

CRANFIELD UNIVERSITY

GIULIA PIZZAGALLI

REMOVAL OF MICROPOLLUTANTS FROM WASTEWATER
COMBINING ADSORPTION AND ELECTROCHEMICAL
REGENERATION

CRANFIELD WATER INSTITUTE
Environmental Technology

MSc by Research
Academic Years: 2015 - 2017

Supervisor: Dr. Pablo Campo-Moreno, Dr. Ana Soares
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ABSTRACT

Increasingly stringent legislations, such as the Water Framework Directive (WFD) and its daughter Directive on Environmental Quality Standards (EQS), have carried important implications for European policy on pollution control for water resources. EQS have been set or proposed for substances which hitherto had not been subjected to monitoring, calling for compliance assessments and new control measures.

To address this challenge, the UK Water Industry Research (UKWIR) financed a Chemicals Investigation Programme (CIP), assessing the source, occurrence and removal of emerging pollutants in the final effluents of wastewater treatment works (WwTWs). A second phase of work, CIP2, now aims to create a justifiable base for future regulatory measures needed to achieve good status (i.e. compliance limits for specific substances), together with a data set on micropollutants' concentrations from trials conducted at pilot and full scale all over the UK.

As part of CIP2, the Arvia ODC (Organic Destruction Cell), a novel technology combining adsorption and electrochemical oxidation, has been investigated at pilot scale. Its overall performance was assessed by evaluating the removal of 68 emerging pollutants and priority substances (pharmaceuticals, steroids, industrial chemicals and heavy metals), by appraising its economic and environmental costs and by weighting its reliability, easiness of maintenance and operation.

Overall, the unit was able to target pharmaceuticals better than any other class of substances, with removals consistently over 50% for the majority of them, being especially effective towards macrolide antibiotics (~ 60-70%) and statins (~70-80%). The majority of determinands (72%) were found to be at concentrations below the set EQS at discharge. However, despite some evidence of promising performance, the ODC appeared to promote the accumulation of metals (i.e. zinc, nickel) in the final effluent and overall showed quite a weak performance in relation to sanitary determinands.

A multi criteria analysis was performed to compare the ODC to alternative tertiary treatments. Although considerably lower than alternative treatment technologies (i.e. GAC or ozonation), energy consumption, normalised at 0.14 kWh/treated m³, represented the major contributing factor to estimated OPEX (1.1 pence/kWh), steadily increasing with population served. The ODC does not require chemical dosing, thus lessening the sludge production and potentially offering lower operational carbon usage than other advanced oxidation processes.

Further testing of the technology was carried on at bench scale, in order to assess the unit's performance in more controlled circumstances (spiked tap water). The trial allowed to single out the main parameters (mainly current density and effluent flow) responsible for the ODC performance and to evaluate to what extent their variation contributed to the removal of carbamazepine, a pharmaceutical compound whose persistence and toxicity in the aquatic environment determined its inclusion in the list of substances investigated in CIP2. The best removal performance (78%) was achieved at intermediate values for the ranges of flow and current density explored (5 L/h, 4 mA/cm²), seemingly allowing a synergic contribution of both adsorption and electrochemical oxidation.

Although the technology has been proved to perform satisfactorily towards specific micropollutants in both trials, it is not applicable with the same degree of success to the removal of the wide range of chemicals investigated in CIP2. Moreover, due to its relative novelty and hitherto lack of full scale applications, the technology still requires stages of development, especially in terms of hydraulics within the unit (i.e. backwash system) and upstream solids capture.

Keywords: Micropollutants, priority substances, Chemicals Investigation Programme, adsorption, electrochemical oxidation.

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LIST OF ABBREVIATIONS

AA-EQS	Annual Average – Environmental Quality Standard
AHP	Analytical Hierarchy Process
AMP	Asset Management Plan
AOP	Advanced Oxidation Process
BDD	Boron Doped Diamond
CA	Carbon Aerogel
CAPEX	Capital Expenditure
CIP	Chemicals Investigation Programme
DE	Direct Electrolysis
DEHP	Bis(2-ethylexyl) phthalate
DET	Direct Electron Transfer
DO	Dissolved Oxygen
DWF	Dry Weather Flow
EA	Environment Agency
EBCT	Empty Bed Contact Time
EC	Energy Consumption
EDCs	Endocrine Disruptive Compounds
EOTR	Electrochemical Oxygen Transfer
EPs	Emerging Pollutants
EQS	Environmental Quality Standard
FE	Final Effluent
FFT	Full Flow to Treatment
GAC	Granular Activated Carbon
HPLC	High Performance Liquid Chromatography
HRT	Hydraulic Retention Time
IBC	Intermediate Bulk Container
ICE	Instantaneous Current Efficiency
IE	Indirect Electrolysis
IQS	Inter-quartile Range
KPI	Key Performance Indicator
LEL	Lower Explosive Limit
MAC-EQS	Maximum Allowable Concentration – Environmental Quality Standard
MCA	Multi-criteria Analysis
MEICA	Mechanical, Electric, Instrumentation, Control and Automation
MeOH	Methanol

NEP	National Environment Programme
NOM	Natural Organic Matter
NSF	Nitrifying Sand Filters
ODC	Organics Destruction Cell
OPEX	Operating Expenditure
PAH	Poly-aromatic Hydrocarbon
PCA	Principal Components Analysis
PCCPs	Pharmaceuticals and Personal Care Products
PCPs	Personal Care Products
PHS	Priority Hazardous Substance
PNEC	Predicted No Effect Concentration
POPs	Persistent Organic Pollutants
PS	Priority Substance
PST	Primary Settlement Tank
SE	Standard Error
SHE	Standard Hydrogen Electrode
SP	Special Pollutant
SRT	Sludge Retention Time
TOC	Total Organic Carbon
TOTEX	Total Expenditure
UKWIR	UK Water Industry Research
WFD	Water Framework Directive
WRA	Water Resources Act
WRC	Water Recycling Centre
WwTW	Wastewater Treatment Works

