

Sonocatalytic persulfate activation for degradation of PFOA and ciprofloxacin in aqueous systems

Jarno Thys

Promotor: Prof. dr. ir. R. Dewil

Copromotor: F. J. Ayala Esmoris, MSc

Masterproef ingediend tot het behalen van de
graad van Master of Science in de industriële
wetenschappen: chemie

Academiejahr 2025-2026

© Copyright KU Leuven

Deze masterproef is een examendocument dat niet werd gecorrigeerd voor eventuele vastgestelde fouten.

Zonder voorafgaande schriftelijke toestemming van zowel de promotor(en) als de auteur(s) is overnemen, kopiëren, gebruiken of realiseren van deze uitgave of gedeelten ervan verboden. Voor aanvragen i.v.m. het overnemen en/of gebruik en/of realisatie van gedeelten uit deze publicatie, kan u zich richten tot: KU Leuven Faculteit Industriële Ingenieurswetenschappen, W. de Croylaan 56, B-3000 Heverlee, email info.iw@kuleuven.be.

Voorafgaande schriftelijke toestemming van de promotor(en) is eveneens vereist voor het aanwenden van de in deze masterproef beschreven (originele) methoden, producten, schakelingen en programma's voor industrieel of commercieel nut, om te refereren naar dit werk in publicaties en voor de inzending van deze publicatie ter deelname aan wetenschappelijke prijzen of wedstrijden.

Preface

This thesis marks the final stage of my Master of Science in Industrial Engineering: Chemistry at KU Leuven. The completion of this work would not have been possible without the support, guidance, and encouragement of several people and institutions, to whom I would like to express my sincere gratitude.

First, I would like to thank the researchers and staff of the University of Aveiro for their valuable contribution to this research by performing the TEM, SEM, BET, and XRD analyses. Their support made the thorough characterization of the synthesized catalysts possible.

I would also like to thank the Unit Pharmaceutical Analysis of the Faculty of Pharmaceutical Sciences at KU Leuven, and Professor Deirdre Cabooter in particular, for making the PFOA analyses possible. Their contribution was essential for evaluating the degradation of this PFAS compound.

I would also like to express my gratitude to Mohammadreza Kamali for making the catalyst characterization possible and for his willingness to answer questions and provide guidance whenever difficulties arose during the project.

My sincere thanks go to my promoter, Professor Raf Dewil, for his guidance throughout this thesis. His insights, constructive feedback, and regular meetings helped me define a clear research trajectory and ensured that the project remained focused and on track.

I am especially grateful to my co-promoter, Francisco Ayala Esmoris, for his continuous support throughout this work. His assistance in the laboratory, readiness to answer questions, and encouragement during both successful and challenging moments were invaluable. I would like to thank him not only for helping me overcome obstacles but also for giving me the freedom to develop this thesis in my own way and take ownership of the research. His support played a crucial role in bringing this work to a successful conclusion.

Finally, I would like to thank my partner, family, friends, and everyone who supported me throughout my studies. Their encouragement and confidence in me have been a constant source of motivation.

Samenvatting

Watervervuiling door zogenaamde opkomende verontreinigingen vormt een steeds grotere milieukundige uitdaging. Tot deze stoffen behoren onder andere per- en polyfluoralkylstoffen (PFAS), die deel uitmaken van de zogenaamde “forever chemicals”, en farmaceutische stoffen zoals het antibioticum ciprofloxacin. Door hun hoge stabiliteit worden deze verontreinigingen slechts gedeeltelijk verwijderd in conventionele waterzuiveringsprocessen. Hierdoor kunnen ze in het milieu aanwezig blijven en mogelijk risico's vormen voor ecosystemen en de menselijke gezondheid.

In deze masterproef werd onderzocht of een geavanceerd oxidatieproces op basis van ultrasone golven, een oxidant en heterogene katalysatoren de afbraak van deze moeilijk afbreekbare stoffen kan verbeteren. Ultrasone golven veroorzaken in water de vorming van microscopisch kleine belletjes, die vervolgens krachtig imploderen. Hierbij ontstaan zeer reactieve omstandigheden. Wanneer dit proces wordt gecombineerd met een oxidant zoals persulfaat en een geschikte katalysator, kunnen reactieve stoffen gevormd worden die organische verontreinigingen kunnen afbreken.

Drie katalysatoren werden gesynthetiseerd en onderzocht: koper(II)oxide (CuO), magnetiet (Fe_3O_4) en een CuO /magnetiet-composiet. Hun werking werd getest voor de afbraak van ciprofloxacin en perfluorooctazuur (PFOA), een veel bestudeerde historische PFAS-verbinding. Van de onderzochte katalysatoren vertoonde magnetiet de meest veelbelovende werking. Dit materiaal combineerde een efficiënte activatie van persulfaat met praktische voordelen, zoals een goedkope synthese en eenvoudige magnetische terugwinning.

Het systeem met ultrasound, persulfaat en magnetiet werd vervolgens verder geoptimaliseerd door de invloed van initiële pH, katalysatordosering en oxidantdosering te onderzoeken. Voor ciprofloxacin werden de beste resultaten behaald onder zure omstandigheden. Meer dan 80% van de verontreiniging werd verwijderd, en de resultaten wezen erop dat de verontreiniging niet alleen werd afgebroken, maar ook gedeeltelijk verder werd omgezet naar eenvoudigere eindproducten. Radicalenvangexperimenten toonden aan dat sulfaatradicalen voornamelijk verantwoordelijk waren voor de afbraak bij lage pH, terwijl hydroxylradicalen belangrijker werden bij neutrale en basische omstandigheden.

Het systeem werd ook toegepast op de afbraak van PFOA. PFOA bleek veel moeilijker af te breken dan ciprofloxacin, wat de hoge stabiliteit van PFAS en hun sterke koolstof-fluorbindingen bevestigt. Hoewel een deel van de PFOA werd verwijderd, kon door de lage beginconcentraties niet betrouwbaar worden vastgesteld in welke mate de stof volledig werd afgebroken of fluor vrijgaf.

Tot slot werd de invloed van meer realistische waterbestanddelen onderzocht. Natuurlijk organisch materiaal had slechts een beperkte invloed op de afbraak, terwijl bicarbonaat- en fosfaationen de efficiëntie duidelijk verminderden. Hergebruiksexperimenten toonden aan dat magnetiet gedurende meerdere cycli actief bleef, hoewel de werking afnam.

Algemeen toont deze studie aan dat de combinatie van ultrasound, persulfaat en magnetiet een veelbelovende aanpak is voor de verwijdering van persistente verontreinigingen uit water. Verder onderzoek is nodig om de afbraak van pollutanten te verbeteren, afbraakproducten te identificeren en de praktische toepassing van deze technologie op grotere schaal te evalueren.

Summary

Water pollution by chemicals of emerging concern is becoming an increasing environmental challenge. These substances include per- and polyfluoroalkyl substances (PFAS), a group often classified among the so-called “forever chemicals”, and pharmaceutically active compounds such as the antibiotic ciprofloxacin. Because these contaminants are highly stable, they are only partially removed by conventional wastewater treatment processes. As a result, they can persist in the environment and may pose risks to ecosystems and human health.

This master’s thesis investigated whether an advanced oxidation process based on ultrasound, an oxidant, and heterogeneous catalysts can improve the degradation of these persistent pollutants. Ultrasonic irradiation creates microscopic bubbles in water that collapse violently, producing highly reactive conditions. When combined with an oxidant such as persulfate and a suitable catalyst, this process can generate reactive species capable of breaking down organic contaminants.

Three catalysts were synthesized and evaluated: copper(II) oxide (CuO), magnetite (Fe₃O₄), and a CuO/Magnetite composite. Their performance was tested for the degradation of ciprofloxacin and perfluorooctanoic acid (PFOA), one of the most widely studied legacy PFAS compounds. Among the investigated catalysts, magnetite showed the most promising overall performance. It combined efficient persulfate activation with practical advantages such as low-cost synthesis and easy magnetic recovery.

The ultrasound/persulfate/magnetite system was then further optimized by studying the influence of initial pH, catalyst dosage, and oxidant dosage. For ciprofloxacin, the best results were obtained under acidic conditions. More than 80% of the contaminant was removed, and the results indicated that the compound was not only degraded but also partly broken down into simpler end products. Radical quenching experiments showed that sulfate radicals were mainly responsible for degradation at low pH, while hydroxyl radicals became more important at neutral and alkaline conditions.

The system was also applied to PFOA degradation. PFOA proved much more difficult to degrade than ciprofloxacin, confirming the high stability of PFAS compounds and their strong carbon–fluorine bonds. Although partial removal was achieved, the low PFOA concentrations used in this study made it difficult to reliably determine the extent to which the compound was completely broken down.

Finally, the influence of realistic water constituents was evaluated. Natural organic matter had only a limited effect on degradation performance, whereas bicarbonate and phosphate ions clearly reduced treatment efficiency. Reuse experiments showed that magnetite remained active over multiple cycles, although its performance decreased.

Overall, this study shows that the combination of ultrasound, persulfate, and magnetite is a promising approach for the removal of persistent contaminants from water. Further research is needed to improve PFAS degradation, identify degradation products, and evaluate the practical application of this technology on a larger scale.

Keywords: Advanced oxidation processes, Sonocatalysis, Persulfate, Ciprofloxacin, PFOA

Abstract

This thesis investigated an ultrasound (US)-assisted advanced oxidation process based on persulfate (PS) activation and heterogeneous catalysis for the degradation of ciprofloxacin (CIP) and perfluorooctanoic acid (PFOA), two persistent chemicals of emerging concern. Copper(II) oxide (CuO), Magnetite (Fe₃O₄), and a CuO/Magnetite composite were synthesized, characterized, and evaluated in combination with low-frequency US and PS. Catalyst screening identified Magnetite as the most promising catalyst due to its efficient PS activation, favorable degradation performance, low-cost synthesis, and magnetic recoverability.

The US/PS/Magnetite system was optimized by studying the influence of initial pH, catalyst dosage, and oxidant dosage. For CIP degradation, the highest performance was obtained under acidic conditions using pH 4, 0.1 g/L Magnetite, and 2.5 mM PS, achieving more than 80% removal within 60 min. These conditions also resulted in the highest apparent mineralization and defluorination. Radical quenching experiments indicated that sulfate radicals were the dominant reactive species under acidic conditions, whereas hydroxyl radicals became more important at neutral and alkaline pH.

The optimized system was subsequently applied to PFOA degradation. Compared to CIP, PFOA showed substantially lower degradation efficiencies, confirming the higher recalcitrance of PFAS compounds. The highest PFOA removal ($47.2 \pm 15.3\%$ within 60 min) was obtained at pH 4 using 0.5 g/L Magnetite and 20 mM PS. However, reliable assessment of defluorination and mineralization was limited by the low PFOA concentrations and associated analytical constraints.

Additional experiments showed that natural organic matter had only a limited effect on CIP degradation, while bicarbonate and phosphate significantly inhibited treatment performance. Reuse experiments indicated a decline in catalyst activity, likely due to catalyst loss, surface fouling, and possible iron leaching. Overall, this work demonstrates that sonocatalytic PS activation using Magnetite is a promising approach for degrading persistent organic contaminants, although further research is needed to improve CIP and PFAS degradation, identify transformation products, and enhance catalyst stability and scalability.

INHOUDSTAFEL

Preface	i
Samenvatting.....	ii
Summary	iii
Abstract.....	iv
Symbolenlijst	viii
Lijst met afkortingen.....	viii
1 Context and Objectives.....	1
1.1 Problem statement.....	1
1.2 Objectives.....	2
2 Literature review	3
2.1 Chemicals of emerging concern: fluorinated contaminants.....	3
2.1.1 Per- and polyfluoroalkyl substances	3
2.1.2 Ciprofloxacin	4
2.1.3 Toxicity of PFAS and CIP	6
2.2 Advanced oxidation processes.....	6
2.2.1 Degradation.....	7
2.2.2 Defluorination	7
2.2.3 Mineralization	8
2.3 Ultrasound and cavitation.....	8
2.4 Sonocatalysis	9
2.5 Oxidants	10
2.6 Catalytic degradation of CECs	11
2.6.1 CuO	12
2.6.2 Magnetite	13
2.6.3 CuO/Magnetite composite	14
2.7 Degradation pathways	14
2.7.1 PFAS	15
2.7.2 CIP.....	16
2.8 Process parameters.....	17
2.9 Identified research gaps.....	19
3 Materials & Methods	21
3.1 Chemicals.....	21

3.2	<i>Catalyst synthesis</i>	21
3.2.1	CuO	21
3.2.2	Magnetite	22
3.2.3	CuO/Magnetite composite	23
3.3	<i>Catalyst characterization</i>	24
3.3.1	Brunauer-Emmett-Teller surface area analysis (BET).....	24
3.3.2	Scanning Electron Microscopy (SEM).....	25
3.3.3	Transmission Electron Microscopy (TEM).....	25
3.3.4	X-Ray Diffraction (XRD)	25
3.3.5	Fourier Transform Infrared Spectroscopy (FT-IR)	25
3.3.6	Zeta potential measurements	26
3.4	<i>Experimental setup</i>	27
3.4.1	Experimental setup without ultrasonic irradiation	27
3.4.2	Experimental setup with ultrasonic irradiation	28
3.5	<i>Analytical methods</i>	29
3.5.1	Degradation – Liquid Chromatography	29
3.5.2	Defluorination - Ion Chromatography	31
3.5.3	Mineralization - Total Organic Carbon	31
3.5.4	Iron leaching - Inductively Coupled Plasma	32
3.6	<i>Experiments</i>	33
3.6.1	Baseline and catalyst performance tests.....	33
3.6.2	Optimization of process parameters for enhanced CIP degradation	34
3.6.3	Optimization of process parameters for enhanced PFOA degradation	34
3.6.4	Radical quenching.....	34
3.6.5	Interference of ions.....	35
3.6.6	Catalyst reusability and iron leaching.....	35
3.7	<i>Design of Experiments</i>	35
4	Results and Discussion	37
4.1	<i>Characterization of the catalysts</i>	37
4.1.1	BET	37
4.1.2	TEM and SEM.....	37
4.1.3	XRD	38
4.1.4	FT-IR.....	40
4.1.5	Zeta potential	41
4.2	<i>Baseline experiments</i>	42

4.3	<i>Experiments leading to catalyst selection</i>	44
4.3.1	Adsorption	45
4.3.2	Ultrasound in the presence of catalysts	45
4.3.3	Persulfate activation by catalysts	46
4.3.4	Catalyst selection: Magnetite	47
4.4	<i>Optimization of process parameters for enhanced CIP degradation</i>	48
4.4.1	CIP degradation	48
4.4.2	Influence of process parameters	49
4.4.3	Contribution of adsorption and degradation	51
4.4.4	Defluorination	52
4.4.5	Mineralization	53
4.4.6	Summary of optimal conditions	54
4.5	<i>Optimization of process parameters for enhanced PFOA degradation</i> .	54
4.5.1	Degradation performance	54
4.5.2	Defluorination	56
4.5.3	Mineralization	57
4.5.4	Summary	57
4.6	<i>Radical quenching experiments for identification of dominant reactive species for CIP degradation</i>	58
4.6.1	Identification of dominant reactive species at different pH conditions	58
4.6.2	Relation between reactive species and degradation pathways ...	61
4.7	<i>System stability and operational robustness</i>	61
4.7.1	Interference of inorganic ions and natural organic matter	61
4.7.2	Reusability of Magnetite as sonocatalyst	62
4.7.3	Leaching of Fe ions	63
4.7.4	Energy consumption	64
5	Conclusion	65
6	Limitations and future research	66
6.1	<i>Limitations</i>	66
6.2	<i>Future research</i>	67
	Referentielijst	69
	Bijlagen	1
Bijlage A	Experimental run order and conditions for enhanced CIP degradation.	1
Bijlage B	Experimental run order and conditions for enhanced PFOA degradation.	2

Symbolenlijst

C_0	Initial concentration of the pollutant	[mg/L = ppm]
C_t	Concentration of the pollutant at sample t	[mg/L = ppm]
k	Pseudo-first-order reaction rate constant	[min ⁻¹]
pH	Acidity	[/]
E_0	Standard redox potential	[V]
λ	XRD-wavelength	[Å]
ζ	Zeta potential	[mV]

Lijst met afkortingen

Abbreviation	Full term
$^1\text{O}_2$	Singlet oxygen
AOPs	Advanced oxidation processes
BET	Brunauer-Emmett-Teller
CB	Conduction band
CECs	Chemicals of emerging concern
C–F	Carbon–fluorine bond
CIP	Ciprofloxacin
CuO	Copper(II) oxide
e^-	Electron
F^-	Fluoride ions
Fe^{2+}/Fe^{3+}	Iron ions
Fe_3O_4	Magnetite
FT-IR	Fourier transform infrared spectroscopy
h^+	Electron hole
$H\cdot$	Hydrogen radical
HA	Humic acid
HGMS	High-gradient magnetic separation
HOMO	Highest occupied molecular orbital
HPLC	High-performance liquid chromatography

IC	Ion chromatography
ICP-OES	Inductively coupled plasma optical emission spectroscopy
LC	Liquid chromatography
LUMO	Lowest unoccupied molecular orbital
NDIR	Non-dispersive infrared detector
NPOC	Non-purgeable organic carbon
$O_2^{\cdot-}$	Superoxide
$OH^{\cdot}$	Hydroxyl radical
PFAS	Per- and polyfluoroalkyl substances
PFBA	Perfluorobutanoic acid
PFCAs	Perfluorocarboxylic acids
PFHpA	Perfluoroheptanoic acid
PFHxA	Perfluorohexanoic acid
PFOA	Perfluorooctanoic acid
PFOS	Perfluorooctane sulfonate
PFPeA	Perfluoropentanoic acid
PhACs	Pharmaceutically active compounds
PI	Periodate
PMS, HSO_5^-	Peroxymonosulfate
PS, $S_2O_8^{2-}$	Persulfate
PZC	Point of zero charge
ROS	Reactive oxygen species
SEM	Scanning electron microscopy
$SO_4^{\cdot-}$	Sulfate radical
TEM	Transmission electron microscopy
TOC	Total organic carbon
UHPLC-QTOF-MS	Ultra-high performance liquid chromatography – quadrupole time-of-flight – mass spectrometry
US	Ultrasound
UV	Ultraviolet
VB	Valence band
WWTPs	Wastewater treatment plants
XRD	X-ray diffraction

1 CONTEXT AND OBJECTIVES

1.1 Problem statement

Chemicals of emerging concern (CECs) are a diverse group of synthetic and naturally occurring substances that are increasingly detected in environmental waters, sediments, and sludge. This group includes pharmaceutically active compounds (PhACs), personal care products, and pesticides, as well as per- and polyfluoroalkyl substances (PFAS). Many CECs exhibit persistence, bioaccumulation potential, and toxicity even at low concentrations, thereby posing significant risks to human health and ecosystems (Salazar et al., 2024; Jonker, 2024).

PFAS are a prominent subclass of CECs and belong to the group of substances commonly referred to as “forever chemicals” due to their extreme chemical stability arising from strong carbon-fluorine (C–F) bonds. These bonds confer high resistance to chemical and biological degradation, resulting in long-term persistence and accumulation in water, soil, and biota (Lu et al., 2023). Consequently, PFAS are widely detected in aquatic environments and have been associated with chronic toxic effects, even at low environmental concentrations, posing serious risks to ecosystems and human health (Brunn et al., 2023; Jonker, 2024).

Conventional wastewater and sludge treatment technologies, such as activated sludge processes, sedimentation, and anaerobic digestion, are generally ineffective at removing these contaminants (Salazar et al., 2024). In sludge treatment, PFAS pose an additional challenge due to their tendency to adsorb onto solid phases, which can lead to secondary pollution (Veciana et al., 2024). Although certain chemical treatment methods can improve removal efficiencies, they often require substantial chemical input and may generate transformation products that are equally or even more toxic than the parent compounds. Therefore, developing efficient degradation strategies while minimizing chemical consumption remains a major challenge. Advanced oxidation processes (AOPs) offer a promising solution (Sharma et al., 2018).

AOPs, which rely on the generation of highly reactive oxygen species (ROS), have emerged as promising techniques for the degradation of persistent contaminants (Sharma et al., 2018). Among these technologies, ultrasound (US) based systems have gained increasing attention due to their ability to induce acoustic cavitation, resulting in localized extreme temperatures and pressures that promote the formation of reactive species capable of degrading contaminants (Salazar et al., 2024). The combination of US with oxidants and heterogeneous catalysts can further enhance oxidant activation and radical generation. However, the practical application of these systems remains limited by high energy demand, incomplete mineralization, and insufficient understanding of the interactions between operational parameters, catalysts, and oxidants (Deng et al., 2023).

Transition metal-based catalysts have attracted considerable interest due to their redox-active properties and potential to promote radical formation. Nevertheless, the influence of catalyst composition, operational conditions, and environmental matrices on degradation efficiency, radical pathways, catalyst stability, and reusability remains insufficiently understood (Liu et al., 2024b; Zhang et al., 2022).

To investigate degradation mechanisms and optimize operational parameters, model compounds are frequently employed prior to studying highly recalcitrant pollutants such as PFAS.

Ciprofloxacin (CIP), a widely detected PhAC, is commonly used for this purpose due to its well-documented degradation pathways and relatively simpler degradation behavior compared to PFAS. Insights obtained from CIP degradation studies can support the optimization and interpretation of PFAS degradation systems.

Although numerous studies demonstrate the potential of US-based AOPs, the lack of systematic insight into catalyst-specific behavior, defluorination efficiency, and performance under realistic conditions hampers their translation from laboratory-scale studies to practical applications.

1.2 Objectives

The main objective of this master's thesis was to develop and evaluate a sonocatalytic activated persulfate (PS, $\text{S}_2\text{O}_8^{2-}$) system for the degradation of fluorinated contaminants, using CIP as a model compound and perfluorooctanoic acid (PFOA) as a representative legacy PFAS compound.

It was hypothesized that the combination of low-frequency US (24 kHz), PS, and heterogeneous catalysts would exhibit a synergistic effect, resulting in enhanced degradation compared to the individual treatment processes. Furthermore, redox-active catalysts were expected to promote PS activation, increase ROS generation, and improve contaminant degradation, mineralization, and defluorination.

To test these hypotheses, the following objectives were defined:

- To synthesize and physicochemically characterize CuO, Magnetite, and CuO/Magnetite composite catalysts.
- To systematically compare the performance of the different catalysts and treatment configurations, including US, PS, catalyst-assisted systems, and their combinations, in order to identify the most effective catalyst and treatment strategy.
- To optimize key operational parameters, including initial pH, catalyst dosage, and oxidant dosage, with the aim of maximizing contaminant degradation while promoting mineralization and defluorination.
- To evaluate the applicability of the optimized treatment system for both CIP and PFOA degradation.
- To investigate the dominant reactive species and degradation mechanisms responsible for contaminant removal under different operating conditions.
- To assess catalyst stability and practical applicability through catalyst reuse experiments, iron leaching analysis, and energy consumption evaluation.
- To investigate the influence of realistic water-matrix constituents, including humic acid, bicarbonate, and phosphate ions, on the performance of the optimized US/PS/Magnetite system.

2 LITERATURE REVIEW

2.1 Chemicals of emerging concern: fluorinated contaminants

Among the broad range of CECs, fluorinated contaminants represent an important class of pollutants due to the presence of fluorine atoms within their molecular structure. This group includes both PFAS and fluorinated PhACs, such as CIP. Owing to their widespread use and frequent detection in aquatic environments, both contaminant groups have received increasing attention in recent years (Kyzas et al., 2022; Deng et al., 2023). Although PFAS and CIP belong to different contaminant classes, both contain fluorine atoms and therefore provide an opportunity to investigate degradation and defluorination processes in fluorinated organic pollutants with distinctly different physicochemical properties. Figure 1 provides an overview of the wide range of CEC categories and illustrates the diversity of contaminants encountered in the environment.

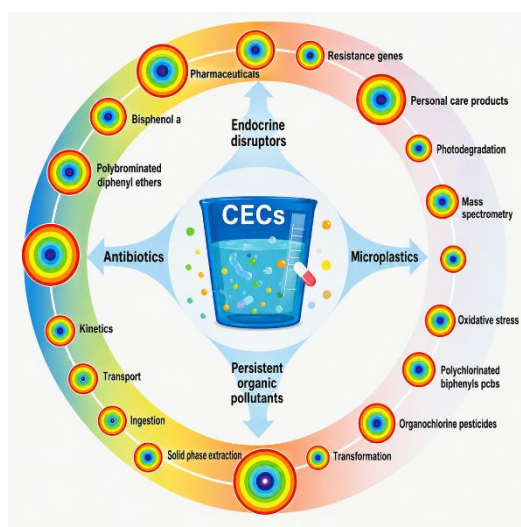


Figure 1: Overview of the wide range of CEC categories (Feng et al., 2023).

2.1.1 Per- and polyfluoroalkyl substances

Among CECs, PFAS (Figure 2) are particularly challenging to degrade due to their exceptional chemical stability. PFAS comprise a large and chemically diverse group of compounds that vary considerably in degree of fluorination, carbon chain length, and functional groups. This structural variability largely contributes to the wide range of physicochemical properties observed within the PFAS family (Glüge et al., 2020; Sidnell et al., 2022; Thakur et al., 2025).

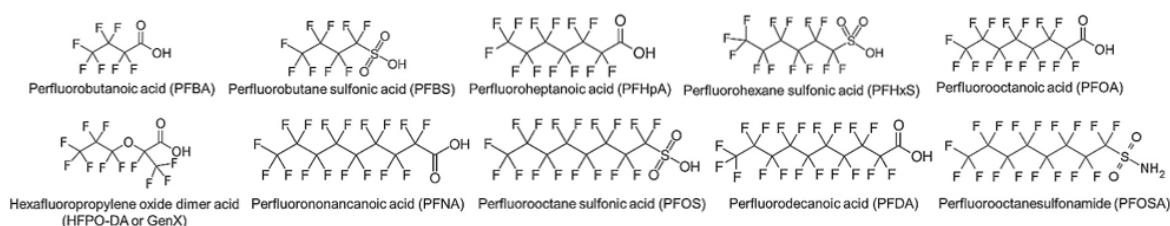


Figure 2: Chemical structures of selected PFAS, illustrating their structural diversity (Jones, 2023).

PFAS are amphipathic molecules composed of two structurally distinct parts: a hydrophobic fluorinated carbon chain and a hydrophilic, typically charged, functional group. The fluorinated carbon chain constitutes the hydrophobic “tail”, whereas the polar functional group acts as the hydrophilic “head” (Tshangana et al., 2025). This amphipathic nature enables PFAS to interact with both aqueous and non-aqueous environments, which partly explains their widespread use in numerous industrial processes and consumer products. The physicochemical behavior, reactivity, and potential toxicity of PFAS can vary substantially depending on the fluorinated chain length and the type of functional group present (Thakur et al., 2025). Common functional groups within the PFAS family include carboxylates ($\text{-COO}^-/\text{-COOH}$), hydroxyl groups (-OH), sulfonates ($\text{-SO}_3^-/\text{-SO}_3\text{H}$), and phosphonates ($\text{-PO}_3\text{H}_2$).

The strong C–F bonds in PFAS render these compounds highly resistant to conventional treatment processes such as biological degradation. The short bond length ($\approx 1.3\text{-}1.4\text{ \AA}$) and high bond dissociation energy of the C–F bond ($\approx 440\text{-}530\text{ kJ/mol}$), combined with the electrostatic and steric shielding provided by the surrounding fluorine atoms of adjacent C–C bonds, make highly fluorinated PFAS exceptionally thermally stable and chemically inert (Sidnell et al., 2022). The exceptional strength of the C–F bond arises from the small atomic radius and high electronegativity of fluorine, which result in a short bond length and strong electrostatic attraction between the carbon and fluorine atoms. Consequently, treatment technologies that can readily cleave weaker carbon–halogen bonds, such as C–Cl bonds, are often ineffective for PFAS degradation, highlighting the need for more powerful treatment approaches such as AOPs. Table 1 compares the average bond dissociation energies of several carbon single bonds, highlighting that the C–F bond is significantly stronger than other common bonds such as C–C and C–O (LibreTexts, 2025).

The reactivity of PFAS is partly influenced by the energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). A smaller HOMO-LUMO energy gap generally corresponds to higher chemical reactivity and may facilitate degradation reactions. ROS are capable of inducing cleavage of C–F bonds, although the efficiency of this process depends on both bond stability and radical reactivity (Yao et al., 2025).

Table 1: Average bond dissociation energies of selected C–X bonds (LibreTexts, 2025).

Bond	Energy (kJ/mol)	Bond	Energy (kJ/mol)	Bond	Energy (kJ/mol)
C–F	485	C–C	347	C–Br	276
C–H	413	C–Cl	339	C–S	259
C–O	358	C–N	305	C–I	240

2.1.2 Ciprofloxacin

Ciprofloxacin (Figure 3), a widely used fluoroquinolone antibiotic, is frequently detected in aquatic environments due to its extensive application in human and veterinary medicine and its incomplete removal during conventional wastewater treatment (Kyzas et al., 2022). The presence of residual CIP in aquatic environments is problematic because it can undergo transformation reactions leading to the formation of potentially toxic intermediates (Kang et al., 2020). In addition, the continuous release of antibiotics such as CIP can exert selective pres-

sure on microbial communities, thereby promoting the development and proliferation of antibiotic-resistant bacteria in aquatic systems. This represents a growing concern for both ecosystem integrity and public health (Michael-Kordatou et al., 2017).

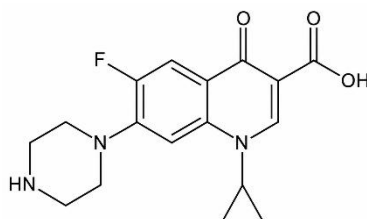


Figure 3: Chemical structure of CIP (drawn using ACD/Labs).

