

DOCTORAL THESIS

Pulsed Corona Discharge
Oxidation of Organic and
Inorganic Pollutants:
From Aqueous Baseline
to Operational Limits in
Source-Separated Urine

Irina Petrotšenko

TALLINN UNIVERSITY OF TECHNOLOGY
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IRINA PETROTŠENKO



TALLINN UNIVERSITY OF TECHNOLOGY

School of Engineering

Department of Materials and Environmental Technology

This dissertation was accepted for the defence of the degree 02/10/2026

Supervisor:

Professor Sergei Preis
School of Engineering
Tallinn University of Technology
Tallinn, Estonia

Opponents:

Dr. Monica Magureanu, Senior researcher
Dept. of Plasma Physics and Nuclear Fusion
National Institute for Laser, Plasma and Radiation
Physics
Magurele, Romania

Kinga Skalska-Tuomi, Postdoctoral researcher
School of Engineering
Department of Separation Science
Lappeenranta–Lahti University of Technology LUT
Mikkeli, Finland

Defence of the thesis: 30/11/2026, Tallinn

Declaration:

Hereby I declare that this doctoral thesis, my original investigation and achievement, submitted for the doctoral degree at Tallinn University of Technology has not been submitted for doctoral or equivalent academic degree.

Irina Petrotšenko

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**Orgaaniliste ja anorgaaniliste
saasteainete oksüdeerimine impulss-
koroonalahenduse abil: vesikeskkonna
mudelsüsteemidest kuni allikapõhiselt
kogutud uriini töötlemise piiranguteni**

IRINA PETROTŠENKO

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List of Publications

The author's name is rendered as Petrotšenko in this thesis and official documents, following Estonian orthography. In international peer-reviewed publications, the name is written as Petrochenko, following standard English transliteration.

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

Petrochenko, I.; Preis, S. (2024). Aqueous bromide oxidized with pulsed corona discharge. *Journal of Electrostatics*, vol. 132, 103978, DOI: 10.1016/j.elstat.2024.103978.

Petrochenko, I., Dulova, N., Simha, P., Preis, S. (2026). Pulsed Corona Discharge for Targeted Oxidation of Carbamazepine in Water and Source-Separated Human Urine. *Plasma Processes and Polymers*, vol. 23, p. e70121, DOI: 10.1002/ppap.70121

Petrochenko, I., Dulova, N., Preis, S. (2026). Pulsed corona discharge in valorisation of urine as a sustainable source of nutrients: targeted oxidation of pharmaceutical residues and inhibition of urea enzymatic hydrolysis. *Processes*, 14(12), 1972. <https://doi.org/10.3390/pr14121972>

Author's Contribution to the Publications

Contribution to the papers in this thesis are:

- I The author carried out the experimental work and respective analyses, interpreted obtained data and wrote the paper with the help of the co-author.
- II The author carried out the experimental work, carried out most of the respective analyses, interpreted obtained data and wrote the paper with the help of co-authors.
- III The author carried out the experimental work and respective analyses, interpreted obtained data and wrote the paper with the help of co-authors.

Introduction

The increasing occurrence of anthropogenic contaminants in the aquatic environment poses a significant threat to global ecosystems and human health. While advanced oxidation processes (AOPs) based on hydroxyl radical ($\text{HO}\bullet$) generation show potential for treating recalcitrant pollutants, commercially available ozonation is often limited by high operational costs and oxidant scavenging in complex matrices. Gas-phase pulsed corona discharge (PCD) provides a more energy-efficient alternative by generating hydroxyl radicals ($\text{HO}\bullet$) from water molecules in situ at the gas-liquid interface. Atomic oxygen and ozone (O_3) formation also contribute to oxidation. Previous research has demonstrated the predominant role of surface-borne radicals in PCD, offering a unique mechanism for targeted, i.e., energy-efficient, oxidation. This work therefore evaluates the operational limits and energy efficiency of PCD for the targeted removal of pollutants in diverse aqueous media, progressing from model aqueous systems to complex source-separated urine matrices to explore its potential for safe and sustainable nutrient recovery. It is based on the premise that the selectivity of gas-phase PCD at the gas-liquid interface enables efficient pollutant degradation even in concentrated high-conductivity matrices while preserving essential nutrients and suppressing the formation of unwanted by-products.

The thesis provides data disclosing the application of PCD to two research subjects: the management of bromide in natural waters and the valorisation of source-separated human urine as a raw material for fertilizer production. The first subject addresses the toxic bromate problem, to which naturally omnipresent bromide is converted during water disinfection. For the first time, the reversible nature of bromide–bromate transformation in PCD was demonstrated, revealing a mechanism for bromate reduction driven by matrix-derived nitrite. This work further establishes the role of organic matter in suppressing the formation of hypobromous species, thus enabling safer PCD disinfection and diminishing the formation potential of trihalomethanes (Publication I). Stable PCD operation was also demonstrated in high-conductivity matrices without electrical breakdown, establishing operational conditions relevant to complex aqueous media.

Operational options for PCD treatment of source-separated human urine were explored through the oxidation of pharmaceutical residues, targeting safe and sustainable fertilizer production and use. The research focused on the oxidation of carbamazepine (CBZ), propranolol (PR), and tetracycline (TC) in a complex urine matrix. Targeted oxidation of amphiphilic CBZ and PR at the gas-liquid interface was demonstrated at moderate energy doses, with the synergistic enhancement observed upon addition of the surfactant sodium dodecyl sulphate (SDS) providing further evidence for the surface-mediated oxidation mechanism. In contrast, hydrophilic TC demonstrated lower efficiency of PCD oxidation. Although SDS addition dramatically improved PCD oxidation of CBZ in aqueous solutions, supporting the mechanism of its surface oxidation, the approach gave a negative result in PCD application to urine treatment (Publications II and III).

A critical aspect of this study is the preservation of nutrients: PCD was found to inactivate urease while leaving urea intact, revealing a novel chemical-free approach for stabilizing source-separated urine and preventing nitrogen loss via enzymatic urea hydrolysis and ammonia volatilization. Finally, the agronomic safety of PCD-treated urine was verified through phytotoxicity assays on *Pisum sativum* peas, confirming the absence of phytotoxic effects at reference application doses (Publication III).

Abbreviations

CBZ	Carbamazepine
DOC	Dissolved organic carbon
E^0	The standard oxidation potential
EC/EC ₀	Electric conductivity
HO•	Hydroxyl radical
PCD	Pulsed corona discharge
pps	Pulses per second
PR	Propranolol
ROS	Reactive oxygen species
SDS	Sodium dodecyl sulphate
TC	Tetracycline
THMs	Trihalomethanes
TPs	Transformation products
UV	Ultraviolet

1 Literature review

The transition toward circular economy has become an objective in addressing the intertwined challenges of resource depletion, environmental degradation, and climate change (Foster et al., 2026). Unlike the traditional linear model of “take-make-dispose,” the circular economy emphasizes the recovery and reuse of materials, aiming to close resource loops and reduce dependence on finite inputs (Rinkinen & Shove, 2023). Within this framework, the nutrient-energy-water nexus has emerged as a critical area of focus, as these systems are deeply interconnected (Pagano et al., 2026). Production of fertilizers requires significant energy input; meanwhile, water systems transport and dilute valuable nutrients, and waste streams often represent untapped reservoirs of recoverable resources rather than liabilities (Ganesapillai et al., 2026).

A particularly pressing issue within this nexus is the sustainability of the global phosphorus supply (McDowell & Haygarth, 2025). Phosphorus is an essential element for agricultural productivity with no synthetic substitute, yet its primary source, phosphate rock, is finite and unevenly distributed globally (Raniero et al., 2025). This concern is compounded by the inefficiency of current phosphorus use and the energy-intensive nature of nitrogen fertilizer production. The Haber-Bosch process, which converts atmospheric nitrogen into ammonia, is responsible for a substantial share of global energy consumption and greenhouse gas emissions (Mingolla & Rosa, 2025; Ouyang et al., 2025). Together, these challenges underscore the need for alternative strategies, such as recovering nutrients from source-separated human urine (Saliu et al., 2023; Mustafa et al., 2026).

However, the path to a circular economy in urine utilization is obstructed by the presence of anthropogenic contaminants that persist in water cycle. In the context of nutrient recovery, the primary barrier is the presence of micropollutants, particularly pharmaceutical residues, which are excreted predominantly via urine and resist conventional degradation (Winker et al., 2008).

In the context of natural water systems and traditional disinfection, the challenge extends to bromide. When untreated or improperly managed, naturally occurring bromide can lead to the formation of regulated, toxic byproducts during disinfection, creating an operational limit for safe water reuse (Petrochenko & Preis, 2024).

Addressing this dual challenge, the removal of pharmaceutical micropollutants for nutrient valorisation and the management of bromide for water safety, requires highly efficient and selective treatment technologies. Conventional wastewater treatment processes are largely inadequate for these tasks, as they focus primarily on bulk organic matter rather than targeted pollutant degradation (Ternes, 1998). This technological gap has led to the emergence of advanced oxidation processes (AOPs) and plasma-based technologies, such as pulsed corona discharge (PCD). By generating reactive species *in-situ*, PCD offers a promising pathway for selective oxidation and improved energy efficiency in complex matrices, bridging the gap between aqueous baselines and real-world operational limits.

1.1 Advanced oxidation processes

Advanced oxidation processes are widely studied for the removal of persistent organic contaminants due to their capacity to generate highly reactive oxygen species (ROS), primarily hydroxyl radicals (HO•). These radicals are capable of degrading and mineralizing recalcitrant compounds that resist conventional treatment, biological and

physico-chemical. The exceptional reactivity of HO• is attributed to its high standard reduction potential ($E^0 = 2.80 \text{ V vs SHE}$) and its strong electrophilic character, allowing it to react with near-diffusion-limited rate constants: $10^9 - 10^{10} \text{ M}^{-1} \text{ s}^{-1}$.

1.1.1 Mechanisms of radical attack

Hydroxyl radicals initiate the degradation of organic molecules through three principal pathways:

- Hydrogen abstraction: HO• removes a hydrogen atom from C-H or O-H bonds, particularly in aliphatic chains, forming water and carbon-centred radicals;
- Electrophilic addition: HO• attacks π -systems in aromatic or unsaturated compounds, such as the tricyclic structure of carbamazepine, forming hydroxycyclohexadienyl radicals;
- Electron transfer: direct one-electron oxidation, which occurs less frequently but is significant for certain functional reactions.

A critical constraint in AOPs is that these reactions often result in partial oxidation rather than complete mineralization. This can generate transformation products (TPs) such as aldehydes, ketones, and carboxylic acids, some of which may exhibit higher toxicity or environmental persistence than the parent molecules. This necessitates safety assessments, such as the phytotoxicity tests conducted in the study.

A primary constraint in hydroxyl radical-based chemistry is the non-selectivity of HO• radical, which reacts indiscriminately with various constituents of the water matrix: carbonate and bicarbonate anions act as scavengers, competing with target pollutants for the radical, and reducing the overall energy efficiency of the process. Scavenging produces carbonate radicals, which possess significantly lower oxidation potentials and are largely ineffective in mineralization of recalcitrant organic compounds. The phenomenon leads to HO• passivation in alkaline media (Buxton et al., 1988). Conversely, in acidic conditions, the carbonate equilibrium shifts toward the formation of free carbon dioxide, thereby reducing the scavenging capacity of the matrix and improving the utilization of hydroxyl radicals for pollutant degradation.

1.1.2 The selectivity and scavenging problem

The non-selective nature of the hydroxyl radical is frequently characterized as the primary set-back for AOPs in environmental engineering, particularly when applied to complex aqueous matrices. This limitation arises directly from the fundamental reactivity of OH•, which reacts rapidly with a vast array of organic and inorganic species. While the property is advantageous for the degradation of diverse or poorly characterized contaminants, it becomes problematic in complex aqueous matrices, where target pollutants typically represent only a minute fraction of the total reactive pool. In natural and engineered water systems, such as surface water or wastewater effluent, the presence of natural organic matter creates a highly competitive reaction environment, where background constituents rapidly scavenge radicals before they can interact with the intended micropollutants. This phenomenon has been widely documented in studies showing that even moderate dissolved organic carbon (DOC) concentrations, typically $10\text{-}50 \text{ mg L}^{-1}$ (Shon et al., 2006) in municipal wastewater disproportionately increase oxidant demand and diminish treatment efficacy.

In the context of source-separated human urine, this challenge represents a major technical limitation for conventional AOPs (Petrochenko, Dulova, & Preis, 2026). Human urine contains very high organic load with reported chemical oxygen demand (COD) of

approximately 3,600 to 19,900 mg O₂ L⁻¹, while untreated domestic wastewater typically contains only 80 to 260 mg L⁻¹ of total organic carbon (TOC), i.e., from 200 to 700 mg O₂ L⁻¹ (Yu et al., 2021). This indicates that urine contains organic matter concentrations that are orders of magnitude higher than those of conventional municipal wastewater. The organic load in urine is dominated by urea, which exhibits significant chemical stability and is generally considered recalcitrant to hydroxyl radical-based oxidation. However, the presence of organic constituents, such as uric acid and creatinine, create a substantial radical scavenging demand due to their higher reactivity. In such a concentrated matrix, the collective scavenging capacity of these background components is so significant that the fraction of radicals available to interact with trace-level target pharmaceuticals becomes negligible (Yang et al., 2022). Consequently, the energy and chemical inputs required to achieve meaningful contaminant removal via traditional bulk-liquid AOPs become prohibitively high, rendering them economically unfeasible.

Beyond organic competition, inorganic ions ubiquitous in water further exacerbate the selectivity issue through secondary scavenging pathways. Species such as bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻) react with OH• to form carbonate radicals (CO₃^{•-}). While these secondary species are more selective, they are significantly less reactive ($E^0 = 1.5\text{V}$), effectively downgrading the oxidative power of the system and redirecting reaction pathways away from target contaminants. This non-selective behaviour also dictates the inefficient use of energy, since a significant portion of the invested oxidative flux is scavenged in non-target reactions. Furthermore, these indiscriminate interactions increase the risk of unintended byproduct formation: in presence of inorganic bromide, non-selective oxidation can trigger the formation of bromate (BrO₃⁻), a regulated potential carcinogen that poses significant toxicity risks. These combined factors, organic scavenging, inorganic interference, and byproduct risks, underscore the need for alternative oxidation strategies, such as PCD, that can manage reactivity spatially at the gas-liquid interface.

1.1.3 Comparison of AOPs

A fundamental challenge in AOP application lies in the inherent conflict between the high oxidation potential of HO• and the non-selective scavenging effects of the matrix. Conventional bulk-phase AOPs, such as assisted ozonation, are fundamentally limited by their reliance on dissolving oxidants into the bulk liquid volume.

As illustrated in Figure 1, the fundamental difference between conventional ozonation and PCD lies in the spatial delivery of reactive species. In ozonation (Figure 1a), the gas is delivered to the bottom of a column, and bubbles rise through the liquid. In high-scavenging matrices like urine, the dissolved ozone and any subsequently generated radicals are immediately consumed by highly concentrated organic constituents before they may react with trace pharmaceuticals. This leads to high energy consumption and unintended oxidation of nutrients (Dodd et al., 2008). In ozonation, the generation of hydroxyl radicals follows a decomposition chain initiated by slow reaction with hydroxyl anions (Equation 1):



In contrast, pulsed corona discharge (Figure 1b) utilizes a sprinkled liquid approach, creating an extended gas-liquid interface. Reactive species, mostly hydroxyl radicals are generated at the interface (Ajo et al., 2017), to which amphiphilic pharmaceutical molecules are driven by natural force as surfactants (Derevshchikov et al., 2021). This allows the surface-borne oxidants to react with target pollutants coincidentally also

gathered at the interface, bypassing the scavenging barrier and significantly improving the energy efficiency (Table 1).

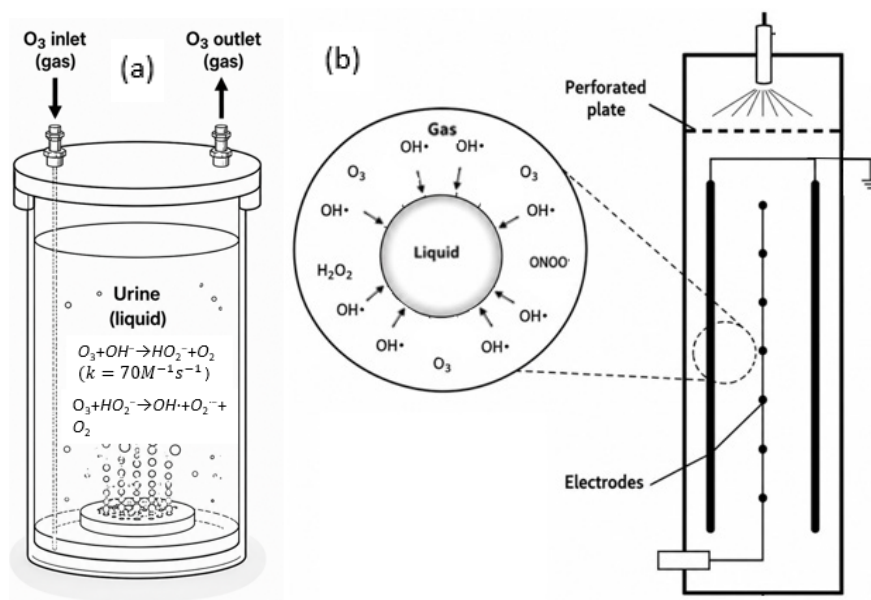


Figure 1. Bulk liquid-phase oxidants in ozonation (a) and surface-borne oxidants in PCD (b)

Table 1. Comparison of HO• production in AOPs

Aspect	UV/H ₂ O ₂	O ₃	PCD
Primary mechanism	H ₂ O ₂ photolysis	O ₃ decomposition → radical chain reaction	Electron impact, avalanche ionization
Key reactions	H ₂ O ₂ + <i>hν</i> → 2HO•	O ₃ + HO ⁻ → HO ₂ ⁻ → radical chain → HO•	e ⁻ + H ₂ O → HO• + H• O + H ₂ O → 2HO• O + O ₂ → O ₃
Characteristic features	Matrix-sensitive; H ₂ O ₂ handling; unfavourable stoichiometry	Matrix-sensitive, bromate formation	Surface-borne OH•, NO _x formation in air
References	(von Gunten, 2003; Miklos et al., 2018)	(Malik et al., 2001; Miklos et al., 2018)	(Preis et al., 2013)

1.2 Pulsed corona discharge

Pulsed corona discharge is a non-thermal plasma-based advanced oxidation technology that offers a fundamentally different approach to reactive species generation compared to conventional bulk-liquid AOPs. In PCD, high-voltage pulses create a plasma zone at the gas-liquid interface, producing short-lived highly reactive species directly at the treated aqueous surface (Ajo et al., 2017). This localized generation enables rapid interaction with target pollutants while potentially limiting non-productive reactions with the bulk liquid matrix. Consequently, PCD represents a promising pathway toward selective

oxidation, bridging the gap between aqueous baselines and the operational limits of complex media such as source-separated urine.

1.2.1 Fundamentals of non-thermal plasma

In non-thermal plasma (NTP), the energy from the electric field is primarily transferred to electrons, reaching temperatures of 10,000 - 100,000 K (1 - 10 eV), while the heavier ions and neutral gas molecules remain near ambient temperature (Malik et al., 2001). This allows for the generation of high-energy chemical environments without the energy penalty of heating the entire aqueous volume, a critical factor when treating large volumes of aqueous matrices.

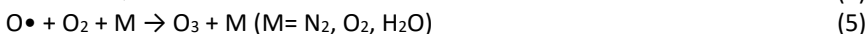
As established by Kornev et al. (Kornev et al., 2017), the efficiency of the PCD system is dictated by the pulse generator's ability to deliver high-voltage pulses with a sharp rise time. In the reactor configuration used in this study (Flowrox Oy, Finland), a thyristor-based pulse generator utilizing magnetic compression stages is employed. This setup shortens the pulse duration to approximately 100 ns. This short duration ensures that the input energy is converted into energetic electrons before a thermal spark can develop, maintaining the non-thermal character of the discharge.

The discharge initiates as streamer discharges - luminous filaments of plasma that propagate through the gas phase. These streamers strike the liquid surface, which is dispersed through a perforated plate to maximize the contact area. Unlike conventional AOPs, PCD provides *in-situ* generation of both ozone and hydroxyl radicals via electron impact dissociation of ambient gas molecules (Equations 2-6):

Direct dissociation and radical formation:



Secondary oxidant formation:



In an air-fed plasma reactor, the discharge inherently produces nitrogen oxides (NO_x), which can lead to the formation of nitric acid, thus impacting the solution pH and the resulting oxidation mechanisms (Ono & Oda, 2003; Măgureanu & Pârvulescu, 2007):



Furthermore, UV emission within the plasma zone initiates the dissociation of H₂O₂, O₂ and H₂O, providing an additional pathway for HO• generation (Măgureanu & Pârvulescu, 2007):



1.2.2 Interface chemistry of amphiphilic molecules

The defining technical advantage of PCD is the spatial localization of the reaction zone at the gas–liquid interface. Because primary reactive species, such as hydroxyl radicals and atomic oxygen (O), possess lifetimes on the scale of microseconds, the majority of oxidation reactions are restricted to a highly reactive boundary layer.

This spatial concentration introduces a selectivity element based on the physicochemical properties of the target contaminants. For the research Subject 2, i.e., urine valorisation, amphiphilic molecules such as propranolol (PR) and carbamazepine (CBZ) tend to partition toward the gas-liquid interface. By congregating at the surface, these molecules are exposed to the highest concentrations of short-lived radicals before these species can be scavenged in the bulk liquid. This surface-active oxidation is the mechanism by which PCD overcomes the ‘fatal barrier’ of complex matrices, (Petrochenko, Dulova, Simha, et al., 2026) mentioned above (see 1.1.2).

Similarly, for Subject 1, the interface chemistry appears to play a role in the bromide-bromate equilibrium. Understanding how the localized oxidative flux interacts with bromide is essential for determining the operational limits for pure water treatment without triggering the accumulation of bromate (Petrochenko & Preis, 2024).

Beyond chemical degradation, the interaction of the plasma discharge with the liquid boundary layer provides microbial inactivation (Machala et al., 2019), although this issue was out of the scope of research. This multi-functional approach positions PCD as a robust technology for both large-scale water safety and decentralized resource recovery systems.

1.3 Subject 1: bromide-bromate problem

The omnipresence of inorganic bromide (Br^-) in natural water presents a significant challenge for the implementation of advanced oxidation and disinfection technologies. Bromide is a naturally occurring anion found in groundwater and surface waters, often because of geological weathering or seawater intrusion. While bromide itself is not considered toxic at typical environmental levels, it acts as a precursor for the formation of bromate during oxidation processes. Bromate is identified as a potential human carcinogen of the Group 2B (WHO, 2026), associated with endocrine disruption and developmental toxicity. Consequently, international regulatory bodies, including the USEPA and the WHO, maintain a strict maximum contaminant level (MCL) of $10 \mu\text{L}^{-1}$ for bromate in drinking water. This threshold defines a critical operational limit for water treatment: the oxidative dose must be sufficient for disinfection and the removal of micropollutants yet controlled enough to prevent exceeding the regulated bromate limit.

1.3.1 Bromide-bromate equilibrium

The transition from bromide to bromate in an oxidative environment is not a single-step reaction but a complex equilibrium involving several short-lived intermediates. The oxidation pathway typically proceeds through the formation of hypobromite (OBr^-) and its conjugate - hypobromous acid (HOBr). These species are highly reactive and can further oxidize into unstable bromite (BrO_2^-) and finally into the stable bromate anion (Equations 11–13):



The formation of bromate in ozonation systems is an exceedingly complex process, often involving up to six different bromine oxidation states as intermediates. As illustrated in Figure 2, the reaction pathways include both direct ozonation and interactions with hydroxyl radicals, making the stabilization of the final BrO_3^- product highly dependent on the oxidant dose and contact time (von Gunten, 2003).

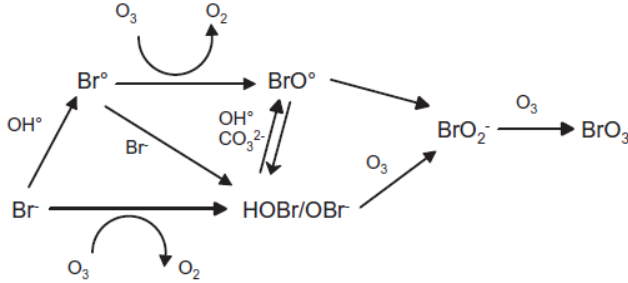


Figure 2. Bromate formation pathways during ozonation (von Gunten, 2003)

The defining distinction of the PCD system is its ability to bypass the relatively slow molecular reaction between O_3 and Br^- that dominates conventional ozonation. Because PCD generates a high-intensity flux of hydroxyl radicals at the gas-liquid interface, it provides an accelerated oxidation pathway via $\text{OH}^\bullet$ (Buxton et al., 1988; von Gunten, 2003):



This radical-mediated pathway (Equations 14–16) is significantly faster than the direct ozone reaction, fundamentally altering the kinetics of the bromine equilibrium. A critical observation within the high-intensity chemical environment of PCD is the reversibility of this equilibrium. Unlike steady state ozonation, where bromate accumulation is typically irreversible, the PCD introduces a reductive pathway driven by the fixation of atmospheric nitrogen. During treatment, the discharge fixes nitrogen and oxygen from the gas phase into nitrogen oxides, which subsequently enter the liquid to form the nitrite ion (Equation 17):



The generated nitrite acts as a reducing agent. Because bromate has a high standard reduction potential, $E^0 = 1.478 \text{ V}$ (Bard et al., 1985), it reacts with the plasma-generated nitrite, restoring bromate back to bromide while the nitrite is oxidized to nitrate (Equation 18):



This reaction provides a mechanistic explanation for the dynamic bromide-bromate equilibrium, although does not explain the deceleration of nitrate formation in the presence of bromate (Table 1 in Petrochenko et al., 2026), since nitrate is the final product of reaction. Hypothetically, the reverse formation of bromide results in its repeated oxidation back to bromate thus competing for the PCD-generated oxidants unavailable for nitric oxides formation. By the other words, the bromide-bromate cycle may reduce the nitrate formation, as observed in the research (see 3.1.4), due to an oxidant expense for alternative reaction with bromide.

As established in aqueous baseline studies of the thesis, achieving disinfection or micropollutant removal without the accumulation of bromate requires understanding of the reactions. If the energy doses are managed to balance the reactions, the formation of regulated bromate may be minimized. This chemical self-regulation effectively extends the technology's operational limits, allowing for effective treatment while staying within the $10\text{ }\mu\text{g L}^{-1}$ safety threshold (WHO, 2017).

1.3.2 Impact of pH and organic scavengers on inorganic speciation

The transformation of bromide in an oxidative environment is fundamentally governed by pH of the aqueous medium, which determines the speciation of reactive bromine intermediates. The primary intermediate, HOBr, exists in a pH-dependent equilibrium with its conjugate base, the OBr⁻, with a pKa of 8.7 at 25 °C (von Gunten, 2003). At circum-neutral pH, both species are present, whereas acidic conditions shift the equilibrium entirely toward HOBr. This speciation is critical because OBr⁻ reacts with molecular ozone approximately 10^6 times faster than HOBr, making the formation of BrO₃⁻ significantly more rapid in alkaline or neutral conditions (Haag & Hoigne, 1983; von Gunten, 2003). Conversely, at low pH, the dominance of HOBr slows the progression toward bromate but increases the likelihood of secondary reactions with other matrix constituents.

The presence of organic scavengers introduces a secondary layer of complexity through competitive kinetic pathways. In any AOP, HO• radicals and ozone are subject to scavenging by dissolved organic matter. The competition between inorganic bromide and organic molecules for available oxidants is a well-documented phenomenon that determines the overall efficiency of disinfection and pollutant removal (Westerhoff et al., 1998). Organic matter acts as an oxidant sink, effectively shielding bromide ions from oxidation; however, this interaction often leads to the formation of total organic bromine. When reactive bromine species (HOBr/OBr⁻) encounter organic scavengers, they can undergo substitution or addition reactions, leading to the formation of regulated halogenated disinfection byproducts such as trihalomethanes (THMs) (Heeb et al., 2014).

In the context of the circular economy and decentralized water treatment, the interplay between these variables represents a major research gap. While the individual effects of pH and DOC on bromide oxidation are understood in conventional ozonation, their behaviour in the high-intensity, interface-based environment of PCD remains underexplored. Specifically, the role of short-chain organic acids in managing the trade-off between bromate suppression and halogenated intermediate formation is a critical area of investigation. Establishing these relationships in a simplified aqueous baseline is a prerequisite for defining the operational limits of PCD before the technology can be applied to highly complex matrices like source-separated urine, where both the organic load and inorganic concentrations are exceptionally high (Larsen et al., 2021).

1.4 Subject 2: urine valorisation

The transition toward a circular economy requires a fundamental shift in how waste streams are managed, moving from disposal to resource recovery. Human urine represents a unique reservoir of essential nutrients: while it constitutes less than 1% of total municipal wastewater volume, it contributes approximately 80% of the nitrogen and 50% of the phosphorus disposed with that (Pathy et al., 2021). Recovering these nutrients at the source provides a pathway to reduce reliance on energy-intensive

industrial processes such as the Haber-Bosch process for nitrogen fixation (Maurer et al., 2006).