Chemicals Investigation Programme substance list (field abbreviations)

NID	Nickel (dissolved)
NIT	Nickel (total)
PBD	Lead (dissolved)
PBT	Lead (total)
CUD	Copper (dissolved)
CUT	Copper (total)
ZND	Zinc (dissolved)
ZNT	Zinc (total)
CDD	Cadmium (dissolved)

CDT	Cadmium (total)
HGD	Mercury (dissolved)
HGT	Mercury (total)
FED	Iron (dissolved)
FET	Iron (total)
ALD	Aluminium (dissolved)
ALT	Aluminium (total)
ALR	Aluminium (reactive)
CRD	Cadmium (dissolved)
CRT	Cadmium (reactive)
DEHP	Di(ethylexyl)phtalate
BDE	Brominated Diphenyl Ether
PFOS	Perfluorooctane Sulfonic Acid
PFOA	Perfluorooctanoic Acid
HBCDD	Hexabromocyclododecane
NOP	Nonylphenol
OCP	Octylphenol
TBT	Tributyltin compounds
FLU	Fluoranthene
BAP	Benzo(a)pyrene
Tricl	Triclosan
CYP	Cypermethrin
TSS	Total Suspended Solids
AMON	Ammoniacal Nitrogen
TOXN	Oxidised Nitrogen
BOD	Biochemical Oxygen Demand
COD	Chemical Oxygen Demand
TP	Total Phosphorus
SRP	Soluble Reactive Phosphorus
TOC	Total Organic Carbon
DOC	Dissolved Organic Carbon
CA	Calcium
S	Sulphide
E1	Oestrone
E2	17 β -oestradiol
EE2	17 α -ethynyloestradiol
DCF	Diclofenac

IBPF	Ibuprofen
ATOV	Atorvastatin
ATOV _o	Ortho-hydroxy-atorvastatin
ATOV _p	Para-hydroxy-atorvastatin
PRPL	Propranolol
ATNL	Atenolol
ERMY	Erythromycin
ERMY _n	Norerythromycin
AZMY	Azithromycin
CLMY	Clarithromycin
CIPR	Ciprofloxacin
RNTD	Ranitidine
METF	Metformin
CBAZ	Carbamazepine
CBAZ _e	10,11 epoxy-carbamazepine
SERT	Sertraline
SERT _n	Norsertaline
FLXT	Fluoxetine
TMXF	Tamoxifen
TXP	Trixylenyl phosphate
BZT	Benzotriazole
TZT	Tolytriazole

1 INTRODUCTION

1.1 Subject overview

Legislation in the field of water and environment, in particular with the European Water Framework Directive (WFD) [1], has broadened the reach of pollution control measures to protect surface waters, stating that each Member State is responsible for ensuring that all surface and ground waters achieve good quality status.

In parallel, the continuous development and improvement of new analytical techniques has determined a significant advancement in the ability to measure and detect substances found in water in the micro ($\mu\text{g/L}$) and nano (ng/L) range of concentration, shedding light on their presence and effects on the water bodies [2] and highlighting the need for stricter legislation on these substances. The Priority Substances Directive (2008/105/EC), derived from the WFD, has represented the first step to raise public awareness on the presence of these trace micropollutants in both wastewater and effluents, identifying an initial list of Priority Substances, including persistent organic pollutants (POPs), pesticides, personal care products (PCPs), toxic chemicals, carcinogenic and endocrine disrupting compounds (EDCs) [3], [4].

In order to answer to the new obligations set by the WFD and the Priority Substances Directive, from 2009 to 2012 the UK Water Industry Research (UKWIR) has collaborated with the water industry, the Environment Agency (EA) and other UK regulators and has implemented the Chemicals Investigation Programme (CIP) to study the occurrence, source and removal of trace substances in wastewater treatment works' (WwTW) effluents, thus establishing a basis for a nation-wide assessment of the risk posed by chemicals in WwTW discharges. CIP aimed at quantifying the risk from these substances and assessing the performance of selected WwTW. It also involved investigations on the sources of these specific contaminants, appraising the effectiveness of different removal technologies both at full scale (i.e. demonstration trials) and at pilot scale, and completing technical investigations on potential methods to reduce these chemicals' concentrations in the final effluents [2], [5].

In 2015, as part of the planning for next period of the water industry's asset management (Asset Management Plan, AMP6, 2015-2020), the CIP started to be updated and taken into a further phase, in a programme known as CIP2, which will focus on more site-specific issues and will further investigate removal technologies with a more rigorous and wider monitoring programme.

1.2 Aim and objectives

The aim of this project is to investigate the efficacy of an advanced wastewater treatment combining adsorption on carbonaceous media and anodic oxidation, called Organic Destruction Cell (ODC) and developed by Arvia Technology (Runcorn, UK), in relation to the removal of substances targeted in CIP2.

In order to reach this aim, the project will be structured in two parts: first, one at pilot scale followed by one at laboratory scale, to achieve a thorough evaluation of the technology.

As for the pilot plant, the main objectives to reach are as follows:

- Evaluate the performance of the unit in removing substances targeted by the CIP2;
- Study the physical hazardous substances removal;
- Identify and contextualise the unit's operating and maintenance parameters;
- Identify the main criticalities of the process, and evaluate the performance towards future design goals;
- Determine the pre-treatment requirements;
- Assess the capital and operational expenditures of the technology (CAPEX, OPEX);
- Appraise the unit's reliability (i.e. frequency and nature of unplanned remedial, maintenance and repair).