CIP exhibits complex acid-base behavior due to the presence of several ionizable functional groups, including the carboxylate group at C-3, the tertiary amine groups on the piperazine ring, and the heterocyclic nitrogen within the quinolone core. These sites give rise to multiple protonation states, reflected in four characteristic pKa values (3.64, 5.05, 6.95, and 8.95). As a result, CIP exists in different molecular forms depending on the solution pH, as seen in Figure 4. Under acidic conditions, the molecule predominantly exists in a cationic form, whereas at neutral pH the zwitterionic species predominates. At higher pH values, further deprotonation leads to the formation of an anionic species (Salma et al., 2016). For the pH conditions investigated in this study, CIP is therefore expected to be predominantly cationic at pH 4, zwitterionic at pH 7, and anionic at pH 10. These pH-dependent changes in speciation may significantly influence interactions between CIP and catalyst surfaces through electrostatic attraction or repulsion, thereby affecting adsorption behavior and degradation efficiency. Consequently, CIP speciation should be considered together with catalyst surface charge characteristics when interpreting the effect of pH on sonocatalytic degradation performance.

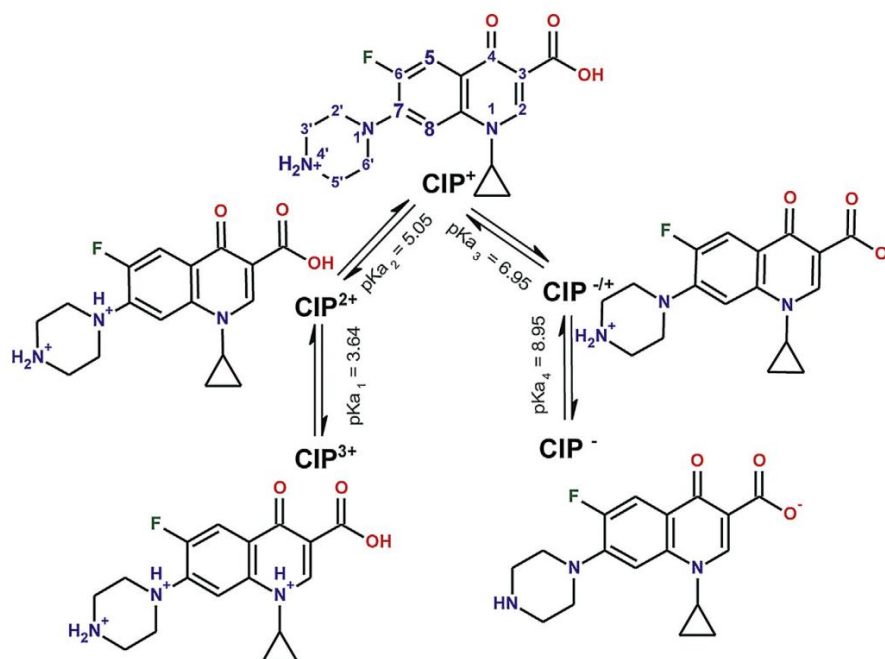


Figure 4: pH dependent protonation and deprotonation equilibria of CIP (Salma et al., 2016).

The commonly depicted neutral CIP structure therefore does not accurately represent the dominant species present under environmentally relevant conditions. Since each protonation state exhibits distinct reactivity and charge distribution, the acid-base equilibria of CIP play a crucial

role in determining its degradation behavior. In addition to influencing interactions with catalyst surfaces, pH-dependent speciation may also affect the reactivity of CIP toward ROS, thereby influencing degradation pathways, transformation kinetics, and the formation and persistence of degradation products (Zhang et al., 2022).

2.1.3 Toxicity of PFAS and CIP

In wastewater treatment plants (WWTPs), PFAS are typically detected in the ng/L to µg/L range. These concentrations overlap with effect thresholds reported for a wide range of aquatic organisms (Lenka et al., 2021). Chronic exposure to environmentally relevant PFAS concentrations has been associated with impaired growth, reproduction, and development in aquatic invertebrates and plankton, as well as endocrine, immune, and developmental disturbances in fish and amphibians (Ma et al., 2022). Due to their persistence, bioaccumulation potential, and continuous release via WWTP effluents, PFAS pose a long-term ecotoxicological risk despite their occurrence at trace concentrations (Ma et al., 2022). Exposure to PFAS has furthermore been associated with a range of adverse human health effects, including metabolic, endocrine, developmental, and carcinogenic outcomes, as summarized by Evangelou and Robinson (2022).

Compared to PFAS, CIP is generally detected at substantially higher concentrations. CIP concentrations in sewage effluents are typically reported in the range of 50 to 500 µg/L, while effluents from pharmaceutical manufacturing facilities may reach concentrations up to approximately 50 mg/L (Zhang et al., 2022). Martins et al. (2012) demonstrated that CIP concentrations reported in aquatic environments overlap with effect thresholds for sensitive organisms such as algae, macrophytes, and crustaceans. In addition, sub-lethal antibiotic concentrations can exert selective pressure on microbial communities, thereby contributing to the development and spread of antibiotic resistance, which represents a growing global threat to human health.

2.2 Advanced oxidation processes

AOPs are treatment technologies that generate ROS, which possess high oxidation potentials and are capable of degrading a wide range of CECs. These ROS react with pollutants through oxidation reactions, enabling the breakdown of compounds that are otherwise resistant to conventional treatment methods. Compared to traditional remediation strategies, AOPs often require relatively low chemical input and can operate under milder conditions, making them attractive and potentially more sustainable technologies for environmental remediation (Salazar et al., 2024).

Although all AOPs rely on ROS generation, they employ different activation mechanisms, including ultraviolet (UV) irradiation, catalytic oxidation, electrochemical activation, plasma discharge, and acoustic cavitation. This diversity forms the basis for the classification into conventional and emerging AOPs, as shown in Figure 5 (Priyadarshini et al., 2022). Emerging technologies, including sonocatalysis, plasma-assisted processes, and advanced Fenton-based systems, are receiving increasing attention due to their efficient ROS generation and their ability to degrade persistent CECs, including PFAS or CIP, under environmentally relevant conditions.

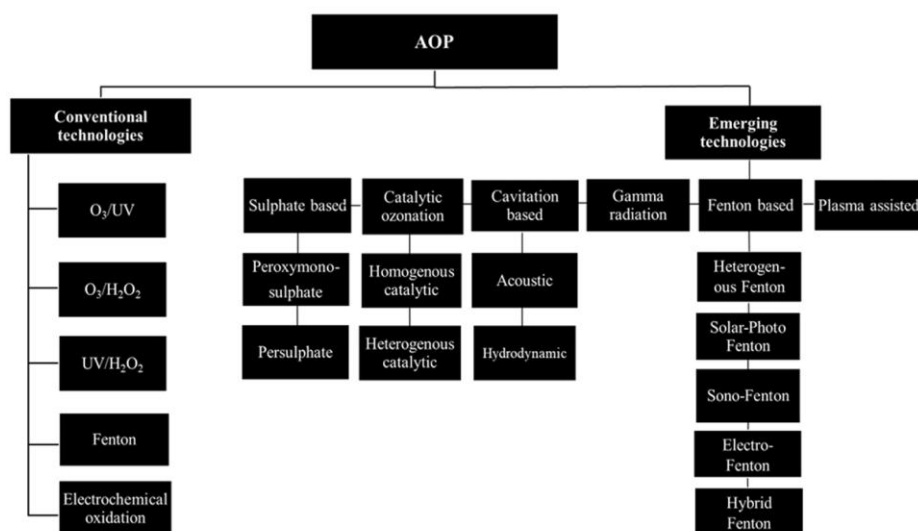


Figure 5: Classification of conventional and emerging AOPs (Priyadarshini et al., 2022).

2.2.1 Degradation

Degradation of CECs refers to the chemical transformation of parent compounds into intermediate products with altered molecular structures. These transformation products may be less, equally, or in some cases more toxic than the original compound, depending on the reaction pathways involved (Sharma et al., 2018).

For PFAS, degradation pathways remain incompletely understood. Evidence suggests that transformation may proceed via stepwise structural modifications, including head-group cleavage or C–C bond scission, while the C–F backbone can remain largely intact. As a result, degradation does not necessarily correspond to detoxification or environmental elimination but may instead lead to the formation of shorter-chain PFAS, which can still exhibit persistence and mobility (Li et al., 2020). Therefore, achieving complete mineralization of these contaminants is of particular importance.

In contrast, the degradation pathways of pharmaceutical compounds such as CIP are generally better understood. Degradation of CIP typically results in the formation of partially oxidized intermediates, which may retain residual biological activity and toxicity. Consequently, degradation alone does not necessarily imply complete detoxification or environmental removal.

2.2.2 Defluorination

Defluorination represents a critical mechanistic step in the transformation of PFAS, involving the cleavage of C–F bonds and the release of inorganic fluoride ions (F⁻). Because the C–F bond is one of the strongest bonds in organic chemistry, defluorination typically proceeds more slowly and requires more energetic conditions than initial structural degradation steps (Deng et al., 2023).

In many treatment systems, PFAS therefore undergo sequential transformation: initial degradation of functional groups and modifications of the carbon backbone, followed by progressive C–F bond cleavage. Complete structural collapse of the fluorinated backbone can only occur after sufficient defluorination, which subsequently enables further degradation toward final mineralization products (Khan, 2025). A similar principle applies to other fluorinated compounds,

such as CIP, in which cleavage of the C–F bond may form part of the transformation pathways leading to further degradation.

Defluorination efficiency is commonly assessed through a fluorine mass balance, although achieving full closure remains challenging. The fluorine mass balance typically consists of three fractions: (i) free fluoride ions, (ii) organically bound fluorine, and (iii) unidentified fluorine species, which may include volatile organofluorine compounds or fluoride adsorbed onto reactor surfaces (Smith et al., 2024; Veciana et al., 2024).

2.2.3 Mineralization

Mineralization represents the complete conversion of organic contaminants into inorganic end products such as CO₂, H₂O, and inorganic ions, including F[−] released through defluorination in the case of fluorinated compounds.

For PFAS, mineralization is particularly challenging due to the exceptional stability of the C–F bonds. Even after significant degradation and partial defluorination, intermediate products may still contain residual fluorinated carbon structures. Only when complete C–F bond cleavage is achieved can full mineralization occur, resulting in the complete loss of the original molecular framework (Deng et al., 2023).

Importantly, defluorination is a prerequisite for mineralization in PFAS systems, since the removal of fluorine atoms weakens the electronic and steric shielding surrounding the carbon backbone. Once C–F bonds are cleaved, the partially defluorinated intermediates become more susceptible to radical attack and subsequent C–C bond scission, thereby promoting step-wise degradation toward inorganic end products (Khan, 2025).

2.3 Ultrasound and cavitation

US has emerged as a promising approach for contaminant removal due to its ability to induce extreme local conditions. These conditions may enhance degradation, defluorination, and ultimately, mineralization (Salazar et al., 2024).

The propagation of ultrasonic waves through aqueous solutions induces alternating compression and expansion cycles, leading to the formation, growth, and subsequent collapse of cavitation bubbles. These cavitation events create localized high-energy “hotspots” within the collapsing bubbles, where transient temperatures and pressures may reach approximately 5000 K and 1000 atm, respectively (Suslick et al., 1990). Although these extreme conditions exist only for very short periods and within a limited volume, while the bulk solution remains close to ambient temperature, they are sufficient to induce pyrolytic-like degradation of pollutants and promote the formation of ROS. In addition, acoustic cavitation can activate both sonocatalysts and oxidants present in the system.

ROS are primarily generated through the sonolysis of water molecules, producing hydrogen radicals (H·) and hydroxyl radicals (OH·). These species can directly react with target pollutants or further participate in secondary reactions leading to the formation of additional ROS, such as superoxide (O₂·[−]). Figure 6 schematically illustrates the formation and collapse of cavitation bubbles (Deng et al., 2023; Pétrier & Wei, 2023).

The frequency of US strongly influences cavitation dynamics and, consequently, pollutant degradation efficiency. Ultrasonic frequencies are typically defined as those above 20 kHz, beyond the human hearing range. Low-frequency US (20-100 kHz) tends to produce larger cavitation bubbles whose collapse is more violent, resulting in higher local energy release. This can enhance catalyst surface activation, and reduce surface fouling, thereby maintaining catalytic activity (Trinh et al., 2025). However, incomplete mineralization has often been reported under low-frequency conditions, which justifies the use of catalysts and oxidants to improve degradation efficiency. In contrast, high-frequency US generates a larger number of cavitation events with shorter lifetimes and reduced maximum bubble size, leading to less intense individual collapse events but a higher spatial density of cavitation activity. Consequently, although the energy released per collapse is lower, the overall radical production rate may increase or exhibit an optimum depending on operating conditions (Nguyen et al., 2017).

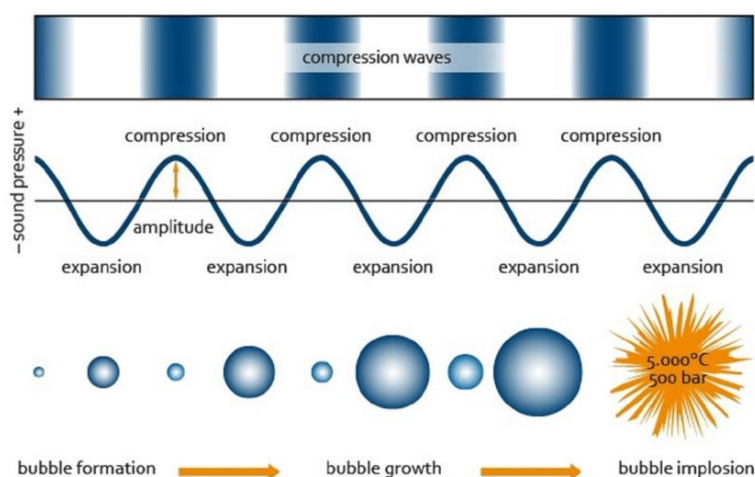


Figure 6: Schematic representation of acoustic cavitation by US (Johansson et al., 2017).

2.4 Sonocatalysis

Sonocatalysts are materials that can enhance the chemical effects of US by promoting ROS formation and improving overall reaction efficiency. In sonocatalytic systems, catalysts can increase interfacial reactivity, facilitate oxidant activation, and improve mass transfer through interactions with acoustic cavitation, thereby enhancing pollutant degradation (Lops et al., 2018).

Some sonocatalysts exhibit piezoelectric properties. In these materials, ultrasonic vibrations induce mechanical deformation that generates internal electric polarization, resulting in charge separation and the formation of electron-hole pairs (e^-h^+). These charge carriers consist of electrons in the conduction band (CB) and holes in the valence band (VB), which can subsequently participate in ROS generation through reduction and oxidation reactions, respectively. Figure 7 illustrates the general mechanism of ROS formation in piezoelectric sonocatalysts (Salazar et al., 2024; Ioannidi et al., 2024).

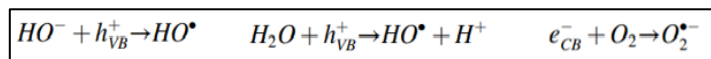


Figure 7: Schematic representation of ROS generation through electron-hole pair formation in piezoelectric sonocatalysts (Ioannidi et al., 2024).

However, the catalysts investigated in this study (CuO, Magnetite, and CuO/Magnetite composite) are not piezoelectric. Therefore, their sonocatalytic activity primarily originates from cavitation-assisted chemical pathways rather than piezo-induced charge separation.

Under US, cavitation bubbles continuously form, grow, and collapse, generating localized extreme temperatures and pressures that promote water sonolysis and ROS formation. In addition, US enhances mass transfer, improves contact between reactants and catalyst surfaces, and continuously renews catalytic active sites by removing adsorbed species (Trinh et al., 2025).

For redox-active catalysts such as Magnetite, sonocatalytic activity is further enhanced through surface redox cycling. The $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple can activate oxidants such as PS very efficiently (Diao et al., 2019), resulting in the generation of sulfate radicals ($\text{SO}_4^{\cdot-}$) and other ROS. US promotes these reactions by increasing surface accessibility and accelerating mass transfer, creating a synergistic interaction between cavitation, oxidant activation, and catalytic redox processes. Consequently, pollutant degradation in US/PS/Magnetite systems is governed primarily by cavitation-induced ROS generation and catalyst-mediated PS activation rather than by piezoelectric charge separation (Kyzas et al., 2022).

2.5 Oxidants

Oxidants are commonly introduced into sonocatalytic systems to enhance the formation of ROS and improve overall degradation and defluorination efficiencies. Their presence can significantly increase the oxidative capacity of the system, thereby accelerating the breakdown of persistent organic contaminants. Table 2 shows the standard oxidation potentials of commonly used oxidants and reactive species in AOPs.

Table 2: Standard oxidation potentials of commonly used oxidants and reactive species in AOPs (Guerra-Rodríguez et al., 2018).

Oxidant	Oxidation potential (V)
Hydroxyl radical ($\text{OH}^{\cdot}$)	2.8
Sulfate radical ($\text{SO}_4^{\cdot-}$)	2.5 - 3.1
Ozone (O_3)	2.1
Persulfate (PS, $\text{S}_2\text{O}_8^{2-}$)	2.1
Peroxymonosulfate (PMS, HSO_5^-)	1.8
Hydrogen peroxide (H_2O_2)	1.8

According to Deng et al. (2023), the effect of oxidant dosage is not strictly linear. At low to moderate concentrations, an increase in oxidant dosage generally enhances pollutant degradation due to increased ROS production. Beyond an optimal dosage, further addition may inhibit degradation efficiency, as excess oxidant can act as a radical scavenger, consuming reactive species and reducing their availability for pollutant oxidation. In addition, high oxidant concentrations may promote the formation of undesired byproducts, some of which can exhibit toxicological relevance.

Among commonly used oxidants, PS is particularly relevant in sonochemical and sonocatalytic systems. Upon activation, PS generates $\text{SO}_4^{\cdot-}$ which possess a high standard oxidation potential ($E_0 = 2.5\text{--}3.1\text{ V}$) and a relatively long half-life ($30\text{--}40\text{ }\mu\text{s}$) (Xue et al., 2022). According to the review by Wang and Wang (2017), both PS and PMS can be activated through various pathways, including thermal activation, alkaline conditions, UV irradiation, activated carbon, transition metals (e.g., Fe^0 , Fe^{2+} , Cu^{2+} , Co^{2+} , Ag^+), US, and hydrogen peroxide. These activation methods promote the generation of sulfate radicals, which are highly reactive oxidizing species capable of effectively degrading emerging contaminants. In sonochemical systems, cavitation-induced extreme conditions and radical formation can further promote PS decomposition into $\text{SO}_4^{\cdot-}$ and secondary ROS.

In addition to sulfate radicals, other reactive species commonly involved in AOPs include $\text{OH}^{\cdot}$, $\text{H}^{\cdot}$, and $\text{O}_2^{\cdot-}$. When oxidants are introduced, additional radical pathways are enabled, expanding the overall ROS pool and increasing the oxidative capacity of the system. The relative contribution of individual reactive species can be evaluated using radical quenching experiments. In this approach, selective scavengers are introduced to preferentially react with specific radicals, thereby suppressing their activity. By comparing pollutant degradation efficiencies with and without scavengers, the contribution of targeted ROS can be quantified (Guerra-Rodríguez et al., 2018; Veciana et al., 2024).

2.6 Catalytic degradation of CECs

The catalytic degradation of CECs is an active and rapidly evolving research field. Heterogeneous catalysts are widely used in AOPs due to their ability to enhance ROS formation, improve oxidant activation, and increase overall reaction efficiency. Among these, metal-oxide based nanomaterials are widely studied because their physicochemical properties can be tailored through controlled synthesis, allowing tuning of surface morphology, active site density, and catalytic reactivity (Khalaj et al., 2017; Liu et al., 2024b).

Copper-based nanomaterials, particularly copper(II) oxide (CuO), have received considerable attention due to their relatively simple and cost-effective synthesis and their favorable catalytic properties (Khalaj et al., 2017). CuO is frequently investigated for the degradation of CECs, including CIP, due to its high surface reactivity and electron transfer capability (Liu et al., 2024b; Zhang et al., 2022). While CuO has been extensively studied in photocatalytic and conventional AOP systems, its performance in sonocatalytic activated PS systems remains comparatively less explored. This makes CuO an interesting candidate for evaluating the role of US in enhancing catalytic degradation. In sonocatalytic systems, such catalysts can additionally interact with cavitation-induced radicals, potentially enhancing interfacial reaction rates.

Magnetite is another widely studied heterogeneous catalyst, primarily due to its dual functionality. First, its intrinsic magnetic properties enable efficient catalyst recovery and reuse via magnetic separation. Second, its $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couple allows direct activation of oxidants such as PS, making it an active catalytic material rather than only a support phase. These properties make Magnetite highly relevant for heterogeneous AOPs targeting organic pollutant degradation (Singh et al., 2024). Although Magnetite has demonstrated promising performance in PS-based oxidation systems, its behavior under combined US and PS activation has received considerably less attention. Furthermore, combining Magnetite with CuO may provide

synergistic effects through interactions between the $\text{Cu}^+/\text{Cu}^{2+}$ and $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couples, while simultaneously retaining the advantages of magnetic catalyst recovery.

However, despite extensive research in photocatalytic and conventional AOP systems, the behavior of CuO, Magnetite, or their combination under US remains less explored. In sonocatalytic environments, pollutant degradation is governed by the combined effects of acoustic cavitation, US-assisted oxidant activation, and surface-mediated redox processes at the catalyst-liquid interface. Figure 8 schematically illustrates these coupled mechanisms (Liu et al., 2024a).

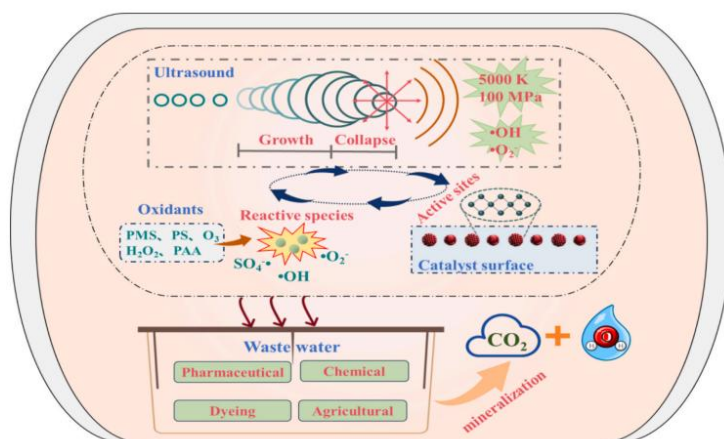


Figure 8: Proposed mechanisms involved in US-assisted heterogeneous catalytic degradation of CECs through cavitation, oxidant activation, and ROS generation (Liu et al., 2024a).

2.6.1 CuO

CuO is a p-type semi-conductor with a narrow band gap of approximately 1.2-1.9 eV (Isherwood, 2016), which contributes to its favorable electron transfer properties and catalytic activity (Khalaj et al., 2017). Its performance can be further improved through structural tuning or coupling with other metal oxides, which enhances charge separation and increases the number of active surface sites (Esmaili-Hafshejani & Nezamzadeh-Ejhieh, 2016; Isherwood, 2016).

In addition, coupling CuO with magnetic materials such as Magnetite enables efficient catalyst recovery through magnetic separation (Singh et al., 2024). Heterogeneous catalysis inherently simplifies catalyst separation, thereby reducing the environmental impact of the treatment process and enabling catalyst reuse and recycling (Zhang et al., 2023). High-gradient magnetic separation (HGMS) systems can be used to recover catalyst particles from treated water or sludge. Figure 9 illustrates a representative HGMS setup.

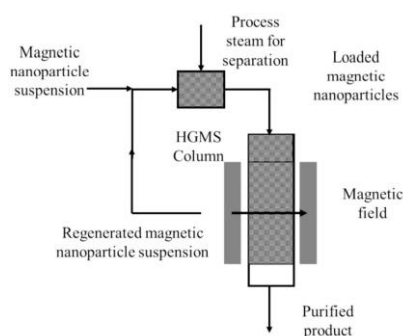


Figure 9: HGMS column for recovery of magnetic nanoparticles (Singh et al., 2024).

Beyond recovery advantages, CuO-based composites may also exhibit enhanced catalytic performance due to interfacial electron transfer between $\text{Cu}^+/\text{Cu}^{2+}$ and $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couples when combined with iron oxides. This can facilitate oxidant activation and improve radical generation efficiency in AOP systems (Singh et al., 2024).

2.6.2 Magnetite

Magnetite or Fe_3O_4 , is a naturally occurring iron oxide with an inverse spinel crystal structure. Fe^{3+} ions occupy tetrahedral sites, while Fe^{2+} and Fe^{3+} ions are distributed over octahedral sites. This arrangement gives rise to its magnetic behavior and electrical conductivity, both of which contribute to its catalytic performance (Malakotian et al., 2019).

The catalytic activity of Magnetite in PS-based systems is primarily governed by $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox cycling. Surface Fe^{2+} species can activate PS, generating $\text{SO}_4^{\cdot-}$ radicals, which can subsequently form $\text{OH}^{\cdot}$ radicals through secondary reactions. These reactive species are responsible for the oxidative degradation of organic contaminants. Under ultrasonic irradiation, cavitation further enhances this process by improving mass transfer and continuously regenerating reactive surface sites. As a result, a synergistic effect is observed between US, PS activation, and Magnetite-mediated redox cycling (Kyzas et al., 2022).

Malakotian et al. (2019) reported the removal of tetracycline antibiotics using PS activated by Magnetite nanoparticles under US. Similarly, Ding et al. (2016) demonstrated the degradation of Norfloxacin using PS activated by Magnetite nanoparticles. Given the structural similarity between Norfloxacin and Ciprofloxacin, these findings suggest strong potential for the degradation of CIP using Magnetite-based catalytic systems.

As illustrated in Figure 10, Fe^{2+} ions on the Magnetite surface react with $\text{S}_2\text{O}_8^{2-}$ to generate $\text{SO}_4^{\cdot-}$ radicals, while Fe^{3+} is simultaneously reduced back to Fe^{2+} , allowing continuous cycling. The produced $\text{SO}_4^{\cdot-}$, and $\text{OH}^{\cdot}$ then attack the contaminant, leading to progressive oxidation and eventual mineralization into CO_2 , H_2O , and smaller by-products. This mechanism highlights why Magnetite is an efficient catalyst in PS-driven sonocatalytic systems (Kyzas et al., 2022).

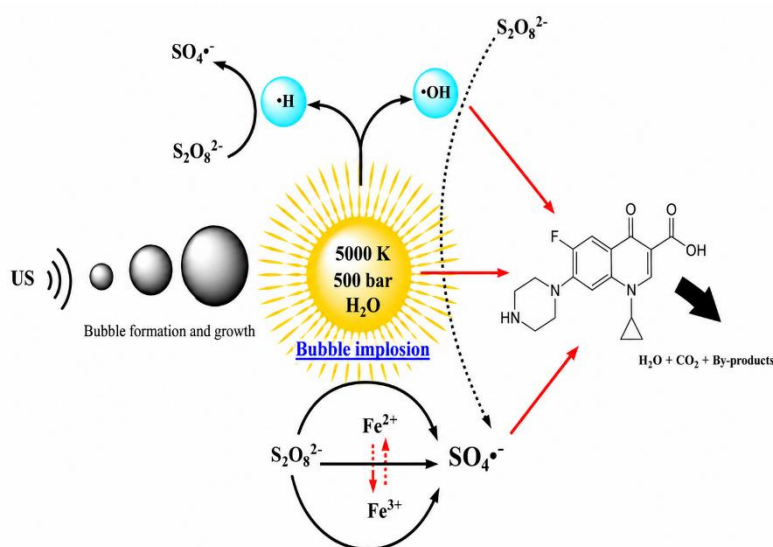


Figure 10: Proposed mechanism for contaminant degradation using Magnetite-activated PS under US (Kyzas et al., 2022).

2.6.3 CuO/Magnetite composite

Combining CuO with Magnetite yields a hybrid catalyst that integrates the catalytic activity of CuO with the magnetic separability and redox functionality of Magnetite. This synergistic combination can enhance overall performance in sonocatalytic systems through improved interfacial electron transfer between $\text{Cu}^+/\text{Cu}^{2+}$ and $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox couples, thereby promoting more efficient oxidant activation and ROS generation.

In addition to improved catalytic efficiency, the Composite offers practical advantages, including facile magnetic recovery, reusability, and potentially lower environmental impact. However, catalyst stability over multiple reaction cycles remains a critical factor for practical application. Deactivation may occur due to surface fouling, leaching of active species, or structural degradation. To maintain performance, regeneration procedures typically involve washing with de-ionized water and organic solvents (e.g. ethanol or methanol), followed by drying at moderate temperatures to restore active sites (e.g., 60 °C for 24 hours) (Saveh et al., 2024; Singh et al., 2024).

From a process engineering perspective, the overall cost of heterogeneous AOP systems is primarily governed by (i) ultrasonic energy input, (ii) oxidant consumption, and (iii) catalyst synthesis, recovery, and potential losses. Therefore, optimization of these parameters is essential for improving both the economic feasibility and scalability of the treatment process.

2.7 Degradation pathways

Understanding degradation pathways is essential for elucidating the reaction mechanisms involved in AOPs and for optimizing contaminant removal efficiency. Mechanistic insight into oxidative reactions, bond cleavage, and structural transformations enables identification of the dominant degradation routes and the reactive species involved.

ROS, particularly $\text{OH}^\cdot$ and $\text{SO}_4^{\cdot-}$ radicals, play a central role in the degradation of organic contaminants in sonocatalytic systems. Their formation, selectivity, and reactivity strongly influence contaminant transformation pathways and overall treatment performance.

Operational parameters such as pH, temperature, ionic strength, and matrix composition can significantly affect both ROS chemistry and degradation efficiency. Inorganic anions such as bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) may act as radical scavengers, reducing the availability of reactive species through competitive reactions. Similarly, natural organic matter, including humic acid (HA), can consume radicals and inhibit degradation processes. In addition, dissolved cations such as Ca^{2+} and PO_4^{3-} may reduce catalytic activity through precipitation or surface deposition on the catalyst, thereby blocking active sites (Zhang et al., 2021).

The ionic strength of the solution can further influence electrostatic interactions between PS and the catalyst surface. Compression of the electrical double layer at the elevated ionic strength may weaken PS adsorption and reduce oxidant activation efficiency, ultimately decreasing ROS generation and contaminant degradation performance (Zhang et al., 2023).

