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

OXIDATION OF TOLUENE BY PULSED CORONA DISCHARGE IN AIR-WATER MIXTURES FOLLOWED BY PHOTOCATALYTIC EXHAUST AIR PURIFICATION

TOLUEENI OKSÜDEERIMINE KOROONA-IMPULSS ELEKTRILAHENDUSEGA VEE- JA ÕHUSEGUDES KOOS JÄRGNEVA FOTOKATALÜÜTILISE ÕHUHEITE PUHASTUSEGA

MASTER THESIS

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Tallinn 2022

AUTHOR’S DECLARATION

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THESIS TASK

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Thesis topic:
(in English) Oxidation of toluene by pulsed corona discharge in air-water mixtures followed by photocatalytic exhaust air purification.
(in Estonian) Tolueeni oksüdeerimine koroona-impulss elektrilahendusega vee- ja õhusegudes koos järgneva fotokatalüütilise õhuheite puhastusega.

Thesis main objectives:

1. Performing a research on oxidation of toluene by pulsed corona discharge
2. Data collection and analysis
3. Making a literature review

Thesis tasks and time schedule:

No	Task description	Deadline
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CONTENTS

PREFACE

The thesis subject was proposed by autor supervisors Juri Bolobajev (researcher) and Maarja Kask (quality manager, AS Ida-Tallinna Keskhaigla). The practical work was conducted at Taltech's Laboratory of Environmental Technology. Juri Bolobajev and Maarja Kask consulted autor, helped with the selection of sources, helped with calculations and checked the work.

I'd want to express my thanks to my supervisors for their aid, patience, encouragemen and inspiration; I'm delighted to work with such excellent people. Additionally, I am grateful to the TalTech professors and lecturers for interesting lectures, practices, seminars and projects that have expanded my range of knowledge in chemical and environmental technology.

The aim of this thesis is to provide information about oxidation of toluene by pulsed corona discharge in air-water mixtures followed by photocatalytic exhaust air purification.

Key words: Plasma Oxidation, Toluene degradation, pulsed corona discharge, photocatalytic air purification, master thesis.

Tallinn,
January 2022
Arina Borissenko

List of abbreviations

AOP – Advanced Oxidation Processes
BTEX – Mixture of benzene, toluene, ethylbenzene and xylene
CNS – Central Nervous System
CSTEE – Scientific committee on toxicity, ecotoxicity and the environment
CD – Corona discharge
EPA – United States Environmental Protection Agency
FTIR - Fourier Tansform Infrared Spectroscopy
HDTMA – Hexadecyltrimethylammonium bromide
HPLC - High-Performance Liquid Chromatography
LD_{50} – The Median Lethal Dose
NTP – Nonthermal Equilibrium Plasma
Ppb – one part per billion
PCD – Pulsed Corona Discharge
PCO – Photocatalytic Oxidation
Ppm – one part per million
Pps – Pulses per second
SEE – Secondary Electron Emission
SMZ - Surfactant Modified Zeolite
SRT - Specific Residence Time
UV- Ultraviolet
VOC - Volatile Organic Compound
WHO - World Health Organization

INTRODUCTION

The anthropogenic impact on the environment has long been known to negatively affect the quality of air and water. For example, the inappropriate treatment and management of hazardous substances in industry may lead to their entering to air or water bodies. Among them are volatile organic compounds (VOCs) that pose a great environmental risk, because being mobile in both aqueous and gaseous phases their spread in environment could have massive effect with dramatically negative consequences. The discharge of VOCs containing wastewaters may inevitably lead to the drinking water pollution. Without any doubt, the presence of VOCs in drinking water deteriorate its quality indicators, making it unusable. Moreover, such components are capable of provoking dangerous diseases, e.g. liver and kidneys failures, disorders of the nervous system, and even oncology.

To cope with water and air pollution caused by VOCs, special technologies are used. They are separation processes, advanced oxidation processes (AOP), ozonation. Separation processes mainly involve methods such as adsorption, and reverse osmosis, which generally transfer a pollutant from one phase to another without decomposing it. A very promising alternative to the separation methods is the use of AOPs, which are aimed to chemically oxidize target pollutant until the formation of less hazardous compound, or even to complete mineralization, where the end products are H_2O and CO_2.

Toluene is a hydrophobic aromatic hydrocarbon with moderate toxicity found in wastewater at concentrations varied in the range between 0.2–12 900 $\mu g\ L^{-1}$. Toluene is widely used in a number of industries including paint and varnish production, oil refining and gas processing. Even dough wastewater containing toluene has undergone appropriate treatment, it may contain residual toluene, which is released into the atmospheric air. In urban air, toluene concentrations fluctuate within the range between 5–150 $\mu g\ m^{-3}$, and in places with high traffic intensity they reach up to 1310 $\mu g\ m^{-3}$. (WHO, 2000; Leusch et al., 2010). Thus, being a classic VOCs representative, this compound has gained significant attention in scientific studies aimed to improve wastewater treatment technologies for VOCs.

In this work, a low-temperature plasma generated by pulsed corona discharge (PCD) for purifying of water and air from toluene was investigated. The present method serves as an alternative approach to traditional AOP technology. The novelty of the present study is that toluene degradation path was monitored in both aqueous and gaseous phases. More importantly, the pulsed corona discharge was combined with a photocatalytic reactor, which allows to remove residual toluene and ozone generated in the PCD outlet gaseous phase.

1. LITERATURE REVIEW

1.1 BTEX, their sources and occurrence in environment

BTEX refers to a mixture of benzene, toluene, ethylbenzene and xylene. These chemicals belong to the class of volatile organic compounds (VOCs) found in petroleum and petroleum products such as gasoline. Being widely spread organic solvents BTEX are employed in several chemical industries like paints and lacquers production as well as in rubber, cosmetic and pharmaceutical products (Cseri, 2018).

The general sources to BTEX exposure commonly derive from contaminated air, or water. Possessing toxic and mutagenic properties (Headley et al., 2001) the long-term exposure to BTEX could result in dramatic consequences to human health. So, their removal from environment is an ultimately important task which deserves the corresponding research.

BTEX compounds are some of the most widely used solvents produced chemicals in the world. BTEX are produced in very large quantities usually from coal or petroleum. BTEX components could be present in environment nature in crude oil, in seawater near sources of oil and natural gas, in some plants, in gas emissions triggered by volcanoes and forest fires.

The main anthropogenic emissions of BTEX compounds into the environment occur through:

- the sources of unintentional emissions, e.g. emissions of gases from automobile and air transport, tobacco smoke, as well as oil spills, leaks of pipelines and underground storage tanks, combustion of coal and biomass;
- processes in which BTEX are used;
- manufactured by BTEX.

BTEX chemicals released into the environment volatilize into the air, partially dissolve in surface waters or groundwater, and can bind to enter soil and sediments. (WHO, 1985; Duan & Li 2017; Department of Environment and Science, 2010)
Being volatile compounds BTEX are generally present in atmosphere, where they are exposed to photochemical reactions induced by sunlight.

1.2 Toluene as BTEX chemical

One of the BTEX elements is toluene (methylbenzene) with a molecular formula C_7H_8. Toluene is formed when one hydrogen atom in a benzene molecule is replaced by a methyl group (Figure 1).

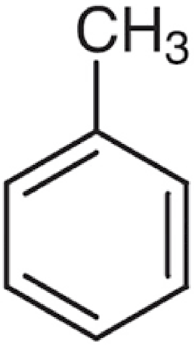

Figure 1. Chemical structure of toluene

Toluene belongs to the category of aromatic hydrocarbons with physical properities represented in Table 1. It is a volatile, transparent, colorless liquid with a sweet, pungent benzene-like odor. Toluene is a flammable chemical that does not react with dilute acids and bases as well as not corrosive. In atmospheric air, it quickly reacts with hydroxyl radicals to form a variety of oxidation products.

Table 1. Physical properties of toluene (Merck, 2021)

Property	Value
Molecular Weight	92.14 g mol^{-1}
Density	0.865 g mL^{-1} at 25ºC
Boiling Point	110-111ºC
Melting Point	-93ºC
Flash Point	4.4ºC
Viscosity	0.560 at 25ºC
Dielectric Constant	2.38 at 23ºC
Dipole Moment	0.375
UV cutoff	286 nm
Refractive Index	1.496 at 20ºC
Vapor Pressure	22 mm Hg at 20°C
Vapor Density	Vapor Density 3.2 (vs. air)

Purified toluene usually contains less than 0.01% benzene, and in industrial products its content can reach 25%. (WHO, 1985)

1.2.1 Sources of toluene and occurrence in environment

Toluene is produced both as a standalone product and as a component of various mixtures. Toluene is used as an independent product:

- for the production of other chemicals, for example, is a raw material for the production of toluene diisocyanate. It is widely used in the production of polyurethane foam, trinitrontoluene and of synthetic chemicals;
- as a solvent in paints, pharmaceuticals, silicone sealants, rubber, adhesives, varnishes and disinfectants;
- as additives, for example, to cosmetics;
- in fuel, toluene is used as an octane booster in gasoline for internal combustion engines, as a fuel for two-stroke and four-stroke engines, and as an admixture for jet fuel. Toluene, produced as a blend, is used for the secondary clarification of gasoline. (WHO, 1985; Duan & Li 2017; Department of Environment and Science, 2010)

The presence of toluene in soil is attributed to its ability for adsorption into this solid matrix. Moreover, the adsorption capacity of toluene increases with decreasing pH. Shifting of soil pH into neutral conditions induces the desorption of toluene, which inevitably leads to its entry into water or air. The remaining part in the soil participates in several types of chemical reactions and undergo biological degradation and biotransformation. Toluene released into natural waters and soil is removed by volatilization and biodegradation. (WHO, 1985)

Unated States Environmental Protection Agency (EPA) made the laboratory experiments on toluene and received results where 40-80% of toluene applied to the surface of sandy soils at concentrations of 0.9 and 0.2 mg/L was released into the air (set half-life 4.9 hours). The rate of evaporation depended on the type of soil and on the content of organic matter. The transfer of toluene from soil to groundwater has dire consequences in the form of contamination of drinking water sources. (EPA, 2005)

As the final link in the food chain, humans could be exposed to toluene through food as well. In the study made by EPA 59 fish meat samples were tested for the presence of toluene and 95% of them contained toluene at concentrations less than 1 mg/kg. Toluene has also been found in fish caught from waters contaminated with crude oil around oil spills and petrochemical plants in Japan. (WHO, 1985)

1.2.2 Common exposure to toluene and its negative impact to aquatic organisms and mammalians including humans

The threshold of acute action of toluene on aquatic biota is 1 mg/L. Aquatic organisms are exposed to toluene through respiration. This leads to a change in the permeability of the gills and as a result poisoning due to the carbon dioxide (CO_2) formation in the body.

The harmful effect of toluene on aquatic organisms, as well as on mammals, is due to its negative impact on central nervous system (CNS). Poisoning effect includes symptoms from mild agitation to lethargy and loss of balance, accompanied by shallow breathing, slow heart rate, loss of sensation and death. (IARC, 1989)

Acute toxicity levels for fish and aquatic invertebrates ranges from 3.7 to 1180 mg L^{-1}, but for most organisms the LD_{50} is approximately 15-30 mg L^{-1}. In addition, toluene is known to inhibit photosynthesis and the process of respiration of marine phytoplankton at a concentration of 34 mg/L. (WHO, 1985)

The study on the toxicity of toluene towards human organism was carried out mainly on people who were exposed to toluene via inhalation in experimental or industrial conditions, or with the deliberate use (as drugs) of solvent mixtures containing toluene. Toluene acts primarily on the CNS. Symptoms from airborne toluene poisoning include euphoria followed by weakness, disorientation, tremors, loss of memory and appetite, nausea, loss of vision, mood instability, tinnitus, diplopia, hallucinations, dysarthria, ataxia, seizures, coma, and even death. Toluene causes irritation of the skin and mucous membranes, and also has the ability to be absorbed into the body through the skin. (EPA, 2012)

Acute, controlled and occupational exposures to toluene in the range between 750-5625 mg m^{-3} induce dose-dependent changes in the CNS. Acute toxicity at high doses (37.500 mg m^{-3} and higher) with exposure time of several minutes, which could occur, for example, during industrial accidents, results in CNS excitation (increased mental activity, euphoria, hallucinations) with a progressive disorder of consciousness, which eventually ends in convulsions and coma. (WHO, 1985)

1.2.3 Reported concentrations of toluene in air and water

As it was stated previously, toluene is an important chemical in industry,which production is widespread in the world. According to industry sources, its worldwide manufacturing in 2018 was 30.2 million tons. 75% of production belongs to USA, Asia and Japan. Conforming to the Scientific committee on toxicity, ecotoxicity and the environment (CSTEE) statistic European production in 1995 was 2.6 million tons. However, much larger quantities, which are not included in this summary report, are generated during the production of petrol. (Statista, 2019)

Humans are exposed to toluene mainly through inhalation of its vapors present in the ambient air, by smoking cigarettes and, to a lesser extent, by consuming food and water contaminated with toluene. Some groups of people are exposed to significant doses of toluene in the workplace. Different countries have established occupational exposure levels for toluene, which could range from 200 to 750 mg m^{-3} for an 8-hour workday and a 40-hour week. (WHO, 1985)

Average atmospheric concentrations of toluene in urban areas range from 2 to 200 µg m^{-3}, whereas in agriculture areas toluene concentration levels could be as low as 0.2 – 4 µg m^{-3}. (WHO, 2004)

Based on the data and estimates available, 86% of the produced toluene ends up in the biosphere (predominantly in the troposphere). The half live of toluene ranges from several days to several months. In urban areas, toluene levels detected in ambient air are 0.0001 – 0.204 mg m^{-3}. Background levels recorded during monitoring at specific locations around the world indicate that populations are exposed to trace amounts of toluene.

