23, 37]. Testing the effect of a mineral scavenger present in real-life situation provides knowledge necessary for understanding oxidation mechanism and assessment of impact. Eqs. 3.1-3.8 describe the sequence of scavenging reactions between •OH and carbonates, in which inert non-reactive bicarbonate- and carbonate-radicals are formed [38]:

$$HCO_3^- + \bullet OH \rightarrow HCO_3^\bullet + OH^- \quad (3.1)$$

$$CO_3^{2-} + \bullet OH \rightarrow CO_3^{\bullet -} + OH^- \quad (3.2)$$

$$HCO_3^{\bullet} \rightleftharpoons CO_3^{\bullet -} + H^+ \tag{3.3}$$

$$CO_3^{\bullet -} + H_2O_2 \longrightarrow HCO_3^{-} + HO_2^{\bullet} \tag{3.4}$$

$$CO_3^{\bullet -} + CO_3^{\bullet -} \longrightarrow CO_2 + CO_4^{2-} \tag{3.5}$$

$$CO_3^{\bullet -} + \text{Natural organic matter} \longrightarrow CO_3^{2-} + \text{products} \tag{3.6}$$

$$H_2CO_3 \rightleftharpoons HCO_3^{-} + H^+ \tag{3.7}$$

$$HCO_3^{-} \rightleftharpoons CO_3^{2-} + H^+ \tag{3.8}$$

Experiments with PCD oxidation of alachlor solutions containing bicarbonate in two various concentrations, 1.0 and 10.0 g L^{-1}, showed a reduced energy efficiency. For bicarbonate concentration of 1.0 g L^{-1}, the efficiency decreased from 5.6 to 4.8 g kW^{-1} h^{-1} at 50% removal of alachlor. At 10.0 g L^{-1}, however, more than twofold decreased efficiency was observed: the efficiency comprised only 2.6 g kW^{-1} h^{-1} at 50% removal. The results are illustrated by Figures 3.3 and 3.4.

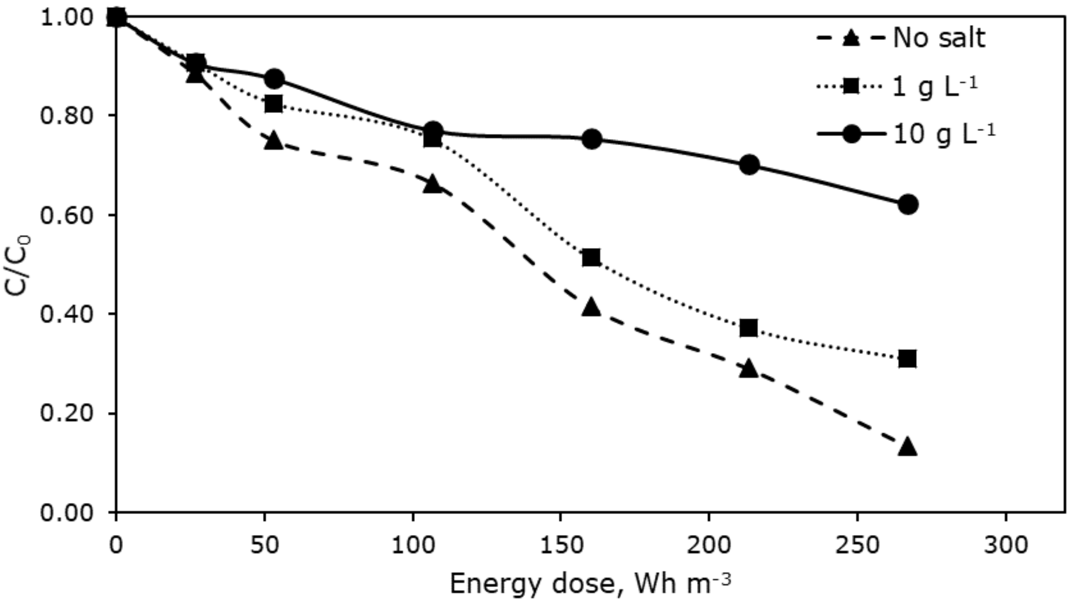


Figure 3.3. Dependence of alachlor relative concentration on delivered energy dose: alachlor initial concentration 2.0 mg L^{-1}, reactor atmosphere air, sodium bicarbonate concentrations 1.0 g L^{-1} and 10.0 g L^{-1}, treated solution flow rate 1.0 m^3 h^{-1}, pulse repetition frequency 200 pps, treatment time 5 min

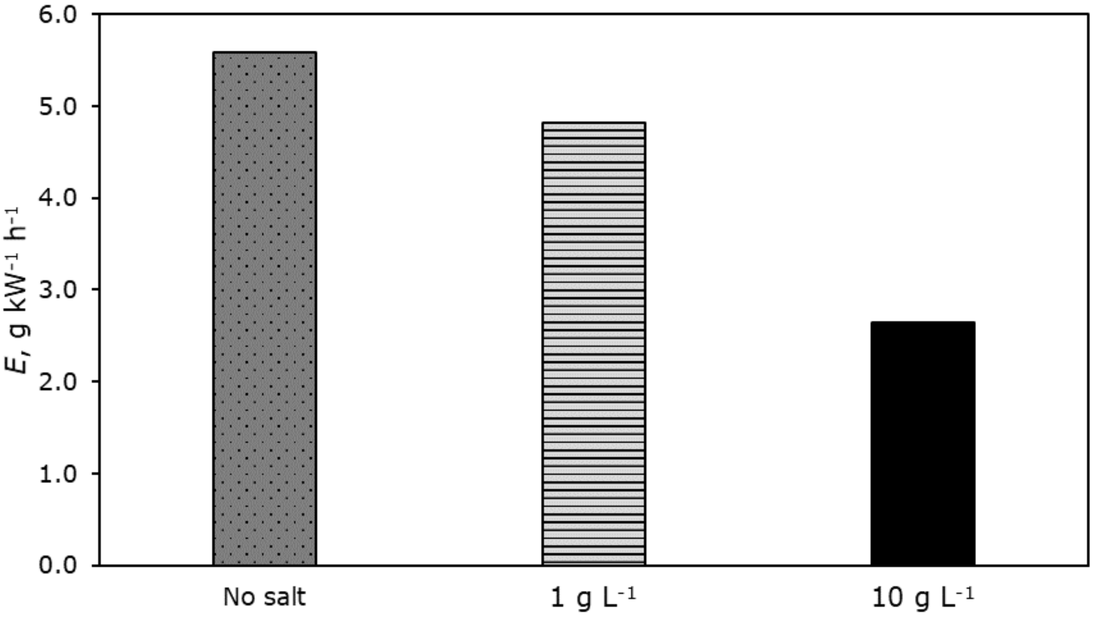


Figure 3.4. Energy efficiencies of alachlor oxidation in presence of sodium bicarbonate: calculations made for 50% removal, for experimental conditions see Fig. 3.3

During five-minute treatment of alachlor solution in presence of sodium bicarbonate in amount of 1.0 g L^{-1}, herbicide concentration decreased for 69.0% while only 37.7% reduction was registered at bicarbonate concentration of 10.0 g L^{-1}. Degradation rate without bicarbonate admixture, as a reminder, was 86.5%. The 50-% removal of alachlor in the experiment with 10 g L^{-1} of $NaHCO_3$ was achieved as late as in 7 min of treatment. This observation indicates noticeable, although moderate scavenging of OH-radicals at bicarbonate concentration (1.0 g L^{-1}) exceeding the target herbicide concentration as much as 500 times indirectly supporting possible domination of the radical reaction at the gas-liquid interface. Non-surfactant radical scavenger shows its substantial impact at the concentration exceeding the target compound's one 5,000 times.

One of the factors reducing the oxidation efficiency in PCD treatment is the treated solution conductivity [34]. Previous studies showed minor contribution of bicarbonate conductivity to the efficiency deterioration in respect to phenol, oxalate and humic acids oxidation [30]. Conductivities of alachlor solutions containing sodium bicarbonate in concentrations of 1.0 and 10.0 g L^{-1} comprised 1.04 and 8.9 mS cm^{-1}, respectively. The latter number is somewhat important for the comparison of the conductivity and bicarbonate impacts. The impact of conductivity is reported in the next chapter.