For the laboratory unit, the planned objectives are:

- Identify and contextualise the ODC's operating and maintenance parameters;
- Evaluate the performance of the unit for the removal of a particularly recalcitrant organic pollutant, carbamazepine;
- Investigate the correlations between removal performance and operational parameters of the unit.

1.3 Research question

The main research questions addressed in this study are as follows:

1. What removal mechanisms are involved in the technology?
2. What are the efficacy and the feasibility of using an ODC as a tertiary technology for hazardous substances removal?
3. What parameters can be optimised in order to improve the technology's performance?
4. What are the main criticalities of the unit, to be improved if a full scale treatment is to be considered?

2 LITERATURE REVIEW

2.1 Introduction

Over the last few decades, the presence of emerging substances in the aquatic environment has been raising concern worldwide, due to their potential toxicological threat to living organisms [6]. In some cases, their release into the aquatic environment has likely occurred for a long time, but they are only now being routinely detected owing to novel and improved detection methods; in other cases, synthesis of new industrial chemicals or changes in use and disposal of the existing ones may have led to the creation of new sources of micropollutants [6], [7].

Micropollutants, thus called because they are present in water at trace concentration - typically ranging from a few ng/L to several µg/L - are also referred to as emerging pollutants (EPs) and consist of a wide array of *“synthetic or naturally occurring chemicals that are not commonly monitored in the environment, but which have the potential to enter the environment and cause known or suspected adverse ecological and (or) human health effects”* [6]. This class of substances includes pharmaceuticals, personal care products, steroid hormones, industrial chemicals and many other compounds [8].

Current wastewater treatment works (WwTWs) were not initially designed to remove a broad spectrum of chemicals and mainly applied for COD and nutrients removal. Micropollutants, due to their persistence and bioactivity, as well as their continuous introduction in the aquatic environment, often tend to bypass the treatment works and be discharged with the final effluent (FE), posing a potential threat to the aquatic wildlife and to the quality of drinking water [9]. Hence, these contaminants' properties and their widespread presence in the environment pose new challenges in the design of methodologies for their removal, as the issues highlighted by the following considerations suggest [9]:

- Despite some effort by the regulators (i.e. the European Directive 2008/15/EC, regulating nonylphenol and di(2-ethylhexyl)phthalate discharge, among others), as of now discharge guidelines and consents have not been established for the vast majority of EPs, as the industrial and technological breakthroughs have outpaced the regulatory practices.
- Emerging pollutants include an extensive and expanding spectrum of compounds, whose different physicochemical properties and low concentration in water make detection and removal very difficult;

- EPs are different in their form and mechanism of action, a fact that renders the identification and the toxicological evaluation from the environmental matrix quite challenging, as there is no standard method for EPs monitoring and most analytical instruments are unable to directly detect compounds at such low levels. Usually, before being analysed, these compounds need to be concentrated through extraction, followed by a multiple-step process, which could be detrimental for certain types of instrumental analysis.
- Some micropollutants are biologically active compounds, not very easily biodegradable, often water soluble and persistent, so that they can bypass treatment in WwTWs. Others, in particular the excreted metabolites and unaltered parent compounds, can be subjected to further transformations in WwTWs and easily end up in WwTWs effluents and surface waters. Here, even though they might be individually present at trace concentration, their combined concentrations and continued infusion into the aquatic environment could have a substantial impact, leading to unwanted synergic effects, even on non-target organisms [10].

2.2 European and UK regulatory framework

The regulatory framework concerning emerging pollutants in the European environment is very complex and includes a set of regulations on their use, emissions and their presence into the aquatic environment and drinking water.

2.2.1 Water Framework Directive and Directive on Environmental Quality Standards

The Water Framework Directive (Directive 2000/60/EC) is the main European regulatory instrument to protect water resources, extending the scope of pollution control to surface waters [1].

In order to reduce the negative effects of chemical substances on water bodies, the WFD identified a list of priority substances that are considered to be especially harmful to or via the aquatic environment due to their toxicity, persistence and bioaccumulation potential. More than 300 contaminants were subjected to risk assessment before a final list of 33 substances was published, which then became Annex X of the Directive.

This first list was then replaced by Annex II of the Directive on Environmental Quality Standards (2008/105/EC, also known as Priority Substances Directive), which set Environmental Quality Standards (EQSs) for some substances that hitherto had not been subjected to monitoring and control. An Environmental Quality Standard (EQS) is defined in

the Directive as “*the concentration of a particular pollutant or group of pollutants in water, sediment or biota, which should not be exceeded in order to protect human health and the environment*”. Two types of EQS were proposed [2]:

- *Annual average – EQS (AA-EQS)*: the average value or concentration of the substance concerned calculated over a one year period;
- *Maximum allowable concentration – EQS (MAC-EQS)*: the maximum allowable concentration of the substance measured specifically. The purpose of this standard is to limit short term pollution peaks.

Member States are required to maintain the concentration of priority substances in their surface waters below EQSs, either by implementing measures to reduce their concentration or by aiming at phasing out their discharge. For this reason, some States are now adjusting their monitoring programmes to the requirements set out by the WFD, whereas the majority have not yet included the issue of emerging pollutants in their policy agenda. However, in some countries such as Germany and the UK, monitoring of emerging pollutants is taking place to some extent within national investigation programmes on the source and occurrence of EPs in the environment [11].

