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**Combination of Advanced Oxidation
Methods for the Energy-Efficient
Abatement of Aqueous and Gaseous
Hazardous Pollutants**

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**Süvaoksüdatsiooniprotsesside
kombineerimine ohtlike saasteainete
energiatõhusaks lagundamiseks vees ja õhus**

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Contents

_Toc76409893List of Publications	6
Author's Contribution to the Publications	7
Introduction	8
Abbreviations	10
1 Literature Overview	11
1.1 Ozonation	11
1.1.1 Enhanced Ozonation with Hydrogen Peroxide	14
1.2 Pulsed Corona Discharge Plasma Treatment.....	14
1.3 Photocatalytic Oxidation	17
1.4 Pollutants Under Consideration	19
1.5 Aim of the Study	20
2 Materials and Methods.....	22
2.1 Chemicals and Materials.....	22
2.2 Experimental Equipment and Procedure	22
2.2.1 Ozonation.....	22
2.2.2 Gas-Phase Pulsed Corona Discharge.....	23
2.2.3 Gas-Phase Photocatalytic Oxidation	25
2.2.4 Combination of Pulsed Corona Discharge with Photocatalytic Oxidation	26
2.3 Analytical Methods.....	27
2.3.1 Analysis of Aqueous Matrix.....	27
2.3.2 Analysis of Gaseous Matrix	28
3 Results and Discussion	29
3.1 Oxidation Energy Efficiency of Aqueous Pollutants by Ozonation and PCD Treatment. Content of Exhaust Air Originating from PCD Equipment	29
3.2 Photocatalytic Treatment of Gaseous Pollutants	33
Conclusions	40
References	41
Acknowledgements.....	47
Abstract.....	48
Lühikokkuvõte.....	50
Appendix 1	53
Appendix 2	62
Appendix 3	81
Curriculum Vitae	95
Elulookirjeldus.....	98

List of Publications

The list of author's publications, on the basis of which the thesis has been prepared:

- I **Kask, M.**; Krichevskaya, M.; Preis, S.; Bolobajev, J. (2021). Oxidation of Aqueous N-Nitrosodiethylamine: Experimental Comparison of Pulsed Corona Discharge with H₂O₂-Assisted Ozonation. *Journal of Environmental Chemical Engineering*, #105102. DOI: 10.1016/j.jece.2021.105102.
- II **Kask, M.**; Bolobajev, J.; Krichevskaya, M. (2020). Gas-Phase Photocatalytic Degradation of Acetone and Toluene, and their Mixture in the Presence of Ozone in Continuous Multi-Section Reactor as Possible Air Post-Treatment for Exhaust from Pulsed Corona Discharge. *Chemical Engineering Journal*, 399, #125815. DOI: 10.1016/j.cej.2020.125815.
- III **Kask, M.**; Krichevskaya, M.; Preis, S.; Bolobajev, J. (2021). Oxidation of Aqueous Toluene by Gas-Phase Pulsed Corona Discharge in Air-Water Mixtures Followed by Photocatalytic Exhaust Air Cleaning. *Catalysts*, 11 (5), #549. DOI: 10.3390/catal11050549.

Author's Contribution to the Publications

Contribution to the papers in this thesis are:

- I The author fulfilled majority of the experiments, supervised the experimental work of a MSc student, interpreted the obtained data, and wrote the paper with the help of co-authors.
- II The author carried out most of the experiments, supervised the experimental work of a MSc student, interpreted the obtained data, and wrote the paper with the help of co-authors. The results were presented by the author at conference "The 6th European Conference on Environmental Applications of Advanced Oxidation Processes"; Portorož, Slovenia, June 26–30, 2019, and at summer school "3rd European Summer School on Environmental Applications of Advanced Oxidation Processes"; Alcoy, Spain, June 3–7, 2019.
- III The author carried out a major part of the experiments, supervised the experimental work a MSc student, interpreted the obtained data, and wrote the paper with the help of co-authors. The author presented the results at the online conference "Athens Conference on Advances in Chemistry"; Athens, Greece, March 10–14, 2021.

Introduction

The presence of hazardous pollutants in the environment has become a great worldwide issue. The population growth has led to extensive production and consumption of goods accompanied by higher quantities of wastewater and air pollution as well as an increasing need for clean potable water. Contaminated water and air, in fact, are also the sources of mankind diseases. To deal with the pollution in water and air, several conventional technologies are in use. These, however, mainly comprise separation techniques like adsorption or membrane processes, e.g., nanofiltration, reverse osmosis, transferring the pollutant from one phase to another without its degradation. A variety of pollutants also demonstrate a refractory character towards bio-oxidation, bringing to front a highly promising application of advanced oxidation processes (AOPs) that are based on the generation and utilisation of reactive oxygen species, principally hydroxyl radicals (HO^\bullet), participating in the formation of harmless end products like H_2O and CO_2 in case of complete mineralisation. Advanced oxidation processes are also effective in disinfection of air and water. In given context, the development of AOP-based technologies deserves a significant attention.

Parameters, that are decisive for the applicability of environmental technologies are energy consumption, installation cost, and ease of operation and maintenance. Ozonation is one of the well-known and commercially available AOP for water treatment, where ozone is synthesised in dielectric barrier discharge (DBD). Though, ozonation has several drawbacks hindering the overall efficacy of the process. For instance, the treatment of water with ozone follows the gas–liquid mass transfer comprising therefore a certain limitation. In addition, *ex situ* synthesis of ozone requires its following transportation into the matrix to be treated and results in higher energy demand compared to electrical discharge process, where the generation of oxidative species occurs *in situ*.

A cost-effective alternative, pulsed corona discharge (PCD), has demonstrated its unequalled energy efficiency in oxidation of aqueous organics because of the more efficient utilisation of *in situ* generated various reactive species, predominantly HO^\bullet and O_3 . However, PCD treatment faces the problem of residual ozone in the exhaust air originating from the setup. Besides, low concentrations of fugitive compounds are also present in the outlet air if volatile organic compounds (VOCs) are treated, therefore requiring additional treatment. Photocatalytic oxidation successfully degrades low concentrations of airborne VOCs as well as ozone at ambient temperature. Photocatalytic reactors with commercial potential operating in continuous mode are under research and development. These reactors are characterised by a fixed area of the photocatalytic surface, while modular reactors allow to steadily increase the photocatalytic surface area by a certain increment and thus are useful for the testing and collection of essential data for the successful application of systems operating in continuous mode.

The thesis was aimed to provide necessary data for the development of cost-effective technologies for the abatement of hazardous organic compounds from water and air. The pollutants under consideration were N-nitrosodiethylamine (NDEA), a water disinfection by-product, known to possess carcinogenic properties, and acetone and toluene, that are VOCs widely used in numerous industries and known to negatively influence the central nervous and respiratory systems. The oxidation kinetics of NDEA as a single pollutant have not been investigated earlier. Toluene and acetone are widely used model water and air pollutants.

The PCD as chemical-free and cost-effective technology was studied for the degradation of NDEA and toluene. In the case of NDEA, the energy efficiency was studied in comparison to traditional ozonation and its combination with H₂O₂. The control parameters were pH, temperature, pulse repetition frequency, the concentration of H₂O₂, and in case of ozonation, O₃ concentration. For the abatement of VOCs and ozone in PCD exhaust air, a unique multi-section photocatalytic reactor, allowing a stepwise increase in the surface coated with a photocatalyst, was used. The reactor was applied for oxidation of toluene, acetone, and their mixture, and O₃ depletion under various operating conditions, including the presence or absence of ozone, variations in initial pollutant concentrations, specific residence time (SRT), and air humidity. The photocatalytic reactor was used in combination with PCD equipment for the post-treatment of the exhaust air containing residual O₃ and toluene at different residence time and SRT. The purpose was to evaluate the feasibility of the combination for the abatement of VOCs in both aqueous and gaseous phases together with O₃ comprising the novelty in research.

The findings made in the study contribute to the possible application of environmentally friendly and energy efficient PCD in water treatment in larger scale as a possible addition or alternative to conventional water treatment technologies, whereas multi-section photocatalytic reactor helps to obtain valuable data for the development of air purifiers working in continuous regime. The novel combination of these technologies contributes to a possible application of the studied approach in closed-loop energy-saving ventilation systems.

Abbreviations

AOP	Advanced oxidation process
DBD	Dielectric barrier discharge
E	Energy efficiency
FTIR	Fourier transform infrared spectroscopy
HPLC	High performance liquid chromatography
NDEA	N-nitrosodiethylamine
PCD	Pulsed corona discharge
PCO	Photocatalytic oxidation
ppm	Parts per million
pps	Pulses per second
RH	Relative humidity
SRT	Specific residence time
VOC	Volatile organic compound

1 Literature Overview

Nowadays, the occurrence of hazardous pollutants in the environment has become a great concern, presenting a detrimental effect on public health. A variety of environmental pollutants are known to be recalcitrant, being only transferred from one medium to another and thus requiring further handling. This concerns conventional treatment processes like bio-oxidation, membrane filtration, coagulation and adsorption (Luo et al., 2014). To deal with this issue, advanced oxidation processes (AOPs) are considered as a viable solution (Gao et al., 2009; Padhye et al., 2010). The target of AOPs is to maximise the generation of one of the most reactive oxidants – hydroxyl radical (HO^\bullet) followed by its utilisation to degrade organic pollutants (Mo et al., 2009 (a)). Oxidation potentials of different oxidants associated with AOPs are depicted in Table 1.

Table 1. Oxidation potential of oxidants associated with AOPs (Wardman, 1989)

Oxidant	Oxidation potential, V
Positively charged hole, h^+ (TiO_2)	3.50
Hydroxyl radical, HO^\bullet	2.80
Atomic oxygen, O^\bullet	2.42
Ozone, O_3	2.07
Hydrogen peroxide, H_2O_2	1.78
Perhydroxyl radical, HO_2^\bullet	1.70

The following chapters 1.1–1.3 provide an overview of the studied AOPs, i.e., ozonation and pulsed corona discharge plasma (PCD) for water treatment, and photocatalytic oxidation (PCO) for air treatment. In chapter 1.4, the properties and occurrence of the studied hazardous pollutants under consideration are discussed.

1.1 Ozonation

Ozonation as a commercially available technology has been extensively studied for the abatement of organic pollutants in water and air (Bourgin et al., 2017; Ridgway et al., 2017; Wang et al., 2018; Kang et al., 2020; Restivo et al., 2021). It is commonly used in water treatment technologies as pre- or post-treatment, mainly to improve taste and odour, and to remove organic and inorganic matter from wastewater (Hoigné, 1998; Kasprzyk-Hordern et al., 2003; Gottschalk et al., 2010). However, due to its selectivity, it is an inefficient method for complete mineralisation of organic substances (Giri et al., 2007). Besides, the high reactivity of O_3 makes it a very unstable gas (Masschelein, 1992) with half-life values varying from seconds to hours dependent on several parameters, e.g., character of medium and temperature. The higher the temperature is, the faster the decomposition of ozone occurs (Ono and Oda, 2003).

For the generation of ozone, a dielectric barrier discharge (DBD) is usually applied. In traditional ozone generators, cylindrical Pyrex (Duran) glass tubes, sometimes also ceramic ones, are mounted inside stainless-steel tubes, high voltage and ground electrodes, with a diameter in the range of 20–50 mm in order to form annular discharge gaps 0.5–1 mm in width. Aluminium films, possessing conductive properties to avoid the creation of thermal plasmas like arc or spark, are connected along with a brush-shaped electrode inside the glass tubes to the high-voltage supply operating the standard

frequency in mains or deriving electricity from a generator. High-performance ozone generators nowadays employ non-glass dielectrics and the voltage derived from a high-frequency switch source (0.5–5 kHz) generating, for instance, a square-wave current. Higher operating frequencies deliver the desired density of power at much lower operating voltages, less than 5 kV in comparison to the typical 20 kV in the past, thus the discharge gap is narrower as a result of lower electrical stress on the dielectrics. Ozone production using DBD ranges from few $\text{mg}\cdot\text{h}^{-1}$ to $\text{kg}\cdot\text{h}^{-1}$. Several hundred discharge tubes are aggregated in large ozone generators (Kogelschatz, 2003; Chu and Lu, 2013). Figure 1 illustrates the ozone generation with DBD.

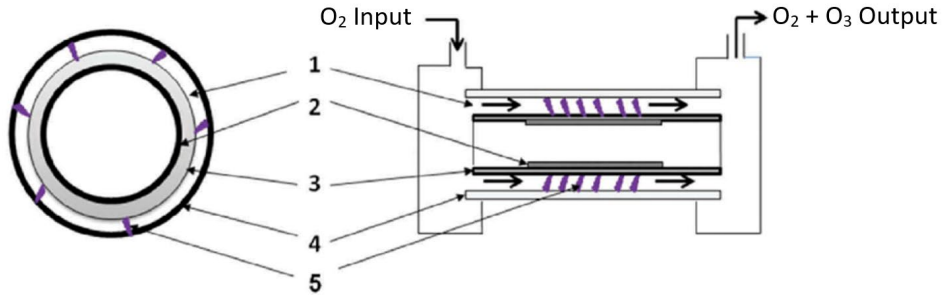


Figure 1. Ozone generation by means of DBD: 1 – discharge gap; 2 – high voltage electrode; 3 – glass tube; 4 – grounded electrode; 5 – plasma (Bechekir et al., 2019)

In DBD ozone generators, oxygen (O_2) is converted to O_3 via two-step reaction. The first step comprises the dissociation of O_2 by electron impact (Eqs. 1–3). If ozone is generated from air, reactions involving N^* and N_2 occur (Eqs. 4–6). The second step is the reaction of atomic oxygen (O^*) with molecular oxygen (Eq. 7) in the presence of a third body (M), i.e., O_2 , N_2 (Magureanu et al., 2013; Magureanu et al., 2018).



High concentration of atomic nitrogen and nitrogen oxide, however, may quench oxygen atoms and assist ozone depletion, whereas O^* high concentration results in dominating recombination into oxygen molecule (Lukes et al., 2005).

Ozonation itself is a pH-sensitive process that involves two types of oxidation reactions, direct and indirect (Gottschalk et al., 2010). Indirect reactions involve the utilisation of short-living HO^* with a lifetime of ca. $0.02 \mu\text{s}$ in water (Ghanbari and Moradi, 2017) and ca. $200 \mu\text{s}$ in air (Magureanu et al., 2013) and proceed mainly at pH over 10 due to the abundance of hydroxide ions (HO^-), which favour the formation of HO^* from ozone. Direct reactions, on the contrary, occur in acidic media at pH lower than 3 by supporting the direct reactions between O_3 and the pollutant, whereas both pathways, direct and indirect, are present at pH range of 3–10 (Kasprzyk-Hordern, 2003). It is

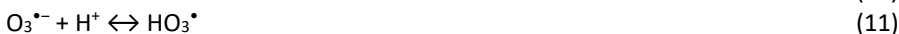
noteworthy that ozonation is considered as AOP only when radical mechanism is dominating.

Molecular O₃ reacts readily via direct reactions with electron-rich moieties in aromatic and aliphatic compounds, i.e., unsaturated bonds, also amino and hydroxyl groups, whereas HO• are significantly less selective, and interact through indirect pathway with most of the organics, by attacking the pollutant normally by abstracting the hydrogen atom or, in the case of unsaturated molecules, by adding to the double bond (Hernandez et al., 2002). The rate constants for ozone and HO•-based reactions are typically in the range of 1.0–10⁶ M⁻¹ s⁻¹ and 10⁸–10¹⁰ M⁻¹ s⁻¹, respectively, thus, indicating that HO•-based reactions present a method of choice in the abatement of ozone-resistant compounds (Gottschalk et al., 2010).

The generation of non-selective HO• through the chain reaction of O₃, that is transported from the ozone generator into the treatment solution and is introduced to water, includes initiation, propagation, and termination reactions. The initiation comprises the reaction between ozone and HO⁻ leading to the formation of superoxide anion (O₂^{•-}) and hydroperoxyl radical (HO₂[•]) (Eq. 8), of which the latter is in acid-base equilibrium with the O₂^{•-} (Eq. 9) (Gottschalk et al., 2010).