1.4.1 Pharmaceutical contaminants of concern

In wastewater and source-separated urine treatment research, pharmaceuticals such as carbamazepine (CBZ), tetracycline (TC), and propranolol (PR) are frequently employed as representative indicator compounds due to their contrasting physicochemical properties and environmental signatures. This triad illustrates the diverse molecular challenges inherent in removing micropollutants from concentrated waste streams (Joss et al., 2006; Verlicchi et al., 2012). While these compounds are well-studied in conventional wastewater, their behaviour in source-separated urine is significantly altered by high ionic strength and elevated pH (≈ 9.0) resulting from the enzymatic hydrolysis of urea. Under these conditions, the persistence of these indicators often exceeds that observed in diluted wastewater, necessitating robust advanced treatment strategies (Winker et al., 2008).

Carbamazepine ($C_{15}H_{12}N_2O$) is an anticonvulsant and mood-stabilizing drug characterized by a stable tricyclic dibenzazepine ring with a carbamoyl side chain (Figure 3). Its aromatic system is resistant to microbial enzymatic attack, resulting in biological removal efficiencies consistently below 10–20% in conventional activated sludge systems (Clara et al., 2004; Onesios et al., 2008). Due to its extreme persistence, CBZ is widely recognized as a reliable anthropogenic marker for contamination in the aquatic environment. In the context of oxidation chemistry, CBZ is considered an ideal probe molecule for hydroxyl radical activity: while its reactivity with molecular ozone is relatively low ($k_{O_3} \approx 0.9 \text{ M}^{-1}\text{s}^{-1}$), its second-order rate constant with $\text{HO}\cdot$ is exceptionally high ($k_{OH} \approx 8.8 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) (Wols & Hofman-Caris, 2012). During oxidation, the primary electrophilic attack occurs at the central C10–C11 double bond of the azepine ring. This leads to the formation of various TPs, most notably 10,11-dihydro-10,11-dihydroxycarbamazepine and acridine. The latter is of particular concern as it necessitates further ecotoxicological assessment due to its potential toxicity (Onesios et al., 2008). The stability of CBZ is particularly high in the context of source-separated urine. It is not susceptible to alkaline hydrolysis, remaining stable even during prolonged urine storage where pH typically rises to 9.0 (Maurer et al., 2006). This persistence ensures that CBZ remains in its parent form throughout the nutrient recovery process unless subjected to intensive advanced oxidation.

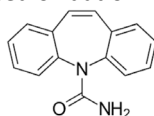


Figure 3. Carbamazepine

Propranolol ($C_{16}H_{21}NO_2$) is a non-selective beta-blocker consisting of a naphthalene ring attached to an isopropyl amino-propanol side chain (Figure 4). Characterized as moderately hydrophobic, PR exhibits variable removal efficiencies in conventional systems, from 20% to 80%, depending on sludge retention times (Gabet-Giraud et al., 2010). The amphiphilic character of PR molecule is a critical parameter for removal via PCD: PR tends to partition toward interface, where the reactive short-lived species are congregating in a highest oxidative flux. This partitioning behaviour of PR is particularly advantageous in complex matrices, where PR may be oxidized before the radicals are

scavenged by the high concentration of reactants present in the bulk liquid. The degradation of PR primarily involves the hydroxylation of the naphthalene ring and cleavage of the side chain, pathways that are highly sensitive to the presence of competing matrix constituents.

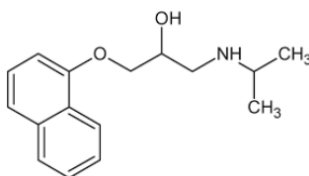


Figure 4. Propranolol

Tetracycline ($C_{22}H_{24}N_2O_8$) is a broad-spectrum antibiotic characterized by a hydronaphthacene skeleton consisting of four fused rings (Figure 5). It is of significant environmental concern because it is excreted unchanged by humans in high proportions, typically from 70% to 90% of consumed quantities, as the active parent compound responsible for the proliferation of antibiotic resistance genes (Kümmerer, 2009). The chemical behaviour of TC is complicated by its multiple ionizable functional groups (pKa values of 3.3, 7.7 and 9.7) and its propensity to form stable chelates with multivalent cations such as Ca^{2+} and Mg^{2+} (Kim & Aga, 2007; Wu et al., 2019). In the alkaline environment of stored urine (pH $\approx$ 9.0), TC exists in its anionic, zwitterionic and anionic forms (Hsu et al., 2018). Its tendency to complex with the abundant mineral content of urine can significantly alter its reactivity with oxidative species and influence its partitioning behaviour at the gas-liquid interface (Ajo et al., 2017).

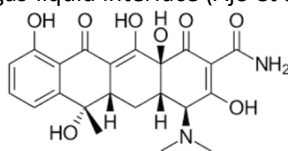


Figure 5. Tetracycline

1.4.2 Matrix effects and targeted surface oxidation

The primary challenge in achieving efficient micropollutant removal in urine is the ‘selectivity’ problem, which manifests as a competition for hydroxyl radicals between trace pharmaceuticals and dominant scavengers. Earlier, the dramatic effect, either accelerating or decelerating, of surfactant sodium dodecyl sulphate (SDS) addition was observed (Onga et al., 2020) and further explained (Onga et al., 2021) in respect of target aqueous pollutants oxidation dependent on their molecular structure. Besides, the dependence of PCD oxidation energy efficiency on the molecular structure of pharmaceuticals was studied (Derevshchikov et al., 2021): pharmaceutical molecules were more efficiently oxidized, and the accelerating effect of SDS was pronounced in respect of amphiphilic molecules. Oxidation of hydrophilic simple-structured molecules was decelerated by SDS addition to the aqueous solutions (Onga et al., 2021). Acceleration of oxidation in presence of SDS is a result of a primary $HO\bullet$ attack on the surfactant: hydroxyl radicals generated at the gas-liquid interface attack the hydrophobic tail of the SDS molecule, removing a hydrogen atom from the CH_3-CH_2 -group and forming a slow-reacting alkyl radical (Equation 19):



The SDS-radical thus acquires a localized affinity for radicalized aromatic rings of the target molecules with high electron densities - structures common in pharmaceuticals like CBZ and PR. The SDS-radical attaches to the target pharmaceutical, forming a covalent surfactant-pollutant bond. The compound is then brought to the gas-liquid interface by the surfactant, where it is exposed to the attack of short-lived oxidants. For molecules with accessible aromatic rings, this approach doubles the oxidation energy efficiency (Onga et al., 2021). However, molecules with abundant hydrophilic functional side-groups and steric obstacles for accessibility demonstrated an opposite surfactant effect screening off the target molecule (Saha et al., 2023): these molecules demonstrated negative or neutral effect of the SDS additions (Onga et al., 2021).

In the context of source-separated urine, additions of a surfactant might appear a factor improving the targeted character of oxidation of pharmaceuticals. If these are transported to the interface by the bonding with SDS, they may escape the bulk liquid scavengers. Consequently, the presence of surfactants, whether added intentionally or present naturally as metabolites, may reinforce targeted oxidation of pharmaceuticals in urine. This hypothesis requires verification carried out in this study.

1.4.3 Nitrogen stabilization

Human urine serves as a concentrated repository for essential plant macronutrients, including nitrogen, phosphorus, potassium, sulphur, calcium, and magnesium, alongside vital micronutrients such as boron, copper, and zinc (Richert et al., 2010). These elements are predominantly found in high-bioavailability forms, making urine a superior alternative to synthetic fertilizers. Within its nutrient pool, urea ($\text{CO}(\text{NH}_2)_2$) is the predominant nitrogenous species. Maintaining nitrogen in urea form is critical for sustainable agricultural management, since urea is the most concentrated solid nitrogen fertilizer, 47% N by weight, offering significant economic and logistical advantages over ammonium sulphate or nitrate (Trenkel, 2013). While urine is sterile in the bladder, it becomes contaminated with urea-splitting bacteria (Udert et al., 2003) during excretion and within collection systems. These bacteria produce urease, which catalyses the rapid hydrolysis of urea into ammonia and carbon dioxide (Equation 20):



This reaction leads to a sharp increase in solution pH spoiling the quality of fertilizer. While conventional urine stabilization relies on prolonged storage ranging from one week to eleven months for pathogens deactivation, this often results in spontaneous hydrolysis and nutrient loss (Jana et al., 2012; Lahr et al., 2016). To mitigate this, previous research has explored the use of chemical inhibitors like N-(n-butyl) thiophosphoric triamide (NBPT) to extend the lifetime of urea during storage (Simha & Ganesapillai, 2017).

Besides, from the perspective of PCD treatment, uncontrolled hydrolysis presents certain inconvenience in working with a liquid of elevated electric conductivity, which leads to energy ohmic losses in the discharge, altering streamer propagation and somewhat reducing the oxidation efficiency (Kornev et al., 2017). A major research gap, and the primary focus of this study, is whether PCD can achieve simultaneous pharmaceutical removal and urease enzyme inactivation. This would provide a 'one-step' stabilization and purification process, eliminating the need for external chemical inhibitors.

1.4.4 Fertilizer safety and plant growth test

The ultimate validation of a urine-derived fertilizer consists of its safety for terrestrial ecosystems. Phytotoxicity assessments are essential to determine whether the treated urine contains residual compounds, either parent pharmaceuticals or their TPs, that could inhibit plant development (van den Broek et al., 2024). These evaluations typically utilize sensitive indicator species to measure germination rates, root elongation, and shoot growth across a range of agronomic doses.

In the context of AOPs, specifically PCD, the chemical removal of a parent pharmaceutical does not always equate to a reduction in the matrix's phytotoxic potential. While studies often focus on acute aquatic toxicity (Onga et al., 2022), the specific response of agricultural crops to oxidation by-products requires standardized phytotoxicity assays to bridge the gap between novel technology and agricultural application. By evaluating the growth of species like the garden pea (*Pisum sativum*) using PCD-treated urine, it is possible to ensure that the oxidation treatment does not result in the accumulation of phytotoxic species, thus confirming the technology's readiness for the circular economy.

1.5 Objectives

Recently, electric discharges have gained significant attention in environmental technology as an energy-efficient method for oxidation of recalcitrant pollutants. Gas-phase pulsed corona discharge offers a promising alternative to conventional ozonation due to its generation of reactive species localized at the gas-liquid interface. However, the successful scale-up of this technology in the context of the circular economy requires a detailed determination of its operational limits when moving from simple aqueous baselines to complex aqueous matrices.

Current work is dedicated to identifying and filling the knowledge gaps related to the application of PCD in two distinct environmental scenarios: the management of inorganic bromide in natural waters and the valorisation of source-separated human urine contaminated with pharmaceuticals. In practice, the high nitrogen content, variable salinity, and presence of surfactants in real urine pose technical challenges, such as oxidant scavenging and ohmic energy losses, that define the technology's feasibility.

The specific objectives of this study include:

- Establishing the fundamental oxidation kinetics of inorganic bromide in an aqueous baseline, specifically exploring the reversibility of the bromide-bromate equilibrium and the role of organic scavengers and pH in suppressing toxic intermediates (Article 1).
- Determining the energy efficiency of pharmaceutical oxidation (CBZ, PR, and TC) across a range of operational conditions, including pulse repetition frequency and pH, in matrices ranging from distilled water to real stabilized human urine (Articles 2 and 3).
- Disclosing the mechanism of targeted surface oxidation by investigating the role of surfactant SDS and natural urine constituents in 'shuttling' hydrophobic pollutants to the gas-liquid interface, thereby bypassing the bulk-liquid scavenging barrier (Article 2).
- Stabilizing nitrogen nutrients in PCD treatment of urine by oxidation of the urease enzyme preserving urea (Article 3).

- Evaluating the agricultural safety of the treated product through standardized phytotoxicity assays on garden peas *Pisum sativum*. Preliminary comparative techno-economic analysis was carried out against the Haber-Bosch and conventional ozonation processes (Article 3).

2 Materials and methods

2.1 Chemicals and materials

Chemicals were of analytical grade and used as received without further purification. Distilled water was used for the preparation of all aqueous solutions, except where real urine matrices were employed.

Propranolol hydrochloride ($C_{16}H_{21}NO_2 \cdot HCl$) and CBZ ($C_{15}H_{12}N_2O$, 97%) were purchased from TCI Europe N.V. (Belgium). Tetracycline ($C_{22}H_{24}N_2O_8$, 98%) was obtained from Sigma Aldrich. Due to the low aqueous solubility of TC (231 mg L^{-1} at 25°C (National Library of Medicine, 2026)), stock solutions were prepared in methanol (CH_3OH , 99%) purchased from Fisher Scientific (UK). While PR stock was prepared in distilled water, the CBZ and TC stocks were prepared in methanol. For bromide-bromate studies, liquid bromine (Br_2 , 99%) was purchased from Thermo Fisher Scientific, Ltd. (USA), while potassium bromide (KBr, 99.7%), potassium bromate ($KBrO_3$, 99%), and sulphuric acid (H_2SO_4 , 96%) were obtained from Lach-Ner Ltd. (Czech Republic). Sodium hydroxide (NaOH, 98%) and sodium oxalate ($Na_2C_2O_4$, 99%) were purchased from Merck KGaA (Germany).

Synthetic urine was prepared according to the protocol by Sarigul et al. (Sarigul et al., 2019). Uric acid ($C_5H_4N_4O_3$, 99%), creatinine ($C_4H_7N_3O$, 98%), urea (CH_4N_2O , 99%), ammonium chloride (NH_4Cl , 99.5%), and trisodium citrate ($Na_3C_6H_5O_7 \cdot 2H_2O$, 98%) were obtained from Sigma Aldrich. Sodium sulphate (Na_2SO_4 , 99%), and sodium chloride (NaCl, 98%) were purchased from Lach-Ner, Ltd, Czech Republic. Additional inorganic components including potassium chloride (KCl, 99%), calcium chloride ($CaCl_2$, 96%), magnesium sulphate ($MgSO_4 \cdot 7H_2O$, 99.5%), dihydrate monobasic sodium phosphate ($NaH_2PO_4 \cdot 2H_2O$, 98%) and dibasic sodium phosphate dodecahydrate ($Na_2HPO_4 \cdot 12H_2O$, 98%) were purchased from Merck KGaA, Germany. Potassium oxalate ($K_2C_2O_4$, 98.5%) used in experiments with bromide oxidation was also purchased from Sigma Aldrich.

Real source-separated urine was obtained from two sources: (I) public urinals in Sweden and (II) donations from research laboratory personnel. To prevent enzymatic urea hydrolysis during storage and transportation, collection tanks were pre-dosed with 10 g L^{-1} of citric acid ($C_6H_8O_7$, 99%, Sigma Aldrich) to maintain pH of approximately 3.0 (Simha et al., 2023), except for samples designated for urease-mediated oxidation experiments.

Surfactant-mediated oxidation was studied using sodium dodecyl sulphate (SDS, $NaC_{12}H_{25}SO_4$, 99%) obtained from Lach-Ner Ltd (Czech Republic).

For enzymatic hydrolysis studies, Jack bean urease solution, 1000 U mL^{-1} in 50% glycerol, was obtained from Merck KGaA. Phytotoxicity and agricultural reuse potential were evaluated using garden pea seeds *Pisum Sativum* obtained from Baltic Agro Eesti (Estonia). The seeding and cutting soil with pH 5.5 - 6.5 employed for germination assays was purchased from ASB Greenworld Eesti (Estonia).

The collected samples pH was measured using a digital S220 pH-meter (Mettler Toledo, Switzerland).

2.2 Experimental setup

Oxidation experiments were performed using a PCD experimental device manufactured by Flowrox Oy (Finland). The device (Figure 6) is comprised of a 40-L storage tank, a high-voltage pulse generator, and a circulation pump that maintains a constant flow of treated solution of $1.0 \text{ m}^3 \text{ h}^{-1}$. The internal architecture of the reactor, detailed previously by

Tikker et al. (Tikker et al., 2020), features a multiple-string electrode configuration. The high-voltage electrodes consist of stainless-steel wires (0.55 mm in diameter) with a total length of 20 m, positioned horizontally between two vertical parallel grounded plates. The gap between the wire electrodes and the grounded plates is 18 mm.

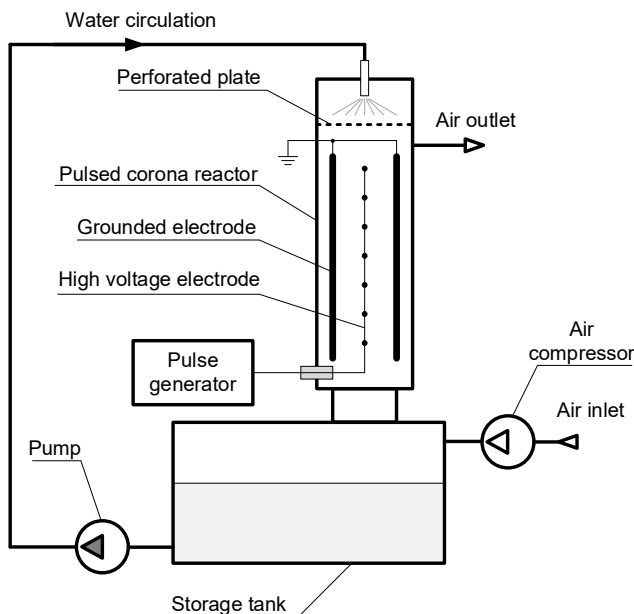


Figure 6. Experimental setup outline

This specific electrode arrangement was designed to minimize energy losses in conductive solutions, following the construction principles described by Kornev et al. (Kornev et al., 2017). The treated solution is fed to the top of the reactor and dispersed through a perforated plate containing 49 perforations of 1.5 mm in diameter. These perforations are aligned in a vertical plane coplanar with the high-voltage string electrodes, ensuring optimal contact between the falling liquid droplets and the PCD streamers. The treated solution is continuously recirculated passing through the discharge zone and falling into the storage tank. The reactor atmosphere consisted of indoor air, purging at a rate of 1.0 L min⁻¹ to maintain a stable gas composition replenishing oxygen consumed in chemical reactions.

The PCD is energized by a pulse generator delivering nanosecond-scale pulses with a voltage amplitude of 18 kV and current of 380 A. The pulse duration is approximately 100 ns. The pulse characteristics and waveforms were monitored using a Rigol DS1102E Mixed Signal Oscilloscope equipped with a Tektronix P6015 high-voltage probe (Tektronix Inc., USA) and a PT-7802 current monitor (PinTek, China). The power delivered to the reactor varied by adjusting the pulse repetition frequency in pulses per second (pps) to 50, 200 and 880, corresponding to output powers of 9, 32 and 123 W, respectively. The energy of a single pulse was calculated as 0.19 at 50 and 200 pps, and 0.15 J at 880 pps by integrating the voltage and current time profiles.

The delivered energy, kWh·m⁻³, was calculated according to Equation 21:

$$\text{Delivered energy} = \frac{P \cdot t}{V} \quad (21)$$

where P is power supplied by the pulse generator, kW, t is the treatment time, h, and V is the treated solution volume, m³.

Nitrate formation was evaluated using energy efficiency with which the anion was created. Efficiency E was determined using the nitrate concentration at the sampling time, the applied pulsed power, and the volume of the treated sample:

$$E = \frac{\Delta C \cdot V}{P \cdot t} \quad (22)$$

where E - nitrate formation energy efficiency, g kW⁻¹ h⁻¹,
 ΔC - the increase in nitrate concentration, g m⁻³,
 V - volume of treated solution sample, m³.

2.3 Analytical methods

2.3.1 Liquid chromatography

Concentrations of CBZ, PR, and TC were quantified using high-performance liquid chromatography coupled with a diode-array detector (HPLC-PDA; Shimadzu, Japan). Chromatographic separation was achieved using a Phenomenex Gemini NX-C18 column (150×2.0 mm, i.d. 1.7 mm) packed with a stationary phase NX-C18 (110 Å, 5 µm). For all methods, an isocratic elution was employed with the column oven temperature maintained at 40 °C and an injection volume of 100 µL.

An isocratic method was used, with mobile phase compositions and flow rates optimized for each compound as follows:

- CBZ: mobile phase consisted of 70% eluate A (water containing 0.3% formic acid) and 30% eluate B (acetonitrile containing 0.3% formic acid). The total flow rate was 0.2 mL min⁻¹ (0.14 mL min⁻¹ of eluate A and 0.06 mL min⁻¹ of eluate B);
- PR: mobile phase was a mixture of eluate A and B in a 3:1 volumetric ratio. The corresponding flow rates were 0.15 and 0.05 mL min⁻¹ for A and B, respectively, with a combined flow rate of 0.2 mL min⁻¹;
- TC: separation was achieved using 85% eluate A and 15% eluate B with individual flow rates of 0.17 and 0.03 mL min⁻¹, respectively, with a combined flow rate of 0.2 mL min⁻¹.

2.3.2 Ion chromatography

Concentrations of bromide, bromate and oxalate were measured using an Eco IC anion chromatograph (Metrohm, USA) equipped with a Metrosep A Supp 5 - 250/4.0 anion column. The mobile phase consisted of an aqueous eluent containing 3.2 mmol/L Na₂CO₃ and 1.0 mmol/L NaHCO₃.

2.3.3 Urea, ammonia and enzyme activity assays

The urea content was determined via enzymatic hydrolysis using urease from *Canavalia ensiformis* (Jack bean). Urea was hydrolyzed to NH₄⁺ / NH₃ at pH 7.2 using lyophilized urease (5 U mg⁻¹, EC 3.5.1.5; Merck, Germany) at a dosage of 5,000 U per gram of expected urea. Samples were incubated at 37 °C for 24 h on a shaker table. To shift the equilibrium toward NH₃ for detection, the solution was alkalized to pH>12 using 10-M NaOH. Ammonia concentration was then quantified as NH₃-N using an ammonia electrode probe (Metrohm AG, Switzerland).

To evaluate urease deactivation during PCD treatment, 10 L of non-acidified human urine was used. To ensure a standardized baseline, the urine was stored at -18°C to prevent spontaneous hydrolysis and thawed at 2°C immediately prior to the experiment. For real-time monitoring of solution conductivity and to evaluate urease deactivation in the storage tank, a Hach HQ430d multi-parameter meter was employed.

2.3.4 Phytotoxicity assay

The evaluation of phytotoxicity was assessed using garden pea plants *Pisum sativum* as per ASTM E1963-22 standard. Tests were carried out placing the seeded pots inside a temperature-controlled chamber at 22± 1°C at 32% relative humidity. The use of LED modules with the peak wavelength of 450 nm helped improve seedling morphogenesis. The canopy's photosynthetic photon flux density (PPFD) was observed and kept at 150±10 µmol m⁻² s⁻¹ with the help of VidalKraft Quantum PAR Meter.

The watering of the plants was automated every three days for one minute at the flow rate of 0.7 L h⁻¹ providing 11.69 mL per plant per event similar to an irrigation load of approximately 27,650 kg ha⁻¹. For over four weeks, the germination and healthy morphogenesis of seedlings were observed, when using the urine sample as a nitrogen supplement.

For each urine dosage level (0 to 4×, Table 2), six independent biological replicates were used in both the untreated control and PCD-treated groups, bringing the total number of *Pisum sativum* seedlings monitored across all conditions to 72.

Table 2. Urine doses and their purpose

Dose level	Relative to agronomic dose	N applied, kg N ha ⁻¹	Urine per pot, mL	Purpose
Control	0	0	0	Negative control
Low	0.25×	6.25	0.53	Sub-threshold sensitivity
Medium-low	0.5×	12.5	1.06	Conservative agronomic
Reference	1×	25	2.11	Reference agronomic dose
Medium-high	2×	50	4.22	Moderate over-application
High	4×	100	8.44	Supra-agronomic stress test

3 Results and discussion

3.1 Subject 1: Oxidation of bromide

Bromide oxidation was evaluated in distilled water at varying concentrations and pH values. These experiments served as the aqueous baseline required to understand the radical-mediated transition of Br^- to its regulated end-product BrO_3^- .

3.1.1 Bromide-bromate equilibrium

A significant finding of this research is that PCD treatment facilitates a reversible bromide-bromate reaction, establishing a dynamic equilibrium rather than a linear one-way transformation. As shown in Figure 7 in circum-neutral media at 200 pps, bromide concentration initially decreased rapidly. However, after approximately 40 minutes of treatment (energy dose of 3.2 kWh m^{-3}), the system reached a steady state where bromide and bromate concentrations plateaued.

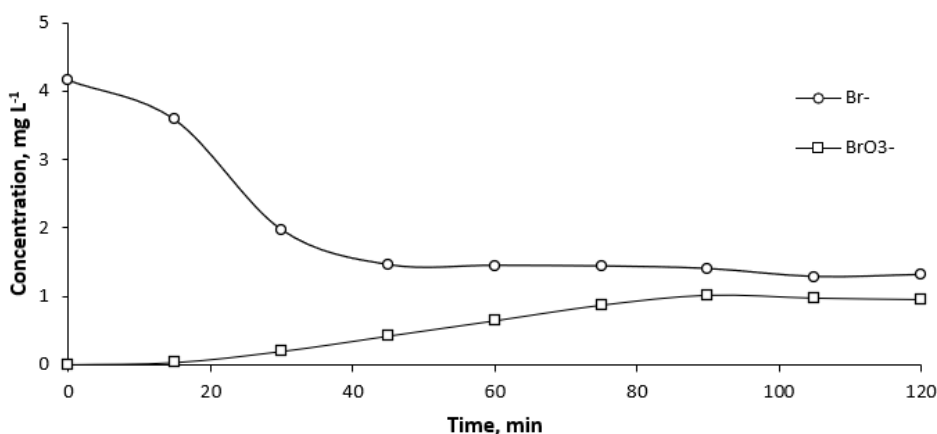


Figure 7. Established equilibrium between the bromine-containing anions: bromide starting concentration 5.0 mg L^{-1} , pulse repetition frequency 200 (32.0 W), circum-neutral pH descending from 9.3 to 3.0

The hypothesis of reversibility was verified by treating a solution containing 4.7 mg L^{-1} of bromate with PCD. As illustrated in Figure 8, the bromate concentration gradually decreased while bromide began to accumulate, reaching a stoichiometric equilibrium with less than 2% misbalance. This deficit is likely attributable to the formation of trace hypobromous acid (HOBr). This reversible character, which is not documented in conventional ozonation, suggests that bromate reduction to bromide occurs as nitrogen oxides transform into nitrite in the acidic medium created by the discharge. Nitrite serves as the reducing agent that prevents the total conversion of Br^- to BrO_3^- . From a practical standpoint, this chemical self-regulation allows the accumulation of toxic bromate to be physically limited by the system's reaction equilibrium.

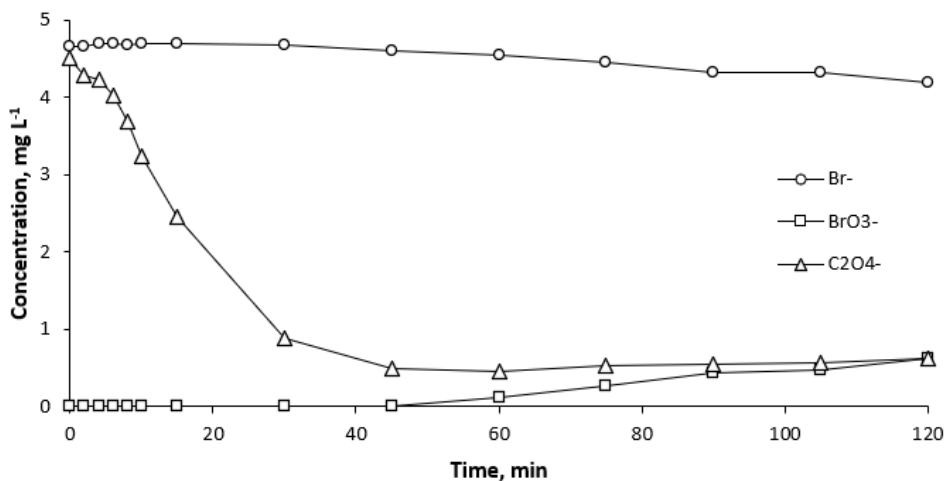


Figure 8. Evolution of bromate and bromide in PCD oxidation: starting bromate concentration 4.7 mg L^{-1} , circum-neutral pH $6.0 \rightarrow 1.7$

3.1.2 The role of organic compounds in bromide oxidation

In water treatment, the primary risk of bromide is the formation of hypobromous intermediates, the HOBr and OBr⁻, which trigger the haloform reaction producing carcinogenic THMs. This research disclosed a critical ‘safety mechanism’ when organic scavengers, represented here by oxalate ($(\text{COO})_2^{2-}$), are present in water.

In circum-neutral media, the addition of oxalate at a 1:1 mass ratio with bromide resulted in a five-fold reduction in the bromide oxidation rate. Crucially, the presence of organic compound resulted in the stoichiometric production of bromate with an almost complete absence of hypobromous intermediates (Figure 9). As shown in Figure 9, the bromide-bromate misbalance dropped to nearly zero in the presence of oxalate.