2.2.2 Chemicals Investigation Programme (CIP) and further update (CIP2)

In order to address the challenges set by the WFD and the Priority Substances Directive, the UK Water Industry Research (UKWIR) has collaborated with the water industry, the Environment Agency (EA) and other UK regulators in the design of a £25 million programme of investigations – the Chemicals Investigation Programme (CIP) – into the source and removal of trace substances in WwTWs effluents, thus establishing the basis for a national-scale assessment of the risk posed by chemicals in WwTW discharges. The programme included three main phases [3]:

- *C1 – Investigations to assess risk from chemicals*: final effluents from 162 WwTWs from England, Scotland and Wales were collected and analysed in order to identify the concentration of chemicals discharged into the water and their compliance with quality criteria;
- *C2 – Investigations to assess WwTWs performance*: the performances of 28 WwTWs were evaluated across primary, secondary and some tertiary treatment processes;
- *C3 – Source investigations*: nine urban catchments across the UK were studied to assess catchment sources of CIP determinands discharged to the sewers.

In preparation for the new Asset Management Plan 6 (AMP6, 2015-2020) of the water industry and for the forthcoming stages of action under the WFD, the CIP is being updated into a new £140 million programme, called CIP2, which focuses on more site-specific issues and incorporates investigations of phosphorus removal technologies. The main aim of CIP2 is a characterisation of EQS compliance at a wider number of WwTWs, either existing CIP sites or works that have not been monitored so far. Furthermore, a continuous survey of trace contaminants in wastewater will be carried on, in order to gain information on a range of substances which will likely be subject to future compliance legislation (AMP7, 2020-2025). Additional parts of the programme consist in:

- *A series of pilot/demonstration scale treatment investigations*, which aim to provide data and technical expertise through full scale testing of technologies selected after AMP5 CIP, as well as pilot scale trials of novel treatment technologies, to ensure the delivery of required improvements in water quality.
- *Investigations into approaches to catchment management*, which will comprehend five catchment studies to investigate catchment-scale issues.

Regarding current compliance with water quality standards, CIP2 has been divided into three main components, each comprehending a number of different endeavours, as shown in **Table 2.1**. The Arvia process for organics removal fits into category C2b.

Table 2.1 - CIP programme main aims and objectives

NEP (National Environment Programme) code	Description	
<i>C1 - Investigations to confirm risk/failure from chemicals</i>	C1a	Effluent screening for current Priority Hazardous Substances (PHS), Priority Substances (PS), Special Pollutants (SP)
	C1b	Effluent screening and process investigations for emerging substances
	C1c	Technical investigations
	C1d	Programme Management and Options Appraisal reports (programme level and site specific)
	C1e	Environmental monitoring upstream and downstream of C1a sites
<i>C2 - Feasibility studies for chemicals</i>	C2a	Full scale demonstration plants of promising technology from AMP5 CIP or linked to PR14 new build
	C2b	Pilot plants - Technology not looked at in AMP5 CIP
	C2c	Catchment study source control investigations for existing and new PHS/PS/SP including undertaking and measuring effectiveness of in the ground water company source control work
	C2d	Programme Management and Options Appraisal reports (programme level and site specific)
<i>P - Investigations/trials into P removal treatment</i>	P1a	Assess pilot plant trials of technologies to achieve 0,1 mgP/L annual average

NEP (National Environment Programme) code	Description	
<i>technologies</i>	P1b	Assess process optimisation techniques to achieve low P effluent concentrations
	P1c	Investigations into innovative technologies (at lab or pilot stage) to assess techniques that could reduce effluent concentrations to 0,1 mg/L or less

CIP2 also revised and further extended the list of substances originally targeted in the Chemicals Investigation Programme, to include priority substances, substances pending review to be classified as priority substances and other substances of specific concern. This project aims at investigating the fate of all the substances listed by CIP2, for a total of 55 determinands:

- **Metals:** nickel, lead, copper, zinc, cadmium, mercury, iron, aluminium, chromium, both dissolved and total fraction;
- **Priority substances:** “penta” congeners 28, 47, 99, 100, 153 and 154 (BDEs), di (2-ethylhexyl) phthalate (DEHP), nonylphenol, nonylphenol with 1, 2 and 3 ethoxylate units, tributyltin compounds (TBT), octylphenols (4-(1,1',3,3'- tetramethylbutyl)-phenol), hexabromocyclododecane, benzo(a)pyrene;
- **Special pollutants:** Perfluorooctane sulfonic acid (PFOS), perfluorooctanoic acid (PFOA), fluoranthene, triclosan, cypermethrin;
- **Steroids:** oestrone (E1), 17 β -oestradiol (E2), 17 α -ethinyloestradiol (EE2);
- **Pharmaceuticals:** diclofenac, ibuprofen, atorvastatin, para and ortho hydroxy atorvastatin, propranolol, atenolol, erythromycin, norerythromycin, azithromycin, clarithromycin, ciprofloxacin, metformin, ranitidine, carbamazepine, 10,11-epoxy carbamazepine, sertraline, norsetraline, fluoxetine, tamoxifen, trixylenyl phosphate, 1,2,3 benzotriazole (tautomers 1H and 2H), tolytriazole (4, 5 methyl benzotriazole).

The determinands' physicochemical properties are reported in **Appendix A**.

2.3 Emerging pollutants' in surface waters and WwTWs

2.3.1 Sources

Many of the selected micropollutants have urban origin and are used daily in households, workplaces or in the urban environment. Although sources and pathways of contamination of many chemicals still remain to be identified with certainty, it is generally believed that emerging pollutants mainly enter the urban water cycle through sewers. This is the case for “down the drain” products, such as detergents, personal care products, pharmaceuticals and their metabolites, and several household chemicals and flame retardants. Municipal

wastewater is further contaminated by diffuse sources of non-domestic pollutants, such as heavy metals, pesticides or hydrocarbons, leached during road wash-off or agricultural and landfill run-off [7], [9], [12]. Hence, WwTWs represent the last barrier where these substances could be removed before reaching natural water bodies and the aquatic environment.