In the propagation stage, the O₂^{•-} reacts with ozone forming an ozonide anion (O₃^{•-}), that promptly decomposes through hydrogen trioxide (HO₃[•]) to HO• (Eq. 10–12). HO• reacts with ozone by generating HO₄[•] (Eq. 13), which decay into HO₂[•] and O₂ (Eq. 14) may re-initiate the chain reactions (Eq. 9 and 10) (Gottschalk et al., 2010).



Although HO• possess a great effect on oxidation of pollutants, their overly high presence in the treated matrix may result in a termination reaction, caused by inefficient self-consumption of radical species (Eq. 15) (Gottschalk et al., 2010).



It is known that gaseous O₃ is sparingly soluble in water (Masschelein, 1992), therefore, its low transfer to aqueous phase clearly affects the oxidation efficiency of some refractory pollutants. To avoid mass transfer limitations and to amplify the mineralisation in ozonation, more extensive decomposition of O₃ with the generation of a vast number of radical species is a desired outcome (de Luis and Lombraña, 2018). As the increase in pH in the treatment solution for such purpose might be costly for radical scavenging by bicarbonates and carbonates accumulated in alkaline solutions (von Gunten, 2003), the addition of hydrogen peroxide serves as a cheaper alternative (de Luis and Lombraña, 2018).

1.1.1 Enhanced Ozonation with Hydrogen Peroxide

The abatement of refractory pollutants could be enhanced with the addition of H₂O₂ into O₃-treated solutions, commercially known as peroxone, for accelerated HO[•] production (von Gunten, 2003; Gottschalk et al., 2010). In addition to the lower cost mentioned above, the high solubility of H₂O₂ in aqueous phase guarantees its simple application (de Luis and Lombraña, 2018). Another advantage of H₂O₂/O₃ system is its non-dependence on the UV transmissivity as is O₃/UV combination, allowing its application also in turbid waters. The reaction of undissociated H₂O₂ with ozone (Eq. 16) is considered negligible, reacting with O₃ predominantly in the form of HO₂⁻ (Eq. 17 and 18) (Gottschalk et al., 2010).



Produced HO₂[•] enters the chain reaction (Eqs. 9–14) to generate HO[•]. Combining the Eqs. 9–14, 16, and 18 gives a net reaction (Eq. 19) as follows (Gottschalk et al., 2010):



The essential factors for the successful progression of the peroxone process are pH, temperature, and the addition of H₂O₂ in appropriate concentration at the right moment into the reactive system (Hernandez et al., 2002; de Luis and Lombraña, 2018). As could be seen from Eq. 19, the molar ratio between O₃ and H₂O₂ is 2:1, which is also considered as an optimum in many applications (Glaze et al., 1987). In fact, the suitable ratio is of particular importance, since H₂O₂ may also act as a scavenger at high concentrations resulting in utilisation of HO[•] (Eq. 20) (Hernandez et al., 2002).



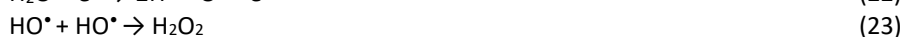
The application of ozone in oxidation of organic pollutants, however, is generally costly due to its *ex situ* production that requires the transportation of relatively long-living ozone into the treatment solution as well as short-living HO[•], which survival is unlikely, thus resulting in higher demand for energy. Another feature that adds to the expenses is the necessity of using dry gases, air or oxygen, for the generation of ozone without a chance for, e.g., humid oxygen reuse. Costly synthesis and application of ozone hinder its implementation in water treatment, dictating the search for cost-effective alternatives (Krichevskaya et al., 2011). One of the promising AOPs, which provides efficient utilisation of various oxidants, for instance HO[•], O₃, H₂O₂, NO[•], atomic oxygen, superoxide anion, generated *in situ* in treatment devices is the application of nonthermal plasma of pulsed corona discharge.

1.2 Pulsed Corona Discharge Plasma Treatment

Corona discharge (CD) occurs near a pin or a thin wire, where an electric field is significantly enhanced, thus ionisation and emission are localised around the pin or wire. Corona discharge is also known as partial discharge since it normally does not extend up to the counter electrode. It can be operated with pulsed voltage or continuous voltage (direct current corona). Pulsed corona is produced by applying ultra-short, generally

sub-microsecond, voltage pulses to an electrode. Such short pulse duration avoids the transition to spark that may damage the electrodes and thus pulsed corona may be used at voltages and currents higher than that of continuous corona. Higher voltages magnify the electric field and cause the increased temperature of electrons resulting in accelerated ionisation and dissociation. From this, pulsed corona is favoured over continuous discharge in environmental applications (Chu and Lu, 2013; Magureanu et al., 2013).

Plasma consists of electrons or negative ions, positive ions, and neutral particles, and can be classified in several ways, for example, based on the thermodynamic equilibrium. Plasma generated in the gas-phase pulsed corona discharge is classified as nonthermal plasma. The main oxidative species formed in nonthermal plasma at atmospheric pressure are HO[•], O₃, H₂O₂, NO[•], atomic oxygen, superoxide anion, but also excited molecules and atoms, negative and positive ions, and free electrons, which formation and abundance depend on the type of plasma source (Schneider et al., 2020). Generally, the dominating ones in pulsed corona discharge are O₃ and HO[•]. All reactive species are mainly formed in the gas-liquid interface, where short-living oxidants generated in the discharge react with pollutants in the boundary layer of water or at close vicinity of gas-liquid interface (Ajo et al., 2017). From the mentioned oxidative species formed by electric discharge, the generation of O₃ and NO[•] was illustrated with Eqs. 1–7 in the previous chapter. Formation of hydroxyl radicals and atomic oxygen in plasma reactions mainly occur via water dissociation in gaseous phase caused by electron impact. The HO[•] recombination leads to the formation of H₂O₂ (Eqs. 21–23) (Lukes et al., 2005; Magureanu et al., 2013).



Electric discharge generation in air causes the formation of nitrogen-containing species, e.g., NO[•] and NO₂[•], which contribute to the decrease in pH while in contact with water, resulting in the formation of nitrous and nitric acids in plasma-treated solutions (Eqs. 24–26). In acidic environment, the peroxyxynitrous acid (O=N-OOH), and in alkaline and neutral media, the formation of peroxyxynitrite (O=N-OO⁻), are also present, of which the anionic and protonated forms of peroxyxynitrite could be directly or indirectly involved in oxidation of the pollutant (Kornev et al., 2013; Magureanu et al., 2013).



In addition to the production of highly reactive radical species and molecules, UV emission that can participate in oxygen, water, and H₂O₂ dissociation, or initiate reverse reactions of NO_x to produce O[•] and subsequently O₃ (Eqs. 27–31), is also generated in electric discharge plasma. Its intensity and wavelength range depend on various parameters, e.g., plasma type and gas composition (Magureanu et al., 2013).



Corona discharges are classified in several different forms depending on the field polarity and electrode configuration. Depending on the pin/wire electrode, either it is anode or cathode, corona is positive or negative. Regarding the electrode configuration, the commonly used design of laboratory scale CD setup is a pin-to-plate electrode pair (Figure 2a), where a needle is placed above the grounded plate and a high voltage pulse is applied to the needle electrode. Such design, however, is suitable only for laboratory studies since its industrial application is energy consuming as the discharge is not spread throughout the whole gaseous volume of the reactor. For the large-scale application in industry, wire-cylinder (Figure 2b) and wire-plate (Figure 2c), especially the first one, are used. Wire-cylinder provides rather homogenous discharge distribution and is simple to implement in a gas-flow system. To enable high gas throughput, multiple wire-cylinder reactors are positioned in parallel (Magureanu et al., 2013).

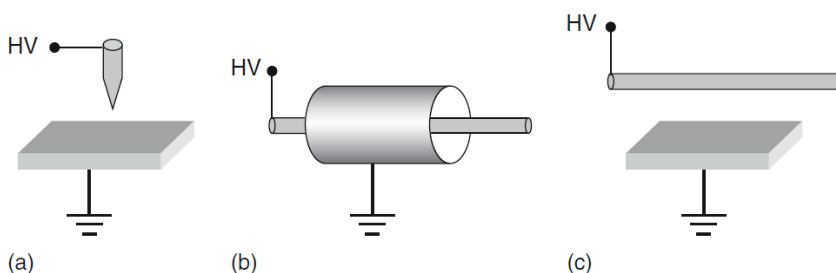


Figure 2. Geometries of corona discharges: a – pin-to-plate; b – wire-cylinder; c – wire-plain. HV – high voltage (Magureanu et al., 2013)

Among the advantages of PCD reactors, the simplicity in design and insensitivity towards gas humidity are important. Moreover, the reactor comprises a closed compartment where the oxidation of the pollutant occurs without a need for ozone synthesis and transport as in the case of ozonation (Preis et al., 2013 (a)). In addition, the system is operated at ambient temperature and pressure and does not need the addition of chemicals (Ajo et al., 2015). In gas-phase PCD, water is sprayed into plasma zone in water droplets and jets, thereby increasing the contact surface of plasma and water. This approach has demonstrated the highest efficiency in comparison to all nonthermal plasma types (Malik, 2010; Kornev et al., 2017).

However, one of the main limitations of PCD in the oxidation of aqueous pollutants is the lack of reliable pulse generators, thus also impeding the widespread use of PCD for commercial purposes since the uncertain operating of the pulse generator may cause the high-temperature spark in the setup (Preis et al., 2013 (b)). Energy transfer efficiency from pulse generator to the reactor is, additionally to the electrode configuration and droplet size, another important feature that affects the stability of the gas-phase PCD. An inappropriate inter-electrode distance may lead to decreasing discharge energy, poor matching of the PCD with generator, and higher residual voltage at the electrodes remaining for a longer time, therefore indicating the inter-electrode distance as a trade-off

between the energy transfer efficiency and spark formation in short inter-electrode gaps. To avoid the spark discharge in the reactor, the installation of a saturating inductor serves as a good solution, contributing to the decrease in voltage pulse duration (Kornev et al., 2017). Another drawback is that nonthermal PCD plasma technology for the treatment of both gaseous and aqueous pollutants may emit low concentrations of certain VOCs, including residual initial compounds, and certain amounts of ozone in the exhaust, therefore requiring post-treatment. However, a combination of PCD treatment with downstream photocatalytic utilization and destruction of ozone along with degradation of VOCs presents a method of choice.

1.3 Photocatalytic Oxidation

Photocatalytic oxidation (PCO) is an AOP in which pollutants react predominantly with reactive oxygen species formed through the activation of a semiconductor catalyst by light photons with appropriate wavelength with the subsequent conversion of organics into H₂O and CO₂ in the case of mineralisation. Photocatalytic oxidation is a promising technology to handle very low concentrations of pollutants at parts per billion (ppb) or parts per million (ppm) levels, which are representative loadings of pollutants in offices and buildings (Boyjoo et al., 2017). The process can be operated at room temperature and under atmospheric pressure, making it suitable for integration in existing heating, ventilation, and air conditioning (HVAC) (Costarramone et al., 2015; Boyjoo et al., 2017). It is a nonselective process with high activity towards various pollutants.

The photocatalytic mechanism on the surface of titanium dioxide (TiO₂), which is the most widely studied catalyst in PCO reactors, is illustrated in Figure 3.

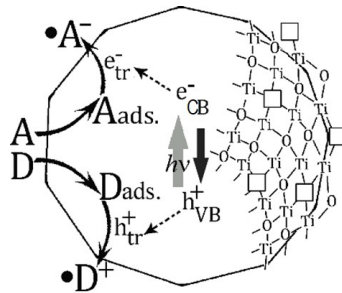
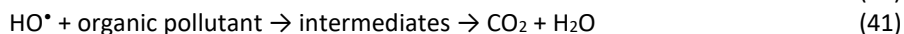
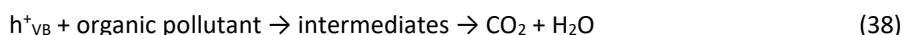


Figure 3. Mechanism of photocatalysis on the surface of TiO₂

The more precise explanation of the mechanism is that the photons reach the surface of the photocatalyst generating highly reactive electron/hole pairs (e⁻/h⁺) by moving the excited electrons from the valence band (h⁺_{VB}) to conduction band (e⁻_{CB}). For excitation, the photon energy (hv) must be equal to or exceeding the band gap energy (E_g) of semiconductor. In heterogeneous photocatalysis, oxygen generally serves as an electron acceptor (A) and H₂O as a donor (D). The photogenerated electrons are distributed on the surface of the catalyst, where they interact with adsorbed organic compounds and oxygen molecules (A_{ads.}). In the latter case, the electrons can generate a superoxide anion (O₂⁻) in a reduction process with adsorbed O₂, which can react with water (D_{ads.}) with subsequent generation of other reactive oxygen species (Eqs. 32–37) (Orellana-Garcia et al., 2016; Ren et al., 2017). It is documented that these trapping (tr) reactions occur in less than 30 ps (Quiroz et al., 2011).



Positive holes (h^+_{VB}) can either directly oxidise the adsorbed organic pollutant resulting in the formation of H_2O and CO_2 in mineralisation or react with water or HO^- by generating HO^{\bullet} . Hydroxyl radicals can non-selectively oxidise organics potentially also leading to mineralisation (Eqs. 38–41) (Orellana-García et al., 2016; Ren et al., 2017).



Concerning the properties of the catalyst, the specific surface area and the abundance of active sites are of high importance (Gogate and Pandit, 2004). In addition, the desirable photocatalyst should be chemically and biologically inert, photoactive and -stable, non-toxic, inexpensive, and applicable under visible and UV radiation (Fujishima et al., 2008). TiO_2 possesses many of the aforementioned characteristics (Gogate and Pandit, 2004; Orellana-García et al., 2016). A high photocatalytic activity is confirmed by wide band gap values of 3.23 and 3.02 eV for anatase and rutile, respectively (Mo et al., 2009 (b); Zhongbia et al., 2008; Irokawa et al., 2006).

For PCO of VOCs like benzene, toluene, acetone, ethanol, acetaldehyde, formaldehyde, and others, continuous reactors have often been used. The photocatalytic reactors for air treatment generally incorporate catalysts immobilised on solid support. Some configurations of simplified photocatalytic reactors are represented in Figure 4. Laboratory scale reactors are commonly coated plate (a) and annular (b) reactors with the catalyst immobilised on the reactor walls. Such reactors, however, are not intended for industrial applications since they are not designed to operate at high flow rates of air but are of utmost importance for kinetics studies. Other reactor configurations such as packed bed (c) and monolith (d) are designed with the purpose to have high catalyst-coated surface area to achieve better performance with the aim of possible commercialisation. Packed bed reactors are of simple construction and may provide high conversion per unit mass of catalyst, yet high radial radiation gradients can occur, and the unit can be difficult to maintain. Monolith reactors are compact and could be easily applied in HVAC systems allowing high throughput and low pressure drop. The main drawback is the quick reduction of light intensity through the monoliths, which could be eliminated, but in a rather challenging way given the small monolith channels' pore size, using individual optical fibres passing through each monolith. Other photocatalytic reactors comprise, for instance, honeycomb, multi-plate, corrugated plate and fluidized bed constructions (Ren et al., 2017; Boyjoo et al., 2017; Zazueta et al., 2013; Passalía et al., 2012).