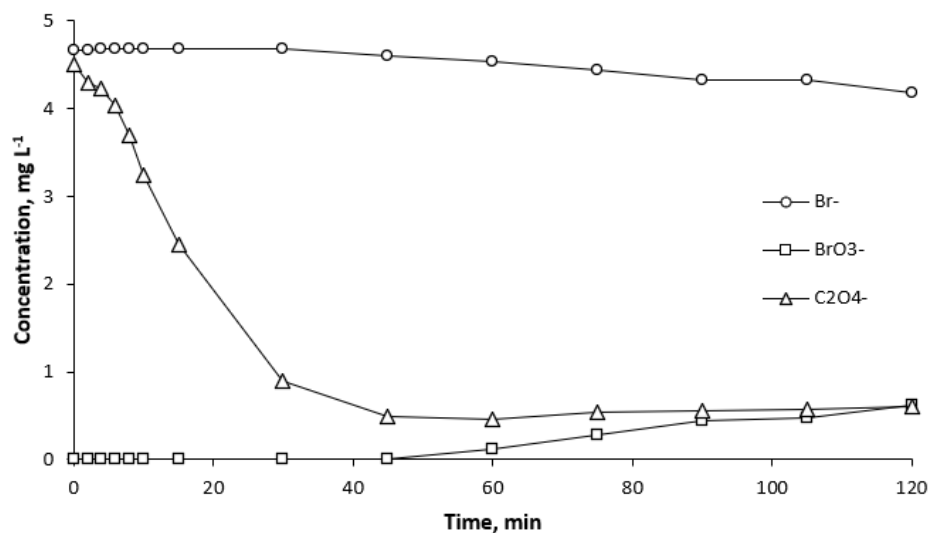


Figure 9. Evolution of bromide, bromate and oxalate in PCD oxidation: starting bromide concentration 4.7 mg L^{-1} , oxalate concentration 4.5 mg L^{-1} , circum-neutral pH $7.3 \rightarrow 6.5$

By eliminating the accumulation of HOBr and OBr⁻, the organic load effectively acts as a protective scavenger against the formation of halogenated organic by-products. This observation provides an additional justification for the safety of applying PCD to potable water treatment containing certain amount of organic matter simultaneous to bromide contents characteristic to natural waters. Extrapolating the knowledge to complex matrices such as human urine, oxidation in competitive conditions ensures minor probability for reactive bromine species converted to bromate or toxic THMs.

3.1.3 Impact of pH

The efficiency of bromide transformation and the resulting distribution of inorganic products were found to be highly sensitive to pH. In acidic media adjusted to pH 2.5, the reaction equilibrium shifted significantly toward bromate formation. At a starting bromide concentration of 5.0 mg L⁻¹, the concentration of bromate nearly doubled compared to circum-neutral conditions, increasing from 1.13 mg L⁻¹ to 2.14 mg L⁻¹. Despite this increase in final product yield, the bromide-bromate misbalance remained relatively stable at approximately 50%, indicating that a substantial portion of the bromine remained in reactive intermediate forms.

The addition of oxalate in acidic conditions revealed a unique kinetic behaviour described as an 'inflection point' in the intermediate species curves. Serious obstacle in the analysis originated from the fact that both hypobromous and oxalic acids were not divided in IC-analysis interfering with each other in chromatograms. As shown in Figure 10, the presence of oxalate in acidic media reduced bromate production approximately twofold compared to oxalate-free conditions. The concentration curve of HOBr/(COOH)₂ initially descends since the organic acid is degraded by the discharge; once the oxalic acid concentration reaches a critical threshold, the curve passes an inflection point and begins to ascend, with HOBr becoming the prevailing species at low pH. This phenomenon is attributed to the increased resistance of hypobromous acid toward oxidation by ROS compared to its conjugate base, OBr⁻, which dominates at higher pH. The higher oxidation potential of HOBr makes it more persistent in acidic environments, thereby slowing the progression to the stable bromate form.

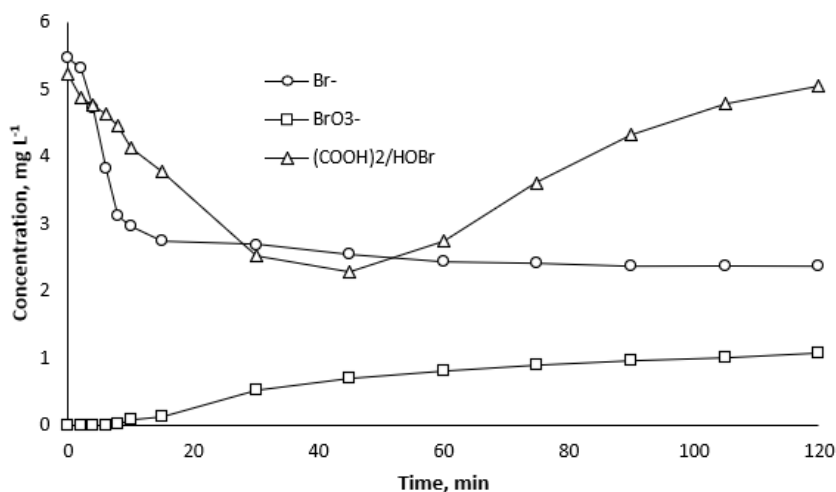


Figure 10. Evolution of bromide and bromate in PCD oxidation: starting bromide concentration 5.3 mg L⁻¹, oxalate concentration 5.2 mg L⁻¹, acidic pH 2.5, hypobromous acid interferes in IC-analysis of oxalic acid

In contrast, bromide exhibited minimal reactivity in alkaline media at pH 11.0. Experimental results showed that only 6.5% of the starting bromide was oxidized over the two-hour treatment period, yielding only 0.52 mg L⁻¹ of bromate. At lower initial bromide concentrations of 1.0 mg L⁻¹, the conversion to bromate was notably more complete with 42% of the initial bromide converted and a significantly smaller share of hypobromous intermediates. These results suggest that lower starting concentrations of bromide allow the oxidative flux to drive the reaction more efficiently toward the final product. Collectively, these pH and concentration-dependent findings demonstrate that the operational limits for managing the bromide-bromate equilibrium are not fixed; they can be effectively tuned by adjusting the initial pH and the scavenger-to-bromide ratio to maximize disinfection while minimizing regulated byproducts.

The minimal reactivity observed in alkaline media represents a significant departure from conventional ozonation theory. According to established literature (Haag & Hoigne, 1983; von Gunten, 2003), high pH typically accelerates the formation of bromate because the hypobromite ion reacts with molecular ozone approximately 10⁶ times faster than its conjugate acid, HOBr. In a standard bulk-liquid ozonation system, alkaline conditions are therefore considered the most productive for bromate formation. However, the PCD reactor demonstrated the opposite effect, where an increase in pH to 11.0 effectively stymied the oxidation process (Petrochenko & Preis, 2024). This phenomenon suggests that in the plasma-liquid interface, the molecular ozone-bromide pathway is subordinate to radical-mediated and reductive nitrogen cycles. The high concentration of OH⁻ ions in alkaline media likely promotes the rapid scavenging of surface-borne hydroxyl radicals, while the simultaneous generation of reducing nitrogen intermediates, such as nitrite, may further inhibit the progression toward stable bromate. Consequently, PCD exhibits an inherent 'alkaline stability' that enhances its safety profile for the treatment of high-pH waste streams, offering a clear operational advantage over traditional bulk-liquid advanced oxidation processes.

The minimal reactivity observed in alkaline media represents a significant departure from conventional ozonation theory. According to previous publications (Haag & Hoigne, 1983; von Gunten, 2003), high pH typically accelerates the formation of bromate because the hypobromite ion reacts with molecular ozone approximately 10⁶ times faster than its conjugate acid, HOBr. In conventional ozonation, alkaline conditions are therefore considered the most productive for bromate formation. However, PCD demonstrated the opposite effect, where an increase in pH to 11.0 effectively stymied the bromide oxidation (Petrochenko & Preis, 2024). This phenomenon suggests that in the plasma-liquid interface, the molecular ozone-bromide pathway is subordinate to radical-mediated and reductive nitrogen cycles. The high concentration of OH⁻ ions in alkaline media likely promotes the rapid scavenging of surface-borne hydroxyl radicals, while the simultaneous generation of reducing nitrogen intermediates, such as nitrite, may further inhibit the progression toward stable bromate. Consequently, PCD exhibits an inherent 'alkaline stability' that enhances its safety profile for the treatment of high-pH waste streams, offering a clear operational advantage over traditional bulk-liquid advanced oxidation processes.

3.1.4 Interaction with nitrogen

Interaction between bromine species and the formation of nitrates was studied. Nitrate is a common byproduct of PCD in air. It was observed that the presence of bromate acts as a strong inhibitor of nitrate formation, reducing the nitrate yield by approximately 30% (Table 3). The presence of bromide and oxalate at various pH values did not exhibit so strong effect as bromate. The red-ox reaction between bromate and nitrite formed in the discharge as an intermediate nitrous species (Kornev et al., 2013), presents a question finding no straightforward answer in the study. This suggests a complex cross-reaction between bromine and nitrogen species at the plasma-liquid interface, the exact mechanism of which requires further investigation but highlights the multi-functional chemical environment in PCD. Hypothetically, bromate producing nitrate and bromide contributes to consumption of oxidants converting bromide to bromate in reversible reaction, thus deflecting a part of ROS from oxidation of nitrous species and formation of nitrate.

Table 3. Efficiencies of nitrate formation in PCD-treated solutions

Experimental conditions	Nitrate formation efficiency, g kW ⁻¹ h ⁻¹
Oxalic acid 5.0 mg L ⁻¹ , pH 2.5	13.9
Bromate 5.0 mg L ⁻¹ , pH 6.0→3.0	9.9
Bromate 5.0 mg L ⁻¹ + bromide 1.0 mg L ⁻¹ , pH 6.0→3.0	8.9
Bromide 1.0 mg L ⁻¹ , pH 2.5	13.2
Bromide 1.0 mg L ⁻¹ , pH 6.5→3.0	13.9
Bromide 1.0 mg L ⁻¹ , pH 11.0	11.5
Bromide 5.0 mg L ⁻¹ , pH 2.5	11.9
Bromide 5.0 mg L ⁻¹ , pH 9.3→3.0	10.6
Bromide 5.0 mg L ⁻¹ , pH 11.0	11.3
Bromide 5.0 mg L ⁻¹ + oxalic acid 5.0 mg L ⁻¹ , pH 2.5	12.8
Bromide 5.0 mg L ⁻¹ + oxalate 5.0 mg L ⁻¹ , pH 7.3→6.5	12.3
Bromide 1.0 mg L ⁻¹ + oxalate 1.0 mg L ⁻¹ , pH 6.5→3.0	13.2

3.2 Subject 2: PCD operational limits in treatment of source-separated urine

The application of PCD to source-separated human urine represents the transition from controlled aqueous baselines to the operational limits of a highly complex organic-inorganic matrix. The presence of a diverse array of metabolites creates a scavenging barrier that dictates the energy efficiency and selectivity of the process.

3.2.1 Energy efficiency and the influence of molecular structure

Oxidation energy efficiencies (E , g kW⁻¹ h⁻¹) for the target pharmaceuticals, CBZ, PR, and TC, were evaluated across four matrices of increasing complexity. As summarized in Table 4, a profound reduction in efficiency was observed when moving from distilled water to real urine.

Table 4. Oxidation energy efficiencies for PCD treatment of CBZ, PR and TC in various aqueous media

Target compound, starting concentration, mg L ⁻¹	Media	Treatment conditions	Energy efficiency at 90% removal, g kW ⁻¹ h ⁻¹
CBZ, 10	Distilled water	50 pps, pH 7.8	54.7
		50 pps, pH 7.8, SDS	75.1
		50 pps, pH 2.5	82.8
	Urea solution (urea conc. 15 g L ⁻¹)	50 pps, pH 7.6	57.0
		50 pps, pH 7.8, SDS	93.1
		200 pps, pH6, SDS	39.3
	Synthetic urine (Appendix 1, Table S1)	200 pps, pH 6	9.5
		200 pps, pH 6, SDS	11.5
	Urine	200 pps, pH 4.0	1.7*
880 pps, pH 4.0		1.6	
PR, 10	Distilled water	50 pps, pH 6.0	32.3
		50 pps, pH 7.0, SDS	57.1
		50 pps, pH 3.0	39.6
	Urine	200 pps, pH 4.0	1.5**
		880 pps, pH 4.0	1.9
		880 pps, pH 4.0, SDS	1.6
TC, 10	Distilled water	50 pps, pH 2.0	38.9
	Urine	200 pps, pH 4.0	0.9***
		880 pps, pH 4.0	0.4****

* 48% removal; **45% removal; ***30% removal; **** 54% removal

Table 4 illustrates the massive energy demand imposed by the urine treatment. In the aqueous baseline under acidic conditions, CBZ exhibited an oxidation efficiency as high as 82.8 g kW⁻¹ h⁻¹. In real urine, this efficiency dropped to 1.6 g kW⁻¹ h⁻¹, representing a reduction of almost two orders of magnitude. Importantly, the results showed that urea itself is not a major scavenger: efficiency in the urea solution (57.0 g kW⁻¹ h⁻¹) remained comparable to the one in distilled water. The primary inhibition is therefore driven by the complex organic metabolites present in real urine, which outcompete the pharmaceuticals for available radicals.

To further disclose the role of molecular structure in overcoming the urine matrix scavenging, the degradations of the indicator pharmaceuticals were compared in Figure 11.

The figure provides an observation of molecular structure-driven selectivity. In distilled water, the degradation curves for all three compounds are relatively clustered, indicating similar oxidation rates in a low-scavenging environment. However, in urine, the curves diverge dramatically. CBZ and PR, which possess amphiphilic structures, reached C/C₀ values of 0.01 and 0.03, respectively. In contrast, TC reached only partial removal (C/C₀ = 0.46) at an efficiency of only 0.42 g kW⁻¹ h⁻¹.

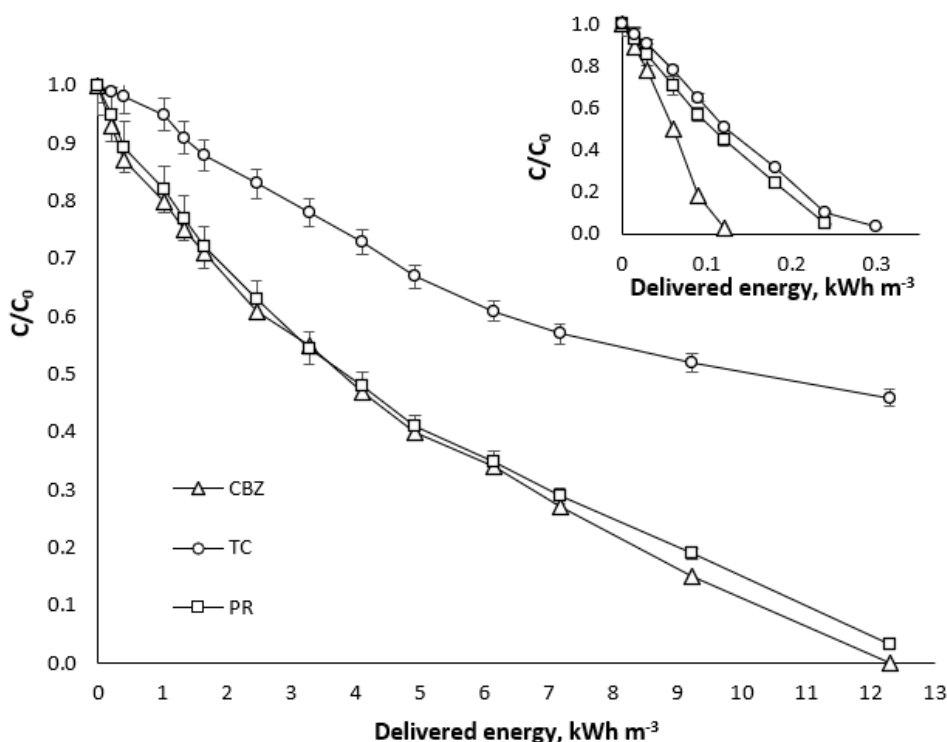


Figure 11. Relative concentrations of CBZ, PR and TC (C/C_0) vs. delivered pulsed energy dose in distilled water (inset) and stabilized source-separated urine. Starting concentration of pharmaceuticals 10.0 mg L^{-1} . Inset (water): pH 3.0, 50 pps (9 W). Main plot (urine): pH 3.0, 880 pps (123 W)

Unlike the amphiphilic CBZ and PR, TC has a structure rich in hydrophilic functional groups (phenolic, alcoholic, and amino), which keeps it sequestered in the bulk liquid, where the radicals are consumed by the urine components before they encounter the TC molecules. These results confirm that the operational limit of PCD in urine treatment is dictated by the target contaminant's ability to partition toward the gas-liquid interface, where it escapes the scavenging barrier. On the other hand, the energy consumption necessary to remove the target pollutant remains viable given the high nutrient value of the treated urine and the energy expense necessary for urine evaporative concentration.

Crucially, PCD achieved pharmaceutical oxidation in acidified urine with an efficiency approximately an order of magnitude higher than conventional ozonation treatment of urine. For comparison, the energy efficiency of ozonation for PR and CBZ in urine comprised $0.26 \text{ g kW}^{-1}\text{h}^{-1}$ and $0.15 \text{ g kW}^{-1}\text{h}^{-1}$, respectively (Dodd et al., 2008). It should be noted that these energy efficiency values for ozonation were obtained using ozone generated from pure oxygen at an energy yield of $13.1 \text{ kWh kg O}_3^{-1}$. Furthermore, although Dodd's experiments utilized lower starting concentrations of 2.3 mg L^{-1} vs 10 mg L^{-1} in the present study, a factor that typically correlates with lower energy efficiency, the PCD maintains a significantly higher oxidative performance. This confirms that PCD is a superior technology for high-strength waste streams, as its surface-active mechanism bypasses the bulk-liquid scavenging that limits conventional ozonation.

3.2.2 Targeted surface oxidation and the role of surfactants

To confirm the PCD oxidation driven by surface interactions, the anionic surfactant SDS was used as an addition interacting with target pollutants to bring those to the gas-liquid interface. In distilled water and urea solutions, the addition of SDS dramatically accelerated oxidation of CBZ and PR by factors of 1.4 to 1.5 (Table 4). This supports the hypothesis elaborated by Onga et al. (Onga et al., 2020, 2021), where the radicalized hydrophobic tails of surfactant molecules form covalent bonds with the radicalized aromatic rings of pharmaceuticals, transporting those to the gas-liquid interface for exposure to the oxidative attack.

However, the application of SDS to oxidation of CBZ in urine revealed a negative tendency: SDS was found to inhibit CBZ oxidation having the negative effect increased with increasing SDS concentration (Figure 12). This inhibition likely stems from the presence of abundant endogenous metabolites in urine that outcompete trace pharmaceuticals for vacant surfactant binding sites. Further increase in SDS additions came across a technical obstacle, the addition of SDS to urine triggered intensive foaming (Figure 13). The foam rapidly filled the interelectrode space, creating a conductive bridge between the high-voltage string electrodes and the grounded plates, resulting in short-circuiting and termination of treatment.

The finding establishes a clear limit: while surfactant-assisted oxidation is a powerful tool in relatively clean waters, it is incompatible with highly loaded matrices like urine.

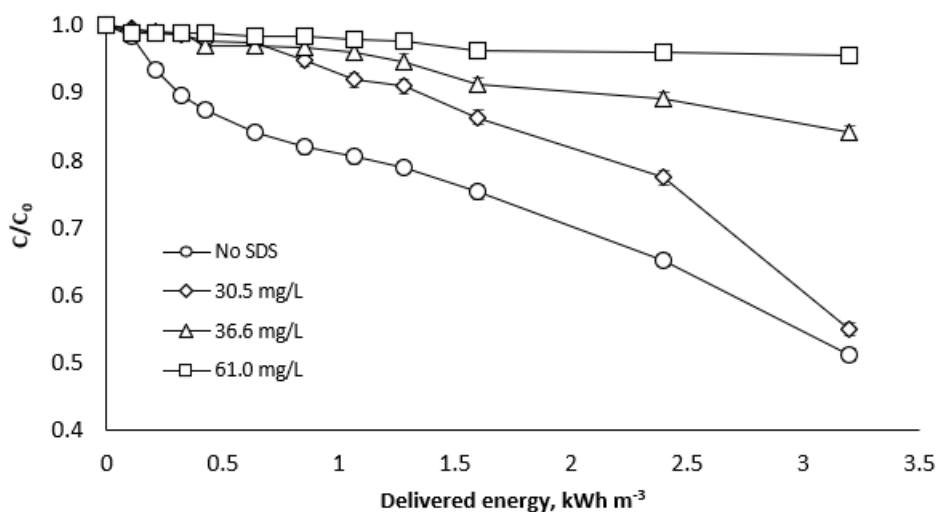


Figure 12. Carbamazepine oxidation in urine at various SDS concentrations vs delivered energy dose: pH 3.0, pulse repetition frequency 200 pps, pulsed powers 32 W, CBZ starting concentration 10.0 mg L⁻¹

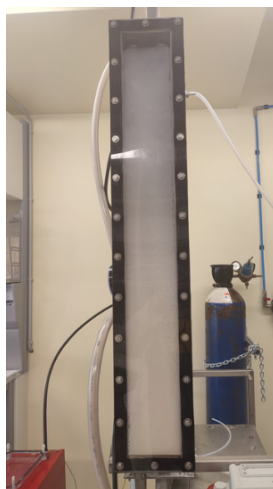


Figure 13. Foaming in PCD reactor with SDS-loaded source-separated urine

3.2.3 Nutrient stability and urease enzyme inhibition

A primary objective of urine valorisation is the preservation of the nitrogen pool in its most concentrated and stable form - urea. A significant achievement of current research was the demonstration of *in-situ* stabilization through the deactivation of the urease enzyme by PCD treatment.

As illustrated in Figure 14, the stabilization effect was evaluated by monitoring the normalized electric conductivity (EC/EC_0) of non-stabilized urine over a two-hour period.

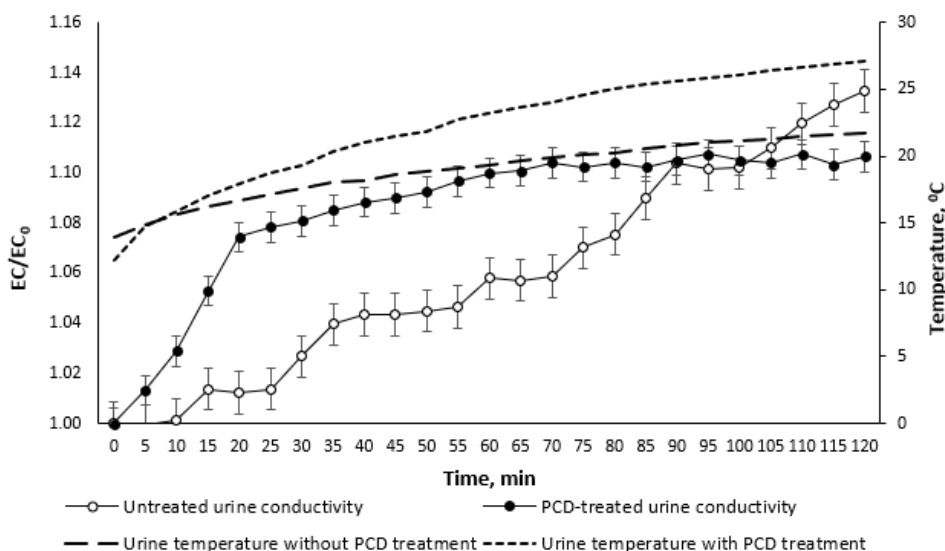


Figure 14. Urease enzyme inhibition observed through normalized electric conductivity (EC/EC_0) in non-stabilized untreated and PCD-treated urine

In the untreated urine sample containing urease, the EC/EC_0 ratio increased steadily from 1.000 to approximately 1.133, with an initial conductivity EC_0 of 13.12 mS cm^{-1} . The

increase was mainly caused by urea hydrolysis into ionic species, ammonium cation and carbonate anion as described in chapter 1.4.3, Equation 20.

In contrast, the PCD-treated sample exhibited a distinct plateauing behaviour. While the conductivity of treated sample initially rose faster than the one of untreated urine, which was likely due to the rapid oxidation of organic compounds into carboxylic acids and formation of nitrates, it reached a steady state after approximately 70 minutes of treatment, stabilizing at EC/EC₀ ratio of 1.10.

The result is further supported by the temperature profiles shown in Figure 14 in dashed lines. The PCD-treated sample reached the final temperature of 27.1 °C, significantly higher than 21.7 °C observed in the untreated sample. Under normal conditions, higher temperatures significantly enhance the activity of the urease enzyme, which should have resulted in a higher conductivity of the treated sample. The fact that the conductivity of PCD-treated sample stopped rising at noticeably lower value than the one of untreated urine despite the higher temperature additionally supports inhibition of the urease enzyme by PCD oxidation. The inhibition is attributed to oxidation, which effectively damages the structure of the enzyme. These findings suggest that PCD may serve as a urea stabilizer, potentially reducing the need for acid. When combined with the fact that no appreciable change in urea and chloride was detected, these results confirm that PCD provides an effective treatment for decentralized nutrient recovery.

3.2.4 Safety and plant growth

The ultimate objective of applying PCD treatment to source-separated urine is the production of a safe pharmaceutical-free fertilizer. The removal of parent pharmaceuticals does not inherently guarantee safety in terms of phytotoxicity, since plasma-induced oxidation products of plentiful organic compounds may exhibit biological activity. To evaluate the risk, phytotoxicity assays using the garden pea *Pisum sativum* were conducted, comparing the performance of untreated stabilized (group A) and PCD-treated urine (group B).

As illustrated in Figure 15, the growth trials involved monitoring the plants through their initial vegetative development stages, from seedling emergence to biomass harvesting.

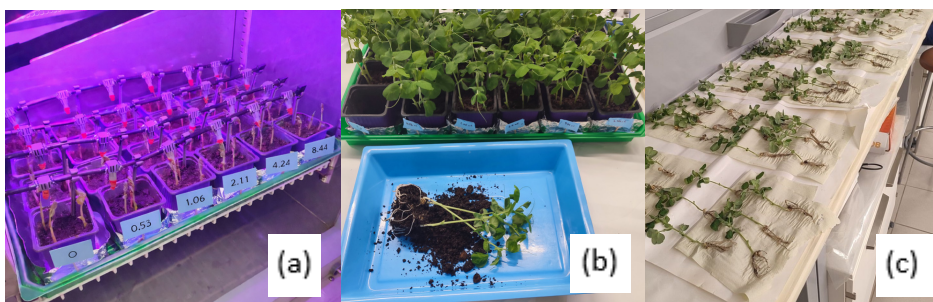


Figure 15. Garden peas *Pisum sativum* plants during the growing phase (a) and in biomass measuring procedures (b and c)

The quantitative results of the biomass accumulation are presented in Figure 16 showing the dry weight of shoots and roots across a range of agronomic dosages (from 0 to 4×, as was indicated in section 1.1.1.1).

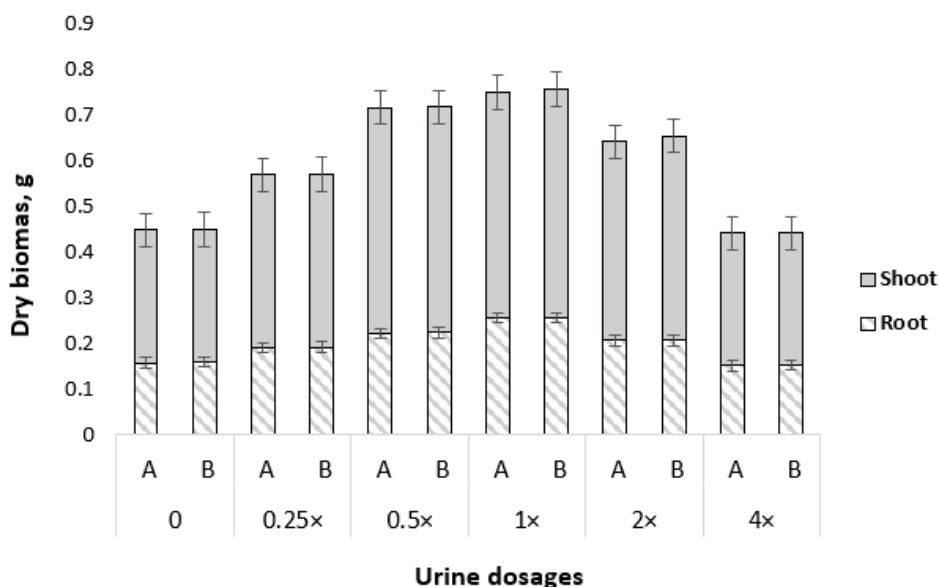


Figure 16. The peas shoot and root average biomass of a single plant while applying urine doses for two treatment groups: untreated urine (group A) and PCD-treated urine (group B)

A critical observation from the data is the identical growth trajectories of groups A and B across urine dosages. There was no statistically significant difference in biomass accumulation or tissue partitioning, i.e., shoot-to-root ratio between the untreated and PCD-treated samples. This result provides definitive proof that the PCD process does not introduce phytotoxic transformation products into the fertilizer matrix.

The growth response followed a characteristic ‘bell curve’ common in nutrient studies. Biomass increased as the dosage rose from 0.25x to the reference agronomic dose 1x, where growth peaked at approximately 0.75 g of total dry biomass. At supra-agronomic doses, 2x and 4x, exceeding the reference dose two and four times, respectively, a decline in biomass was observed. This decline is attributed to the nutrient overdose, inherent salinity and/or osmotic stress of urine rather than the PCD treatment itself, as the inhibition was equally present in both the untreated and treated groups.

Furthermore, as a leguminous crop, *Pisum sativum* relies on symbiotic nitrogen fixation. The successful growth in all treated samples suggests that the supplemental nitrogen provided by the stabilized urine was effectively utilized without damaging the soil-rhizobia interface. These results confirm that PCD-treated urine is a viable and safe alternative to synthetic fertilizers. When combined with the high removal rates of recalcitrant drugs and the successful inhibition of the urease enzyme, the technology meets all the necessary operational requirements for integration into a decentralized circular economy.