2.7.1 PFAS

The degradation of PFOA in aqueous systems can proceed through multiple radical-driven and thermally induced pathways, depending on the catalyst system and oxidant employed. According to Deng et al. (2023), in US-assisted systems combined with PS, $\text{OH}^\cdot$ radicals and $\text{SO}_4^{\cdot-}$ radicals are generally identified as the dominant reactive species. The degradation process is commonly initiated through cavitation-induced pyrolytic-like reactions and decarboxylation of PFOA, leading to the formation of perfluoroalkyl radicals such as $\text{C}_7\text{F}_{15}^\cdot$. Once generated, these radicals may undergo several competing transformation pathways.

In $\text{SO}_4^{\cdot-}$ mediated pathways, $\text{C}_7\text{F}_{15}^\cdot$ can react with $\text{SO}_4^{\cdot-}$ radicals to form intermediates such as $\text{C}_7\text{F}_{15}\text{OSO}_3^\cdot$ and $\text{C}_7\text{F}_{15}\text{OH}$, which subsequently undergo hydrolysis and oxidation to form shorter-chain intermediates such as $\text{C}_6\text{F}_{13}\text{COF}$. Due to its instability in aqueous media, $\text{C}_6\text{F}_{13}\text{COF}$ readily hydrolyses into shorter-chain perfluorocarboxylic acids (PFCAs), including PFHpA, PFHxA, PFPeA, and PFBA (Deng et al., 2023). Parallel, $\text{OH}^\cdot$ -mediated pathways may also occur, involving direct oxidation of $\text{C}_7\text{F}_{15}^\cdot$ to $\text{C}_7\text{F}_{15}\text{OH}$, followed by sequential C–F bond cleavage and chain shortening reactions.

The degradation pathways proposed by Deng et al. (2023) are particularly relevant to the present study, as both systems rely on the combination of US, PS activation, and a redox-active catalyst. Therefore, sulfate radical- and hydroxyl radical-mediated degradation pathways provide the most appropriate mechanistic framework for interpreting the results obtained with the US/PS/Magnetite system investigated in this work.

Comparable degradation products and chain-shortening reactions have also been reported in US-driven piezocatalytic systems using PTFE-based catalysts (Yao et al., 2025). However, unlike the Magnetite catalyst investigated in this study, PTFE-based materials exhibit piezoelectric properties that generate additional charge carriers and ROS through piezo-induced electron-hole pair formation. Consequently, the underlying ROS generation mechanism differs from that expected in the present US/PS/Magnetite system, although several downstream degradation steps appear to be similar.

Following deprotonation of PFOA into $\text{C}_7\text{F}_{15}\text{COO}^\cdot$, oxidative reactions involving holes and superoxide radicals generate $\text{C}_7\text{F}_{15}\text{COO}^\cdot$ radicals, which subsequently undergo Kolbe decarboxylation to produce $\text{C}_7\text{F}_{15}^\cdot$ and CO_2 . Subsequent reactions with $\text{OH}^\cdot$ radicals induce progressive C–F bond cleavage, resulting in intermediates such as $\text{C}_6\text{F}_{13}\text{COF}$ and hydrolyzed products including $\text{C}_6\text{F}_{13}\text{COOH}$ (PFHpA), alongside HF formation. Continued oxidation promotes sequential removal of CF_2 units, ultimately forming shorter-chain PFCAs, F^- ions, and CO_2 , as final mineralization products. These findings reinforce the crucial role of both decarboxylation and hydroxyl radical attack in PFOA degradation.

Although perfluorooctane sulfonate (PFOS) differs structurally from PFOA due to the presence of a sulfonate rather than a carboxylate functional group, several comparable degradation behaviors and defluorination pathways have been reported in catalytic systems. Veciana et al. (2024) demonstrated that PFOS degradation may initiate through hydrated electron-induced cleavage of the terminal sulfonate group. By breaking this C–S bond, $\text{C}_8\text{F}_{17}^\cdot$ is formed. Subsequent oxidation reactions may lead to intermediates including PFOA, followed by progressive chain-shortening and defluorination reactions.

Overall, current studies consistently highlight the dominant role of radical-mediated oxidation, decarboxylation, functional group transformation, and sequential chain shortening in PFAS

degradation pathways, although the relative importance of these mechanisms strongly depends on catalyst composition, oxidant system, and operational conditions. For the present study, degradation pathways reported for US-assisted PS activation systems are considered the most relevant mechanistic basis for interpreting PFOA degradation, while piezocatalytic pathways provide complementary insight into possible chain-shortening and defluorination reactions.

2.7.2 CIP

The degradation pathways of CIP are strongly influenced by its molecular structure. The most reactive sites include the piperazine ring, the fluorine substituent, the carboxyl group, and the cyclopropyl group (Zhang et al., 2023). Among these, the piperazine ring is generally considered the primary site for oxidative attack and degradation initiation (Zhang et al., 2022).

Figure 11 illustrates the proposed degradation pathways of CIP in a CuO/PI system. Although this pathway was reported for PI-based systems, similar transformation mechanisms may occur in PS-based catalytic systems involving CuO, Magnetite, or CuO/Magnetite composites, due to the generation of comparable ROS.

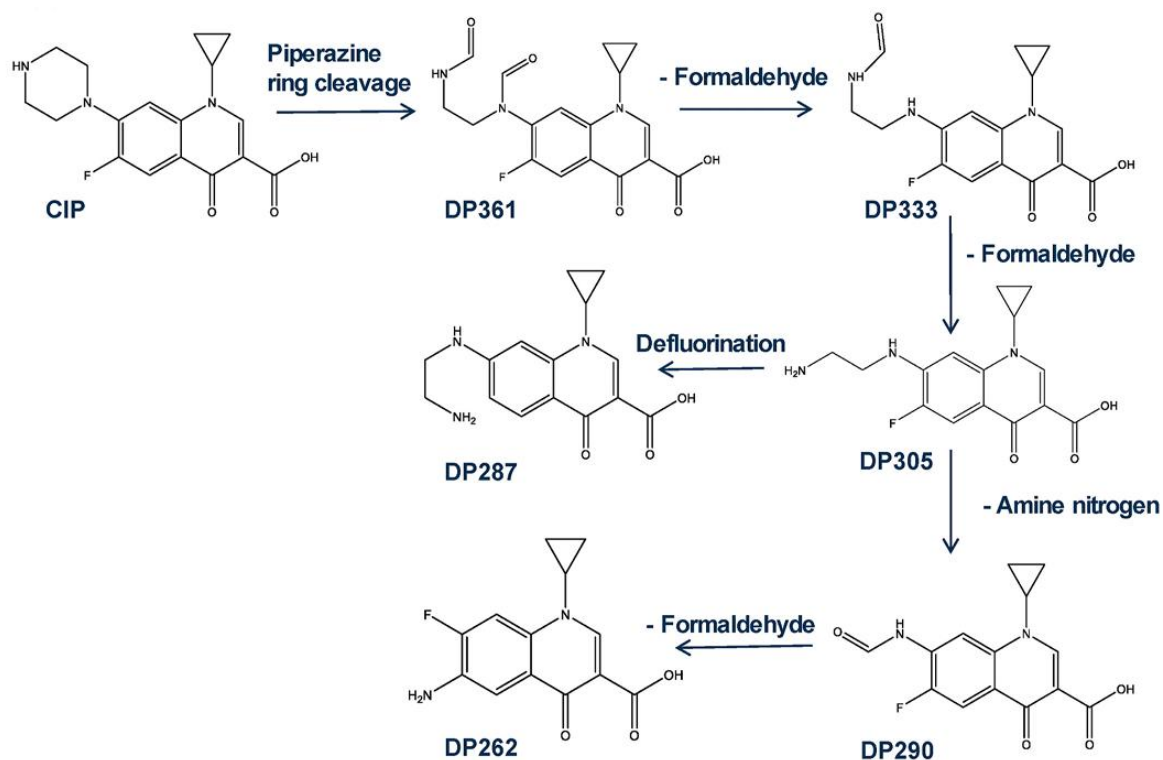


Figure 11: Proposed degradation routes of CIP with CuO/PI (Zhang et al., 2022).

The degradation process commonly begins with cleavage of the piperazine ring, followed by the formation of intermediate compounds through reactions such as dealkylation, hydroxylation, decarboxylation, and fragmentation into smaller organic molecules (Zhang et al., 2021; Zhang et al., 2023). Some of these intermediates may exhibit different physicochemical properties and toxicological behavior compared to the parent compound.

$\text{SO}_4^{\cdot-}$ radicals are generally considered the dominant oxidizing species in PS-based systems and primarily react through electron transfer pathways. $\text{OH}^{\cdot}$ radicals may additionally contribute through non-selective oxidation pathways, including radical addition and hydrogen abstraction mechanisms. Superoxide radicals may also participate in secondary reaction pathways, although their contribution is generally considered less significant. Similarly, singlet oxygen ($^1\text{O}_2$) appears to play only a minor role in CIP degradation (Zhang et al., 2021).

Recent studies further suggest the coexistence of radical and non-radical degradation pathways. In particular, direct oxidation by activated PS species may contribute to contaminant transformation depending on the catalyst type and operational conditions (Zhang et al., 2021).

The incorporation of US enhances CIP degradation through intensified cavitation effects and increased ROS generation. Cavitation-induced localized extreme conditions can accelerate PS activation and promote structural transformation of CIP molecules. High-performance liquid chromatography (HPLC) analysis frequently reveals the formation of intermediate products associated with piperazine ring cleavage, aromatic hydroxylation, and progressive dealkylation reactions (Ma & Wang, 2022).

2.8 Process parameters

Reactor operating conditions strongly influence the efficiency of sonocatalytic degradation processes. Figure 12 schematically illustrates the main parameters affecting the sonocatalytic degradation of CECs.

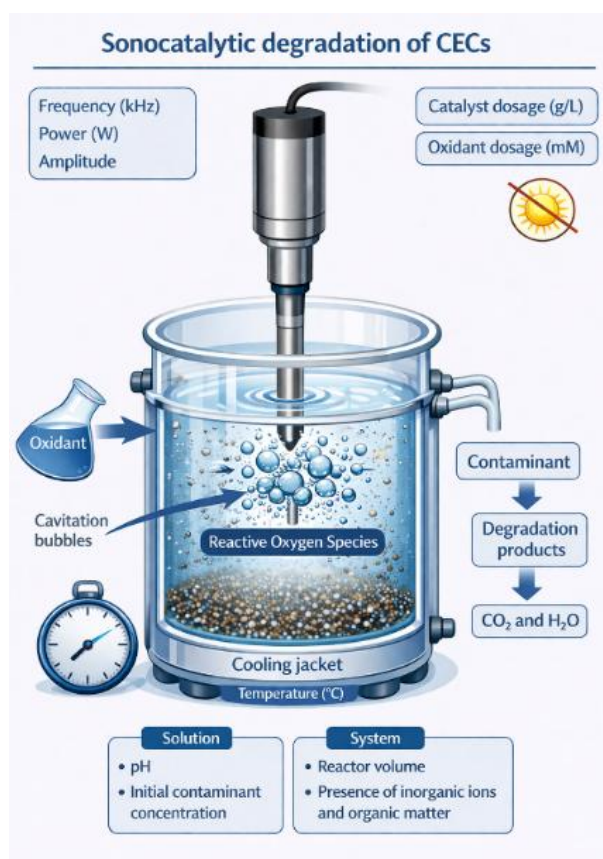


Figure 12: Main operational parameters affecting sonocatalytic degradation of CECs (generated with ChatGPT, OpenAI).

US power is an important operational parameter, as increasing power enhances cavitation intensity and radical generation, thereby maintaining the availability of active catalytic sites and reducing surface fouling during operation (Deng et al., 2023; Trinh et al., 2025).

Catalyst dosage also significantly affects degradation performance. An adequate catalyst concentration is required to provide sufficient active surface sites and promote efficient oxidant activation. However, excessive catalyst loading may induce particle agglomeration, reduce the effective surface area, and hinder ultrasonic wave propagation through the solution. Consequently, an optimal catalyst dosage must be determined for each system, depending on catalyst morphology, surface characteristics, and pollutant concentration (Salazar et al., 2024).

Similarly, oxidant dosage directly influences ROS generation and overall degradation efficiency. Increasing oxidant concentration generally enhances radical production and pollutant degradation up to an optimal level. Beyond this optimum, excess oxidant may consume reactive radicals through side reactions, thereby decreasing the availability of ROS for pollutant oxidation and reducing overall process efficiency (Deng et al., 2023).

Reaction time is another important operational parameter. Longer treatment durations typically improve degradation and mineralization efficiencies due to prolonged exposure to reactive species. However, extended reaction times also increase energy consumption and operational costs. Therefore, a balance must be established between degradation performance, mineralization efficiency, and process economics (Priyadarshini et al., 2022).

The pH of the solution strongly affects both catalyst behavior and ROS chemistry. Variations in pH can influence radical stability, oxidant reactivity, catalyst surface charge, and pollutant speciation. Changes in pH alter the zeta potential of the catalyst and the protonation state of pollutants, thereby affecting adsorption behavior, mass transfer, and interactions between pollutants, radicals, and catalyst surfaces. Furthermore, the redox potential and activation pathways of oxidants are also pH-dependent, which may significantly influence degradation mechanisms and overall treatment efficiency (Ioannidi et al., 2024).

In PS-based AOPs, pH strongly influences the dominant reactive species. Sulfate radicals are generally more relevant under acidic to neutral conditions. However, above approximately pH 8.5-9, $\text{SO}_4^{\cdot-}$ can react with OH^- to form $\text{OH}^\cdot$, causing a shift toward hydroxyl radical-dominated oxidation. This conversion is kinetically favored over the reverse reaction. Although $\text{OH}^\cdot$ may enhance the degradation of some organic compounds, it is less selective than $\text{SO}_4^{\cdot-}$ and is more easily consumed by natural water matrix components. Therefore, pH affects not only catalyst surface charge and pollutant speciation, but also the relative contribution of $\text{SO}_4^{\cdot-}$ and $\text{OH}^\cdot$ to the degradation process (Lee et al., 2020).

Finally, the composition of the water matrix can strongly influence sonocatalytic performance. Inorganic ions and natural organic matter may act as radical scavengers, reducing the availability of reactive species for pollutant degradation. In sludge-containing systems, additional inhibition may occur due to adsorption of contaminants onto solid particles, which limits pollutant accessibility, or due to scavenging reactions involving sludge constituents themselves (Deng et al., 2023).

2.9 Identified research gaps

Recent advances in AOPs have highlighted the potential of sonocatalytic systems for the degradation of CECs, including persistent compounds such as PFAS and CIP. Despite the growing number of studies in this field, several scientific and technological gaps remain unresolved.

For PFAS, significant challenges persist due to the exceptional stability of the C–F bond. Current studies commonly report partial degradation or transformation into shorter-chain PFAS rather than complete mineralization. Consequently, limited information is available regarding overall defluorination efficiency, inorganic fluoride formation, and fluorine mass balance closure. In addition, hybrid systems integrating US, PS, and heterogeneous catalysts remain relatively unexplored for PFAS degradation, despite their potential to generate highly reactive species such as $\text{SO}_4^{\cdot-}$ and $\text{OH}^{\cdot}$ radicals. The dominant degradation pathways in such systems are still not fully understood, particularly regarding the relative contribution of radical and non-radical mechanisms, as well as the influence of localized extreme conditions generated during acoustic cavitation.

Similarly, although CIP is frequently used as a model contaminant in degradation studies, its behavior in hybrid systems combining US, PS, and heterogeneous metal oxide catalysts such as CuO or Magnetite has not been systematically evaluated. Most published studies primarily focus on apparent pollutant removal or structural transformation, while considerably less attention is given to defluorination pathways, fluoride release, and fluorine mass balance. As a result, the extent of complete contaminant mineralization and the environmental fate of fluorinated intermediates remain insufficiently understood.

From a materials perspective, systematic comparative studies evaluating different catalysts, including CuO, Magnetite, and potential hybrid combinations, are still scarce. The physico-chemical behavior of these catalysts under US, including changes in surface chemistry, defect formation, active site availability, and PS activation efficiency, remains insufficiently characterized. Furthermore, catalyst stability, reusability, and metal leaching under combined cavitation and oxidative conditions are rarely investigated, despite their importance for long-term process performance and environmental safety.

Another important limitation in current research is the predominant use of simplified laboratory systems. Most sonocatalytic studies are performed in ultrapure water, thereby neglecting the complexity of realistic matrices such as wastewater or sludge. In these systems, inorganic ions, natural organic matter, and suspended solids may significantly influence degradation efficiency by scavenging reactive species, competing for active sites, or altering pollutant availability and transport behavior.

Finally, several challenges persist at the process and engineering level. The scalability of sonocatalytic systems is limited by the high energy demand associated with US, as well as by reactor design constraints and non-uniform acoustic field distribution. Moreover, comprehensive techno-economic analyses and energy-normalized performance evaluations remain largely absent from the literature, hindering the assessment of their practical feasibility and industrial applicability. Future research should therefore extend beyond laboratory-scale degradation studies and focus on realistic water matrices, catalyst durability, process optimization, and the economic and energetic viability of sonocatalytic treatment systems.

Based on the identified research gaps, the present thesis specifically aims to address the following aspects:

- Comparative evaluation of CuO, Magnetite, and CuO/Magnetite composite catalysts in sonocatalytic activated PS systems, followed by detailed investigation of the most promising catalyst, Magnetite.
- Assessment of pollutant degradation, mineralization, and defluorination during the treatment of both PFOA and CIP, providing insight into the extent of contaminant transformation beyond parent compound removal.
- Investigation of the influence of key operational parameters, including pH, catalyst dosage, and oxidant dosage, on degradation performance through a systematic experimental design approach.
- Elucidation of degradation mechanisms through radical quenching experiments and evaluation of the dominant reactive species involved in CIP degradation.
- Evaluation of catalyst stability, reusability, and iron leaching, as well as the influence of inorganic ions and natural organic matter on process performance under more environmentally relevant conditions.

3 MATERIALS & METHODS

3.1 Chemicals

All chemicals used in this study were of analytical or high-purity grade and were employed as received without further purification. The contaminants investigated included PFOA (>95%, Sigma-Aldrich) and CIP (>98%, Acros Organics). Stock solutions of CIP and PFOA were prepared in 1 L volumetric flasks using Milli-Q water at concentrations of 50 ppm and 100 ppm, respectively. All volumetric flasks were wrapped in aluminum foil and stored in the dark to prevent photodegradation.

The catalysts were synthesized using iron(III) chloride (FeCl_3 , $\geq 98\%$, Acros Organics), iron(II) sulfate (FeSO_4 , $\geq 98\%$, Acros Organics), ammonium hydroxide (NH_4OH , 28-30%, Sigma-Aldrich), copper(II) sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, >98%, Fisher Chemicals), sodium hydroxide (NaOH , $\geq 98\%$, Acros Organics), and ethanol (99%, Fisher Chemicals). Sodium chloride (NaCl) was used for zeta potential measurements, while the solution pH was adjusted using hydrochloric acid (HCl , $\geq 37\%$, Fisher Chemicals) or NaOH .

Potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$, >99%, Fisher Scientific) was used as oxidant, and sodium thiosulfate (thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$) was used as quenching agent to terminate PS-based reactions by reducing residual oxidant species. For radical scavenging experiments, 1-octanol (>99%, Sigma-Aldrich) was used as scavenger for $\text{SO}_4^{\cdot-}$ and $\text{OH}^{\cdot}$ radicals, tert-butanol (TBA, $\geq 99\%$, Fisher Scientific) for $\text{OH}^{\cdot}$ radicals, while L-ascorbic acid (LAA, $\geq 99\%$, Sigma-Aldrich) was used to target $\text{O}_2^{\cdot-}$ species.

For liquid chromatography, ammonium formate (NH_4HCO_2), formic acid (HCOOH), acetonitrile (ACN, CH_3CN), and ammonium acetate ($\text{NH}_4\text{CH}_3\text{CO}_2$) were used for mobile phase preparation. For ion chromatography, sodium bicarbonate (NaHCO_3), and sodium carbonate (Na_2CO_3) were used. Reverse aqua regia ($\text{HNO}_3/\text{HCl} = 3:1$ v/v) was used for ICP sample digestion. Interference experiments were performed using NaHCO_3 , sodium phosphate (Na_3PO_4) and humic acid (HA).

3.2 Catalyst synthesis

3.2.1 CuO

CuO was synthesized through a precipitation-based method, as schematically illustrated in Figure 13, where the numbered steps correspond to the numbers indicated in parentheses throughout the procedure. In a typical synthesis (Davarazar et al., 2022), 5 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was dissolved in 250 mL Milli-Q water under continuous stirring (1). Separately, 4.9 g of NaOH was dissolved in 100 mL of Milli-Q water, and the resulting solution was added dropwise to the copper-containing solution to initiate precipitation of copper species (2). During this process, the reaction mixture was maintained at 60-70 °C. After the complete addition of the NaOH solution, the suspension was stirred for an additional 30 minutes at the same temperature to allow the precipitation process to proceed to completion (3).

After completion of the precipitation reaction, the entire suspension containing the CuO particles was transferred to a Büchner funnel and vacuum filtered to collect the solid phase (4). The resulting filter cake was washed three times with 20 mL of ethanol per wash to remove residual ions and unreacted precursors (5). The washed CuO was then dried overnight at 60 °C and subsequently ground into a fine powder prior to use (6).

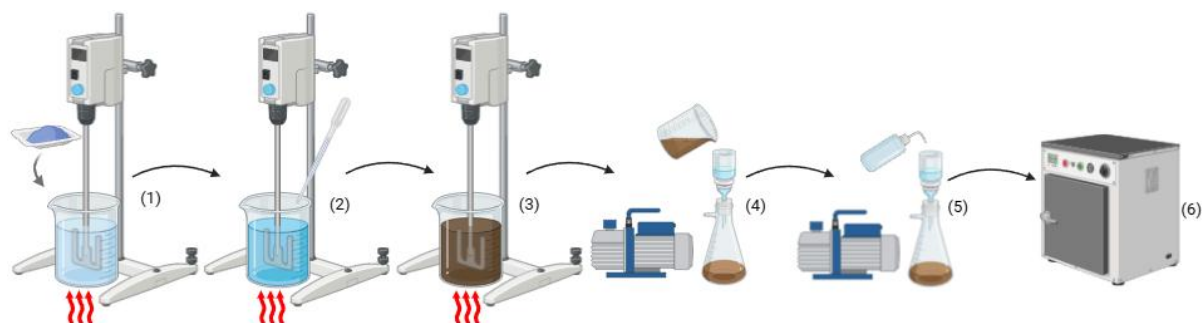


Figure 13: Schematic overview of the CuO synthesis procedure.

3.2.2 Magnetite

Magnetite nanoparticles were synthesized following a co-precipitation approach, as schematically illustrated in Figure 14, where the numbered steps correspond to the numbers indicated in parentheses throughout the procedure. A mixture of 2.197 g of FeCl_3 and 2.890 g of FeSO_4 was dissolved in 200 mL of Milli-Q water under continuous overhead stirring at 200 rpm, while the suspension was maintained at 60-70 °C (1). These quantities correspond to approximately 13.5 mmol Fe(III) and 19.0 mmol Fe(II), resulting in an Fe(III)/Fe(II) molar ratio of 0.71. The synthesis was performed according to a previously established laboratory protocol (Ning et al., 2025). Magnetic stirring was avoided to prevent interference with the Magnetite formation, as the developing particles rapidly adhered to magnetic components.

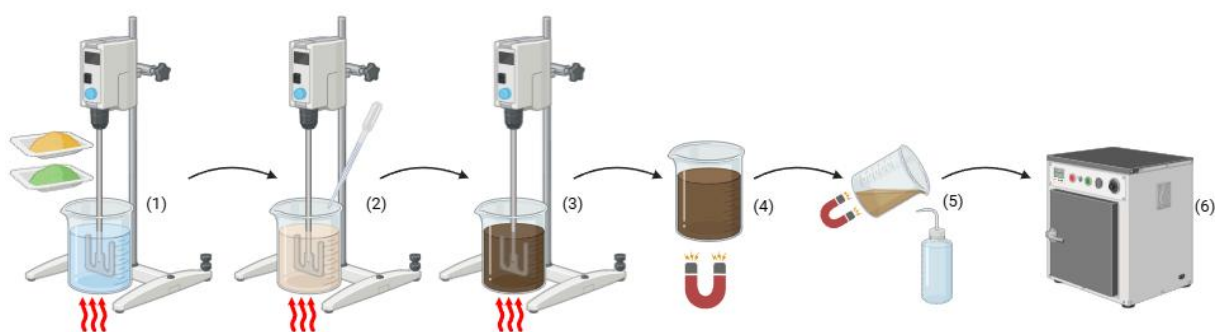


Figure 14: Schematic overview of the Magnetite and Composite synthesis procedure.

The synthesis was conducted under ambient atmospheric conditions without the use of an inert gas atmosphere. Consequently, partial oxidation of Fe(II) during synthesis cannot be excluded, potentially resulting in the formation of minor amounts of maghemite ($\gamma\text{-Fe}_2\text{O}_3$) alongside Magnetite. The phase composition was therefore evaluated through XRD characterization.

Once the iron salts were fully dissolved, 20 mL of NH_4OH (28-30%) was introduced slowly into the system in a dropwise manner to initiate precipitation (2). The mixture was allowed to react

for an additional 30 minutes under the same temperature and stirring conditions to ensure complete nucleation and growth of the Magnetite phase (3).

After the reaction, the solid Magnetite particles were isolated by placing a strong permanent magnet against the exterior bottom wall of the beaker, enabling magnetic separation (4). The supernatant was decanted while maintaining the magnet in place. The collected solids were subsequently washed three times with 20 mL of ethanol per wash to remove residual impurities (5). For washing, the magnet was removed to allow suspension and full contact between the particles and the solvent, after which the particles were again magnetically separated.

The washed catalyst was dried overnight at 60 °C and subsequently ground into a fine powder to ensure homogeneity prior to use (6). Figure 15 shows a picture of the synthesis process.



Figure 15: Picture of the Magnetite synthesis procedure performed in the lab.

3.2.3 CuO/Magnetite composite

The composite catalyst was synthesized by depositing a copper oxide phase onto pre-formed Magnetite using a precipitation-based procedure similar to the CuO synthesis described earlier. In this case, Magnetite was introduced into the copper-containing solution before precipitation, allowing copper species to form in the presence of the magnetic support. The procedure is schematically illustrated in Figure 14, where the numbered steps correspond to the numbers indicated in parentheses throughout the procedure. 5 g of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was dissolved in 250 mL of demineralized water, after which the Magnetite powder was dispersed into this solution under continuous stirring (1).

Separately, a second solution was prepared by dissolving 4.9 g of NaOH in 100 mL of demineralized water. The copper-containing suspension was heated to 60-70 °C on a hot plate while being stirred with a non-magnetic overhead stirrer at 200 rpm to avoid interference with the magnetic particles (1). Once the temperature stabilized, the NaOH solution was introduced dropwise to the copper-Magnetite suspension (2). During this process, a visible color change occurred, consistent with the precipitation of copper species onto the Magnetite surface (3).

Following the reaction, the solid composite particles were separated magnetically by placing a strong permanent magnet along the exterior bottom wall of the beaker. While holding the magnet in place, the supernatant was decanted (4). The collected solids were washed three times with 20 mL of ethanol per wash, with the magnet temporarily removed during washing to allow proper mixing and renewed contact between the particles and solvent, followed by magnetic separation after each wash (5).

The resulting composite catalyst was dried overnight at 60 °C and subsequently ground into a fine, homogeneous powder suitable for further use in degradation experiments (6). Figure 16 shows the first color change during the synthesis process.

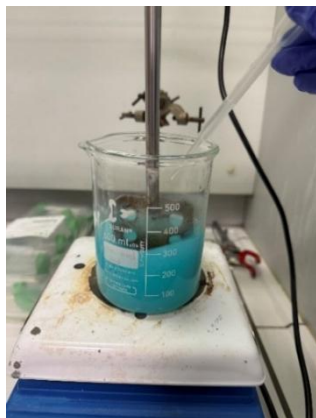


Figure 16: Picture of the CuO/Magnetite composite synthesis procedure performed in the lab.

3.3 Catalyst characterization

All catalysts used in this thesis were systematically characterized to confirm successful synthesis, assess purity, and establish structure-property relationships relevant to catalytic performance. Properties such as surface area, porosity, crystallinity, surface composition, and surface charge strongly influence adsorption behavior, oxidant activation, ROS generation, and catalyst stability. Comprehensive characterization is therefore essential for interpreting the observed catalytic activity and comparing the synthesized materials with literature-reported systems.

3.3.1 Brunauer-Emmett-Teller surface area analysis (BET)

BET analysis is a widely used technique for determining the specific surface area and porosity of solid materials. The method is based on physical gas adsorption at the surface of a material and is particularly relevant for catalytic materials, where a high surface area and accessible pore structure can significantly improve adsorption capacity and increase the availability of active sites, thereby enhancing heterogeneous catalytic performance (Salazar et al., 2024). In sonocatalytic systems, a large surface area is especially beneficial because acoustic cavitation improves mass transfer and continuously renews catalyst surfaces through the removal of adsorbed intermediates and by-products (Pétrier & Wei, 2023).

Prior to BET analysis, samples are typically degassed to remove moisture and adsorbed impurities from the surface and pore structure. Subsequently, the material is exposed to an adsorptive gas, commonly nitrogen, at cryogenic temperatures. By analyzing the obtained adsorption–desorption isotherms, important textural parameters such as specific surface area, pore volume, and pore size distribution can be determined (Naderi, 2014).

BET surface area measurements were performed using nitrogen adsorption with a Micromeritics Gemini V instrument (Micromeritics Instrument Corp., USA). Prior to analysis, the samples

were evacuated for 10 min at an evacuation rate of 133.3 kPa/min. Measurements were conducted using nitrogen as adsorptive gas at 77.300 K.