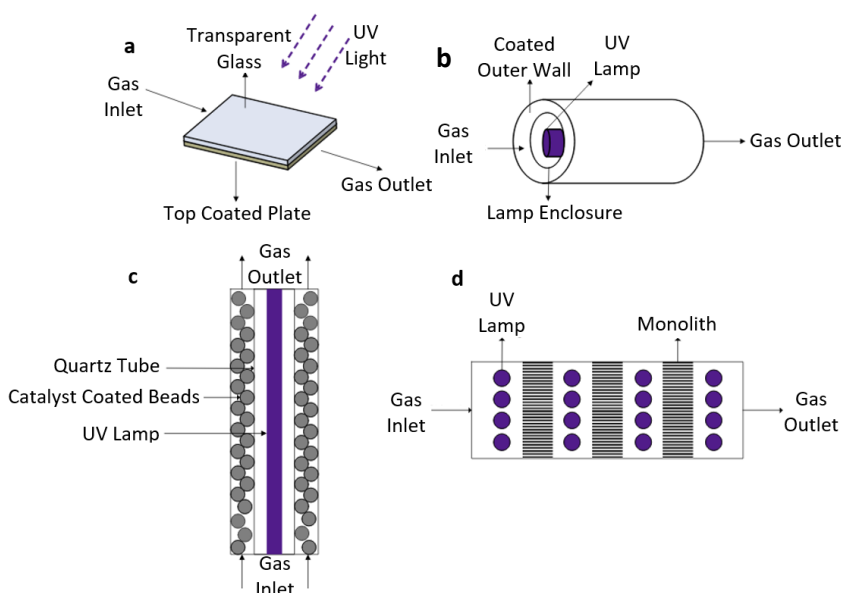


Figure 4. Configurations of gas-phase photocatalytic reactors: a – coated plate; b – annular; c – packed bed; d – monolith (top view) (Boyjoo et al., 2017)

Two main limitations in photocatalytic reactors are the mass and photon transfer. New photocatalytic materials for the absorption of visible light could increase the efficiency of photocatalytic oxidation. Another intensification technique includes a novel configuration of light source, reactor design, and optimal operating conditions. Parameters such as pollutant concentration, light intensity, air flow rate, and relative air humidity affect the rate of photocatalysis (Boyjoo et al., 2017). Photocatalytic decomposition of VOCs generally leads, however, to the formation of intermediates and by-products, which could be more toxic than the initial compound. Hence, the incomplete decomposition of VOCs in oxidation processes is one of the challenges to be faced. Besides, on some occasions, the by-products cause the poisoning of the catalyst requiring regeneration (Orellana-García et al., 2016). Application of ozone may serve as a solution to eliminate this problem, helping to avoid rapid blocking of active sites by degradation intermediates via their heterogeneous reactions with ozone.

1.4 Pollutants Under Consideration

N-nitrosodiethylamine (NDEA) is a water disinfection by-product formed in chlorination or chloramination of potable and waste waters. It is one out of about 300 existing nitrosamines, of which roughly 80-90% are known for their carcinogenic, mutagenic, and teratogenic properties (Xu et al., 2010; Zhou et al., 2012; Mazari et al., 2019). N-nitrosodiethylamine has been linked to the development of gastrointestinal tumours in humans (CSWRCB, 2021), thus having the allowable limit in water established in a few countries. For instance, State of California Department of Public Health and Australian Government have set the NDEA notification level in drinking water at $10 \text{ ng}\cdot\text{L}^{-1}$, and Norwegian Public Health Institute the acceptable limit of $4 \text{ ng}\cdot\text{L}^{-1}$ for NDEA in drinking water (Sørensen et al., 2015; CSWRCB, 2021). Since nitrosamines are known for their

recalcitrance towards conventional water treatment technologies, AOPs are considered as a viable solution (Gao et al., 2009; Padhye et al., 2010).

Toluene and **acetone** are hazardous VOCs present in the environment. Toluene is a hydrophobic aromatic hydrocarbon occurring in industrial wastewaters, originating from paint and coating production, oil refinery, and gas processing with reported concentrations ranging from 0.2 to 12,900 $\mu\text{g}\cdot\text{L}^{-1}$ (Mrowiec, 2014; Cseri et al., 2018; Anjum et al., 2019). Wastewaters subjected to the relevant treatment may still contain residual toluene (Mrowiec, 2014) that can be released to the ambient air, thereby possessing a harmful impact on ecosystems. In places with high traffic density, toluene concentration can reach 1,310 $\mu\text{g}\cdot\text{m}^{-3}$, and in urban air it can range from 5 to 150 $\mu\text{g}\cdot\text{m}^{-3}$ (Schneider et al., 2001; Batterman et al., 2007). Toluene along with acetone may also be detected in the indoor air. The main sources are paintings, tobacco smoke and several household products (Debono et al., 2009; Mo et al., 2009 (b)). Toluene being also a component of gasoline enters the indoor air with vehicle exhausts from outdoors (Batterman et al., 2007). For instance, the indoor concentrations of toluene in winter and summer in Windsor, Canada reached up to 12 and 30 $\mu\text{g}\cdot\text{m}^{-3}$, respectively, whereas in the case of acetone the reported concentrations were accordingly 32 and 137 $\mu\text{g}\cdot\text{m}^{-3}$ (Stocco et al., 2008). Human exposure to toluene and acetone has been reported to affect the central nervous and respiratory systems, also causing skin and eye irritation (Mo et al., 2009 (b); Debono et al., 2009). Toluene and acetone are both also known as model pollutants used to evaluate the efficiency of air purifiers (Costarramone et al., 2015), providing a reasonable basis for the comparison of their abatement with various methods in different matrices.

Ozone, widely used in environmental technologies due to its oxidative properties towards organic pollutants as discussed above, is also a toxic air pollutant. Although it occurs naturally in stratosphere forming a protective layer to avoid harmful effect of UV-light to living organisms, its presence at the ground level may damage respiratory system by aggravating lung diseases such as asthma, chronic bronchitis, and emphysema depending on the level of exposure. Ozone as a pollutant is not emitted directly into the atmosphere but is formed under sunlight via chemical reactions between VOCs and nitrogen oxides (NO_x), originating principally from industries and electric utilities, also from car exhaust. Ozone is also the main ingredient of the photolytic “smog”. Unhealthy levels of ozone are more likely reached on hot sunny days in urban areas; however, high levels can still be detected in colder climates. The existing ambient air quality standards established in 2015 require ozone concentrations to not exceed 0.070 ppm (0.14 $\text{ng}\cdot\text{m}^{-3}$) as averaged across three consecutive years as the fourth-highest daily maximum 8-hour concentration (EPA, 2021). From this, it is obvious that residual ozone originating from water treatment requires further handling and could be utilised as an oxidant in air photocatalytic post-treatment.

1.5 Aim of the Study

The development of novel energy efficient technologies as well as the subsequent improvement of the existing ones for efficient water and air treatment is one of the main goals in environmental technology. Commercially available ozonation is costly, whereas PCD, requiring additional studies and improvements for its large-scale application, is a promising method for the energy efficient oxidation of various hazardous organic compounds. Ozone, an oxidant, and toxic air pollutant present together with VOCs in PCD exhaust air requires post-treatment. Combination of electric discharge treatment

with downstream catalytic utilisation and destruction of ozone along with the degradation of VOCs presents a method of choice since photocatalytic oxidation successfully degrades low concentrations of airborne VOCs at ambient temperature. In addition to organic pollutants, both technologies are lethal to multiple microorganisms in water and air.

This thesis is aimed to provide data necessary for the development of cost-effective technologies for the abatement of hazardous organic compounds from water and air. The objectives of the study include:

- Clarify the PCD energy-efficiency of an unexampled PCD equipment in comparison to commercially used traditional ozonation and its combination with H₂O₂ in aqueous NDEA degradation, the oxidation kinetics of which as a single pollutant have not been studied earlier;
- studying the impact of process control parameters, i.e., initial pollutant concentration, residence time and specific residence time (s·cm⁻²), and humidity, on the degradation of acetone and toluene, and their mixture in the presence and absence of ozone using the unique continuous multi-section photocatalytic reactor with adjusting catalytic surface area for the development of air purification technologies; monitoring the depletion of ozone as toxic air pollutant throughout these experiments;
- evaluating the feasibility of the innovative combination of PCD equipment with photocatalytic reactor for the abatement of toluene in both aqueous and gaseous phases; this objective fills the gap in combined PCD-photocatalytic treatment for the elimination of the VOC in both phases.

The strategic structure of the study is illustrated in Figure 5.

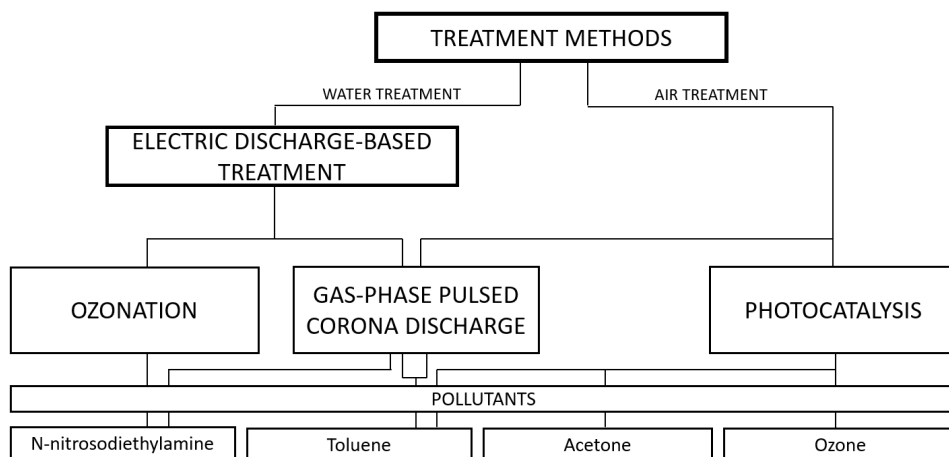


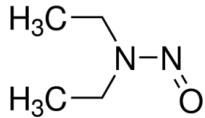
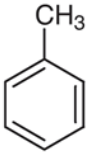
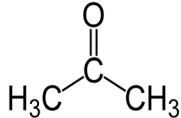
Figure 5. The strategic structure of the study

2 Materials and Methods

2.1 Chemicals and Materials

All used reagents were of analytical grade. Aqueous solutions were prepared using distilled water. Studied organic pollutants – N-nitrosodiethylamine, acetone, and toluene, were purchased from Sigma-Aldrich (Germany). Their chemical structure and physicochemical properties are depicted in Table 2.

Table 2. The properties of N-nitrosodiethylamine, acetone, and toluene

Properties	N-nitrosodiethylamine (NDEA)	Toluene	Acetone
Molecular structure			
Classification	Nitrosamine	Volatile organic compound	Volatile organic compound
CAS nr	55-18-5	108-88-3	67-64-1
Chemical formula	C ₄ H ₁₀ N ₂ O	C ₇ H ₈	C ₃ H ₆ O
Molecular mass, g mol ⁻¹	102.14	92.14	58.08
Solubility in water, g L ⁻¹	106.0 (24 °C)	0.526 (25 °C)	1.0 (25 °C)

2.2 Experimental Equipment and Procedure

2.2.1 Ozonation

Paper I-Experimental Equipment and Procedure

Conventional ozonation was performed in a 600 mL batch glass reactor filled with NDEA solution with initial concentration (C_0) of 10 μM ; ozone-containing air with ozone concentration of 1 or 2 $\text{mg}\cdot\text{L}^{-1}$ was fed to the solution at the flow rate of 2.5 $\text{L}\cdot\text{min}^{-1}$. Flow distribution of O_3 -containing gas is depicted in Figure 6.

Ozonation in acidic (pH 3.0) and neutral (pH 7.0) media were conducted in 50-mM phosphate buffers prepared according to Henderson-Hasselbach equation (Po and Senozan, 2001) ensuring the stability of pH throughout the experiments since preliminary treatment tests showed the decrease in pH, shifting the process towards molecular oxidation. Adjustment of pH 12.0 was provided with the addition of 10 M NaOH solution. In $\text{O}_3/\text{H}_2\text{O}_2$ experiments, hydrogen peroxide with a final concentration of 50 μM in treatment solution, was added into the reactor before the start of ozonation. Residual oxidants in samples were quenched with the addition of sodium sulphite. All experiments were conducted at an ambient temperature of 22 ± 2 °C.

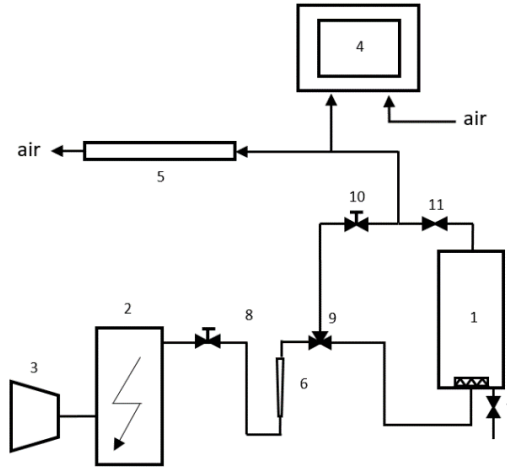


Figure 6. Schematic outline of ozonation gas distribution system: 1 – reactor; 2 – O₃ generator; 3 – compressor; 4 – O₃ monitor; 5 – residual O₃ decomposition column; 6 – rotameter; 7 – sampling port; 11 – gate valve; 8, 10 – gate valves with manual actuator; 9 – 3-way valve

Aqueous ozone was measured by means of colorimetric indigo method (Clesceri et al., 2005) calculating dissolved ozone concentration using Eq. 42:

$$C_{O_3} = \frac{100 \cdot \Delta A}{f \cdot b \cdot V} \quad (42)$$

where C_{O_3} is ozone concentration, mg·L⁻¹, ΔA is the difference between sample and blank absorbance, b is the cell path length, cm, V is the volume of sample, mL, and f is an extinction coefficient with a value of 0.42.

The energy efficiency E , g·kW⁻¹·h⁻¹, was calculated at 50% of NDEA oxidation in ozonation or O₃/H₂O₂ using Eq. 43:

$$E = \frac{\Delta C \cdot V}{t \cdot P + E_{H_2O_2} C_{H_2O_2} V} \quad (43)$$

where ΔC is the decrease of pollutant concentration, g·m⁻³, V is the volume of treated sample, m³, t is the treatment time, h, and P is the power consumed by ozone synthesis, kW, $E_{H_2O_2} C_{H_2O_2} V$ is the energy consumption for H₂O₂, kWh·g H₂O₂⁻¹. The value of power was calculated from the initial concentration of gaseous O₃, mg O₃·L⁻¹, the energy consumed by O₃ synthesis comprising 30 kWh·kg O₃⁻¹, and the flow rate of ozone-containing air, L·min⁻¹ (Katsoyiannis et al., 2011).

2.2.2 Gas-Phase Pulsed Corona Discharge

Paper I and III-Experimental Equipment

The PCD equipment (Flowrox Oy, Finland) (Figure 7) consists of 154 L reactor with 40 L storage tank, pulse generator, and circulation pump (Iwaki Co. Ltd., Japan). The treatment solution was dispersed into the plasma zone through a perforated plate with 51 holes of 1 mm diameter. High voltage pulses (ca 20 kV) were applied between horizontal high voltage electrodes made of stainless-steel wire of 0.55 mm in diameter and total length of 20 m, and two vertical grounded stainless-steel parallel plates.

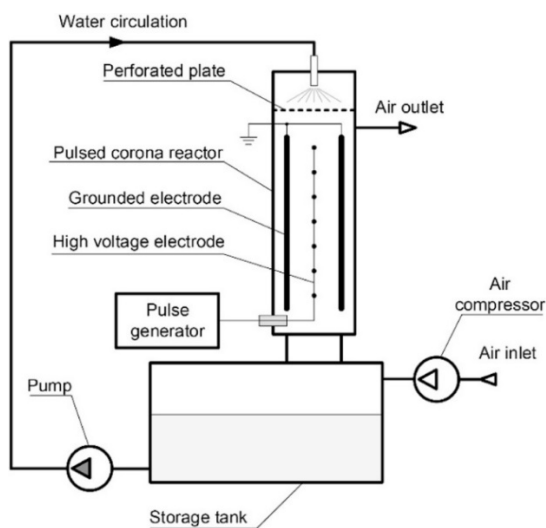


Figure 7. Schematic illustration of PCD device

Paper I-Experimental Procedure

The 10 L aqueous solution sample with initial NDEA concentration of 10 μM was pumped to the distribution box at the top of the plasma reactor and sprayed into the electric discharge zone. The experiment started once the pulse generator was turned on. It applied high voltage pulses with the repetition frequencies of 200 and 880 pulses per second (pps) providing output powers of 32 and 123 W, respectively. For sampling, the generator was turned off and the treated solution was allowed to circulate with a flow rate of 1.0 $\text{m}^3\cdot\text{h}^{-1}$ for four minutes for equalizing the content. The procedure was repeated for each sample collected at incremental time intervals. Alkaline and acidic media were attained by adding either 5 M NaOH or 5 M H_2SO_4 to the NDEA solution, respectively. In PCD/ H_2O_2 experiments, hydrogen peroxide was added into the storage tank filled with the solution before the start of treatment, resulting in an initial concentration of 50 μM . The experiments were carried out at ambient temperature of 22 ± 2 $^\circ\text{C}$.