3.2.5 Techno-economic and environmental considerations

To contextualize the findings made in the research within the framework of the circular economy, a comparative energy analysis was performed in respect of nitrogen nutrient production to evaluate the viability of PCD-treated urine against conventional synthetic fertilizer production, i.e., ammonia. The total energy expense for producing a concentrated urine-derived fertilizer is estimated at 33.4 kWh kg⁻¹ N, comprising 1.8 kWh

kg⁻¹ N for PCD taken as the highest experimental energy dose of 12.3 kWh m⁻³ of urine, and 31.6 kWh kg⁻¹ N for the subsequent dewatering step.

When compared to the Haber-Bosch benchmark of 12.5 kWh kg⁻¹ N for industrial ammonia production, the proposed system initially appears to have a higher energy demand. However, this comparison must be viewed through the lens of decentralized resource management and industrial symbiosis.

First, the energy demand is highly dependent on the final application of the product. In a decentralized local reuse scenario, such as an eco-village or an urban farming project excluding long-distance transportation, the dewatering step could be entirely bypassed. If the PCD-treated urine is applied locally as a liquid fertilizer, the energy footprint drops to just 1.8 kWh kg⁻¹ N, which is nearly seven times more efficient than the Haber-Bosch process. This suggests that PCD is an exceptionally low-energy solution for local nutrient loops where the 'logistical penalty' of transporting heavy liquid volumes is minimized.

Second, in scenarios where concentration and dewatering are necessary for transport, the energy efficiency can be further optimized by utilizing industrial waste heat. The dewatering step (31.6 kWh kg⁻¹ N) is primarily a thermal process. If the treatment facility is integrated into an industrial park or near a power plant that generates waste heat as an emission, this 'free' energy source can be harnessed to drive the concentration process. In such a model, the actual electrical energy requirement remains restricted to the 1.8 kWh kg⁻¹ N consumed by the PCD reactor, making the overall system highly competitive with centralized manufacturing.

The gap between the energy costs of urine valorisation and synthetic production is significantly bridged by the environmental 'credits' inherent in decentralized production. These include:

- contaminant abatement: unlike conventional fertilizer production, the PCD process eliminates pharmaceutical residues, preventing their entry into aquatic ecosystems and avoiding the future costs of downstream environmental remediation;
- nutrient resilience: the recycling of nitrogen, potassium and phosphorus reduces the reliance on finite mineral resources and carbon-intensive industrial processes;
- reduced distribution costs: producing fertilizer-at-source eliminates the energy-intensive transport and logistics associated with distributing synthetic products from centralized hubs.

These considerations confirm that the PCD treatment of source-separated urine is not merely a wastewater treatment technology, but a scientifically and economically viable pillar of a sustainable circular economy.

Conclusions

The research presented in this thesis demonstrates that the gas-phase pulsed corona discharge (PCD) is a highly effective and multi-functional technology for the treatment of complex aqueous matrix of urine, effectively bridging the gap between fundamental aqueous baselines and the practical operational limits of decentralized nutrient recovery. By studying the transformation of inorganic and organic pollutants, the research has disclosed the critical role of the gas-liquid interface in overcoming the scavenging barriers inherent in high-strength waste streams like source-separated human urine.

In the investigation of inorganic pollutants, the study established that the bromide-bromate transition in PCD is a reversible process. Unlike conventional ozonation, where bromate accumulation is a linear consequence of oxidant dose, the PCD system reaches a dynamic equilibrium between bromide and bromate within a relatively short treatment duration. This equilibrium is heavily influenced by the chemical environment. Specifically, the presence of organic scavengers in circum-neutral media suppresses the formation of unstable hypobromous intermediates. This finding is of significant practical importance for water safety, as the elimination of these intermediates effectively minimizes the potential for the haloform reaction, i.e., the subsequent production of regulated trihalomethanes. Furthermore, the observation that bromate inhibits nitrogen oxidation by reducing nitrate yields highlights the complex chemistry of PCD, where reactions between inorganic species define the final product composition.

Regarding the valorisation of source-separated urine, the research confirms that PCD achieves a high degree of targeted oxidation determined by molecular structure of pollutants, and interphase action of PCD. The technology demonstrated energy efficiencies for the removal of amphiphilic pharmaceuticals, such as carbamazepine and propranolol, that are an order of magnitude higher than those reported for conventional ozonation. This targeted character is a direct result of the partitioning of hydrophobic molecules toward the gas-liquid interface, where they are attacked by a short-lived surface-borne radicals before they can be sequestered by bulk-liquid scavengers. In contrast, the poor removal rates of hydrophilic compounds like tetracycline define a clear operational limit, suggesting that the effectiveness of PCD in complex matrices is intrinsically linked to the target contaminant's molecular structure.

The study also identified critical physico-chemical limits for the technology's application. While surfactants like SDS enhance oxidation in dilute waters by acting as a molecular 'shuttle', their use in urine treatment appeared bringing negative consequences, decelerating oxidation of target pharmaceutical pollutants.

From the other hand, PCD offers a significant advantage as a one-step stabilizer. The treatment effectively deactivates the urease enzyme, thereby locking nitrogen in its urea form and preventing ammonia volatilization. This dual-benefit approach, abating pharmaceuticals while preserving nutrient integrity at moderate energy expense comprises the main benefit of PCD application to urine valorisation. Phytotoxicity assays confirmed that PCD-treated urine is as safe as untreated one for plants as fertilizer. From a techno-economic perspective, the maximum experimentally tested energy requirement of $1.8 \text{ kWh kg}^{-1} \text{ N}$ seems to be promising for decentralized liquid fertilizer production, making PCD a scientifically and economically viable pillar for the transition toward a resilient circular economy.

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Abstract

Pulsed corona discharge oxidation of organic and inorganic pollutants: from aqueous baseline to operational limits in source-separated urine

The global transition toward circular economy necessitates the development of innovative technologies capable of recovering essential resources from anthropogenic waste streams while ensuring environmental safety. Within the nutrient-energy-water nexus, human urine represents a concentrated reservoir of nitrogen, potassium and phosphorus, yet its valorisation as a fertilizer is hindered by the presence of persistent pharmaceutical residues and the rapid enzymatic loss of nitrogen. Conventional advanced oxidation processes (AOPs), such as ozonation, often fail to treat these high-strength matrices efficiently due to the ‘fatal barrier’ of radical scavenging, where bulk matrix constituents consume the oxidative flux before it can reach trace contaminants. The doctoral thesis investigates gas-phase pulsed corona discharge (PCD) as a superior alternative, exploring its mechanisms and operational limits across two distinct research subjects: aqueous bromide management and urine-derived nutrient recovery.

The first phase of research established an aqueous baseline by investigating the oxidation of bromide. Bromide is a naturally occurring precursor to bromate, a regulated potential carcinogen. Through PCD experimental studies, the reversible bromide-bromate reaction was observed, reaching a dynamic equilibrium that prevents the total conversion of bromide to toxic bromate. The study disclosed that the presence of organic scavengers, such as oxalates, fundamentally alters the speciation of bromine. In circum-neutral media, these scavengers suppress the accumulation of hypobromous acid and hypobromite, the primary agents responsible for the formation of toxic halogenated organic byproducts. By navigating these pH and matrix-dependent pathways, the research demonstrates that PCD can achieve disinfection and pollutants removal while maintaining inorganic speciation within safe regulatory limits.

The second phase of the study explored the operational limits of PCD in the context of the circular economy - the treatment of source-separated human urine. Using carbamazepine, propranolol, and tetracycline as indicator compounds, the research demonstrated that PCD achieves targeted oxidation through interface-based reactions. The results show that molecular amphiphilicity is the primary determinant of success: amphiphilic drugs partition to the gas-liquid interface and escape the bulk-liquid scavenging of surface-borne oxidants, leading to energy efficiencies an order of magnitude higher than conventional bulk-liquid treatments such as ozone application. However, the study also identified a feasibility limit regarding surfactant addition: while sodium dodecyl sulphate (SDS) enhances amphiphiles oxidation in diluted waters, it fails when applied in high-organic waste streams like urine.

Beyond contaminant removal, the research addressed the critical challenge of nutrient stabilization. The enzymatic hydrolysis of urea by urease leads to significant nitrogen loss. This research provides a proof that PCD deactivates the urease enzyme, stabilizing the nitrogen pool in its molecular urea form. The safety of the fertilizer product was comprehensively validated through phytotoxicity assays on garden pea *Pisum sativum*. The trials showed that PCD-treated urine maintains growth trajectories identical to untreated samples, confirming the absence of phytotoxic transformation products.

A preliminary techno-economic analysis concludes the work by comparing the PCD process to industrial benchmarks. While producing concentrated fertilizer is energy-intensive, the decentralized application of safe PCD-stabilized urine requires only 1.8 kWh kg⁻¹ N. This is significantly lower than the energy demand of the Haber-Bosch process, even before accounting for the environmental ‘credits’ of pharmaceutical removal and nutrient recycling. Collectively, the findings of this thesis provide a scientific roadmap for scaling up PCD as a robust decentralized technology for water purification and sustainable agricultural reuse, bridging the gap between theoretical oxidation mechanisms and real-world environmental challenges.

Lühikokkuvõte

Orgaaniliste ja anorgaaniliste saasteainete oksüdeerimine impulss-koroonalahenduse abil: vesikeskkonna mudel-süsteemidest kuni allikapõhiselt kogutud uriini töötlemise piiranguteni

Üleilmne üleminek ringmajandusele eeldab uuenduslike tehnoloogiate arendamist, mis võimaldavad antropogeensetest jäätmevoogudest ressursse tõhusalt tagasi võita, tagades samal ajal keskkonnoahutuse. Toitainete–energia–vee seose (ingl *water–energy–food nexus*) kontekstis on inimuriin kontsentreeritud lämmastiku, fosfori ja kaaliumi allikas. Selle kasutamist väetisena piiravad aga püsivad ravimijäägid ning urea kiire ensümaatilise lagunemine, mis põhjustab märkimisväärset lämmastikukadu. Olemasolevad süvaoksüdatsiooniprotsessid (ingl *advanced oxidation processes*, AOP), näiteks osoonimine, ei suuda suure orgaanilise koormusega maatrikseid tõhusalt töödelda radikaalide püüdmise tõttu, mille korral maatriksi põhikomponendid tarbivad oksüdeerijad enne, kui need jõuavad mikroreostusaineteni. Käesolevas doktoritöös uuritakse gaasifaasi koroon-impulss-elektrilahendust (KIEL) kui alternatiivset oksüdatsioonitehnoloogiat, selgitades selle toimemehhanisme ja rakenduspiire bromiidi oksüdeerimisel ning inimuriinist toitainete taaskasutamisel.

Uurimistöö esimeses etapis käsitleti bromiidi oksüdeerumist vesilahustes. Bromiid on looduslikult esinev bromiidi lähteühend, samas kui bromaat on kantserogeenne joogivee kõrvalsaadus. Katsed näitasid, et KIEL-is kujuneb bromiidi ja bromiidi vahel dünaamiline tasakaal, mis takistab bromiidi täielikku muundumist bromiidi. Lisaks selgus, et orgaaniliste ühendite, näiteks oksalaadi, olemasolu muudab oluliselt broomiühendite reaktsiooniradasid. Neutraalses keskkonnas pärsib oksalaat hüpobroomishappe ja hüpobromiti teket, vähendades seeläbi toksiliste halogeenitud orgaaniliste kõrvalsaaduste moodustumise riski. Tulemused näitavad, et pH ja maatriksi koostise sihipärane juhtimine võimaldab KIEL-protsessis eemaldada saasteaineid, piirates samal ajal ohtlike anorgaaniliste kõrvalproduktide teket.

Töö teises etapis hinnati KIEL-i sobivust tekkekohas eraldatud inimuriini töötlemiseks. Indikaatorühenditena kasutati karbamasepiini, propranolooli ja tetratsükliini. Tulemused näitasid, et KIEL võimaldab selektiivset oksüdatsiooni gaasi-vedeliku faasipiiril ning protsessi määravaks teguriks on ravimimolekulide amfiifiilsus. Amfiifiilsed ühendid akumuleeruvad faasipiirile, vältides vedeliku mahus toimuvat oksüdeerijate püüdmist, mistõttu saavutati ligikaudu suurusjärgu võrra suurem energiatõhusus kui osoonimisel. Samas määrati kindlaks ka tehnoloogia rakenduspiirid: kuigi naatriumdodetsüülsulfaat (SDS) soodustab amfiifiilsete ühendite oksüdeerumist lahjades vesilahustes, ei paranda see protsessi efektiivsust suure orgaanilise aine sisaldusega maatriksites, näiteks uriinis.

Lisaks mikroreostusainete eemaldamisele käsitleti töös toitainete stabiliseerimist. Urea ensümaatilise hüdrolyüsi ureaasi toimetel ammoniaagiks põhjustab märkimisväärset lämmastikukadu, kuid käesolevas töös näidati, et KIEL inaktiveerib ureaasi ning stabiliseerib lämmastiku urea kujul. Saadud väetise ohutust hinnati fütotoksilisuskatsetega aedhernel (*Pisum sativum*). KIEL-iga töödeldud ja töötlemata uriiniga väetatud taimede kasv ei erinenud statistiliselt, mis kinnitab, et töötlemise käigus ei moodustunud fütotoksilisi kõrvalsaadusi.

Doktoritöö lõpetab tehnilis-majanduslik eelanalüüs, milles võrreldakse KIEL-protsessi olemasolevate tehnoloogiatega. Kuigi kontsentreeritud väetise tootmine on energiamahukas, nõuab KIEL-iga stabiliseeritud uriini detsentraliseeritud kasutamine vaid $1,8 \text{ kWh kg}^{-1} \text{ N}$, mis on oluliselt väiksem kui Haber–Boschi protsessi energiavajadus. Seejuures ei hõlma võrdlus ravimijääkide eemaldamisest ja toitainete ringlussevõttust tulenevat täiendavat keskkonnakasu. Käesolev doktoritöö annab uued teadmised gaasifaasi plasmaoksüdatsiooni mehhanismidest suure orgaanilise koormusega vesilahustes ning loob teadusliku aluse KIEL-tehnoloogia rakendamiseks ravimijääkide eemaldamisel ja toitainete ringlussevõtul detsentraliseeritud veekäitlussüsteemides.

Appendix 1

Table S1. Synthetic urine composition

Ingredient	Empiric formula	Concentration, g L ⁻¹
Sodium sulphate	Na ₂ SO ₄	1.7
Uric acid	C ₅ H ₄ N ₄ O ₃	0.25
Trisodium citrate	Na ₃ C ₆ H ₅ O ₇ ·2H ₂ O	0.72
Creatinine	C ₄ H ₇ N ₃ O	0.881
Urea	CH ₄ N ₂ O	15.0
Potassium chloride	KCl	2.308
Sodium chloride	NaCl	1.756
Calcium chloride	CaCl ₂	0.185
Ammonium chloride	NH ₄ Cl	1.266
Potassium oxalate	K ₂ C ₂ O ₄	0.035
Magnesium sulphate	MgSO ₄ ·7H ₂ O	1.0082
Dihydrate monobasic sodium phosphate	NaH ₂ PO ₄ ·2H ₂ O	2.912
Dibasic sodium phosphate dodecahydrate	Na ₂ HPO ₄ ·12H ₂ O	0.831

Appendix 2

Paper I

Petrochenko, I.; Preis, S. (2024). Aqueous bromide oxidized with pulsed corona discharge. Journal of Electrostatics, vol. 132, 103978, DOI: 10.1016/j.elstat.2024.103978.



Aqueous bromide oxidized with pulsed corona discharge

Irina Petrochenko, Sergei Preis*

Laboratory of Environmental Technology, Department of Materials and Environmental Technology, Tallinn University of Technology, 5 Ehitajate tee, 19086 Tallinn, Estonia

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ABSTRACT

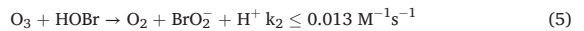
Bromide in treated natural waters is oxidized to toxic bromate with ozone. For the novelty of pulsed corona discharge (PCD) in water treatment, its potential in bromide transformation needs clarification. Experimental research into bromide-bromate conversion dependent on control parameters, including pulse repetition frequency, pH, Br^- concentration, and presence of organics, was undertaken. Bromide transformed to bromate in acidic and circum-neutral media; transformation of bromate to bromide was also observed. Bromide was poorly oxidized in alkaline media. Oxidation of bromide was obstructed with oxalate. Formation of nitrate was noticeably decelerated by bromate.

1. Introduction

Fresh water contains enough bromide to create more than $10 \mu\text{g L}^{-1}$ of bromate after ozonation, which is the USEPA's maximum allowable concentration [1]. Bromate is toxic and is thought to be a human carcinogen: studies on animals showed bromate causing cancer at relatively low dosages. Investigations also showed mutagenicity of bromate causing a change in a gene or chromosome. Bromide is naturally found in geological formations such as limestone, granite, and shale with quantities ranging from 0.3 to 24 mg kg^{-1} [2]. The concentration of bromide in surface water is in the range of a few $\mu\text{g L}^{-1}$ to several mg L^{-1} . Bromide levels below $20 \mu\text{g L}^{-1}$ do not cause problems, although higher levels are becoming a problem by bromate formation [3].

There are two main ways bromate ends up in drinking water: oxidation of bromide and infiltration of bromate with wastewaters. Minor amounts may also appear in water reservoirs under solar radiation [4].

Generation of bromate as a disinfection by-product when bromide reacts with ozone is shown in Eqs. (1)–(5) [5].



Hydroxyl radical reacts with bromide at the reaction rate constant as high as $10^{10} \text{ M}^{-1}\text{s}^{-1}$, initiating a fast chain reaction [5].

Bromate is generated in ozonation reacting with a mixture of ozone and HO-radicals. Its production is exceedingly difficult, with up to six bromine oxidation states involved (Fig. 1) [6].

At acidic conditions ($\text{pH} < 4$), the direct reaction with molecular ozone takes precedence, but at $\text{pH} > 10$, radical oxidation prevails with both mechanisms acting in neutral media [7]. In some wastewaters, radical oxidation may be significant even at pH 2, dependent on the contents of contaminants and reaction promoters in treated water [8].

Application of pulsed corona discharge (PCD) is a cost-effective oxidation method, similar in its chemical nature to other advanced oxidation processes (AOPs), generating HO-radicals mainly at the gas-liquid interface [9]. This, together with the PCD advanced energy efficiency in oxidation of aqueous pollutants [10], makes the behaviour of bromide in plasma treatment falling into the area of PCD safety, deserving studies. Oxidizing pollutants mainly with HO-radicals [11], PCD requires a separate approach to its actions on bromide due to oxidation potential of the radical exceeding the one of molecular ozone, 2.8 eV against 2.07 eV, respectively [12,13]. The objective of the research is to establish the performance of PCD in respect to bromide, focusing on the control parameters' impact - pulse repetition frequency, pH, starting Br^- concentration, and presence of organic compounds. Oxalate was chosen as an organic competitor for its structural simplicity,

* Corresponding author.

E-mail address: sergei.preis@taltech.ee (S. Preis).

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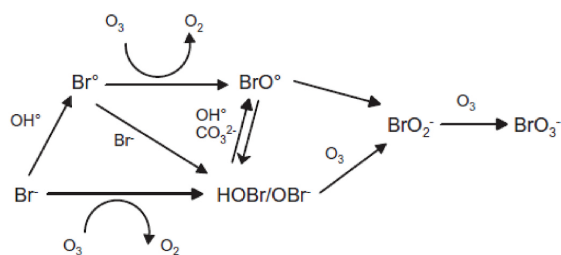


Fig. 1. Bromate formation pathways in ozonation [6].

moderate oxidation rate, being fully mineralized without intermediates. The authors failed to find published data on aqueous bromide oxidation by means of electric discharge.

2. Materials and methods

2.1. Chemicals

The bromine liquid (Br_2 , 99 %) was purchased from Thermo Fischer Scientific, Ltd. (USA). Potassium bromide (KBr, 99.7 %), potassium bromate (KBrO_3 , 99 %) and sulphuric acid (H_2SO_4 , 96 %) were obtained from Lach-Ner Ltd. (Czech Republic). Sodium hydroxide (NaOH, 98 %) and sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$, 99 %) were purchased from Merck KGaA (Germany).

2.2. Analyses

Anion concentrations were measured using anion chromatograph Eco IC (Metrohm, USA) equipped with anion column Metrosep A Supp5 – 250/4.0 and standard eluent (Metrohm, USA). pH was measured using S220 digital pH-meter (Mettler Toledo, Switzerland).

2.3. Experiments

The experimental equipment (Fig. 2) manufactured by Flowrox Oy (Finland) consists of PCD reactor with the storage tank of 40 L capacity,

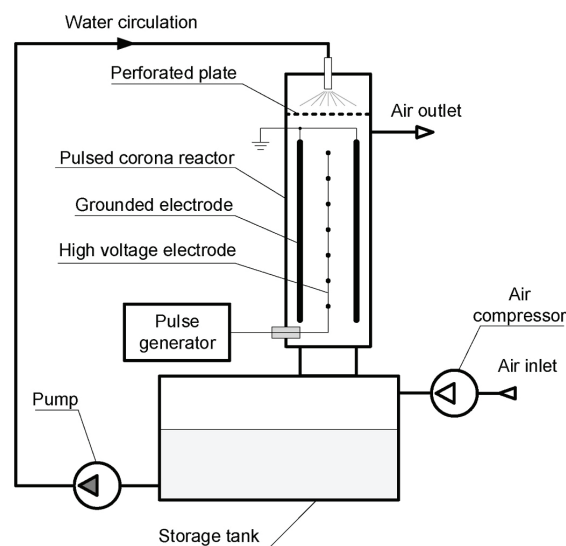


Fig. 2. Experimental setup outline.

pulse generator and circulation pump providing the treated solutions' flow rate of $1.0 \text{ m}^3 \text{ h}^{-1}$. The detailed description of the PCD device is given by Tikker et al. [13]. The multiple string electrodes of 0.55 mm in diameter and.

20 m of total length are positioned horizontally between vertical parallel plates. The electrode system configuration was chosen to provide smaller conductivity losses using construction described by Kornev et al. [14]. The distance between wire electrodes and the grounded plate is 18 mm. Treated solutions were dispersed through the perforated plate with 49 perforations of 1.5 mm diameter positioned in a vertical plane with the high voltage string electrodes. Pulses of voltage amplitude of 18 kV, current of 380 A, and 100 ns duration with power delivered to the reactor of 9W, 32 W and 123 W at 50, 200 and 880 pulses per second (pps), respectively, were provided by the pulse generator. The pulse characteristics were quantified with a Rigol DS1102E Mixed Signal Oscilloscope, a Tektronix P6015 high voltage probe (Tektronix Inc., USA) and a current monitor PT-7802 (PinTek, China). The energy of a pulse delivered to the reactor was 0.19 and 0.15 J at 50 and 200, and 880 pps, respectively, calculated by integration of voltage and current time profiles [14]. After passing the plasma zone, treated water falls to a storage tank, from where it is circulated back to the top of reactor. Indoor air was used as the discharge atmosphere purged at the 1.0 L min^{-1} rate considered being sufficient for minor reactivity of the treated dissolved substances.

The delivered energy was calculated using Eq. (6):

$$\text{Delivered energy} = \frac{P \cdot t}{V} \quad (6)$$

where P is power supplied by the pulse generator, kW, t is the treatment time, h, and V is the treated solution volume, m^3 .

Bromide was dissolved in distilled water with concentrations 1.0 and 5.0 mg L^{-1} in 10-L samples used as potassium salt. The concentrations were chosen for reliability of the quantification of bromide and the products of oxidation. The sample was treated in the PCD reactor at 200 pps for 2 h with sampling for analyses every two minutest within the first 30 min of treatment, and every 15 min for the rest of experimental time. After the PCD was switched off prior the sampling, the treated solution was continuously mixed with the pump for the volume averaging for 4 min. During the 2-h treatment, the temperature of solution increased from initial $20 \pm 1^\circ \text{C}$ to $25 \pm 1^\circ \text{C}$.

Nitrate formation was assessed by the energy efficiency, with which the anion was formed. The efficiency E was calculated knowing the nitrate concentration at the sampling time, the applied pulsed power and the volume of treated sample:

$$E = \frac{\Delta C \cdot V}{P \cdot t} \quad (7)$$

where E – nitrate formation energy efficiency, $\text{g kW}^{-1} \text{ h}^{-1}$,
 ΔC – the increase in nitrate concentration, g m^{-3} ,
 V – volume of treated solution sample, m^3 .

3. Results and discussion

3.1. The impact of pulse repetition frequency

The pulse repetition frequency meeting the experiment needs in measurement of bromine ionic forms was chosen from the experimental results obtained from the PCD treatment of bromide solutions. The tests at various pulse repetition frequencies were conducted at 5.0 mg L^{-1} of starting bromide concentration, and 10 L of solution volume treated for 2 h. At this time, the equilibrium between the bromine-containing anions was achieved by using 200 and 880 pps, whereas 50 pps demonstrated slower achievement of equilibrium (Figs. 3 and 4). Evolution of unadjusted pH in the PCD-treated bromide solution characteristic for the discharge in air forming nitric acid is shown in Fig. 5. Formation of

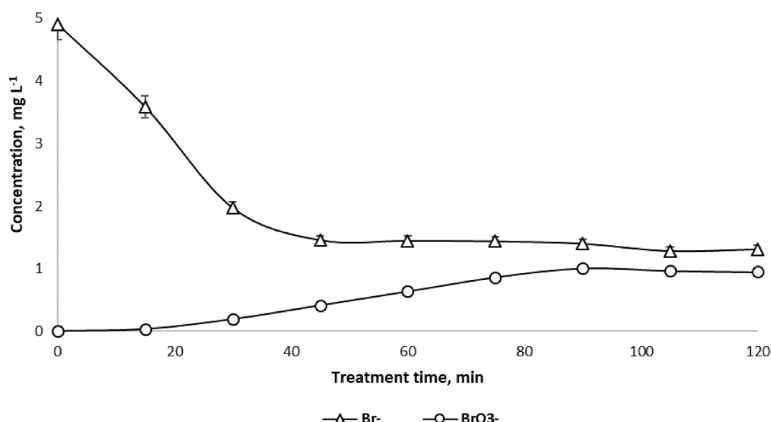


Fig. 3. Equilibrium between the bromine-containing anions: pulse repetition frequency 200 pps, bromide starting concentration 5.0 mg L^{-1} , circum-neutral pH descending from 9.3 to 3.0.

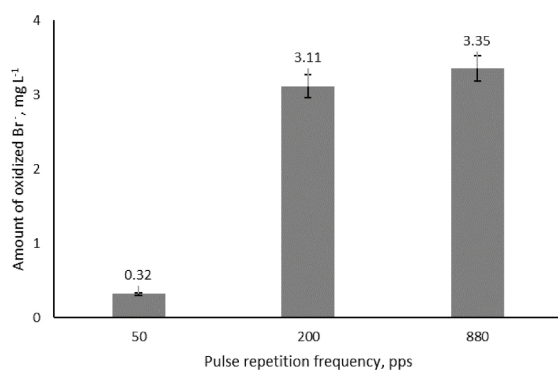


Fig. 4. Effect of pulse repetition frequency on amount of oxidized Br^- after 2 h of treatment: circum-neutral pH descending from 9.3 to 3.0, bromide starting concentration 5.0 mg L^{-1} , energy doses delivered to the reactor at 50, 200 and 880 pps are 1.8, 6.4 and 12.6 kWh m^{-3} , respectively.

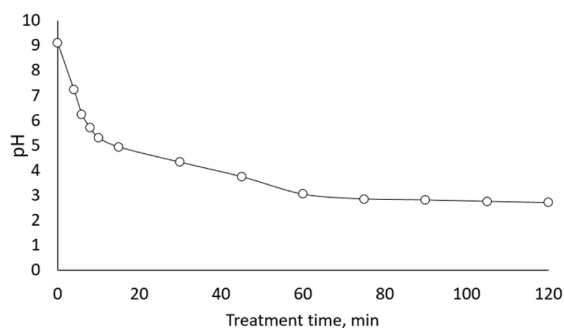


Fig. 5. Evolution of unadjusted pH in the PCD-treated bromide solution: pulse repetition frequency 200 pps, bromide starting concentration 5.0 mg L^{-1} .

nitrate following a linear pattern in time is shown in Fig. 6. Concerning nitrite, the authors did not notice appearance of it in PCD-treated samples explained by its oxidation further to nitrates as described in Refs. [15,16]: nitrite observed earlier in a spark discharge, was not quantified

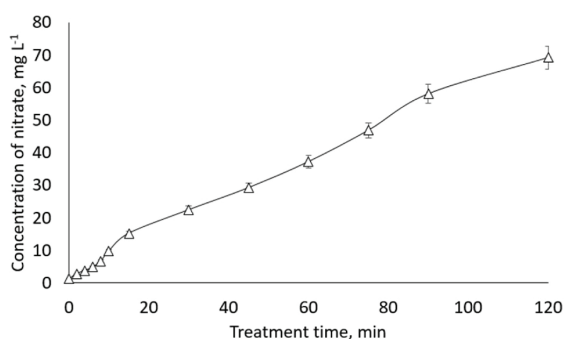


Fig. 6. Evolution of nitrate concentration in the PCD-treated bromide solution: pulse repetition frequency 200 pps, bromide starting concentration 5.0 mg L^{-1} , unadjusted pH decreasing from 9.3 to 3.0.

in PCD neither previously, nor in the present study.