2.3.2 Removal mechanisms in WwTWs

A certain decrease in micropollutants' concentration has been registered within conventional WwTWs, due to physical, chemical or biological processes occurring during sewage treatment and depending on the chemicals' physicochemical properties [12]. However, the fate and the metabolic degradation of many of these substances have not yet been fully understood, and neither has a process succession able to guarantee removal to Predicted No Effect Concentrations (PNEC) [2].

The four main processes involved in micropollutants removal within WwTW as follows [12]:

- Sorption;
- Volatilisation;
- Abiotic degradation;
- Biological transformation.

Sorption and volatilisation determine the pollutant's transfer from one compartment (water) to another (solid phase or gas phase), whereas abiotic degradation converts pollutants to a simpler form due to the occurrence of abiotic reactions, i.e. hydrolysis or photolysis.

Microbial populations either use micropollutants as substrates or transform them into different compounds, which may result in a more toxic or persistent to biodegrade pollutant [2].

2.3.2.1 Sorption

Sorption is a physicochemical phenomenon occurring when a pollutant migrates to a solid or liquid phase from which it can be removed by a physical process.

Generally speaking, the sorption potential of a substance can be assessed by its octanol/water coefficient ($\text{Log } K_{ow}$), which is considered to be a good indicator of hydrophobicity and environmental fate. The interpretation of $\text{Log } K_{ow}$ values and fate of substances in WwTWs can be classified as follows [13]:

- $\text{Log } K_{ow} < 2.5$: hydrophilic substance with high bioavailability, sorption to sludge is not expected to contribute to the removal of pollutants, which are transported with the liquid phase of the wastewater;

- $2.5 < \text{Log } K_{ow} < 4$: moderately hydrophobic substance with some sorption potential, fate is more dependent on the wastewater matrix complexity;
- $\text{Log } K_{ow} > 4$: strongly hydrophobic, sorption to sludge and suspended matter likely to be dominant.

Sorption onto sludge thus represents an important removal mechanism, especially for hydrophobic substances, as the mechanisms governing it are mainly two [12]:

- *Hydrophobic interactions*, between hydrophobic pollutants and suspended solids, extracellular polymeric substances or the lipophilic cell membrane of the microorganisms;
- *Van der Waals type electrostatic interactions* between positively charged groups of the pollutant and mainly negatively charged surfaces of the microorganisms and effluent organic matter.

Furthermore, the removal of a hazardous substance can be affected by the presence of dissolved or colloidal organic matter, which enhances the apparent solubility of hydrophobic substances, rendering them more stable in the aqueous phase and limiting their potential for adsorption onto sludge.

2.3.2.2 Volatilisation

Volatilisation refers to the passage of a substance from a liquid to a gaseous phase and essentially depends on the volatility of the compound (Henry's law constant, K_H) at which the process operates conditions (aeration, agitation, temperature and atmospheric pressure).

Compounds with low aqueous solubility, low vapour pressure and low molecular mass are easily transferred into the atmosphere. As a general law, compounds with a Henry's constant over $10^{-3} \text{ atm}/(\text{mol m}^3)$ can be removed by volatilisation [14]. According to Rogers [15], the material losses of organic compounds during sewage treatment can be predicted using an empirical correlation between K_H and $\text{Log } K_{ow}$:

- $K_H > 1 \times 10^{-4}$ and $K_H/\text{Log } K_{ow} > 1 \times 10^{-9}$ high volatilisation potential;
- $K_H < 1 \times 10^{-4}$ and $K_H/\text{Log } K_{ow} < 1 \times 10^{-9}$ low volatilisation potential.

However, according to Luo et al., volatilisation of micropollutants is negligible for pharmaceuticals and oestrogens, but the process could be intensified with the aid of additional air supply [8].

2.3.2.3 Abiotic degradation

Organic micropollutants could also be abated during conventional sewage treatment by means of abiotic reactions such as hydrolysis or photolysis [2], [12].

Hydrolysis involves the cleavage of chemical bonds by the addition of water molecules. Temperature, pH, moisture and inorganic matter can have an influence on chemical degradation.

Photolysis occurs when a photon is absorbed by a compound, leading to chemical cleavage of the chemical bond. However, this process rarely occurs in conventional WwTWs due to the high turbidity of the wastewater matrix, which inhibits the penetration of light into the water.

2.3.2.4 Biological transformation

Biodegradation refers to the biological decomposition of substances by microorganisms, which employ organic micropollutants as a growth substrate. These substrates, along with other organic compounds, can provide energy (catabolism) or act as a carbon source (anabolism) for their cell development (maintenance, growth and reproduction). For many hydrophilic organic micropollutants, biotransformation represents the main removal mechanism during sewage treatment [12].

The biodegradation of a substance is influenced by a wide array of factors, among which micropollutants' and wastewater properties, the microbial community undertaking the biodegradation and WwTWs operational parameters.

Emerging pollutants' properties of interest are mainly those impacting bioavailability and transport, such as Log K_{ow} , pK_a and diffusivity [2], and the presence of particular functional groups (i.e. linear compounds with short side chains, unsaturated aliphatic compounds and compounds possessing electron donating functional groups) [8].

The wastewater properties affecting biodegradation are mainly temperature, pH, redox conditions, acidity, alkalinity [8]. The composition of the matrix also plays a significant role: availability of enough substrate to support the biological community's growth, existence of other phases or substances that create a bond with the organic pollutant, rendering it more or less biodegradable, the presence of biodegradation inhibitors or substances affecting the metabolism through co-metabolism or substrate competition [2].