3.3.2 Scanning Electron Microscopy (SEM)

SEM is commonly used to investigate the morphology and microstructure of catalytic materials. By scanning the sample surface with a focused electron beam, high-resolution images can be obtained, providing information regarding particle size, morphology, aggregation, and surface texture. In catalyst characterization, SEM is particularly valuable for evaluating structural homogeneity, particle dispersion, and morphological changes resulting from synthesis procedures. These properties can directly influence surface accessibility, mass transfer, and catalyst stability during heterogeneous and sonocatalytic reactions (Bergström, 2015; Herrero et al., 2023).

3.3.3 Transmission Electron Microscopy (TEM)

TEM complements SEM by providing detailed information on the internal structure and nanoscale morphology of materials. In TEM, a high-energy electron beam is transmitted through an ultrathin sample, enabling visualization of particle size, crystal structure, lattice fringes, and the dispersion of active phases at nanometer resolution. TEM is especially useful for investigating the crystallinity, porosity, and interfacial structure of sonocatalysts, which are important parameters influencing catalytic activity and radical generation during pollutant degradation processes (Inkson, 2016).

3.3.4 X-Ray Diffraction (XRD)

XRD is a widely applied analytical technique used to determine the crystalline structure, phase composition, and crystallinity of solid materials. The technique is based on the interaction between incident X-rays and the periodically arranged atomic planes within crystalline materials. When monochromatic X-rays with a wavelength in the order of approximately 0.1 nm interact with a crystal lattice, constructive interference occurs at specific diffraction angles according to Bragg's law. The resulting diffraction pattern is characteristic for a given crystalline phase and can therefore be used to identify crystal structures, evaluate phase purity, and assess structural changes or crystallinity. In the field of heterogeneous catalysis and composite materials, XRD is commonly employed to confirm successful material synthesis, identify crystalline phases, and evaluate the structural stability of catalysts after preparation or treatment (Bergström, 2015; Ebrahimi & Ahari, 2024).

XRD measurements were performed using an X'Pert-PRO diffractometer equipped with a Cu anode source. The analyses were carried out in continuous scanning mode at 25 °C. Diffraction patterns were recorded over a 2θ range from 10° to 130° using Cu K α 1 radiation ($\lambda = 1.54060$ Å). The instrument was operated at 45 kV and 40 mA. All measurements were conducted with a step size of 0.0260° and a scan step time of 96.3900 s.

3.3.5 Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR is a widely applied, rapid and non-destructive analytical technique used to identify surface functional groups and chemical bonds in materials and is therefore highly valuable for

catalyst characterization. In FT-IR analysis, the sample is exposed to infrared radiation within the mid-infrared region of the electromagnetic spectrum, typically ranging from 4000 to 400 cm^{-1} . This region corresponds to molecular vibrational energies that are lower in frequency and longer in wavelength than those of visible light.

The infrared spectrum is commonly divided into distinct regions associated with different types of chemical bonds. Single-bond stretching vibrations, including O–H, C–H and N–H vibrations, typically appear in the range between 2500 and 4000 cm^{-1} . Double-bond vibrations are generally observed between 1500 and 2000 cm^{-1} , while triple-bond vibrations occur at higher energies, between 2000 and 2500 cm^{-1} . The lower wavenumber region, approximately 650 to 1500 cm^{-1} , is known as the fingerprint region and contains complex absorption patterns characteristic of the overall molecular structure.

FT-IR spectroscopy is particularly useful for confirming metal–oxygen bonds, identifying surface hydroxyl groups, and detecting adsorbed species or surface modifications that may influence catalytic performance. In heterogeneous catalysts, these surface functionalities can strongly affect adsorption behavior, oxidant activation, and catalyst stability (Herrero et al., 2023).

3.3.6 Zeta potential measurements

Zeta potential measurements are used to characterize the surface charge of catalyst particles suspended in an aqueous medium. The zeta potential originates from the electrical double layer formed at the solid-liquid interface when a catalyst comes into contact with water. It reflects the potential difference between the slipping plane of the particle and the bulk solution and therefore provides an indirect measure of the electrostatic interactions between the catalyst surface and surrounding species.

In heterogeneous catalytic systems, surface charge plays a crucial role in determining the interaction between the catalyst and charged contaminants. Many organic pollutants and fluorinated compounds exist in different ionic forms depending on the solution pH, while the surface charge of metal oxide catalysts also varies with pH. Zeta potential measurements therefore allow evaluation of electrostatic attraction or repulsion between the catalyst and contaminants under different experimental conditions. Favorable electrostatic interactions can enhance adsorption of contaminants onto the catalyst surface, which is often a prerequisite for efficient heterogeneous catalytic degradation.

The point of zero charge (PZC) is a key parameter derived from zeta potential analysis and corresponds to the pH at which the net surface charge of the catalyst is zero. At pH values below the PZC, the catalyst surface is predominantly positively charged, whereas above the PZC it becomes negatively charged. This pH-dependent behavior strongly influences adsorption mechanisms and can determine whether cationic or anionic contaminants are preferentially attracted to the catalyst surface.

In sonocatalytic systems, the importance of surface charge is further amplified by enhanced mass transfer induced by acoustic cavitation. Although US promotes mixing and radical formation in the bulk solution, electrostatic interactions at the catalyst-solution interface remain critical for bringing contaminants into close proximity with reactive surface sites and short-lived radicals. Zeta potential measurements therefore provide essential insight into how pH affects catalyst-contaminant interactions, adsorption behavior, and ultimately catalytic performance.

By linking surface charge characteristics to degradation efficiency, zeta potential analysis contributes to understanding structure-performance relationships and supports optimization of operational parameters such as pH in heterogeneous (sono)catalytic degradation processes (Kamble et al., 2022; Khalaj et al., 2018).

3.4 Experimental setup

Aqueous contaminant solutions were prepared using Milli-Q water. CIP solutions were prepared at concentrations of 5 ppm and 10 ppm, while PFOA solutions were prepared at 1 ppm. These working solutions were prepared from stock solutions with concentrations of 50 ppm for CIP and 100 ppm for PFOA.

In experiments involving a catalyst, systems were initially allowed to reach adsorption equilibrium prior to degradation. In experiments with an oxidant, the oxidant was subsequently added to initiate the degradation process. A similar approach was applied in US-assisted experiments, where US irradiation was used to trigger degradation after the adsorption phase. In combined systems including both oxidant and US, the oxidant was added, followed immediately by the application of US to start the reaction.

Figure 17 provides a schematic overview of the sampling and sample preparation procedure, where the numbered steps correspond to the numbers indicated in parentheses throughout the procedure. Samples of 1.5 mL were collected in Eppendorf tubes at predefined time intervals (1). In experiments involving PS, samples were immediately quenched with an excess of thiosulfate to terminate radical reactions (2). Subsequently, samples were centrifuged for 5 min at 14,000 rpm (3) to remove suspended solids (4), followed by filtration through 0.22 μm syringe filters (5). The filtrate was transferred into HPLC vials for analysis of the parent compound concentration (6).

Mineralization was evaluated by TOC analysis. For this purpose, 20 mL samples were collected at the beginning and at the end of the degradation experiment. End-point samples were quenched with thiosulfate prior to analysis. Defluorination was assessed by IC using 10 mL samples collected at the end of the experiment after quenching.

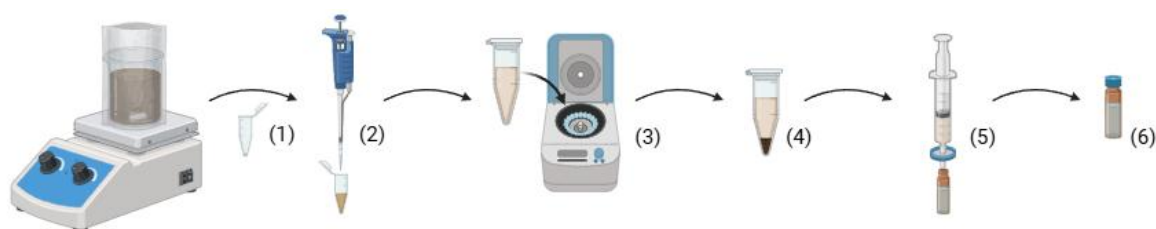


Figure 17: Schematic overview of the sampling and sample preparation procedure (Created with BioRender).

3.4.1 Experimental setup without ultrasonic irradiation

Experiments without US were conducted in beakers containing either 250 mL or 500 mL of solution. When a catalyst was used, it was added at a dosage of 1 g/L. The beakers were placed on a magnetic stirring plate to ensure homogeneous dispersion of the catalyst and were

covered with aluminum foil to minimize contamination, evaporation, or photocatalytic interference. The reaction mixtures were stirred continuously throughout the experiment. Figure 18 shows a representative figure and a picture of the experimental setup without US.



Figure 18: Experimental setup without US used in the lab.

3.4.2 Experimental setup with ultrasonic irradiation

The experiments are conducted in a batch reactor with a working volume of 500 mL, equipped with low-frequency sonotrode operating at 24 kHz. The reactor temperature was maintained at 20 °C by external cooling through a cooling jacket. Figure 19 and Figure 20 show a picture of the experimental setup with US and a representative figure of the sonotrode. Appropriate safety measures were applied during operation: ear protection was worn at all times and precautions were taken to prevent splashes and aerosols. Care was taken not to touch the glass reactor with the sonotrode.

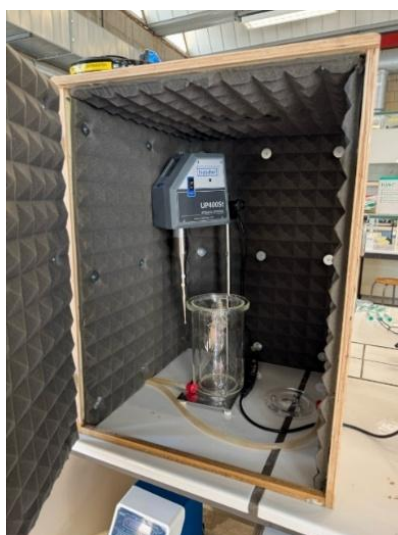


Figure 19: Experimental setup used for US experiments.

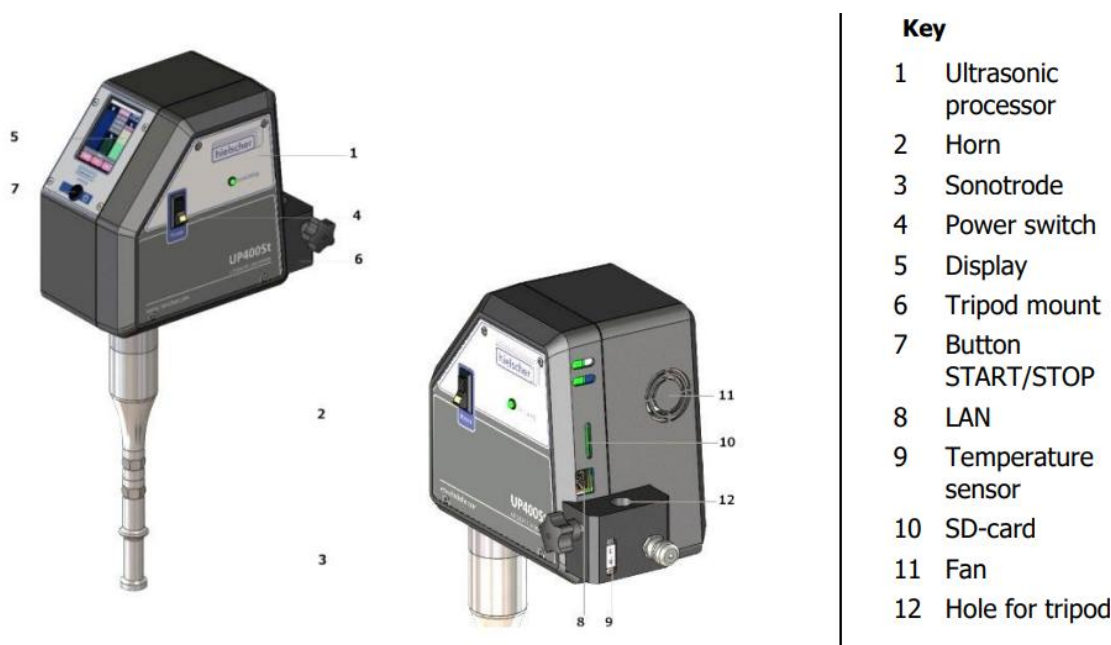


Figure 20: Sonotrode used in the experimental setup (UP400St Operating Manual).

3.5 Analytical methods

Several analytical techniques were employed to evaluate contaminant degradation during sonocatalytic treatment experiments. The degradation of CECs was monitored through the decrease in parent compound concentration using Liquid Chromatography (LC). Defluorination of fluorinated compounds was assessed using Ion Chromatography (IC) by quantifying released fluoride ions. However, neither degradation nor defluorination alone necessarily indicates complete mineralization. Therefore, Total Organic Carbon (TOC) analysis was additionally performed to evaluate the extent of organic carbon conversion into inorganic end products. In addition, inductively coupled plasma (ICP) was used to quantify iron leaching and assess catalyst stability during treatment.

3.5.1 Degradation – Liquid Chromatography

The degradation of contaminants was monitored by measuring the concentration of the parent compound using LC. By following the decrease in parent compound concentration, degradation efficiencies and reaction kinetics can be evaluated. In addition, the simultaneous analysis of transformation products enables identification of potential degradation pathways and intermediate formation.

CIP analysis

The HPLC analysis (Figure 21) was performed using an Agilent 1100 system USA equipped with a Zorbax Eclipse Plus C18 column (4.6 × 100 mm, 3.5 μm). The mobile phase consisted of 10 mM ammonium formate, adjusted to pH 2.8 with formic acid (7:3 dilution with water), and ACN. Equal volumes of both solvents were prepared, with both mobile phases degassed in an ultrasonic bath for 30 minutes prior to use. The elution gradient increased from 10% to 90%

CH₃CN over 8 minutes, followed by a return to 10% within 4 minutes to allow column equilibration. The flow rate was 1.0 mL/min, the injection volume was 10 µL, and the column temperature was maintained at 30 °C. CIP was detected at 275 nm, and each sample was analyzed over a total run time of approximately 16 minutes.



Figure 21: HPLC system used for CIP analysis.

PFOA analysis

Ultra-high performance liquid chromatography–quadrupole time-of-flight–mass spectrometry (UHPLC-QTOF-MS, Figure 22) analyses were carried out using a Waters ACQUITY UHPLC system coupled to an Agilent 6530 Quadrupole Time-of-Flight mass spectrometer (Agilent Technologies, Waldbronn, Germany), equipped with a diode array detector for complementary UV detection. Separation was achieved on a UHPLC BEH C18 column (2.1 × 100 mm, 1.7 µm particle size; Waters, Milford, USA).

The mobile phase consisted of two eluents, where solvent A was 5 mM ammonium acetate in water and solvent B consisted of 2% water with 5 mM ammonium acetate in ACN. Prior to use, both mobile phases were degassed with helium. A gradient elution was applied starting at 95% A and 5% B at 0 min. The proportion of solvent B was then increased to 80% at 9 min (20% A : 80% B), followed by a further increase to 95% B at 10 min (5% A : 95% B). At 11 min, the system was returned to the initial conditions and re-equilibrated until 15 min (95% A : 5% B). The flow rate was maintained at 0.3 mL min⁻¹, and an injection volume of 5 µL was used for all analyses.



Figure 22: UHPLC-QTOF-MS system used for PFOA analysis.

3.5.2 Defluorination - Ion Chromatography

Defluorination refers to the cleavage of C–F bonds, resulting in the release of inorganic F^- ions into the aqueous phase. For highly fluorinated compounds such as PFAS, this parameter is a key indicator of bond cleavage due to the exceptional stability of the C–F bond and its contribution to environmental persistence (Khan, 2025). In this study, defluorination was assessed by quantifying released F^- using IC.

IC (Metrohm 930 Compact IC Flex, Figure 23) was used for the separation and quantification of fluoride in aqueous samples. Samples were automatically injected using an autosampler (858 Professional Sample Processor) and introduced into an ion-exchange chromatographic system. Separation is based on electrostatic interactions between the analyte ions and the charged stationary phase, whereby ions with higher affinity for the stationary phase are retained longer, resulting in separation according to retention time.

After chromatographic separation, fluoride ions were detected using a conductivity detector. The signal was processed using MagIC Net software (Metrohm), which generates a chromatogram of conductivity versus retention time. Fluoride was identified based on its characteristic retention time, and quantification was performed by peak area integration using external calibration, yielding concentrations expressed in $mg\ F^-/L$.

To ensure optimal separation and sensitivity, an anion-exchange system was used with a carbonate-based eluent consisting of $NaHCO_3$ (1 mM) and Na_2CO_3 (3.5 mM). A suppressor system was applied to reduce background conductivity from the eluent, thereby improving the signal-to-noise ratio and enhancing detection sensitivity for fluoride quantification.



Figure 23: Ion chromatography system used for fluoride analysis.

3.5.3 Mineralization - Total Organic Carbon

TOC analysis was used to evaluate the extent of contaminant mineralization following sonocatalytic treatment. Whereas HPLC analysis specifically monitors the decrease in parent compound concentration, TOC analysis measures the total amount of organic carbon remaining in the sample, including transformation products and degradation intermediates. As a result, TOC provides a more comprehensive assessment of treatment performance by evaluating the conversion of organic contaminants into inorganic end products such as CO_2 and H_2O . A significant decrease in TOC therefore indicates a higher degree of mineralization and more complete degradation.

Organic carbon concentrations were determined using a TOC analyzer (Shimadzu TOC-L, Figure 24). TOC was analyzed using the non-purgeable organic carbon (NPOC) method. In this approach, inorganic carbon species are first removed prior to analysis, thereby avoiding the indirect difference measurement associated with conventional TOC determination and reducing potential analytical errors. For the investigated samples, NPOC was considered equivalent to TOC because no significant amounts of volatile organic compounds were present, which was confirmed experimentally during analysis.

For NPOC determination, samples were first acidified with HCl, converting inorganic carbon species into CO₂, which was subsequently removed by purging. After removal of inorganic and volatile carbon fractions, the remaining organic material was oxidized to CO₂ by high-temperature combustion (± 720 °C). The generated CO₂ was quantified using a non-dispersive infrared detector (NDIR), and the corresponding organic carbon concentration was reported in mg C/L.



Figure 24: TOC analyzer used for mineralization analysis.

3.5.4 Iron leaching - Inductively Coupled Plasma

Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, Figure 25) was used to quantify dissolved iron released from the catalyst during sonocatalytic treatment. Determining iron leaching is important for evaluating catalyst stability and assessing the potential contribution of homogeneous iron-mediated PS activation pathways.



Figure 25: ICP-OES system used for leaching analysis.

Prior to analysis, samples were digested using reverse aqua regia ($\text{HNO}_3/\text{HCl} = 3:1$ v/v) to ensure complete dissolution of dissolved and particulate iron species. The digested samples were subsequently introduced into an inductively coupled argon plasma, where temperatures of approximately 6000-8000 K atomized and excited the elements present. As the excited atoms and ions returned to lower energy states, they emitted element-specific radiation at characteristic wavelengths.

Iron concentrations were determined using a Spectro Arcos ICP-OES system. The emitted radiation was separated into its spectral components by the optical system and detected using charge-coupled device detectors. Quantification was performed through calibration with iron standards using the Smart Analyzer software.

3.6 Experiments

3.6.1 Baseline and catalyst performance tests

Experiments were conducted to establish baseline conditions and to evaluate the performance of different catalysts (CuO, Magnetite and CuO/Magnetite composite) for the degradation of CIP. These experiments were used to assess potential differences in catalytic activity and to determine whether the composite material provided improved performance compared to the individual components.

Batch experiments (1 h) were performed to evaluate the individual and combined effects of US, PS, and catalyst addition on CIP degradation. The investigated experimental conditions are summarized in Table 3. A catalyst dosage of 1 g/L was applied in all experiments involving catalysts.

Table 3: Overview of the baseline and catalyst screening experiments.

Experiment	CIP (ppm)	PS (mM)	Catalyst
CIP alone: CIP	5	/	/
Sonolysis: CIP + US	5	/	/
PS oxidation: CIP + PS	5	15	/
US-activated PS oxidation: CIP + US + PS	5	15	/
Adsorption: CIP + CAT	5	/	CuO, Magnetite, and Composite
Sonocatalysis: CIP + US + CAT	5	/	CuO, Magnetite, and Composite
Catalytic PS activation: CIP + CAT + PS	5	15	CuO, Magnetite, and Composite
	10	1	CuO, Magnetite, and Composite
	10	0.5	Magnetite

These experiments were used to evaluate adsorption behavior, catalytic activity, and potential synergistic effects between US, PS activation, and catalyst composition. For catalyst screening

experiments involving PS activation, a PS concentration of 15 mM was initially selected to ensure sufficient oxidant availability and to maximize the likelihood of observing catalytic effects. This concentration is consistent with upper dosage ranges frequently reported in PFAS degradation studies, where further increases in oxidant concentration often provide limited additional benefit. Lower PS concentrations (1 and 0.5 mM) were subsequently investigated to evaluate catalyst performance under less oxidant-rich conditions and to obtain more clearly distinguishable degradation kinetics. At high PS concentrations, degradation can occur too rapidly, making it difficult to assess differences in catalytic activity and reaction rates between catalysts.

3.6.2 Optimization of process parameters for enhanced CIP degradation

Systematic experiments were performed to optimize the degradation of CIP using PS activation in combination with Magnetite as catalyst. CIP was initially used as a model contaminant at an initial concentration of 5 ppm to evaluate and optimize process parameters prior to application to more persistent fluorinated compounds.

The effect of operational parameters was investigated by varying the initial solution pH (pH 4, 7, and 10), oxidant dosage (0.1, 1.3, and 2.5 mM), and catalyst dosage (0.1, 0.55, and 1 g/L). pH adjustments were performed using HCl and NaOH. These experiments were performed using Magnetite as the catalyst under batch conditions to identify optimal degradation performance.

3.6.3 Optimization of process parameters for enhanced PFOA degradation

Systematic experiments were performed to evaluate the degradation of PFOA using PS activation in combination with Magnetite as catalyst. PFOA was selected as a representative legacy PFAS compound to assess system performance under fluorinated contaminant conditions.

The effect of operational parameters was investigated by varying the initial solution pH (pH 4, 7, and 10), oxidant dosage (5, 12.5, and 20 mM), and catalyst dosage (0.5, 1, and 1.5 g/L). pH adjustments were performed using HCl and NaOH. These experiments were performed under batch conditions using Magnetite as catalyst to evaluate degradation efficiency and parameter sensitivity for PFOA.

3.6.4 Radical quenching

Radical quenching experiments were performed to identify the dominant reactive species involved in CIP degradation under different pH conditions. Selected radical scavengers were added to the reaction system under optimized conditions to evaluate their effect on degradation efficiency and to infer the contribution of specific ROS.

1-Octanol, tert-butanol, and L-ascorbic acid were used as radical scavengers. 1-Octanol was added at a concentration of 480 μL per 500 mL solution, tert-butanol at 780 μL per 500 mL, and L-ascorbic acid at 88 mg per 500 mL.

1-Octanol was used to evaluate the combined contribution of hydroxyl radicals ($\text{OH}\cdot$) and sulfate radicals ($\text{SO}_4\cdot^-$), whereas tert-butanol was used as a preferential scavenger for $\text{OH}\cdot$ radicals. By comparing the inhibition observed in the presence of 1-octanol and tert-butanol, the

relative contribution of sulfate radical-mediated oxidation could be inferred. A stronger suppression of degradation in the presence of 1-octanol compared to tert-butanol was therefore interpreted as an indication of $\text{SO}_4^{\cdot-}$ involvement in the degradation process. L-Ascorbic acid was used to assess the contribution of superoxide radicals ($\text{O}_2^{\cdot-}$).

The effect of these scavengers on CIP degradation was therefore used as an indirect indication of the involvement of $\text{OH}^{\cdot}$ radicals, $\text{SO}_4^{\cdot-}$ radicals, and $\text{O}_2^{\cdot-}$ radicals. Since no separate experiments were conducted to evaluate direct reactions between the scavengers and PS, potential interactions between the scavengers and the oxidant cannot be completely excluded.

3.6.5 Interference of ions

The effect of inorganic ions and natural organic matter on CIP degradation was investigated by introducing selected background constituents into the reaction system. These experiments were conducted to evaluate potential inhibition effects and to simulate environmentally relevant water matrix conditions.

The influence of inorganic carbon was assessed using HCO_3^- (5 mM), while phosphate ions (PO_4^{3-} , 0.5 mM) were added to evaluate potential catalyst poisoning effects due to surface complexation and active site blocking. In addition, humic acid (10 mg/L) was used as a model compound for natural organic matter to assess its impact on radical scavenging and competitive adsorption.

3.6.6 Catalyst reusability and iron leaching

The stability and reusability of the Magnetite catalyst were evaluated using CIP as model contaminant under the previously optimized conditions. Five consecutive degradation cycles were performed to assess the loss of catalytic activity during repeated operation. After each cycle, the treated solution was removed by magnetic separation of the catalyst followed by decantation of the supernatant. The recovered catalyst was then dried in an oven and reused directly in the next cycle without washing or additional regeneration.

No washing step was applied between cycles, because preliminary handling showed that washing resulted in substantial catalyst loss during recovery. As a result, the catalyst dosage was not fully restored to its initial value in each cycle, and a gradual decrease in catalyst mass occurred during repeated use. The catalyst mass was therefore monitored after each cycle to evaluate catalyst recovery efficiency and to relate performance loss to both catalyst deactivation and physical catalyst loss.

In addition, catalyst stability was assessed by quantifying the release of iron into the aqueous phase. Metal leaching was analyzed to evaluate potential structural degradation and dissolution of Magnetite during operation.

3.7 Design of Experiments

A fractional factorial screening design (2^{3-1} , Resolution III) was applied to evaluate the influence of key process parameters on degradation performance. Three factors (initial pH, catalyst dosage, and oxidant dosage) were investigated at two levels, resulting in four factorial runs. Each

condition was performed in triplicate, and two center points were included to assess potential curvature in the system response. As all experiments were conducted using a single batch reactor, the complete design was performed within one experimental block. The order of the individual experimental runs, including replicates and center points, was randomized to minimize systematic bias arising from time-dependent effects such as catalyst aging or variations in ultrasonic performance.

A fractional factorial design was selected as a screening approach to limit the number of required experiments while still enabling identification of the most influential process parameters. Due to the Resolution III structure of the design, main effects are confounded with two-factor interactions. Therefore, the estimated effects should be interpreted as indicative trends rather than as fully independent parameter effects. A full factorial design would allow independent estimation of all main effects and interaction effects. However, the fractional factorial design was considered sufficient for the screening objectives of this study and was used primarily to identify promising operating conditions for further investigation. The factor levels and corresponding experimental conditions are presented in Table 4. The experimental run order and corresponding conditions are provided in *Bijlage A* and *Bijlage B*.

Table 4: Experimental design matrix used for the optimization of process parameters affecting CIP and PFOA degradation.

Pollutant	Initial pH (<i>I</i>)		Catalyst dosage (g/L)		Oxidant dosage (mM)	
	Low	High	Low	High	Low	High
CIP	4	10	0.1	1.0	0.1	2.5
PFOA	4	10	0.5	1.5	5.0	20.0

The results of the optimization experiments were statistically evaluated using a regression-based analysis of variance. The coded factor levels of initial pH, catalyst dosage, and oxidant dosage were used as independent variables, while contaminant degradation efficiency was used as the response variable. The significance of the overall model was assessed from the ANOVA output, and the contribution of each process parameter was evaluated based on the p-values of the regression coefficients. A significance level of $p < 0.05$ was applied.

In addition, one-way ANOVA was used to compare the complete experimental parameter combinations. Where relevant, pairwise Welch's t-tests were performed to identify differences between individual groups. For multiple comparisons, Bonferroni correction was applied.

4 RESULTS AND DISCUSSION

4.1 Characterization of the catalysts

4.1.1 BET

The BET results are summarized in Table 5. All synthesized materials exhibited mesoporous structures, with average pore widths between 11 and 13 nm. The specific surface area increased from CuO (34.7 m²/g) to Magnetite (47.6 m²/g), while the CuO/Magnetite composite exhibited the highest surface area (55.3 m²/g). The relatively high surface areas and mesoporous structures are beneficial for catalytic applications, as they provide a large number of accessible active sites and facilitate mass transfer of reactants. The increased surface area of the Composite further suggests successful integration of both catalyst components without significant pore blockage.

Table 5: Specific surface area and pore characteristics of CuO, Magnetite, and CuO/Magnetite composite determined by BET analysis.

	CuO	Magnetite	Composite
BET Surface Area (m²/g)	34.7	47.6	55.3
Pore volume (cm³/g)	0.174	0.153	0.150
Average pore width (nm)	13.2	12.1	11.6

4.1.2 TEM and SEM

TEM analysis (Figure 26) revealed that Magnetite consisted predominantly of quasi-spherical nanoparticles that formed agglomerated clusters, which is commonly observed for magnetic iron oxide materials due to magnetic interactions between particles.

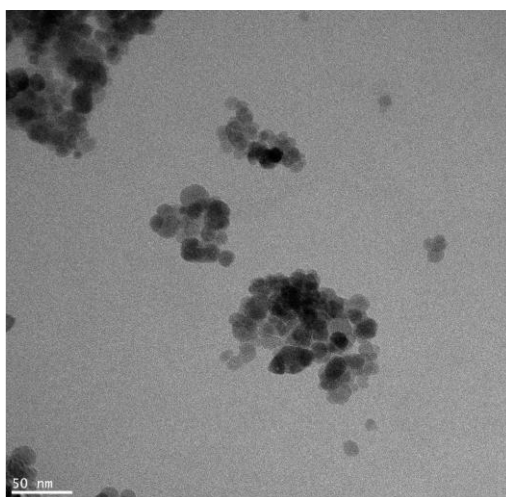


Figure 26: TEM image of Magnetite.

SEM images (Figure 27 and Figure 28) of the CuO/Magnetite composite revealed strongly agglomerated particles with rough and irregular surface morphologies. The porous appearance

observed in the SEM images is consistent with the mesoporous character identified by BET analysis. Although the individual CuO and Magnetite phases could not be visually distinguished, the observed morphology is consistent with successful composite formation.