Sampling at 200 pps appeared more convenient giving better chance for establishing the kinetic curves of bromine-containing species. Pulse repetition frequency affects the balance of short- and long-living oxidants, mainly HO-radical and ozone, respectively [11]. The balance between the oxidant species might make a difference in the bromide-bromate ratio and the rate of achievement of equilibrium between bromide and bromate. The authors, however, did not find the difference between 200 and 880 pps in these circumstances, making a choice in favour of 200 pps (Fig. 4). The absence of such difference may be explained by slow oxidation of bromide (Fig. 3), taking about 40 min for bromide-bromate equilibrium established, and, thus, a uniform composition of the oxidants' mixture. Since the 1-h equilibrium was achieved at 200 pps with the delivered energy of 3.2 kWh m^{-3} close to the one at 880 pps with the delivered energy of 12.3 kWh m^{-3} , the frequency of 200 pps was chosen also from the spent energy, and thus treated solution heating point. The bromide oxidation appears to be slow, showing no effect of increased rate of the energy/oxidants delivery within the experimental conditions.

3.2. PCD oxidation of bromine-containing species

The bromide-bromate equilibrium in PCD-treated bromide solution brings to an idea of the reverse character of bromide oxidation. The

authors failed to find a reference to the reversible bromide oxidation, the available references indicate one-way transformation of aqueous bromide to bromate [4,17–19], thus making the fact of the observed equilibrium unexplained.

To verify the hypothesis of reverse bromide oxidation, the authors undertook an experimental study in PCD oxidation of bromate and bromide-bromate mixtures. The results of bromate oxidation in circum-neutral medium, transited during the experiment to the acidic one due to the nitrate formation in PCD [15], showed gradual accumulation of bromide corresponding to the equally gradual decrease in bromate (Fig. 7): the misbalance of the reaction with the starting bromate concentration of 4.7 mg L^{-1} did not exceed 2 %. The equilibrium by the end of 2-h experiment reached concentrations of bromide and bromate at 0.4 and 4.0 mg L^{-1} , respectively.

The experiments with a mixture of bromate and bromide with respective concentrations of 4.5 and 1.0 mg L^{-1} showed a good hit on target equilibrium, providing minor change in concentrations: by the end of 2-h treatment, bromate concentration slightly decreased to 4.3 mg L^{-1} , whereas bromide concentration also decreased to 0.5 mg L^{-1} . The misbalance of reaction comprised 14 %, the reason of which is described below.

The quantification of bromide and bromate did not meet an obstacle: both IC-peaks were well-distinguished and quantitatively reliable. However, the unknown peaks also appeared in chromatograms besides the bromide and bromate together with the inevitable nitrate. The authors encountered obstacles in quantification of the peaks characteristic for the intermediate bromine-containing compounds. Thus, the hypobromite quantification is practically impossible for its unstable character. However, the hydrolysis of diatomic bromine in aqueous solution (Eqs. (8) and (9)) provided the IC-peaks identical to the ones observed in bromide PCD-oxidized solutions [19,20].



Earlier, Morrison et al. also described in their review bromate formation pathways, which include presence of hypobromous forms in ozonated bromine solutions [1]. 0.5 mL of liquid bromine comprising about 1.5 g of Br_2 was diluted in 100 mL of distilled water making bromine stock solution. Further dilutions of this solution were IC-analysed to provide bromide concentrations close to the ones used in the PCD experiments. Being aware of the approximate quantification of hypobromite and hypobromous acid showing different peaks at various pH of diluted solutions, the authors were able to clarify the balance of bromine-containing species in the treated solutions approaching from

the stoichiometry of the bromine hydrolysis (Fig. 8a and b). The peaks characteristic for hypobromous forms were the only ones observed in the IC-chromatograms, no other unknown peaks were encountered: hypobromite peak appeared at the seventh minute, whereas hypobromous acid's peak came up at the 33rd-35th minute (Fig. 9). This gives the authors reason to assume hypobromous forms to be the only relatively stable intermediate compounds in bromide oxidation. One should notice that hypobromous acid and hypobromite provided distinct peaks in the IC-chromatograms: being both observed in circum-neutral media, only hypobromous acid was detected at pH below 2.5 (Fig. 8b). The assessment of the atomic balance in treated solutions accounting for estimated hypobromous forms showed good coverage on misbalance between bromide and bromate.

3.3. Roles of bromide initial concentration and pH in bromide-bromate equilibrium

The initial bromide concentrations of about 5.0 and 1.0 mg L^{-1} were tested for the bromate formation in circum-neutral media. At the bromide concentration of 5.0 mg L^{-1} , the unadjusted pH of solution was 9.3 , and at 1.0 mg L^{-1} pH was 6.5 . After 2 h of treatment, the pH dropped to 2.7 and 2.9 in the solutions containing 5.0 and 1.0 mg L^{-1} of bromide, respectively, which belongs to circum-neutral range, as called in this study. The effect of nitrates formed in PCD to pH was discussed earlier (see 3.2).

The quantitative difference in the composition of bromine-containing products of oxidation is seen from the bromine balance in experiments with different bromide concentrations. At initial bromide concentration of 5.0 mg L^{-1} , about 69 %, i.e., 3.45 mg L^{-1} of bromide was oxidized. However, only $1.13 \text{ mg L}^{-1} \text{ BrO}_3^-$ was formed, which corresponds to $0.71 \text{ mg L}^{-1} \text{ Br}$, making the reaction bromine misbalance as big as 54 %. Hypobromous forms were found to fill the balance (see above), making the role of those substantial. At the five-fold smaller initial bromide concentration of 1.0 mg L^{-1} , 75 % of bromide was oxidized into $0.67 \text{ mg L}^{-1} \text{ BrO}_3^-$, i.e., $0.42 \text{ mg L}^{-1} \text{ Br}$, making the bromide-bromate misbalance almost 1.5 times smaller than at 5.0 mg L^{-1} concentration, 37 %. This makes the share of hypobromous forms substantially smaller at lower bromide starting concentration. Besides, the yield of bromate at lower bromide concentration appears to be much higher: 42 % of bromide at 1.0 mg L^{-1} was converted to bromate, whereas only 14 % of $5.0 \text{ mg L}^{-1} \text{ Br}^-$ were oxidized to bromate, leaving the bulk of bromine-containing compounds in hypobromous forms. By the other words, lower initial concentration of bromide results in more complete oxidation to bromate with lesser amount of hypobromous forms.

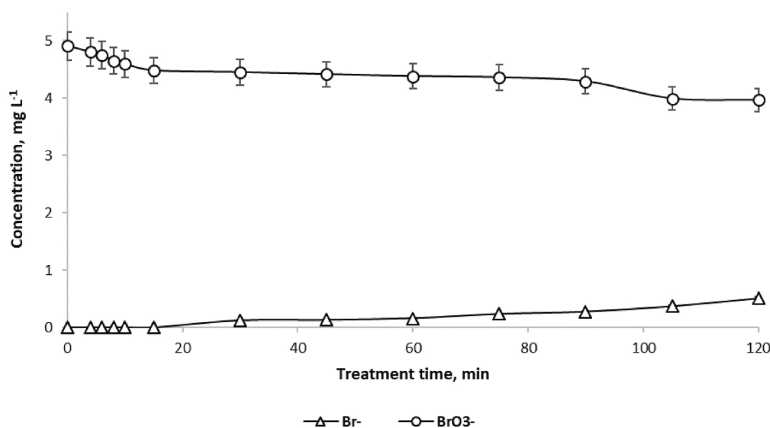


Fig. 7. Evolution of bromate and bromide in PCD oxidation: starting bromate concentration 4.7 mg L^{-1} , circum-neutral pH $6.0 \rightarrow 1.7$.

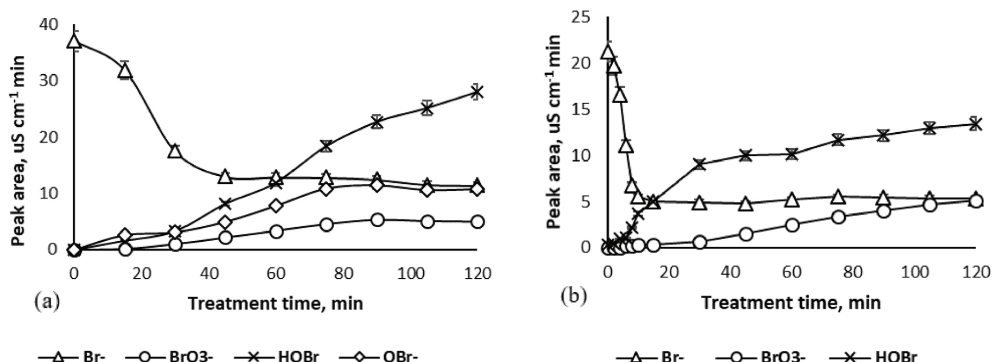


Fig. 8. Observed peaks of hypobromite and hypobromous acid in circum-neutral (a) and acidic (b) media in PCD-treated solutions: circum-neutral pH descending from 9.3 to 3.0, acidic pH 2.5, starting bromide concentration 5.0 mg L^{-1} .

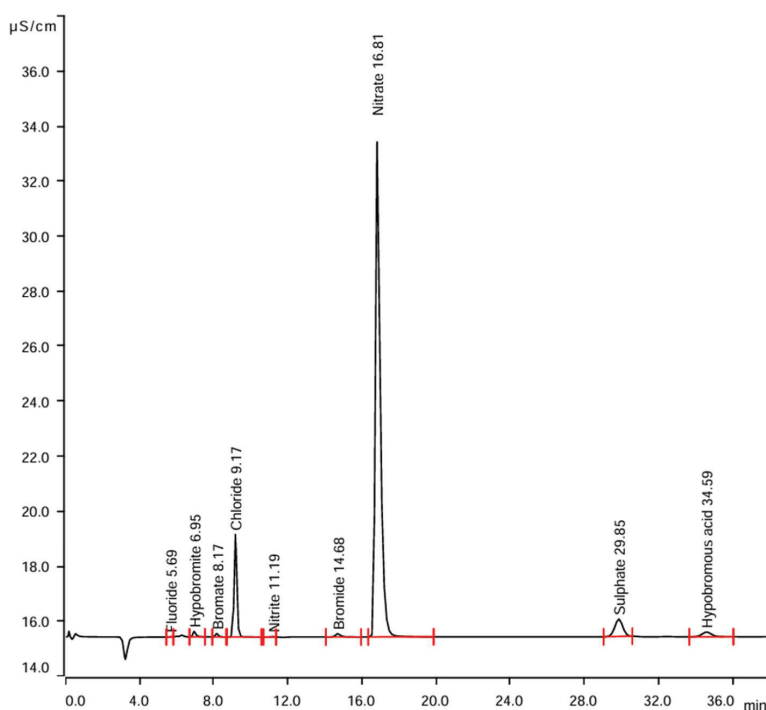


Fig. 9. IC-chromatogram of PCD-treated bromide solution: treatment time 75 min, circum-neutral pH descending from 9.3 to 3.0, starting bromide concentration 5.0 mg L^{-1} , fluoride as an internal standard, nitrate and nitrite – PCD side products, chloride and sulfate – impurities.

In acidic media adjusted with 4-M H_2SO_4 to pH 2.5, the equilibrium of reaction at the bromide starting concentration of 5.0 mg L^{-1} shifted towards bromate formation: the concentration of bromate increased from 1.13 in circum-neutral solution to 2.14 mg L^{-1} in acidic one (Fig. 10). One can see that the yield of bromate almost doubled in acidic solution, although the bromide-bromate misbalance remained almost unchanged with its 50 % in acidic medium, i.e., in acidic solution more of bromide was oxidized.

Interestingly, at lower initial bromide concentration of 1.0 mg L^{-1} , neither the amount of resultant bromate nor the bromide-bromate misbalance underwent significant changes in acidic solution compared to the circum-neutral medium: the resultant bromate concentration of

0.54 mg L^{-1} was observed together with the bromide-bromate misbalance of 46 %, i.e., the equilibrium deviated within 20 % of the IC-readings below 1.0 mg L^{-1} . The contents of hypobromous species also did not change with pH within circum-neutral and acidic range at the lower bromide concentration.

Alkaline media were adjusted with 4-M NaOH solution to pH 11.0. The results are shown in Fig. 10: only 6.5 % of bromide at its starting concentration of 5.0 mg L^{-1} was oxidized in 2 h of PCD treatment, producing 0.52 mg L^{-1} of bromate. The bromide-bromate balance showed here the negligible misalignment of 0.35 %. At the lower bromide concentration used in this study, the conversion to bromate was not noticed at negligible decrease in bromide concentration of around 2

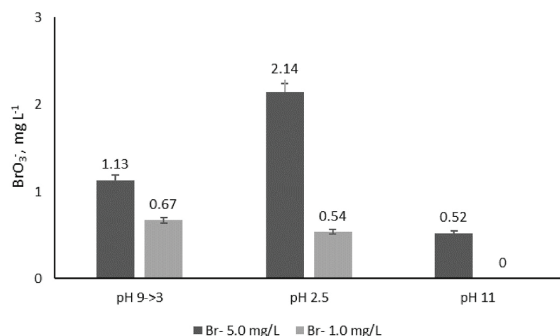


Fig. 10. Dependence of bromate yield on pH at various starting bromide concentrations in PCD-treated bromide solutions.

%, i.e., 0.02 mg L⁻¹.

3.4. Effect of oxalate admixture

Earlier, the authors found that nitrate formation in PCD is obstructed by the presence of organic compounds in treated solutions: pollutants compete for reactive oxygen species (ROS) with nitrogen oxides converted to nitrates. This observation had an exception – the presence of oxalate and formate, in contrast, accelerated the formation of nitrates [16]. Considering oxidation of bromide to bromate, the presence of organic admixtures presents an interest from the treatment safety standpoint. The authors choose oxalate as an admixture interfering with bromide oxidation for its structural simplicity, slow-to-moderate oxidation reaction, and the absence of oxidation intermediates potentially complicating the picture: oxalate is straightforwardly mineralized to carbon dioxide and water, incorporation of bromine into its structure is also impossible.

The amount of oxalate added to the bromide solution comprised 5.0 mg L⁻¹, corresponding to the 1:1 mass ratio with bromide, i.e., 1.1:1.0 M ratio, conveniently close to a unity. Alkaline conditions were not tested for negligible oxidation of bromide. Besides, oxidation of oxalate in alkaline media is also very slow explained in detail earlier [13], the authors do not expect an effect of two slow reactions to each other, tests with addition of oxalate to bromide solutions were conducted in circum-neutral and acidic conditions. Due to the buffering properties of oxalate solutions [21], pH of bromide-oxalate aqueous mixture naturally

stabilized at 7.3. Looking ahead, the buffering capacity stabilized the PCD-treated solution effectively enough to end up with pH 6.5 in 2 h of treatment even with only 20 % of remaining oxalate. The results of bromide-bromate equilibrium and degradation of oxalate in circum-neutral solution are shown on Fig. 11. One can see that the addition of oxalate substantially inhibited bromide oxidation, reducing also bromate formation (Fig. 12). Thus, the amount of oxidized bromide in presence of oxalate comprised only 0.38 mg L⁻¹, which is seven times smaller than in its absence, i.e., 2.67 mg L⁻¹. The amount of bromate formed in presence of oxalate in neutral medium comprised 0.62 mg L⁻¹, which is in stoichiometric ratio with oxidized bromide. The IC-peaks characteristic for hypobromous species were not observed in samples from PCD-treatment of neutral solutions, confirming negligible misbalance on bromine-containing species in presence of oxalate.

The fact attracting special attention consists of the bromide-bromate misbalance close to zero, pointing to the absence of hypobromous forms in presence of oxalate in PCD-treated neutral medium. By the other words, obstructing bromide oxidation, oxalate promotes oxidation of hypobromous forms down to the highest degree of oxidation, i.e., bromate. The disclosure of such reaction mechanism lays beyond the subject of this study, deserving, however, special attention in safety questions concerning PCD applications. This observation may witness reduced trihalomethane formation potential in haloform reaction of organic compounds [22] with hypobromous species eliminated in presence of oxalate, which deserves confirmation in further research.

Experiments in acidic medium at pH 2.5 revealed the unfortunate coincidence of IC-peaks of oxalic and hypobromic acids, both peaks were observed at 33rd/35th minute of chromatogram. As a result, the curves of these acids at the concentration-time experimental diagram remain unmeasurable, only bromide and bromate concentrations may be reliably quantified. Knowingly, oxalate PCD-degradation accelerates at low pH [23], which is related to HO-radical oxidation potential increasing with lowering pH from 1.9 to 2.8 V in neutral and acidic media, respectively [12]. The experimental test at pH 2.5 with PCD oxidation of oxalic acid undertaken in this research (graphically not shown) showed its content in 2 h of treatment at about 10 % of residual concentration, i. e., oxalate remains till the end of treatment confirming moderate oxidation rate. Evolutions of oxalic acid concentration, however, are not seen in presence of hypobromous acid formed in bromide oxidation for the interference in IC-analysis: the curve descending on account of oxalic acid degradation passes the inflection point with further ascending with formation of hypobromous acid prevailing at low pH (Fig. 13).

Bromide oxidation rate in presence of oxalic acid is visibly slower

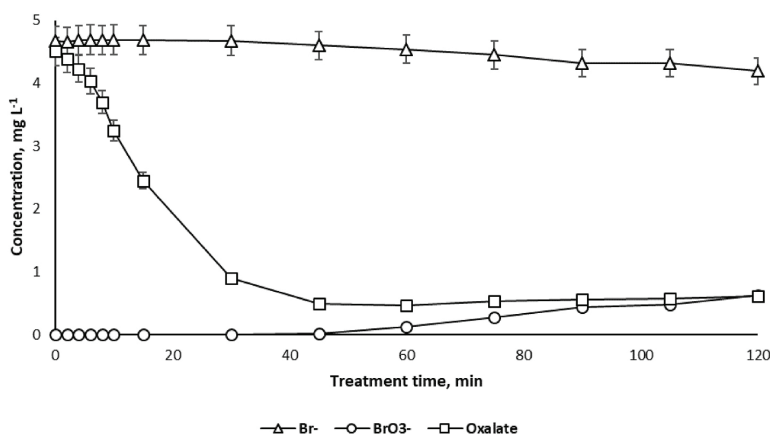


Fig. 11. Evolution of bromide, bromate and oxalate in PCD oxidation: starting bromide concentration 4.7 mg L⁻¹, oxalate concentration 4.5 mg L⁻¹, circum-neutral pH 7.3 → 6.5.

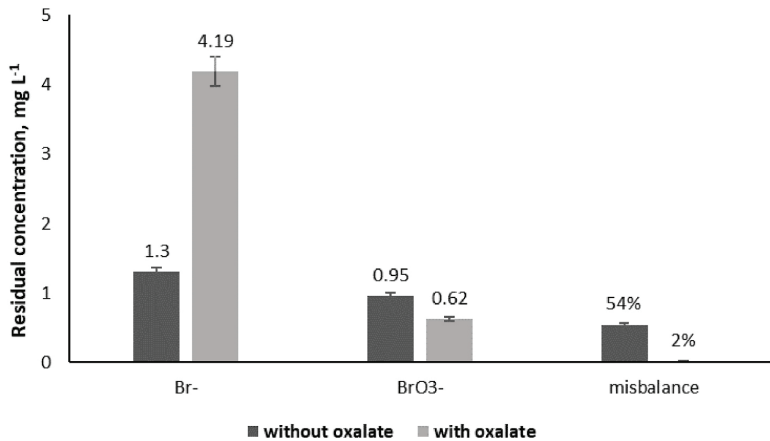


Fig. 12. Effect of oxalate addition on bromide oxidation and bromate formation in neutral medium: PCD treatment time 2 h at 200 pps, bromide initial concentration 4.7 mg L⁻¹, oxalate initial concentration 4.5 mg L⁻¹, circum-neutral pH 7.3 → 6.5.

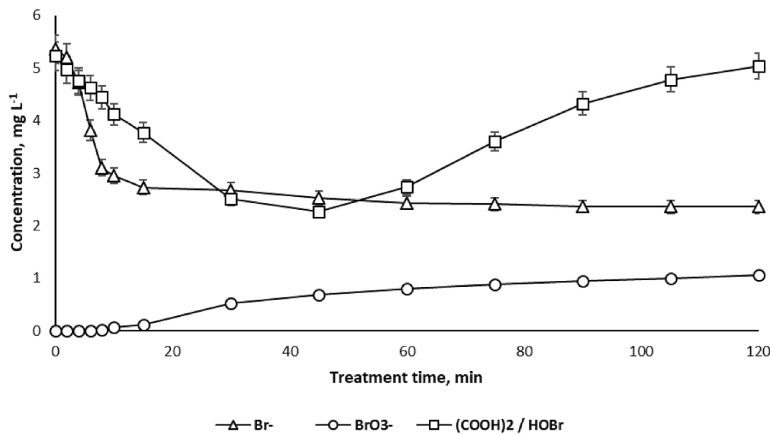


Fig. 13. Evolution of bromide and bromate in PCD oxidation: starting bromide concentration 5.3 mg L⁻¹, oxalate concentration 5.2 mg L⁻¹, acidic pH 2.5, hypobromous acid interferes in IC-analysis of oxalic acid.

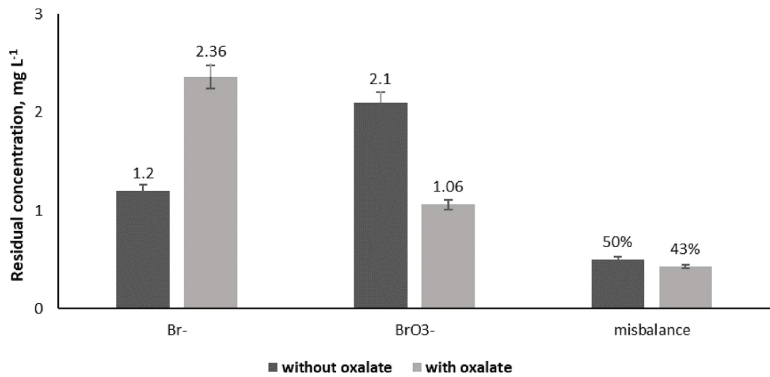


Fig. 14. Effect of oxalate addition on bromide oxidation and bromate formation at pH 2.5: starting bromide concentration 5.3 mg L⁻¹, oxalate concentration 5.2 mg L⁻¹.

than the one in absence of the latter, e.g., the decrease of bromide concentration for 30 % is achieved in 4.5 and 7.0 min without and with oxalate, respectively. The equilibrium concentration of bromide in 2 h treatment takes higher position in presence of oxalic acid at 2.36 mg L^{-1} gradually decreasing (Fig. 13), whereas in absence of oxalic acid bromide concentration reached about 1 mg L^{-1} in 10 min and remained at this level till the end of experiment (Fig. 8b). Bromate in presence of oxalic acid was formed in consistently smaller amounts around 1 mg L^{-1} (Fig. 14). In absence of organic acid, the concentration of bromate reached 2.1 mg L^{-1} . Under the circumstance, the bromide-bromate molecular misbalance in 2 h of treatment did not differ much with or without oxalic acid, comprising 43 % and 50 %, respectively. This fact indicates the indifference of the bromate formation mechanism via hypobromous acid towards the presence of oxalic acid in acidic media, the amount of hypobromous acid seems to remain proportional to the quantity if oxidized bromide. The difference with bromide oxidation in neutral solution, where no hypobromite was accumulated, may be explained by the difference in two hypobromous species' redox potential: higher oxidation potential of hypobromous acid [12] makes it more resistant than hypobromite towards oxidation with ROS produced in PCD. Slow oxidation kinetics of hypobromous acid with ozone prevailing in acidic media also supports its refractory character compared to hypobromite ion (Eq. (5)) [5].

3.5. Impact of bromine-containing species and oxalate on nitrate formation

The nitrate production in PCD was studied earlier showing its efficiency fitting in the span from 10 to $14 \text{ g kW}^{-1} \text{ h}^{-1}$ in similar PCD reactors in distilled water and oxalate solutions [23]. One can see that bromide and oxalate in various pH conditions left the nitrate formation efficiency within this span, whereas the presence of bromate noticeably obstructed formation of nitrate, making the yield as low as $9\text{--}10 \text{ g kW}^{-1} \text{ h}^{-1}$ (Table 1), the reason of which remains unknown: the bromide-bromate transformations are obviously involved into nitrogen oxidation, although this observation requires additional studies. The highest yields of nitrate were observed with addition of oxalic acid only, $13.9 \text{ g kW}^{-1} \text{ h}^{-1}$. Small additions of bromide in amount of 1.0 mg L^{-1} did not show big impacts on the nitrate yield, although small reduction was visible. Bigger reduction in the yields was observed with higher bromide concentrations, with ($12.3\text{--}12.8 \text{ g kW}^{-1} \text{ h}^{-1}$) or without ($10.6\text{--}11.9 \text{ g kW}^{-1} \text{ h}^{-1}$) oxalate. Alkaline media also showed smaller yields of nitrate.

4. Conclusions

Bromide appeared slowly oxidizable to bromate in aqueous solutions treated with non-thermal plasma of PCD in a reversible reaction ending up at certain bromide-bromate equilibrium dependent on operation factors. The equilibrium established in acidic and circum-neutral media in about 1 h at the delivered energy dose of about 3.2 kWh m^{-3} at the pulse repetition frequency of 200 pps, i.e. the delivered power of 32 W. About 60 % of bromide was oxidized giving about 10 mol. % of bromate. The rest of bromine was converted to hypobromous species, hypobromite and hypobromous acid dependent on pH. In alkaline solutions, minor oxidation of bromide was observed, consistently producing negligible amounts of bromate. The bromide-bromate equilibrium witnesses for a reversible reaction, verified in bromate PCD-treatment: bromate in circum-neutral media decreased for about 10 % giving stoichiometric amount of bromide, no hypobromous species were detected. Smaller concentration of PCD-treated bromide (1.0 mg L^{-1}) also resulted in equilibrium with smaller bromide-bromate misbalance. Admixtures of oxalate in circum-neutral bromide solutions substantially, about five times, reduced bromide oxidation with stoichiometric production of bromate at almost complete absence of hypobromous intermediates. The latter circumstance gives a reason to expect

Table 1
Efficiencies of nitrate formation in PCD-treated solutions.

Experimental conditions	Nitrate formation efficiency, $\text{g kW}^{-1} \text{ h}^{-1}$
Oxalic acid 5.0 mg L^{-1} , pH 2.5	13.9
Bromate 5.0 mg L^{-1} , pH $6.0 \rightarrow 3.0$	9.9
Bromate 5.0 mg L^{-1} + bromide 1.0 mg L^{-1} , pH $6.0 \rightarrow 3.0$	8.9
Bromide 1.0 mg L^{-1} , pH 2.5	13.2
Bromide 1.0 mg L^{-1} , pH $6.5 \rightarrow 3.0$	13.9
Bromide 1.0 mg L^{-1} , pH 11.0	11.5
Bromide 5.0 mg L^{-1} , pH 2.5	11.9
Bromide 5.0 mg L^{-1} , pH $9.3 \rightarrow 3.0$	10.6
Bromide 5.0 mg L^{-1} , pH 11.0	11.3
Bromide 5.0 mg L^{-1} + oxalic acid 5.0 mg L^{-1} , pH 2.5	12.8
Bromide 5.0 mg L^{-1} + oxalate 5.0 mg L^{-1} , pH $7.3 \rightarrow 6.5$	12.3
Bromide 1.0 mg L^{-1} + oxalate 1.0 mg L^{-1} , pH $6.5 \rightarrow 3.0$	13.2

suppression of haloform reaction producing trihalomethanes in treated solutions. In acidic media, hypobromous acid was formed in presence of oxalic one due to, presumably, higher resistance of the former towards oxidation with the PCD-generated ROS. Production of bromate in acidic solution of bromide and oxalic acid was also reduced twice compared to the bromide oxidation with no oxalate.

Bromide and oxalate only minorly affected the nitrate formation in PCD-treated solutions dependently on pH and bromide concentrations. However, bromate appeared to be strong inhibitor of nitrate formation, reducing the yield of nitrates for about 30 %. The explanation of this phenomenon lays, presumably, in complex reactions between the bromine and nitrogen species, and requires further studies.

From the practical standpoint, the fact of slow bromide PCD oxidation gives a chance for safe water treatment at the energy dose sufficient for disinfection.

CRediT authorship contribution statement

Irina Petrochenko: Writing – original draft, Methodology, Investigation, Data curation. Sergei Preis: Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix 3

Paper II

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RESEARCH ARTICLE

Pulsed Corona Discharge for Targeted Oxidation of Carbamazepine in Water and Source-Separated Human Urine

Irina Petrochenko¹ | Niina Dulova¹ | Prithvi Simha² | Sergei Preis¹ 

¹Laboratory of Environmental Technology, Department of Materials and Environmental Technology, Tallinn University of Technology, Tallinn, Estonia | ²Department of Energy and Technology, Swedish University of Agricultural Sciences, Uppsala, Sweden

Correspondence: Sergei Preis (sergei.preis@taltech.ee)

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ABSTRACT

Pharmaceutical residues in human urine present a critical barrier to its recycling as a circular fertilizer. Gas-phase pulsed corona discharge (PCD) generating short-living radicals at the plasma-liquid interface was applied for targeted and energy-efficient oxidation of anticonvulsant carbamazepine (CBZ) in urine. In aqueous solution, CBZ was rapidly degraded with energy efficiency reaching 50 g kWh⁻¹. In real urine, CBZ oxidation was hindered (1.6 g kWh⁻¹) by competing endogenous organic compounds consuming reactive species. Complete CBZ oxidation was achieved in urine with no detectable loss of plant-essential nutrients (urea, ammonia) or chloride. Compared to conventional ozonation, PCD achieved an order of magnitude higher energy efficiency in CBZ oxidation. The study demonstrates PCD as a targeted pharmaceutical degradation method valorizing human urine.