Toluene concentrations in air are influenced by regional differences in production, use, emissions, meteorological processes, location and sampling method. For example, monitoring of atmospheric air in the town Kohtla-Järve near the Viru Keemia Grupp plant showed that the concentration of toluene in the air in March 2016 varied from 1.22 µg m^{-3} to 19.83 µg m^{-3} (Figure 2). (Keskkonnaamet, 2016)

Additionally to air contominations by toluene, it can be also found in several water sources, e.g. in drinking water (0 – 0.027 mg L^{-1}), well waters (0.005 – 0.1 mg L^{-1}) and in raw water (0.001 – 0.015 mg L^{-1}) (WHO, 1985). For example, the toluene content in Ordovician groundwater of the borehole of Avinurme town in Mustvee municipality was found to be 0.11 µg L^{-1}. (EERC, 2013)

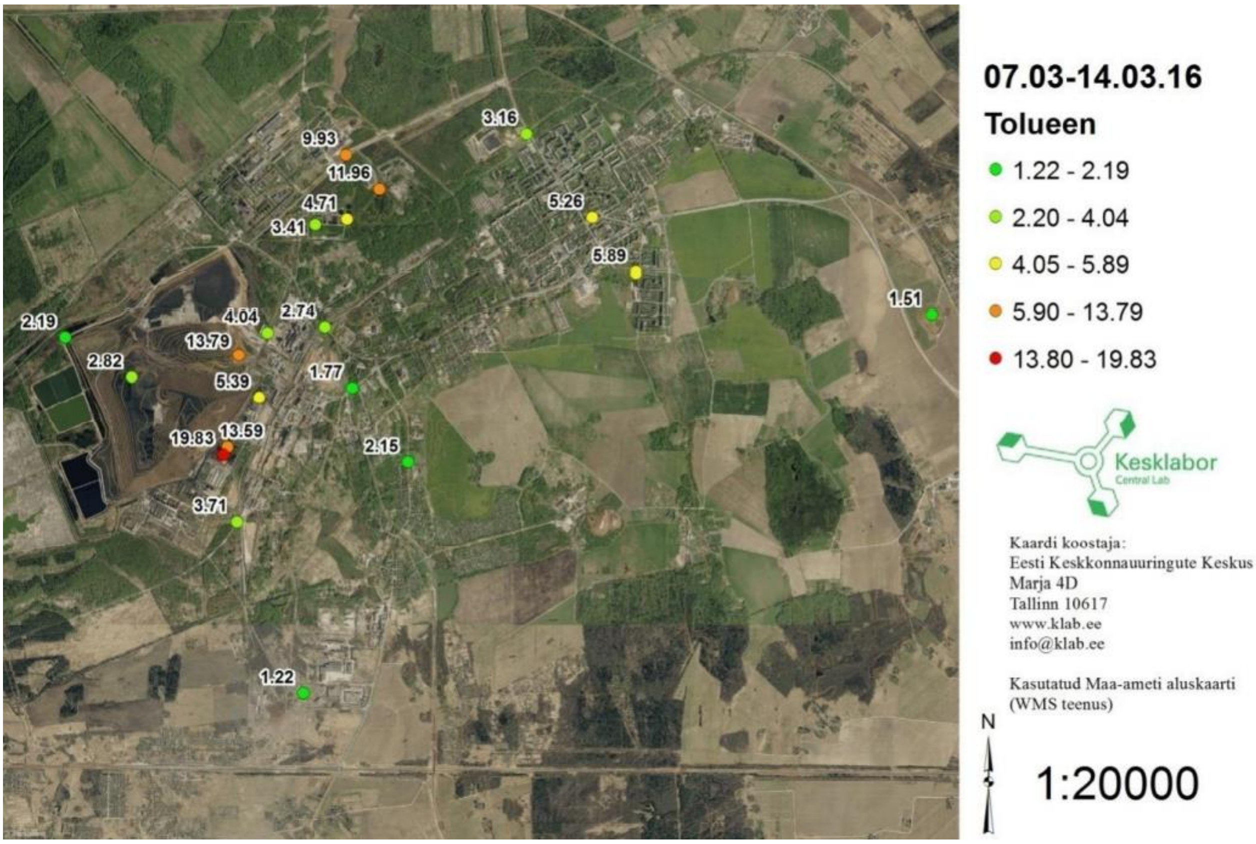

Figure 2. Periodic average concentration of toluene in Kohtla-Järve, 07.03-14.03.2016 (Keskkonnaamet, 2016)

1.2.4 Public health guidelines and government regulations towards toluene

In order to protect people and environment from toluene exposure, the specific guidelines intended for minimizing toluene presence in atmosphere, indoor air, water etc. are to be established. For example, the threshold limits for toluene concentration in air have been set by Estonian Government in "RT I 2001, 77, 460" directive (Table 2) (Töökeskkonna keemiliste ohutegurite piirnormid, 2001). In other derective "RT I 2010, 57, 374" are spesified standarts of groundwater quality and in regulation number 77 limits for toluene contsentrations that can be found in surface water (Table 3) (Veeseadus, 2010; Veeseadus, 2015).

Table 2. Toluene limits in air set by Estonian Government (Töökeskkonna keemiliste ohutegurite piirnormid, 2001)

Toluene limits	mg m^{-3}	ppm
Exposure limit (average concentration of the chemical in the inhaled air during the working day or working week)	200	50
Short-term exposure limit (maximum permissible concentration of the chemical in the inhaled air over a period of 15 minutes)	400	100
Limit values for ambient air pollution	200	50

Table 3. Toluene water pollution limits set by Estonian Government (Veeseadus, 2010; Veeseadus, 2015)

Toluene limits	µg L^{-1}
Threshold number for groundwater	0.5
Limit for groundwater and surface water	50

1.3 Technologies available for the removal of toluene from water and air

The anthropogenic load on the biosphere threatens with irreversible imbalance in ecological systems and calls into question the safe existence of living organisms. In this regard, it is necessary to pay continuous attention to environmental protection: monitor water and air quality, improve air and wastewater purification systems of industrial enterprises and cities, develop new and more effective methods of water and air purification.

In terms of chemical properties, toluene belongs to a group of aromatic hydrocarbons, the compounds of which are present in the wastewater of plastics, resins, varnishes, paints, in the rubber and petrochemical industries. Due to the exchange of liquid and air, which occurs in ventilated tanks or tanks with intensive stirring, toluene, due to its volatility, quickly enters the gaseous phase from the liquid phase. Thus, toluene is emitted into the atmosphere from various industries.

To avoid the release of toluene into the environment, the factories use technologies for the removal of toluene from wastewater and air. Available technologies is Advanced Oxidation Processes, Ozonation, Plasma oxidation, Separation processes, Pulsed corona discharge, Photocatalysis.

1.3.1 Advanced Oxidation Processes

Advanced oxidation processes (AOP) include a set of chemical treatment procedures designed to remove from water and wastewater the toxic or non-degradable materials such as aromatic hydrocarbons, pesticides, petroleum components, and volatile organic compounds by oxidation through the reactions with hydroxyl radicals ($OH^{\bullet}$). Radicals are used to either decompose organic and inorganic pollutants, or to disinfect water by killing pathogenic microorganisms. The HO• is the most powerful oxidizing agent after fluorine with an oxidizing potential (reduction oxidation potential HO• radicals is in the range of 1.9 – 2.85V and fluorine reduction oxidation is 2.87V). It exhibits higher oxidation rates than conventional oxidizing agents such as H_2O_2 or $KMnO_4$. In practical applications, the term AOP usually refers to a subset of such chemical processes like the use of O_3, H_2O_2, and UV light. (Chirwa & Bamuza-Pemu, 2010)

Table 4 illustrates the general classes of AOP. Differences in the various methods lie in the mechanism of formation of HO•. These classes include chemical processes, photolytic processes, photochemical processes, and photocatalysis. (Chirwa & Bamuza-Pemu, 2010)

Table 4. Classification of advanced oxidation processes (Chirwa & Bamuza-Pemu, 2010)

Advanced Oxidation Processes				
Chemical Processes:	Photolytic Processes:	Photochemical Processes:	Physical Processes:	Photocatalysis:
O_3	UV	O_3 / UV	Ultrasonic Cavitation	Titanium Dioxide / UV
H_2O_2	Vacuum UV	H_2O_2 / UV	Hydrodynamic Cavitation	Zinc Oxide / UV
O_3 / H_2O_2		O_3 / H_2O_2 / UV		Tungsten Oxide / UV
H_2O_2 / Fe (II)		H_2O_2 / Fe (II) / UV		

1.3.2 Ozonation

Historically the first AOP processes implemented in water treatment are chemical-based systems that use a single oxidant for pollutant degradation. Among them, ozonation is the example of an AOP process that can be used in water treatment either solely, or in combination with H_2O_2 as well as with ultraviolet radiation.

For more than eight decades, ozone has been utilized as a reagent in chemical synthesis, an industrial chemical, and an oxidant for water treatment. Ozone is a strong oxidant and disinfectant, with high thermodynamic oxidation potential (2.07V). In theory, ozone should be able to oxidize inorganic molecules to their most stable oxidation states while also oxidizing organic chemicals to carbon dioxide and water. In fact, ozone's oxidation processes are very selective. It is particularly useful in organic synthesis for cleavage of several chemical bonds, e.g. including those present in aromatic compounds. However, in terms of ozone application in water treatment, the oxidation rates may be too slow. (Glaze et al., 1987)

The following reactions (Equations 1-6) explain the ozonation mechanism (Chirwa & Bamuza-Pemu, 2010):

$$O_3 + OH^- \rightarrow HO_2 + O_2^- \quad (1)$$
$$HO_2 \leftrightarrow H^+ + O_2^- \quad (2)$$
$$O_2^- + O_3 \rightarrow O_2 + O_3^- \quad (3)$$
$$O_3^- + H^+ \rightarrow HO_3 \quad (4)$$
$$HO_3 \rightarrow O_2 + OH\bullet \quad (5)$$
$$O_3 + OH\bullet \rightarrow HO_2 + O_2 \quad (6)$$

The poor solubility of ozone in water is one of its main disadvantages as an oxidant. Another factor is the relatively high overall cost for producing the ozone as an oxidant for complete organic pollutants breakdown. The use of O_3 in water treatment is limited by mass transfer, and engineering methods to improve mass transfer rates would improve its oxidant efficacy even further.