3.3 Effect of conductivity

The experiments with increased conductivity for establishing ohmic losses were performed using NaCl and Na_2SO_4 [34]. Both sodium chloride and sulphate were dissolved in distilled water in amounts of 5.6 and 8.5 g L^{-1}, respectively, to reach the electric conductivity of solutions equal to 10 mS cm^{-1} at 20 °C. The experiments showed slight reduction of oxidation efficiency in presence of both sodium salts indicating insignificant ohmic losses (Fig. 3.5). What is more important, no big difference was observed between salts indicating absent electrolytic phenomena otherwise theoretically capable of additional degradation of alachlor. Figure 3.6 demonstrates calculated energy efficiencies of alachlor PCD oxidation in conductive solutions. According to Fig 3.6, oxidation in presence of chloride appeared to be less efficient than with sulphate, while the angles of their slopes in Fig. 3.5 differ by one ten thousandth. Such noticeable difference in oxidation energy efficiencies is related to the starting alachlor concentrations: 1.23 mg L^{-1} and 1.56 mg L^{-1} for experiments with chloride and sulphate, respectively. The dependence of energy efficiency of oxidation on alachlor initial concentration will be discussed in chapter 3.6. The values of energy efficiencies at 50% removal of alachlor were obtained using equations of the straight lines given on Fig. 3.5 and equal to 4.9, 4.7 and 3.6 g kW^{-1} h^{-1} for experiments without presence of salt, with sulphate and chloride, respectively. The removal of alachlor was found to be around 75% in 5 min of treatment for both salts.

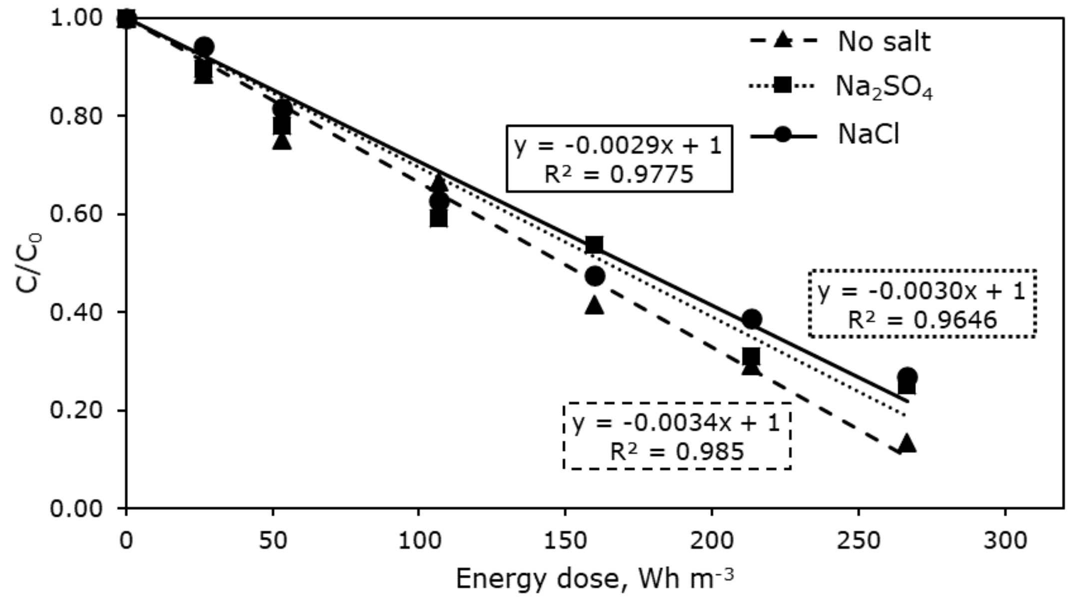


Figure 3.5. Dependence of alachlor relative concentration on delivered energy dose: alachlor initial concentration 2 mg L^{-1}, reactor atmosphere air, sodium chloride concentration 5.6 mg L^{-1}, sodium sulphate concentration 8.5 mg L^{-1}, conductivity of salt containing solutions 10 mS cm^{-1} at 20 °C, treated solutions flow rates 1 m^3 h^{-1}, pulse repetition frequency 200 pps, treatment time 5 min

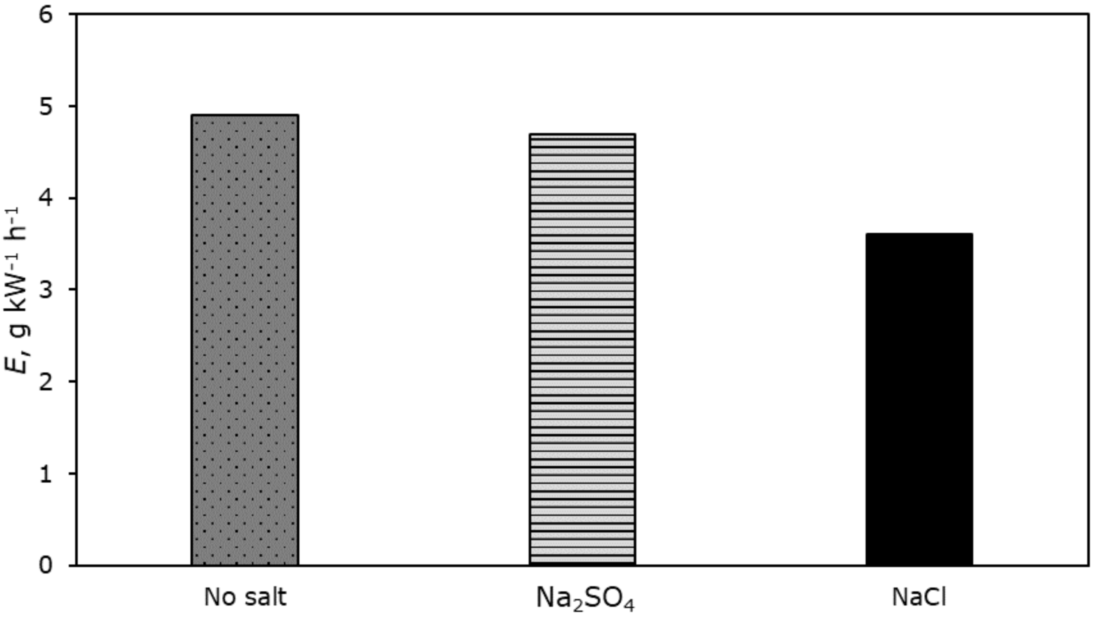


Figure 3.6. Energy efficiencies of alachlor oxidation in conductive solutions: calculations made for 50% removal, for experimental conditions see Fig. 3.5

Weak impact of conductivity to the energy efficiency indicates that substantial impact of bicarbonate to alachlor oxidation is predominantly due to radical scavenging, not ohmic losses with increased conductivity.

3.4 Effect of surfactant

The effect of surfactant on oxidation efficiency of various aqueous pollutants was studied in previous works [30, 39], showing inconsistent, at the first sight, impacts towards different substances. The addition of SDS surfactant was reported to significantly improve oxidation of reactive azo-dyes, whereas simple molecules of phenolic compounds and oxalate demonstrate screening effect of SDS in respect of surface-borne radicals reducing the oxidation efficiency. To study the possible effect of surfactant on alachlor oxidation, SDS was added to treated solution in amount of 100 mg L^{-1}. The attempt was unfortunate due to SDS interfering the alachlor and metazachlor extraction with dichloromethane; accurate quantification appeared to be impossible. This task thus remains for further studies.

3.5 Determination of degradation products

The attempts of oxidation products identification were performed in experiments with alachlor starting concentration of 2 mg L^{-1}. The products concentrations, being definitely below the starting concentration of the parent compound, was low enough to lose them in the 'noise' of chromatograms. Identification of oxidation products was performed using alachlor initial concentration increased ten times, i.e. 20 mg L^{-1}. The applied energy dose of 1,067 Wh m^{-3} resulted in 86.7% alachlor concentration reduction after 20 min of treatment at 200 pps. The alachlor oxidation efficiency comprised 21.2 g kW^{-1} h^{-1} at 50% removal, almost four times exceeding the one observed at 2 mg L^{-1}. This result shows oxidation efficiency improved with increased concentration of the target compound.