The energy efficiency E , $\text{g}\cdot\text{kW}^{-1}\cdot\text{h}^{-1}$, was calculated at 50% NDEA oxidation using Eq. 44:

$$E = \frac{\Delta C \cdot V}{W} \quad (44)$$

where ΔC is the decrease in pollutants concentration, $\text{g}\cdot\text{m}^{-3}$, V is the volume of treated sample, m^3 , and W is the consumption of energy, kWh.

Delivered energy, $\text{kWh}\cdot\text{m}^{-3}$ was calculated using Eq. 45:

$$\text{Delivered energy} = \frac{P \cdot t}{V} \quad (45)$$

where P is the power, kW, t is the sampling time, h, and V is the volume of treatment solution, m^3 .

2.2.3 Gas-Phase Photocatalytic Oxidation

Paper II and III-Experimental Equipment

Photocatalytic oxidation was carried out in a multi-section continuous reactor consisting of five sequential sections, each equipped with UVA lamp and TiO₂-coated (P25, Evonik) borosilicate glass plates with the surface area of 120 cm². The schematic illustration of the system with photocatalytic reactor is depicted in Figure 8.

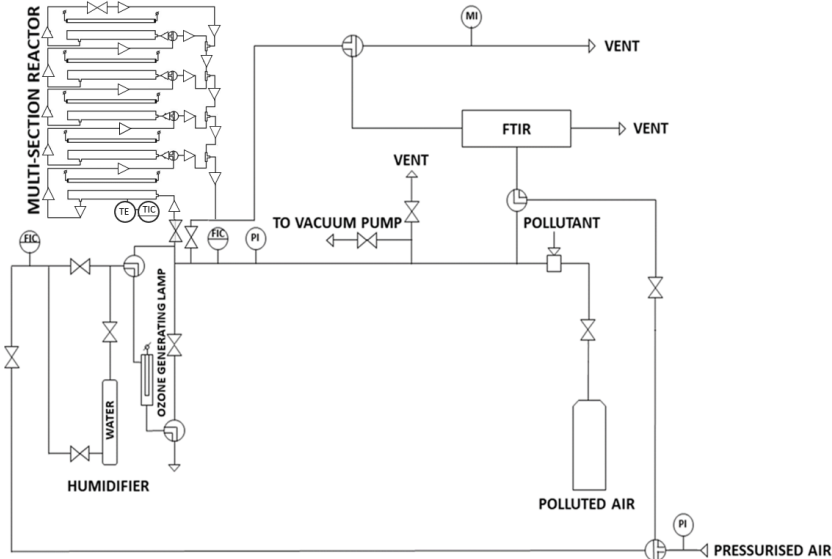


Figure 8. Schematic illustration of the system with photocatalytic reactor: FIC – flow indicator controller; MI – moisture indicator; PI – pressure indicator; TE – temperature element; TIC – temperature indicator controller

UVA-emitting fluorescent lamps (Philips, Actinic T8) with the power of 15 W were placed 6 cm above each section of the reactor. The irradiance of 3.5 mW·cm⁻² was measured at a distance corresponding to the level of the surface of the catalyst by a fibre optic spectrometer (USB-2000 + UV-VIS-ES) using cosine corrector (CC-3-UV-S, field of view 180°); the measured irradiance corresponded to 1.3 × 10⁻⁶ Einstein·s⁻¹ in one section of the reactor. The internal cross-sectional dimensions of the reactor section are 0.9 × 4.9 cm and length 29.5 cm resulting in a volume of 130 mL. The glass wall thickness is 0.2 cm. Temperature in the reactor was measured with a temperature controller supplied with K-type thermocouple (Omega, CN9000A). The gas flow rate was controlled by means of a flow metering valve (Swagelok, SS-6MG-MM) and measured by a mass flow meter (Kobold, MAS-1009-A).

Applied ozone in Paper II was generated by the UVC lamp (LSE Lighting, GPH287T5VH/4) emitting at wavelengths of 254 and 185 nm. The relative air humidity (RH) was 6 ± 1% (1.2 g·m⁻³) or 40 ± 5% (8.2 g·m⁻³) determined at 22 ± 1 °C by hygrometer/psychrometer (TPI, 597) (Paper II).

Conversion, %, was calculated using Eq. 46:

$$\text{Conversion (\%)} = \frac{C_0 - C_t}{C_0} \cdot 100 \quad (46)$$

where C_0 and C_t , ppm, are inlet and outlet concentration of pollutant, respectively.

Paper II-Experimental procedure

The air polluted with either acetone or toluene (inlet concentration, C_0 (acetone) and C_0 (toluene), of 20, 40, or 60 ppm) or their mixture (inlet concentration of 20 ppm of each compound) was treated in the photocatalytic reactor. The respective amounts of pollutants were injected through the injection port into the feed tank, which had been previously vacuumed. The gas mixture was allowed to evaporate for 20 min followed by the filling of the tank with compressed air to pressure of 3 bars and left for 90 min in order to balance the fluctuations in the concentration. Thereupon, it was directed into the modular reactor using up to five sections, from where the outlet gas of VOCs and ozone was led into Fourier transform infrared spectroscopy (FTIR). For the measurement of initial concentrations, the reactor was omitted by directing the gaseous mixture directly into the gas cell of FTIR.

The flow rates of 0.5 and 1.0 L·min⁻¹ were applied, providing accordingly residence times of 16.0 and 8.0 s per reactor section and specific residence times (SRT) of 0.13 and 0.065 s·cm⁻². The temperature in the reactor maintained by the heat of the lamp was 41 ± 2 °C.

2.2.4 Combination of Pulsed Corona Discharge with Photocatalytic Oxidation

Paper III-Experimental Equipment

The PCD reactor was combined with the photocatalytic one, both described in detail above, to treat residual toluene and ozone containing air exhaust. The 3D illustration of the combination is shown in Figure 9. The exhaust gas was subjected to photocatalytic treatment in the multi-section photocatalytic reactor.

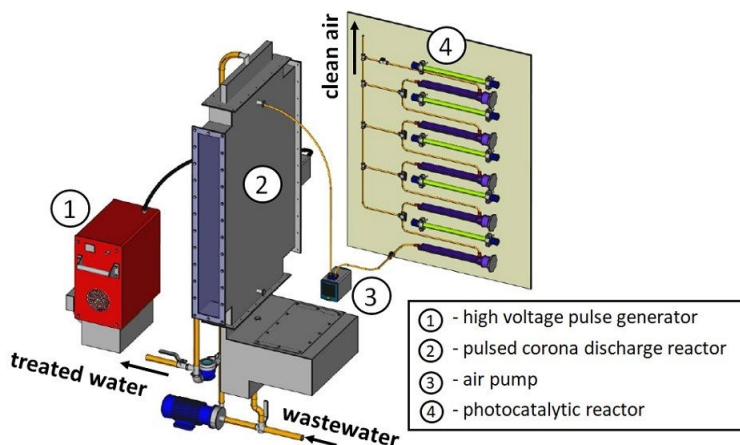


Figure 9. 3D illustration of combined PCD and photocatalytic reactor

Paper III-Experimental procedure

Solutions initially containing approximately 10, 30, and 50 mg·L⁻¹ of toluene provided equilibrium aqueous concentrations of 1.0, 3.7, and 6.3 mg·L⁻¹ in 10 L aqueous solutions at 20 ± 2 °C. These concentrations consistently provided equilibrium airborne toluene concentrations in the air phase of 0.4, 1.0, and 1.6 mg·L⁻¹, respectively, in the overall free gaseous volume of the hermetically closed PCD reactor of 144 L. In experiments at temperature elevated to 30 ± 2 °C, the equilibrium in solutions containing 30 mg L⁻¹ was established at aqueous concentration of 2.5 mg·L⁻¹ and airborne toluene content of

1.2 mg·L⁻¹. Treatment solution was recirculated for 10 min prior to the start of the experiment, and for 5 min prior to sampling after treatment to reach equilibrium concentrations of toluene in liquid and gas phases. The applied pulse repetition frequencies were 50, 200, and 880 pps, providing output powers of 9, 32, and 123W, respectively. Acidic and alkaline media were attained by adding either 5 M H₂SO₄ or 5 M NaOH to the treatment solution, respectively. Otherwise, the experimental procedure in PCD reactor is identical as previously described. An inbuilt spiral coil heater was used to obtain a higher temperature of the solution. The equilibrium state of toluene in gas–liquid system verified implementing Henry’s law (Eq. 47) (Sander, 2015) showed that the measured concentrations were close to the theoretically calculated ones:

$$H = H_0 \cdot \exp \left[\frac{\ln H}{\left(\frac{1}{T}\right)} \right] \left(\frac{1}{T} - \frac{1}{T_0} \right) \quad (47)$$

where H is Henry’s law solubility constant, H_0 is Henry’s law solubility constant at reference temperature, mol·kg⁻¹·bar⁻¹ (Leighton and Calo, 1981), T is the treated solution temperature, K, T_0 is a reference temperature of 298.15 K.

The energy efficiency E , g·kW⁻¹·h⁻¹, was calculated at 40% of toluene oxidation (Eq. 44).

The gas samples from PCD reactor were directed into the photocatalytic modular reactor for exhaust air post-treatment using an air pump (KNF Neuberger S.A.S, France) at flow rates of 0.5, 1.0, and 2.0 L·min⁻¹ that provided residence times of 16.0, 8.0, and 4.0 s per section and specific residence times (SRT) of 0.13, 0.065 and 0.033 s·cm⁻², respectively. The outlet gas of the photocatalytic reactor was directed into FTIR for the measurement of concentrations. The temperature in the reactor comprised 38 ± 1 °C maintained by the heat of the lamp.

2.3 Analytical Methods

2.3.1 Analysis of Aqueous Matrix

Paper I and III

Concentrations of aqueous solutions were measured using 9300 HPLC System high-performance liquid chromatography (YL Instrument Co., Republic of Korea) equipped with a UV/Vis detector and Waters XBridge C18 column (130 Å pore size, 3.5 µm particle size, 150 mm in length and 3.0 mm inner diameter). Eluent flow rate was 0.2 mL·min⁻¹ at the sample run time of 13 min. Isocratic elution was applied using 0.1% CH₃COOH in ultrapure water and acetonitrile: 80% and 20%, respectively, in Paper I and 70% and 30%, respectively, in Paper II. Measurements were duplicated showing a deviation of the results up to 5%.

pH was measured with S220 digital pH-meter (Mettler Toledo, Switzerland) (Paper I and II) and conductivity with multiparameter meter HQ430d (Hach Company, USA) (Paper I). Measurements (Paper I) of (i) aqueous O₃ concentration by means of indigo method at wavelength 600 nm, (ii) the concentration of H₂O₂ formed in PCD treatment using titanyl sulphate method at 410 nm (Kasprzyk-Hordern et al., 2003), and (iii) the concentration of Fe²⁺ determined by o-phenanthroline method at 410 nm (Merck, 1974) were performed by means of HeLios UV-Vis spectrophotometer (Thermo Electron Corporation, USA).

2.3.2 Analysis of Gaseous Matrix

Paper II and III

Concentrations of pollutants in the gas flow were measured using FTIR (Interspec 200-X, Estonia) with the Specac Tornado 8 m 1.33 L gas cell in the range of 500–4000 cm^{-1} . The spectra were collected every 5 min (Paper III) and 10 min (Paper II) for each reactor's section. For quantitative analysis, the peaks of acetone and toluene were measured at the IR bands 1250–1177 and 2964–2838 cm^{-1} (Paper II), respectively, and at 733–727 cm^{-1} only for toluene (Paper III). Peak of ozone was monitored at the IR band 1100–970 cm^{-1} . The gaseous intermediate products observed in the study, such as carbon monoxide (Paper II, III) and formic acid (Paper III), were analysed at the IR bands 2225–2050 and 1150–1070 cm^{-1} , respectively. All existing peaks, except ozone, were integrated using Essential FTIR software (Operant LLC, USA) and quantitative database (FDM, HiRes VPFTIR for Quant, USA) (Papers II and III). In Paper I, ozone was produced from dry air using A2ZS-10GLAB O₃ generator (A2Z Ozone Inc., USA) and O₃ gaseous concentration in ozonation as well as the residual O₃ concentration in the exhaust air of PCD were determined with an ozone monitor (PCI-WEDECO Environmental Technologies, Inc., USA). In Papers II and III, the concentration of ozone was determined using FTIR calibrated by either colorimetric indigo method (Clesceri et al., 2005) (Paper II), or MP-6060 ozone analyser (Anseros Klaus Nonnenmacher GmbH, Germany) (Paper III) for calibration. All experiments were duplicated indicating the standard deviation less than 5%.

Catalytic coating was prepared by hand-spraying sonicated slurry of TiO₂ (5 wt%) in ethanol onto glass plates by means of

an aero spray (Stanley, 150119XSTN, USA) followed by drying at room temperature. The TiO₂ surface density was $1.4 \pm 0.2 \text{ mg}\cdot\text{cm}^{-2}$ and thickness of the coating measured using the surface profiler TENCOR P-10, USA, was in the range of 1 μm . The surface of the catalyst (Paper II, Figure S1 in Supplementary material) was visualised with field emission scanning electron microscopy (FE SEM, Dual-Beam Helios Nanolab 600, FEI, USA). The water contact angle was measured at $22 \pm 1 \text{ }^\circ\text{C}$ with DSA 25 (KRÜSS Instrument, Germany) applying the sessile drop fitting method.

The reference experiments, i.e., adsorption and photochemical degradation were carried out in Paper II. No decomposition of acetone, toluene, or ozone was observed under the UVA irradiation in the absence of the catalyst. No degradation of acetone and toluene was observed in the presence of ozone and the absence of TiO₂ catalyst coatings under the studied operating conditions. Slight adsorption (less than 5%) of acetone was detected in dark conditions on TiO₂ coating, whereas no decrease in toluene and ozone concentrations was detected in the FTIR spectrum referring to the lack of adsorption.

Regeneration of the catalyst was needed after the photocatalytic treatment of toluene in the absence of ozone. The air containing ozone passed through the UVA irradiated reactor for 30 min followed by the solitary UVA irradiation for 60 min. Otherwise, the photocatalytic surface was treated under UVA irradiation for 60 min.

3 Results and Discussion

3.1 Oxidation Energy Efficiency of Aqueous Pollutants by Ozonation and PCD Treatment. Content of Exhaust Air Originating from PCD Equipment

The oxidation efficiencies of (i) aqueous NDEA by ozonation, PCD, and their H₂O₂-assisted treatment, and (ii) aqueous toluene by PCD at various experimental conditions are depicted in Table 3a–s. Since toluene is a volatile compound, the energy efficiency values of simultaneous gas-phase oxidation by PCD are also shown in Table 3l–s.