1 | Introduction

Several factors necessitate the exploration of alternative nutrient sources, including the growing demand for agricultural fertilizers, the uneven global distribution of mineral and energy resources, and the environmental damage caused by raw material excavation and processing [1]. Among potential alternatives, human excreta, particularly human urine, have attracted attention due to their high nutrient content [2]. Urine accounts for about 85%–90% of nitrogen and 50% of phosphorus and potassium present in household wastewater, effectively containing all nutrients essential for plant growth [3]. When urine is collected separately at the source, referred to as source-separated urine, it becomes a widely available and renewable source of nutrients that could contribute significantly to meeting agricultural needs while reducing reliance on synthetic fertilizers [4]. Globally, human urine can substitute

approximately one-fourth of the synthetic nitrogen and phosphorus demand in agriculture [5].

One of the major challenges of recycling urine-derived nutrients is the presence of pharmaceutical residues resulting from their contemporary consumption. Pharmaceuticals are primarily excreted via urine rather than feces [6], and even after long-term storage, these compounds remain stable and are retained in the urine matrix [7]. While the actual risk to human health and the environment from pharmaceuticals in urine used as fertilizer may be low [8], public and stakeholder concerns, including those from farmers and the food industry, about potential contamination can hinder the acceptance and implementation of urine recycling [9]. An example of a pharmaceutical contaminant in human urine is carbamazepine (CBZ), an anticonvulsant commonly used to treat epilepsy and bipolar disorder. More than 70% of administered CBZ is excreted via

urine, either unchanged or as metabolites [10]. CBZ is highly persistent in the environment and resistant to conventional wastewater treatment, with studies showing it accumulates in soils irrigated with treated wastewater and is taken up by crops, while the actual human health risks remain understudied [11]. In controlled laboratory experiments focused on direct photolysis, CBZ exhibits long degradation periods, with reported half-lives ranging from approximately 84 h to 87.5 days [12, 13]. Degradation via biotransformation is even slower, with estimated half-lives spanning from 125 to 315 days [12, 14]. Field studies in natural aquatic systems, such as a Swedish lake and the Baltic Sea, indicate even stronger persistence, with estimated half-lives of around 3.5 years [15, 16]. This remarkable stability makes CBZ a representative model compound for studying the challenges of pharmaceutical removal from source-separated urine intended for agricultural reuse.

The removal of pharmaceuticals from urine is challenging due to its complex chemical composition, which contains a wide variety of endogenous and exogenous organic compounds that can interfere with treatment processes [17]. Guidelines from the World Health Organization suggest that storing urine stabilizes nutrients and reduces pathogen content [18]. However, storage alone is not sufficient to remove micro-pollutants, such as pharmaceuticals and their metabolites [7]. Several advanced oxidation processes (AOPs), recognized as promising for degrading emerging contaminants, have been studied for their effectiveness and limitations in degrading pharmaceuticals in urine. AOPs utilize highly reactive hydroxyl or sulfate radicals, which effectively oxidize recalcitrant pollutants and enhance the biodegradability of wastewater. Electrochemical oxidation, ozonation, photocatalysis, and Fenton oxidation processes are among the approaches explored for pharmaceutical removal from urine, each offering distinct mechanisms of oxidant generation and potential for pollutant removal. However, the performance of these AOPs is deteriorated by high concentrations of organic compounds in urine, competing with the target pollutants, operational pH, and the potential formation of undesirable byproducts [19–21]. Moreover, most AOPs act broadly, oxidizing not only pharmaceuticals but also essential plant nutrients, which undermines the objective of preserving the fertilizer value of urine. For instance, AOPs applied to hydrolyzed urine result in the formation of chlorinated byproducts and unselective oxidation of organic and inorganic constituents, including chloride, ammonia, and urea [22, 23]. In this context, pulsed corona discharge (PCD), a radical-based oxidation process characterized by high energy efficiency [24], presents a promising alternative for achieving targeted pharmaceutical degradation.

PCD plasma, generated by applying high voltage pulses across an inter-electrode gap sprayed with the treated liquid, produces short-living oxidants primarily at the gas-liquid interface [25]. Involving these transient oxidants in the oxidation of pollutants contributes to a more energy-efficient oxidation compared to conventional application of ozone, which relies on the formation of relatively stable ozone molecules via the reverse “oxygen-ozone-oxygen” reaction in dielectric barrier discharge. Another feature of PCD, that is, the formation of oxidant species predominantly at the plasma-liquid interface, enables targeted oxidation of compounds with complex molecular structures containing aromatic rings, as found in many

pharmaceuticals [26]. These molecules are preferentially exposed to radical attack at the aqueous surface. To confirm this hypothesis and further enhance selectivity, the surfactant sodium dodecyl sulfate (SDS) was added to promote covalent bonding between its radicalized hydrophobic tail and aromatic rings. Such formations are localized at the plasma-liquid interface, being attacked by reactive species, thereby improving targeted oxidation of hydrophobic pharmaceutical compounds like CBZ [27].

The aim of this study was to evaluate the potential of PCD for targeted pharmaceutical oxidation from complex matrices, including synthetic and real source-separated human urine, while preserving their fertilizer value. Specifically, the study was conducted to determine (i) the influence of matrix types on PCD efficiency and selectivity in CBZ oxidation, (ii) the impact of additives of SDS on enhancing selectivity for CBZ removal, (iii) the optimum process parameters, and (iv) the energy efficiency of CBZ oxidation in PCD treatment of urine. Collectively, these insights are intended to advance the development of PCD as a promising, targeted, and energy-efficient approach for safe nutrient recovery from human urine.

2 | Materials and Methods

2.1 | Chemicals

Oxidation experiments were conducted using CBZ dissolved in distilled water, urea solutions, synthetic urine, and real source-separated urine. The synthetic urine was prepared according to a protocol [28], and its composition is detailed in Table 1. Urine was collected from public urinals in Sweden, where collection tanks were pre-dosed with 10 g L^{-1} of citric acid to prevent enzymatic urea hydrolysis [29]. The main constituents and properties of urine are listed in Table 2.

CBZ ($\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}$, 97%) was purchased from TCI Europe N.V., Belgium. Methanol (CH_3OH , 99%) for dissolution of CBZ was purchased from Fisher Scientific, UK. Sodium sulphate (Na_2SO_4 , 99%), SDS ($\text{NaC}_{12}\text{H}_{25}\text{SO}_4$, 99%), and sodium chloride (NaCl , 98%) were purchased from Lach-Ner, Ltd, Czech Republic. Uric acid ($\text{C}_5\text{H}_4\text{N}_4\text{O}_3$, 99%), trisodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$, 98%), creatinine ($\text{C}_4\text{H}_7\text{N}_3\text{O}$, 98%), urea ($\text{CH}_4\text{N}_2\text{O}$, 99%), ammonium chloride (NH_4Cl , 99.5%), and potassium oxalate ($\text{K}_2\text{C}_2\text{O}_4$, 98.5%) were obtained from Sigma Aldrich. Potassium chloride (KCl , 99%), calcium chloride (CaCl_2 , 96%), magnesium sulfate ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 99.5%), dihydrate monobasic sodium phosphate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, 98%), and dibasic sodium phosphate dodecahydrate ($\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$, 98%) were purchased from Merck KGaA, Germany. A 2-M solution of sulfuric acid (Lach-Ner, Ltd, Czech Republic) was used to adjust the pH of synthetic CBZ solutions.

2.2 | Experiments

The experimental setup (Figure 1), designed by Flowrox Oy, Finland, consists of a PCD reactor equipped with a 40 L storage tank, a pulse generator, and a circulation pump that maintained a treated solution flow rate of $1.0 \text{ m}^3 \text{ h}^{-1}$. A detailed description of the PCD device has been provided previously [27, 30]. The reactor's electrode system includes multiple wires of 0.55 mm in

TABLE 1 | Synthetic urine composition.

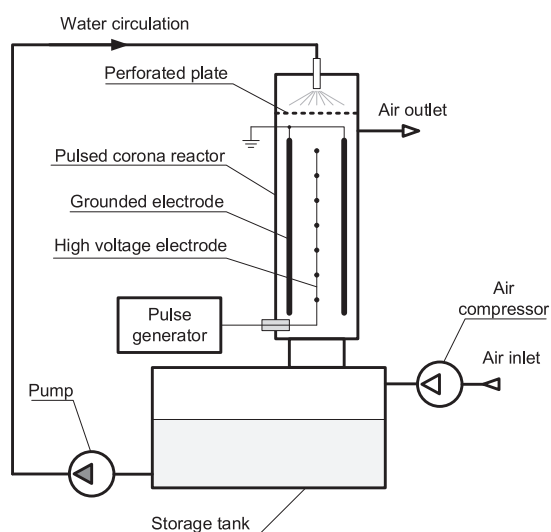
Ingredient	Empiric formula	Concentration, g L⁻¹
Sodium sulfate	Na ₂ SO ₄	1.7
Uric acid	C ₅ H ₄ N ₄ O ₃	0.25
Trisodium citrate	Na ₃ C ₆ H ₅ O ₇ · 2H ₂ O	0.72
Creatinine	C ₄ H ₇ N ₃ O	0.881
Urea	CH ₄ N ₂ O	15.0
Potassium chloride	KCl	2.308
Sodium chloride	NaCl	1.756
Calcium chloride	CaCl ₂	0.185
Ammonium chloride	NH ₄ Cl	1.266
Potassium oxalate	K ₂ C ₂ O ₄	0.035
Magnesium sulfate	MgSO ₄ · 7H ₂ O	1.0082
Dihydrate monobasic sodium phosphate	NaH ₂ PO ₄ · 2H ₂ O	2.912
Dibasic sodium phosphate dodecahydrate	Na ₂ HPO ₄ · 12H ₂ O	0.831
pH		6.0
Electric conductivity, mS cm ⁻¹		13.1 ± 0.1

TABLE 2 | Acid-stabilized urine major constituents.

Ingredient	Empiric formula	Concentration, g L⁻¹
Citric acid	C ₆ H ₈ O ₇	7.13
Urea	CO(NH ₂) ₂	9.92
Ammonium	NH ₄ -N	0.65
Chlorine	Cl ⁻	3.91
Calcium	Ca ²⁺	0.058
Potassium	K ⁺	3.08
Magnesium	Mg ²⁺	0.082
Orthophosphate	PO ₄ -P	0.494
Sulfate	SO ₄ ²⁻	0.994
pH		3.0
Electrical conductivity, mS cm ⁻¹		10.4 ± 0.1

diameter totaling 20 m in length, positioned horizontally between two vertical parallel plates. This configuration was selected to minimize conductivity losses, based on the design outlined by Kornev et al. [31]. The air gap between the wire electrodes and the grounded plate was 18 mm. The treated solutions were dispensed through a perforated plate containing 49 holes, each 1.5 mm in diameter, arranged in a vertical plane with the high-voltage string electrodes.

The pulse generator delivered 100-ns voltage pulses with a peak of 18 kV and a peak current of 380 A, providing power outputs of 9.0, 32.0, and 123.0 W at 50, 200, and 880 pulses per second (pps), respectively. The pulse characteristics were measured using a Rigol DS1102E Mixed Signal Oscilloscope, a Tektronix P6015 high-voltage probe (Tektronix Inc., USA), and a PT-7802 current monitor (PinTek, China). The energy per pulse

**FIGURE 1** | Experimental setup outline.

delivered to the reactor was calculated by integrating the voltage and current time profiles, yielding 0.19 J at 50 and 200 pps, and 0.15 J at 880 pps [31]. The treated solution passed through the plasma zone, drained into the storage tank, and was re-circulated back to the top of reactor. Indoor air is used as the discharge atmosphere, purged at a rate of 1.0 L min⁻¹ to maintain adequate oxygen concentration.

Experimental PCD studies on CBZ oxidation were carried out in four aqueous matrices: distilled water; urea solution containing 15 g L⁻¹ of the latter, matching the concentration typically found in urine; synthetic urine containing, besides urea, a few other organic and mineral compounds (Table 1); and source-separated urine stabilized with citric acid at pH 3.0 [29].

The energy delivered to the PCD reactor, kWh m^{-3} , was calculated using Equation 1:

$$\text{Delivered energy} = \frac{P \cdot t}{V} \quad (1)$$

where P is power supplied by the pulse generator, kW, t — treatment time, h, and V —treated solution volume, m^3 .

The energy efficiency of CBZ oxidation, $\text{g kW}^{-1} \text{h}^{-1}$, was calculated using Equation 2:

$$E = \frac{\Delta C \cdot V}{W} \quad (2)$$

where ΔC is the decrease in CBZ concentration, g m^{-3} , V —volume of treated solution, m^3 , and W —energy consumption as a product of power delivered to the reactor and the time of treatment, kWh. The energy efficiency was calculated for 90% CBZ removal, except for experiments with real urine, where the efficiency was taken for 50% removal at an energy dose of 3.2 kWh m^{-3} .

A stock solution of CBZ was prepared by dissolving CBZ in methanol at a concentration of 25 g L^{-1} . This stock was used to spike the test matrices, resulting in a final CBZ concentration of 10 mg L^{-1} in all experiments. The selection of this concentration ensured reliable quantification of CBZ during analysis, particularly in the complex matrix of source-separated urine, where high background interference can obscure chromatographic detection. While data on the concentration of pharmaceuticals in human urine vary widely, Özel Duygan et al. [32] estimated concentrations of certain pharmaceuticals in source-separated urine in Switzerland ranging from a few tens to a few hundreds of $\mu\text{g L}^{-1}$.

The samples underwent treatments at 200 pps, providing pulsed power output of 32 W for a total duration of 1 h. Samples were taken at specific time intervals: zero-sample, and subsequently at 2, 4, 6, 8, 12, 16, 20, 24, 30, 45, and 60 min of treatment. Prior to each sampling, the electric discharge was switched off, and the treated solution was recirculated and mixed using the pump for at least 4 min to ensure uniformity of concentrations. The temperature of the solution gradually increased from $20^\circ\text{C} \pm 1^\circ\text{C}$ at the start to $25^\circ\text{C} \pm 1^\circ\text{C}$ by the end of the treatment.

In experiments assessing the effect of the surfactant SDS, molar mass 288.4 g mol^{-1} , it was added to achieve molar ratios ranging from 2.5:1 to 5:1 relative to the initial CBZ concentration, molar mass 236.3 g mol^{-1} . These molar ratios were selected based on preliminary experience with other substances [27]. For the selected CBZ concentration of about 10 mg L^{-1} , this corresponded to SDS concentrations from 30.5 to 61.0 mg L^{-1} .

2.3 | Analyses

Samples were analyzed for residual CBZ content using high-performance liquid chromatography combined with a diode array detector (HPLC-PDA, Shimadzu, Japan) equipped with a Phenomenex Gemini column ($150 \times 2.0 \text{ mm}$, 1.7 mm) packed with a stationary phase NX-C18 ($110 \text{ \AA}$, $5 \mu\text{m}$). An isocratic

method was used, with a mobile phase consisting of 60% eluate A (water containing 0.3% formic acid, flow rate 0.02 mL min^{-1}) and 40% eluate B (acetonitrile containing 0.3% formic acid, flow rate 0.08 mL min^{-1}). The total flow rate was 0.1 mL min^{-1} ; the injection volume was $100 \mu\text{L}$, and the oven temperature was 40°C . The samples withdrawn from the PCD reactor were injected into the HPLC sampling port in a sequence of three injections. The results of HPLC analysis demonstrated deviations in repeated measurements not exceeding 5% from the average value. pH was measured using a S220 digital pH-meter (Mettler Toledo, Switzerland).

The urea content in urine samples was determined using urease from *Canavalia ensiformis* (Jack bean), which catalyzes urea hydrolysis to ammonia and carbon dioxide. Ammonia was determined as $\text{NH}_3\text{-N}$ using an ammonia probe electrode (Metrohm AG, Switzerland). Before measurements, urea was hydrolyzed to $\text{NH}_4^+/\text{NH}_3$ at pH 7.2 using lyophilized urease (5 U/mg, EC 3.5.1.5; Merck, Germany) at a dosage of 5000 U urease per g of expected urea concentration, in centrifuge tubes with O-rings. The tubes were incubated at 37°C for 24 h on a shaker table for optimal temperature and contact with the enzyme. To shift the equilibrium towards NH_3 , the solution was alkalinized to $\text{pH} > 12$ by the addition of 0.5 mL of 10-M sodium hydroxide solution [33]. Cations and anions in real urine were quantified using an automated Gallery Discrete Analyzer (ThermoFisher Scientific, USA), applying the instrument's standardized colorimetric protocols.

3 | Results and Discussion

3.1 | Impact of pH on CBZ Oxidation

CBZ PCD-oxidation in aqueous solution was tested for the impact of pH. Since the source-separated urine used in the study was stabilized with citric acid at pH 3.0 [29], CBZ degradation was tested under acidic and circum-neutral conditions in aqueous solutions. This makes the oxidative treatment of urine at low pH reasonable, although pH is known to be a crucial factor of oxidation kinetics: pollutants dissociation state and mechanism of radical decomposition of ozone are pH-dependent [34]. In conventional ozonation, oxidation of CBZ was observed to proceed more rapidly under acidic conditions due to the faster reaction of molecular ozone [35]. Since ozone is also present amongst the active oxidation species formed in PCD plasma, its enhanced reactivity at low pH likely contributes to the trends of CBZ oxidation observed in our study. As shown in Figure 2, CBZ was oxidized more rapidly at low pH, indicating that acidic conditions enhance oxidation efficiency while simultaneously stabilizing urea by preventing enzymatic ureolysis during PCD treatment. The observation gives grounds to assert that oxidation of CBZ acquires certain benefits in acidic conditions, in which further experiments with urine and urine-modeling aqueous solutions were carried out.

3.2 | Energy Efficiency of CBZ Oxidation

The results demonstrated that CBZ underwent oxidation in all tested environments, aqueous solutions, and urine (Figure 3). However, its degradation rate decreased as the complexity of the composition increased, likely due to the presence of

competing organic compounds. In distilled water, CBZ exhibited the fastest decline in concentration, reaching near-complete degradation with minimal delivered energy and a high oxidation efficiency of $50.2 \text{ g kW}^{-1} \text{ h}^{-1}$.

Urea did not interfere with CBZ during PCD-oxidation: the target pollutant was oxidized almost as efficiently as in distilled water, yielding an energy efficiency of $49.2 \text{ g kW}^{-1} \text{ h}^{-1}$. This observation indicates that urea is not a scavenger of hydroxyl radicals. In synthetic urine, CBZ followed a decline pattern like that in aqueous solutions, although with a noticeable lag in oxidation for about 0.5 kWh m^{-3} , likely due to competing constituents, for example, creatinine, which was oxidized more rapidly than CBZ at its experimental concentration, thus consuming the oxidants [36]. Once this interference was overcome, CBZ degradation accelerated, resulting in an energy efficiency of $18.1 \text{ g kW}^{-1} \text{ h}^{-1}$ within the energy span from 0.5 to 1.0 kWh m^{-3} . In contrast, CBZ degradation in source-separated urine was significantly slower, with an oxidation energy efficiency of $1.6 \text{ g kW}^{-1} \text{ h}^{-1}$. This likely reflects the presence of readily oxidizable endogenous organic compounds in urine that compete with CBZ for oxidants. The total concentration of endogenous organic compounds in urine, excluding urea, ranges from 1.4 g L^{-1} [37] to 3.2 g L^{-1} [38],

which is orders of magnitude higher than the initial CBZ concentration (10 mg L^{-1}). Many of these organics, including amino acids, creatinine, and carbohydrates, exhibit high reactivity with hydroxyl radicals, with the second-order reaction rate constants in the range of 10^7 – $10^9 \text{ M}^{-1} \text{ s}^{-1}$ [39]. Their abundance and reactivity contribute to the rapid scavenging of oxidants, reducing the overall oxidation efficiency of CBZ.

Nevertheless, pulsed energy dose as low as 3.2 kWh m^{-3} resulted in almost 50% degradation of the initial CBZ concentration, highlighting the selectivity of PCD for CBZ oxidation at relatively low energy input. Complete CBZ degradation in urine was achieved at a pulsed energy dose of 12.3 kWh m^{-3} (Figure 4). To put this in perspective, one should realize that emerging urine recycling technologies concentrate nutrients by water removal, using nitrification-distillation and alkaline/acid stabilization-dehydration with energy recovery from steam condensation. The technology foresees energy demands in the range of 100 – 150 kWh m^{-3} of urine, possibly covered by waste heat [40]. This makes the energy required by PCD for complete CBZ degradation as small as 8% – 12% of the energy demand for these nutrient-concentrating processes. This suggests that integrating PCD for pharmaceutical removal may be an

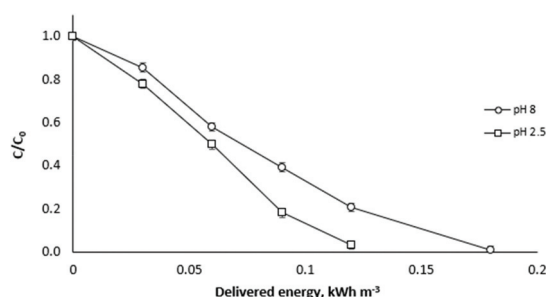


FIGURE 2 | Carbamazepine oxidation in distilled water solutions at various pH vs delivered energy dose: pulse repetition frequency 50 pps, pulsed power 9 W, CBZ starting concentration 10.0 mg L^{-1} .

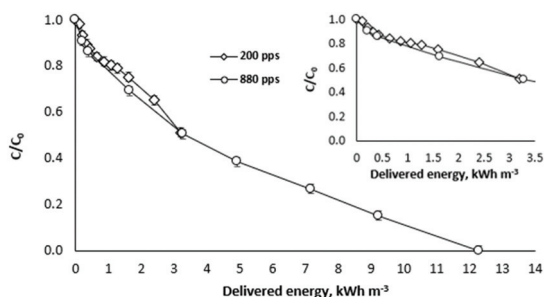


FIGURE 4 | Carbamazepine oxidation in urine at various pulse repetition frequencies vs delivered energy dose: pH 3.0, pulsed powers 32 and 123 W, CBZ starting concentration 10.0 mg L^{-1} .

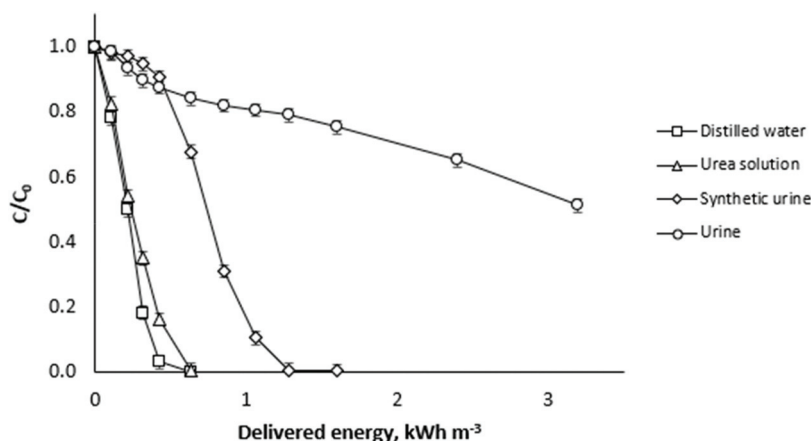


FIGURE 3 | Carbamazepine oxidation in aqueous solutions and urine vs delivered energy dose: pH 3.0, pulse repetition frequency 200 pps, pulsed power 32 W, CBZ starting concentration 10.0 mg L^{-1} , urea concentration in aqueous solution and synthetic urine 15 g L^{-1} .

energetically justified approach for producing clean fertilizer from urine.

The concentration of pollutants is known to determine oxidation kinetics, that is, the energy efficiency of their removal, and the treatment duration required to achieve the desired outcome. Realistic concentrations of pharmaceuticals in urine, which are orders of magnitude lower than those used in the study, may require shorter treatment times and thus lower energy doses. The authors found earlier that at concentrations of $\mu\text{g L}^{-1}$ range, CBZ was rapidly removed from biologically treated wastewater with the energy dose as small as 0.1 kWh m^{-3} . It is also worth mentioning that the identified CBZ transformation products visible at high CBZ concentrations of mg L^{-1} range, acridine-9-carbaldehyde, hydroxyl-acridine-9-carbaldehyde, 10,11-dihydro-CBZ 10,11-epoxide 1-(2-benzaldehyde)-4-hydroquinazoline 2-one (BQM) and 1-(2-benzaldehyde)-4-hydro-quinazoline-2,4-dione (BQD), were below the detection limit at lower CBZ concentrations, indicating their concurrent degradation with CBZ [41].

To contextualize these results, the energy efficiency of PCD was compared with that of conventional ozone application. According to Dodd et al. [42], ozonation of CBZ in enzymatically hydrolyzed urine containing other pharmaceuticals achieved a maximum energy efficiency of about $0.15 \text{ g kW}^{-1} \text{ h}^{-1}$ for 90% degradation. This value was obtained under conditions of ozone generated from pure oxygen at an energy yield of $13.1 \text{ kWh kg}^{-1} \text{ O}_3$, which should be doubled when synthesized from air. Their experiments used a CBZ starting concentration of 2.36 mg L^{-1} , lower than the one in the present study, 10 mg L^{-1} . Although energy efficiency tends to decrease with decreasing substrate concentration [43], the observed order-of-magnitude difference suggests that PCD offers a more energy-efficient approach for CBZ degradation due to its targeted oxidation mechanism driven by short-living reactive species formed at the plasma-liquid interface [25].

The inset in Figure 4 compares CBZ degradation in urine at two different pulse repetition frequencies. The curves are nearly identical, indicating that increasing the frequency from 200 to 880 pps does not reduce energy efficiency. This suggests that ozone is consumed rapidly between pulses, and the longer intervals between pulses at lower frequency provide no meaningful advantage in terms of oxidant utilization. Instead, operating at a higher frequency is preferable, as it accelerates the treatment process without compromising energy efficiency.

The oxidation energy efficiency may also be influenced by the conductivity of the treated solution, which may partly explain the decreased performance of PCD in urine with a conductivity of $10.4 \pm 0.1 \text{ mS cm}^{-1}$. However, this effect appears to be minor since synthetic urine with a conductivity of $13.1 \pm 0.1 \text{ mS cm}^{-1}$ demonstrated significantly higher energy efficiency for CBZ oxidation than urine. Previous studies have shown that electric conductivity as high as 10.0 mS cm^{-1} reduced the energy efficiency of textile dyes oxidation by only about 15%–25% compared to solutions in distilled water [31]. Thus, the high organic content in urine, not conductivity, is the primary factor for the lower CBZ oxidation efficiency observed.

Importantly, no measurable oxidation of urea, chloride, or ammonia was observed during PCD treatment of urine. Urea concentrations remained stable across all energy doses, within a 2% analytical margin, and both chloride and ammonia levels

showed no consistent change. Nitrate formation was detected, but at a relatively low level, with an efficiency of $1.5\text{--}1.7 \text{ g kW}^{-1} \text{ h}^{-1}$, compared to yields of $8\text{--}16 \text{ g kW}^{-1} \text{ h}^{-1}$ reported for dilute aqueous solutions [24]. Overall, these results demonstrate that PCD degrades CBZ while preserving key nutrients in urine.

A passing observation is worth noting: synthetic urine is a poor substitute for human urine in targeted oxidation studies. While it mimics basic inorganic composition well, it lacks the broad range of oxidizable organics present in real urine, which significantly affects competition for oxidants. As discussed in more detail elsewhere [44], this difference can lead to misleading conclusions about treatment performance and selectivity.

3.3 | Surface Reaction in PCD-Oxidation of CBZ

To explore whether CBZ oxidation during PCD is driven by surface interactions, SDS was added to treated solutions. The surfactant can facilitate the accumulation of hydrophobic compounds at the gas-liquid interface, exposing these to surface-borne short-living oxidants [30]. As shown in Figures 5 and 6, SDS addition accelerated CBZ degradation in all aqueous solutions.

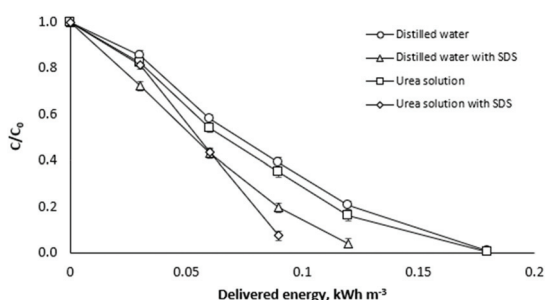


FIGURE 5 | Carbamazepine oxidation in distilled water and urea solution with and without SDS additions vs delivered pulsed energy: pH 6.0, pulse repetition frequency 200 pps, pulsed power 32 W, urea concentration 15.0 g L^{-1} , SDS concentration 61.0 mg L^{-1} , CBZ starting concentration 10.0 mg L^{-1} .