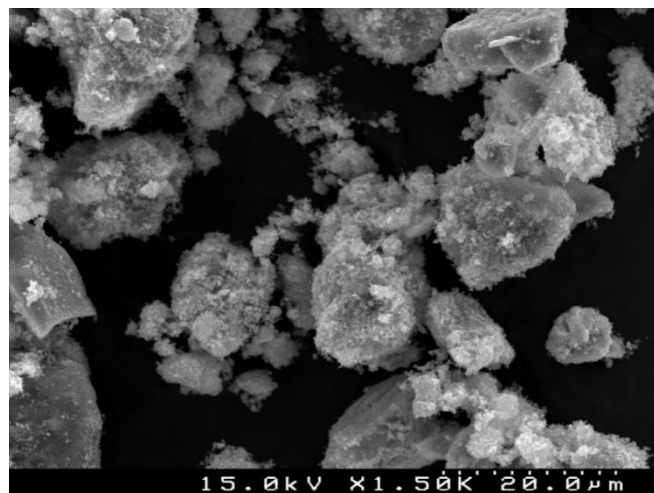


Figure 27: SEM image of CuO/Magnetite composite at 1.50k magnification.

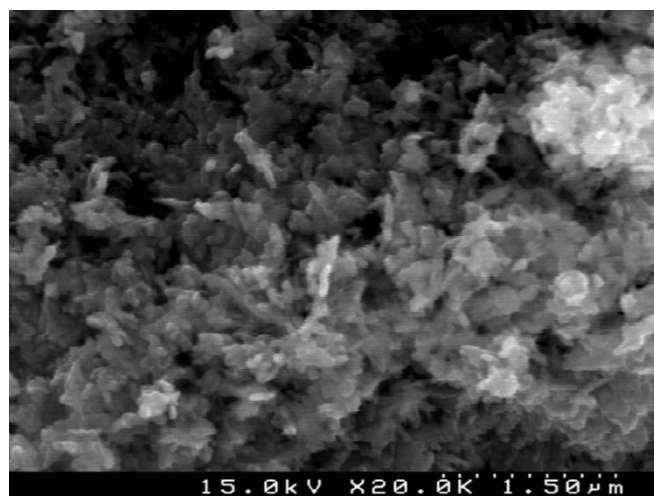


Figure 28: SEM image of CuO/Magnetite composite at 20.0k magnification.

4.1.3 XRD

The XRD diffractograms (Figure 29, Figure 30 and Figure 31) confirmed the successful synthesis of the targeted catalyst phases. Characteristic diffraction peaks corresponding to crystalline CuO were observed in the CuO sample, while the Magnetite diffractogram showed the typical reflections associated with crystalline Fe_3O_4 . No additional crystalline impurity phases were detected.

The CuO/Magnetite composite exhibited diffraction peaks originating from both CuO and Magnetite, confirming the presence of both phases within the synthesized material. The absence of additional diffraction peaks indicates that no significant crystalline impurities were formed during synthesis. These results demonstrate that the intended catalyst materials were successfully synthesized and retained their crystalline structures after composite formation.

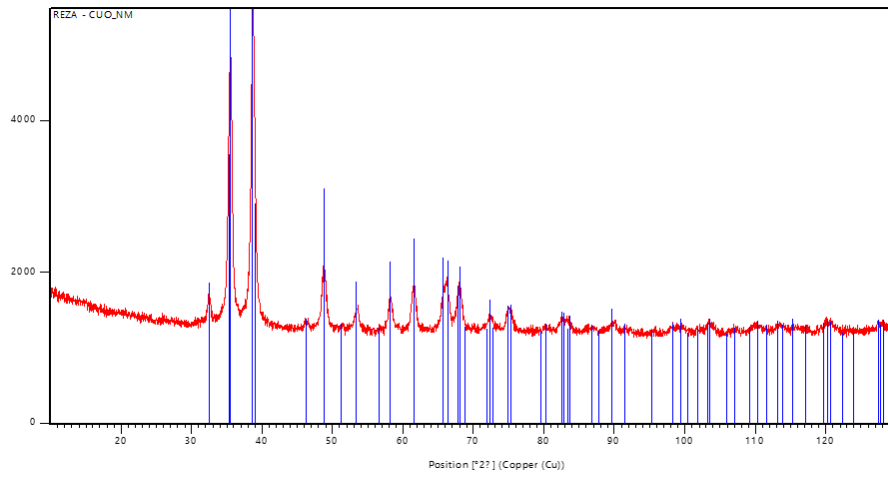


Figure 29: XRD diffractogram of CuO. The red diffractogram represents the experimentally measured sample, while the blue reference peaks correspond to the characteristic diffraction planes of CuO.

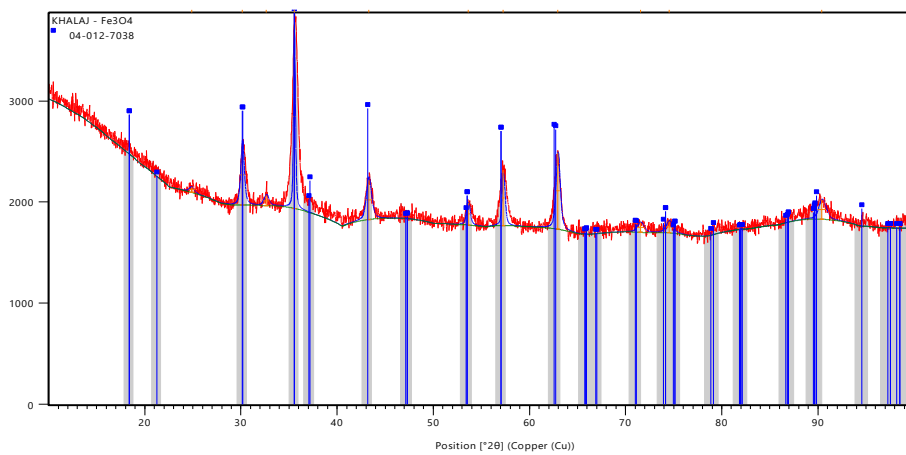


Figure 30: XRD diffractogram of Magnetite. The red diffractogram represents the experimentally measured sample, while the blue reference peaks correspond to the characteristic diffraction planes of Magnetite.

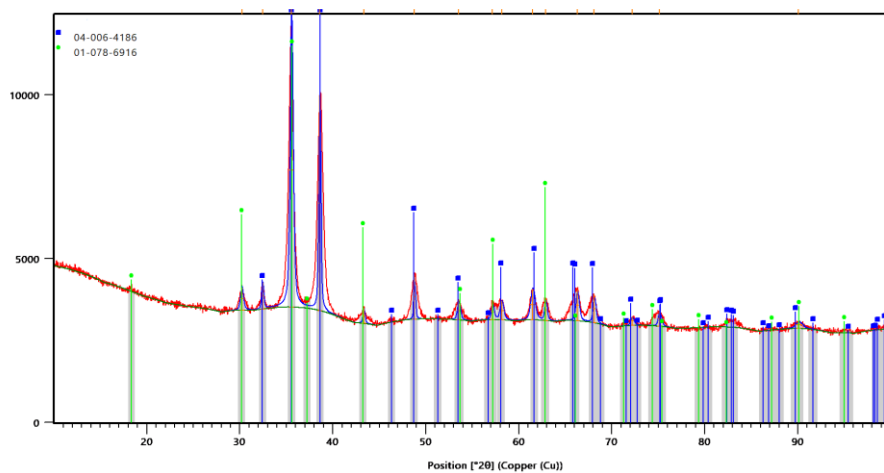


Figure 31: XRD diffractogram of CuO/Magnetite composite. The red diffractogram represents the experimentally measured sample, while the blue and green reference peaks correspond to the characteristic diffraction planes of CuO and Magnetite, respectively.

4.1.4 FT-IR

The FT-IR spectra (Figure 32, Figure 33 and Figure 34) confirmed the presence of the characteristic metal–oxygen vibrations associated with the synthesized catalyst materials. CuO exhibited the expected Cu–O absorption bands below 600 cm^{-1} , while Magnetite showed the characteristic Fe–O stretching vibrations in the $400\text{--}600\text{ cm}^{-1}$ region.

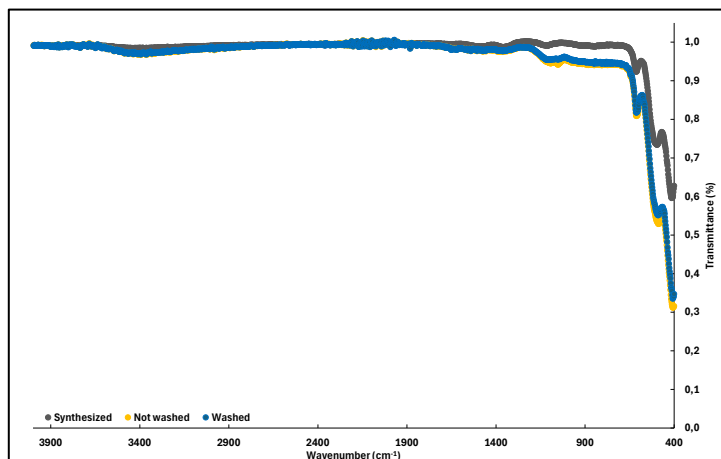


Figure 32: FT-IR spectra of CuO, comparing newly synthesized, not washed, and washed.

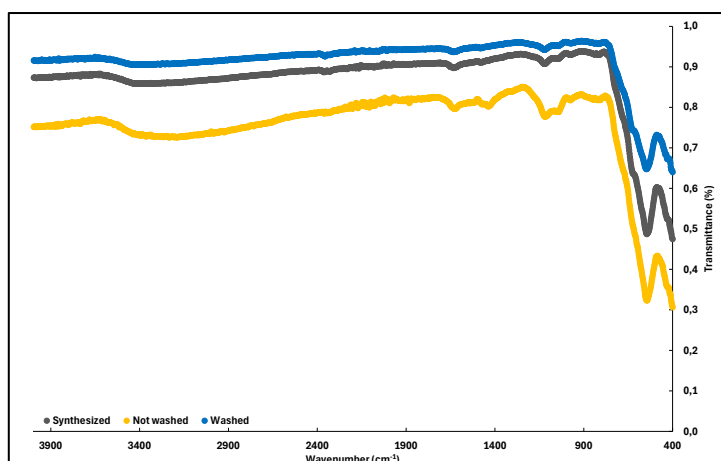


Figure 33: FT-IR spectra of Magnetite, comparing newly synthesized, not washed, and washed.

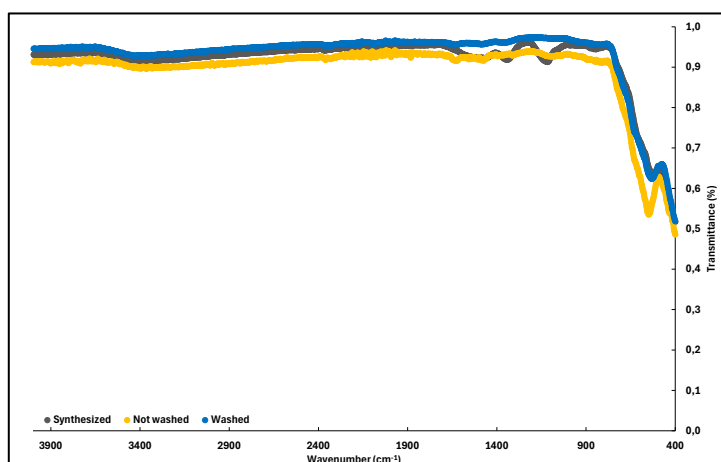


Figure 34: FT-IR spectra of CuO/Magnetite composite, comparing newly synthesized, not washed, and washed.

Comparison of the freshly synthesized, used, and washed catalysts revealed only minor differences in the FT-IR spectra. The characteristic Cu–O and Fe–O bands remained present after use, indicating that the catalyst structures were largely preserved during the degradation experiments. Additional broad bands observed around 3400 cm⁻¹ for some used samples may be attributed to adsorbed water, hydroxyl groups, or residual surface species. However, no major structural changes were observed.

The FT-IR results therefore suggest that the synthesized catalysts remained chemically stable throughout the performed degradation experiments.

4.1.5 Zeta potential

The zeta potential measurements were performed in 10 mM NaCl solution for all catalysts, both immediately after dispersion and after 24 h of equilibration. No significant differences were observed between these two conditions, indicating stable surface charge characteristics over time. For the selected catalyst, Magnetite, the zeta potential was additionally determined as a function of pH, with all measurements performed in triplicate (Table 6, Figure 35).

Table 6: Zeta potential values of the investigated catalysts and Magnetite at different pH conditions.

Average zeta potential (mV)	
CuO	26.367 ± 2.964
Composite	-24.550 ± 2.179
Magnetite	pH
	3.0
	18.067 ± 1.935
	3.9
	17.867 ± 1.380
	4.8
	17.567 ± 0.902
	7.0
	16.500 ± 1.082
	8.0
	1.667 ± 1.185
	10.0
	-25.567 ± 1.301

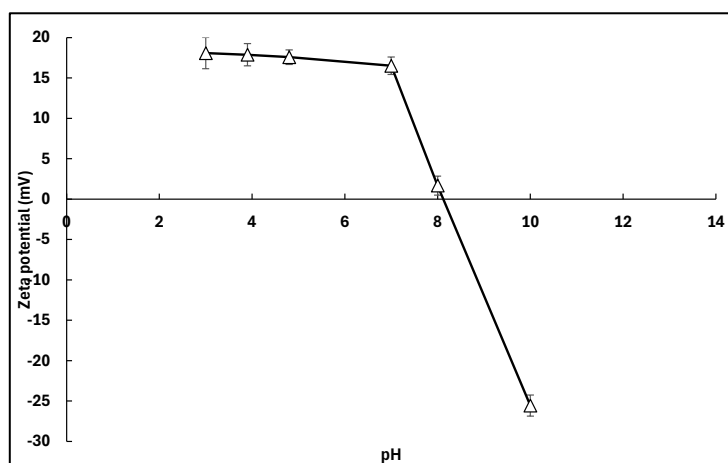


Figure 35: Zeta potential of Magnetite at different pHs.

The results demonstrate a strong pH dependence of the Magnetite surface charge. At acidic pH values, the Magnetite surface is positively charged, with zeta potential values around +18 mV at pH 3. This positive surface charge gradually decreases with increasing pH, approaching near-neutral conditions around pH 8, which corresponds to the point of zero charge (PZC). Above this pH, the surface becomes negatively charged, reaching approximately -25 mV at pH 10. Although the observed PZC ($\approx$ pH 8) is slightly higher than the commonly reported range for Magnetite (pH 6.0-7.5), such deviations can be attributed to differences in experimental conditions, including ionic strength, surface hydration, possible buffering effects of the material, or limited data density around the charge inversion region.

These surface charge variations have important implications for adsorption and PS activation. Under acidic conditions, the positively charged Magnetite surface enhances electrostatic attraction of negatively charged PS ions, potentially promoting PS activation and $\text{SO}_4^{\cdot-}$ generation (Silvestri et al., 2021). In this regime, electrostatic interactions with anionic PFAS such as PFOA are also influenced, potentially enhancing their approach to the catalyst surface, although steric and interfacial effects may still limit strong adsorption. For CIP, which exhibits pH-dependent speciation and can exist in cationic, zwitterionic, or anionic forms depending on the pH, electrostatic interactions will vary accordingly, with neutral to zwitterionic species expected to show reduced electrostatic repulsion and therefore more favorable surface interaction near neutral pH.

Near the PZC, where the surface charge approaches neutrality, adsorption of both oxidant species and organic contaminants is expected to be governed more by non-electrostatic interactions, such as hydrogen bonding and hydrophobic effects. Under alkaline conditions, the negatively charged Magnetite surface may hinder PS adsorption (Silvestri et al., 2021) and shift the oxidative pathway towards $\text{OH}^{\cdot}$ dominated mechanism. In addition, electrostatic repulsion of anionic species such as PFOA may reduce their surface association, whereas CIP speciation under these conditions is expected to be predominantly anionic, further limiting adsorption.

Overall, the zeta potential results provide key mechanistic insight into the observed pH-dependent degradation behavior, highlighting the role of surface charge in governing both reactant adsorption and radical generation pathways.

Overall, the BET, TEM/SEM, XRD, and FT-IR analyses confirmed the successful synthesis of CuO, Magnetite, and the CuO/Magnetite composite. The materials exhibited mesoporous structures, high surface areas, characteristic crystalline phases, and the expected chemical bonding environments. These properties indicate that the synthesized materials are suitable candidates for PS activation and sonocatalytic degradation experiments.

4.2 Baseline experiments

Baseline experiments were performed to evaluate the individual contribution of US, PS, and their combined application toward CIP degradation in the absence of a catalyst. These experiments establish a baseline for evaluating the contribution of US-assisted oxidant activation and for assessing the additional effect of catalyst incorporation during subsequent sonocatalytic experiments.

The degradation performance was evaluated by monitoring the normalized CIP concentration (C_t/C_0) as a function of reaction time during 1 h experiments. Lower C_t/C_0 values correspond to higher degradation efficiencies. The corresponding degradation efficiency was calculated as $(1 - C_t/C_0) \times 100\%$.

Figure 36 shows the evolution of the normalized CIP concentration during continuous stirring in the absence of US, PS, or catalyst addition. No decrease in CIP concentration was observed over the 1 h experimental period, indicating that CIP remained stable under the applied mixing conditions. This confirms that any concentration decrease observed in subsequent degradation experiments originates from oxidative degradation processes rather than from spontaneous degradation, volatilization, or adsorption to the reactor walls.

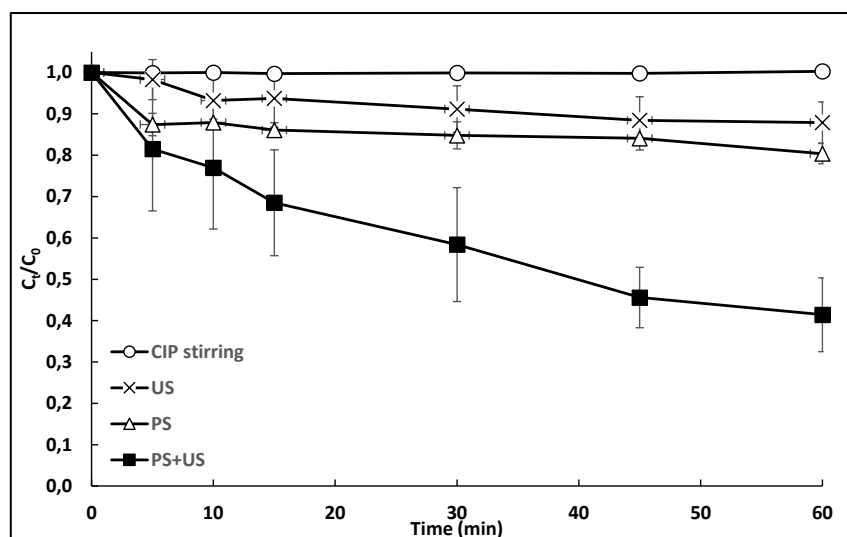


Figure 36: Evolution of the normalized CIP concentration during baseline experiments using stirring only, US, PS (15 mM), and the combined US/PS system. Experiments were performed for 1 h using an initial CIP concentration of 5 ppm.

Low-frequency US alone resulted in limited CIP degradation, with only $12.1 \pm 5.0\%$ removal after 1 h. The relatively low degradation efficiency suggests that cavitation-induced radical formation or pyrolytic-like reactions was insufficient to achieve extensive degradation of CIP under the applied operating conditions. Although acoustic cavitation can promote ROS formation through water sonolysis, the degradation efficiency observed in the absence of additional oxidants or catalytic activation pathways remained limited under the applied operating conditions. This suggests that US alone was not sufficient to achieve extensive pollutant degradation within the investigated reaction time. Further experiments, such as radical quenching tests, would be required to confirm the specific contribution of cavitation-induced radical formation. In addition, the practical relevance of prolonged US treatment should be evaluated together with the corresponding energy consumption.

PS alone (15 mM) resulted in a degradation efficiency of $19.6 \pm 2.4\%$ after 1 h. Although PS possesses a high oxidation potential after activation, its direct reaction with CIP remained relatively limited in the absence of external activation pathways.

Combining US with 15 mM PS significantly enhanced CIP degradation. The US/PS system achieved $58.6 \pm 8.9\%$ degradation after 1 h, demonstrating a clear synergistic effect between US and PS. The enhanced degradation can be attributed to cavitation-assisted activation of PS, resulting in the formation of highly reactive $SO_4^{\cdot-}$ and additional ROS. During cavitation bubble collapse, localized high temperatures and pressures promote PS decomposition and

accelerate radical generation, thereby substantially increasing the oxidative capacity of the system.

Despite the strong improvement, complete degradation was not achieved within the investigated reaction time. This behavior may partly be attributed to PS depletion during the reaction, radical recombination reactions, and sulfate radical scavenging at elevated oxidant concentrations. Nevertheless, the obtained baseline results are higher than those reported by Ma and Wang (2022), who observed only limited CIP removal using low-frequency US, PS, and US/PS. However, this comparison should be interpreted with caution, since their PS concentration was 1.5 mM, whereas 15 mM PS was used in the presented baseline experiments. Table 7 summarizes the degradation efficiencies and observed pseudo-first-order rate constants for the baseline experiments.

Table 7: Summary of degradation efficiencies and pseudo-first-order rate constants obtained during the baseline experiments.

System	Degradation efficiency (%)	Observed k-values (min ⁻¹)
US	12.1 ± 5.0	0.0021 ± 0.0009
PS	19.6 ± 2.4	0.0042 ± 0.0006
US/PS	58.6 ± 8.9	0.0143 ± 0.0014

The significantly higher degradation efficiency and observed k-value for the combined system confirms the existence of a synergistic interaction between US and PS. Nevertheless, the incomplete degradation obtained after 1 h indicates that additional improvements remain necessary. These results establish an important baseline for the subsequent sonocatalytic experiments. The addition of catalysts may further enhance PS activation, increase ROS generation, and improve overall degradation efficiency through combined cavitation and surface-mediated catalytic effects.

4.3 Experiments leading to catalyst selection

Prior to evaluating the removal performance of the investigated sonocatalysts, adsorption experiments were performed to determine the time required to reach adsorption-desorption equilibrium. Establishing this equilibrium is important to distinguish between pollutant removal due to adsorption and removal resulting from oxidative degradation during subsequent sonocatalytic experiments.

The performance of CuO, Magnetite, and a CuO/Magnetite composite was subsequently evaluated under US and PS activation conditions. These experiments were conducted to identify the most suitable catalyst for further optimization studies involving CIP and PFOA degradation.

Unless stated otherwise, all figures present the normalized CIP concentration (C_t/C_0) as a function of reaction time. In catalyst-containing systems, the observed removal represents the combined effect of adsorption and degradation, since only the parent compound concentration was monitored.

4.3.1 Adsorption

Preliminary adsorption experiments performed under static conditions showed only limited CIP adsorption on the investigated catalysts. Only CuO exhibited a moderate adsorption capacity of approximately 30%, while Magnetite and the CuO/Magnetite composite showed negligible adsorption. Since US treatment inherently promotes mixing and mass transfer, adsorption under stirred conditions was considered more representative for the subsequent degradation experiments.

Adsorption experiments were therefore performed using 5 ppm CIP and 1 g/L catalyst under continuous stirring at 350 rpm. Figure 37 shows the evolution of the normalized CIP concentration during the adsorption period.

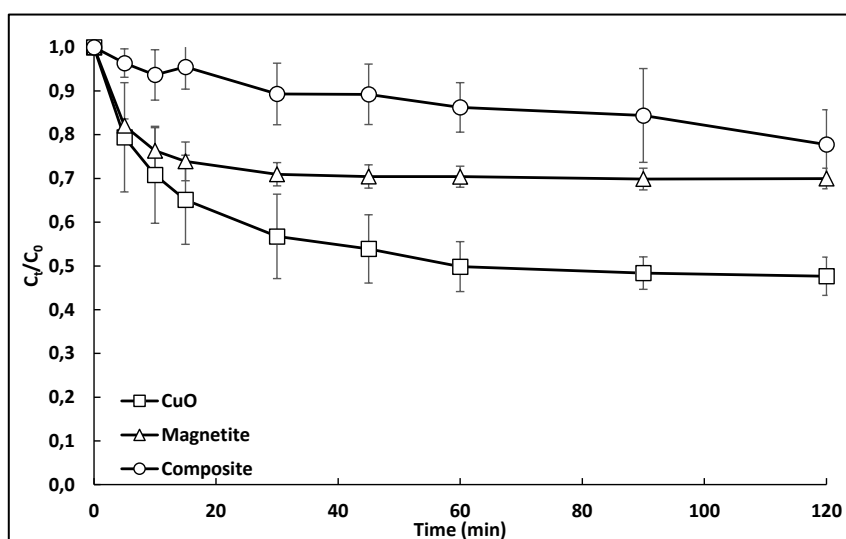


Figure 37: Adsorption of CIP (5 ppm) on CuO, Magnetite, and CuO/Magnetite composite (1 g/L) under continuous stirring.

The highest adsorption capacity was observed for CuO, which reached approximately 60% removal after 60 min. Magnetite exhibited a lower adsorption capacity of approximately 30%, but adsorption equilibrium was already reached after 30 min. The CuO/Magnetite composite showed intermediate adsorption behavior, although relatively large error bars were observed, indicating lower reproducibility compared to the individual catalysts.

Based on these results, an adsorption period of 60 min was applied for CuO and the CuO/Magnetite composite prior to degradation experiments, whereas 30 min was considered sufficient for Magnetite.

4.3.2 Ultrasound in the presence of catalysts

The performance of the investigated catalysts under US was evaluated in the absence of PS. Figure 38 presents the removal of CIP obtained with US and catalyst addition.

Overall, only limited CIP removal was observed for all catalysts, indicating that catalyst addition alone was insufficient to substantially enhance degradation under the applied US conditions. Magnetite showed the highest removal efficiency and the highest observed pseudo-first-order rate constant ($k = 0.0051 \text{ min}^{-1}$), followed by the CuO/Magnetite composite ($k = 0.0045 \text{ min}^{-1}$) and CuO ($k = 0.0011 \text{ min}^{-1}$).

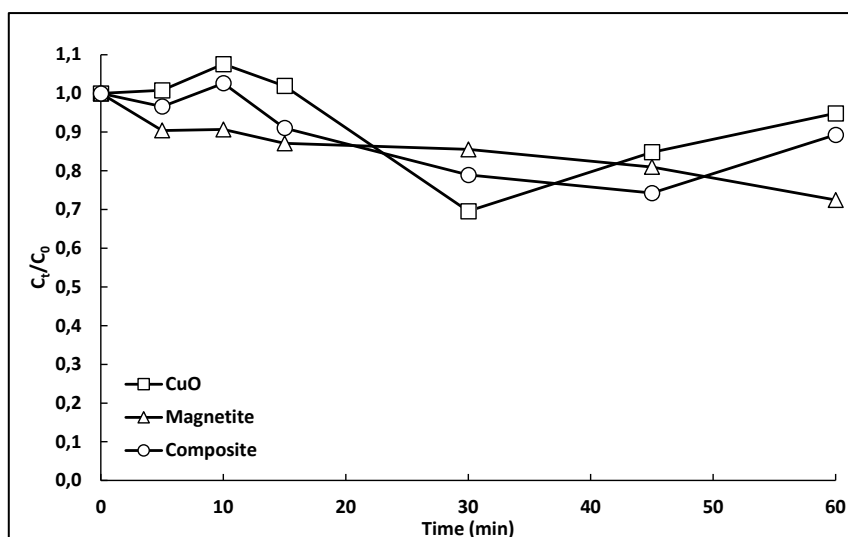


Figure 38: Removal of CIP (5 ppm) using US in the presence of CuO, Magnetite, and CuO/Magnetite composite (1 g/L).

Some fluctuations in the normalized CIP concentration profiles were observed, especially in cases where the overall removal was limited. These variations are most likely related to experimental or analytical variability, such as sampling, catalyst separation, filtration, or temporary adsorption-desorption interactions between CIP and the catalyst surface. Under US, these adsorption-desorption dynamics may be further influenced by enhanced mixing, particle dispersion, and cavitation-induced surface renewal.

The relatively low removal efficiencies suggest that US alone generated insufficient reactive species for extensive CIP degradation. This is in line with Hou et al. (2011), who reported only limited tetracycline degradation using US/Magnetite in the absence of PS, while substantially higher degradation was obtained when PS was added. Although this comparison involves a different pollutant and a higher initial pollutant concentration, it supports the importance of combining sonocatalysis with PS activation to achieve high degradation efficiencies.

4.3.3 Persulfate activation by catalysts

Initial experiments performed using 15 mM PS resulted in nearly complete CIP removal within the first sampling interval for all investigated catalysts. Although these results confirmed the strong PS activation capacity of the catalysts, the reaction proceeded too rapidly to allow meaningful comparison of degradation kinetics. Therefore, lower PS concentrations were investigated.

Figure 39 compares the degradation performance obtained using 1 mM PS for all catalysts and 0.5 mM PS for Magnetite. Under these conditions, CuO and Magnetite achieved respectively $96.4 \pm 3.7\%$ and $96.7 \pm 0.7\%$ CIP removal after 60 min, while the CuO/Magnetite composite reached $84.1 \pm 4.7\%$ removal. The corresponding pseudo-first-order rate constants were $0.0589 \pm 0.0380 \text{ min}^{-1}$ for CuO, $0.1374 \pm 0.1509 \text{ min}^{-1}$ for Magnetite, and $0.0241 \pm 0.0027 \text{ min}^{-1}$ for the Composite. A similarly high CIP degradation efficiency using CuO-activated PS was reported by Xing et al. (2019), who observed nearly complete CIP removal using 1 mM PS, confirming the ability of CuO to effectively activate PS for CIP degradation.