Table 3. Energy efficiencies of NDEA oxidation in ozonation and PCD, and toluene oxidation in PCD treatment

	Ozonation conditions for NDEA	Efficiency of NDEA oxidation for 50%, g·kW ⁻¹ ·h ⁻¹	
		Aqueous	
(a)	C ₀ =10 μM, O ₃ [2 mg·L ⁻¹], pH=7.0, 22°C	0.034	
(b)	C ₀ =10 μM, O ₃ [2 mg·L ⁻¹], pH=12.0, 22°C	1.10	
(c)	C ₀ =10 μM, O ₃ [1 mg·L ⁻¹], pH=7.0, 22°C	0.029	
(d)	C ₀ =10 μM, O ₃ [2 mg·L ⁻¹]/H ₂ O ₂ [50 μM], pH=7.0, 22°C	0.84	
(e)	C ₀ =10 μM, O ₃ [1 mg·L ⁻¹]/H ₂ O ₂ [50 μM], pH=7.0, 22°C	0.70	
	PCD treatment conditions for NDEA	Efficiency of NDEA oxidation for 50%, g·kW ⁻¹ ·h ⁻¹	
		Aqueous	
(f)	C ₀ =10 μM, 200 pps, pH=3.0, 22°C	1.42	
(g)	C ₀ =10 μM, 200 pps, initial pH=7.0, 22°C	1.01	
(h)	C ₀ =10 μM, 200 pps, pH=12.0, 22°C	0.93	
(i)	C ₀ =10 μM, 880 pps, initial pH=7.0, 22°C	0.59	
(j)	C ₀ =10 μM, (200 pps)/H ₂ O ₂ [50 μM], initial pH=7.0, 22°C	1.05	
(k)	C ₀ =10 μM, (880 pps)/H ₂ O ₂ [50 μM], initial pH=7.0, 22°C	0.51	
	PCD treatment conditions for toluene	Efficiency of toluene oxidation for 40%, g·kW ⁻¹ ·h ⁻¹	
		Aqueous	Airborne
(l)	C ₀ =6.3 mg·L ⁻¹ , 880 pps, initial pH 7.0, 20°C	7.5	22.3
(m)	C ₀ =6.3 mg·L ⁻¹ , 200 pps, initial pH 7.0, 20°C	8.6	27.0
(n)	C ₀ =6.3 mg·L ⁻¹ , 50 pps, initial pH 7.0, 20°C	10.5	29.3
(o)	C ₀ =3.7 mg·L ⁻¹ , 200 pps, initial pH 7.0, 20°C	7.5	23.0
(p)	C ₀ =1.0 mg·L ⁻¹ , 200 pps, initial pH 7.0, 20°C	6.4	13.7
(q)	C ₀ =3.7 mg·L ⁻¹ , 200 pps, pH 3.0, 20°C	7.6	22.4
(r)	C ₀ =3.7 mg·L ⁻¹ , 200 pps, pH 12.0, 20°C	7.6	24.9
(s)	C ₀ =2.5 mg·L ⁻¹ , 200 pps, initial pH 7.0, 30°C	5.3	29.5

As is known, ozonation is a pH-sensitive process, thus the NDEA treatment solutions were buffered to maintain the desired pH throughout the experiments. The decomposition of NDEA by mere ozonation at pH 7.0 indicated energy efficiency values of 0.029 and

0.034 g·kW⁻¹·h⁻¹ at gaseous ozone concentration of 1 and 2 mg·L⁻¹, respectively (Table 3a, c; Paper I, Figure 3). Only minor, if any, oxidation was observed under acidic conditions, whereas the increase of pH to 12.0 demonstrated a significantly higher energy efficiency of 1.10 g kW⁻¹·h⁻¹ at gaseous ozone concentration of 2 mg·L⁻¹ due to the abundance of generated HO^{*} (Table 3a, b; Paper I, Figure 6). Relatively low degradation efficiency of NDEA in ozonation at pH 7.0 was substantially improved with the addition of H₂O₂, explained by the accelerated decomposition of O₃ into HO^{*} (Eq. 19) providing the increased oxidation efficiency of 0.70 and 0.84 g·kW⁻¹·h⁻¹ at gaseous ozone concentration of 1 and 2 mg·L⁻¹, respectively (Table 3d, e; Paper I, Figure 3). The influence of ozone gas–liquid transfer on the oxidation kinetics was tested by measuring aqueous ozone content in the NDEA solution in time of ozone delivery at pH 3.0 indicating rapid saturation of the treated water with ozone reaching an equilibrium concentration at about 250 μg·L⁻¹ in less than 1 min (Paper I, Figure S1 in Supplementary material). This indicates the mass transfer in the reactor is proceeding faster than the oxidation reaction, making the latter control the process rate.

In PCD treatment, the choice of suitable pulse repetition frequency in energy-efficient prospective is of great importance. The changes in pulse repetition demonstrated a different NDEA degradation pattern (Figure 10a) resulting in energy efficiencies of 1.01 and 0.59 g·kW⁻¹·h⁻¹ at 200 and 880 pps, respectively (Table 3g, i), thereby referring to the role of long-living O₃ in NDEA oxidation, since longer periods of time between pulses provide an extra time for O₃ transfer and reactions (Panorel et al., 2011; Preis et al., 2013 (a)). Unlike NDEA, ozone plays a minor role in aqueous toluene oxidation as only moderate variations in energy efficiency (Figure 10b) were observed, comprising 10.5, 8.6, and 7.5 g·kW⁻¹·h⁻¹ at 50, 200, and 880 pps, respectively (Table 3l–n). This is explained by the low concentration of gaseous ozone due to its reaction with toluene in air. For instance, within the first 5 min of PCD treatment, gaseous ozone concentration of 0.22 mg·L⁻¹ in the reactor (Paper III, Figure 3) may provide 0.07 mg·L⁻¹ of equilibrium aqueous ozone according to Henry's law (Gottschalk et al., 2010) affirming the smaller role of ozone in aqueous toluene oxidation. Additionally, toluene is a hydrophobic compound that possesses notably lower water solubility compared to NDEA (Table 2) referring to the occurrence of degradation process at the gas–liquid interface mostly with interface-borne short-living HO^{*} (Ajo et al., 2017). It also explains the need for shorter treatment time and thus lower delivered energy in toluene decomposition seen in Figure 10b since HO^{*}-based reactions generally proceed at least two orders of magnitude faster in comparison to O₃-based ones (Gottschalk et al., 2010).

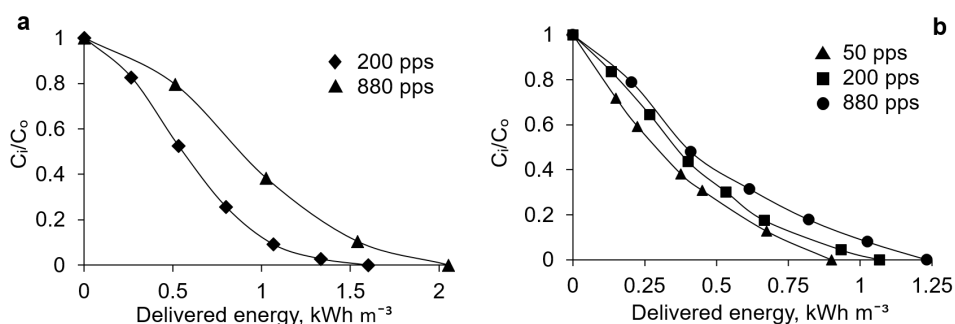


Figure 10. NDEA (a) and toluene (b) delivered energy-dependent PCD-oxidation at pulse repetition frequencies of 200 and 880 pps for NDEA and 50, 200, and 880 pps for toluene. NDEA: $C_0=10 \mu\text{M}$, initial pH=7.0, 22°C; toluene: $C_0=6.3 \text{ mg L}^{-1}$, initial pH 7.0, 20°C

From Figure 10a one can also see a rather unusual stepwise oxidation pattern with the initial slower phase followed by degradation acceleration. This phenomenon could be explained by the occurrence of Fenton reactions in PCD setup as both H_2O_2 and Fe^{2+} were detected and quantified in concentrations growing with time and H_2O_2 also with pulse repetition frequency (Paper I, Figure 5). H_2O_2 is generated in PCD via recombination of HO^\bullet (Eq. 23) and Fe^{2+} enters the aqueous phase through the leaching from the surface of electrodes and reactor walls made of stainless-steel.

In the experiments on NDEA and toluene oxidation, the pulse frequency of 200 pps appeared to be the most optimal one for further study, affording a longer time of treatment for accurate sampling. Since different initial equilibrium concentrations of 1.0, 3.7, and 6.3 $\text{mg}\cdot\text{L}^{-1}$ were studied for toluene PCD oxidation, indicating accordingly energy efficiency values of 6.4, 7.5, and 8.6 $\text{g}\cdot\text{kW}^{-1}\cdot\text{h}^{-1}$ (Table 3m, o, p), the initial equilibrium concentration of 3.7 $\text{mg}\cdot\text{L}^{-1}$ was chosen for the same purpose as pulse frequency of 200 pps (Paper III, Figure 1a and Figure 2).

For comparative reasons, the importance of using buffered solutions was also clarified by testing PCD oxidation efficiency in conductive medium to provide stable pH as in acidic and alkaline solutions the pH remained practically unchanged throughout the treatment, whereas in neutral solutions the formation of carboxylic acids (Panorel et al., 2013) and nitrate (Kornev et al., 2013) resulted in pH decrease from 7.0 ± 0.1 to 4.2 ± 0.4 in case of NDEA and to 4.5 ± 0.2 in case of toluene. 50 mM phosphate buffer solution for pH 7.0 possessed a conductivity of $7.0 \pm 0.1 \text{ mS}\cdot\text{cm}^{-1}$ at 22 °C, which, however, demonstrated no effect on energy efficiency of complete oxidation of target compound compared to non-buffered media (Paper I, Table S1 in Supplementary material). Further discussion therefore handles PCD oxidation in non-buffered solutions. PCD oxidation of NDEA in alkaline and neutral conditions indicated similar efficiencies of 0.93 and 1.01 $\text{g}\cdot\text{kW}^{-1}\cdot\text{h}^{-1}$, respectively, whereas the acidic medium, contrary to ozonation, demonstrated the highest energy efficiency of 1.42 $\text{g}\cdot\text{kW}^{-1}\cdot\text{h}^{-1}$, exceeding the efficiency at neutral conditions of about 30% (Paper I, Figure 7). This tendency may be explained by the surface oriented HO^\bullet attack, although HO^\bullet also possesses higher redox potential in acidic medium (Wardman, 1989) as well as the radical-scavenging bicarbonates are absent in the acidic medium. Contrary to ozonation, PCD did not benefit from the addition of H_2O_2 making it evident, that the concentration of leached Fe^{2+} -ions limit the rate of Fenton oxidation discussed earlier as the content of H_2O_2 differs twofold (Table 3g, i, j, k). At neutral pH of natural water, the comparison of ozonation at gaseous ozone concentration of 2 $\text{mg}\cdot\text{L}^{-1}$ with PCD treatment at 200 pps in NDEA oxidation exhibited a considerable difference: PCD efficiency of 1.01 $\text{g}\cdot\text{kW}^{-1}\cdot\text{h}^{-1}$ surpassed 0.034 $\text{g}\cdot\text{kW}^{-1}\cdot\text{h}^{-1}$ of ozonation by at least an order of magnitude, which also exceeded the $\text{O}_3/\text{H}_2\text{O}_2$ combination for 20% (Table 3a, d, g).

In toluene PCD-oxidation, the variations in pH possessed no effect on the aqueous toluene degradation (Table 3o, q, r) although alkaline medium promotes additional HO^\bullet production via aqueous ozone decomposition (Kasprzyk-Hordern et al., 2003). As was explained earlier, this is due to the low concentration of gaseous ozone that is in accordance with an even lower equilibrium aqueous ozone content, therefore contributing to the generation of additional HO^\bullet in water only to some extent. The increase in temperature from 20 ± 2 °C to 30 ± 2 °C in the treatment solution, containing 3.7 $\text{mg}\cdot\text{L}^{-1}$ of aqueous toluene in equilibrium with air, provided a toluene aqueous concentration of 2.5 $\text{mg}\cdot\text{L}^{-1}$ and resulted in a remarkably lower energy efficiency of 5.3 $\text{g}\cdot\text{kW}^{-1}\cdot\text{h}^{-1}$ in toluene PCD oxidation (Table 3s).

The oxidation energy efficiency of airborne toluene exceeds the ones of aqueous toluene by about three times in most of the cases (Table 3l–s) pointing to toluene degradation with interface-borne HO^{*} at the gas-phase side (Ajo et al., 2017). The difference increased by about five times with temperature growth, which is consistent with the higher equilibrium concentration of 1.2 mg·L⁻¹ in gas-phase in comparison with 1.0 mg·L⁻¹, and the lower oxidation rate of aqueous admixtures at elevated temperatures (Onga et al., 2020).

The exhaust air originating from PCD setup contains residual ozone as well as a low concentration of fugitive compounds if VOCs are treated. Residual ozone, formed in NDEA PCD oxidation, was quantified at pH 3.0, 7.0, and 12.0 reaching of 0.73 mg O₃·L⁻¹ in acidic and neutral mediums and 0.66 mg O₃·L⁻¹ in alkaline (Table 4a–c). Slightly lower content of gaseous ozone residues at the highest pH is addressed to the enhanced decomposition of O₃ in alkaline solutions.

Since toluene is a volatile compound, its presence in the exhaust air is principally inevitable. In addition to ozone and toluene, a minor presence of carbon monoxide, the product of incomplete oxidation, was observed at the end of the PCD treatment (Table 4d–k).

Table 4. Toluene, O₃, and CO concentrations in PCD outlet gas

	PCD treatment conditions for NDEA	Sampling time, min	Concentration, mg·L ⁻¹		
			O ₃		
(a)	C ₀ =10 μM, 200 pps, pH=3, 22°C	25	0.73		
(b)	C ₀ =10 μM, 200 pps, pH=7, 22°C	30	0.73		
(c)	C ₀ =10 μM, 200 pps, pH=12, 22°C	45	0.66		
	PCD treatment conditions for toluene	Sampling time, min	Concentration, mg·L ⁻¹		
			Toluene	O ₃	CO
(d)	C ₀ =6.3 mg·L ⁻¹ (aq), C ₀ =1.6 mg·L ⁻¹ (gas), 880 pps, initial pH 7.0, 20°C	6	0.057	0.61	0.051
(e)	C ₀ =6.3 mg·L ⁻¹ (aq), C ₀ =1.6 mg·L ⁻¹ (gas), 200 pps, initial pH 7.0, 20°C	20	0.080	0.40	0.042
(f)	C ₀ =6.3 mg·L ⁻¹ (aq), C ₀ =1.6 mg·L ⁻¹ (gas), 50 pps, initial pH 7.0, 20°C	60	0.10	0.22	0.033
(g)	C ₀ =3.7 mg·L ⁻¹ (aq), C ₀ =1.0 mg·L ⁻¹ (gas), 200 pps, initial pH 7.0, 20°C	12.5	0.061	0.39	0.028
(h)	C ₀ =1.0 mg·L ⁻¹ (aq), C ₀ =0.4 mg·L ⁻¹ (gas), 200 pps, initial pH 7.0, 20°C	5	0.065	0.34	0.016
(i)	C ₀ =3.7 mg·L ⁻¹ (aq), C ₀ =1.0 mg·L ⁻¹ (gas), 200 pps, pH 3.0, 20°C	12.5	0.057	0.42	0.030
(j)	C ₀ =3.7 mg·L ⁻¹ (aq), C ₀ =1.0 mg·L ⁻¹ (gas), 200 pps, pH 12.0, 20°C	12.5	0.065	0.044	0.030
(k)	C ₀ =2.5 mg·L ⁻¹ (aq), C ₀ =1.2 mg·L ⁻¹ (gas), 200 pps, initial pH 7.0, 30°C	12.5	0.096	0.22	0.029

In PCD-oxidation of toluene, concentrations of both outlet gas constituents, ozone, and CO, were decreasing with declining pulse repetition frequencies at rather similar toluene content at the end of the treatment (Table 4d–f). This might refer to the potential similarity in PCD and PCO, where lower ozone in a gas phase causes the formation of lower yield of CO, observed in photocatalytic oxidation of toluene which is described in upcoming chapter. Besides, lower toluene initial concentration resulted in a lower carbon monoxide yield at almost equal O₃ content (Table 4e, g, h). The reduced

carbon monoxide yield at lower ozone concentrations monitored at higher temperature also fits into the correlation between gaseous ozone concentration and CO production (Table 4f, k). However, the PCD oxidation experiments at various pH values indicate principally identical CO yield at ozone concentrations expectedly being an order of magnitude lower in alkaline media as a result of rapid decomposition and, thus, the ozone chemisorption (Table 4g, l, j). From this, it could be concluded that CO is a toluene oxidation product without a particular role of ozone, formed through the predominant mechanism of degradation via HO[•]. It is also seen in Table 4 that in NDEA oxidation, the difference in O₃ concentration between acidic as well as neutral and alkaline is around 10%, while in the case of toluene, the disparity is about tenfold. In PCD outlet gas, two times higher residual O₃ content was observed at the end of NDEA treatment compared to that of toluene oxidation (Table 4b, h, where 10 μM corresponds to ca. 1 mg·L⁻¹ of NDEA), which could be addressed to the reaction between ozone and toluene in gas-phase confirmed by the measurements of gas-phase ozone concentrations exhibiting slower gaseous ozone concentration growth at higher toluene concentration (Paper III, Figure 3).