The removal of pollutants by biodegradation also depends on the amount of microorganisms undertaking the process (indirectly, sludge concentration) and their specific type (sludge composition) [12].

Solid Retention Time (SRT) within the reactor, to allow microbial acclimatisation and the establishment of a diverse microbial community, and Hydraulic Retention Time (HRT), i.e. the amount of time allowing for sorption and biodegradation, are two noteworthy operational parameters affecting biodegradation [8].

2.3.3 Occurrence and fate in WwTWs

The fate of emerging pollutants during sewage treatment depends both on internal and external factors. Whereas internal factors are micropollutant related, mainly to their physicochemical properties (hydrophobicity, biodegradability and volatility), external factors are linked to treatment type, to the mixture of micropollutants in the wastewater matrix as well as to its pH and temperature [8]. **Table 2.2** describes the fate of selected classes of micropollutants in conventional WwTWs, while **Table 2.3** presents the concentration of chosen EPs in surface water and in the final effluents, together with their EQSs and average values of removal in conventional treatment works.

Table 2.2 - Occurrence, effects and fate of various classes of micropollutants (adapted from [12])

Class	Subclasses and use	Occurrence	Effects	Fate
Surfactants	Detergents and cleaners, personal care, textiles, paint additives, lacquers and plastic	Directly discharged into sewers because of high consumption. Concentrations relatively high (> 40 mg/L).	Potential development of bacterial resistance. Variable toxicity to aquatic flora and fauna (invertebrates and fish). Potential for bioaccumulation [16]	Most are easily biodegradable and well removed in WwTWs. Mainly removed by biodegradability and adsorption. Still found at high concentration in the effluent, due to influent high concentration.
Pharmaceuticals	Analgesic and anti-inflammatory drugs, antidiabetics, antihypertensives, lipid regulators, β -blockers	About 3000 compounds are commercially available in Europe. These compounds are excreted via urine and faeces, partially as the original molecule (not metabolised in the body) and partially as metabolites, which are mainly hydroxylated, hydrolysed or conjugated forms of the parent compounds.	Possible cocktail effects, difficult to evaluate, as the threshold of many substances cannot easily be assessed. Potential for antimicrobial and cross resistance of different bacteria.	The majority of pharmaceuticals are removed less than 50%. They have low volatility and are not expected to be stripped. Removal by sorption can be significant for positively charged pharmaceuticals. Most pharmaceuticals have high solubility, low hydrophobicity and negative charge, which mean low affinity for biological sludge. Thus they are mostly found in the dissolved phase biodegradation is the main removal mechanism.
Steroids (E1, E2, EE2)	Natural hormones and contraceptives	Excreted through urine	Endocrine disruption in fish and other aquatic animals. Abnormal development of reproductive, neurological, cardiovascular, metabolic and immune system [2], [17].	Natural oestrogens can be removed by bacteria in WwTWs. Secondary treatment with activated sludge effective for E2 and EE2, with efficiency 85%, and lower removals for E1 because it is a metabolic intermediate of E2 [17].
Antimicrobials (PCP)	Soaps (liquid and bars), toothpastes, deodorants and shave gels.	Concentrations in crude wastewater relatively high. They do not undergo metabolic changes prior to their release in water [7].	Potential for bioaccumulation [7].	Due to their hydrophobicity, they are normally well removed onto sludge. In many cases their concentration in the final effluent still exceeds proposed thresholds.
Plasticisers and plastic additives (phthalates)	PVC pipes	Widespread use, medium to high concentrations	Disruption of endocrine activity and other human health problems (alteration of reproduction and neurodevelopment)	Partially to well removed in WwTWs (60-95%), partly by sorption but mainly by biodegradation

Class	Subclasses and use	Occurrence	Effects	Fate
Anticorrosives (benzotriazoles)	De-icing fluids for aircrafts, brake fluids, industrial cooling systems, dishwashing detergents	Relatively high concentration (3 mg/d per capita released in sewers)	Potentially toxic for aquatic organisms, growth inhibition. Effects worse in winter months, when concentrations are higher [18]	Highly polar and water soluble, removal generally low, on average between 20-30%. High concentration in effluents.
Flame retardants (brominated)	Building materials, electrical devices, upholstered furniture, textiles	Present in water in many forms (different congeners), frequently detected in crude wastewater	Potential for bioaccumulation	Usually well removed, mostly during secondary treatment. Due to their hydrophobicity and their low potential for degradation, mainly adsorbed on sludge and aquatic sediments.
Perfluorinated compounds	Water proofing sprays, stain or water resistant textiles	Detected in wastewater and sludge in concentrations up to hundreds of ng/L. Highest concentrations are from PFOS and PFOA. [19]	Potential for bioaccumulation. Adverse effects on human growth, implications in birth weight, fertility disorders, phenomena of early menopause in women, carcinogenesis and thyroid malfunction [19]	Due to their persistence and non-degradability, not significantly removed in WwTW, effluent concentrations similar to influent.
Polycyclic aromatic hydrocarbons (PAHs)	Most have not industrial use. Naphthalene in lubricants, bathroom products, wood preservatives.	Widely spread through the environment. Subject to wet and dry deposition, they end up in waters due to urban runoff occurring during rain events. Concentrations in wastewater relatively low.	Highly carcinogenic, mutagenic and teratogenic. Sediment contamination.	Highly variable removal, depending on the compound. High molecular weight compounds (usually more toxic) are usually better removed (80%). Concentrations in final effluent are quite low, but several PAHs are still above the proposed EQS for surface waters.