The obtained MS spectra were compared with the NIST database allowing to identify the primary alachlor degradation products. The difference of 1 m/z value with actual molecular weight was considered to be a measurement uncertainty. As observed in previous research [22], hydroxyl radicals attack organic compounds several ways: (1) abstracting H from C–H, O–H and N–H bonds, (2) adding to C–C bonds and (3) conjugating aromatic rings. The discovered intermediates were found to appear through four main degradation pathways: (1) dehalogenation, (2) cyclization reactions, (3) ether bond cleavage and (4) hydroxylation of the aromatic ring.

Compound 1 with RT of 14.305 min and m/z value of 248 was found in every sample except 0- and 0.5-min samples. It can correspond to N-(2,6-diethylphenyl)-N-(methoxymethyl)-2-oxoacetamide. It should be pointed out that its peak was slightly growing on chromatograms indicating the moderate growth in concentration. The author failed to find information about this intermediate published earlier. Compound 1 could be generated by dehalogenation, where –Cl is substituted with –OH and subsequent cleavage of hydrogen atom to form double bond with oxygen.

Compound 2 with RT of 13.990 min and m/z value of 238 corresponds to 2-chloro-N-(2,6-diethylphenyl)-N-methylacetamide. The formation of this by-product is related to detachment of ether group or partial loss of the lateral group of N and may result in formation of various by-products. The author either failed to find published information on this intermediate as an alachlor degradation product.

Compound 3 with RT of 13.370 min and m/z value of 251 corresponds to 7-acetyl-1-(2-chloroacetyl)-2,3-dihydro-1H-indol-3-one. It was formed during cyclization – typical reaction for oxidation of alachlor by •OH and hydroxylation of lateral chain. The presence of this compound in reaction mixture was also found earlier in alachlor ozonation [6], ZVI activating persulfate oxidation [15] and Fenton process [22].

Compound 4 with RT of 10.230 min and m/z value of 223 corresponds to 2-chloro-1-(7-ethyl-2,3-dihydro-1H-indol-1-yl)ethan-1-one. This intermediate was also formed due to cyclization reaction similarly to the compound 3, and may serve as precursor for the occurrence of compound 8 (see below). Compound 4 is an alachlor biotransformation by-product reported previously. [6] It was also solidary reported to be the oxidation product of alachlor oxidation [5, 6, 15 and 22].

Compound 5 with RT of 10.935 min and m/z value of 225 corresponds to 2-chloro-N-(2,6-diethylphenyl)acetamide formed by C–N bond cleavage. It also has CAS registry number® 6967-29-9. In addition, this compound was reported as one of the major alachlor metabolites formed in the environment [6], mammalian bodies, human liver microsomes and urine [22]. It was also found among reaction products in several studies [5, 6, 15 and 22].

Compound 6 with RT of 11.680 min and m/z value of 253 corresponds to N-(2-chloroacetyl)-N-(2,6-diethylphenyl)formamide. The formation of described intermediate is related to the ether bond cleavage. Compound 6 was not found by the author among products reported earlier.

Compound 7 with RT of 15.250 min and m/z value of 254 corresponds to 2-chloro-N-(2,6-diethylphenyl)-N-(hydroxymethyl)acetamide. Demethylation of alachlor or hydroxylation of compound 2 are probable pathways of formation of compound 7. It was also reported by Pipi et al. [5] and Bolobajev et al. [22] as an alachlor oxidation intermediate.

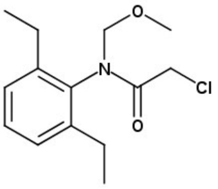
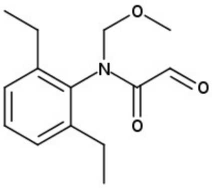
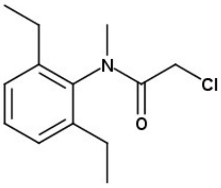
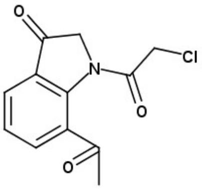
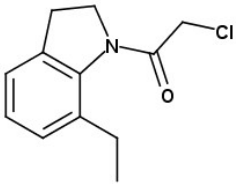
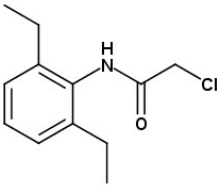
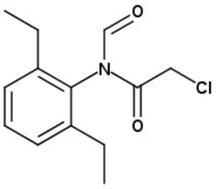
Compound 8 with RT of 15.390 min and m/z value of 237 corresponds to 1-(2-chloroacetyl)-7-ethyl-2,3-dihydro-1H-indol-3-one. The described compound forms via cyclization and hydroxylation reactions. The presence of this compound among reaction products was not reported in available literature.

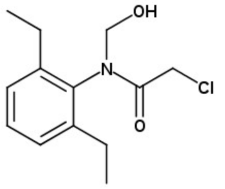
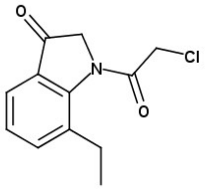
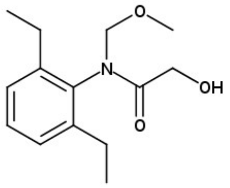
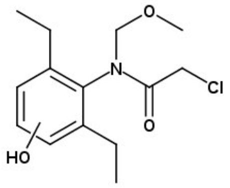
Compound 9 with RT of 14.550 min and m/z value of 251 corresponds to N-(2,6-diethylphenyl)-2-hydroxy-N-(methoxymethyl)acetamide with CAS registry number® 56681-55-1. It forms by dehalogenation, where –Cl is substituted by –OH. This intermediate was also found earlier by Bolobajev et al. [22].

Compound 10 with RT of 15.540 min and m/z value of 284 corresponds to 2-chloro-N-(2,6-diethyl-X-hydroxyphenyl)-N-(methoxymethyl)acetamide, in which X denotes the ordinal number of carbon in aromatic ring to which hydroxyl group is attached. The described compound forms by electrophilic substitution involving attachment of hydroxyl group to the aromatic ring. Compound 10 was also described in [5, 15 and 22].

Analysis of chromatograms showed more oxidation products than described here. Determination of undescribed compounds was unsuccessful due to unclear mass spectra or presence of ‘noise’. All identified oxidation by-products are presented in Table 3.1. Fig. 3.7 demonstrates GC-MS chromatogram of the sample taken after 20 min of treatment. The degradation pathway of alachlor is proposed in Fig. 3.8.

Table 3.1. Alachlor oxidation by-products identified by GC-MS: MW – molecular weight, RT – retention time

Compound	**MW, g mol^{-1}**	**RT, min**	**Structure**
Alachlor	269	13.0	
1	249	14.3	
2	239	14.0	
3	251	13.4	
4	223	10.2	
5	225	10.9	
6	253	11.7	

Compound	**MW, g mol^{-1}**	**RT, min**	**Structure**
7	255	15.3	
8	237	15.4	
9	251	14.6	
10	285	15.5	

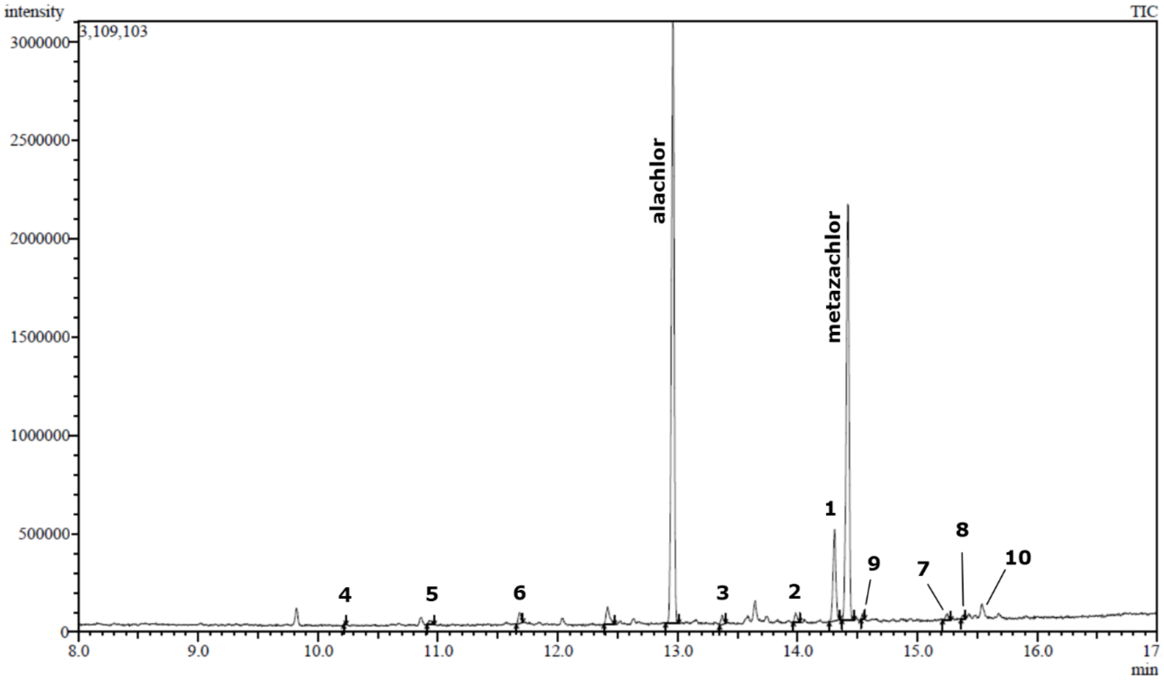


Figure 3.7. GC-MS chromatogram obtained from the sample. Sample was taken after 20 min of treatment by PCD