In 2009 the Superior School of Chemical Engineering of National Polytechnic Institute conducted a study aimed to the degradation of BTEX by means of ozone generated in the gaseous phase. The tests were carried out in a tubular reactor (L = 1.5 m and d = 2.5 cm) (Figure 3). The overall experimental part was divided into two stages: first, pollutants were evaporated in oxygen flow to compose a gaseous mixture containing BTEX; second, liberated BTEX was decomposed by ozone in a tubular reactor. The efficiency of ozonation was determined by measuring the VOC content at the tubular reactor's output. The concentration obtained at the reactor's input was compared to the concentration obtained at the reactor's output. (Franco et al., 2012)

According to the acquired data, BTEX breakdown begins immediately after these organics are distributed throughout the reactor, but as one would expect, there is a significant disparity in the rates of interaction of organics with ozone. Thus, xylene decomposes more rapidly than the other BTEX components. On the other hand, under certain reaction circumstances, benzene cannot be entirely destroyed.

The findings of the experiments indicate that ozonation in the gaseous phase is effective at reducing BTEX emissions. The breakdown dynamics and degree of decomposition were dependent on the ozonation kinetics and operating conditions of the investigated VOCs. The degradation efficiency of original VOCs and intermediates were achieved under experimental settings including a flow rate of 0.2 L min^{-1} and an ozone content of 35 mg L^{-1}. (Franco et al., 2012)

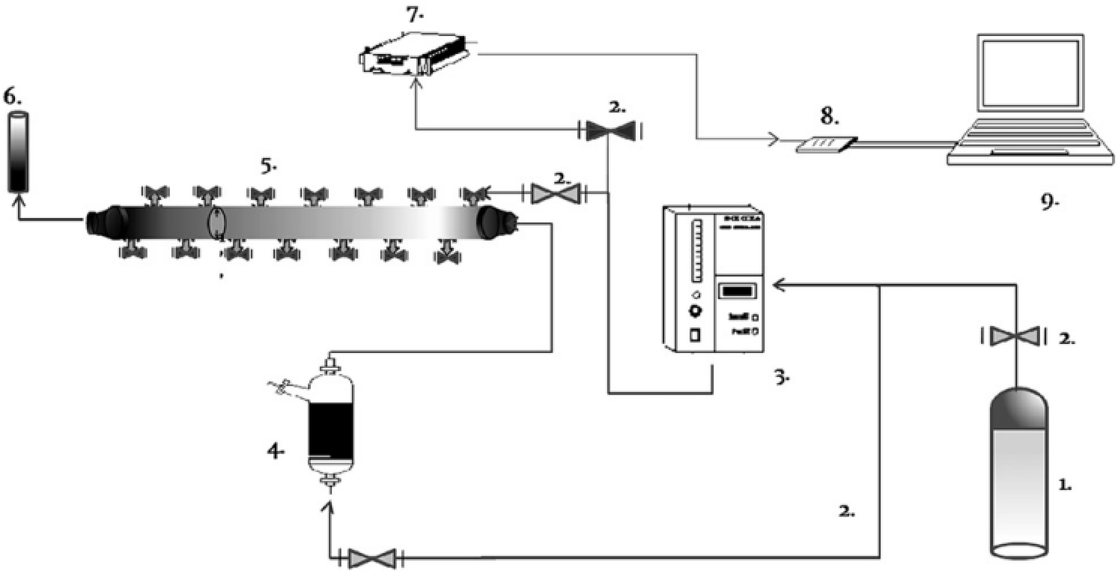

Figure 3. Schematic diagram of the ozonation: (1) oxygen tank, (2) valve step, (3) ozone generator, (4) reactor with model solution, (5) tubular gaseous phase reactor (6) activated carbon, (7) ozone analyzer, (8) data acquisition board, (9) data visualization (Franco et al., 2012)

1.3.3 Fenton reagent (H_2O_2/Fe(II))

In the treatment of organics in water and soil, the Fenton process is becoming more popular. Fenton reagent is a catalytic oxidative mixture that typically comprises a peroxide-based oxidant (usually H_2O_2) and a catalyst (transitional metals, commonly ferrous salts or oxides). The decomposition of H_2O_2 induced by Fe^{2+} ions results in the formation of very reactive and non-selective HO•. Equations 7-13 describe the chemistry of the process:

$$Fe^{2+} + \bullet OH \rightarrow Fe^{3+} + OH^{-} + \bullet OH \quad (7)$$
$$Fe^{3+} + H_2O_2 \rightarrow [Fe{-}{-}{-}OOH]^{2+} + H^{+} \quad (8)$$
$$[Fe{-}{-}{-}OOH]^{2+} \rightarrow Fe^{2+} + HO_2\bullet \quad (9)$$
$$Fe^{2+} + HO_2\bullet \rightarrow Fe^{3+} + HO_2^{-} \quad (10)$$
$$Fe^{3+} + HO_2\bullet \rightarrow Fe^{2+} + H^{+} + O_2 \quad (11)$$
$$\bullet OH + H_2O_2 \rightarrow H_2O + HO_2\bullet \quad (12)$$
$$2HO_2\bullet \rightarrow H_2O + O_2 \quad (13)$$

Nowadays, the Fenton process has been widely researched and several improved procedures like the electro-Fenton, photo-Fenton UV-Fenton and others Fenton-like systems have been presented. Combination of UV light and the Fenton reaction mixture possesses synergistic effect, where UV light promotes the decomposition of hydrogen peroxide as well as increases the overall oxidation efficiency. It is known that hydrogen peroxide can be directly decomposed into HO• by UV radiation instead of the usual decomposition of hydrogen peroxide catalyzed by iron. (Yan et al, 2016)

Compared with other conventional pollutants chemical removal approaches, e.g. physical absorption, photo-catalytic oxidation, the UV-Fenton process demonstrates significant benefits such as its high degradation ability, the absence of secondary contamination and low operating cost.

Interestingly, the UV-Fenton process is regarded to be a promising technology in landfill gas treatment for the elimination of BTEX. The tests were conducted at room temperature. Deionized water was used to fill the bubble column, and the initial pH was corrected using NaOH and HCl. H_2O_2 and $FeSO_4$ were added immediately after the carrier gas was directed into the bubble column (Luchun Yan et al, 2016).

Hydrogen peroxide was the predominant source of oxidants (i.e., HO•) in the Fenton reaction. Certain amount of the organic pollutants was immediately decomposed by UV light. The Fenton process was responsible for the degradation of organic matter entered the aqueous phase by means of gas-liquid mass transfer. Again, UV light supported the Fenton-based oxidation of BTEX pollutants. So, the utilization of hydrogen peroxide was significantly enhanced. This was usually ascribed to UV-synergistic light's action. The suggested UV-Fenton system (Figure 4) demonstrated specific properties via BTEX degradation, including high oxidation ability, huge handling capacity, and reuse of chemicals, such as Fe(II) salts. Contrary to that, the mere Fenton process and UV treatment were less effective for BTEX oxidation. (Luchun Yan et al., 2016)

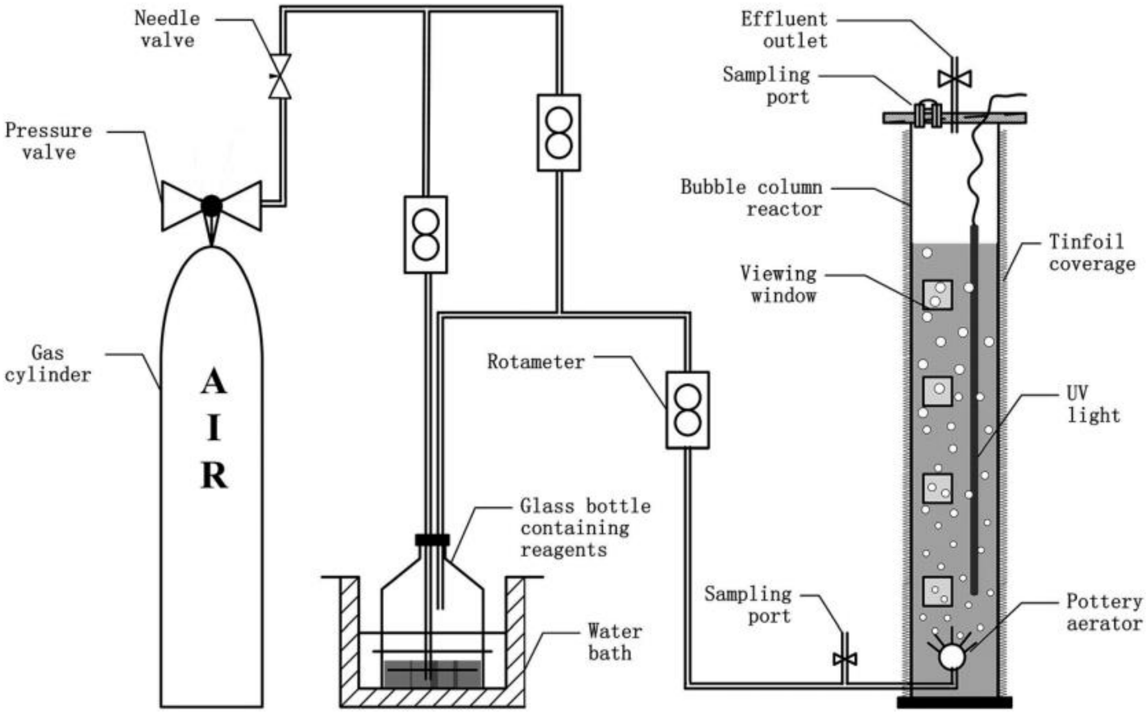

Figure 4. Schematic UV-Fenton system (Luchun Yan et al, 2016)

1.3.4 Separation processes

BTEX has been successfully removed from wastewaters using a variety technologies based on conventional separation processes. Adsorption, biological treatment, membrane filtration, biodegradation, thermal oxidation, catalytic and chemical oxidation, absorption, condensation, solvent extraction, and air stripping are common approaches for removing of volatile organic chemicals. (Eydi et al., 2018)

Among them, adsorption remains the most flexible and commonly utilized process because of its high efficiency and ease of operation. Due to the ability to recover both the adsorbent and the adsorbate, it is one of the finest and the cost-effective substitutes for treating water contaminations.

Activated carbon, zeolites, modified clays, polymeric resins, coal, fly ash, metal oxides, and silicas are some of the adsorbents utilized in the adsorption process. In order to increase the sorption properties of functional material, most of them need preliminary conditioning, for example, zeolites are mostly hydrophilic. So, their surfaces are frequently chemically transformed to increase the material hydrophobicity allowing thereupon adsorbing organic molecules.

For this purpose, the long chain cationic surfactant hexadecyltrimethylammonium bromide ($C_{19}H_{42}BrN$ or HDTMA) is used. When zeolites are treated with HDTMA, its cationic exchange sites are occupied with HDTMA’s organic cations to produce a surfactant layer. Because organic molecules are bigger than zeolite pore diameters, surfactant molecules are bonded to the exterior surface, leaving the interior pore open to adsorbate molecules. As a result, in the synthesis of organo-zeolites, cation exchange capacity is a significant feature. Organic compound adsorption on surfactant modified zeolite (SMZ) is already recognized to be an effective approach for removing pollutants from water. SMZ may concurrently adsorb polar and non-polar molecules from water. It is a feasible alternative to other adsorbents due to relatively low cost of modified zeolites. (Ehsan Farsouni Eydi et al., 2018)

1.3.5 Plasma Oxidation & Pulsed corona discharge

Such a phenomenon as plasma began to be studied back in the 17th century. In nature, people can encounter plasma in the form of lightning or the aurora borealis.
Plasma is known as the fourth state of matter and comprises positive ions, electrons or negative ions, and neutral particles. It make up more than 99% of visible matter in the celestial sphere. Plasma is generated when a large quantity of energy is delivered to a gas by an electric discharge, the electrons that escape from atoms or molecules enable ions to move more freely and create additional electrons and ions via collisions. The higher is the quantity of free electrons and ions, the more changeable become the electrical properties of gas. The latter results in the formation of ionized gas or plasma.

For example, the mechanism of plasma generation from a solid state of matter is shown in Figure 5.