Table 2.3 - Occurrence and fate of selected trace metals and micropollutants

Substance	CAS number	Family	Surface waters [ng/L]	Reference for surface waters	Effluent concentration [ng/L] ¹	EQSs ² [ng/L]	Removal in WwTW [%] ³
METALS							
Nickel	7440-02-0	-	-	-	4,900/4,300 ⁴	4,000	31/6
Lead	7439-92-1	-	-	-	800/400	1,200	89/57
Copper	7440-50-8	-	-	-	8,300/5,600	1,000	86/63
Zinc	7440-66-6	-	-	-	30,900-24,400	12,900	75/16
Cadmium	7440-43-9	-	-	-	50/24	80	85/89
Mercury	7439-97-6	-	-	-	16/11		79/32
Iron	7439-89-6	-	-	-	170,000/59,000	730,000	78/61
Aluminium (reactive)	7429-90-5	-	-	-	68,000/20,000	50,000	93/44
Chromium	7440-47-3	-	-	-	700/600	3,400	73/-
PRIORITY SUBSTANCES							
Di-(2-ethylhexyl) phthalate (DEHP)	117-81-7	Plastic additives	140-980	[8]	2,400	1,300	94
BDE 47	5436-43-1	Brominated flame retardant	-	-	0.7-8	0.5	91
BDE 99	32534-81-9	Brominated flame retardant	-	-	0.6-9	0.5	93
Nonylphenols	25154-52-3**	Non-ionic surfactant	1.3-179600	[8]	-	300	-
4-nonylphenol monoethoxylate	25154-52-3**	Non ionic-surfactant	up to 20000 ⁵	[20]	6,000	300	90
4-nonylphenol diethoxylate	25154-52-3**	Non ionic-surfactant	up to 9000	[20]	6,000	300	90
Octylphenols	140-66-9	Non-ionic surfactant	0.04-4300	[8]	1,000	100	80
Benzo(a)pyrene	50-32-8	PAHs	up to 240	[2]	1.1	0.2	70

¹ [12]. The effluent concentrations all refer to the European or UK value found in literature;

² AA-EQSs for CIP2, supplied by Atkins Ltd. Pharmaceuticals refer to PNECs (Predicted No Effect Concentration) instead of EQSs;

³ [12].

⁴ The first value refers to the total fraction, the second to the dissolved one;

⁵ The notation "up to" indicates the maximum value found in literature;

Substance	CAS number	Family	Surface waters [ng/L]	Reference for surface waters	Effluent concentration [ng/L] ¹	EQSs ² [ng/L]	Removal in WwTW [%] ³
SPECIAL POLLUTANTS							
Perfluorooctane sulfonic acid (PFOS)	335-67-1	Perfluorinated compound	up to 174	[21]	13	0.7	1
Pefluorooctanoic acid	1763-23-1	Perfluorinated compound	up to 1341	[21]	12	0.7	1
Fluoranthene	206-44-0	PAHs	-	-	10	6.3	80
Triclosan	3380-34-5	Biocides	<0.1-2300	[2]	200	100	90
STEROIDS							
Oestrone	53-16-7	Natural hormone	<0.1-38	[8]	12	3	76
17β-oestradiol	50-28-2	Natural hormone	<0.3-15.5	[2]	1.3	1	90
17α-ethynyloestradiol	57-63-6	Contraceptive	<0.1-30.8	[2]	0.5	0.1	60
PHARMACEUTICALS							
Diclofenac	15307-86-5	Anti-inflammatory	<0.8-1043	[2]	260	50	20
Ibuprofen	15687-27-1	Anti-inflammatory	1-2370	[22]	330	10	80
Atorvastatin	134523-00-5	Anti-cholesterol	up to 51	[23]	-	1,700	-
o-hydroxy-atorvastatin	214217-86-4	Anti-cholesterol	up to 1.2	[23]	-	1,700	-
p-hydroxy-atorvastatin	163217-70-7	Anti-cholesterol	up to 2.0	[23]	-	1,700	-
Propranolol	525-66-6	β-blocker	<0.5-107	[22]	140	100	28
Atenolol	29122-68-7	β-blocker	<1-487	[22]	843	148,000	41
Erythromycin	114-07-8	Antibiotic	<0.5-159	[22]	830	200	45
Azithromycin	83905-01-5	Antibiotic	-	-	220-408	90	39
Clarithromycin	81103-11-9	Antibiotic	up to 20.3	[2]	130-276	13	33
Ciprofloxacin	86393-32-0	Antibiotic	av 9 ⁶	[2]	96	8.9	69
Metformin	657-24-9	Anti-diabetic	up to 150	[20]	10,347-27,800	13,450	57
Ranitidine	66357-35-5	Aastric antacid	<3-32	[22]	7	310	52
Carbamazepine	298-46-4	Anticonvulsant	<0.5-251	[22]	832	2,500	16
Fluoxetine	54910-89-3	Anti-depressant	5.8-14	[22]	-	47	-
Tamoxifen	10540-29-1	Anti-oestrogen	<4-212	[22]	-	490	-
1,2,3 Benzotriazole (tautomers)	95-14-7	Corrosion inhibitor	up to 3,500	[18]	6,600	2	26

⁶ The notation "av" indicates the average value found in literature.

The reported concentrations of emerging pollutants in WwTW's influent and effluent reveal significant spatial and temporal variations, due to rate of production, specific sales and practises, human metabolism (excretion rate), daily water consumption per capita, environmental persistence and efficacy of the wastewater treatment. Studies suggest that the concentrations of Pharmaceutical and Personal Care Products (PPCP) is well correlated with their production amounts and their patterns of usage and consumption [8].