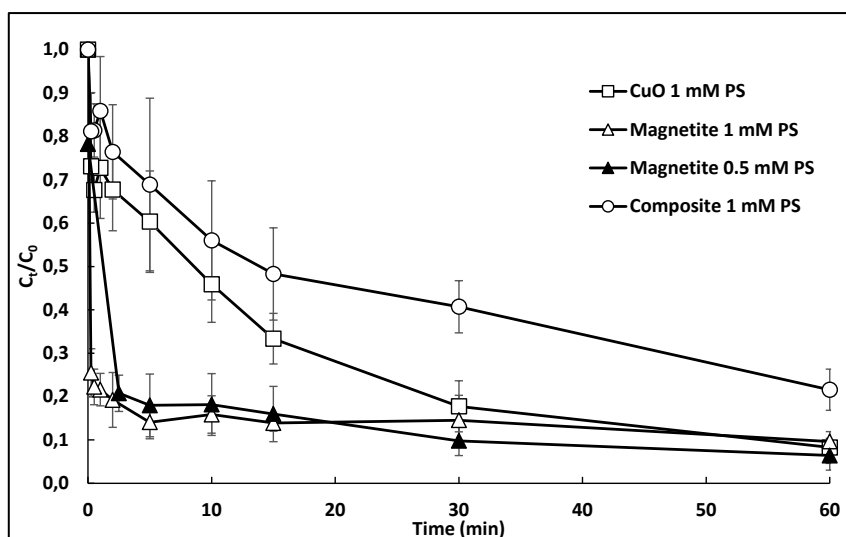


Figure 39: Effect of PS (1 and 0.5 mM) and catalysts (1 g/L) on the removal of CIP (10 ppm).

To further evaluate the PS activation efficiency of Magnetite, the PS concentration was reduced to 0.5 mM. Despite the lower oxidant dosage, Magnetite still achieved $93.5 \pm 3.4\%$ removal, confirming its strong PS activation capability even under less favorable operating conditions.

4.3.4 Catalyst selection: Magnetite

The performed experiments demonstrated that all investigated catalysts were capable of activating PS and promoting CIP degradation. However, important differences were observed in terms of degradation efficiency, reproducibility, catalyst handling, and practical applicability.

The CuO/Magnetite composite showed the least favorable performance, exhibiting lower degradation efficiencies and larger experimental variability compared to the individual catalysts. Although CuO achieved final degradation efficiencies comparable to Magnetite, its degradation proceeded more slowly, and its performance did not exceed that of Magnetite under any of the investigated conditions.

Magnetite consistently showed the most favorable overall behavior. In the US-only experiments, Magnetite achieved the highest degradation rate among the investigated catalysts. Under PS activation conditions, Magnetite achieved removal efficiencies comparable to CuO while maintaining high performance even when the PS concentration was reduced from 1.0 to 0.5 mM. This demonstrates the strong PS activation capability of Magnetite and suggests efficient ROS generation. Similar observations have been reported in the literature, where Magnetite effectively activated PS for the degradation of norfloxacin, a structurally related fluoroquinolone antibiotic, achieving degradation efficiencies exceeding 90% within 60 min. The authors attributed this performance to efficient generation of sulfate and hydroxyl radicals through Fe(II)-mediated PS activation pathways (Ding et al., 2016).

In addition to its degradation performance, Magnetite offers several practical advantages. The material can be synthesized easily and at relatively low cost, exhibits excellent magnetic separability, and has been widely reported in the literature as an effective catalyst for PS activation and pollutant degradation. Based on both experimental results and practical considerations, Magnetite was selected as the most suitable catalyst for the subsequent optimization experiments involving CIP and PFOA degradation.

4.4 Optimization of process parameters for enhanced CIP degradation

Following catalyst selection, the complete US/PS/Magnetite system was optimized for CIP degradation. Three process parameters were investigated: initial pH (4-10), catalyst dosage (0.1-1.0 g/L), and oxidant dosage (0.1-2.5 mM). The selected experimental conditions are summarized in Table 8.

Prior to each degradation experiment, the solution pH was adjusted using HCl or NaOH and the catalyst was allowed to equilibrate with the CIP solution for 30 min to establish adsorption-desorption equilibrium. In addition to CIP removal, defluorination and mineralization efficiencies were evaluated using IC and TOC analysis, respectively.

4.4.1 CIP degradation

The degradation profiles obtained under the five investigated operating conditions are summarized in Figure 40, while the corresponding degradation efficiencies and observed pseudo-first-order rate constants are presented in Table 8.

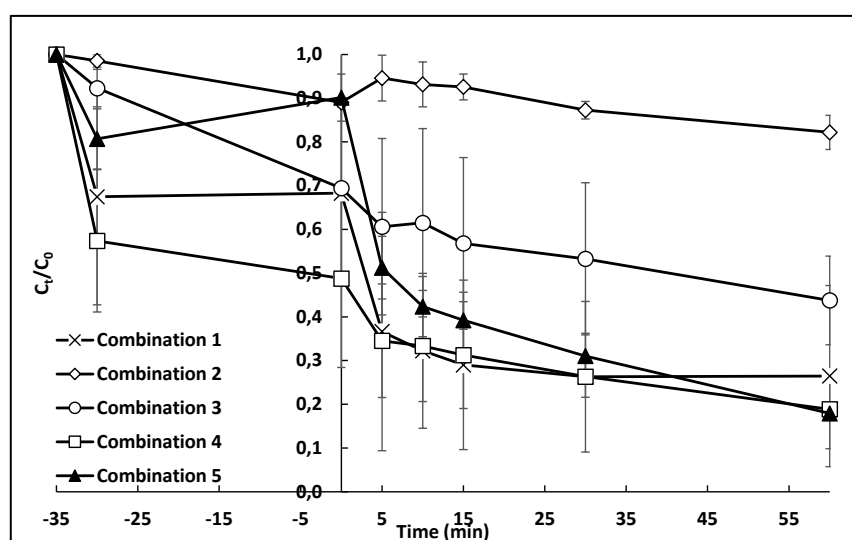


Figure 40: Degradation profiles of CIP under the five investigated operating conditions.

Table 8: Experimental combinations of process parameters for enhanced CIP degradation, including corresponding removal efficiencies and observed pseudo-first-order rate constants.

Nr.	Initial pH (l)	Catalyst dosage (g/L)	Oxidant dosage (mM)	Removal (%)	Observed k-value (min ⁻¹)
1	4	1.00	0.1	73.5 ± 20.7	0.0204 ± 0.0099
2	10	0.10	0.1	17.8 ± 3.5	0.0022 ± 0.0004
3	10	1.00	2.5	56.2 ± 10.1	0.0070 ± 0.0028
4	7	0.55	1.3	81.1 ± 0.4	0.0131 ± 0.0082
5	4	0.10	2.5	82.1 ± 8.1	0.0280 ± 0.0154

A clear influence of the initial solution pH on CIP degradation was observed. Both alkaline conditions (pH 10, conditions 2 and 3) resulted in substantially lower degradation efficiencies compared to the acidic and neutral conditions. The lowest degradation efficiency was obtained for condition 2 ($17.8 \pm 3.5\%$), whereas conditions both 4 and 5 achieved removals exceeding 80%.

Among the investigated conditions, condition 5 (pH 4, 0.1 g/L Magnetite, 2.5 mM PS) exhibited the highest observed rate constant and consistently high degradation performance. Condition 4 (pH 7, 0.55 g/L Magnetite, 1.3 mM PS) achieved a comparable removal efficiency while requiring less oxidant and no pH adjustment.

The results indicate that efficient CIP degradation can be achieved under both acidic and neutral conditions, whereas alkaline conditions are considerably less favorable.

4.4.2 Influence of process parameters

As a first step, the relative influence of the investigated process parameters was evaluated using a regression-based ANOVA performed on the coded experimental design. The model included initial pH, catalyst dosage, and oxidant dosage as independent variables, with CIP degradation efficiency as the response variable. The overall regression model was statistically significant (Significance F = 0.00136), indicating that the investigated parameters explained a significant part of the variation in CIP degradation. The model showed an R^2 value of 0.777, meaning that approximately 77.7% of the variability in degradation efficiency was explained by the selected process parameters.

The regression analysis showed that initial pH had the strongest influence on CIP degradation. A significant negative effect was obtained for initial pH (coefficient = -20.79, $p = 0.00068$), indicating that increasing the pH from acidic to alkaline conditions reduced degradation efficiency. Oxidant dosage also showed a significant positive effect (coefficient = 12.14, $p = 0.0179$), whereas catalyst dosage showed a positive but statistically non-significant effect at the 95% confidence level (coefficient = 7.86, $p = 0.0971$). Based on the absolute regression coefficients, the relative influence of the investigated parameters followed the order: initial pH > oxidant dosage > catalyst dosage.

As shown in Figure 41, the effect of initial pH was clearly reflected in the experimental results. Lower degradation efficiencies were obtained at pH 10 compared with pH 4 and pH 7. A grouped one-way ANOVA confirmed a significant difference between the investigated pH levels ($p = 0.00199$). Pairwise Welch's t-tests with Bonferroni correction showed no significant difference between pH 4 and pH 7, whereas pH 10 differed significantly from both pH 4 and pH 7. These results indicate that acidic and neutral conditions resulted in comparable CIP removal efficiencies, while alkaline conditions were significantly less favorable.

This behavior can be explained by the pH-dependent surface charge of Magnetite and the corresponding changes in radical chemistry. Zeta potential measurements demonstrated that Magnetite possessed a positive surface charge under acidic conditions, became closer to neutral around pH 7, and exhibited a negative surface charge under alkaline conditions. Under acidic conditions, the positively charged Magnetite surface can promote the adsorption and activation of negatively charged PS ions, enhancing sulfate radical generation. In contrast, under alkaline conditions sulfate radicals are progressively converted into hydroxyl radicals, while electrostatic interactions between Magnetite and PS become less favorable.

These observations are consistent with the radical quenching experiments, which identified sulfate radicals as the dominant oxidizing species at pH 4, a mixed sulfate/hydroxyl radical system at pH 7, and predominantly hydroxyl radical-driven degradation at pH 10. The superior degradation observed at acidic and neutral pH therefore appears to be closely related to more efficient PS activation and sulfate radical generation.

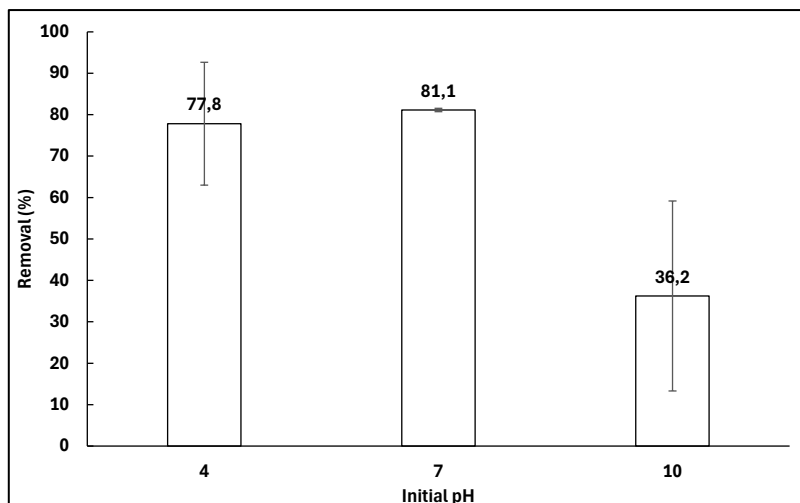


Figure 41: Influence of initial pH on CIP removal.

The influence of catalyst dosage (Figure 42) was considerably smaller than that of pH. This was confirmed by the regression analysis, where catalyst dosage showed no statistically significant effect on CIP degradation within the investigated range ($p = 0.0971$). A grouped one-way ANOVA also showed no significant difference between the investigated catalyst dosages ($p = 0.344$). Although differences in average removal efficiency were observed between catalyst dosages, these differences were not statistically significant. These results suggest that even the lowest investigated catalyst dosage provided sufficient active sites for PS activation and CIP degradation. Increasing the catalyst dosage therefore did not result in a statistically significant improvement in degradation performance, indicating that catalyst dosage was not the limiting factor within the investigated operating window.

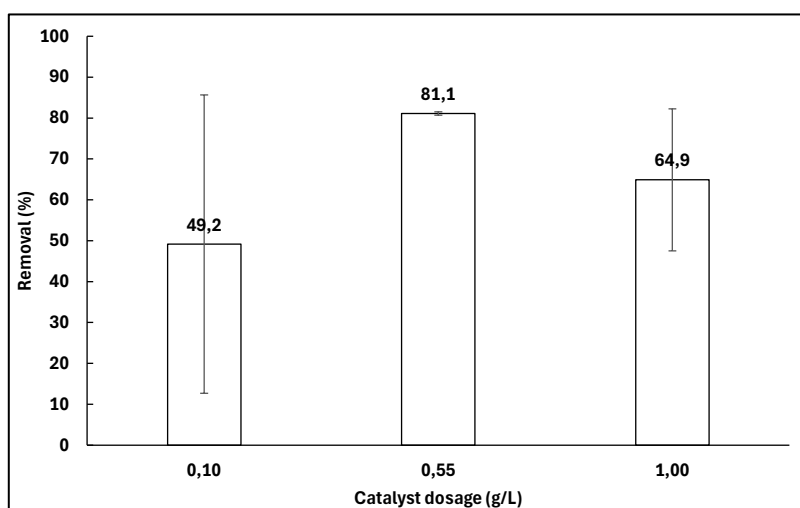


Figure 42: Influence of catalyst dosage on CIP removal.

The effect of oxidant dosage is shown in Figure 43. The regression analysis indicated that oxidant dosage had a significant positive effect on CIP degradation ($p = 0.0179$), suggesting

that increasing the oxidant dosage contributed to improved degradation efficiency. However, when the results were grouped only by oxidant dosage, one-way ANOVA did not show a significant difference between the dosage levels ($p = 0.201$), and the pairwise comparisons were not significant. This difference can be attributed to the simultaneous variation of pH and catalyst dosage within the experimental design. Therefore, the regression-based analysis is considered more appropriate for evaluating the individual contribution of oxidant dosage, as it accounts for the combined influence of all investigated parameters.

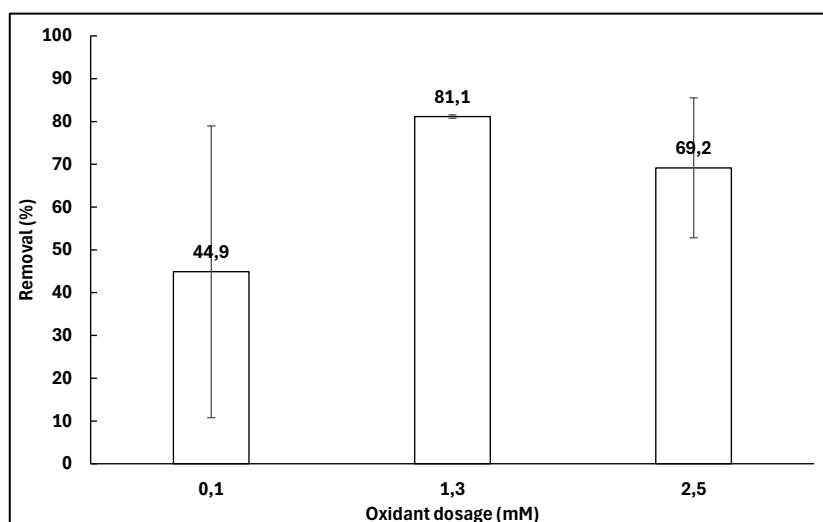


Figure 43: Influence of oxidant dosage on CIP removal.

Overall, the statistical analysis confirmed that initial pH was the dominant parameter controlling CIP degradation in the US/PS/Magnetite system. Oxidant dosage also contributed significantly to the degradation efficiency, whereas catalyst dosage had a comparatively smaller and statistically non-significant effect within the investigated range.

4.4.3 Contribution of adsorption and degradation

Figure 44 distinguishes the contribution of adsorption and degradation to the overall CIP removal. This distinction is important because adsorption merely transfers the pollutant from the aqueous phase to the catalyst surface, whereas degradation results in chemical transformation of the contaminant.

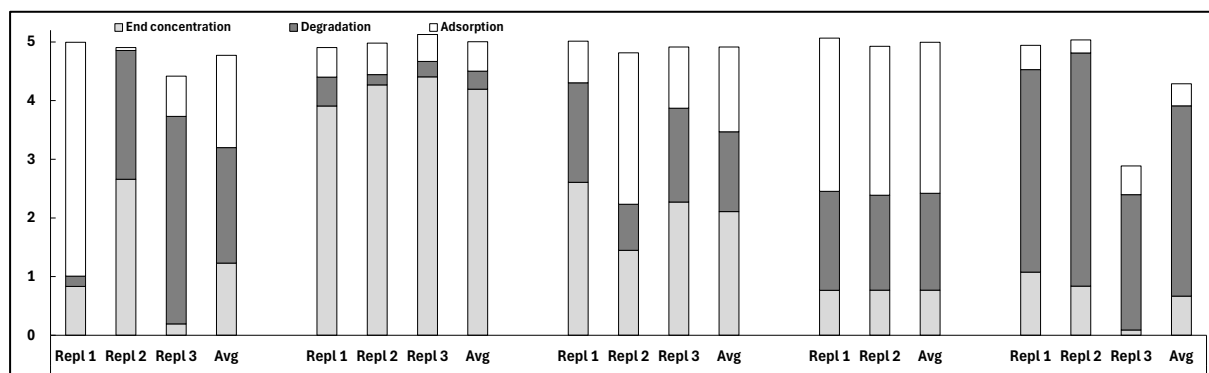


Figure 44: Contribution of adsorption and degradation of CIP for each condition.

The highest adsorption contribution was observed under neutral conditions (condition 4). This can be explained by the speciation of CIP and the surface charge of Magnetite. Around neutral

pH, CIP predominantly exists in its zwitterionic form, while Magnetite possesses a near-neutral surface charge. These conditions favor adsorption interactions between the pollutant and catalyst surface.

In contrast, adsorption was less pronounced at pH 4. Under acidic conditions both CIP and Magnetite are positively charged, resulting in electrostatic repulsion and reduced adsorption. Despite the lower adsorption, degradation remained highly efficient, indicating that enhanced PS activation and sulfate radical generation compensated for the reduced adsorption capacity.

4.4.4 Defluorination

Defluorination efficiency was evaluated based on the F^- concentration measured at the end of the degradation experiments. Fluoride release is an important indicator of C–F bond cleavage and therefore provides information beyond the disappearance of the parent CIP molecule. The defluorination efficiencies obtained under the investigated conditions are presented in Figure 45. Overall, relatively low defluorination efficiencies were observed for all conditions. The highest apparent defluorination was obtained for condition 5 (pH 4, 0.1 g/L Magnetite, 2.5 mM PS), which was also identified as the most effective condition for CIP degradation.

The generally low defluorination efficiencies suggest that, although CIP degradation occurred, complete removal of the fluorinated part of the molecule was limited within the investigated reaction time. In addition, the maximum theoretical fluoride concentration resulting from complete defluorination of 5 ppm CIP is only approximately 0.286 mg/L. Such low fluoride concentrations are close to the detection limit of the analytical method and may contribute to increased measurement uncertainty.

Consequently, the defluorination results should be interpreted primarily as qualitative indicators of C–F bond cleavage rather than as precise quantitative values. A one-way ANOVA was performed to evaluate whether the apparent defluorination differed significantly between the investigated conditions. No statistically significant differences were observed at $\alpha = 0.05$ ($p = 0.158$), indicating that the observed differences should be interpreted with caution. Nevertheless, the higher apparent defluorination observed under acidic conditions follows the same trend as the degradation results and is therefore consistent with the superior degradation performance obtained for condition 5.

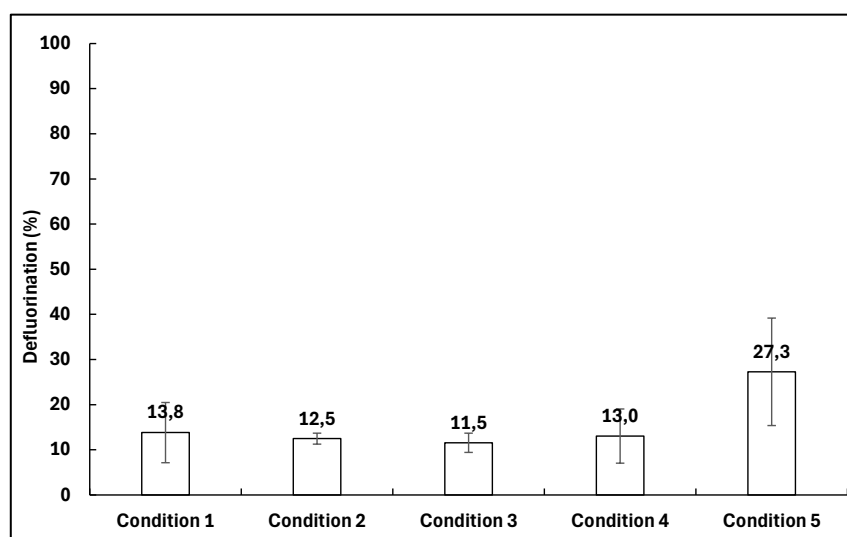


Figure 45: Defluorination efficiency under each condition for the optimization CIP removal.

4.4.5 Mineralization

Mineralization was assessed using TOC analysis and provides information on the extent to which the organic carbon present in CIP was converted into inorganic carbon species. In contrast to degradation, which only reflects the disappearance of the parent compound, mineralization is a more stringent indicator of treatment efficiency.

The mineralization results obtained under the investigated conditions are shown in Figure 46. The highest apparent mineralization was observed for condition 5, which is in agreement with the degradation and defluorination results. However, the reliability of the TOC measurements should be interpreted with caution.

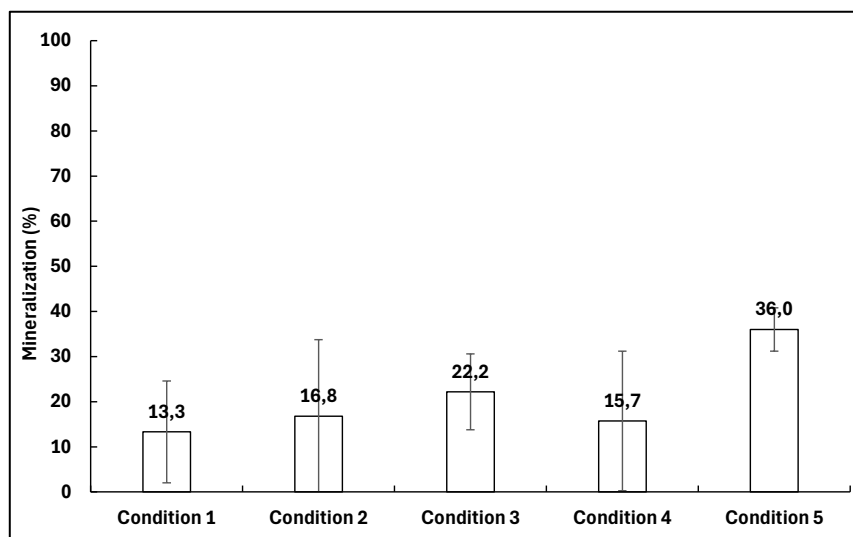


Figure 46: Mineralization efficiency under each condition for the optimization of CIP removal.

At a CIP concentration of 5 ppm, the theoretical carbon concentration corresponds to only approximately 3.08 mg C/L. This value was calculated from the molecular formula of CIP ($C_{17}H_{18}FN_3O_3$), by multiplying the initial CIP concentration by the carbon mass fraction of the molecule: $5 \text{ mg}_{\text{CIP}}/\text{L} \times [(17 \times 12.01 \text{ g}_C/\text{mol}) / 331.34 \text{ g}_{\text{CIP}}/\text{mol}]$. Furthermore, the samples required a tenfold dilution prior to analysis to satisfy instrument requirements, resulting in very low carbon concentrations being measured. In addition, residual PS, quenching agents, and dissolved inorganic species may have introduced matrix effects that influenced the TOC measurements.

As a result, the absolute mineralization values reported in Figure 46 may not accurately reflect the true extent of mineralization. A one-way ANOVA was performed to evaluate whether the apparent mineralization differed significantly between the investigated conditions. No statistically significant differences were observed at $\alpha = 0.05$ ($p = 0.258$), indicating that the differences between the conditions should be interpreted with caution. Therefore, the higher apparent mineralization observed for condition 5 cannot be considered a statistically confirmed improvement. Nevertheless, this trend is consistent with the degradation and defluorination results, as condition 5 also showed the highest CIP degradation efficiency and apparent defluorination.

To confirm these observations, future studies should employ higher initial pollutant concentrations and complementary analytical techniques, such as identification of transformation products by mass spectrometry.

4.4.6 Summary of optimal conditions

Based on the degradation, defluorination and mineralization results, condition 5 (pH 4, 0.1 g/L Magnetite, 2.5 mM PS) was identified as the most effective operating condition for CIP removal. This condition achieved high degradation efficiency while also providing the highest apparent defluorination and mineralization performance.

Nevertheless, condition 4 (pH 7, 0.55 g/L Magnetite, 1.3 mM PS) achieved comparable degradation while operating at a more environmentally relevant pH and requiring less chemical adjustment. As many wastewater and sludge streams are naturally near neutral pH, this condition may represent a more practical option for future applications.

Overall, the results demonstrate that solution pH was the dominant parameter controlling CIP degradation in the US/PS/Magnetite system. This was confirmed by the regression-based ANOVA, which showed a significant negative effect of initial pH on degradation efficiency. Oxidant dosage also contributed significantly to the response, whereas catalyst dosage did not show a statistically significant effect within the investigated range. In addition, grouped comparison of the pH levels showed that pH 10 resulted in significantly lower degradation than pH 4 and pH 7, while no significant difference was observed between acidic and neutral conditions.

4.5 Optimization of process parameters for enhanced PFOA degradation

4.5.1 Degradation performance

Unlike the CIP experiments, only a limited optimization study could be performed for PFOA degradation due to the long analytical turnaround times associated with PFAS analysis. Therefore, the objective of this section was not to fully optimize the process, but rather to identify preliminary trends and promising operating conditions for further investigation.

The combinations of process parameters investigated for PFOA degradation are summarized in Table 9, while the corresponding removal efficiencies are presented in Figure 47.

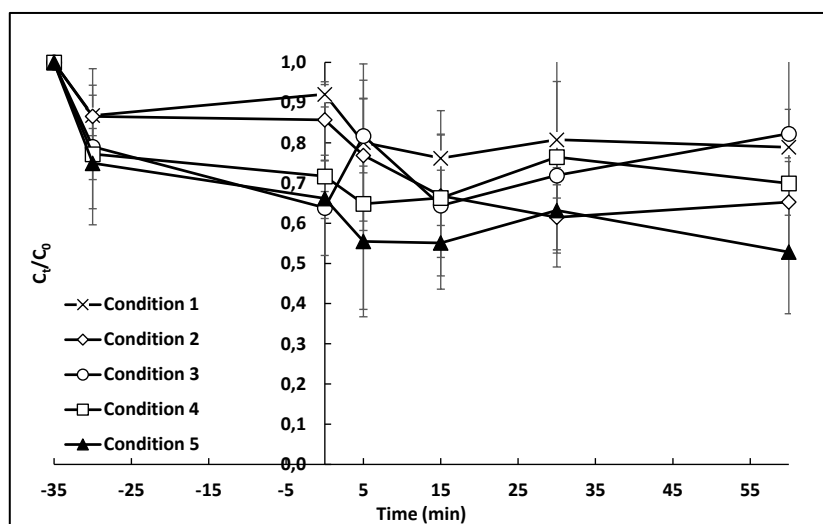


Figure 47: Degradation profiles of PFOA under the five investigated operating conditions.

Table 9: Experimental combinations of process parameters for optimizing PFOA (1 ppm) degradation, including corresponding removal efficiencies and observed pseudo-first-order rate constants.

Nr.	pH (/)	Catalyst dosage (g/L)	Oxidant dosage (mM)	Removal (%)	Observed k-value (min ⁻¹)
1	10	0.5	5.0	21.1 ± 27.1	-0.0002 ± 0.0006
2	10	1.5	20.0	34.7 ± 3.3	0.0159 ± 0.0119
3	4	1.5	5.0	17.7 ± 6.0	-0.0055 ± 0.0074
4	7	1.0	12.5	30.1 ± 5.4	0.0004 ± 0.0060
5	4	0.5	20.0	47.2 ± 15.3	0.0031 ± 0.0099

Among the investigated conditions, condition 5 (pH 4, 0.5 g/L Magnetite, 20 mM PS) achieved the highest PFOA removal of 47.2 ± 15.3%. In contrast, condition 3 (pH 4, 1.5 g/L Magnetite, 5 mM PS) resulted in the lowest removal efficiency of 17.7 ± 6.0%. However, the relatively large standard deviation observed for condition 5 indicates that the apparent improvement should be interpreted with caution.

Overall, the effect of initial pH (Figure 48) appeared limited compared to the trends observed for CIP degradation. Average removals remained within a similar range for pH 4, 7 and 10, suggesting that PFOA degradation was less sensitive to changes in solution pH under the investigated conditions. This was confirmed by the one-way ANOVA performed for the different pH levels, which showed no statistically significant effect of pH on PFOA removal ($p = 0.974$).

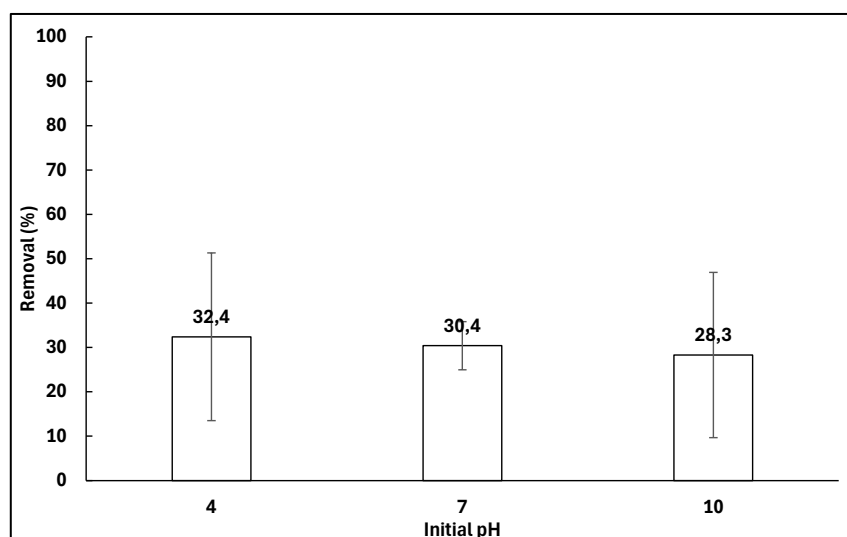


Figure 48: Influence of initial pH on PFOA removal.