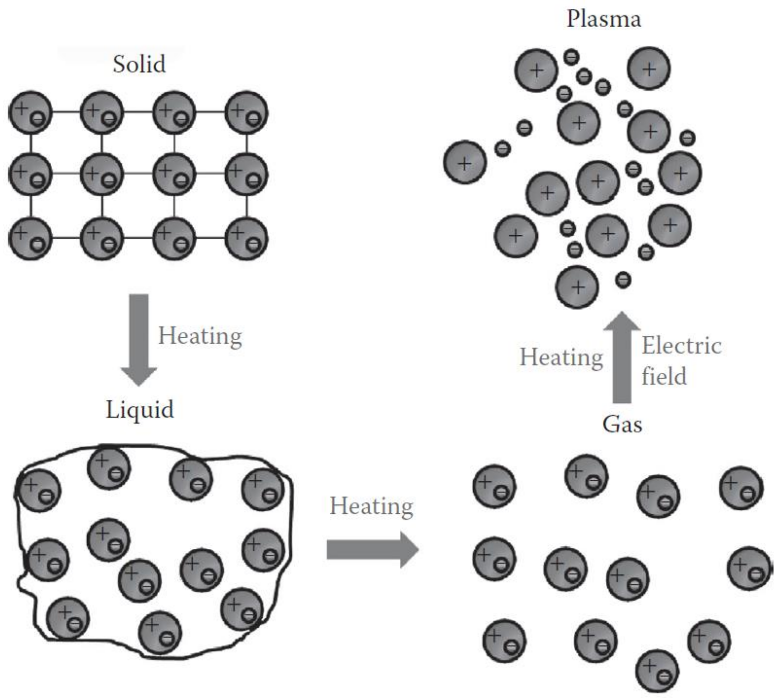

Figure 5. Transformation of state of aggregation (Chu & Lu, 2013)

This phenomenon can be divided into several classes as following (Chu & Lu, 2013):

- High-Pressure Plasma
- Low-Pressure Plasma
- Thermal Equilibrium Plasma
- Nonthermal Equilibrium Plasma (NTP)
- Local Thermal Equilibrium Plasma

The NTP electron temperature is much highter than that of ions and neutrals (Chu & Lu, 2013). Because of the powerful electrons that contribute to plasma chemistry processes and the ability to quickly oxidize contaminants at ambient temperature, NTP may save energy and be alternative to traditional approaches. Nonthermal equilibrium plasma possesses a non-selective oxidation properties and may serve as a perfect tool in environmental technologies aimed to chemical degradation/oxidation of organic pollutants. Therefore, many research studies have placed the particular attention on the plasma generating methods including electric discharge reactors, which are known to have high efficacy in the degradation of organic matter, e.g. VOCs. (Yao et al, 2018) Corona discharge (CD), glow discharge, arc discharge, capacitively linked discharge, inductively coupled discharge, wave heated plasma - all produce NTP. This types of plasma generation could be successfully implemented in environmental engineering, aeronautics and aerospace engineering, biomedicine, textile technology and analytical chemistry. (Chu & Lu, 2013)

CD as one of the most widely used NTP, has gained attention in the area of VOC abatement, owing to its simple discharge reactor construction and capacity to treat large volumes of gas pollutants without pressure drop. (Yao et al, 2018). Conventional ozonation is frequently replaced with Pulsed corona discharge (PCD) ozonation, which is an energy-efficient alternative that generates ozone and HO• in humid air and most likely on the treated surface of the water (Eq. 14): (S. Preis et al. 2013)

$$\bar{e} + H_2O > \bar{e} + H\bullet + HO\bullet \quad (14)$$

Yao et al. (2018) reported the study on the implementation of corona discharge as a method for degradation of toluene in the gas phase. The experimental setup (Figure 6) comprised corona discharge reactor, high-voltage direct current (DC) source, optical detection system, surface potential test system and gas analysis equipment. The positive corona discharge method used a wire-plate reactor manufactured of plexiglass.

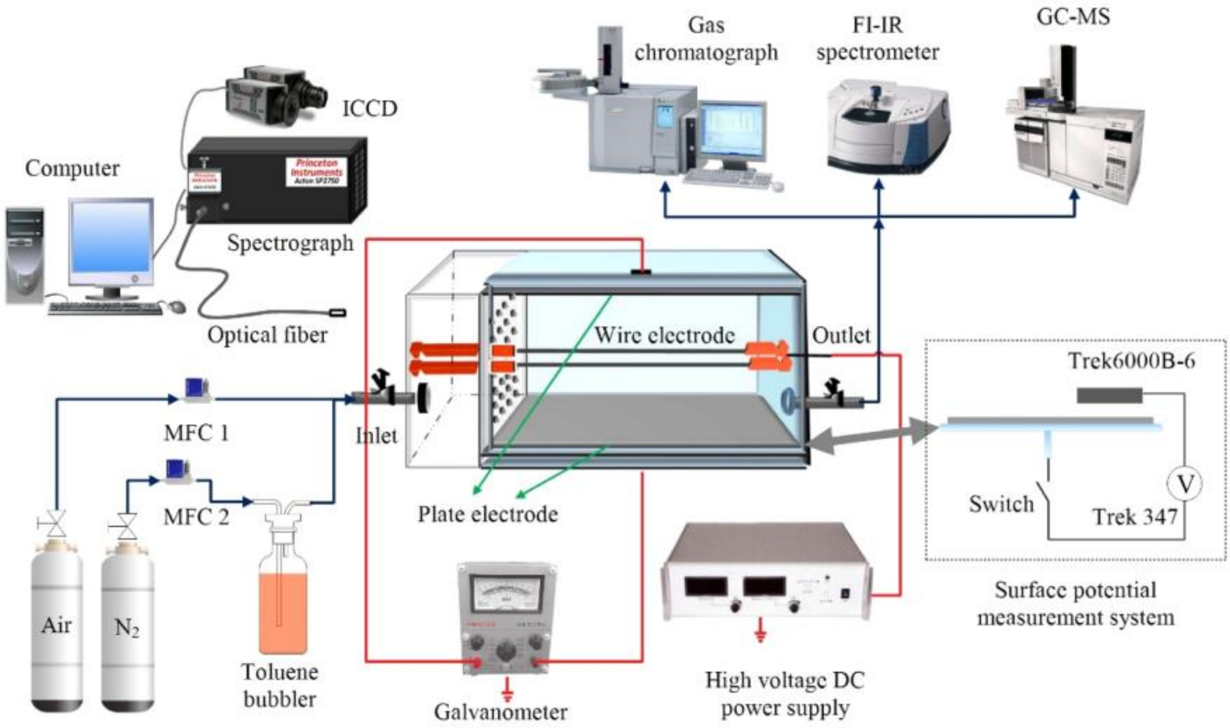

Figure 6. Schematic of the experimental setup (Yao et al., 2018)

Compressed air was used in toluene feeding system to dilute the vaporized toluene which was produced by bubbling toluene liquid in the presence of a N_2 gas stream. In order to determine the toluene degradation efficiency gaseous samples from the reactor influent and effluent were analyzed for the presence of toluene and CO_2 concentrations. (Yao et al, 2018) (Figure 7).

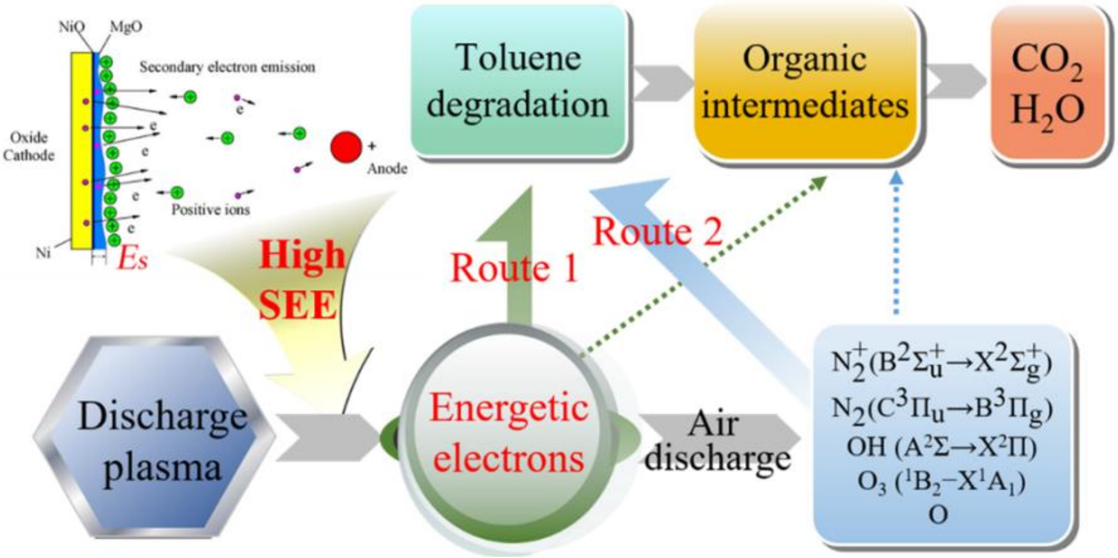

Figure 7. The toluene degradation mechanism (Yao et al., 2018)

The secondary electron emission (SEE) yields of the produced MgO/NiO/Ni and NiO/Ni cathodes were determined using a SEE yield measuring method.

In comparison to discharges with Ni cathodes, discharges with oxide cathodes result in an increase of O_3 concentration. Due to the fact that O_3 creation is caused by plasma and toluene breakdown (Eq. 15–17), it is evident that a competitive process for oxygen atoms exists between toluene molecule degradation and O_3 molecule synthesis.

$\bar{e} + O_2 \rightarrow \bar{e} + O + O$ (15)
$O + O_2 + M \rightarrow O_3 + M$, (where M are air molecules) (16)
$C_6H_5{\cdot}CH_3 + O \rightarrow C_6H_5CH_2O + H$ (17)

Additionally, oxygen atoms are thought to be critical in the degradation of toluene based on the presence of organic intermediates such as the synthesis of benzaldehyde throughout the process (Eq. 17) (Yao et al, 2018).

1.3.6 Photocatalysis in gaseous phase

The growing concern about human health risks associated with indoor air pollution has greatly increased the global interest towards photocatalytic oxidation (PCO) for VOC elimination.

Gas phase photocatalysis is a process that degrades organic contaminants in the air by using the synergetic interaction of light, a semiconductor catalyst, and O_2 or H_2O producing oxidizing agents as a result. Oxygen and water adsorption on the surface of photocatalyst may generate reactive radicals, e.g. HO•, HO_2• etc., that are also present in water matrix during the photolytic processes. Suggesting that photocatalytic oxidation (PCO) is capable of removing organic contaminants from the air. Chemisorption and photochemistry studies on H_2O, O_2, and CO_2 advanced the concept of PCO removal of VOCs for air purification. Photocatalysis has a plenty of benefits over traditional processes such as adsorption or filtering because organic contaminants could be completely oxidized to CO_2 and H_2O, whereas physical methods of separation transfer pollutants from one matrix to another without destroying them. (Boyjoo et al., 2017; Gholami et al., 2014)

Since the process of photocatalysis is generally conducted under ambient conditions, it is compatible with heating, ventilation, and air conditioning equipment. Additionally, photocatalysis demonstrates high efficacy at low concentrations of pollutants (ppb or ppm), which are common for contaminated air in workplaces and buildings.

The mechanism of photocatalysis comprises the generation of electron-hole pairs (Figure 8) on the surface of semiconductor caused by the electromagnetic irradiation (usually UV light). The holes may either directly oxidize adsorbed contaminants or form highly reactive HO• from water adsorbed on the catalyst as well. HO• is known to be very reactive oxidant. After that, the charge transfer loop is ended by mixing the leftover electron with O_2. The following equation (Eq. 18) summarizes the photocatalytic oxidation of organic pollutants (Boyjoo et al., 2017):

$$\text{Organic Pollutants} + O_2 \xrightarrow{\text{Catalyst + UV Light}} CO_2 + H_2O + \text{Mineral Acid} \qquad (18)$$

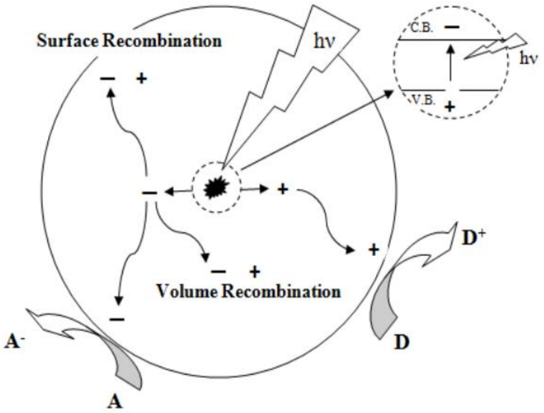

Figure 8. The scheme of electron-hole pair generation (Ipek & Uner 2012)

Numerous investigations on the photocatalytic degradation of environmental contaminants utilizing semiconductors such as TiO_2, Fe/TiO_2, and ZNO/TiO_2 have been conducted. TiO_2 is a metal oxide, which exists in nature in four well-known polymorphs: anatase (tetragonal), brookite (orthorhombic), rutile (tetragonal), and TiO_2 with monoclinic crystalline structure. The anatase form has been discovered to have the most advantageous photocatalytic oxidation (PCO) features, since it is the most active form in terms of photocatalytic properties. Irradiation with a wavelength of less than 385 nm results in the formation of electron–hole pairs in anatase. In the majority of commercial PCO procedures, the anatase form is utilized.