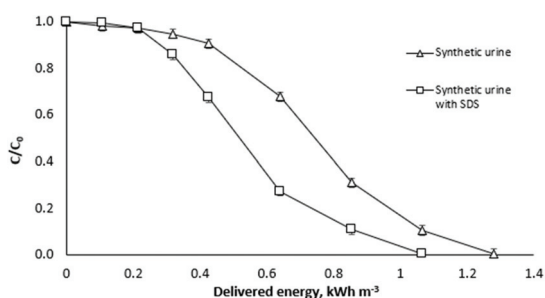
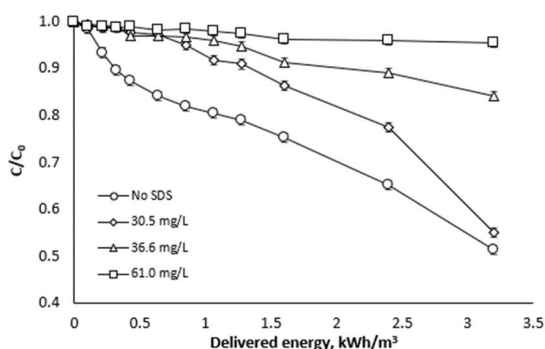


FIGURE 6 | Carbamazepine oxidation in synthetic urine with and without SDS additions vs delivered pulsed energy: pH 6.0, pulse repetition frequency 200 pps, pulsed power 32 W, urea concentration 15.0 g L^{-1} , SDS concentration 61 mg L^{-1} , CBZ starting concentration 10.0 mg L^{-1} .

TABLE 3 | Energy efficiency with the addition of SDS.

Treated solutions	Energy efficiency, g kW ⁻¹ h ⁻¹	
	Without SDS	With SDS
Water	50.2	71.9
Urea solution	49.2	76.0
Synthetic urine	7.0 ^a	8.6 ^a

^aCalculated for the pulsed energy dose span from 0 to 1.1 kWh m⁻³.**FIGURE 7** | Carbamazepine oxidation in urine at various SDS concentrations vs delivered energy dose: pH 3.0, pulse repetition frequency 200 pps, pulsed powers 32 W, CBZ starting concentration 10.0 mg L⁻¹.

In distilled water, urea solution, and synthetic urine, CBZ oxidation rate increased by factors of 1.43, 1.54, and 1.23, respectively, compared to the reference experiments without SDS (Table 3). This supports the hypothesis that CBZ PCD-oxidation involves surface-mediated processes, and that enhancing its localization at the gas–liquid interface through SDS addition can further accelerate degradation. The proposed mechanism involves interactions between the hydrophobic radicalized tail of SDS and the aromatic radical of CBZ, which may bring the latter near the plasma–liquid interface and increase its exposure to reactive oxygen species [30].

In contrast to aqueous solutions, the addition of SDS to urine inhibited CBZ oxidation (Figure 7), with the reaction rate decreasing further at higher surfactant concentrations. This inhibition likely stems from interactions between SDS and abundant organic metabolites in urine, which compete with CBZ for both oxidants and vacant covalent bond SDS-sites at the gas–liquid interface. The surfactant may preferentially interact with these endogenous compounds, which are present at far higher concentrations than CBZ, effectively shielding the target pharmaceutical from oxidation. Ultimately, adding SDS to urine did not enhance CBZ oxidation, thus proving counterproductive.

4 | Conclusions

The study demonstrates that PCD provides a feasible approach for the targeted oxidation of pharmaceuticals in source-separated urine. The experiments showed energy-efficient PCD-oxidation of CBZ in aqueous solutions and synthetic urine, showing high energy efficiencies. Oxidation of CBZ was found

to be pH-dependent with enhanced degradation under acidic conditions, which is compatible with urine recycling technologies that involve acidification for stabilizing urea. High urea concentrations, 15 g L⁻¹, did not noticeably affect CBZ oxidation, indicating that urea does not act as a scavenger of reactive oxidants. However, the presence of endogenous organic compounds in urine significantly hindered CBZ oxidation, reducing energy efficiency. Nevertheless, targeted oxidation of CBZ remained high in urine, with key nutrients such as urea preserved during PCD treatment, even at energy doses up to 12.3 kWh m⁻³ required for complete CBZ degradation. Notably, PCD achieved CBZ oxidation in acidified urine with energy efficiency approximately an order of magnitude higher than conventional ozone treatment of hydrolyzed urine.

The role of surface reactions at the plasma–liquid interface was confirmed by the observed acceleration of CBZ oxidation upon SDS addition in aqueous solutions and synthetic urine. In contrast, oxidizable organic compounds in urine altered the effect of SDS: its addition reduced CBZ oxidation efficiency with greater inhibition at higher SDS concentrations.

These findings highlight the importance of considering matrix complexity in treatment studies, as synthetic urine does not fully replicate the inhibitory effects of natural organic matter present in real urine. Overall, this study highlights the potential of PCD for micro-pollutant removal from source-separated urine while also emphasizing the need for further optimization to improve energy efficiency and address matrix-related limitations in urine treatment.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The authors have nothing to report.

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Appendix 4

Paper III

Petrochenko, I., Dulova, N., Preis, S. (2026). Pulsed corona discharge in valorisation of urine as a sustainable source of nutrients: targeted oxidation of pharmaceutical residues and inhibition of urea enzymatic hydrolysis. *Processes*, 14(12), 1972. <https://doi.org/10.3390/pr14121972>

Article

Pulsed Corona Discharge in Valorisation of Urine as a Sustainable Source of Nutrients: Targeted Oxidation of Pharmaceutical Residues and Inhibition of Urea Enzymatic Hydrolysis

Irina Petrochenko , Niina Dulova  and Sergei Preis 

Laboratory of Environmental Technology, Department of Materials and Environmental Technology, Tallinn University of Technology, Tallinn 19086, Estonia; irina.petrotsenko@taltech.ee (I.P.); niina.dulova@taltech.ee (N.D.)
* Correspondence: sergei.preis@taltech.ee; Tel.: +372-6203365

Abstract

Human urine is a sustainable source of nutrients with significant fertilizer potential. The presence of pharmaceutical residues, however, obstructs its use in agriculture. Also, the loss of ammonia formed in enzyme-catalyzed hydrolysis of urea in stored urine compromises the approach. This study presents gas-phase pulsed corona discharge (PCD) used in the oxidation of pharmaceuticals and enzymes, improving the applicability of urine as a fertilizer. The prioritized beta-blocker propranolol (PR) and antibiotic tetracycline were chosen as target micropollutants for the experimental study, demonstrating enhanced oxidation relative to matrix constituents. Tetracycline showed its more recalcitrant character in urine than PR for its more pronounced matrix-mediated scavenging or complexation. The PCD oxidation significantly lowered the urease enzyme activity, thus preventing nitrogen loss through ammonia volatilization. According to the phytotoxicity assessment using the *Pisum sativum* garden peas test, urine PCD-treated with the energy dose sufficient to substantially degrade pharmaceuticals is not phytotoxic when applied at recommended agronomic doses. The findings reveal the use of PCD as an energy-efficient technology for producing safe and stable urine-derived fertilizer.

Keywords: advanced oxidation process; antibiotic; beta-blocker; emerging contaminants; hydroxyl radical; nitrogen conservation; ozone; phytotoxicity; urea; urease inactivation; urine valorisation



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1. Introduction

Following the ongoing transition to sustainable agricultural and waste practices, interest in closing nutrient cycles, together with minimizing reliance on synthetic mineral fertilizers, is growing [1]. Synthetic fertilizers leave substantial energy footprints, deteriorating the environment through their mining, production, and transportation at an uneven global geographical distribution of raw materials [2]. Alternative nutrient sources within the context of the circular economy are explored, answering these challenges—waste streams are re-evaluated as valuable resources [3].

Domestic wastewater fractions are attracting increasing attention in nutrient recovery. Human urine contains most of the nitrogen and a significant proportion of phosphorus and potassium excreted by humans [4]. Urine allows efficient recovery of nutrients when collected separately at the source due to their high content and low pathogen loads [5].

Urine contains most of the nutrients found in domestic wastewater: approximately 90% of nitrogen, 45–80% of phosphorus, and 70–95% of potassium. Multiple studies show that the implementation of urine recycling could largely meet the global demand for fertilizers [6].

Despite advantages, the reuse of urine-derived nutrients faces critical barriers related to chemical contamination. Human urine is a primary excretion pathway for a wide range of pharmaceuticals and their metabolites, many of which are biologically active [7]. These pharmaceutical residues may persist in urine at concentrations relevant for soil ecosystems, crops, and downstream aquatic environments, raising concerns regarding environmental safety and regulatory acceptance [8]. Conventional urine treatment, including storage, dilution, or biological processing, is not designed to remove micropollutants and has been shown to be insufficient for eliminating many pharmaceutical compounds [9]. Consequently, the development of affordable treatment technologies capable of degrading pharmaceutical residues while preserving the nutrient value of urine is a prerequisite for its safe and sustainable reuse in agriculture.

Representative examples of pharmaceutical contaminants relevant to the reuse of source-separated urine are the non-selective beta-blocker propranolol (PR) and the broad-spectrum antibiotic tetracycline (TC). Propranolol, widely prescribed for cardiovascular conditions, is extensively metabolized in the human body, but a notable fraction is excreted through urine either as the parent compound or as environmentally active metabolites [10]. Propranolol is frequently detected in aquatic environments worldwide with recorded concentrations up to $0.52 \mu\text{g L}^{-1}$ due to its widespread use and incomplete removal during wastewater treatment [11]. It has been reported in influent and effluent at municipal wastewater treatment plants, hospital wastewater, surface and groundwater at concentrations ranging from ng L^{-1} to low $\mu\text{g L}^{-1}$, sometimes exceeding predicted threshold concentrations [12]. Propranolol exhibits a relatively high octanol-water partition coefficient, $\log K_{ow} \approx 3.5$, indicating potential for bioaccumulation and enhanced bioavailability in aquatic organisms [13]. Ecotoxicological studies have shown that PR may induce sub-chronic physiological and behavioural effects in aquatic species at environmentally relevant concentrations [14]. Compared with other beta-blockers, PR is associated with higher toxicity, which may be partly attributed to its aromatic structure and limited susceptibility to biodegradation [15]. Based on screening frameworks incorporating occurrence, persistence, bioaccumulation, and toxicity known as OPBT criteria, PR ranks among high-priority emerging contaminants requiring focused monitoring and targeted removal strategies [16]. Similarly, TC, a widely used antibiotic in human and veterinary medicine, is predominantly excreted in unchanged form in urine at rates of about 70%, contributing to its entry into wastewater streams [17,18]. Environmental monitoring studies report TC residues across water matrices, including surface water, groundwater, and wastewater, often in the ng L^{-1} to low $\mu\text{g L}^{-1}$ range, reflecting continuous release from municipal, agricultural, and pharmaceutical sources [19]. For example, TC concentrations of 0.074 to 0.520 ng L^{-1} have been registered in river water, with higher levels observed in mariculture and areas influenced by wastewater effluent [20]. Relatively high persistence of TC in aqueous systems, attributable to its hydrophilic nature and resistance to biodegradation, contributes to its widespread distribution and slow attenuation in the environment [21]. Tetracyclines are also capable of contributing to the spread of antibiotic resistance genes, raising concerns for the ecosystem and public health [22]. Given its prevalence, persistence, and potential ecological impact, TC serves as a representative model antibiotic for studies in its removal from complex matrices, such as urine and wastewaters. Understanding the oxidation of PR and TC is therefore critical to developing an effective and targeted approach to mitigating environmental risks without compromising the nutrient value of urine-derived fertilizer.

Degradation of pharmaceutical residues in urine presents a significant technical challenge due to the chemical complexity of the matrix, containing a wide range of endogenous metabolites and exogenous organic molecules readily interacting with reactive species used in the treatment. These molecules may substantially reduce the effectiveness of treatment by competing for oxidants or altering reaction pathways [23]. Although storage of source-separated urine has been recommended as the first step to stabilize nitrogen, phosphate, and other plant nutrients while reducing pathogen loads [24], storage alone does not remove micro-pollutants to environmentally acceptable levels [25]. In response to this limitation, a variety of advanced oxidation processes (AOPs) have been explored for their capacity to oxidize micropollutants, including pharmaceuticals, in reactions with hydroxyl radicals [26]. AOPs encompass ozonation and its combinations with UV and peroxides, electrochemical oxidation, photocatalysis, and Fenton-based methods, generating radicals through distinct mechanisms and energy inputs [27].

An additional complication stems from the non-selective nature of hydroxyl radicals in the bulk liquid, which also react with nutrient-containing molecules, undermining the objective of preserving fertilizer quality. For example, when applied to hydrolyzed urine, electrochemical oxidation has been associated with the generation of chlorinated byproducts and extensive oxidation of inorganic nitrogen and organic constituents [28].

Gas-phase pulsed corona discharge (PCD), a radical-based oxidation technique noted for its high energy efficiency and potential for targeted oxidation, emerges as a promising alternative for pharmaceutical degradation while mitigating nutrient loss in urine [29]. The plasma is generated by applying high-voltage pulses across an inter-electrode gap, through which the treated liquid is dispersed, leading to the formation of highly reactive, short-living oxidants predominantly at the gas–liquid interface. The direct participation of these oxidants in pollutant degradation results in a more energy-efficient oxidation compared with conventional ozonation, which utilizes energy of only relatively stable ozone molecules through repetitive ‘oxygen-ozone-oxygen’ conversion reactions in dielectric barrier discharges. This characteristic of PCD favours targeted oxidation mechanisms and enables preferential transformation of compounds with complex molecular architectures, particularly aromatic structures commonly present in pharmaceutical molecules [30].

The objective of this work is to assess the potential of PCD in the oxidation of PR and TC contaminants in source-separated human urine without compromising its nutrient content and fertilizer potential. To achieve this, the experimental study was undertaken evaluating (i) the effects of aqueous matrices on the efficiency of PCD oxidation, (ii) the operating conditions to maximize the treatment performance, and (iii) the energy demand associated with urine PCD treatment. Together, this study aims to support the advancement of PCD as an energy-efficient technology for safe recovery and reuse of nutrients from human urine.

Enzymatic hydrolysis of urea, the essential nitrogen-containing constituent of urine, with its transformation into volatile ammonia partially lost during further treatment, storage, and transportation, is considered a factor that reduces fertilizer quality. Urease is a protein enzyme of complex three-dimensional structure, with its activity dependent on key amino acids at the active site [31]. Strong oxidants formed in PCD may attack the active moieties of urease, thereby partially or completely preventing urea hydrolysis, thus stabilizing nitrogen content in urine. Hydroxyl radicals cause irreversible oxidative denaturation of enzymes [32]. They readily oxidize amino acid side chains, particularly cysteine, histidine, methionine, and tryptophan, and may cleave peptide bonds while disrupting metal centres within the enzyme’s active site. In plasma–liquid systems, the oxidative effects result in the permanent loss of enzymatic activity without the possibility of protein refolding [33].

Experimental research was undertaken to verify the hypothesis of nitrogen stabilization using real-time monitoring of electrical conductivity (EC) as a validated kinetic proxy. Since the enzymatic breakdown of urea into cationic ammonium (NH_4^+) and anionic carbonate (CO_3^{2-}) improves solution conductivity, the suppression of the EC-rise rate serves as direct evidence of urease deactivation. This approach provides a quantitative measure of urea hydrolysis without real-time analysis of total nitrogen or nitrogen species during the active treatment phase [34].

A critical step in evaluating a treatment technology applied to the source-separated human urine for agricultural reuse is phytotoxicity assessment: the removal of pharmaceuticals may happen along with biological effects arising from transformation products of matrix components. Oxidative treatment is capable of partial oxidation of organic constituents of urine, producing intermediates with unknown biological activity. Testing provides an integrative measure of treatment safety, complementing analytical measurements of pharmaceutical degradation [35].

Seed germination and initial root development are highly sensitive to chemical stress and are therefore well suited for detecting subtle phytotoxic effects. The ASTM E1963-22 Standard Guide for Conducting Terrestrial Plant Toxicity Tests provides a structured framework for evaluating growth inhibition and developmental responses following exposure to test media [36]. The guide emphasizes reproducibility, controlled exposure conditions, and the use of quantitative endpoints that are directly relevant to agricultural performance.

2. Materials and Methods

2.1. Chemicals and Substrates

For oxidation experiments, the stock solutions were made with PR dissolved in distilled water and TC in methanol. This difference is determined by low TC solubility in water, 231 mg L^{-1} at 25°C [37]. Propranolol hydrochloride ($\text{C}_{16}\text{H}_{21}\text{NO}_2\cdot\text{HCl}$, 99%) was purchased from TCI Europe N.V., Haven, Belgium. Tetracycline ($\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_8$, 98%) and citric acid ($\text{C}_6\text{H}_8\text{O}_7$, 99%) were obtained from Sigma Aldrich, St. Louis, MI, USA, and methanol (CH_3OH , 99%)—Fisher Scientific, Loughborough, UK. Peas *Pisum Sativum* were obtained from Baltic Agro Eesti, Lehmja, Estonia. Soil for seeding and cuttings with a pH 5.5–6.5 was purchased from ASB Greenworld Eesti, Nurme, Estonia. Jack beans urease solution in 50% glycerol, 1000 U mL^{-1} , was obtained from Merc KGaA, Darmstadt, Germany.

Urine was collected from donations of research laboratory personnel to the collection tanks pre-dosed with 10 g L^{-1} of citric acid at pH 3.0 to prevent enzymatic urea hydrolysis, except for urine used in urease oxidation experiments (see below).

2.2. Experiments

The PCD experiments were carried out in a batch mode using an aqueous-media recirculating plasma treatment device engineered by Flowrox Oy (Lappeenranta, Finland), schematically shown in Figure 1. The experimental equipment consisted of a plasma reactor connected to a 40 L storage tank, a high-voltage pulse generator, and a circulation pump providing a constant liquid throughput of $1.0 \text{ m}^3 \text{ h}^{-1}$. Rather than single-pass exposure, the treated solution repeatedly traversed the plasma zone, allowing cumulative interaction with plasma-generated reactive species.

The reactor employed a wire-plate electrode configuration optimized to limit conductivity-related energy losses [38]. Forty wire electrodes, 0.55 mm in diameter and with a combined length of 20 m, were mounted horizontally between two vertically oriented parallel plates. The spacing between the wire electrodes and the grounded plate was set at 18 mm. Liquid was distributed into the discharge zone through a perforated feed plate.

Perforations were positioned in a line coinciding with the vertical plane of the high-voltage wire electrodes. The distributor contained 49 evenly spaced openings with a diameter of 1.5 mm, ensuring uniform exposure of the liquid to the plasma at the gas–liquid interface. Electrical excitation was provided by nanosecond-scale high-voltage pulses with a duration of 100 ns and a peak amplitude of 18 kV, producing peak currents of approximately 380 A. Pulse repetition frequencies of 50, 200, and 880 pulses per second (pps) were applied, corresponding to average power inputs of 9.0, 32.0, and 123.0 W, respectively.

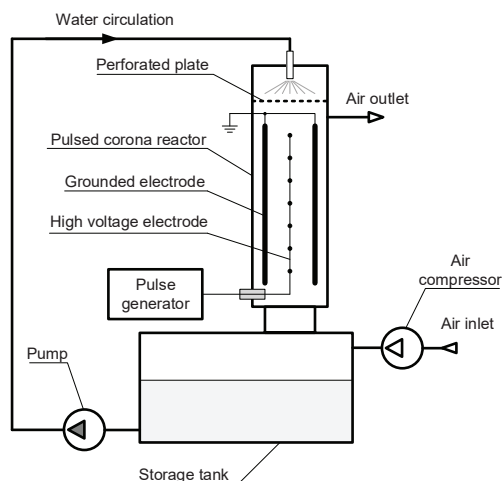


Figure 1. Experimental setup outline.

Voltage and current waveforms were recorded using a Rigol DS1102E mixed-signal oscilloscope (RIGOL Technologies EU GmbH, Gilching, Germany) in combination with a Tektronix P6015 high-voltage probe (Tektronix, Inc., Beaverton, OR, USA) and a PT-7802 current monitor (Guangzhou Pintech Co. Ltd., Guangzhou, China). The energy delivered per pulse was calculated by numerical integration of the recorded waveforms and amounted to 0.19 J at 50 and 200 pps, decreasing to 0.15 J at 880 pps. Ambient air served as discharge gas and was continuously supplied at 1.0 L min^{-1} to maintain a stable oxygen concentration in the reactor.

Experimental PCD studies on PR and TC oxidation were carried out in distilled water and source-separated urine.

The energy dose delivered to the PCD reactor, kWh m^{-3} , was calculated using Equation (1):

$$\text{Delivered energy dose} = P \cdot t / V \quad (1)$$

where P is power supplied by the pulse generator, kW, t —treatment time, h, and V —treated solution volume, m^3 .

The energy efficiency E of PR or TC oxidation, $\text{g kW}^{-1} \cdot \text{h}^{-1}$, was calculated using Equation (2):

$$E = \Delta C \cdot V / (P \cdot t) \quad (2)$$

where ΔC is the decrease in PR or TC concentration, g m^{-3} , and V —volume of treated solution, m^3 .

Stock solutions of PR and TC were prepared with concentrations of 25 g L^{-1} . Aliquots of the stock solutions were added to the tested samples to obtain an initial pharmaceutical concentration of 10 mg L^{-1} in all experiments. This concentration level was selected to allow

accurate and reproducible analytical quantification in source-separated urine, where matrix complexity and elevated background signals interfere with chromatographic detection.

To ensure a homogeneous sample composition, the electrical discharge was temporarily halted before each sampling event, and the solution was allowed to circulate and mix within the system for a minimum of four minutes. Over the course of treatment, the liquid temperature increased gradually from an initial 20 ± 1 °C to approximately 25 ± 1 °C within one hour at the maximum pulsed power applied, 123 W.

2.3. Analyses

Quantitative analyses of PR and TC were carried out using high-performance liquid chromatography coupled with a diode-array detector (HPLC–PDA; Shimadzu, Kyoto, Japan). Separation was achieved on a Phenomenex Gemini NX-C18 column (150×2.0 mm, 1.7 mm) packed with a stationary phase NX-C18 (110 Å, 5 µm) operated under isocratic conditions.

For PR quantification, the mobile phase consisted of a mixture of eluate A, composed of water acidified with 0.3% formic acid, and eluate B, acetonitrile containing 0.3% formic acid, in a volumetric ratio of 3:1. Corresponding flow rates for eluates A and B were 0.15 and 0.05 mL min^{−1}, respectively. In the TC analysis, the mobile phase composition was adjusted to 85% eluate A and 15% eluate B, with individual flow rates of 0.17 and 0.03 mL min^{−1}, respectively. For both analytical methods, the eluent combined flow rate was maintained at 0.2 mL min^{−1}. Samples were injected at a volume of 100 µL, and chromatographic separation was performed with the column oven temperature set to 40 °C. Solution pH values were monitored using a digital S220 pH meter (Mettler Toledo, Greifensee, Switzerland).

2.4. Urease Deactivation

To evaluate the urease deactivation with PCD, the experiments with elevated enzyme concentrations were carried out following in situ EC of urine. An EC electrode (Hach HQ430d, Hach Company, Loveland, CO, USA) submerged directly into the recirculation storage tank was used to avoid ammonia loss during the sampling. A 120 min urease PCD deactivation test was conducted using 10 L of non-acidified human urine. To ensure a standardized fresh baseline, urine was collected and frozen at −18 °C to prevent spontaneous hydrolysis. Before the experiment, the urine sample was slowly thawed at 2 °C. Freshly thawed urine in an amount of 10 L was pumped into the PCD reactor and dosed with Jack bean urease solution in 50% glycerol in an amount of 5.0 mL containing 1000 U mL^{−1}, to initiate accelerated urea hydrolysis. The resulting enzyme concentration in urine thus achieved 500 U L^{−1}. Immediately, the PCD was applied to the circulated urine continuously for 120 min at a pulse repetition frequency of 880 pps, providing 123 W of pulsed power. The total delivered energy dose was thus provided as high as 24.6 kWh m^{−3}. As a reference experiment, 10 L of urine, identically dosed with urease, was circulated in the PCD reactor for 120 min without plasma treatment, with EC monitored. In both experiments, EC was monitored in real time at five-minute intervals. The normalized conductivity ratio (EC/EC₀) served as a kinetic proxy for urea hydrolysis.

2.5. Phytotoxicity Test

A phytotoxicity test was conducted using pea plants (*Pisum sativum*) [36]. For pea crops, nitrogen requirements are generally much lower than for non-leguminous vegetables, due to symbiotic associations with nitrogen-fixing bacteria (*Rhizobium*) formed by peas, covering most of the plant's nitrogen needs. Peas require only a small supplemental nitrogen beyond what is biologically fixed in the soil. Typical agronomic recommendations for peas suggest only 20 to 30 kg N ha^{−1} at sowing before nitrogen fixation becomes fully active [39]. Excess nitrogen inhibits nodulation and biological nitrogen fixation.

The test was conducted using two urine samples: one untreated citric acid-stabilized urine, and another PCD-treated with the maximum energy dose relevant to the study, 12.6 kWh m^{−3}. The previous study demonstrated the indifference of urea and ammonia contents towards the pulsed energy dose delivered to the urine treatment, and a small increase in nitrates due to their formation in air-phase PCD [29]. The treated urine sample was spiked at the start with 10 mg L^{−1} of PR, which was almost entirely oxidized by the end of treatment (Figure 2). The experiment was conducted using six independent biological replicates (*n* = 6) for each dosage level (from 0 to 4×, Table 1) within both the untreated and PCD-treated groups. This resulted in a total of 72 *Pisum sativum* seedlings monitored.

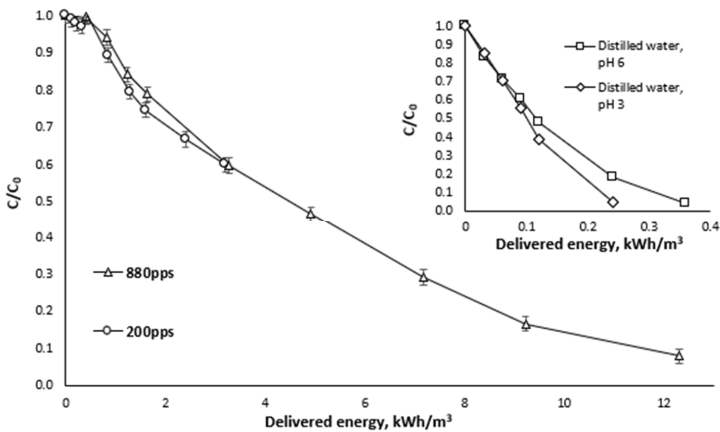


Figure 2. Propranolol concentration vs. delivered pulsed energy dose in distilled water (inset) and urine: starting PR concentration 10.0 mg L^{−1}; oxidation in water at pulse repetition frequency 50 pps (9.0 W), starting pH 3.0 and 6.0; oxidation in stabilized source-separated urine at pH 3.0, pulse repetition frequency 200 (32.0 W) and 880 (123.0 W) pps.

Table 1. Urine doses and their purpose.

Dose Level	Relative to Agronomic Dose	N Applied, kg N ha ^{−1}	Urine per Pot, mL	Purpose
Control	0	0	0	Negative control
Low	0.25×	6.25	0.53	Sub-threshold sensitivity
Medium-low	0.5×	12.5	1.06	Conservative agronomic
Reference	1×	25	2.11	Reference agronomic dose
Medium-high	2×	50	4.22	Moderate over-application
High	4×	100	8.44	Supra-agronomic stress test

The conditions of testing were maintained in accordance with the ASTM E1963-22 [36]. Testing was conducted in a temperature-controlled chamber at 22 ± 1 °C. Illumination was provided by blue-enhanced LED modules (peak wavelength ≈ 450 nm) specifically designed for the seedling emergence stage. The photosynthetic photon flux density (PPFD) was maintained at 150 ± 10 μmol m^{−2} s^{−1} at the plant canopy level, verified using a VidalKraft Quantum PAR Meter. This blue-rich spectrum (400–500 nm) was selected to optimize seedling morphogenesis and ensure healthy growth during the four-week observation period. Air relative humidity in the chamber at 22 °C was maintained at 32%. The plants were watered automatically once every three days for a duration of one minute at a flow rate of 0.7 L h^{−1}, providing 11.69 mL per plant per event. This corresponds

to an irrigation load of approximately $27,650 \text{ kg ha}^{-1}$ per event, which is equivalent to 2.77 mm of precipitate, ensuring soil moisture without leaching during the seedling emergence phase. The initial soil pH was measured prior to the seedling as 6.1. The nitrogen application rates were standardized to an agricultural dose of 25 kg N ha^{-1} and recalculated for the pot surface area of 42.25 cm^2 , yielding a target of $10.56 \text{ mg N per pot}$. To ensure precise nitrogen loading for the phytotoxicity assays, the total nitrogen (N_{tot}) content of the urine batch was determined by aggregating the nitrogen contributions of its primary components: urea (9921 mg L^{-1}) and ammonia-nitrogen ($\text{NH}_4\text{-N } 667 \text{ mg L}^{-1}$), both measured using a Thermo Scientific Gallery discrete analyzer. Accounted for the nitrogen mass fraction of urea (46.6%), the estimated N_{tot} of the batch was 5.3 g L^{-1} . Based on this concentration and the surface area of the experimental pots, an application volume of 2.11 mL was established as the reference agronomic dose ($1\times$). Urine was dosed to the pots once for three days before watering.

The phytotoxicity test was repeated twice with variation in the seed tray arrangement to avoid a possible impact of unevenness in illumination. The plant growth was assessed during the early growth stage, comprising four weeks: harvested shoots and roots were separated, weighed to determine the fresh biomass, oven-dried at 70°C until constant weight, and reweighed for dry biomass. Biomass data were used to evaluate potential phytotoxic effects of the applied urine doses.