The catalyst dosage (Figure 49) showed a slight negative trend, as increasing the catalyst dosage from 0.5 to 1.5 g/L did not improve degradation and was associated with somewhat lower average removal efficiencies. This may be related to particle agglomeration, shielding of ultrasonic waves, or radical scavenging at excessive catalyst dosages. However, statistical analysis did not confirm a significant effect of catalyst dosage on PFOA removal ($p = 0.929$).

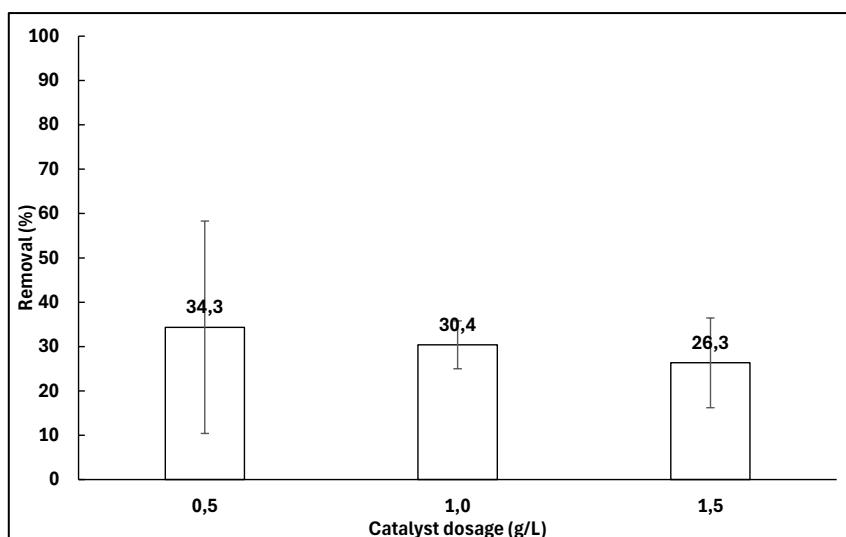


Figure 49: Influence of catalyst dosage on PFOA removal.

The oxidant dosage (Figure 50) showed a more pronounced, although not statistically significant, trend. Increasing the oxidant dosage from 5 to 20 mM PS resulted in higher average PFOA removal efficiencies, increasing from $19.9 \pm 17.7\%$ at 5 mM PS to $40.74 \pm 11.9\%$ at 20 mM PS. This observation may be related to the highly recalcitrant nature of PFOA, for which extensive radical generation is required to initiate degradation and C–F bond cleavage. Nevertheless, the one-way ANOVA for oxidant dosage showed that this trend was not statistically significant ($p = 0.186$).

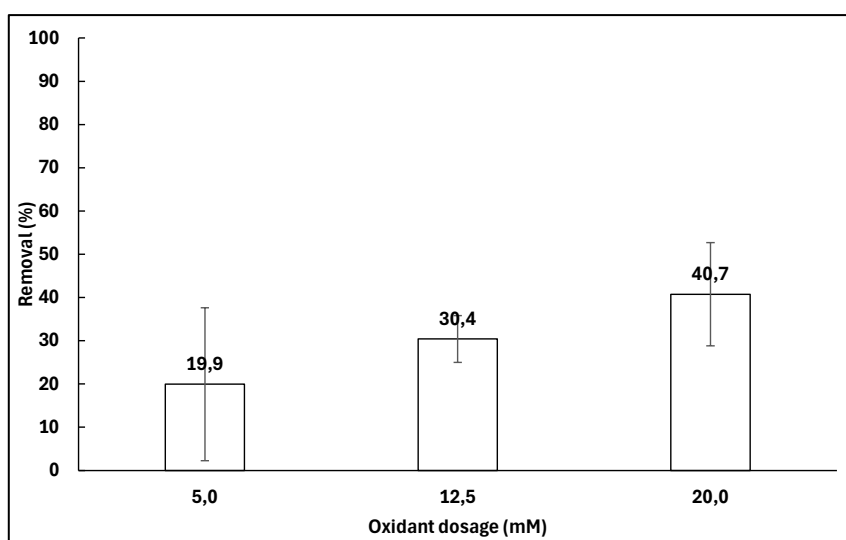


Figure 50: Influence of oxidant dosage on PFOA removal.

Overall, the parameter-based ANOVA results showed no statistically significant effect of pH, catalyst dosage, or oxidant dosage on PFOA removal. Therefore, the observed trends should be interpreted as preliminary indications rather than statistically confirmed effects.

4.5.2 Defluorination

Defluorination is considered one of the most important indicators of PFAS degradation, as it directly reflects cleavage of the highly stable C–F bonds. However, reliable quantification of defluorination was not possible within the scope of this study.

At the applied PFOA concentration of 1 mg/L, complete defluorination would theoretically yield only approximately 0.688 mg/L fluoride. Considering the low pollutant concentration and the expected partial defluorination, the resulting fluoride concentrations were likely close to the detection and quantification limits of the analytical method.

Consequently, the measured fluoride concentrations did not allow reliable determination of defluorination efficiencies. Future studies should employ higher initial PFOA concentrations or more sensitive fluoride quantification methods to accurately assess C–F bond cleavage.

4.5.3 Mineralization

Mineralization was evaluated using TOC analysis. However, interpretation of the obtained results was complicated by the extremely low carbon concentration associated with the applied PFOA dosage.

At a PFOA concentration of 1 mg/L, the theoretical carbon concentration corresponds to only approximately 0.232 mg C/L. Furthermore, all samples were diluted tenfold prior to analysis to satisfy instrument requirements, resulting in even lower carbon concentrations during measurement.

The measured TOC values showed considerable variability and exceeded the theoretical maximum carbon concentration initially present in the samples. This indicates that matrix effects, analytical uncertainty, or interference from residual reagents may have significantly influenced the measurements.

Therefore, no reliable conclusions regarding mineralization efficiency can be drawn from the obtained TOC data. Future studies should employ higher pollutant concentrations and complementary analytical techniques, such as identification of transformation products by LC-MS/MS, to better assess the extent of PFOA mineralization.

4.5.4 Summary

Within the investigated experimental domain, condition 5 (pH 4, 0.5 g/L Magnetite, and 20 mM PS) showed the highest average PFOA removal efficiency and was therefore considered the most promising condition. However, statistical analysis showed that this condition was not significantly different from the other tested conditions, as confirmed by one-way ANOVA ($p = 0.237$).

The multiple linear regression model was not statistically significant (Significance $F = 0.366$), and none of the individual parameters showed a significant effect on PFOA removal. In addition, the low adjusted R^2 value of 0.039 indicated that only a limited fraction of the experimental variability could be explained by the model. Although higher PS concentrations appeared to improve PFOA removal, this trend was not statistically significant.

Because reliable defluorination and mineralization data could not be obtained, the extent of actual PFOA destruction could not be fully assessed. Therefore, these results should be regarded as preliminary, and additional experiments with more replicates are required to confirm the observed trends and further optimize the process.

4.6 Radical quenching experiments for identification of dominant reactive species for CIP degradation

Radical quenching experiments were performed to identify the dominant ROS involved in CIP degradation within the US/PS/Magnetite system under different pH conditions. Scavengers were added to suppress specific radical pathways, including $\text{SO}_4^{\cdot-}$, $\text{OH}^{\cdot}$, and $\text{O}_2^{\cdot-}$. However, it should be noted that radical scavengers are not always fully selective and may react with more than one ROS. Therefore, the quenching experiments were interpreted as qualitative indications of the dominant radical pathways rather than as absolute proof of the exclusive involvement of a single reactive species. The degradation profiles obtained in the presence of scavengers were compared with the corresponding reference experiments performed under identical operating conditions.

4.6.1 Identification of dominant reactive species at different pH conditions

At pH 4, experiments were performed using 1 g/L Magnetite, 2.5 mM PS, and 5 ppm CIP. As shown in Figure 51, the addition of the superoxide scavenger caused no significant decrease in degradation efficiency, suggesting that $\text{O}_2^{\cdot-}$ played only a minor role in the degradation process under acidic conditions.

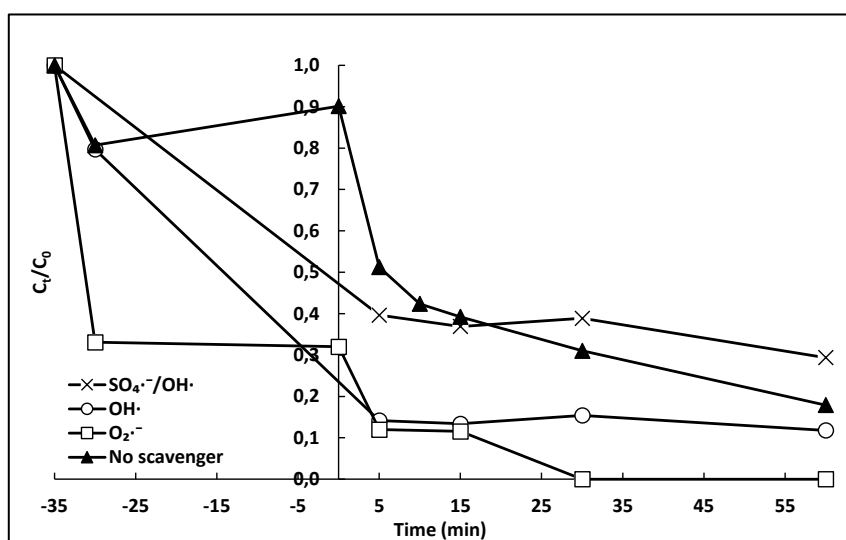


Figure 51: Radical quenching experiments in the US/PS/Magnetite system at pH 4.

In contrast, the addition of the scavenger targeting sulfate radicals strongly suppressed CIP degradation. Although this scavenger is not fully selective and can also quench $\text{OH}^{\cdot}$ radicals, comparison with the hydroxyl radical scavenging experiment allows a more careful interpretation. Since the hydroxyl radical scavenger did not inhibit CIP degradation, whereas the scavenger targeting sulfate radicals caused a pronounced decrease in removal efficiency, the observed inhibition can mainly be attributed to the suppression of $\text{SO}_4^{\cdot-}$ -mediated oxidation. This indicates that sulfate radicals played a major role in CIP degradation under acidic conditions.

The hydroxyl radical scavenger did not inhibit CIP removal. Instead, a faster initial decrease in CIP concentration was observed compared to the experiment without scavenger, while the final removal efficiency was slightly higher. This suggests that freely available $\text{OH}^{\cdot}$ radicals were unlikely to be the dominant reactive species at pH 4. The altered degradation profile may

indicate that the hydroxyl radical scavenger affected the reaction matrix or reaction kinetics rather than selectively suppressing the main degradation pathway.

Overall, these observations suggest that $\text{SO}_4^{\cdot-}$ -based pathways were the primary contributors to CIP degradation under acidic conditions, whereas the contribution of $\text{OH}^{\cdot}$ radicals appeared to be limited. This interpretation is consistent with the higher stability of sulfate radicals under acidic conditions and the efficient activation of PS by Magnetite. Moreover, zeta potential measurements showed that Magnetite possessed a strongly positive surface charge under acidic conditions (approximately +18 mV), which likely promoted electrostatic attraction between the catalyst surface and negatively charged PS ions. This favorable interaction may have enhanced surface-mediated PS activation and sulfate radical generation at the catalyst interface.

The final pH remained strongly acidic, ranging from pH 2.41 to 3.41, which is consistent with conditions under which sulfate radicals are expected to remain relatively stable, while conversion toward hydroxyl radicals is less favored.

At pH 7, experiments were conducted using 0.55 g/L Magnetite, 1.3 mM PS, and 5 ppm CIP (Figure 52). Similar to the acidic conditions, the addition of the superoxide scavenger had little influence on CIP degradation, indicating a limited contribution of $\text{O}_2^{\cdot-}$ radicals.

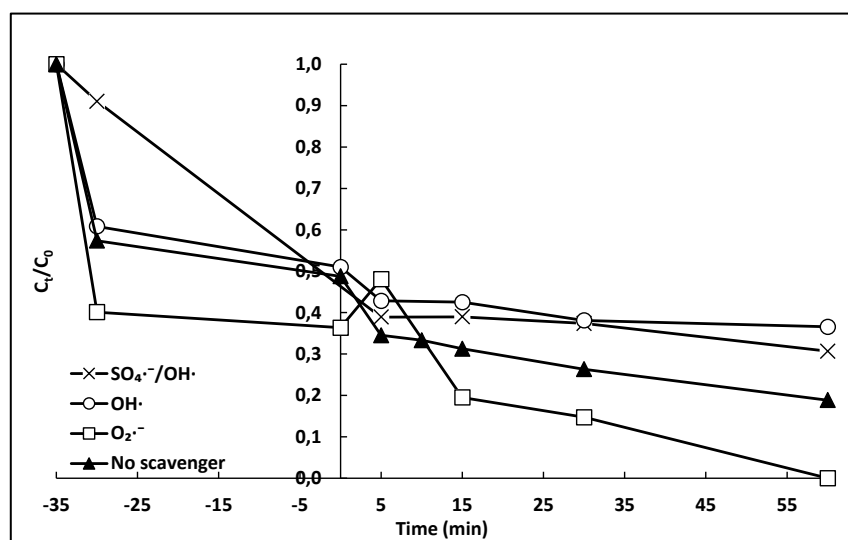


Figure 52: Radical quenching experiments in the US/PS/Magnetite system at pH 7.

Both the scavenger targeting sulfate radicals and the hydroxyl radical scavenger resulted in a noticeable decrease in degradation efficiency compared to the reference experiment without scavenger addition. Since the sulfate radical scavenger is not fully selective and may also react with hydroxyl radicals, the observed inhibition cannot be attributed exclusively to $\text{SO}_4^{\cdot-}$. Instead, the results indicate that radical-mediated oxidation involving $\text{SO}_4^{\cdot-}$ and/or $\text{OH}^{\cdot}$ contributed significantly to CIP degradation under neutral initial pH conditions.

The comparable inhibition observed in the presence of both scavengers suggests that a mixed radical system was present. This behavior can be explained by partial conversion of sulfate radicals into hydroxyl radicals at near-neutral pH, resulting in the simultaneous contribution of both reactive species. Although Magnetite still exhibited a slightly positive surface charge at neutral pH, the reduced zeta potential compared to acidic conditions may have weakened electrostatic interactions with PS anions and altered interfacial radical generation behavior.

Interestingly, the final pH decreased to approximately pH 3.8-4.77 during the experiments, indicating acidification of the reaction medium during CIP degradation. This pH decrease may additionally promote sulfate radical stability during the later stages of the reaction, meaning that the radical system may have shifted during treatment.

At pH 10 (Figure 53), the addition of the superoxide scavenger again had little effect on the degradation profile, indicating that $O_2^{\cdot-}$ was not a dominant reactive species under alkaline conditions.

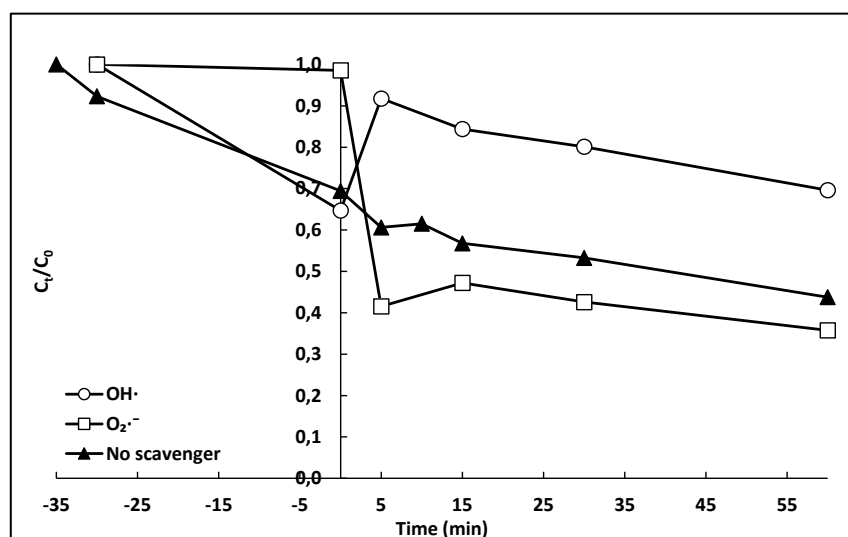


Figure 53: Radical quenching experiments in the US/PS/Magnetite system at pH 10.

A substantial decrease in degradation efficiency was observed in the presence of the hydroxyl radical scavenger, suggesting that $OH^{\cdot}$ radicals played a major role in CIP degradation at high pH. In contrast, the sulfate radical quenching experiment produced inconsistent results, preventing reliable interpretation of the contribution of $SO_4^{\cdot-}$ under these conditions. Therefore, the role of sulfate radicals at pH 10 cannot be conclusively determined based on the available quenching results.

Nevertheless, the predominance of hydroxyl radicals at alkaline pH is consistent with the known conversion of sulfate radicals into hydroxyl radicals under alkaline conditions. This suggests that the alkaline reaction environment may have favored hydroxyl radical-dominated oxidation rather than sulfate radical-dominated oxidation. In addition, zeta potential measurements showed that Magnetite became strongly negatively charged at alkaline pH (approximately -25 mV), which likely reduced electrostatic attraction between the catalyst surface and negatively charged PS anions. This reduced interaction may have suppressed surface-mediated PS activation and shifted the degradation mechanism toward hydroxyl radical-dominated oxidation in the bulk solution.

Although the final pH values remained alkaline, ranging from pH 7.63 to 8.33, a clear decrease from the initial pH of 10 was observed. This acidification may be related to the formation of acidic intermediates during CIP degradation and/or the consumption of alkaline species during radical reactions. Therefore, the system remained alkaline overall, but the observed pH decrease indicates that the reaction environment changed during treatment.

4.6.2 Relation between reactive species and degradation pathways

Overall, the quenching experiments (Table 10) demonstrated that the dominant reactive species involved in CIP degradation strongly depended on the solution pH. Under acidic conditions, sulfate radicals appeared to be the primary oxidizing species. At neutral pH, both sulfate and hydroxyl radicals seemed to contribute significantly to degradation, suggesting the presence of a mixed radical system. Under alkaline conditions, hydroxyl radicals appeared to become dominant due to the conversion of $\text{SO}_4^{\cdot-}$ into $\text{OH}^{\cdot}$ radicals at elevated pH.

In contrast, superoxide radicals showed only a minor contribution under all investigated conditions. These observations are consistent with the pH-dependent radical conversion mechanisms commonly reported for PS-based AOP and help explain the differences in degradation behavior observed throughout the optimization experiments.

Table 10: Relationship between initial solution pH, Magnetite surface charge (zeta potential), final reaction pH, and the dominant reactive species contributing to CIP degradation.

Initial pH	Final pH range	Magnetite surface charge	Dominant reactive species
4	2.41 – 3.41	Positive	$\text{SO}_4^{\cdot-}$
7	3.8 – 4.77	Slightly positive	$\text{SO}_4^{\cdot-}$, $\text{OH}^{\cdot}$
10	7.63 – 8.33	Negative	$\text{OH}^{\cdot}$

The observed shift in dominant reactive species with increasing pH appears closely linked to both radical conversion chemistry and changes in Magnetite surface charge behavior, which influence PS activation and interfacial oxidation pathways.

4.7 System stability and operational robustness

Additional experiments were performed to evaluate the operational robustness and practical applicability of the US/PS/Magnetite system for CIP degradation. The influence of inorganic ions and natural organic matter commonly present in real wastewater matrices was investigated to assess potential interference effects. Furthermore, catalyst reusability, iron leaching behavior, and energy consumption were evaluated to determine the long-term stability and feasibility of the sonocatalytic system.

4.7.1 Interference of inorganic ions and natural organic matter

Interference experiments were performed at pH 7, representing conditions commonly encountered in wastewater treatment systems. The obtained degradation profiles were compared with the optimized reference conditions at pH 7 using 0.55 g/L Magnetite, 1.3 mM PS, and 5 ppm CIP. Figure 54 shows the influence of inorganic ions and natural organic matter on CIP degradation within the US/PS/Magnetite system.

The addition of humic acid, used as a model compound for natural organic matter, resulted in only limited changes in degradation efficiency. This observation suggests that the sonocatalytic system maintained its oxidative performance even in the presence of organic background constituents, indicating potential applicability in complex wastewater or sludge-containing matrices.

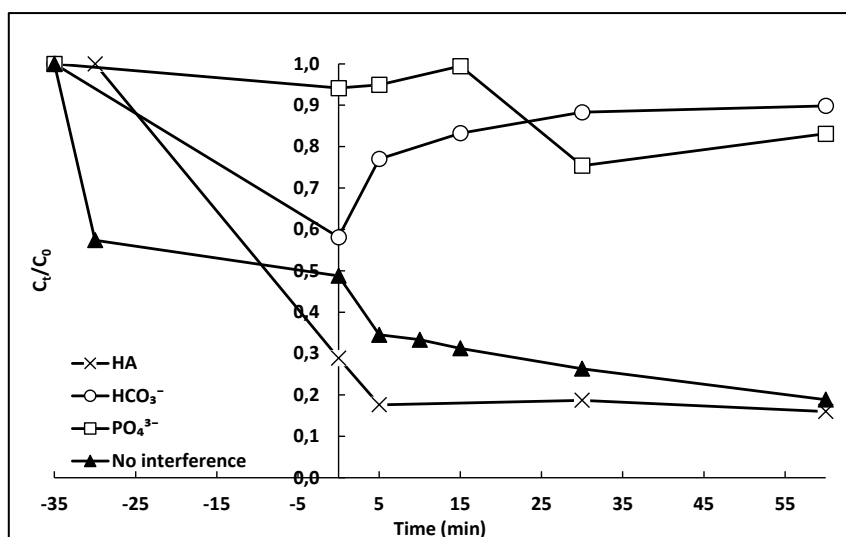


Figure 54: Influence of inorganic ions and natural organic matter on CIP degradation in the US/PS/Magnetite system under optimized conditions at pH 7.

In contrast, the presence of HCO_3^- ions significantly suppressed CIP degradation. Besides influencing the solution pH, HCO_3^- ions are known radical scavengers that can react with hydroxyl radicals and sulfate radicals to form less reactive carbonate radicals. This radical scavenging effect likely reduced the overall oxidative capacity of the system.

PO_4^{3-} ions also strongly inhibited degradation efficiency. This behavior is consistent with the strong affinity of PO_4^{3-} species toward iron oxide surfaces, which may result in catalyst surface poisoning through competitive adsorption and blockage of catalytically active sites involved in PS activation.

4.7.2 Reusability of Magnetite as sonocatalyst

Figure 55 illustrates the degradation efficiency during consecutive reuse cycles of Magnetite within the US/PS/Magnetite system. A progressive decrease in degradation efficiency was observed with increasing reuse cycles, indicating gradual deactivation of the catalyst.

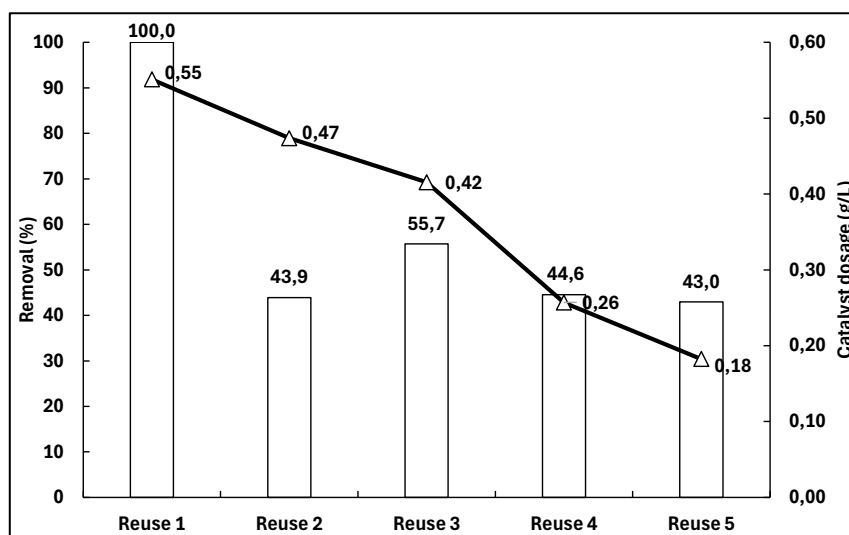


Figure 55: CIP degradation efficiency and catalyst dosage during consecutive reuse cycles of Magnetite in the US/PS/Magnetite system.

Several mechanisms may have contributed to this performance loss. Intermediate products formed during CIP degradation may have accumulated on the catalyst surface, thereby blocking active sites involved in PS activation and pollutant adsorption. In addition, no washing was applied between reuse cycles, which likely enhanced surface fouling effects.

A gradual decrease in catalyst mass was also observed during the reuse experiments. Approximately 67% of initial catalyst mass was lost after five cycles. This reduction may partly originate from ultrasonic fragmentation of Magnetite particles, mechanical washout during recovery, and possibly iron leaching into the aqueous phase. The progressively darker coloration of the treated solution after each reuse cycle further suggests the presence of suspended or dissolved iron-containing species.

These results indicate that although Magnetite exhibits promising sonocatalytic activity, additional stabilization strategies may be required to improve long-term operational stability. Immobilization of the catalyst on membranes or solid supports, combined with intermediate washing, may help preserve catalytic activity and reduce catalyst loss during repeated operation.

4.7.3 Leaching of Fe ions

During the reuse experiments, progressively darker coloration of the treated solutions was observed together with incomplete catalyst recovery after each cycle (Figure 56). While the solution remained nearly transparent after reuse 1, increasingly intense brown coloration was observed during subsequent cycles, reaching a maximum during reuse 3.



Figure 56: Solutions obtained after consecutive reuse cycles of Magnetite.

ICP analysis confirmed the occurrence of iron leaching (Table 11). The normalized iron leaching increased from only 0.458 mg Fe/g catalyst after reuse 1 to 45.4 mg Fe/g catalyst and 201 mg Fe/g catalyst after reuse 2 and reuse 3, respectively. Although lower values were obtained during reuse 4 and reuse 5 (137 and 202 mg Fe/g catalyst, respectively), iron leaching remained substantially higher than during the first cycle. The ICP results are therefore consistent with the observed increase in solution coloration and indicate progressive release of iron-containing species during repeated sonocatalytic operation.

Table 11: Iron leaching measured by ICP-OES following consecutive reuse cycles of Magnetite.

Reuse	Iron leaching (mg Fe/kg solution)	Catalyst dosage (g/L)	Iron leaching (mg Fe/g catalyst)
1	0.2525	0.5512	0.4582
2	21.5108	0.4736	45.4197
3	83.7278	0.4156	201.4625
4	35.1757	0.2568	136.9770
5	36.8539	0.1824	202.0497

The observed iron release likely originates from catalyst surface erosion, particle fragmentation, and partial dissolution induced by acoustic cavitation. Besides indicating gradual catalyst degradation, dissolved iron species may also contribute to PS activation through homogeneous catalytic pathways, potentially generating additional sulfate radicals.

4.7.4 Energy consumption

US represents the primary energy input of the sonocatalytic system and therefore plays an important role in evaluating process feasibility. During the experiments, the ultrasonic power output remained relatively constant between 60 and 80 W throughout the 1 h treatment period. This corresponds to a total supplied energy of approximately 220-290 kJ per experiment and a power density of 120-160 W/L.

The supplied ultrasonic energy contributes both to acoustic cavitation and to the generation of ROS responsible for pollutant degradation. Although ultrasonic treatment alone resulted in only limited CIP degradation, the combination with PS and Magnetite substantially enhanced oxidation efficiency, indicating that the supplied energy was utilized more effectively in the coupled sonocatalytic system.

Nevertheless, the relatively high energy demand associated with US remains an important consideration for large-scale implementation. Further optimization of catalyst dosage, oxidant dosage, and ultrasonic operating conditions may improve the overall energy efficiency of the process.

5 CONCLUSION

This thesis investigated the degradation of CECs using US-assisted advanced oxidation systems based on PS activation and sonocatalysis. The results demonstrated that combining US with PS and heterogeneous catalysts substantially enhanced pollutant degradation compared to the individual processes alone.

Among the investigated catalysts, Magnetite showed the most promising overall performance for CIP degradation due to its efficient PS activation, favorable degradation efficiency, low-cost synthesis, and simple magnetic recovery. In comparison, CuO and CuO/Magnetite composites exhibited less favorable performance under the investigated conditions.

Optimization experiments demonstrated that degradation efficiency was primarily governed by the initial pH, whereas catalyst dosage and oxidant dosage showed a more limited influence within the investigated ranges. The optimal conditions for CIP degradation were identified as pH 4, 0.1 g/L Magnetite, and 2.5 mM PS. Radical quenching experiments and zeta potential measurements indicated that sulfate radicals ($\text{SO}_4^{\cdot-}$) dominated under acidic conditions, while hydroxyl radicals ($\text{OH}^{\cdot}$) became increasingly important at neutral and alkaline pH. The enhanced performance at acidic pH was attributed to favorable electrostatic interactions between PS anions and the positively charged Magnetite surface, promoting sulfate radical generation.

The developed US/PS/Magnetite system was also evaluated for PFOA degradation. Compared to CIP, PFOA proved substantially more resistant toward degradation, highlighting the difficulty of breaking the highly stable C–F bonds characteristic of PFAS compounds. Due to experimental and analytical limitations, only a preliminary optimization study could be performed. Nevertheless, the obtained results indicated that the most favorable degradation behavior occurred under acidic conditions combined with elevated oxidant dosages. Although defluorination and mineralization could not yet be quantified with sufficient reliability, the preliminary results suggest that oxidant dosage plays an important role in determining PFOA degradation efficiency.