The Figure 9 shows an example of the photocatalytic experimental setup with annular packed bed reactor. Authors reported that using the present air treatment assembly toluene degradation rates rose either with UV intensity increase, or initial pollutant concentration decrease. (Gholami et al., 2014)

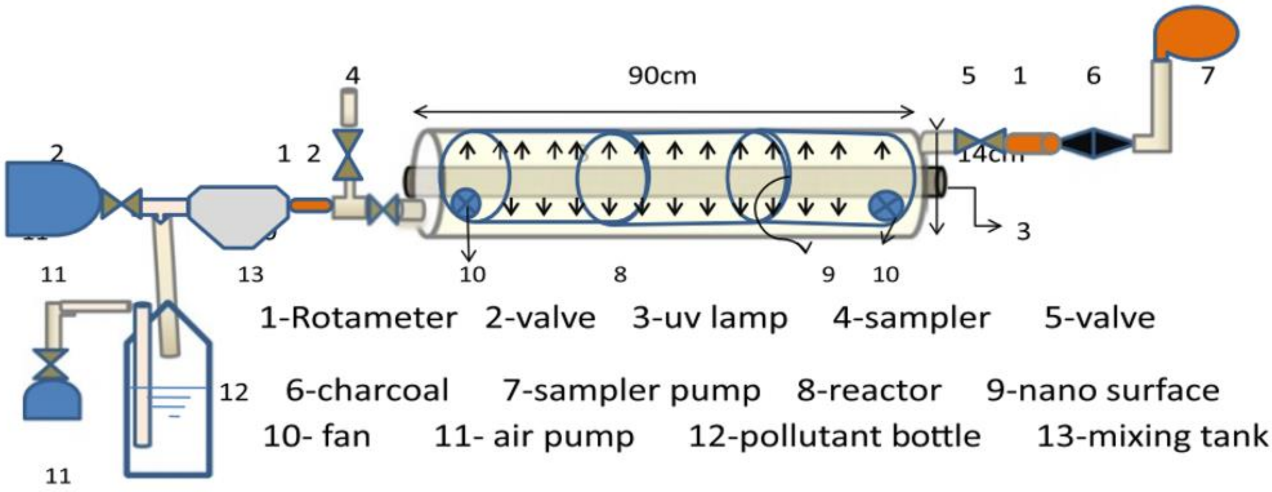

Figure 9. Photocatalysis setup scheme with annular packed bed reactor (Gholami et al., 2014)

Toluene can be found in high concentrations in polluted air both indoors and outdoors, making it one of the most studied model pollutants in PCO studies. The light source is critical to PCO as it affects the first phase of electron-hole pair generation induced by photocatalysis. The following equations explain the breakdown processes of toluene (Eq. 19–27). (Boyjoo et al., 2017)

$2HO_2 \rightarrow O_2 + H_2O_2$ (19)
$H_2O_{2,ads} + O_2{}^{-}{}_{,ads} \rightarrow OH^{-} + HO\bullet + O_2$ (20)
$HO\bullet + C_6H_5CH_{3,ads} \rightarrow H_2O + C_6H_5CH_2\bullet$ (21)
$C_6H_5CH_2\bullet + O_2{}^{-}{}_{,ads} \rightarrow C_6H_5CH_2OO\bullet$ (22)
$C_6H_5CH_2OO\bullet + \bar{e} \rightarrow C_6H_5CH_2O + OH^{-}$ (23)
$C_6H_5CH_2O_{ads} + HO\bullet\ {}^{-}\!\!\rightarrow C_6H_5CO\bullet + H_2O$ (24)
$C_6H_5CO\bullet + O_{2\,,ads} \rightarrow C_6H_5COOO\bullet$ (25)
$C_6H_5COOO\bullet + C_6H_5CHO_{ads} \rightarrow C_6H_5CO\bullet + C_6H_5COOOH_{ads}$ (26)
$C_6H_5COOOH_{ads} + C_6H_5CHO_{ads} \rightarrow 2C_6H_5COOH_{ads}$ (27)
$2C_6H_5COOH_{ads} \rightarrow C_6H_6 + CO_2$ (28)

The partial oxidation produces benzaldehyde, benzoic acid, and trace amounts of benzyl alcohol and phenol as intermediates. It is known that certain oxidation intermediates, e.g. benzene, formed during the oxidation of toluene contaminate the photocatalyst's surface. Palladium was found to increase the resistance of TiO_2 towards the deactivation induced by oxidation intermediates. The presence of palladium in TiO_2-based photocatalysts could reduce the formation of benzene preventing therefore catalysts contamination. (Boyjoo et al., 2017)

2. MATERIALS AND METHODS

2.1 Reagents and chemicals

Toluene (C_7H_6, ≥ 99%), sodium hydroxide (NaOH, ≥98%), acetic acid glacial (CH_3COOH, ≥99.7), were purchased from Sigma-Aldrich (St. Louis, MO, USA). Acetonitrile (CH_3CN for HPLC, ≥ 99.9%) and sulfuric acid (H_2SO_4, 96%) were obtained from Honeywell (Charlotte, North Carolina, US) and Lach-Ner (Czech Republic), respectively.

All other reagents were of analytical grade at greater than 95% purity used without further purification. Toluene aqueous solutions were prepared using distilled water.

2.2 Determination of toluene

2.2.1 Determination of toluene in liquid phase

The concentration of toluene in liquid phase was determined using a high-performance liquid chromatography (HPLC, YL Instrument Co., Republic of Korea) equipped with a UV/Vis detector and a C18 column (Waters XBridge, 130 Å pore size, 3.5 μm particle size, 150 mm length, and 3.0 mm inner diameter). Eluent flow rate was set to 0.2 mL min^{-1} throughout the 13-minute sample run. Isocratic elution was performed using 70% ultrapure water pre-acidified with acetic acid (0.1% solution, w/w) and 30% acetonitrile. pH of studied solutions was adjusted with either 5-M H_2SO_4, or 5-M NaOH and determined using a digital pH meter (S220 Mettler Toledo, Switzerland).

2.2.2 Determination of toluene in gaseous phase

The residual toluene and O_3 concentrations in air were assessed using Fourier transform infrared spectroscopy (FTIR, Interspec 200-X, Estonia). Gaseous samples were collected in the Specac Tornado 8-m 1.33-L gas cell and analyzed in the 500–4000 cm^{-1} wavelength range. The spectrum was taken in each gaseous sample and analyzed using essential FT-IR software (Operant LLC) equipped with a quantitative database (FDM, HiRes VPFTIR for Quant). The concentration of O_3 in gaseous samples was assessed using either FTIR spectroscopy, or MP-6060 ozone analyzer (Anseros Klaus Nonnenmacher GmbH, Germany). All measurements were repeated to ensure that the standard deviation was less than 5%.

2.3 Combined pulsed corona discharge and photocatalysis setup

The present research was aimed to combine PCD and photocatalysis. A composite approach allows simultaneous removing of toluene from polluted water and air. Figure 10 demonstrates a principal scheme of studied setup. The PCD reactor was responsible for the oxidation of target pollutant in aqueous and gaseous phases, whereas the following photocatalytic treatment served as a polishing step for purification of air exhaust.

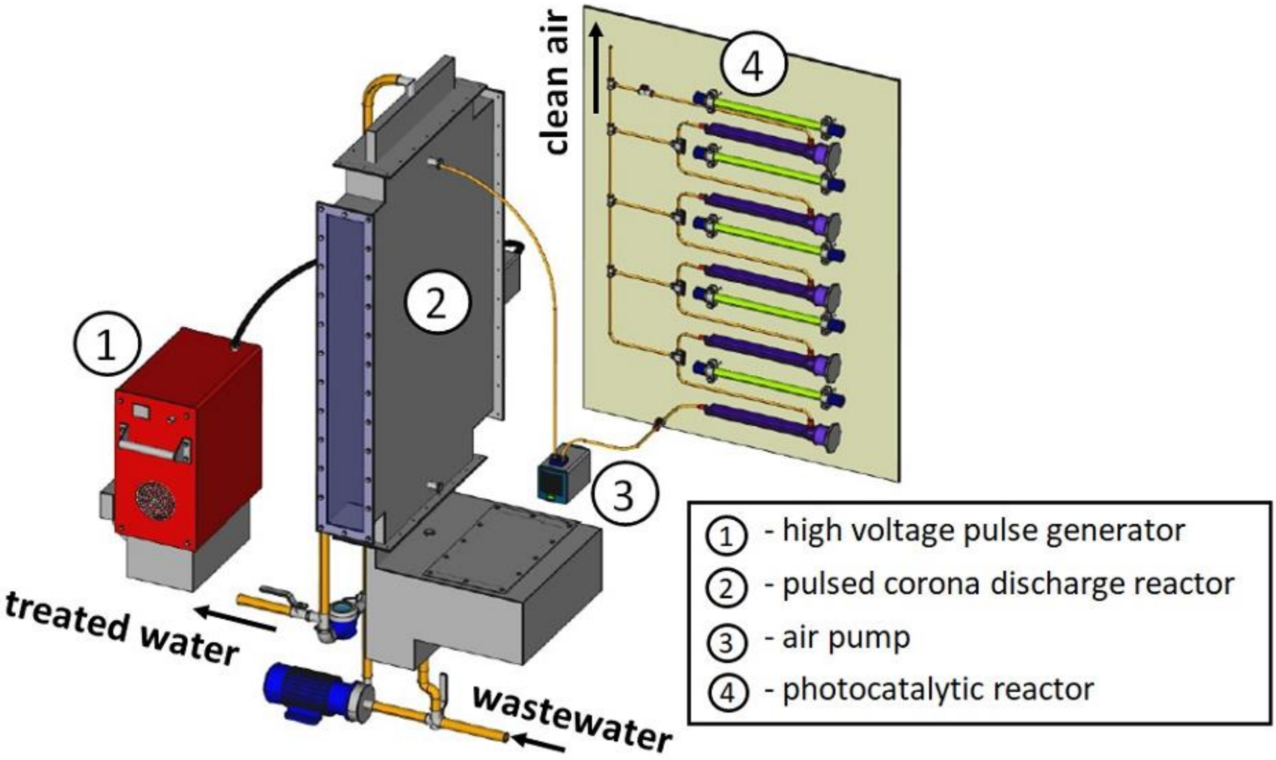

Figure 10. 3D illustration of the PCD equipment with the photocatalytic reactor.

2.3.1 Pulsed Corona Discharge

The PCD setup (Flowrox Oy, Finland) consists of a 154L reactor with a 40L storage tank, a pulse generator, and a circulation pump (Iwaki Co. Ltd., Japan) (Figure 11). A perforated plate with 51 holes of 1 mm diameter was used to spread aqueous solution into into the plasma zone. High voltage pulses (20 kV) were applied between two horizontal voltage electrodes constructed of 0.55 mm diameter stainless-steel wire with a total length of 20 m and two vertical grounded stainless-steel parallel plates having repetition frequencies of 50, 200, and 880 pps producing 9, 32, and 123 W of output power, respectively.