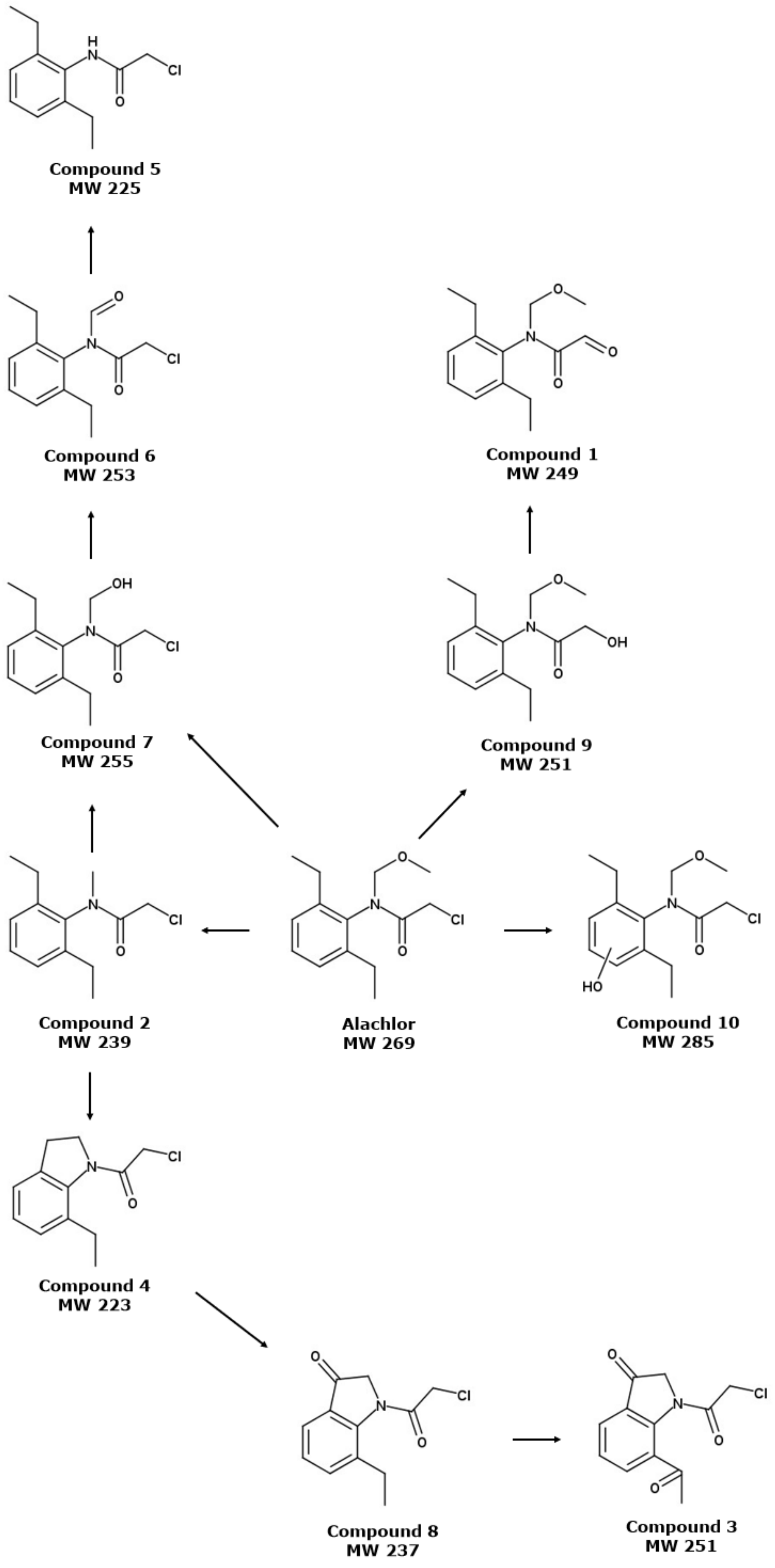


Figure 3.8. Probable degradation pathway of alachlor

3.6 The results analysis in comparison with preceding alachlor oxidation studies

3.6.1 Comparison to AOPs

Energy efficiency of alachlor oxidation was calculated using published data primarily on ozonation, although other AOPs were also considered. Table 3.2 provides a brief overview on energy efficiencies of alachlor oxidation in AOPs. Calculations were made considering energy expense for ozone synthesis of 15 kWh kg^{-1} O_3 in oxygen, and 30 kWh kg^{-1} O_3 when using air [40]. The costs of 50% H_2O_2 of 0.8217 EUR kg^{-1}, $FeSO_4$ 0.7163 EUR kg^{-1} and electric energy 0.0342 EUR kW^{-1} h^{-1} were used [41]. Costs of used chemicals were converted to the energy expense. The examples of calculations are shown in Eqs. 3.9–3.16.

An example of ozonation energy efficiency calculations was taken with the following parameters: ozone production 1.68 mg min^{-1}; treatment time 10 min; alachlor initial concentration 120 mg L^{-1}; treated solution volume 1 L; removal rate 55.7%; ozone was produced from air [20].

$$E = \frac{C_0 \cdot V \cdot p}{Q \cdot t \cdot W} \tag{3.9}$$

where E – energy efficiency of oxidation, g kW^{-1} h^{-1},

C_0 – alachlor initial concentration, g L^{-1},

V – volume of treated solution, L,

p – concentration decrease, %,

Q – ozone production, kg min^{-1},

t – treatment time, min,

W – energy consumption for ozone synthesis, kWh kg^{-1}.

$$E = \frac{0.12 \cdot 1 \cdot 0.557}{1.68 \cdot 10^{-6} \cdot 10 \cdot 30} = 132.6 \text{ g kW}^{-1} \text{ h}^{-1} \tag{3.10}$$

The data from the study of Bagal et al. [16] was used as an example of ultrasound energy efficiency considering following reaction conditions: power applied 100 W; sonication time 50 min; alachlor initial concentration 20 mg L^{-1}; treated solution volume 0.1 L; concentration reduction 50%.

$$E = \frac{C_0 \cdot V \cdot p}{t \cdot W} \tag{3.11}$$

where E – energy efficiency of oxidation, g kW^{-1} h^{-1},

C_0 – alachlor initial concentration, g L^{-1},

V – volume of treated solution, L,

p – concentration decrease, %,

t – sonication time, h,

W – applied power, kW.

$$E = \frac{0.02 \cdot 0.1 \cdot 0.5}{50/60 \cdot 0.1} = 1.2 \cdot 10^{-2} \text{ g kW}^{-1} \text{ h}^{-1} \tag{3.12}$$

Ultrasound/H_2O_2 [16] oxidation efficiency was calculated by using several parameters: power applied 100 W; sonication time 0.5 h; alachlor initial concentration 20 mg L^{-1}; treated solution volume 0.1 L; hydrogen peroxide concentration 200 mg L^{-1}; concentration reduction 50%.

$$E = \frac{C_0 \cdot V \cdot p}{t \cdot W + C_{HP} \cdot V \cdot q/f} \tag{3.13}$$

where E – energy efficiency of oxidation, g kW^{-1} h^{-1},

C_0 – alachlor initial concentration, g L^{-1},

V – volume of treated solution, L,

p – concentration decrease, %,

t – treatment time, h,

W – Applied power, kW,

C_{HP} – hydrogen peroxide concentration, kg L^{-1},

q – hydrogen peroxide purchase cost, EUR kg^{-1},

f – electric energy cost, EUR kWh^{-1}.