3. Results and Discussion

3.1. Energy Efficiency of Propranolol Oxidation

The oxidative degradation of PR by PCD demonstrated a dependence on the solution pH and the complexity of the matrix (Figure 2). In distilled water at neutral pH, complete removal of PR at a pulse frequency of 50 pps (9.0 W) was achieved within 24 min, corresponding to a specific energy consumption (SEC) of 0.36 kWh m^{-3} . During the treatment, the pH in neutral solutions decreased from 6.55 to 6.35. At pH 3.0, which remained stable during the treatment, PR was oxidized within 16 min, making SEC decrease to 0.24 kWh m^{-3} (Figure 2 inset). These numbers give the PR oxidation energy efficiencies at 50% removal, 43.3 and $45.3 \text{ g kW}^{-1}\cdot\text{h}^{-1}$ for neutral and acidic solutions, respectively. For 90% removal, the efficiencies comprised 32.3 and $39.6 \text{ g kW}^{-1}\cdot\text{h}^{-1}$ in circum-neutral and acidic media, respectively.

The kinetic behaviour of oxidized PR, influenced by solution acidity, is explained by both the speciation of the target pollutant and the behaviour of plasma-generated oxidants, ozone, and hydroxyl radicals [40]. Propranolol, a secondary amine with a pKa of approximately 9.53, exists predominantly in its protonated cationic form under acidic conditions [41]. This state likely enhances its susceptibility to electrophilic attack by hydroxyl radicals generated at the gas–liquid interface [42]. The beneficial character of acidic medium for PR oxidation determined the application of the condition to the PR treatment in acid-stabilized urine in further experiments.

Oxidation of PR in source-separated urine demonstrated a significant inhibitory effect on oxidation efficiency. This decrease in energy efficiency is attributed to a pronounced ‘matrix effect’, when high concentrations of endogenous organic metabolites act as competitive radical scavengers. In the urine matrix at 200 pps (32.0 W), the PR concentration was reduced to $C/C_0 = 0.57$ after 60 min of treatment, requiring SEC of 3.2 kWh m^{-3} . The energy efficiency of PR oxidation at this energy dose comprised $1.45 \text{ g kW}^{-1}\cdot\text{h}^{-1}$. This should be doubled when PCD is applied in oxygen [43]. While the pulse repetition frequency increased to 880 pps (123.0 W), facilitating almost complete PR removal within the same 60 min timeframe, it necessitated SEC reaching 12.3 kWh m^{-3} . The energy efficiency of this pulsed power comprised $0.81 \text{ g kW}^{-1}\cdot\text{h}^{-1}$ at 90% removal. It is worth noting, however, that

SEC of 3.2 kWh m^{-3} showed equal oxidation of PR indifferent towards the applied pulsed power (Figure 2), i.e., all available short- and long-living oxidants, including ozone, are consumed fast even at the highest frequency, and no energy efficiency benefits are obtained at low pulse repetition frequency. This observation enables urine treatment at maximum available pulsed power, i.e., at the highest treatment intensity.

According to Dodd et al. [44], ozonation of PR in partially hydrolyzed urine containing other pharmaceuticals achieved a maximum energy efficiency of about $0.26 \text{ g kW}^{-1} \cdot \text{h}^{-1}$ for 90% degradation. This value was obtained under conditions in which ozone was generated from pure oxygen, with an energy yield of $13.1 \text{ kWh kg O}_3^{-1}$. Their experiments used a PR starting concentration of 2.33 mg L^{-1} , which was lower than the 10 mg L^{-1} in the present study. Although energy efficiency tends to decrease with decreasing substrate concentration [43], the observed order-of-magnitude difference suggests that PCD offers a more energy-efficient approach for PR degradation due to its targeted oxidation mechanism driven by short-living reactive species formed at the plasma–liquid interface [45]. SEC of the PCD treatment was also compared against the benchmarks for urine ozonation, using the ozone demand relative to the total nitrogen, modelled at 1.5 g O_3 per $\text{g of N}_{\text{tot}}$ [43]. For 5.3 g L^{-1} of N_{tot} in this study, this correlates to an ozone dose of $7.95 \text{ g O}_3 \text{ L}^{-1}$. Utilizing the above-mentioned energy yield in oxygen [43], the calculated SEC for conventional ozonation would reach 104 kWh m^{-3} , which is doubled with air to be compared with 12.3 kWh m^{-3} observed with PCD [46]. This order-of-magnitude difference confirms that while PR is highly reactive toward molecular ozone ($k_{\text{O}_3} \approx 10^5 \text{ M}^{-1} \text{ s}^{-1}$), the generation of reactive species at the gas–liquid interface in PCD bypasses the massive bulk-phase scavenging and is significantly more efficient than molecular ozone delivery.

3.2. Energy Efficiency of Tetracycline Oxidation

Trials in neutral aqueous solutions were confounded by TC's propensity for hydrolysis and precipitation, as reported earlier [17–19]. Therefore, PCD experiments were conducted under acidified conditions (pH 3.0) to ensure TC remained in its protonated soluble form. In acidified distilled water, TC proved highly susceptible to PCD-driven oxidation; its complete degradation was achieved within 20 min at a low pulse repetition frequency (50 pps, 9.0 W), requiring a specific energy dose of 0.3 kWh m^{-3} (Figure 3 inset). The energy efficiency of TC oxidation thus comprised 43.6 and $38.9 \text{ g kW}^{-1} \cdot \text{h}^{-1}$ at 50% and 90% removal, respectively, which are close to the numbers observed in PR oxidation. High energy efficiency in water is consistent with short-living hydroxyl radicals participating in oxidation and their electrophilic attack on the phenolic and other electron-rich moieties of the TC molecule at low pH. For comparison, Jeong et al. reported near-complete degradation of TC at $50 \text{ }\mu\text{M}$ concentration, i.e., 22.2 mg L^{-1} , using γ -radiolysis at a dose of 2.5 kGy , which corresponds to an estimated energy yield of approximately $32 \text{ g kW}^{-1} \cdot \text{h}^{-1}$ [47]. Under the circumstances, PCD oxidation demonstrates energy efficiency surpassing the bulk-phase radical generation by ionizing radiation.

Tetracycline content in urine at 200 pps was reduced to $C/C_0 = 0.7$ after 60 min of treatment, demonstrating the energy efficiency of $0.93 \text{ g kW}^{-1} \cdot \text{h}^{-1}$. When the delivered energy dose increased to 12.3 kWh m^{-3} at a pulse repetition frequency of 880 pps, i.e., nearly 40 times the dose required in water, partial removal of TC was achieved at $C/C_0 = 0.46$ at the energy efficiency of $0.44 \text{ g kW}^{-1} \cdot \text{h}^{-1}$. Tetracycline thus exhibited degradation in urine noticeably slower than PR, explained by the difference in molecular structures of these substances. In contrast to the amphiphilic molecular structure of PR, i.e., combining hydrophilic and hydrophobic moieties located at diametrically opposite ends, the TC molecule is of non-amphiphilic, i.e., non-surfactant character, containing plentiful functional hydrophilic groups—phenolic, alcoholic, keto- and amino-groups, determining a multi-functional molecu-

lar structure interacting with the surrounding chemical environment, i.e., exhibiting stronger ‘matrix effect’. These groups may facilitate the formation of stable coordination complexes with various organic and inorganic substances, such as polyvalent metal ions [48], or dissolved organic matter [49,50], potentially shielding the TC molecule from oxidative attacks at the plasma–liquid interface or altering the degradation pathways toward less efficient routes. The observed difference between PR and TC in oxidation in urine leads to an important notice: the interaction of the target micropollutant with urine components and, consequently, the effectiveness of PCD oxidation depends on the molecular structure of the target contaminant. This necessitates investigating the behaviour of diverse micropollutant structures in urine to comprehensively assess PCD efficiency in safe fertilizer production. The hypothesis is supported by observations made earlier with tricyclic carbamazepine (CBZ), which is poor in functional groups, oxidation of which in urine was also more efficient than that of TC [29].

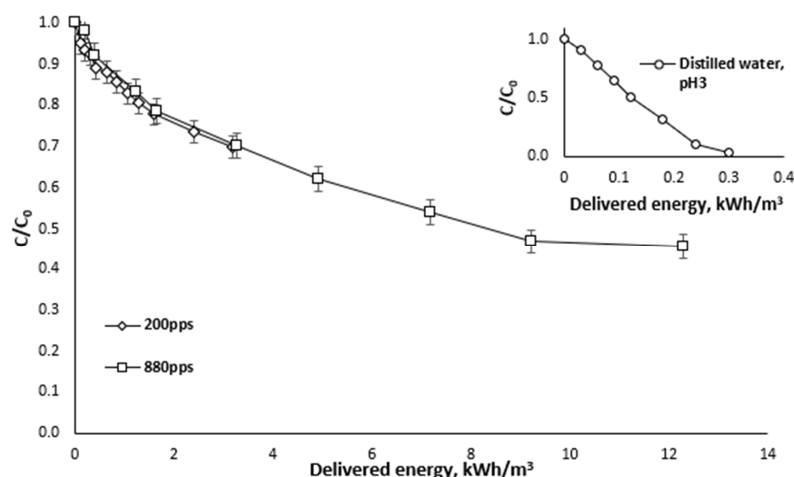


Figure 3. Tetracycline concentration vs. delivered pulsed energy dose in distilled water (inset) and urine: starting TC concentration 10.0 mg L^{-1} ; oxidation in water at pulse repetition frequency 50 pps (9.0 W), starting pH 3.0; oxidation in stabilized source-separated urine at pH 3.0, pulse repetition frequency 200 (32.0 W) and 880 (123.0 W) pps.

3.3. Phytotoxicity Testing

The experimental design followed a dose–response relationship ranging from sub-threshold sensitivity to supra-agronomic stress, as detailed in Table 1. As illustrated in Figure 4, both untreated and PCD-treated urine exerted a pronounced stimulatory effect on early plant development at agronomic doses ($\leq 1 \times$). At the $1 \times$ reference dose, 25 kg N ha^{-1} , total dry biomass increased by 30% for group A and 31% for group B compared to the non-fertilized negative control. Morphological measurements (Table 2) confirmed this trend, with mean root lengths reaching 66.5 and 67.0 mm in groups A and B, fertilized with untreated and PCD-treated urine, respectively. These root lengths exceeded those in the negative control row, 55.8 mm, by about 20%. These observations confirm that urine-derived nutrients are bioavailable, providing a significant ‘starter’ effect during the early life of the pea plants.

Comparison between untreated urine, group A, and PCD-treated urine, group B, revealed no significant difference in plant performance across the urine dose range. Growth trajectories were closely aligned with nitrogen input levels, showing no impact of potential plasma-induced transformation products (Figure 4 and Table 2). The fact that the biomass accumulation and tissue partitioning, i.e., shoot-to-root ratio, were nearly identical for

both groups suggests that the PCD treatment did not negatively affect nutrient availability, i.e., it preserved the functional integrity of the urine as a nutrient source.

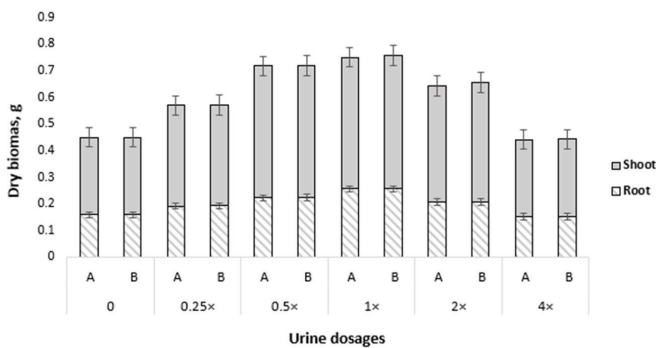


Figure 4. The pea shoot and root biomass at application of urine dosages for two treatment groups: untreated urine, group A, and PCD-treated urine, group B.

Table 2. Morphological parameters of *Pisum sativum* seedlings (mean $\pm$ SD, $n = 6$).

Dose Range	Untreated Urine			PCD-Treated Urine		
	Shoot, cm	Root, cm	S/R Ratio	Shoot, cm	Root, cm	S/R Ratio
0	12.3 $\pm$ 0.5	5.6 $\pm$ 0.5	2.21	12.3 $\pm$ 0.5	5.6 $\pm$ 0.5	2.21
0.25 $\times$	14.2 $\pm$ 0.3	6.1 $\pm$ 0.3	2.31	14.3 $\pm$ 0.3	6.2 $\pm$ 0.3	2.30
0.5 $\times$	15.5 $\pm$ 0.5	6.4 $\pm$ 0.5	2.42	15.6 $\pm$ 0.5	6.5 $\pm$ 0.5	2.41
1 $\times$	17.0 $\pm$ 0.6	6.7 $\pm$ 0.6	2.56	17.1 $\pm$ 0.6	6.8 $\pm$ 0.6	2.51
2 $\times$	16.0 $\pm$ 0.6	5.9 $\pm$ 0.5	2.74	15.8 $\pm$ 0.6	5.7 $\pm$ 0.5	2.77
4 $\times$	12.3 $\pm$ 0.3	4.5 $\pm$ 0.3	2.72	12.3 $\pm$ 0.4	4.4 $\pm$ 0.4	2.79

Growth inhibition was observed only at supra-agronomic application doses. At the 2 $\times$ dose, 50 kg N ha^{−1}, minor reductions in root elongation and biomass were detected. These effects remained sublethal and were consistent with nutrient-induced physiological stress. The highest application rate of 4 $\times$, 100 kg N ha^{−1}, resulted in a ‘point of zero-net-benefit’, where the biomass accumulation dropped back to the level of the non-fertilized control. This inhibition is attributed primarily to rhizosphere acidification and ammonium-related toxicity, common consequences of excessive nitrogen overfeed, rather than any inherent toxicity from the PCD process itself. This nitrogen overfeed suppressed root development and negated the stimulatory potential of the urine-derived nutrients. The absence of additional inhibitory effects in the PCD-treated row compared to the untreated one confirms the toxicological safety of the plasma treatment.

Analysis of the growth data confirmed that the results remained consistent regardless of the sample order or the tray position in the chamber. The uniformity of the biomass accumulation across the replicates indicates that the potential impact of uneven illumination was successfully neutralized. Consequently, the observed stimulatory and inhibitory effects can be confidently attributed to the nutrient loading and the PCD treatment process.

3.4. Urease Enzyme Deactivation

To evaluate the impact of PCD treatment on nitrogen stability by deactivating the urease enzyme and thus preserving urea, EC was monitored as a real-time substitute for enzymatic urea hydrolysis (see Section 1). By monitoring the rate of the EC/EC0 increase

relative to the treatment time, the degree of urease deactivation in the complex urine matrix may be indirectly assessed (Figure 5).

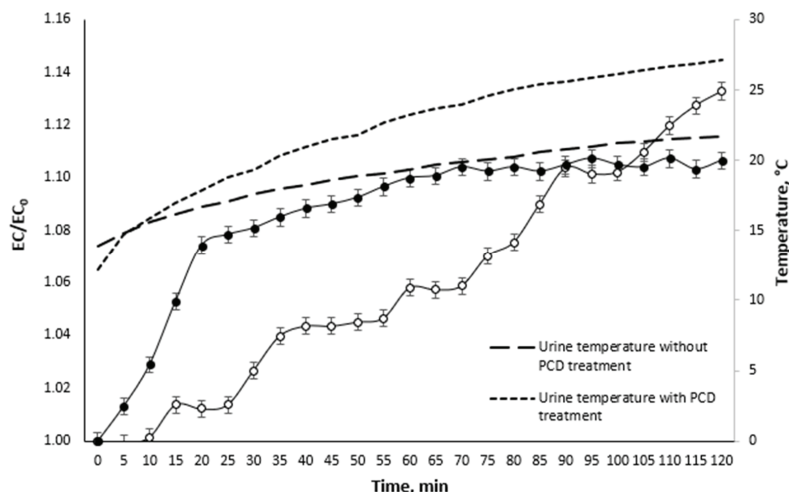


Figure 5. Normalized electric conductivity (EC/EC_0) and temperature dependent on treatment time in processing of non-stabilized urine containing urease: ○—untreated urine (reference sample without PCD application); $EC_0 = 13.12 \text{ mS cm}^{-1}$; ●—PCD-treated urine; $EC_0 = 12.11 \text{ mS cm}^{-1}$; starting concentration of urease 500 U L^{-1} , pulse repetition frequency 880 pps (123.0 W); urine sample volume 10 L; urine circulation rate $1 \text{ m}^3 \text{ h}^{-1}$. Dashed lines represent temperature profiles for the untreated and PCD-treated urine.

In the untreated urine containing urease enzyme, the normalized electric conductivity EC/EC_0 demonstrated a steady increase from 1.000 to 1.133 at the $EC_0 = 13.12 \text{ mS cm}^{-1}$. The continuous rise is determined by urea hydrolysis, and, to some extent, the rise in temperature from 13.9 to 21.7 °C during the trial. One should keep in mind that the temperature of urine not only affects its EC but, in the presence of urease enzyme, also accelerates urea hydrolysis, making the role of temperature more complex. It is therefore difficult to distinguish the effect of temperature from that of hydrolysis. Consequently, the observed increase in EC must be considered a combined phenomenon reflecting both temperature and the enzymatic hydrolysis of urea. The pH of untreated urine rose during the trial from 6.2 to 9.0, i.e., by 2.8 units; recalculated conditionally to the increase in hydroxyl-ion concentration, this means about 630 times.

The PCD-treated sample with $EC_0 = 12.11 \text{ mS cm}^{-1}$ demonstrated a higher temperature growth due to the discharge energy dissipation, reaching a final temperature of 27.1 °C in two hours. Higher temperature should have accelerated the enzymatic reaction rate and, as a result, led to higher EC by the end of treatment. However, after about one hour of treatment, the EC/EC_0 ratio reached a plateau at approximately 1.08–1.10, yielding to the final one of steadily growing untreated urine. This observation indicates the deactivation of urease, rendering it unable to further hydrolyze urea, confirming that PCD effectively stabilizes urea. PCD treatment itself does not impact urea concentration as observed earlier [29].

The rapid increase in EC during the first 20 min of treatment may be explained by the oxidation of abundant endogenous organic components in urine and the formation of ionized products, such as salts of carboxylic acids, which contributed to the increased EC. The pH of the PCD-treated urine also increased, although to a smaller extent, from 6.6 to 8.7, i.e., 2.1 units, indicating that the hydroxyl-ion concentration increased only 128 times.

This observation may also be explained by the formation of carboxylic acids neutralizing ammonium formed in urea hydrolysis.

Although ambient air in the PCD reactor facilitates formation of nitrates [51], the contribution of these ions to EC is minor for the amount formed in urine: the energy yield of nitrates is only $1.6 \text{ g kW}^{-1} \cdot \text{h}^{-1}$ [51]. Thus, the concentration of nitrates in treated urine at the energy dose of 24.6 kWh m^{-3} may not exceed 39 mg L^{-1} .

3.5. Practical Implications and Techno-Economic Considerations

While PCD treatment effectively neutralizes pharmaceutical contaminants, the resulting effluent remains a dilute liquid. For viable agricultural scaling, nutrient concentration via dewatering is a critical determinant of operational feasibility [52,53]. Advanced technologies, such as membrane distillation and alkaline dehydration with heat recovery, present SEC values ranging from 150 to 220 kWh m^{-3} . Applying these benchmarks to the nitrogen-rich urine with a mean total Kjeldahl nitrogen of 6.95 g L^{-1} [53] allows for a more rigorous economic assessment [53,54]. The total energy expenditure for producing a stabilized, pharmaceutical-free, concentrated fertilizer, including both PCD treatment, $1.8 \text{ kWh kg}^{-1} \text{ N}$, and dewatering, $31.6 \text{ kWh kg}^{-1} \text{ N}$, is approximately $33.4 \text{ kWh kg}^{-1} \text{ N}$. One should notice that the energy expense in PCD, although minor as compared to dewatering, was based on the complete removal of PR and its initial concentration as high as 10 mg L^{-1} , which is expected to be smaller at realistic concentrations in urine.

While this value exceeds the primary energy demand for ammonia production in the Haber–Bosch process, comprising $12.5 \text{ kWh kg}^{-1} \text{ N}$ [54], the gap is significantly bridged when the intrinsic value of contaminant removal and nitrogen recycling is factored into the total environmental credit of the system [53]. This integrated approach provides a decentralized, circular pathway that addresses chemical safety and nutrient preservation in ways conventional synthetic production cannot match. In addition, one should keep in mind the turnover of phosphorus and potassium nutrients covered by the approach, which contributes to the sustainability of agriculture and wastewater management.

4. Conclusions

The study demonstrated PCD as a reliable and effective technology for the valorization of source-separated human urine, successfully oxidizing certain pharmaceutical contaminants and providing nitrogen stability. The experimental results confirm that PCD achieves high removal efficiencies for PR and, to a lesser extent, TC. While PR was readily oxidized in both aqueous and urine matrices, the degradation of TC in urine was significantly attenuated. This recalcitrance is attributed to a complex matrix effect involving competitive radical scavenging and the screening of TC through its complexation by endogenous organic compounds. Despite these inhibitory factors, target pollutant oxidation is still possible by increasing the delivered pulsed energy dose, confirming that PCD can overcome the chemical complexity of urine. The examples of amphiphilic PR and hydrophilic TC logically support the previously stated claim that targeted oxidation is facilitated by the amphiphilic molecular structure of the target substance.

Urea is effectively stabilized by the PCD deactivation of the urease enzyme: by suppressing enzymatic urea hydrolysis, PCD treatment mitigates the risk of ammonia volatilization, thereby preserving the total nitrogen content. The dual functionality, providing chemical safety and nutrient preservation at moderate energy expenditure, distinguishes PCD from other treatment methods.

Phytotoxicity assessments on *Pisum sativum* further validated the safety of the PCD-treated urine: with reference to agronomic doses, no inhibitory effects were observed; PCD-treated urine promoted vegetative development identical to that of the untreated

reference sample. The absence of negative plant responses at these nitrogen doses indicates that the transformation products generated during PCD oxidation do not pose a biological risk. Inhibitory effects in both urine samples were observed only at supra-agronomic doses, being consistent with nutrient-induced stress rather than inherent treatment toxicity.

From a techno-economic perspective, although the energy demand for PCD treatment and subsequent dewatering at approximately 33.4 kWh kg^{−1} N is higher than the Haber–Bosch benchmark, the process offers a unique value proposition. By enabling the decentralized production of safe, stabilized, and contaminant-free liquid fertilizer, PCD facilitates the transition toward a circular nutrient economy.

Future research should focus on the more efficient removal of antibiotics and other hydrophilic pharmaceuticals; studies on PCD interactions with dewatering issues, such as removal of lipids; and long-term impacts of PCD-treated urine on soil fertility.

Author Contributions: Conceptualization, I.P. and S.P.; methodology, I.P.; software, N.D.; validation, I.P., N.D. and S.P.; formal analysis, S.P.; investigation, I.P.; resources, N.D. and S.P.; data curation, I.P.; writing—original draft preparation, I.P.; writing—review and editing, S.P.; visualization, I.P.; supervision, S.P.; project administration, S.P.; funding acquisition, S.P. All authors have read and agreed to the published version of the manuscript.

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Abbreviations

The following abbreviations are used in this manuscript:

AOP	Advanced oxidation process
CBZ	Carbamazepine
EC	Electrical conductivity
HPLC	High-performance liquid chromatography
N _{tot}	Total content of nitrogen
OH	Hydroxyl radical
OPBT	Occurrence, persistence, bioaccumulation, and toxicity criteria
PCD	Pulsed corona discharge
pps	Pulses per second
PR	Propranolol
SEC	Specific energy consumption
TC	Tetracycline
UV	Ultra-violet

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Curriculum Vitae

Personal data

Name:	Irina Petrotšenko
Date of birth:	30.10.1988
Place of birth:	Tallinn
Citizenship:	Estonian

Contact data

E-mail:	irina.petrotsenko@taltech.ee
---------	------------------------------

Education

2022–2026	Tallinn University of Technology, Department of Materials and Environmental Technology, Doctoral Studies
2017–2019	Tallinn University of Technology, MSc in Engineering
2008–2017	Tallinn University of Technology, BSc in Engineering (gap 5 years)
2004–2007	Tallinn Lasnamäe High School

Language competence

English	Fluent
Estonian	Fluent
Russian	Native speaker
German	Basics

Defended thesis

Master's Degree, 2019, Effect of ozone on photocatalytic degradation of acetone vapour on P25 TiO₂ coatings, Tallinn University of Technology, Department of Materials and Environmental Technology. Supervisors Marina Kritševskaja, Maarja Kaasik.

Main areas of scientific work

1. Biosciences and Environment; 1.8 Research relating to the State of the Environment and to Environmental Protection; CERCS CLASSIFICATION: T270 Environmental technology, pollution control

4. Natural Sciences and Engineering; 4.12. Process Technology and Materials Science; CERCS RESEARCH FIELD: T150 Material technology; SPECIFICATION: Environmental Technology

4. Natural Sciences and Engineering; 4.11. Chemistry and Chemical Technology; CERCS CLASSIFICATION: T350 Chemical technology and engineering

Participation in research projects

ETAG22018 Utilization of aluminium-bearing raw materials for the production of aluminium metal, other materials and compounds

Awards

2025	Kristjan Jaak Scholarship for short-term research visit to the Swedish University of Agricultural Sciences (SLU), 1–6 December 2025
2025	Tallinn City Council Scholarship

Attendance at conferences and training schools

2026	Oral presentation at Future Frontiers: PhD Conference on Emerging Technologies, May 5–6, 2026, Tartu, Estonia
2025	Oral presentation at Future Frontiers: PhD Conference on Emerging Technologies, May 6–7, 2026, Tartu, Estonia
2025	Oral presentation at 7th International Conference on the Environmental Applications of Advanced Oxidation Processes, June 10 – 13, 2025, Paestum, Italy
2024	Attendance with a poster presentation at the 4th European School on Environmental Applications of Advanced Oxidation Processes, November 4 - 6, 2024, Thessaloniki, Greece

Supervised dissertations

Svetlana Ivanova, Master's Degree, 2024, (sup) Sergei Preis; Irina Petrotšenko, Oxidation of Bromide During the Treatment of Aqueous Solutions with Pulsed Corona Discharge, Tallinn University of Technology, School of Engineering, Department of Materials and Environmental Technology

Elulookirjeldus

Isikuandmed

Nimi: Irina Petrotšenko
Sünniaeg: 30.10.1988
Sünnikoht: Tallinn
Kodakondsus: Eesti

Kontaktandmed

E-post: irina.petrotsenko@taltech.ee

Hariduskäik

2022–2026	Tallinna Tehnikaülikool, materjali- ja keskkonnatehnoloogia instituut, doktoriõpe
2017–2019	Tallinna Tehnikaülikool, tehnikateaduse magister (MSc)
2008–2017	Tallinna Tehnikaülikool, tehnikateaduse bakalaureus (BSc) (vaheaeg 5 aastat)
2004–2007	Tallinna Lasnamäe Gümnaasium, keskharidus

Keeleoskus

Inglise keel	Väga hea
Eesti keel	Väga hea
Vene keel	Emakeel
Saksa keel	Algtase

Kaitstud lõputööd

Magistrikraad, 2019, Osooni mõju atsetooniauru fotokatalüütilisele lagundamisele P25 TiO₂ pinnakatetel (*Effect of ozone on photocatalytic degradation of acetone vapour on P25 TiO₂ coatings*), Tallinna Tehnikaülikool, materjali- ja keskkonnatehnoloogia instituut. Juhendajad: Marina Kritševskaja, Maarja Kaasik.

Teadustöö põhisuunad

1. Bio- ja keskkonnateadused; 1.8. Keskkonnaseisundit ja keskkonnakaitset käsitlevad uuringud; CERCS KLASSIFIKAATOR: T270 Keskkonnatehnoloogia, saastekontroll

4. Loodusteadused ja tehnika; 4.12. Protsessitehnoloogia ja materjaliteadus; CERCS VALDKOND: T150 Materjalitehnoloogia; TÄPSUSTUS: Keskkonnatehnoloogia

4. Loodusteadused ja tehnika; 4.11. Keemia ja keemiatehnoloogia; CERCS KLASSIFIKAATOR: T350 Keemiatehnoloogia

Osalemine teadusprojektides

ETAG22018 Alumiiniumi sisaldava toorme kasutamine alumiiniummetalli, muude materjalide ja ühendite tootmiseks

Tunnustused

2025	Kristjan Jaagu välissõidu stipendium lühiajaliseks teadustööks Rootsi Põllumajandusülikoolis (SLU), 1.–6. Detsember 2025
2025	Tallinna Raestipendium

Osalemine konverentsidel ja koolitustel

2026	Suuline ettekanne konverentsil „Future Frontiers: PhD Conference on Emerging Technologies“, 5.–6. mai 2026, Tartu, Eesti
2025	Suuline ettekanne konverentsil „Future Frontiers: PhD Conference on Emerging Technologies“, 6.–7. mai 2025, Tartu, Eesti
2025	Suuline ettekanne konverentsil „7th International Conference on the Environmental Applications of Advanced Oxidation Processes“, 10.–13. juuni 2025, Paestum, Itaalia
2024	Osalemine posterettekandega koolitusel „4th European School on Environmental Applications of Advanced Oxidation Processes“, 4.–6. november 2024, Thessaloniki, Kreeka

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