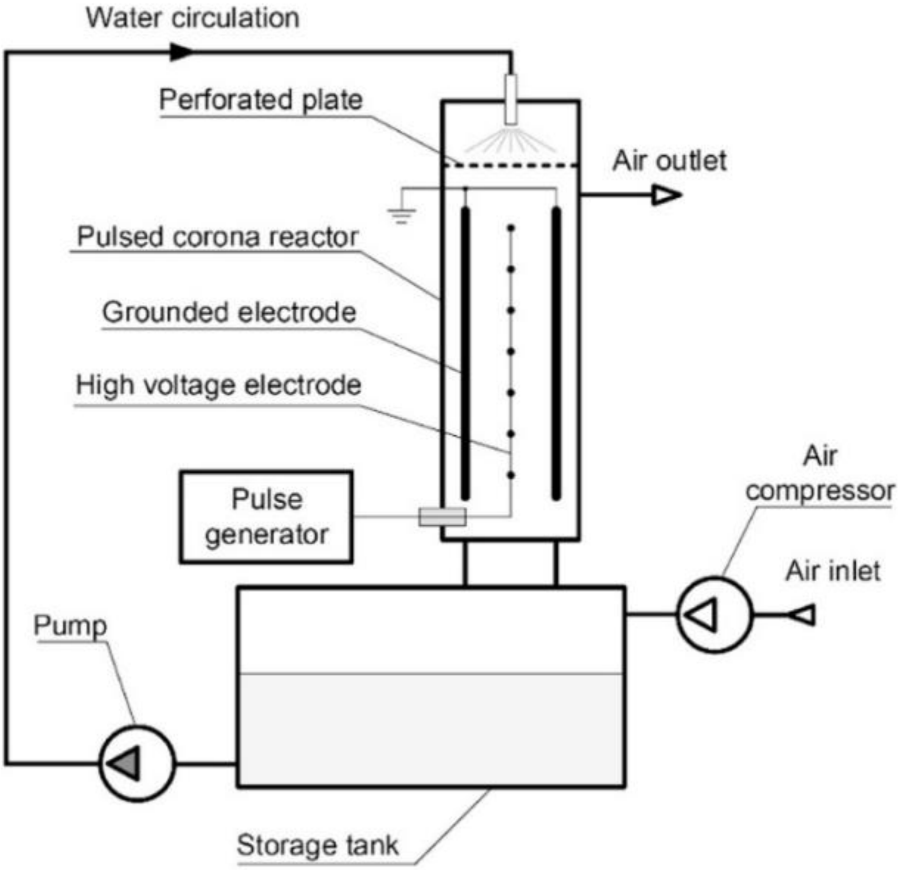

Figure 11. Schematic illustration of PCD equipment (Kask et al., 2021)

Precise dosing of aqueous toluene into the reactor comprised several challenges. Toluene belongs to VOCs and being dissolved in water tends to rapidly evaporate to the ambient air. To prevent the significant evaporation, toluene solutions were stored in hermetically closed jars and supplied into the PCD reactor using a peristaltic pump (Masterflex, USA). In the beginning of each experiment 10 L of freshly prepared toluene aqueous stock solutions were pumped into PCD reactor. At 20°C, equilibrium aqueous concentrations of toluene were found to be 1.0, 3.7, and 6.3 mg L^{-1} which were obtained from stock solutions originally containing roughly 10, 30, and 50 mg L^{-1} of toluene. These values consistently resulted in equilibrium airborne toluene concentrations of 0.4, 1.0, and 1.6 mg L^{-1} in the PCD reactor's total free gaseous volume. At a temperature of 30 °C, equilibrium was attained in solutions containing 30 mg L^{-1} with an aqueous concentration of 2.5 mg L^{-1} and an airborne toluene content of 1.2 mg L^{-1}. To increase the temperature of the solution, an integrated spiral coil heater was used.

2.3.2 Calculation of toluene equilibrium concentrations in gas-liquid system

The amount of toluene in both gaseous and aqueous phases is determined by Henry's law, according to which the equilibrium concentration of volatile compound in water is proportional to its partial pressure above liquid (Eq. 29) (Sander, 2015).

$$C_{aq} = k_H \cdot P_i \tag{29}$$

,where C_{aq} – molar concentration of toluene in aqueous phase, mol L^{-1};
k_H – Henry's law toluene solubility constant (water-air partitioning coefficient), mol kg^{-1} bar^{-1};
P_i – toluene partial pressure above water solution under equilibrium conditions, bar.

The temperature dependence of Henry's equilibrium constant could be generally estimated using Eq. 30:

$$k_H = k_{H_0} \times exp^{d\left[\frac{lnH}{\left(\frac{1}{T}\right)}\right]\left(\frac{1}{T}-\frac{1}{T_0}\right)} , \tag{30}$$

where k_H is Henry's law solubility constant;
k_{H_0} is Henry's law solubility constant at reference temperature, mol kg^{-1} bar^{-1};
T is the temperatuure of toluene solution, K;
T_0 is a reference temperature of 298.15 K;
According to Leighton et al. (1981), d(lnH)/d(1/T) and k_{H_0} are 3700 and 0.15, respectively.

The process of toluene evaporation and the formation of equilibrium concentration are schematically illustrated in Figure 12.

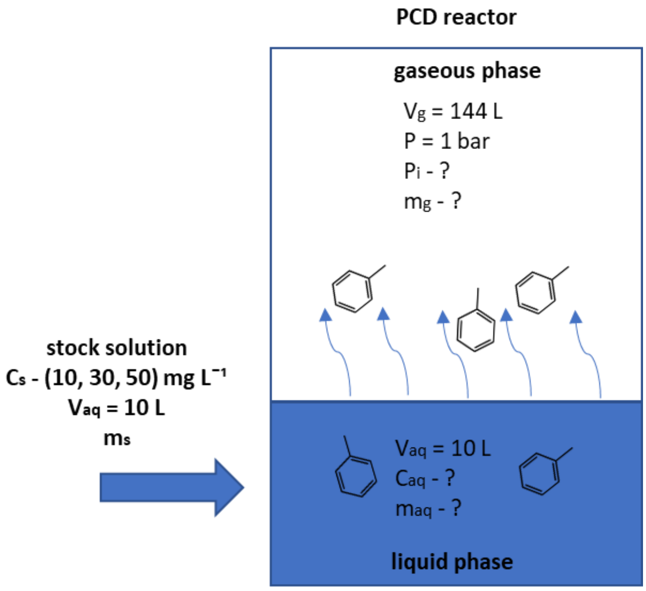

Figure 12. Schematic illustration of toluene equilibrium state in both aqueous and gaseous phases

According to that, toluene evaporates from water in the reactor chamber until the equilibrium between aqueous and gaseous phases is achieved. Toluene mass-equilibrium could be described in terms of mass-balance using Eq. 31 and Eq. 32:

$$m_s = m_{aq} + m_g \tag{31}$$

$$\frac{C_S \cdot V_{aq}}{1000} = C_{aq} \cdot V_{aq} \cdot Mr + \frac{10^5 \cdot C_{aq} \cdot V_g \cdot Mr}{1000 \cdot k_H \cdot R \cdot T}, \tag{32}$$

where m_s, m_{aq}, and m_g are toluene masses in stock solution, aqueous, and gaseous phases, respectively;

C_s – aqueous concentrations of toluene in stock solution, mg L^{-1};

C_{aq} – aqueous concentrations of toluene in the PCD reactor in equilibrium, mol L^{-1};

V_{aq} – volume of aqueous phases in the reactor chamber, m^3;

V_g – volume of gaseous phases in the reactor chamber, m^3;

Mr – toluene molar mass (92.14 g mol^{-1});

R – universal gas constant (8.314 m^3 Pa K^{-1} mol^{-1});

T – temperature, K;

10^5 is the coefficient for the conversion of pressure units (from bars to Pascals) and 1000 considers the conversion between mg ang g, or L and m^3.

Using mass-balance from Eq. 31 the following equilibrium concentrations were calculated (Table 5).

Table 5. Toluene concentrations.

Toluene concentration in stock solution (C_s), mg L^{-1}	Toluene equilibrium concentration in aqueous phase (C_{aq}), mg L^{-1}	Toluene equilibrium concentration in gaseous phase (C_g), mg L^{-1}
10	2.26	0.54
30	6.77	1.61
50	11.29	2.69

Although the calculated equilibrium concentrations are somewhat higher than measured ones, this difference could be considered as acceptable because of certain losses of toluene during the preparation and dosing of stock solution. Being volatile compound toluene tends to rapidly evaporate during its dissolving in water, and thus, the overall procedure of solution preparation and dosing became technically sophisticated and needed special methodology.

Toluene aqueous solutions were treated in a recirculation regime in which they were constantly sprayed into electric discharge zone using circulation pump at the flow rate of 1.0 m^3 h^{-1}. The PCD reactor was hermetically sealed to prevent toluene vapor leaks into ambient air.

The process efficiency was assessed in terms of energy consumption by PCD setup using Eq. 33 (Onga, 2020). Energy efficiency E (g kW^{-1} h^{-1}) was calculated at the point, where 40% of toluene was oxidized.

$$E = \frac{\Delta C \cdot V}{W}, \qquad (33)$$

where ΔC is the decrease in toluene concentration, g m^{-3};
V is the volume of treated sample, m^3;
and W is the consumption of energy, kWh.

Delivered energy, kWh m^{-3} was calculated using Eq. 34:

$$\text{Delivered energy} = \frac{P \cdot t}{V} \qquad (34)$$

To achieve equilibrium concentrations of toluene in the liquid and gas phases, 10 L of toluene solution was recirculated in PCD reactor for 10 minutes before starting the PCD treatment and for 5 minutes prior each sample withdrawal from the reactor. Gas samples from the PCD reactor were collected and analyzed for the presence of toluene and ozone using an air pump (KNF Neuberger S.A.S., France). After PCD treatment, the gaseous exhaust was directed to the photocatalytic reactor for the following processing.

2.3.3 Photocatalytic Oxidation

The photocatalytic treatment of air exhaust from a PCD reactor was carried out using TiO_2-coated (P25, Evonik) glass plates in the presence of UVA-emitting fluorescent lamps (Philips, Actinic T8, 15 W) in a multi-section continuous reactor consisting of five sequential sections with a volume of 130 mL each (0.9×4.9×29.5 cm) and wall thickness of 0.2 cm (Figure 13). Thus, the catalyst-coated surface area per section was 120 cm^2, with a TiO_2 surface density of 1.4 ± 0.2 mg cm^{-2} and a coating thickness of about 1 μm.

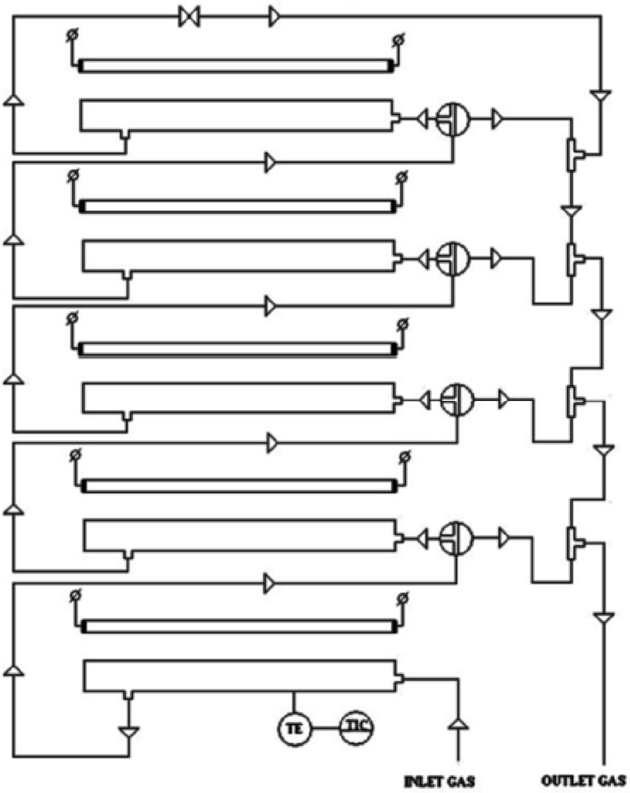

Figure 13. Schematic illustration of photocatalytic reactor, where TIC – temperature indicator controller, TE – temperatuure (Kask et al., 2021)

The air temperature (38±1°C) within the reactor maintained by the heat from UV lamps and the use of the reflector was measured using a temperature controller equipped with a K-type thermocouple (Omega, CN9000A). A flow metering valve was used to regulate the gas flow rate (Swagelok, SS-6MG-MM). The flow rates of 0.5, 1.0, and 2.0 L min^{-1} were used to get 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}.