$$E = \frac{0.02 \cdot 0.1 \cdot 0.5}{0.5 \cdot 0.1 + 200 \cdot 10^{-6} \cdot 0.1 \cdot 0.8217/0.0342} = 2.0 \cdot 10^{-2} \text{ g kW}^{-1} \text{ h}^{-1} \tag{3.14}$$

Research [16] was used for demonstrating calculations of energy efficiency of sono-Fenton, considering applied power 100 W; sonication time 2.5 min; alachlor initial concentration 20 mg L^{-1}; treated solution volume 0.1 L; hydrogen peroxide concentration 70 mg L^{-1}; ferrous sulphate concentration 35 mg L^{-1}; concentration reduction 50%.

$$E = \frac{C_0 \cdot V \cdot p}{t \cdot W + C_{HP} \cdot V \cdot q/f + C_{FS} \cdot V \cdot i/f} = \frac{C_0 \cdot V \cdot p}{t \cdot W + V/f \cdot (C_{HP} \cdot q + C_{FS} \cdot i)} \tag{3.15}$$

where E – energy efficiency of oxidation, g kW^{-1} h^{-1},

C_0 – alachlor initial concentration, g L^{-1},

V – volume of treated solution, L,

p – concentration decrease, %,

t – treatment time, h,

W – Applied power, kW,

C_{HP} – hydrogen peroxide concentration, kg L^{-1},

C_{FS} – ferrous sulphate concentration, kg L^{-1},

q – hydrogen peroxide purchase cost, EUR kg^{-1},

i – ferrous sulphate purchase cost, EUR kg^{-1},

f – electric energy cost, EUR kWh^{-1}.

$$E = \frac{0.02 \cdot 0.1 \cdot 0.5}{2.5/60 \cdot 0.1 + 0.1/0.0342 \cdot (70 \cdot 10^{-6} \cdot 0.8217 + 35 \cdot 10^{-6} \cdot 0.7163)} = 0.2 \text{ g kW}^{-1} \text{ h}^{-1} \tag{3.16}$$

Table 3.2. Calculated energy efficiencies of alachlor oxidation using AOPs. C_0 – alachlor initial concentration; E – energy efficiency of oxidation; N/A – not available

Process	**C_0, mg L^{-1}**	**Treated solution volume, L**	**Removal rate, %**	**E, g kW^{-1} h^{-1}**	**Reference**
Ozonation	120	1	55.7	132.6	[20]
			91.2	72.4	
Ozonation	100	N/A	50	N/A[a]	[21]
			90	N/A[a]	
Ozonation	5.4	0.5	50	2.8	[42]
			90	2.2	
Ozonation	100	$7.5 \cdot 10^{-2}$	50	25.6	[43]

Process	C_0, mg L^{-1}	Treated solution volume, L	Removal rate, %	E, g kW^{-1} h^{-1}	Reference
			90	13.2	
Ozonation	0.2	0.5	95	2.4	[44]
Ozonation	0.2	0.5	95	2.2	[44]
Ozonation	0.2	0.5	95	0.9	[44]
Ozonation	0.2	0.5	95	1.1	[44]
Ultrasound	20	0.1	50	$1.2 \cdot 10^{-2}$	[16]
			86.4	$8.6 \cdot 10^{-3}$	
Ultrasound/H_2O_2	20	0.1	50	$2.0 \cdot 10^{-2}$	[16]
			90	$1.5 \cdot 10^{-2}$	
Sono-Fenton	20	0.1	50	0.2	[16]
			90	0.1	
Ultrasound	50	1	6.5	$3.3 \cdot 10^{-2}$	[17]
Sono-Fenton	50	1	100	0.5	[17]
Fenton	27.0	0.03	90	N/A[b]	[22]

[a] The authors did not present the volume of treated solution.

[b] The authors provided no sufficient data to calculate oxidation energy efficiency. Particularly, there were no data concerning residual concentration of $FeSO_4$ and H_2O_2 in reaction mixture.

The experimental results shown in Table 3.3 were compared to other studies on alachlor oxidation described in Table 3.2. Energy efficiency of oxidation was chosen as the main criteria for showing the most efficient process. Straightforward comparison of efficiencies is complicated by the differences in experimental conditions, although the source [42] describes ozonation under conditions similar to the present work: starting concentration of alachlor was at 5.4 mg L^{-1} (Table 3.2). The energy efficiency of ozonation given in [42], however, yields to the one in the present research 2-3 times even with 2.7 times lower concentration of alachlor (Table 3.3).

Table 3.3. Energy efficiency of oxidation by PCD. C_0 – alachlor initial concentration; E – energy efficiency of oxidation

Process description	C_0, mg L^{-1}	Removal rate, %	E, g kW^{-1} h^{-1}
50 pps	2	50	7.4
		90	6.3
200 pps	2	50	5.6
		86.5	5.0

Process description	***C$_0$*, mg L^{-1}**	**Removal rate, %**	***E*, g kW^{-1} h^{-1}**
200 pps / NaHCO$_3$ 1 g L^{-1}	2	50	4.8
		69.0	4.2
200 pps / NaHCO$_3$ 10 g L^{-1}	2	37.7	2.5
		50	2.6[a]
200 pps / NaCl	2	50	3.6[b]
		73.1	3.5
200 pps / Na$_2$SO$_4$	2	50	4.7[b]
		74.8	4.7
200 pps	20	50	21.2
		86.7	16.9

[a] Value was calculated based on experimental data extrapolation. Half of the initial concentration decrease was observed in 7 min of treatment.

[b] Value was calculated using the equation of the straight line of degradation.

PCD treatment of alachlor with initial concentration of 20 mg L^{-1} and its reduction to 50% demonstrated energy efficiency of 21.2 g kW^{-1} h^{-1}, while the best result out of sonochemichal processes was shown by sono-Fenton and equals to 0.2 g kW^{-1} h^{-1}. Thus, the efficiency of PCD is around 100 times higher. However, compared to ozonation [43] with initial alachlor concentration of 100 mg L^{-1} and energy efficiency of 25.6 g kW^{-1} h^{-1} for 50% concentration reduction, PCD still claims to be promising technology, since oxidation efficiency of alachlor depends on its initial concentration, i.e. increasing the concentrations in experiments with PCD could lead to increased efficiency surpassing that of ozonation.

The description of the reaction kinetics for PCD systems is complicated due to the presence of a number of oxidants including ozone, •OH, atomic oxygen etc., which participate in the degradation of substrate. However, it is generally assumed that oxidation undergoes in accordance with a second order reaction kinetics, where the concentration of oxidants is substituted by the power (P) divided by the total volume (V) of the plasma zone (Eq. 3.17) [45]:

$$\frac{dC}{dt} = -\frac{k_2 \cdot C \cdot P}{V} \tag{3.17}$$

Where C – pollutant concentration, mol m^{-3},

t – treatment time, min,

P – Power delivered to the reactor, W, *V* – Volume of plasma zone, m^3,

k_2 – second order reaction rate constant, m^3 J^{-1}.

Integrating equation 3.17 between t_0 and t results in equation 3.18:

$$\ln\left(\frac{C_0}{C}\right) = \frac{k_2 \cdot P}{V} \cdot t \qquad (3.18)$$

Plotting the left side of Eq. 3.18 against t yields a straight line with slope $k_2 P \cdot V^{-1}$ (Fig. 3.9), which allows determining the second order reaction rate constant for degradation of alachlor. One can see the PCD degradation of alachlor fitting satisfactorily in the present model possessing the highest rate constant at 200 pps. Considering the volume of plasma zone to be 0.013 m^3, the corresponding second order rate constants were calculated (Table 3.4). The disproportional growth in alachlor oxidation rate (three times lower second order reaction rate coefficient) with ten-fold increased concentration may be explained by the change in substrate-oxidant ratio with possible change in reaction stoichiometry.