As shown in Table 4d–k the trace concentrations of toluene are present in the exhaust air after PCD treatment remaining at about 0.06–0.10 mg·L⁻¹. The complete oxidation of toluene by PCD may be a time- and energy-consuming task, and besides, residual O₃ is also considered an air pollutant. Thus, gaseous exhaust air containing residual O₃ or additionally trace amounts of VOCs requires further treatment. In such case, photocatalysis presents a reasonable approach.

3.2 Photocatalytic Treatment of Gaseous Pollutants

For successful abatement of VOCs by photocatalytic oxidation, the suitable process parameters should be opted. The changeable operating conditions comprised the presence and absence of ozone, changes in pollutant initial concentration, in residence time and specific residence time (SRT), and in relative humidity (RH) for the degradation of artificially contaminated air containing acetone and toluene, and their mixture. The humid O₃-containing exhaust air originating from PCD equipment allowed studying only the influence of residence time and SRT as manually changeable parameters.

An explanation for the connection between residence time and SRT lies in the doubling of SRT by decreasing the gas flow rate two times that enables following VOCs' conversion at the same residence time, but at twice the smaller catalyst area. For instance, the TiO₂-coated surface of 240 cm² is used at residence time of 16 s and SRT of 0.065 s·cm⁻², whereas at the same residence time and SRT of 0.13 s·cm⁻² photocatalytic process is operated over 120 cm² allowing to follow the changes in process performance either by increasing the overall residence time by adding the operating reactor sections or by increasing the residence time in one section and exploring the degradation over smaller catalyst surface area.

In the photocatalytic oxidation of acetone and toluene as single pollutants, the use of ozone did not indicate any major effect on the oxidation of acetone within the whole range of the studied inlet concentrations of 20, 40, and 60 ppm corresponding to 0.076, 0.15, and 0.23 mg·L⁻¹, respectively, whereas in the case of toluene, ozone apparently influenced toluene conversion at highest inlet concentration of 60 ppm through accelerated degradation of adsorbed intermediates (Figure 11a, b).

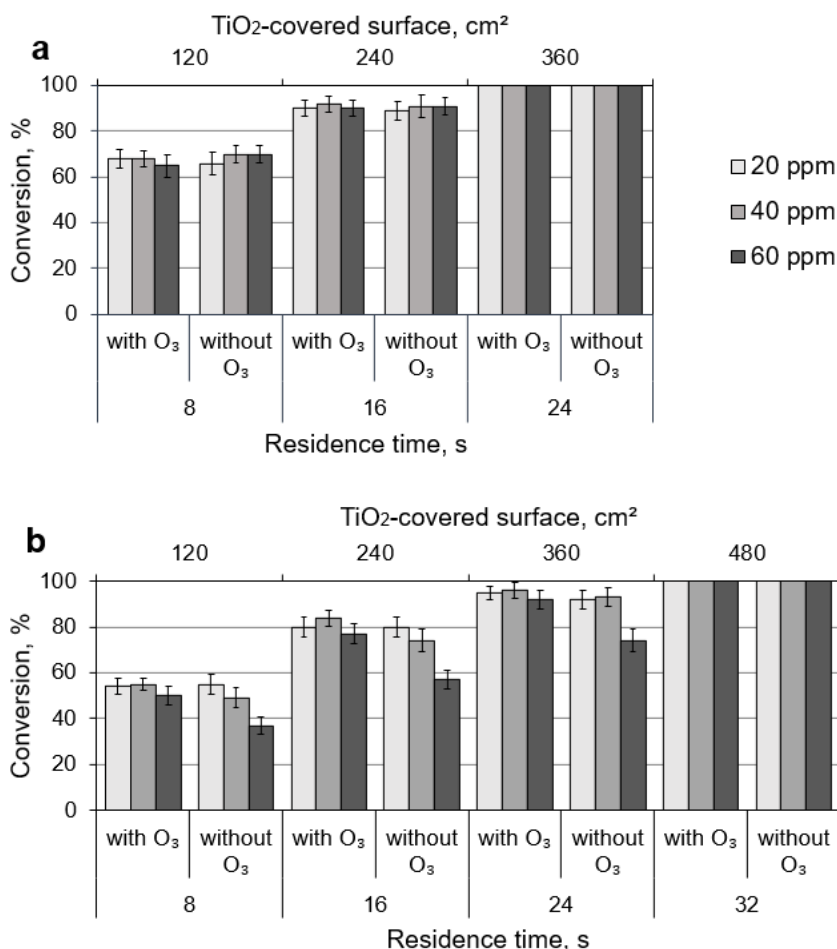


Figure 11. Influence of acetone (a) and toluene (b) concentrations on their conversion in the presence and absence of ozone. RH 6%, SRT=0.065 s·cm⁻²

Rapid deactivation of the catalyst surface by oxidation intermediates is previously reported in the literature (Augugliaro et al., 1999; d'Hennezel, 1998; Cao et al., 2000). The probable reason for the valid effect of ozone on toluene oxidation in fact is the prevention of rapid clogging of active sites by the degradation intermediates via their heterogeneous reactions with ozone. In comparison to acetone, the blocking of catalyst's active sites at higher toluene inlet concentrations is, supposedly, due to the benzene ring, which is more resistant towards oxidative degradation.

Since VOCs' inlet concentration of 20 ppm was the lowest one to allow following the degradation of the initial compounds using more than one section of the reactor, the subsequent discussion covers the results obtained at this concentration. As could be expected, the increase in residence time and TiO₂-coated area increased the efficacy of photocatalytic oxidation, resulting in complete degradation of toluene at the residence time of 32 s (SRT of 0.065 and 0.13 s·cm⁻²; coated area of 480 and 240 cm², respectively), while complete abatement of acetone was examined at residence time of 24 s and 16 s (SRT of 0.065 and 0.13 s·cm⁻²; coated area of 360 and 120 cm², respectively) (Figure 12).

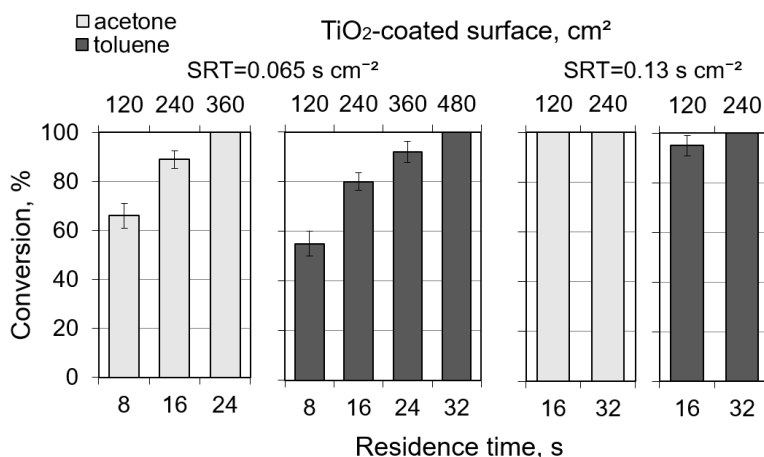


Figure 12. Influence of residence time on acetone and toluene conversion as a single VOC in the absence of ozone. $C_0(\text{acetone})=20 \text{ ppm}$, $C_0(\text{toluene})=20 \text{ ppm}$, RH 6%

Figure 12 also demonstrates a higher conversion of acetone and toluene at residence time of 16 s at SRT of $0.13 \text{ s}\cdot\text{cm}^{-2}$ and thus a smaller catalytic surface (coated area of 120 cm^2) compared to the SRT of $0.065 \text{ s}\cdot\text{cm}^{-2}$ (240 cm^2).

The photocatalytic degradation was also compared at different RH values of 6%, which is considered as dry air, and at RH of 40% considered as relative indoor air humidity. The higher air humidity in the presence as well as in the absence of ozone, however, showed no major influence on the oxidation of single VOCs, neither did the presence of ozone at RH of 6% in air polluted with acetone or toluene.

It is known that there are plenty of hydroxyl groups on the TiO_2 surface potentially enabling the adsorption of aromatic compounds through $\text{OH}\cdots\pi$ -electron type complex or water via hydrogen bonding (Nagao and Suda, 1989) possibly resulting in a competitive sorption process under varying experimental conditions. Water adsorption through hydrogen bonding was also confirmed in the present research by the surface wettability test. The water contact angle of TiO_2 -covered surface was measured indicating the value of 0° for an as-prepared sample, thereby showing its hydrophilicity even without the UV treatment (Banerjee et al., 2015). Thus, in the oxidation of single VOCs, the increase in the number of precursors of radicals, such as ozone and hydroxyl anions, did not assist the degradation, whereas the increase in SRT and concentration of pollutants augmented the number of pollutants degraded under the studied conditions.

The increase in RH to 40% slightly inhibited the oxidation of VOCs mixture only at longer SRT in the absence of ozone ($0.13 \text{ s}\cdot\text{cm}^{-2}$, 16 s, 120 cm^2) and in the presence of ozone at shorter SRT ($0.065 \text{ s}\cdot\text{cm}^{-2}$, 8–24 s, $120\text{--}360 \text{ cm}^2$) (Figure 13).

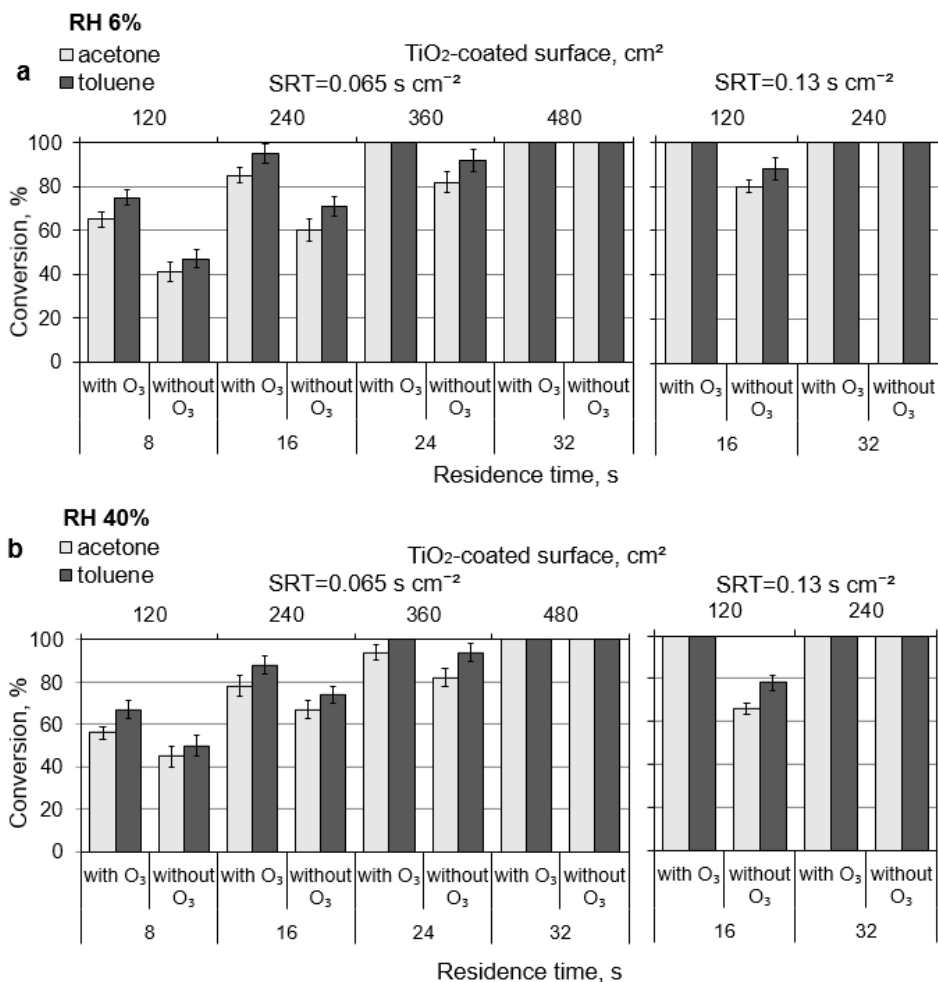


Figure 13. Influence of residence time on acetone and toluene conversion in the mixture in the absence and presence of ozone at RH of 6 (a) and 40% (b). $C_0(\text{acetone})=20$ ppm, $C_0(\text{toluene})=20$ ppm

The minor negative impact of higher relative humidity of 40% in the presence of ozone at shorter SRT could be explained by the competitive adsorption between water vapour and ozone for the active sites on the surface of the photocatalyst. At the same time, the use of ozone tends to advance the oxidation of both VOCs, which is in accordance with the foregoing assumption on the promotion of the degradation of toluene by accelerated oxidation of its intermediates. In addition, toluene presence seemingly inhibited the degradation of acetone in all experimental runs (RH of 6 and 40%, with and without ozone, SRT of 0.065 and 0.13 s·cm⁻²) explained by the adsorption–desorption equilibria, i.e., intermediate products of toluene oxidation impede the adsorption and degradation of acetone.

The complete degradation of the mixture was reached in the absence of ozone at the residence time of 32 s (SRT of 0.065 and 0.13 s·cm⁻²; coated area of 480 and 240 cm², respectively) at both humidity levels, whereas in the presence of ozone, the complete degradation was achieved at the residence time of 24 s (360 cm²) at SRT of 0.065 s·cm⁻² (except for acetone at RH of 40%) and 16 s (120 cm²) at SRT of 0.13 s·cm⁻².

In comparison to single VOCs, higher toluene conversions in the presence of ozone at SRT of $0.065 \text{ s}\cdot\text{cm}^{-2}$ and RH of 6% in the mixtures were presumably attained as a result of additionally formed radicals from acetone degradation, while the conversion of acetone in the mixture was only slightly lower than that of solitary acetone. In the absence of ozone, the catalyst deactivation with adsorbed by-products of toluene resulted in reduced conversions of acetone in the mixtures compared to that of a single VOC (Figure 13), while the toluene conversions remained practically unchanged. The degradation at SRT of $0.065 \text{ s}\cdot\text{cm}^{-2}$ and RH of 40% followed the same pattern, however, somewhat lower conversions of both compounds were noticed in the presence of ozone in comparison to that of RH of 6%, which is, as mentioned before, apparently due to the water vapour competitive adsorption.

As ozone is a toxic air pollutant, its degradation in the air mixture is required. In all studied conditions, ozone was completely degraded possibly via the reactions shown in literature overview (Eqs. 10–14). Ozone was fully degraded at RH of 6% and SRT of $0.065 \text{ s}\cdot\text{cm}^{-2}$ at residence time of 32 s (TiO_2 -coated surface of 480 cm^2), except for (i) in the presence of higher concentration of acetone (Paper II, Figure 5) or toluene (40 and 60 ppm), or (ii) in the presence of VOCs mixture (20 ppm of each pollutant) requiring residence time of 24 s (360 cm^2). This is also consistent with the previous assumption on the oxidative ability of ozone towards higher concentrations of by-products indicating faster depletion of ozone. For the total ozone degradation at higher air humidity of 40% in comparison with 6%, the VOCs' inlet concentrations of 20 ppm and their mixture needed shorter residence time of 24 and 16 s corresponding to 360 and 240 cm^2 , respectively. The presence of a higher content of water vapour favoured the ozone depletion (Masschelein, 1992) and thus somewhat lower concentrations of ozone entered the reactor. The increase in SRT up to $0.13 \text{ s}\cdot\text{cm}^{-2}$ at VOCs' inlet concentration of 20 ppm resulted in the decrease in residence time necessary for complete ozone degradation: at RH of 6% from 32 to 16 s (TiO_2 -coated surface from 480 to 240 cm^2) and at RH of 40% 24 to 16 s (from 360 to 240 cm^2). Although at longer SRT, the imperceptible amount of ozone exited the first reactor section, application of the second reactor section was needed resulting in an overall treatment time of 32 s. For the mixture, the requisite residence time for ozone depletion was 8 s less than in the case of single compounds. The need for lower residence time in order to degrade ozone at SRT of $0.065 \text{ s}\cdot\text{cm}^{-2}$ is because of the overall higher concentration of organics, which is also in accordance with the obtained results using higher VOCs concentrations.