3. RESULTS AND DISCUSSION

3.1 Oxidation of toluene by PCD in aqueous phase

The oxidation of PCD could be characterized using a second-order kinetic law (Eq. 35) (Preis et al., 2013):

$$\frac{dC}{dt} = \frac{k_2 \cdot C \cdot P}{V}, \qquad (35)$$

where k_2 is the second-order reaction rate constant of compound degradation induced by PCD, $m^3\ J^{-1}$;
C is the toluene concentration, mol m^{-3};
P is the pulsed corona discharge power, W;
V is the plasma zone volume, m^3.

The second-order kinetic constants and efficiency values of aqueous toluene PCD oxidation for this study are listed in Table 6.

Table 6. The second-order kinetic constants and efficiency values for PCD oxidation in aqueous toluene.

PCD treatment conditions	k_2 10^{-7}, $m^3\ J^{-1}$	R^2	Efficiency of toluene oxidation for 40%, g $kW^{-1}\ h^{-1}$	
			Aqueous	Airborne
(a) C_0=6.3 mg L^{-1} , 880 pps, initial pH 7.0, 20°C	6.9	0.9981	7.5	22.3
(b) C_0=6.3 mg L^{-1} , 200 pps, initial pH 7.0, 20°C	8.3	0.9964	8.6	27.0
(c) C_0=6.3 mg L^{-1} , 50 pps, initial pH 7.0, 20°C	10.7	0.9905	10.5	29.3
(d) C_0=3.7 mg L^{-1} , 200 pps, initial pH 7.0, 20°C	12.4	0.9994	7.5	23.0
(e) C_0=1.0 mg L^{-1} , 200 pps, initial pH 7.0, 20°C	37.0	0.9938	6.4	13.7
(f) C_0=3.7 mg L^{-1} , 200 pps, pH 3.0, 20°C	12.5	0.9887	7.6	22.4
(g) C_0=3.7 mg L^{-1} , 200 pps, pH 12.0, 20°C	13.0	0.9943	7.6	24.9
(h) C_0=2.5 mg L^{-1} , 200 pps, initial pH 7.0, 30°C	12.2	0.9984	5.3	29.5

Figure 14 and Table 6 (a, b, c) illustrates the oxidation of aqueous toluene at its equilibrium concentration of 6.3 mg L^{-1} at pulse repetition frequencies of 50, 200, and 880 pulses per second (pps). It shows that oxidation rates increase with pulse repetition frequency, whereas energy efficiencies (Figure 14, B) possess modest variations resulting in 10.5, 8.6, and 7.5 g kW^{-1} h^{-1} at 50, 200, and 880 pps, respectively. The difference in energy efficiencies could indicate that at lower repetition frequencies the role of ozone in toluene oxidation increases, because the longer is the pause between pulses, the higher could be the contribution of long-living ozone towards the degradation of the compound. However, the molecular oxidation of organics by ozone is generally slow and the present difference of energy efficiencies is not remarkable.

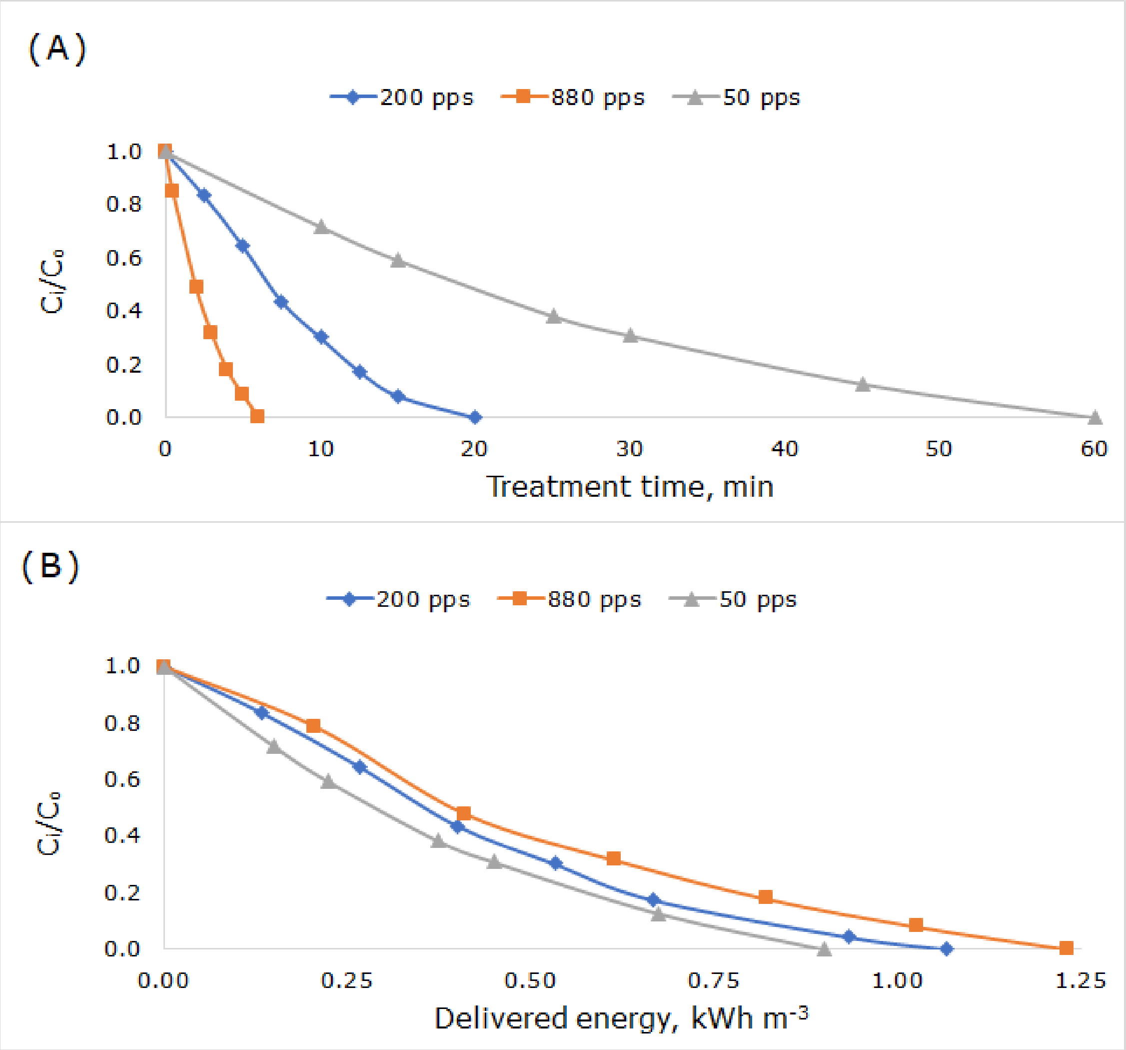

Figure 14. Degradation of aqueous toluene dependent on treatment time (A) and delivered energy (B) at pulse repetition frequencies of 50, 200, and 880 pps: C_0=6.3 mg L^{-1}, starting pH 7.0, 20°C.

3.2 Oxidation of toluene by PCD in aqueous and gaseous phase

Further experiments were conducted with various toluene concentrations (Table 6 (b, d, e)) at a constant pulse repetition frequency of 200 pps. Figure 15 depicts toluene degradation over the time in both aqueous and gaseous phases, as well as the differences in oxidation rates depending on the aqueous toluene starting concentration. As the method of sampling considered 5 min pause before sample withdrawal from the reactor, this ensured achieving toluene equilibrium between phases. Therefore, toluene concentration reduction in both phases followed similar pattern.

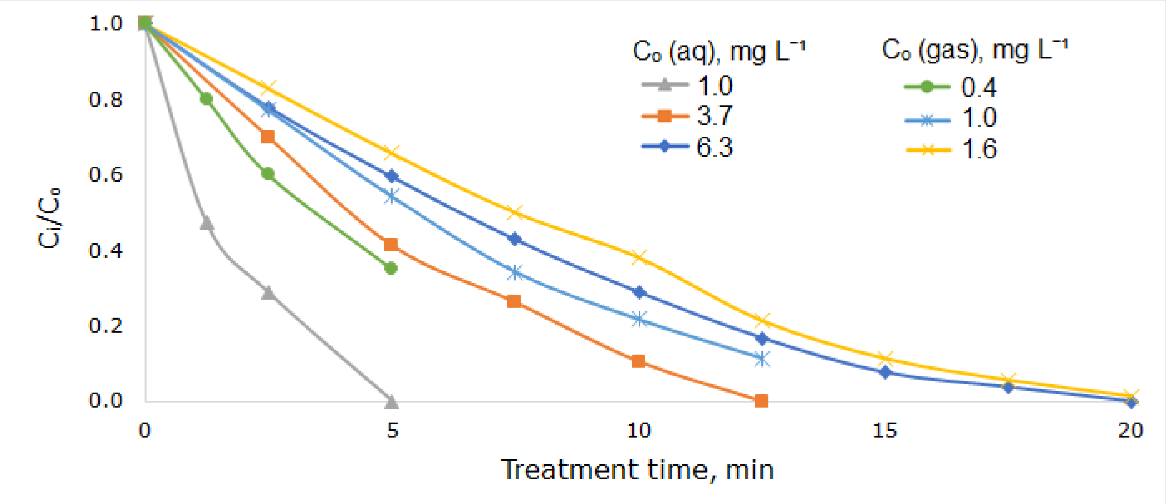

Figure 15. Simultaneous toluene PCD oxidation in aqueous and gaseous phases dependent on treatment time at different concentrations: pulse repetition frequency of 200 pps, initial pH 7.0, 20°C.

Table 6 (b, d, e) illustrates the influence of toluene oxidation energy efficiency on its initial concentration: values of 6.4, 7.5, and 8.6 g kW^{-1} h^{-1} correspond to initial equilibrium aqueous toluene concentrations of 1.0, 3.7, and 6.3 mg L^{-1}. As it can be seen in Table 6 the efficiencies of airborne toluene oxidation are generally two to three times higher than that of aqueous one, which could be explained by the role of interface-borne HO• in the gas phase. More importantly, the successful result of airborne toluene degradation confirms the relevance of volatile pollutants abatement by PCD in gas-liquid systems.

At higher temperatures (30°C) the difference rose to about fivefold. Obviously, this was caused by a larger gas-phase equilibrium concentration.

3.3 Ozone measurements in gaseous phase

The profile of gaseous ozone concentration points to its unambiguous participation in the oxidation process: the higher is the toluene concentration, the slower is the rise of the ozone concentration (Figure 16). Additionally, concentration values also indicate ozone consumption during oxidation (Preis et al., 2013).

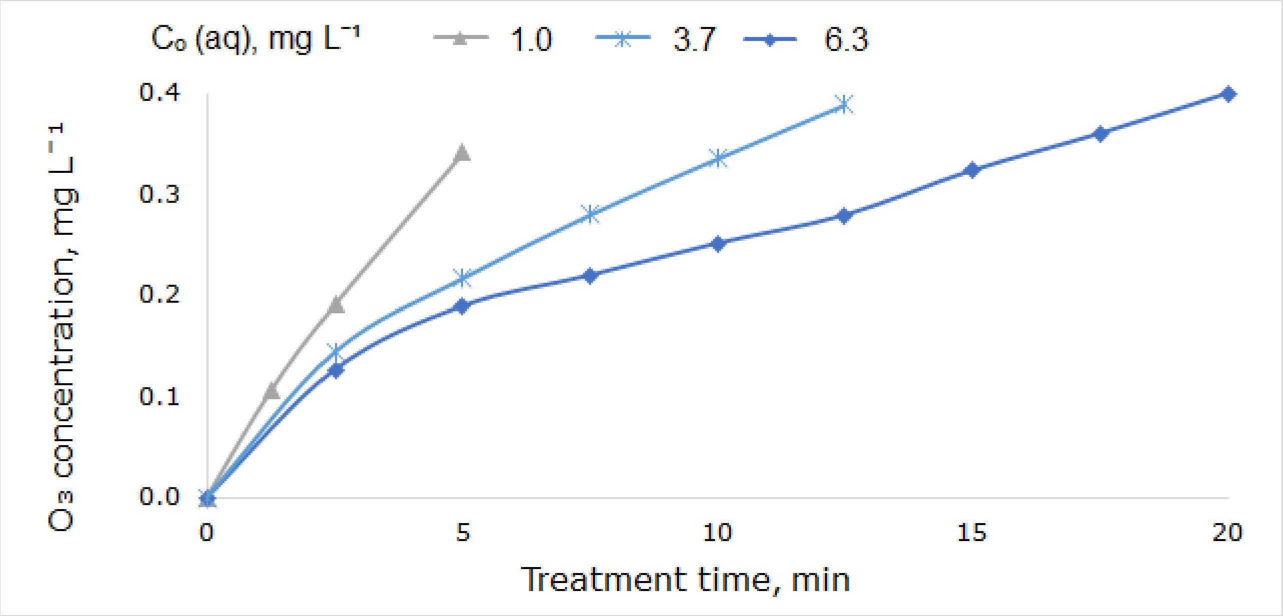

Figure 16. Gaseous ozone in PCD reactor in time of treatment dependent on initial aqueous toluene concentration: pulse repetition frequency 200 pps, pH 7.0, 20 °C.