Additional CIP degradation experiments demonstrated that the sonocatalytic system maintained relatively stable performance in the presence of humic acid, indicating potential applicability in complex wastewater matrices. In contrast, HCO_3^- and PO_4^{3-} ions significantly inhibited degradation due to radical scavenging effects and catalyst surface poisoning, respectively.

CIP catalyst reuse experiments revealed a gradual loss of degradation efficiency during repeated operation. Catalyst mass loss, iron leaching, and surface fouling likely contributed to the observed deactivation behavior, indicating that further improvements in catalyst stabilization, recovery, and regeneration are required.

Overall, this work demonstrates the strong potential of US-assisted PS activation using Magnetite for the degradation of organic micropollutants. At the same time, the results highlight the importance of further optimizing radical generation pathways, catalyst stability, and operational efficiency to improve the applicability of sonocatalytic AOPs for wastewater treatment.

6 LIMITATIONS AND FUTURE RESEARCH

6.1 Limitations

Several limitations should be considered when interpreting the results obtained in this study. Although the experiments provided important mechanistic and operational insights into US-assisted PS activation for pollutant degradation, further experimental refinement remains necessary.

A major limitation concerned the experimental development of the PFOA degradation system. The original objective of this thesis primarily focused on PFAS degradation, particularly PFOA. However, optimization and mechanistic investigation of the PFOA system were strongly limited by the long waiting times associated with UHPLC-QTOF-MS analysis, which was performed at an external laboratory location. Because analytical feedback was obtained only after extended delays, rapid iterative optimization of experimental conditions was not feasible during the course of the study.

As a result, experimental work increasingly shifted toward CIP degradation, for which faster analytical measurements could be performed locally using HPLC. This allowed more extensive optimization, mechanistic analysis, radical quenching experiments, interference studies, and catalyst evaluation for the CIP system. In contrast, for PFOA mainly preliminary optimization experiments could be performed, while more detailed investigations such as baseline experiments, radical quenching studies, extensive parameter optimization, degradation pathway analysis, and operational stability experiments could not yet be completed.

The statistical robustness of several experiments was also limited. Radical quenching experiments, catalyst reuse experiments, and interference studies involving inorganic ions and natural organic matter were performed without experimental replicates due to time limitations. While the observed trends were clear and chemically consistent with literature findings, future work should include replicate measurements to improve statistical reliability and experimental reproducibility.

Furthermore, the statistical robustness of the optimization study differed between both target pollutants. While the CIP optimization was supported by a statistically significant regression model, the limited experimental dataset available for PFOA restricted the statistical power of the analysis. Therefore, the observed PFOA trends should be regarded as preliminary and require further confirmation.

Several analytical limitations also remained for the PFOA degradation experiments. Although degradation trends could be observed, reliable quantification of defluorination and mineralization remained difficult under the investigated experimental conditions. Additional analytical optimization and higher pollutant concentrations may therefore be required to obtain more accurate fluorine balance and mineralization data.

Additional uncertainty may have been introduced during the preparation and storage of PS stock solutions used in the baseline experiments. After dissolution, the persulfate solution was rapidly cooled and stored at low temperature, which likely induced partial crystallization within

the stock solution. As a result, the effective PS concentration added during the baseline experiments may have differed slightly from the intended dosage, potentially influencing the observed degradation efficiencies for the PS and US/PS systems.

Finally, the current study was performed using a batch reactor configuration under laboratory-scale conditions. While this setup allowed detailed investigation of degradation behavior and reaction mechanisms, it does not fully represent realistic large-scale wastewater treatment conditions. Important operational factors such as continuous flow behavior, long-term catalyst stability, sludge interactions, and energy efficiency therefore still require further investigation.

6.2 Future research

Further optimization of the US/PS/Magnetite system remains necessary to improve both degradation efficiency and operational feasibility. Although promising degradation efficiencies were obtained for both CIP and PFOA, additional optimization remains possible for both systems. The current results provide important mechanistic guidelines regarding the influence of pH, radical behavior, catalyst dosage, oxidant dosage, and surface charge interactions, which can be used to direct future optimization strategies more efficiently.

For CIP degradation, additional studies should focus on the mechanistic differences between acidic and neutral operating conditions, particularly regarding adsorption behavior, radical generation, mineralization efficiency, and degradation kinetics. Although acidic conditions resulted in the highest degradation efficiency, neutral conditions may remain more attractive for practical wastewater treatment applications due to reduced chemical adjustment requirements.

Future optimization studies should also investigate gradual or stepwise PS addition strategies instead of single-dose oxidant addition. Controlled PS dosing may reduce radical self-scavenging effects at elevated oxidant dosage and maintain more stable reactive species generation throughout the treatment process, potentially improving overall oxidation efficiency and oxidant utilization.

For PFOA degradation, substantially more optimization remains necessary due to the extreme stability of PFAS compounds. The influence of higher oxidant dosages, alternative catalyst dosage, longer treatment times, and modified ultrasonic operating conditions should be further investigated. In addition, radical quenching experiments combined with zeta potential analysis may provide further insight into the dominant degradation mechanisms involved in PFAS oxidation under different pH conditions.

Further mechanistic understanding could be obtained by identifying degradation intermediates and transformation pathways using advanced analytical techniques such as mass spectrometry. Such analyses would provide valuable information regarding mineralization pathways, fluorine release behavior, and the potential formation of toxic intermediates during degradation.

Future research should also evaluate the applicability of the sonocatalytic system in real wastewater matrices containing multiple pollutants, inorganic ions, and natural organic matter. In particular, experiments involving sludge-containing systems would be highly relevant, since many organic micropollutants and PFAS compounds accumulate in sludge phases. Both pollutant desorption followed by aqueous-phase treatment and direct sludge treatment approaches should therefore be investigated.

Additional work is also required to improve catalyst stability and long-term operational performance. Future reuse experiments should evaluate catalyst washing and regeneration procedures, as well as strategies to reduce catalyst loss and iron leaching during ultrasonic treatment. Immobilization of Magnetite onto membranes or solid supports may improve catalyst recovery and enhance process stability during repeated operation.

Future studies should additionally focus on reducing the energy demand associated with US. Optimization of ultrasonic frequency, power density, irradiation mode, and reactor geometry may improve cavitation efficiency and lower the specific energy consumption of the process. In particular, the use of combined ultrasonic frequencies, such as dual-frequency or multi-frequency irradiation, could be investigated to determine whether simultaneous cavitation at different frequencies enhances radical generation, mass transfer, and degradation efficiency. Evaluation of degradation efficiency relative to supplied energy input will be essential for assessing the large-scale feasibility of sonocatalytic wastewater treatment systems.

Finally, future studies should investigate alternative reactor configurations better suited for large-scale implementation. Continuous or semi-continuous reactor systems may improve process scalability and energy efficiency compared to the current batch configuration. Reactor designs combining continuous influent treatment with immobilized sonocatalysts and optimized ultrasonic irradiation zones may provide promising opportunities for practical wastewater treatment applications.

Referentielijst

- ACD/Labs. (2026). ACD/ChemSketch [Software]. Advanced Chemistry Development, Inc. Retrieved from <https://www.acdlabs.com/>
- Bergström, J. (2015). Experimental characterization techniques. In Elsevier eBooks (pp. 19–114). <https://doi.org/10.1016/b978-0-323-31150-2.00002-9>
- BioRender.com. (2026). BioRender [Software]. Retrieved from <https://app.biorender.com/>
- Brunn, H., Arnold, G., Körner, W., Rippen, G., Steinhäuser, K. G., & Valentin, I. (2023). PFAS: forever chemicals—persistent, bioaccumulative and mobile. Reviewing the status and the need for their phase out and remediation of contaminated sites. In *Environmental Sciences Europe* (Vol. 35, Issue 1). Springer. <https://doi.org/10.1186/s12302-023-00721-8>
- Davarazar, M., Kamali, M., Venâncio, C., Gabriel, A., Aminabhavi, T. M., & Lopes, I. (2022). Activation of persulfate using copper oxide nanoparticles for the degradation of Rhodamine B containing effluents: Degradation efficiency and ecotoxicological studies. *Chemical Engineering Journal*, 453, 139799. <https://doi.org/10.1016/j.cej.2022.139799>
- Deng, J., Fang, Y., Hou, C., Zhang, Y., Li, M., Han, J., Du, W., Tang, C., & Hu, X. (2023). Ultrasonic assisted activation of persulfate for the treatment of spent porous biochar: Degradation of adsorbed PFOA and adsorbent regeneration. *Journal Of Environmental Chemical Engineering*, 11(6), 111146. <https://doi.org/10.1016/j.jece.2023.111146>
- Ding, D., Liu, C., Ji, Y., Yang, Q., Chen, L., Jiang, C., & Cai, T. (2016). Mechanism insight of degradation of norfloxacin by Magnetite nanoparticles activated persulfate: Identification of radicals and degradation pathway. *Chemical Engineering Journal*, 308, 330–339. <https://doi.org/10.1016/j.cej.2016.09.077>
- Diao, Z., Dong, F., Yan, L., Chen, Z., Qian, W., Kong, L., Zhang, Z., Zhang, T., Tao, X., Du, J., Jiang, D., & Chu, W. (2019). Synergistic oxidation of Bisphenol A in a heterogeneous ultrasound-enhanced sludge biochar catalyst/persulfate process: Reactivity and mechanism. *Journal of Hazardous Materials*, 384, 121385. <https://doi.org/10.1016/j.jhazmat.2019.121385>
- Ebrahimi, F., & Ahari, M. F. (2024). Mechanics of active materials. In Elsevier eBooks (pp. 234–268). <https://doi.org/10.1016/b978-0-323-90646-3.00043-5>
- Esmaili-Hafshejani, J., & Nezamzadeh-Ejhieh, A. (2016). Increased photocatalytic activity of Zn(II)/Cu(II) oxides and sulfides by coupling and supporting them onto clinoptilolite nanoparticles in the degradation of benzophenone aqueous solution. *Journal of Hazardous Materials*, 316, 194–203. <https://doi.org/10.1016/j.jhazmat.2016.05.006>
- Evangelou, M. W. H., & Robinson, B. H. (2022). The phytomanagement of PFAS-Contaminated land. *International Journal of Environmental Research and Public Health*, 19(11), 6817. <https://doi.org/10.3390/ijerph19116817>
- Evich, M. G., Davis, M. J. B., McCord, J. P., Acrey, B., Awkerman, J. A., Knappe, D. R. U., Lindstrom, A. B., Speth, T. F., Tebes-Stevens, C., Strynar, M. J., Wang, Z., Weber, E. J., Henderson, W. M., & Washington, J. W. (2022). Per- and polyfluoroalkyl substances

- in the environment. *Science*, 375(6580), eabg9065. <https://doi.org/10.1126/science.abg9065>
- Feng, W., Deng, Y., Yang, F., Miao, Q., & Ngien, S. K. (2023). Systematic Review of Contaminants of Emerging Concern (CECS): distribution, risks, and implications for water quality and health. *Water*, 15(22), 3922. <https://doi.org/10.3390/w15223922>
- Glüge, J., Scheringer, M., Cousins, I. T., DeWitt, J. C., Goldenman, G., Herzke, D., Lohmann, R., Ng, C. A., Trier, X., & Wang, Z. (2020). An overview of the uses of per- and polyfluoroalkyl substances (PFAS). *Environmental Science Processes & Impacts*, 22(12), 2345–2373. <https://doi.org/10.1039/d0em00291g>
- Guerra-Rodríguez, S., Rodríguez, E., Singh, D., & Rodríguez-Chueca, J. (2018). Assessment of Sulfate Radical-Based Advanced Oxidation Processes for water and Wastewater Treatment: a review. *Water*, 10(12), 1828. <https://doi.org/10.3390/w10121828>
- Herrero, Y. R., Camas, K. L., & Ullah, A. (2023). Characterization of biobased materials. In *Elsevier eBooks* (pp. 111–143). <https://doi.org/10.1016/b978-0-323-91677-6.00005-2>
- Hou, L., Zhang, H., & Xue, X. (2011). Ultrasound enhanced heterogeneous activation of peroxydisulfate by magnetite catalyst for the degradation of tetracycline in water. *Separation and Purification Technology*, 84, 147–152. <https://doi.org/10.1016/j.seppur.2011.06.023>
- Inkson, B. (2016). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) for materials characterization. In *Elsevier eBooks* (pp. 17–43). <https://doi.org/10.1016/b978-0-08-100040-3.00002-x>
- Ioannidi, A. A., Bampos, G., Antonopoulou, M., Oulego, P., Boczkaj, G., Mantzavinos, D., & Frontistis, Z. (2024). Sonocatalytic degradation of Bisphenol A from aquatic matrices over Pd/CeO₂ nanoparticles: Kinetics study, transformation products, and toxicity. *The Science Of The Total Environment*, 919, 170820. <https://doi.org/10.1016/j.scitotenv.2024.170820>
- Isherwood, P. (2016). Copper zinc oxide: Investigation into a p-type mixed metal oxide system. *Vacuum*, 139, 173–177. <https://doi.org/10.1016/j.vacuum.2016.09.026>
- Johansson, Ö., Pamidi, T., Khoshkhoo, M., & Sandström, Å. (2017). Sustainable and energy efficient leaching of tungsten (W) by ultrasound controlled cavitation. *ResearchGate*. https://www.researchgate.net/publication/322552455_Sustainable_and_energy_efficient_leaching_of_tungsten_W_by_ultrasound_controlled_cavitation
- Jones, B. (2023, June 23). You probably have “forever chemicals” in your body. Here’s what that means. *Vox*. Consulted on 13 March 2026. <https://www.vox.com/2022/8/25/23318667/pfas-forever-chemicals-safety-drinking-water>
- Jonker, M. T. O. (2024). Per- and Polyfluoroalkyl Substances in Water (2008–2022) and Fish (2015–2022) in The Netherlands: Spatiotemporal Trends, Fingerprints, Mass Discharges, Sources, and Bioaccumulation Factors. *Environmental Toxicology and Chemistry*. <https://doi.org/10.1002/etc.5846>
- Kamble, S., Agrawal, S., Cherumukkil, S., Sharma, V., Jasra, R. V., & Munshi, P. (2022). Revisiting Zeta Potential, the Key Feature of Interfacial Phenomena, with Applications and Recent Advancements. *ChemistrySelect*, 7(1). <https://doi.org/10.1002/slct.202103084>

- Khalaj, M., Kamali, M., Khodaparast, Z., & Jahanshahi, A. (2017). Copper-based nanomaterials for environmental decontamination – An overview on technical and toxicological aspects. *Ecotoxicology and Environmental Safety*, 148, 813–824. <https://doi.org/10.1016/j.ecoenv.2017.11.060>
- Khan, M. F. (2025). Recent Progress and Challenges in Microbial Defluorination and Degradation for Sustainable Remediation of Fluorinated Xenobiotics. In *Processes* (Vol. 13, Issue 7). Multidisciplinary Digital Publishing Institute (MDPI). <https://doi.org/10.3390/pr13072017>
- Kyzas, G. Z., Mengelizadeh, N., Saloot, M. K., Mohebi, S., & Balarak, D. (2022). Sonochemical degradation of ciprofloxacin by hydrogen peroxide and persulfate activated by ultrasound and ferrous ions. *Colloids and Surfaces a Physicochemical and Engineering Aspects*, 642, 128627. <https://doi.org/10.1016/j.colsurfa.2022.128627>
- Lee, J., Von Gunten, U., & Kim, J. (2020). Persulfate-Based Advanced Oxidation: Critical Assessment of Opportunities and roadblocks. *Environmental Science & Technology*, 54(6), 3064–3081. <https://doi.org/10.1021/acs.est.9b07082>
- Li, F., Duan, J., Tian, S., Ji, H., Zhu, Y., Wei, Z., & Zhao, D. (2020). Short-chain per- and polyfluoroalkyl substances in aquatic systems: Occurrence, impacts and treatment. *Chemical Engineering Journal*, 380, 122506. <https://doi.org/10.1016/j.cej.2019.122506>
- Libretexts. (2025, April 3). Bond Energies. Chemistry LibreTexts. [https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_\(Physical_and_Theoretical_Chemistry\)/Chemical_Bonding/Fundamentals_of_Chemical_Bonding/Bond_Energies](https://chem.libretexts.org/Bookshelves/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Chemical_Bonding/Fundamentals_of_Chemical_Bonding/Bond_Energies)
- Liu, S., Long, Z., Liu, H., Zhang, J., Zhang, G., & Liang, J. (2024). Machine learning predict the degradation efficiency of aqueous refractory organic pollutants by ultrasound-based advanced oxidation processes. *Journal of Water Process Engineering*, 66, 106022. <https://doi.org/10.1016/j.jwpe.2024.106022>
- Liu, Y., Kamali, M., Chen, X., Rossi, B., Appels, L., & Dewil, R. (2024). Photocatalytic defluorination of ciprofloxacin by nitrogen-defected g-C₃N₄ under simulated sunlight: Mechanistic insight and pathway analysis. *Chemical Engineering Journal*, 493, 151950. <https://doi.org/10.1016/j.cej.2024.151950>
- Lops, C., Ancona, A., Di Cesare, K., Dumontel, B., Garino, N., Canavese, G., Hernández, S., & Cauda, V. (2018). Sonophotocatalytic degradation mechanisms of Rhodamine B dye via radicals generation by micro- and nano-particles of ZnO. *Applied Catalysis B: Environmental*, 243, 629–640. <https://doi.org/10.1016/j.apcatb.2018.10.078>
- Lu, J., Lu, H., Liang, D., Feng, S. S., Li, Y., & Li, J. (2023). A review of the occurrence, monitoring, and removal technologies for the remediation of per- and polyfluoroalkyl substances (PFAS) from landfill leachate. *Chemosphere*, 332(May), 138824. <https://doi.org/10.1016/j.chemosphere.2023.138824>
- Ma, T., Ye, C., Wang, T., Li, X., & Luo, Y. (2022). Toxicity of per- and polyfluoroalkyl substances to aquatic invertebrates, planktons, and microorganisms. *International Journal of Environmental Research and Public Health*, 19(24), 16729. <https://doi.org/10.3390/ijerph192416729>

- Ma, X., & Wang, Z. (2022). Removal of Ciprofloxacin from Wastewater by Ultrasound/Electric Field/Sodium Persulfate (US/E/PS). *Processes*, 10(1), 124. <https://doi.org/10.3390/pr10010124>
- Malakotian, M., Asadzadeh, S. N., Khatami, M., Ahmadian, M., Heidari, M. R., Karimi, P., Firouzeh, N., & Varma, R. S. (2019). Protocol encompassing ultrasound/Fe₃O₄ nanoparticles/persulfate for the removal of tetracycline antibiotics from aqueous environments. *Clean Technologies and Environmental Policy*, 21(8), 1665–1674. <https://doi.org/10.1007/s10098-019-01733-w>
- Martins, N., Pereira, R., Abrantes, N., Pereira, J., Gonçalves, F., & Marques, C. R. (2012). Ecotoxicological effects of ciprofloxacin on freshwater species: data integration and derivation of toxicity thresholds for risk assessment. *Ecotoxicology*, 21(4), 1167–1176. <https://doi.org/10.1007/s10646-012-0871-x>
- Michael-Kordatou, I., Karaolia, P., & Fatta-Kassinos, D. (2017). The role of operating parameters and oxidative damage mechanisms of advanced chemical oxidation processes in the combat against antibiotic-resistant bacteria and resistance genes present in urban wastewater. *Water Research*, 129, 208–230. <https://doi.org/10.1016/j.watres.2017.10.007>
- Naderi, M. (2014). Surface area. In Elsevier eBooks (pp. 585–608). <https://doi.org/10.1016/b978-0-12-384746-1.00014-8>
- Nguyen, T. T., Asakura, Y., Koda, S., & Yasuda, K. (2017). Dependence of cavitation, chemical effect, and mechanical effect thresholds on ultrasonic frequency. *Ultrasonics Sonochemistry*, 39, 301–306. <https://doi.org/10.1016/j.ultsonch.2017.04.037>
- Ning, J., Kamali, M., Crauwels, S., & Appels, L. (2025). The triple action of pinewood biochar-based materials to improve biogas yields: pH regulation, DIET, and colonization. *Journal of Environmental Management*, 380, 125185. <https://doi.org/10.1016/j.jenvman.2025.125185>
- OpenAI. (2026). ChatGPT (GPT-5.3) [Large language model used to generate the figure]. <https://chat.openai.com>
- Pétrier, C., & Wei, Z. (2023). The use of power ultrasound for water treatment. In *Power Ultrasonics: Applications of High-Intensity Ultrasound*, Second Edition (pp. 797–815) <https://doi.org/10.1016/B978-0-12-820254-8.00024-5>
- Priyadarshini, M., Das, I., Ghangrekar, M. M., & Blaney, L. (2022). Advanced oxidation processes: Performance, advantages, and scale-up of emerging technologies. *Journal of Environmental Management*, 316, 115295. <https://doi.org/10.1016/j.jenvman.2022.115295>
- Salazar, H., Zarandona, A., Zhang, Q., & Mendez, S. (2024). Unlocking the potential of sonophotocatalysis for enhanced water remediation. *Chemical Engineering Journal*, 505, 159173. <https://doi.org/10.1016/j.cej.2024.159173>
- Salma, A., Thoröe-Boveleth, S., Schmidt, T. C., & Tuerk, J. (2016). Dependence of transformation product formation on pH during photolytic and photocatalytic degradation of ciprofloxacin. *Journal of Hazardous Materials*, 313, 49–59. <https://doi.org/10.1016/j.jhazmat.2016.03.010>

- Saveh, H., Mazloom, G., & Abdi, J. (2024). Synthesis of magnetic layered double hydroxide (Fe₃O₄@CuCr-LDH) decorated with ZIF-8 for efficient sonocatalytic degradation of tetracycline. *Journal of Environmental Management*, 362, 121338. <https://doi.org/10.1016/j.jenvman.2024.121338>
- Sharma, A., Ahmad, J., & Flora, S. J. S. (2018). Application of advanced oxidation processes and toxicity assessment of transformation products. *Environmental Research*, 167, 223–233. <https://doi.org/10.1016/j.envres.2018.07.010>
- Sidnell, T., Wood, R. J., Hurst, J., Lee, J., & Bussemaker, M. J. (2022). Sonolysis of per- and poly fluoroalkyl substances (PFAS): A meta-analysis. *Ultrasonics Sonochemistry*, 87, 105944. <https://doi.org/10.1016/j.ultsonch.2022.105944>
- Silvestri, D., Krawczyk, K., Pawlyta, M., Krzywiecki, M., Padil, V. V., Torres-Mendieta, R., Ghanbari, F., Dinc, O., Černík, M., Dionysiou, D. D., & Waclawek, S. (2021). Influence of catalyst zeta potential on the activation of persulfate. *Chemical Communications*, 57(63), 7814–7817. <https://doi.org/10.1039/d1cc01946e>
- Singh, A., Sinha, M. K., & Khuntia, S. (2024). Synthesis, retrieval, and industrial applications of magnetic nanoparticles in recent times. *Journal of Water Process Engineering*, 69, 106792. <https://doi.org/10.1016/j.jwpe.2024.106792>
- Smith, S. J., Lauria, M., Higgins, C. P., Pennell, K. D., Blotevogel, J., & Arp, H. P. H. (2024). The need to include a fluorine mass balance in the development of effective technologies for PFAS destruction. *Environmental Science & Technology*, 58(6), 2587–2590. <https://doi.org/10.1021/acs.est.3c10617>
- Suslick, K., Doktycz, S., & Flint, E. (1990). On the origin of sonoluminescence and sonochemistry. *Ultrasonics*, 28(5), 280–290. [https://doi.org/10.1016/0041-624x\(90\)90033-k](https://doi.org/10.1016/0041-624x(90)90033-k)
- Swadhina Priyadarshini Lenka, Melanie Kah, Lokesh P. Padhye. A review of the occurrence, transformation, and removal of poly- and perfluoroalkyl substances (PFAS) in wastewater treatment plants, *Water Research*, Volume 199, 2021, 117187, ISSN 0043-1354, <https://doi.org/10.1016/j.watres.2021.117187>.
- Thakur, A., Khusnutdinova, A. N., Navarro-Márquez, M., Kumar, V., Ma, H., Golyshin, P. N., Lyu, T., Yakunin, A. F., Kumar, G., Nithya, K., Soto, G. G., Iqbal, H. M., Gutierrez, T., Coulon, F., & Parra-Saldívar, R. (2025). Comprehensive strategies for the remediation of per- and polyfluoroalkyl substances (PFAS): Mechanisms, technologies, and future perspectives. *Ecotoxicology and Environmental Safety*, 306, 119374. <https://doi.org/10.1016/j.ecoenv.2025.119374>
- Trinh, Q. T., Golio, N., Cheng, Y., Cha, H., Tai, K. U., Ouyang, L., Zhao, J., Tran, T. S., Nguyen, T., Zhang, J., An, H., Wei, Z., Jerome, F., Amaniampong, P. N., & Nguyen, N. (2025). Sonochemistry and sonocatalysis: current progress, existing limitations, and future opportunities in green and sustainable chemistry. *Green Chemistry*, 27(18), 4926–4958. <https://doi.org/10.1039/d5gc01098e>
- Tshangana, C. S., Nhlengethwa, S. T., Glass, S., Denison, S., Kuvarega, A. T., Nkambule, T. T. I., Mamba, B. B., Alvarez, P. J. J., & Muleja, A. A. (2025). Technology status to treat PFAS-contaminated water and limiting factors for their effective full-scale application. *Npj Clean Water*, 8(1). <https://doi.org/10.1038/s41545-025-00457-3>

- Veciana, A., Steiner, S., Tang, Q., Pustovalov, V., Llacer-Wintle, J., Wu, J., Chen, X., Manyiwa, T., Ultra, V. U., Garcia-Cirera, B., Puigmartí-Luis, J., Franco, C., Janssen, D. J., Nyström, L., Boulos, S., & Pané, S. (2024). Breaking the Perfluorooctane Sulfonate Chain: Piezocatalytic Decomposition of PFOS Using BaTiO₃ Nanoparticles. *Small Science*, 4(12), 2400337. <https://doi.org/10.1002/smssc.202400337>
- Wang, J., & Wang, S. (2017). Activation of persulfate (PS) and peroxymonosulfate (PMS) and application for the degradation of emerging contaminants. *Chemical Engineering Journal*, 334, 1502–1517. <https://doi.org/10.1016/j.cej.2017.11.059>
- Xing, S., Li, W., Liu, B., Wu, Y., & Gao, Y. (2019). Removal of ciprofloxacin by persulfate activation with CuO: A pH-dependent mechanism. *Chemical Engineering Journal*, 382, 122837. <https://doi.org/10.1016/j.cej.2019.122837>
- Xue, Y., Kamali, M., Yu, X., Appels, L., & Dewil, R. (2022). Novel CuO/Cu₂(V₂O₇)/V₂O₅ composite membrane as an efficient catalyst for the activation of persulfate toward ciprofloxacin degradation. *Chemical Engineering Journal*, 455, 140201. <https://doi.org/10.1016/j.cej.2022.140201>
- Yao, S., Lin, J., He, S., Bai, Y., Jin, M., Zhu, F., Fang, J., & Wang, M. (2025). Highly efficient degradation of perfluoroalkyl substances (PFAS) by a novel polytetrafluoroethylene piezocatalyst. *Journal of Hazardous Materials*, 488, 137317. <https://doi.org/10.1016/j.jhazmat.2025.137317>
- Zhang, X., Kamali, M., Van Beeck, R., Hens, W., Truyen, J., Cabooter, D., & Dewil, R. (2023). Degradation of ciprofloxacin using Magnetite nanoparticle-activated periodate: Kinetic, mechanistic and toxicity evaluation. *Chemical Engineering Journal*, 478, 147323. <https://doi.org/10.1016/j.cej.2023.147323>
- Zhang, X., Kamali, M., Xue, Y., Li, S., Costa, M. E. V., Cabooter, D., & Dewil, R. (2022). Periodate activation with copper oxide nanomaterials for the degradation of ciprofloxacin - A new insight into the efficiency and mechanisms. *Journal of Cleaner Production*, 383, 135412. <https://doi.org/10.1016/j.jclepro.2022.135412>
- Zhang, Y., Zhang, C., Zhou, Z., Wu, Y., & Xing, S. (2021). Degradation of ciprofloxacin by persulfate activation with CuO supported on Mg Al layered double hydroxide. *Journal of Environmental Chemical Engineering*, 9(5), 106178. <https://doi.org/10.1016/j.jece.2021.106178>

Bijlagen

Bijlage A Experimental run order and conditions for enhanced CIP degradation.

Bijlage B Experimental run order and conditions for enhanced PFOA degradation.

Bijlage A EXPERIMENTAL RUN ORDER AND CONDITIONS FOR ENHANCED CIP DEGRADATION.

CIP	Initial pH (l)	Catalyst dosage (g/L)	Oxidant dosage (mM)
A	4	1.00	0.1
B	10	0.10	0.1
C	4	1.00	0.1
D	10	1.00	2.5
E	10	0.10	0.1
F	7	0.55	1.3
G	10	0.10	0.1
H	10	1.00	2.5
I	4	0.10	2.5
J	4	1.00	0.1
K	7	0.55	1.3
L	4	0.10	2.5
M	10	1.00	2.5
N	4	0.10	2.5

Bijlage B EXPERIMENTAL RUN ORDER AND CONDITIONS FOR ENHANCED PFOA DEGRADATION.

PFOA	Initial pH (l)	Catalyst dosage (g/L)	Oxidant dosage (mM)
AA	10	0.5	5.0
BB	10	1.5	20.0
CC	7	1.0	12.5
DD	10	1.5	20.0
EE	4	1.5	5.0
FF	10	1.5	20.0
GG	4	1.5	5.0
HH	10	0.5	5.0
II	4	0.5	20.0
JJ	10	0.5	5.0
KK	7	1.0	12.5
LL	4	0.5	20.0
MM	4	0.5	20.0
NN	4	1.5	5.0

FACULTEIT INDUSTRIËLE INGENIEURSWETENSCHAPPEN

W. de Croylaan 56
3001 HEVERLEE, België
info.iw@kuleuven.be
www.iw.kuleuven.be