In addition to ozone, the elimination of gaseous by-products formed in VOCs oxidation is of great importance. Plenty of studies report the detection of several adsorbed by-products on the surface of the catalyst (Bianchi et al., 2014; Huang and Li, 2011; Mo et al., 2009 (a); Sleiman et al., 2009), therefore, the present research was focused on the detection and monitoring of gas phase intermediates and by-products, which are essential from the practical point of view. The identified gaseous oxidation products in most experiments (VOCs in the inlet from 20 to 60 ppm) were water vapour, carbon dioxide (CO_2), and carbon monoxide (CO). Besides, the formation of ca. 5 ppm of formic acid (HCOOH) was detected at toluene inlet concentration of 60 ppm in the presence of ozone, nevertheless, at a residence time of 32 s (SRT of $0.065 \text{ s}\cdot\text{cm}^{-2}$, 480 cm^2) there were no traces of formic acid in the outlet gas flow (Paper II, Figure S2 in Supplementary material). Interestingly, at the same conditions, except the presence of ozone, the formation of gaseous formic acid was not noticed, possibly referring to the adsorption of HCOOH , if any, on the catalyst's surface in the absence of O_3 (Schirolin et al., 2009;

d’Hennezel et al., 1998) whereas the presence of ozone facilitates the generation of higher amount of HCOOH followed by its partial desorption into the gaseous phase. CO was not present in the outlet flow of the reactor at acetone inlet concentration of 20 ppm in the presence and absence of ozone, confirming the total degradation of acetone in the gas phase, whereas low levels of CO (≤ 7 ppm) were observed at higher concentrations of 40 and 60 ppm. In the case of toluene PCO, the variations in toluene inlet concentration from 20 to 60 ppm resulted in the formation of CO from 2 to 8 ppm in the absence of ozone and from 13 to 20 ppm in the presence of ozone. Regarding carbon monoxide, its formation in the VOCs’ oxidation within the whole range of studied concentrations was promoted by ozone. The higher CO yield in the presence of ozone confirmed the above-mentioned discussion on the larger number of formed reactive oxygen species as well as the more profound degradation of the intermediate products. In the photocatalytic treatment of mixtures of VOCs, the concentrations of formed CO were comparable or slightly higher, not exceeding 2 ppm difference, than those detected in the case of isolated toluene which is in accordance with the earlier discussion. No significant influence of higher RH of 40% on the formation of CO in PCO of toluene (20 ppm) was observed in the presence of ozone, while the formation of CO was influenced by humid conditions in the absence of ozone, resulting in higher concentrations. Higher amount of water vapour hindered the further oxidation of CO to CO₂, which is consistent with what has been reported earlier (Soliman, 2019). Carbon monoxide yields correspond to residence times, where the complete conversion of initial pollutants was accomplished.

In the combined treatment of PCD and PCO, rather low inlet concentrations of toluene in the saturated exhaust air originating from PCD setup (Table 5) became undetectable over a TiO₂-coated area of 120 cm² within various tested residence times of 4, 8, and 16 s, i.e., correspondingly at SRT values of 0.033, 0.065, and 0.13 s·cm⁻² (Figure 14).

Table 5. Toluene, O₃, and CO concentrations in PCD outlet gas entering photocatalytic reactor

	PCD treatment conditions for toluene	Sampling time, min	Concentration, mg·L ⁻¹		
			Toluene	O ₃	CO
(a)	C ₀ =6.3 mg·L ⁻¹ (aq), C ₀ =1.6 mg·L ⁻¹ (gas), 880 pps, initial pH 7.0, 20°C	20	0.034	0.29	0.038
(b)	C ₀ =3.7 mg·L ⁻¹ (aq), C ₀ =1.0 mg·L ⁻¹ (gas), 200 pps, initial pH 7.0, 20°C	12.5	0.046	0.29	0.024
(c)	C ₀ =1.0 mg·L ⁻¹ (aq), C ₀ =0.4 mg·L ⁻¹ (gas), 200 pps, initial pH 7.0, 20°C	5	0.042	0.24	0.014

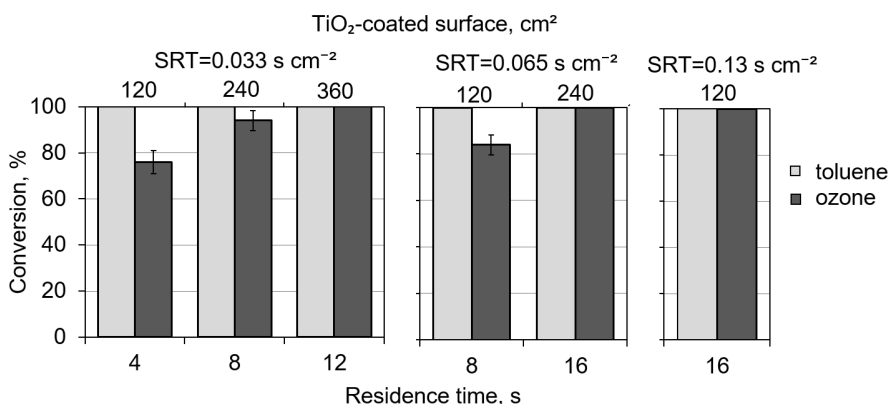


Figure 14. Conversion of airborne toluene and ozone in photocatalytic reactor dependent on residence time at the TiO₂-coated surface, PCD treatment conditions: C₀=3.7 mg L⁻¹ (aq), C₀=1.0 mg L⁻¹ (gas), 200 pps, starting pH 7.0, 20 °C

The fast oxidation of residual toluene is explained by the role of residual plentiful ozone (Pichat et al., 2000). Since no major difference in O₃ conversion was noticed at several residual toluene concentrations, Figure 14 only illustrates the results obtained at an aqueous toluene starting equilibrium concentration of 3.7 mg·L⁻¹ (Table 5b). Ozone was fully degraded at the longest SRT of 0.13 s·cm⁻² provided by a residence time of 16 s over a TiO₂-covered photocatalytic surface of 120 cm², although at SRT of 0.065 and 0.033 s·cm⁻², the O₃ degradation accordingly required 240 and 360 cm² corresponding to residence times of 16 and 12 s, respectively. At lower SRTs of 0.033 and 0.065 s·cm⁻² provided by the respective residence times of 4 and 8 s over TiO₂-coated surface of 120 cm², complete ozone depletion was not observed indicating the need for a larger area of the photocatalyst to ensure the time limit for O₃ degradation. The gradual O₃ depletion within a time span longer than the one essential for the total oxidation of residual toluene confirms a deep oxidation of toluene degradation by-products under the experimental conditions; the accelerated ozone depletion in the presence of toluene oxidation by-products adsorbed on TiO₂-coated surface was mentioned above.

The photocatalytic treatment of the PCD exhaust air resulted in a slight addition of the CO produced from residual toluene in amounts of 0.002–0.007 mg·L⁻¹. Variations in the CO outlet concentrations are determined by differences in the residual toluene concentrations in the air that enters the photocatalytic reactor. The probable reason for the presence of CO residues is the influence of water vapor described above. The yield of CO, however, does not exceed the maximum permissible concentration for an eight-hour exposure in a working zone comprising 0.058 mg·L⁻¹ (CREIA, 2011), thus proving the feasibility of the combined PCD and PCO treatment.

Conclusions

Pulsed corona discharge (PCD), photocatalytic oxidation, and their combination were studied for the energy efficient abatement of hazardous environmental pollutants. Water disinfection by-product N-nitrosodiethylamine (NDEA) was degraded as a single pollutant by PCD for the first time. A multi-section photocatalytic reactor, which allows increasing the surface of the catalyst along with the extension of residence time stepwise by adding the reactor sections, was used for the degradation of acetone, toluene, their mixture, and ozone under variable process parameters. Modular reactors with adjustable photocatalytic surface area, that allow the characterisation of the recalcitrance of volatile organic compounds (VOCs), have not been applied earlier in oxidation in continuous mode. An innovative combination of PCD with photocatalytic oxidation was studied for the elimination of residual ozone originating from PCD treatment, in which toluene was oxidised in both phases, aqueous and gaseous. Previous research in this field has not considered the combined technologies to control the removal of VOCs in both phases.

Pulsed corona discharge treatment demonstrated its unequalled energy efficiency in NDEA and toluene oxidation. The difference in energy efficiencies at different pulse repetition frequencies pointed to the role of O₃-induced oxidation of NDEA, whereas in the case of toluene, reactions with surface-borne HO* were dominating. At neutral pH of natural water, PCD surpassed traditional ozonation in oxidation of aqueous NDEA in energy efficiency by about twenty-nine times, surpassing also the O₃/H₂O₂ combination by about 20%. In toluene oxidation at pH 7.0, the PCD treatment showed energy efficiencies in aqueous and gaseous toluene oxidation reaching up to 10.5 and 29.6 g·kW⁻¹·h⁻¹, respectively. Residual O₃ was detected in the outlet gas of PCD in both NDEA and toluene treatment, also demonstrating the presence of low concentrations of toluene and its by-product CO in the latter case.

In photocatalytic treatment, the positive effect of ozone in toluene oxidation was conditioned by its assistance in regeneration of the catalyst deactivated by toluene oxidation by-products. The increase in specific residence time (SRT) demonstrated enhanced conversion of ozone and VOCs, i.e., acetone and toluene. Properly selected conditions of photocatalytic oxidation over TiO₂-coated surface allowed complete degradation of VOCs, their mixture, and ozone, resulting in the formation of gaseous oxidation products such as water, CO₂, and minor amount of carbon monoxide. CO yield, however, did not exceed the permissible concentration for an eight-hour exposure.

The findings in the study contribute to the possible application of energy efficient chemical-free PCD in water treatment in larger scale as a possible addition and/or alternative to conventional water treatment technologies, whereas multi-section photocatalytic reactor with adjustable catalytic surface allowed to obtain necessary data for the development of effective technologies for the decomposition of air pollutants. The novel combination of PCD and photocatalytic reactor contributes to a possible application of the studied approach in closed-loop energy-saving ventilation systems.

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Abstract

Combination of Advanced Oxidation Methods for the Energy-Efficient Abatement of Aqueous and Gaseous Hazardous Pollutants

The presence of hazardous pollutants in the environment has become a worldwide concern due to their detrimental effect on living organisms. A variety of pollutants possess refractory character towards bio-oxidation, and separation techniques, which transfer the pollutant from one phase to another, requiring further handling. A viable solution to deal with such issue is the application of advanced oxidation processes (AOPs) with the aim to degrade organics, mainly by means of highly reactive hydroxyl radicals (HO^\bullet), into harmless products like H_2O and CO_2 in as energy efficient way as possible.

One of the well-known commercially available AOP for water treatment is ozonation, yet expensive synthesis and application of ozone dictates the search for cost-effective alternatives. Pulsed corona discharge (PCD) has demonstrated its unequalled energy efficiency in the oxidation of aqueous organics as a result of more efficient utilisation of reactive species, predominantly HO^\bullet and O_3 , compared to traditional ozonation. However, PCD treatment faces the problem of residual ozone in the air exhaust discharged from the setup. Besides, low concentrations of fugitive compounds are present in the air exhaust if volatile organic compounds (VOCs) are treated, therefore requiring a post-treatment. Photocatalytic oxidation successfully degrades low concentrations of airborne VOCs at ambient temperature. Combination of electric discharge treatment with downstream catalytic utilisation and destruction of ozone along with degradation of VOCs thus presents a method of choice. The pollutants under consideration in the present thesis were N-nitrosodiethylamine (NDEA), acetone and toluene. NDEA, a water disinfection product, is known to possess carcinogenic properties, while toluene and acetone, VOCs widely used in numerous industries, may affect the central nervous and respiratory systems.

The objective of the study was (i) to carry out the comparative study of PCD energy efficiency and traditional ozonation and its combination with H_2O_2 in aqueous NDEA abatement, the oxidation kinetics of which as a single pollutant have not been investigated earlier by either of treatment technologies; (ii) to study the influence of changing process parameters, i.e., initial pollutant concentration, residence and specific residence time (SRT), and humidity, on the degradation of acetone and toluene, and their mixture in the presence and absence of ozone using the unique continuous multi-section photocatalytic reactor with adjusting catalytic surface area for the development of air purifiers; monitoring of ozone depletion was also under the scope of the study; (iii) to evaluate the feasibility of the innovative advanced combination of PCD and photocatalytic reactor for the abatement of toluene in both, aqueous and gaseous phases, and O_3 from gaseous phase, since previous studies in the field has not considered the combined technologies to control the elimination of VOCs in both phases.

Ozonation was performed by continuously feeding O_3 -containing gas flow through a 600-mL batch glass reactor containing aqueous NDEA. The air-filled plasma reactor is 154 L in volume and includes a pulse generator that applies high voltage pulses to the electrodes: horizontal high voltage electrodes are concluded between two grounded vertical parallel plates, all made of stainless steel. A solution of 10 L in volume containing either NDEA or toluene was treated in PCD equipment in recirculation mode: the treated

water was pumped to the distribution box at the top of the plasma reactor and dispersed to the electric discharge zone through a perforated plate with 51 holes of 1 mm in diameter. In toluene oxidation, the gas samples from PCD reactor were directed into the photocatalytic modular reactor for post-treatment. The exhaust air, air polluted with acetone or toluene, or their mixture were treated under UV-A irradiation in the presence and absence of ozone over the photocatalytic surface of P25 TiO₂ in a continuous photocatalytic reactor consisting of five sequential sections, each with a volume of 130 mL. A slurry containing 5% wt. of TiO₂ in ethanol was sprayed onto borosilicate glass plates comprising 120 cm² per reactor section followed by drying at room temperature.

Pulsed corona discharge treatment demonstrated its unequalled energy efficiency in NDEA and toluene oxidation. At neutral pH of natural water, PCD surpassed traditional ozonation in the oxidation of aqueous NDEA in energy efficiency by about twenty-nine times, surpassing also the H₂O₂-assisted ozonation by about 20%. In toluene oxidation at pH 7.0, the PCD treatment showed energy efficiencies in aqueous and gaseous toluene degradation reaching up to 10.5 and 29.6 g·kW⁻¹·h⁻¹, respectively. Application of different pulse repetition frequencies resulted in a notable difference in energy efficiencies pointing to the role of O₃-induced oxidation of NDEA, whereas in the case of toluene, reactions with surface-borne HO[•] were favoured. Residual O₃ was detected in the exhaust air of PCD in both NDEA and toluene treatment, also showing the presence of low concentrations of toluene and its oxidation by-product CO in the latter case.

In photocatalytic oxidation, ozone exhibited a positive effect on toluene degradation via its assistance in regeneration of the catalyst surface deactivated by toluene by-products. The increase in SRT enhanced the conversion of ozone and VOCs, i.e., acetone and toluene. All airborne pollutants were photocatalytically degraded over TiO₂ coated surface under properly selected conditions resulting in the formation of gaseous oxidation products such as water, CO₂, and minor amount of CO in case of toluene. The latter, however, did not exceed the permissible concentration for an eight-hour exposure.

The findings in the study contribute to the possible application of energy efficient chemical-free PCD equipment in water treatment in large scale, whereas the continuous multi-section photocatalytic reactor helped to obtain valuable data for the development of energy efficient air purifiers. The studied approach of combination of PCD equipment and photocatalytic reactor provide a possible solution for application in closed-loop energy-saving ventilation systems.