3.4 Influence of temperature and pH.

The role of pH and temperature was investigated at toluene initial equilibrium concentration of 3.7 mg L^{-1}. While the pH of acidic and alkaline solutions remained constant during the treatment, the pH of neutral solutions decreased from 7.0±0.1 to 4.5±0.2 in 12.5 minutes owing to the production of carboxylic acids and inorganic acids such as nitric and nitrous acids. Variations in pH had little influence on the degradation of aqueous toluene (Table 6 (d, f, g)), despite the fact that basic pH conditions increase the breakdown of aqueous ozone, generating additional HO• radicals and in theory alkaline pH should promote the oxidation. However, due to extremely low concentration of ozone dissolved in water this effect was not remarkable. For example, according to Henry's law for ozone, 0.22 mg L^{-1} of gaseous ozone in the reactor (Figure 15) may yield only 0.07 mg L^{-1} of equilibrium aqueous ozone within the first 5 minutes of treatment. This finding verifies the insignificant role of ozone observed in other experiments, where various pulse repetition frequencies were studied. With respect to toluene behavior in aqueous phase depending on pH in the range between 3.0 and 12.0, this had no effect on the non-dissociating toluene molecule's reactivity with discharge-generated HO• in a PCD reactor. (Kask et al., 2021)

The solution, containing 3.7 mg L^{-1} of aqueous toluene was adiabatically heated from 20±2 to 30±2 °C (Table 6 (d) and (h)), which resulted in concentration decrease in aqueous phase to 2.5 mg L^{-1} due to toluene evaporation in accordance with Henry’s law. The higher temperature resulted in a significantly reduced energy efficiency of 5.9 g kW^{-1} h^{-1}. This finding implies that toluene oxidation occurs at the gas-liquid interface (Ajo et al., 2017), since the increased airborne toluene concentration results in a faster rate of oxidation on the gas-phase side.

Along with toluene and ozone, FTIR analysis of the air exhaust from the PCD reactor showed the presence of a trace amounts of carbon monoxide, a by-product of incomplete oxidation of organics (Table 7).

Table 7. Concentrations of toluene, O_3, and CO in PCD output gas.

PCD treatment conditions	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	6	0.057	0.61	0.051
(b) 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
(c) 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
(d) 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
(e) 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
(f) 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
(g) 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
(h) 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

Additionally, it was discovered that a lower ozone concentration in the gas phase and a lower starting toluene concentration result in a reduced carbon monoxide production (Table 7 (b, d, e)).

After PCD treatment trace concentrations of toluene (about 0.06–0.10 mg L^{-1}, Table 7 (b, d, e)) and residual ozone remained in outlet gas. The latter is also considered as air pollutant. Therefore, the additional treatment of the gaseous exhaust by photocatalytic oxidation is highly recommendable.

3.5 Purification of gaseous exhaust by photocatalytic oxidation

Toluene, O_3, and CO residues from the PCD reactor were introduced into the photocatalytic reactor at the quantities specified in Table 8.

Table 8. Toluene, O_3, and CO concentrations in the PCD output gas entering the photocatalytic reactor.

PCD treatment conditions	Sampling time, min	Concentration, mg L^{-1}		
		Toluene	O_3	CO
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	0.034	0.29	0.038
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_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

The results of photocatalytic air exhaust treatment are shown in Figure 17 at a starting equilibrium concentration of 3.7 mg L^{-1} for aqueous toluene. O_3 was completely degraded at the longest SRT of 0.13 s cm^{-2}, as determined by a residence time of 16 s over a TiO_2-covered photocatalytic surface of 120 cm^2. At SRTs of 0.065 and 0.033 s cm^{-2}, O_3 depletion needed 240 and 360 cm^2, respectively, with residence durations of 16 and 12 s. Ozone did not completely degrade at lower SRTs of 0.033 and 0.065 s cm^{-2} produced by residence durations of 4 and 8 s over 120 cm^2 of TiO_2 coating. Consequently, this indicates the need for a larger area of the photocatalyst to ensure the limiting degradation time of O_3.

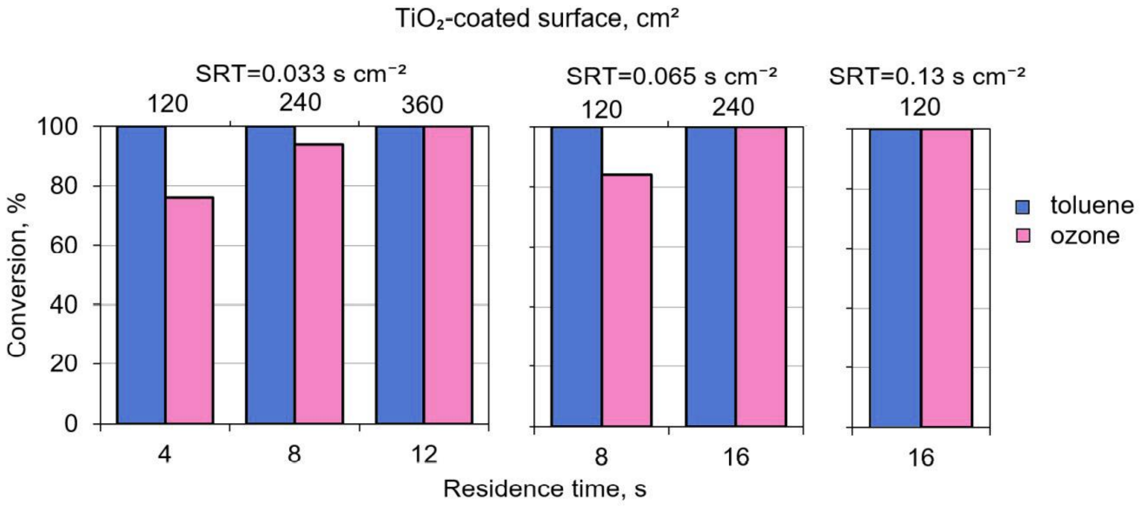

Figure 17. Conversion of airborne toluene and ozone in photocatalytic reactor dependent on residence time at the TiO_2-coated surface, PCD treatment conditions: C_0=3.7 mg L^{-1} (aq), C_0=1.0 mg L^{-1} (gas), 200 pps, starting pH 7.0, 20°C

The rapid decomposition of residual toluene is explained by the presence of ozone in exhaust. Pichat et al. observed that ozone facilitated the direct (Eq. 36) or indirect (Eq. 37) capture of electrons transferred to the TiO_2 conduction band under the influence of photons. O_3• may react with water adsorbed on the TiO_2 surface, increasing the formation of HO• (Eq. 38). Additionally, scavenging of photogenerated electrons with ozone inhibits hole-electron recombination, hence amplifying the generation of HO• from hydroxyl-anions at the photocatalyst surface (Eq. 39). (Pichat et al., 2000)

$\bar{e} + O_3 \rightarrow O^{\bullet -} + O_2$ (k = $1.8 \cdot 10^9$ L mol^{-1} s^{-1}) (36)

$\bar{e} + O_2 \rightarrow O_2^{\bullet -}$ and $O_2^{\bullet -} + O_3 \rightarrow O_3^{\bullet -} + O_2$, (k = $2.1 \cdot 10^{11}$ L mol^{-1} s^{-1}) (37)

$O_3^{\bullet -} + H_2O \rightarrow HO^{\bullet} + HO^{-} + O_3$ (38)

$HO_s^{-} + h^{+} \rightarrow HO^{\bullet}$ (39)

SUMMARY

In this work, a combination of Pulsed Corona Discharge and photocatalysis was used. The pulsed corona discharge (PCD) showed energy efficient degradation of toluene. However, the PCD process was accompanied by the formation of ozone known to be an air-borne pollutant. The residual VOCs were also present in air exhaust. To remove ozone and residual toluene, a multi-section photocatalytic reactor was used, to increase the catalyst surface with increasing residence time by adding reactor sections. The subsequent photocatalytic treatment successfully breaks down low concentrations of VOCs in the air, converting them into harmless H_2O and CO_2 products.

In the course of work, the following conclusions can be drawn:

- The treatment of aqueous toluene using a gas-phase pulsed corona discharge in conjunction with photocatalytic treatment of exhaust air removes residual toluene and ozone while creating trace levels of CO.
- A small difference in energy efficiencies obtained at various pulse repetition frequencies points to the moderate role of O_3-induced oxidation of toluene. The increase of temperature in treated toluene solution from 20 to 30°C resulted in decreased oxidation efficiency of aqueous toluene for about 20% showing higher oxidation rates in the gas phase.
- The dependence of toluene oxidation efficiency on pH of treated solution indicates the significant role of $HO^{\bullet}$ generated by PCD.
- The residual concentrations of toluene, ozone as well as trace quantities of CO were detected in PCD outlet gas. Properly adjusted photocatalytic oxidation conditions, i.e. gas residence time, enabled to achieve the complete removal of toluene and ozone from the exhaust air.

Thus, the studied combination of PCD treatment and photocatalysis may serve as an efficient and self-supported method for VOCs degradation. The obtained knowledge represents an important contribution in the field, which allows achieving considerable breakthrough in water and air purification technologies aimed to VOCs abatement.

KOKKUVÕTE

Selles töös kasutati koroona-impulss elektrilahendust koos fotokatalüüsiga. Koroona-impulss elektrilahendus (KIEL) näitas tolueeni energiasäästlikku lagunemist, kuid sellega kaasnes osooni moodustumine, mis on teadaolevalt õhu kaudu leviv saasteaine. Lenduvate orgaaniliste ühendite (LOÜ) jäägid esinesid ka väljatõmbeõhus. Osooni ja jääktolueeni eemaldamiseks kasutati mitmeosalist fotokatalüütilist reaktorit. Selleks, et suurendada katalüsaatori pinda koos viibimisaja pikendamisega oli lisatud lisasektsioone. Järgnev fotokatalüütiline töötlemine lagundas edukalt madala kontsentratsiooniga LOÜ-d, mille tulemusel tekkisid H_2O ja CO_2.

Töö käigus on tehtud järgmised järeldused:

- Tolueeni vesilahuse töötlemine gaasifaasi KIEL-i abil koos väljatõmbeõhu fotokatalüütilise töötlemisega eemaldab jääktolueeni ja osooni, tekitades samal ajal CO jälgi.
- Väike erinevus energiatõhususes, mis saadakse erinevatel impulsside kordussagedustel, viitab O_3 indutseeritud tolueeni oksüdatsiooni mõõdukale rollile. Temperatuuri tõus töödeldud tolueenilahuses 20°C-lt 30°C-le põhjustas tolueeni vesilahuse oksüdatsioonitõhususe vähenemise umbes 20% võrra, mis näitab kõrgemat oksüdatsioonikiirust gaasifaasis.
- Tolueeni oksüdatsiooni efektiivsuse sõltuvus töödeldud lahuse pH-st näitab KIEL poolt tekitatud HO-radikaalide olulist rolli.
- KIEL-i väljalaskegaasis tuvastati nii tolueeni, osooni kui ka süsinikdioksiidi jääkkontsentratsioonid. Õigesti reguleeritud fotokatalüütilise oksüdatsiooni tingimused, st gaasi viibimisaeg reaktoris, võimaldasid saavutada tolueeni ja osooni täieliku eemaldamise heitõhust.

Töös saadud tulemused näitavad, et KIEL-i ja fotokatalüüsi uuritud kombinatsioon võib olla tõhus ja iseseisvalt toimiv meetod LOÜ lagunemiseks. Saadud teadmised on valdkonna oluline panus, mis võimaldab saavutada märkimisväärset läbimurret lenduvate orgaaniliste ühendite vähendamises vee- ja õhupuhastustehnoloogiates.

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