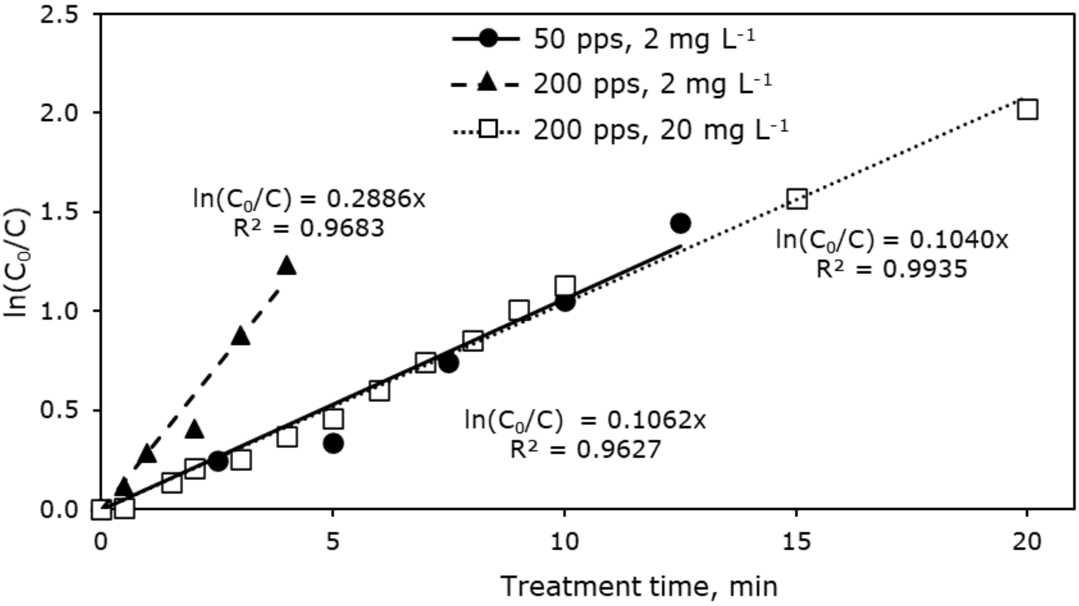


Figure 3.9. Verification of equation 3.18. Determination of the second order rate constant for the degradation of alachlor by PCD: initial concentrations of alachlor 2 and 20 mg L^{-1}, pulse repetition frequencies 50 and 200 pps

Table 3.4. The second order reaction rate coefficients for alachlor degradation by PCD

Pulse repetition frequency	**C_0, mg L^{-1}**	**Second order reaction rate coefficient $k_2 \cdot 10^{-6}$, m^{3}J^{-1}**	**Determination coefficient R^2**
50	2.0	2.7	0.963

Pulse repetition frequency	**C_0, mg L^{-1}**	**Second order reaction rate coefficient $k_2 \cdot 10^{-6}$, m^3J^{-1}**	**Determination coefficient R^2**
200	2.0	2.1	0.968
200	20	0.74	0.994

The solution of Eq. 3.18 is shown by Eq. 3.19 and proposes an exponential decay in pollutant concentration as a function of treatment time which fits the shape of alachlor degradation demonstrated by Figure 3.10.

$$C = C_0 \cdot \exp\left(-\frac{k_2 \cdot P}{V} \cdot t\right) \tag{3.19}$$

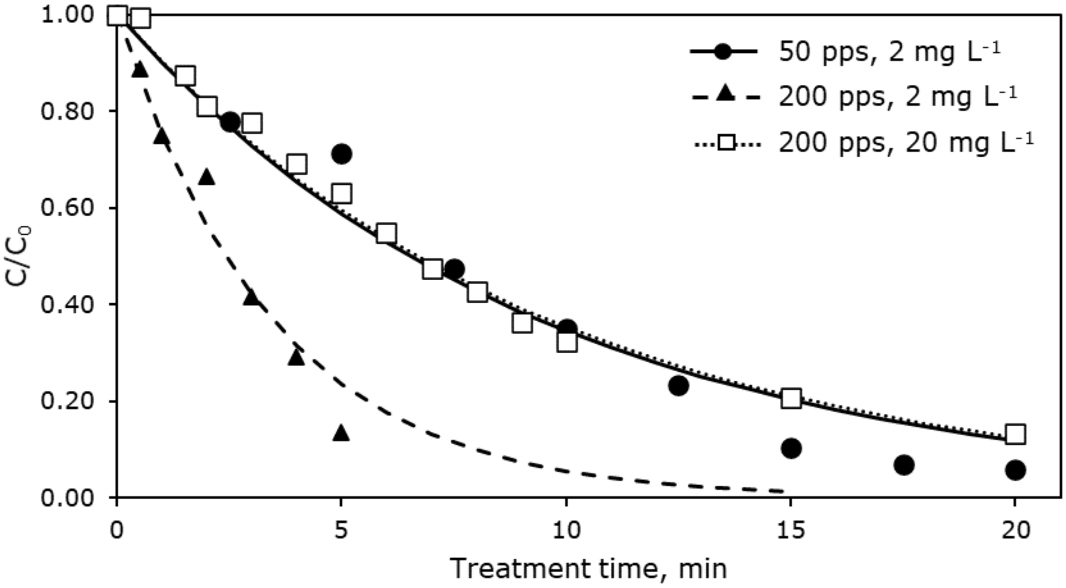


Figure 3.10. Removal efficiency of alachlor at different frequencies of pulses. Simulation curves fits with obtained experimental data. For conditions see Fig. 3.9

Therefore, the higher is the concentration of alachlor in reaction mixture, the more herbicide can be degraded using the same energy dose that reflects in increased values of energy efficiencies of oxidation. This fact is also confirmed by current research: oxidation efficiency of alachlor in experiment with initial concentration of 20 mg L^{-1} under the same conditions as experiment with initial concentration of 2 mg L^{-1} was at least 3.5 times higher.

3.6.2 Dielectric barrier discharge oxidation of alachlor

The author came across the description of alachlor oxidation using dielectric barrier discharge (DBD) [19]. This type of discharge is known to be reliably stable using pulses of longer duration, although having no future in real-life application for extreme inefficiency of energy utilization [46]. Nevertheless, DBD is often used in research work as a simple and reliable source of non-thermal plasma. The initial concentration of alachlor in the cited work was 1.0 mg L^{-1}. The lowest energy consumption for alachlor elimination by an order of magnitude EE/O was 10.4 kWh m^{-3} achieved in combination of DBD with residual ozone utilization in a sequential bubble column. The alachlor elimination efficiency thus comprised 0.09 g kW^{-1} h^{-1}, which yields to PCD studies in this research at least 1.5 orders of magnitude.

3.6.3 Comparison of degradation products

The identified PCD degradation products were analysed as compared to the lists of products determined in other works. The PCD treatment products were found similar to other AOPs in composition having, however, some of them unique for different technologies, although the discrepancies are not dramatic (see 3.5).

In contrast, the products originated from DBD treatment were found to have one or more hydroxyl groups bound to the aromatic ring. Moreover, only DBD method led to formation of product with aromatic ring cleavage. This is a very important observation, since the loss of aromaticity is not often observed in AOPs. [19] However, all those compounds only occurred during single-pass reactor configuration and their presence in the batch process was not confirmed. The formation of products from batch process included double bonded oxygen addition, dealkylation, hydroxylation and dechlorination steps which are similar to other studies.

SUMMARY

Aqueous alachlor herbicide oxidation by promising pulsed corona discharge treatment was studied. The novelty of research is guaranteed by the newly developed water treatment method applied to alachlor removal with the energy efficiency surpassing other AOPs. The objective of the research was to establish the PCD oxidation energy efficiency in comparison with already known and widely applied water treatment technologies. Identification of degradation products presents a separate objective of the study. Several conclusions were derived from the experimentally obtained data:

1. The difference in oxidation efficiencies at two different frequencies confirmed the predominant role of •OH in alachlor degradation. It also indicated certain role of ozone in herbicide oxidation, direct or via forming OH-radicals, realized at longer treatment times. Increased frequency, from the other hand, results in accelerated oxidation.

2. Bicarbonates act as hydroxyl radical scavengers, thus noticeably reducing the efficiency of oxidation. In addition, they increase the conductivity of solution; however ohmic losses insignificantly affect the efficiency.

3. Derived from analysis of chromatograms and mass-spectra, several degradation products were identified with pathways of their formation. Most of the determined intermediates were identified in other AOPs showing insignificant difference with the mechanism of those.