Lühikokkuvõte

Süvaoksüdatsiooniprotsesside kombineerimine ohtlike saasteainete energiatõhusaks lagundamiseks vees ja õhus

Ohtlike saasteainete esinemine keskkonnas on oma kahjuliku mõju tõttu elusorganismidele kerkinud ülemaailmseks probleemiks. Mitmed saasteained on biooksüdatsioonile vastupidavad ning separatsiooniprotsesside puhul toimub saasteaine lagundamise asemel selle transport ühest maatriksist teise, nõudes seega lisa puhastusetappi. Paljulubavateks töötlemisprotsessideks on süvaoksüdatsiooniprotsessid (SOP), mis põhinevad saasteainete lagundamisel tugevate oksüdantide, peamiselt hüdroksüülradikaalide (HO^{\bullet}), abil.

Üheks laialdaselt veetötluses kasutusel olevaks SOP-ks on osoonimine. Osooni sünteesimine *ex situ* ja selle rakendamine muudab antud tehnoloogia aga üsna kulukaks, mistõttu on oluline pöörata tähelepanu kulutõhusama alternatiivi leidmisele. Koroonaimpulss elektrilahendus (KIEL) on osutunud mitmete saasteainete oksüdeerimisel vägagi energiatõhusaks meetodiks ning seda just KIEL reaktoris *in situ* tekkivate oksüdantide, enamasti HO^{\bullet} ja osoon, tõttu. KIEL tehnoloogia üheks puuduseks on jääkosooni esinemine seadmest väljuvas õhus, mis võib lisaks sisaldada veel ka lenduvaid orgaanilisi ühendeid (LOÜ). Sellest johtuvalt on vajalik heitgaasi edasine töötlemine. Järeltötlusena sobib fotokatalüütiline oksüdatsioon, mis võimaldab lagundada madalaid LOÜ-de kontsentratsioone. Käesolevas töös olid vaatluse all kolm saasteainet: N-nitrosodietüülamiin (NDEA), toluen ja atsetoon. NDEA on kantserogeenne vee desinfitseerimisel kloorühenditega tekkiv kõrvalprodukt. Toluen ja atsetoon on tööstuses laialt kasutusel olevad LOÜ-d, mis võivad avaldada kahjulikku mõju närvisüsteemile ja hingamisteedele.

Töö üheks eesmärgiks oli võrrelda omavahel KIEL-i ja osoonimise ning viimase kombinatsiooni vesinikperoksiidiga, energiaefektiivsusi NDEA lagundamisel vesifaasis. NDEA lagundamise kineetikat SOP-dega üksiku saasteainena ei oldud vaarasemalt uuritud. Töö eesmärgiks oli ka uurida erinevate töötingimuste, nagu saasteaine algne kontsentratsioon, viibe- ja eriviibeaeg ja suhteline õhuniiskus, mõju tolueni ja atsetooni ning nende segu lagundamisele osooni juuresolekul ja ilma, kasutades unikaalset fotokatalüütilist pidevas režiimis töötavat reaktorit, mis võimaldab muuta fotokatalüütilise pinna suurust vastavalt vajadusele. Oluline oli jälgida ka osooni kui toksilise õhusaasteaine lagundamist. Saadud tulemused on väärtuslikud tõhusate õhupuhastustehnoloogiate välja töötamiseks. Lisaks seati töös eesmärk hinnata KIEL-i ja fotokatalüütilise reaktori kombineerimise otstarbekust tolueni lagundamiseks nii vedelkui gaasifaasist ja osooni lagundamiseks gaasifaasist, kuna varasemalt puudusid uuringud LOÜ-de lagundamiseks kombineeritud tehnoloogiaid kasutades.

Osoonimise katsed viidi läbi 600 ml NDEA lahust sisaldavas segureaktoris, millest puhuti pidevalt läbi osooni sisaldavat gaasi. Gaasifaasiline KIEL-i reaktor on mahult 154 l ning hõlmab endas lisaks veel pulsigeneraatorit, mis rakendab elektroodidele kõrgpinge impulsse. Kõrgpinge elektroodid asetsevad horisontaalselt kahe maandatud vertikaalse paralleelse elektroodi vahel. Lahust töödeldi retsirkuleerivas režiimis. 10 l töötlemislahust, mis sisaldas vastavalt kas NDEA-d või tolueni, pumbati plasmareaktori ülemises osas asuvasse jaotuskambrisse ja piserdati plasmatsiooni läbi perforatsiooniga plaadi. Tolueni töötlemise puhul koguti hetkel, mil tolueni kontsentratsiooni vees enam ei tuvastatud, gaasiproovid, mis suunati edasiseks töötamiseks fotokatalüütilisse reaktoris. KIEL reaktorist pärineva tolueni ja osooni sisaldava heitgaasi ning kunstlikult valmistatud

gaasisegude, mis sisaldasid vastavalt kas atsetooni, tolueni, või mõlemat saasteainet ja mida töödeldi osooni juuresolekul ja ilma, puhastamiseks kasutati fotokatalüütilist reaktorit. Reaktor koosneb viiest sektsioonist, millest igaüks on mahult 130 ml ning varustatud UVA lambiga. Iga sektsiooni sisse on paigutatud 120 cm² suurune borosilikaatklaas, mis kateti käsitsi spreitamise teel suspensiooniga, mis sisaldas 5 massi% TiO₂ etanoolis. Katted kuivatati toatemperatuuril.

KIEL tehnoloogia osutus nii NDEA kui ka tolueni lagundamisel energiatõhusaks meetodiks. Loodusliku vee tavapärase neutraalse pH juures ületas KIEL NDEA lagundamisel traditsioonilist osoonimist ligikaudu 29 korda ning osooni kombineerimist vesinikperoksiidiga ligikaudu 20%. Tolueni oksüdeerimise puhul neutraalses keskkonnas ulatusid KIEL-i energiaefektiivsuse väärtused vee- ja gaasifaasis vastavalt 10.5 ja 29.6 g·kW⁻¹·h⁻¹. Erinevate pulsisageduste rakendamine tõi NDEA lagundamise puhul kaasa märgatava erinevuse energiaefektiivsuses, viidates seega osooni mõjule lagundamisprotsessis. Tolueni puhul oli erinevus pigem väike, mis viitab hoopis HO[•] rollile. Nii NDEA kui ka tolueni töötlemisel tuvastati KIEL seadmest väljuvas heitgaasis jääkosooni ning tolueni puhul ka madalaid tolueni ning selle laguprodukti – CO, kontsentratsioone.

Fotokatalüütilisel töötlemisel takistas osooni juuresolek katalüsaatori pinna saastumist tolueni laguproduktidega. Eriviibeaja suurendamisega kaasnes osooni ja LOÜ-de – atsetoon ja toluen, kõrgem konversioon. Sobilikud katsetingimused tagasid õhusaasteainete lagundamise veeks ja süsihappegaasiks. Tolueni puhul tuvastati ka CO teket, mis siiski ei ületanud lubatavat kontsentratsiooni kaheksatunnise kokkupuute korral.

Töös uuritud saasteainete energiatõhusat lagundamist tõestanud kemikaalivaba KIEL tehnoloogia võib tulevikus leida laialdasemat kasutust. Pidevas režiimis töötava mitmesektsioonilise katalüütilise õhupuhastusreaktoriga saadud tulemused omavad kõrget väärtust olemasolevate õhupuhastusreaktorite arendamisel ja uute välja töötamisel. KIEL reaktori ja fotokatalüütilise reaktori innovaatilist kombinatsiooni saab potentsiaalselt rakendada suletud energiasäästlikes ventilatsioonisüsteemides.

Appendix 1

Paper I

Kask, M.; Krichevskaya, M.; Preis, S.; Bolobajev, J. (2021). Oxidation of Aqueous N-Nitrosodiethylamine: Experimental Comparison of Pulsed Corona Discharge with H₂O₂-Assisted Ozonation. *Journal of Environmental Chemical Engineering*, 9, #105102.

Appendix 2

Paper II

Kask, M.; Bolobajev, J.; Krichevskaya, M. (2020). Gas-Phase Photocatalytic Degradation of Acetone and Toluene, and their Mixture in the Presence of Ozone in Continuous Multi-Section Reactor as Possible Air Post-Treatment for Exhaust from Pulsed Corona Discharge. *Chemical Engineering Journal*, 399, #125815.

Appendix 3

Paper III

Kask, M.; Krichevskaya, M.; Preis, S.; Bolobajev, J. (2021). Oxidation of Aqueous Toluene by Gas-Phase Pulsed Corona Discharge in Air-Water Mixtures Followed by Photocatalytic Exhaust Air Cleaning. *Catalysts*, *11*, #549.

Curriculum Vitae

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Defended dissertations

Master's Degree, 2017, Photocatalytic effect of Metal-Doped Organic Aerogels on Trimethoprim Degradation, Tallinn University of Technology, School of Engineering, Department of Materials and Environmental Technology. Supervisors: Juri Bolobajev, Anna Goi.

Involvement in research projects

PRG776 Innovative energy-efficient abatement of aqueous and airborne hazardous pollutants combining pulsed corona discharge plasma with catalysis/photocatalysis

VEU17119 Toward a smart & integral treatment of natural radioactivity in water provision services

IUT1–7 Chemical engineering approach to removal of priority pollutants and emerging micropollutants from water/wastewater and soil: implementation and optimization of advanced oxidation technologies

Awards

- 2021 Tallinn city Rae scholarship
- 2019 TalTech Development Fund, Rickard Kruusberg “Adventure through studies!” scholarship
- 2019 European Cooperation in Science & Technology (COST) scholarship
- 2019 Baltic Sea region university consortium for Science and Technology (BALTECH) scholarship
- 2019 Dora Plus program (activity 1.1) scholarship

Attendance at conferences and training schools

- 2021 Attendance with an oral presentation at online conference “Athens Conference on Advances in Chemistry”; March 10–14, 2021, Athens, Greece
- 2020 Attendance with poster presentation at Graduate School of Functional Materials and Technologies (GSFMT) scientific conference; February 4–5, 2020, Tallinn, Estonia
- 2019 Attendance with an oral presentation at training school “Aerogels processing, modelling and environmental-driven applications”; October 21–23, 2019, Coimbra, Portugal (COST scholarship)
- 2019 Attendance at summer school “4th International PhD Summer School”; August 26–30, 2019, Trakai, Lithuania (BALTECH scholarship)
- 2019 Attendance with a poster presentation at conference “The 6th European Conference on Environmental Applications of Advanced Oxidation Processes”; June 26–30, 2019, Portorož, Slovenia (Dora Plus scholarship)
- 2019 Attendance at summer school “3rd European Summer School on Environmental Applications of Advanced Oxidation Processes” with poster presentation; June 3–7, 2019, Alcoy, Spain (GSFMT financial support)
- 2019 Attendance with poster presentation at Estonian Chemistry Days, April 18, 2019, Tallinn, Estonia
- 2019 Attendance with poster presentation at Graduate School of Functional Materials and Technologies (GSFMT) scientific conference; February 4–5, 2019, Tartu, Estonia
- 2018 Attendance at summer school “Wastewater and biosolids management (WWSS18)”; July 22–27, 2018, Patras, Greece (GSFMT financial support)

Supervised dissertations

Sofia Pereskoka, Master's Degree, 2021, (sup) Maarja Kask; Juri Bolobajev, Application of ferrocene aerogel and iron-doped organic aerogel in Fenton-like and photolytic processes for oxidation of N-nitrosodiethylamine and trimethoprim in water – a comparative study, Tallinn University of Technology School of Engineering, Department of Materials and Environmental Technology.

Marko Jaaksaar, Master's Degree, 2020, (sup) Juri Bolobajev; Maarja Kask, Application of ozonation, photolysis and O₃/H₂O₂ combination for the oxidation of N-nitrosodimethylamine and N-nitrosodiethylamine – a comparative study, Tallinn University of Technology School of Engineering, Department of Materials and Environmental Technology.

Irina Petrotšenko, Master's Degree, 2019, (sup) Marina Kritševskaja; Maarja Kask, Effect of ozone on photocatalytic degradation of acetone vapour on P25 TiO₂ coating, Tallinn University of Technology School of Engineering, Department of Materials and Environmental Technology.

Publications

Kask, M.; Krichevskaya, M.; Preis, S.; Bolobajev, J. (2021). Oxidation of Aqueous Toluene by Gas-Phase Pulsed Corona Discharge in Air-Water Mixtures Followed by Photocatalytic Exhaust Air Cleaning. *Catalysts*, 11 (5), #549. DOI: 10.3390/catal11050549.

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Kaitstud lõputööd

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Osalemine uurimisprojektides

PRG776 Ohtlike vee ja õhu saasteainete lagundamine innovatiivse energiatõhusa kombineeritud impulss-koroona elektrilahenduse ja katalüüsi/fotokatalüüsiga

VEU17119 Parima veetöötlustehnoloogia rakendamine põhjavee kõrgeenenud loodusliku radioaktiivsuse korral

IUT1-7 Keemiatehnikapõhine lähenemisviis prioriteetsete saasteainete ja uute esilekerkivate mikrosaasteainete kõrvaldamisele veest/reoveest ja pinnasest: täiustatud oksüdatsioonitehnoloogiatega kasutamine ja optimeerimine

Tunnustused

- 2021 Tallinna linna Raestipendium
- 2019 TalTech arengufond, Rickard Kruusbergi nimeline stipendium "Seikle õpingute läbi!"
- 2019 European Cooperation in Science & Technology (COST) stipendium
- 2019 Baltic Sea region university consortium for Science and Technology (BALTECH) stipendium
- 2019 Dora Pluss programmi (tegevus 1.1) stipendium

Konverentsidel ja treeningkoolides osalemine

- 2021 Suulise ettekandega esinemine online konverentsil "Athens Conference on Advances in Chemistry"; 10.–14.03.2021, Ateena, Kreeka
- 2020 Posterettekandega esinemine Funktsionaalsete materjalide ja tehnoloogiate doktorikooli (FMTDK) teaduskonverentsil; 4.–5.02.2020, Tallinn, Eesti
- 2019 Suulise ettekandega esinemine treeningkoolitusel "Aerogels processing, modelling and environmental-driven applications"; 21.–23.10.2019, Coimbra, Portugal (COST stipendium)
- 2019 Enesetäiendamine suvekoolis "4th International PhD Summer School"; 26.–30.08.2019, Trakai, Lithuania (BALTECH stipendium)
- 2019 Posterettekandega esinemine konverentsil "The 6th European Conference on Environmental Applications of Advanced Oxidation Processes"; 26.–30.06.2019, Portorož, Sloveenia (Dora Pluss stipendium)
- 2019 Posterettekandega esinemine suvekoolis "3rd European Summer School on Environmental Applications of Advanced Oxidation Processes"; 3.–7.06.2019, Alcoi, Hispaania (FMTDK poolne finantseerimine)
- 2019 Posterettekandega esinemine Eesti Keemiaseltsi 100. aastapäeva teaduskonverentsil, 18.04.2019, Tallinn, Eesti
- 2019 Posterettekandega esinemine Funktsionaalsete materjalide ja tehnoloogiate doktorikooli (FMTDK) teaduskonverentsil; 4.–5.02.2019, Tartu, Eesti
- 2018 Enesetäiendamine suvekoolis "Wastewater and biosolids management (WWSS18)"; 22.–27.07.2018, Patra, Kreeka (FMTDK poolne finantseerimine)

Juhendatud magistritööd

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Marko Jaaksaar, magistrikraad, 2020, (juh) Juri Bolobajev; Maarja Kask, Osoneerimise, fotolüüsi ja O₃/H₂O₂ kombinatsiooni kasutamine N-nitrosodimetüülamiini ja N-nitrosodietüülamiini oksüdeerimiseks vees – võrdlev uuring, Tallinna Tehnikaülikool, Inseneriteaduskond, Materjali- ja keskkonnatehnoloogia instituut.

Irina Petrotšenko, magistrakraad, 2019, (juh) Marina Kritševskaja; Maarja Kask, Osooni mõju atsetooniauru fotokatalüütilisele oksüdeerimisele P25 TiO₂ katetega, Tallinna Tehnikaülikool, Inseneriteaduskond, Materjali- ja keskkonnatehnoloogia instituut.

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