4. The energy efficiency of PCD oxidation was found to exceed that of sonochemical methods by more than two orders of magnitude. The energy efficiency of PCD treatment at tested 20 mg L^{-1} concentration was found close to the one of ozonation at the alachlor five-fold higher concentration. Dielectric barrier discharge showed energy efficiency at least 15 times lower than PCD.

KOKKUVÕTE

Käesolevas töös uuriti herbitsiidi alakloor lagundamist koroona impulsslahenduse abil. Töö uudsuseks on hiljuti välja töötatud veepuhastusmeetod, mille energiaefektiivsus ületab teisi süvaoksüdatsiooniprotsesse alakloori lagundamise näitel. Töö eesmärgiks oli uurida PCD oksüdatsioonivõimet, arvutada välja energiaefektiivsused ja võrrelda saadud tulemusi teiste tuntud ja laialt kasutatavate veepuhastustehnoloogiatega. Eraldi eesmärgiks oli lagunemisproduktide identifitseerimine. Eksperimentaalsete andmete põhjal tehti järgmised järeldused:

1. Oksüdatsiooni efektiivsuste erinevus kahel erineval sagedusel kinnitas •OH domineerivat rolli alakloori lagunemisel. Samuti näitas see pikema töötlemisaja jooksul osooni rolli oksüdeerimisel, otsesel või kaudsel ehk OH-radikaalide abil. Sageduse tõstmine suurendab oksüdatsiooni kiirust.

2. Bikarbonaadid käituvad hüdroksüülradikaalide püüdjana, vähendades märgatavalt oksüdatsiooni efektiivsust. Lisaks tõstavad bikarbonaadid reaktsioonisegus elektrijuhtivust, kuid oomilised kaod on tühised ning ei mõjuta märkimisväärselt efektiivsust.

3. Kromatogrammide ja mass-spektride analüüsi käigus leiti reaktsioonisegus mitmeid lagunemisprodukte. Nendest kümme identifitseeriti ning pakuti välja nende võimalik tekkeviis.

4. Leitud oksüdatsiooni energiaefektiivsus oli PCD korral sada korda suurem võrreldes meetoditega, mis põhinevad ultrahelil. Kahjuks ei leitud kirjandusest uuringuid, mis käsitleks alakloori lagundamist süvaoksüdatsiooniprotsessidega samal algkontsentatsioonil. Seetõttu, ei saa järeldada mis tehnoloogia on efektiivsem. Sellest hoolimata on koroona impulsslahendus perspektiivne meetod, mis andis tulemuseks praktiliselt samaväärse efektiivsuse kui osoneerimine viis korda suurema herbitsiidi algkontsentratsiooni korral. Võrreldes antud meetodit dielektrik-barjäärlahendusega, võib kindlusega öelda, et koroona impulsslahendus on soodsam ja majanduslikult otstarbekam tehnoloogia.

5. Identifitseeritud lagunemisprodukte võrreldi teistes uuringutes leitud produktidega. Selgus, et suurem osa teistes süvaoksüdatsiooniprotsessides määratud produktidest leidusid ka antud reaktsioonisegus. Seega pole reaksioonisegud peale töötlemist unikaalsed ning nende erinevus ei ole märkimisväärne.

LIST OF REFERENCES

[1] Ikehata, K., El-Din, M. G. Aqueous Pesticide Degradation by Ozonation and Ozone-Based Advanced Oxidation Processes: A Review (Part I). – *Ozone: Science & Engineering: The Journal of the International Ozone Association*, 2005, 27 (2), 83-114. [*Online*] Taylor & Francis Online (08.02.2020)

[2] Kumar, N. K. H., Jagannath, S. Cytological effects of herbicide alachlor in somatic cells of maize (*Zea mays* L.) and soybean (*Glycine max* Merrill.). – *Biocatalysis and Agricultural Biotechnology*, 2020, 24, 101560. [*Online*] ScienceDirect (17.03.2020)

[3] Badriyha, B. N., Ravindran, V., Den, W., Pirbazari, M. Bioadsorber efficiency, design, and performance forecasting for alachlor removal. – *Water Research*, 2003, 37 (17), 4051-4072. [*Online*] Europe PubMed Central (08.02.2020)

[4] Marican, A., Durán-Lara, E. F. A review on pesticide removal through different processes. – *Environmental Science and Pollution Research*, 2017, 25, 2051-2064. [*Online*] Springer (08.02.2020)

[5] Pipi, A. R. F., De Andrade, A. R., Brillas, E., Sirés, I. Total removal of alachlor from water by electrochemical processes. – *Separation and Purification Technology*, 2014, 132, 674-683. [*Online*] ScienceDirect (08.02.2020)

[6] Qiang, Z., Liu, C., Dong, B., Zhang, Y. Degradation mechanism of alachlor during direct ozonation and O_3/H_2O_2 advanced oxidation process. – *Chemosphere*, 2010, 78, 517-526. [*Online*] ScienceDirect (11.11.2019)

[7] Babu, D. S., Srivastava, V., Nidheesh, P. V., Kumar, M. S. Detoxification of water and wastewater by advanced oxidation processes. – *Science of the Total Environment*, 2019, 696, 133961. [*Online*] ScienceDirect (18.02.2020)

[8] Piai, L., Blokland, M., van der Wal, A., Langenhoff, A. Biodegradation and adsorption of micropollutants by biological activated carbon from a drinking water production plant. – *Journal of Hazardous Materials*, 2020, 388, 122028. [*Online*] ScienceDirect (16.02.2020)

[9] Tosun, J., Schaub, S., Fleig, A. What determines regulatory preferences? Insights from micropollutants in surface waters. – *Environmental Science and Policy*, 2020, 106, 136-144. [*Online*] ScienceDirect (17.03.2020)

[10] Liu, J., Lu, G., Yang, H., Dang, T., Yan, Z. Ecological impact assessment of 110 micropollutants in the Yarlung Tsangpo River on the Tibetan Plateau. – *Journal of Environmental Management*, 2020, 262, 110291. [*Online*] ScienceDirect (16.03.2020)

[11] Ahmad, J., Naeem, S., Ahmad, M., Usman, A. R. A., Al-Wabel, M. I. A critical review on organic micropollutants contamination in wastewater and removal through carbon nanotubes. – *Journal of Environmental Management*, 2019, 246, 214-228. [*Online*] ScienceDirect (19.03.2020)

[12] Rosenfeld, P. E., Feng, L. G. H. Chapter 11 – Pesticides. – *Risks of Hazardous Wastes*, 2011, 127-154. [*Online*] ScienceDirect (08.02.2020)

[13] Gupta, P. K. Chapter 24 – Herbicides and fungicides. – *Biomarkers in Toxicology*, 2014, 409-431. [*Online*] ScienceDirect (01.05.2020)

[14] Acquavella, J. F., Delzell, E., Cheng, H., Lynch, C. F., Johnson, G. Mortality and cancer incidence among alachlor manufacturing workers 1968–

99. – *Occupational and Environmental Medicine*, 2004, 61 (8), 680-685. [*Online*] Europe PubMed Central (01.05.2020)

[15] Wang, Q., Shao, Y., Gao, N., Chu, W., Deng, J., Shen, X., Lu, X., Zhu, Y., Wei, X. Degradation of alachlor with zero-valent iron activating persulfate oxidation. – *Journal of the Taiwan Institute of Chemical Engineers*, 2016, 63, 379-385. [*Online*] ScienceDirect (11.11.2019)

[16] Bagal, M. V., Gogate, P. R. Sonochemical degradation of alachlor in the presence of process intensifying additives. – *Separation and Purification Technology*, 2012, 90, 92-100. [*Online*] ScienceDirect (11.11.2019)

[17] Wang, C., Liu, C. Decontamination of alachlor herbicide wastewater by a continuous dosing mode ultrasound/Fe^{2+}/H_2O_2 process. – *Journal of Environmental Sciences*, 2014, 26, 1332-1339. [*Online*] ScienceDirect (11.11.2019)

[18] Cave, M., Falkner, K. C., McClain, C. Chapter 27 – Occupational and Environmental Hepatotoxicity. – *Zakim and Boyer's Hepatology (Sixth Edition)*, 2012, 476-492. [*Online*] ScienceDirect (02.05.2020)

[19] Wardenier, N., Gorbanev, Y., Van Moer, I., Nikiforov, A., Van Hulle, S. W. H., Surmont, P., Lynen, F., Leys, C., Bogaerts, A., Vanraes. P. Removal of alachlor in water by non-thermal plasma: Reactive species and pathways in batch and continuous process. – *Water Research*, 2019, 161, 549-559. [*Online*] ScienceDirect (07.02.2020)

[20] Li, H.-Y., Qu, J.-H., Liu, H.-J. Decomposition of alachlor by ozonation and its mechanism. – *Journal of Environmental Sciences*, 2007, 19, 769-775. [*Online*] ScienceDirect (12.01.2020)

[21] Li, H., Huang, Y., Cui, S. Removal of alachlor from water by catalyzed ozonation on Cu/Al_2O_3 honeycomb. – *Chemistry Central Journal*, 2013, 7 (1), 143. [*Online*] ResearchGate (12.01.2020)

[22] Bolobajev, J., Trapido, M., Goi, A. Improvement in iron activation ability of alachlor Fenton-like oxidation by ascorbic acid. – *Chemical Engineering Journal*, 2015, 281, 566-574. [*Online*] ScienceDirect (16.02.2020)

[23] Wang, J., Chen, H. Catalytic ozonation for water and wastewater treatment: Recent advances and perspective. – *Science of the Total Environment*, 2020, 704, 135249. [*Online*] ScienceDirect (24.03.2020)

[24] Umar, M., Roddick, F., Fan, L., Aziz, H. A. Application of ozone for the removal of bisphenol A from water and wastewater – A review. – *Chemosphere*, 2013, 90, 2197-2207. [*Online*] ScienceDirect (24.03.2020)

[25] Ma, S., Kim, K., Chun, S., Moon, S. Y., Hong, Y. Plasma-assisted advanced oxidation process by a multi-hole dielectric barrier discharge in water and its application to wastewater treatment. – *Chemosphere*, 2020, 243, 125377. [*Online*] ScienceDirect (15.03.2020)

[26] Wang, J., Wang, Z., Vieira, C. L. Z., Wolfson, J. M., Pingtian, G., Huang, S. Review on the treatment of organic pollutants in water by ultrasonic technology. – *Ultrasonics – Sonochemistry*, 2019, 55, 273-278. [*Online*] ScienceDirect (01.05.2020)

[27] Chaplin, B. P. Chapter 17 – Advantages, Disadvantages, and Future Challenges of the Use of Electrochemical Technologies for Water and Wastewater Treatment. – *Electrochemical Water and Wastewater Treatment*, 2018, 451-494. [*Online*] ScienceDirect (02.05.2020)

[28] Ma, F., Zhu, Y., Wu, B., Zhang, Q., Xu, D., Xu, J., Wang, B., Gu, Q., Li, F. Degradation of DDTs in thermal desorption off-gas by pulsed corona discharge plasma. – *Chemosphere*, 2019, 233, 913-919. [*Online*] ScienceDirect (15.03.2020)

[29] Ajo, P., Kornev, I., Preis, S. Pulsed Corona Discharge Induced Hydroxyl Radical Transfer Through the Gas-Liquid Interface. – *Scientific Reports*, 2017, 7(1), 16152. [*Online*] ResearchGate (03.03.2020)

[30] Wang, Y.-X., Kornev, I., Wei, C.-H., Preis, S. Surfactant and non-surfactant radical scavengers in aqueous reactions induced by pulsed corona discharge treatment. – *Journal of Electrostatics*, 2019, 98, 82-86. [*Online*] ScienceDirect (01.03.2020)

[31] Method and device for a liquid purifying and use of device. Authors: Preis, S., Kornev, I., Hatakka, H., Kallas, J., Yavorovskiy, N. Patent of Finland No. 125772, priority date May 23, 2013, issued February 15, 2016

[32] Pokryvailo, A., Wolf, M., Yankelevich, Y., Wald, S., Grabowski, L. R., van Veldhuizen E. M., Rutgers, W. R., Reiser, M., Glocker, B., Eckhardt, T., Kempenaers, P., Welleman, A. High-Power Pulsed Corona for Treatment of Pollutants in Heterogeneous Media. – *IEEE Transactions on Plasma Science*, 2006, 34 (5), 1731-1743. [*Online*] ResearchGate (12.04.2020)

[33] Tikker, P., Kornev, I., Preis, S. Oxidation energy efficiency in water treatment with gas-phase pulsed corona discharge as a function of spray density. – *Journal of Electrostatics*, 2020, 106, 103466. [*Online*] ScienceDirect (08.05.2020)

[34] Kornev, I., Saprykin, F., Preis, S. Stability and energy efficiency of pulsed corona discharge in treatment of dispersed high-conductivity aqueous solutions. – *Journal of Electrostatics*, 2017, 89, 42-50. [*Online*] ScienceDirect (03.03.2020)

[35] Preis, S., Panorel, I. C., Kornev, I., Hatakka, H., Kallas, J. Pulsed corona discharge: the role of ozone and hydroxyl radical in aqueous pollutants oxidation. – *Water Science & Technology*, 2013, 68 (7), 1536-1542. [*Online*] ResearchGate (03.03.2020)

[36] Preis, S., Panorel, I. C., Llauger Coll, S., Kornev, I. Formation of nitrates in aqueous solutions treated with pulsed corona discharge: the impact of organic pollutants. – *Ozone: Science and Engineering*, 2014, 36 (1), 94-99. [*Online*] ResearchGate (03.03.2020)

[37] Hoigné, J., Bader, H. Rate constants of reactions of ozone with organic and inorganic compounds in water—II: Dissociating organic compounds. – *Water Research*, 1983, 17 (2), 185–194. [*Online*] ScienceDirect (20.05.2020)

[38] Acero, J. L., von Gunten, U. Influence of Carbonate on the Ozone/Hydrogen Peroxide Based Advanced Oxidation Process for Drinking Water Treatment. – *Ozone: Science & Engineering*, 2000, 22 (3), 305-328. [*Online*] Taylor & Francis Onlone (20.05.2020)

[39] Onga, L., Kornev, I., Preis, S. Oxidation of reactive azo-dyes with pulsed corona discharge: Surface reaction enhancement. – *Journal of Electrostatics*, 2020, 103, 103420. [*Online*] ScienceDirect (16.02.2020)

[40] Katsoyiannis, I. A., Canonica, S., von Gunten, U. Efficiency and energy requirements for the transformation of organic micropollutants by ozone,

O_3/H_2O_2 and UV/H_2O_2. – *Water Research*, 2011, 45 (13), 3811-3822. [*Online*] ScienceDirect (01.05.2020)

[41] Krichevskaya, M., Klauson, D., Portjanskaja, E., Preis, S. The Cost Evaluation of Advanced Oxidation Processes in Laboratory and Pilot-Scale Experiments. – *Ozone: Science & Engineering*, 2011, 33 (3), 211-223. [*Online*] Taylor & Francis Onlone (01.05.2020)

[42] Beltrán, F. J., Gonsález, M., Rivas, F. J., Acedo, B. Determination of Kinetic Parameters of Ozone during Oxidations of Alachlor in Water. – *Water Environment Research*, 2000, 72 (6), 689-697. [*Online*] ResearchGate (12.01.2020)

[43] Qu, J., Li, H., Liu, H., He, H. Ozonation of alachlor catalyzed by Cu/Al_2O_3 in water. – *Catalysis Today*, 2004, 90, 291-296. [*Online*] ScienceDirect (01.05.2020)

[44] Liu, Z., Yang, Y., Shao, C., Ji, Z., Wang, Q., Wans, S., Guo, Y., Demeestere, K., Hulle, S. V. Ozonation of trace organic compounds in different municipal and industrial wastewaters: Kinetic-based prediction of removal efficiency and ozone dose requirements. – *Chemical Engineering Journal*, 2020, 387, 123405. [*Online*] ScienceDirect (09.02.2020)

[45] Kornev, I., Preis, S. Aqueous Benzene Oxidation in Low-Temperature Plasma of Pulsed Corona Discharge. – *Journal of Advanced Oxidation Technologies*, 2016, 19 (2), 284-289. [*Online*] ResearchGate (21.05.2020)

[46] Preis, S., Klauson, D., Gregor, A. Potential of electric discharge plasma methods in abatement of volatile organic compounds originating from the food industry. – *Journal of Environmental Management*, 2013, 114, 125-138. [*Online*] ScienceDirect (21.05.2020)