Some compounds in the effluent can be discharged at relatively high concentrations still, sometimes higher than their respective EQSs: the presence of some substances, such as human metabolites and/or transformation products in the effluent, can lead to a FE concentration exceeding the influent one, as these products could be transformed back to parent compound during biological treatment (e.g. metformin, carbamazepine, erythromycin). Other factors could be further contributing to negative removals, i.e. fluctuations in daily concentration during the sampling period, analytical uncertainty, or desorption of molecules from sludge and suspended particulate matter [8], [12].

Generally, hydrophobic and easily biodegradable pollutants are largely removed during conventional treatment (>70%), whilst polar and poorly biodegradable ones (most pharmaceuticals and biocides) do not reach 50% removal, thus representing a greater risk of contamination for surface waters [12].

However efficient treatment may be, after organic micropollutants are removed from wastewater, they are concentrated into primary and secondary sewage sludge depending on their hydrophobicity and general tendency to be adsorbed on flocs. Conventionally, sludge treatment in WwTWs involves processes of dewatering, thickening and digestion to reduce quantities and volumes, and then compacting to form a cake. Sludge quantities may also be reduced by thermal processes (i.e. incineration, pyrolysis or wet-air oxidation) before ultimately being disposed. Landfill and land application are the most widespread means of disposal [24], especially the latter, as sludge can be used as a fertiliser owing to its richness in nutrients [25].

According to Mailler et al. [26], while PFOS, PFOA and many pharmaceuticals, including ciprofloxacin and propranolol, generally show low concentrations in treated sludge and an overall good propensity to elimination, other compounds, such as alkylphenols (NOP and ethoxylates), DEHP and some PAHs tend to remain in treated sludge. As such, residual organic micropollutants in sludge could create another potential pathway of aquatic or soil contamination from WwTWs, impacting soil organisms or being transferred up to the food chain, especially when sludge is landfilled or repurposed for agriculture [4], [25].

Furthermore, an element of risk is posed by wash-off of sewage sludge into water bodies, which could lead to exceedance of the more stringent EQSs set for surface waters [4].

Although organic micropollutants in sludge are not being regulated yet, as a review of the Sewage Sludge Directive (86/278/CE) [25] concentration limits are being implemented to ensure the sludge's safe use in agriculture, together with advanced treatment to reduce micropollutants concentrations in sludge (i.e. low-frequency ultrasound [25], advanced oxidation [27]).

2.4 Tertiary treatment

Apart from source control to avoid micropollutants' release - via regulations and substitution of harmful chemicals - and improvement and/or optimisation of existing treatment technologies, another step to ensure a reduction in their discharge from WwTWs would be the addition of complementary advanced treatments (tertiary treatments).

Up to now, advanced processes of physicochemical nature are primarily applied, removing pollutants from wastewater either physically, by adsorption (i.e. activated carbon) or membrane filtration (micro-, ultra-, nano-filtration and reverse osmosis), or chemically (oxidation with ozone, peroxide, $\bullet\text{OH}$ radicals) [12]. Other alternatives for tertiary treatment exploit biological processes, such as biodegradation and the use of microbial pure cultures for targeted biodegradation, whereas constructed wetlands combine all three processes to achieve micropollutants removal [2].

However, many of these methods currently suffer from major drawbacks: filtration and adsorption alone do not always guarantee compliance to discharge consents, chemical oxidations have low capacity rates and necessitate transportation and storage of harmful reagents, whilst advanced oxidation processes (AOPs) determine considerable investment costs [28]

2.5 Basis of electrochemical oxidation of organic pollutants

In this framework, oxidative electrochemical solutions offer a versatile, efficient and cost effective alternative to these tertiary technologies, as electrons can be considered a "clean reagent" [29] and organics mineralisation can be achieved on electrodes of specific material avoiding chemicals' use and with the only aid of electric energy [30].

In electro-oxidation, pollutants can be removed by two main processes [28]:

- Direct Electrolysis (DE), where pollutants exchange electrons directly with the anode surface without any other substance participation:

- Indirect Electrolysis (IE), where some electro-active species generated at the anode act as intermediaries to carry electrons from the organic compounds to the electrode.

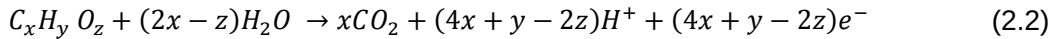
2.5.1 Direct Electrolysis

In direct electrolysis, organics contained in the bulk of wastewater are electrolysed after adsorption on the anode surface, without the involvement of any other substance other than the electron (Direct Electron Transfer, DET):

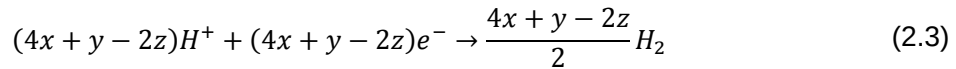


where R_{ads} represents the reagents of adsorption, P_{ads} the products of adsorption and n is the number of electrons involved in the reaction [28].

In general, anodic oxidation reactions occur simultaneously with the transfer of oxygen from water to the reaction products using electric energy, in a reaction called Electrochemical Oxygen Transfer (EOTR) [31]. For a generic organic compound, water is used in the electrolytic cell [28]:



Meanwhile, protons released by this reaction are discharged at the cathode to form gaseous hydrogen H_2 , according to **(2.3)** [28]:

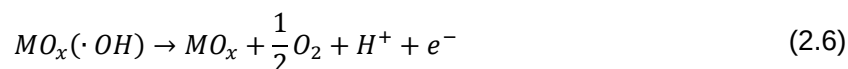
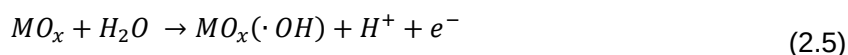


However, the main problem in conducting this reaction at low potential, before oxygen evolution, is the possibility of a decrease in catalytic activity due to the formation of a polymer film on the anodic surface. This deactivation mainly depends on the adsorption properties of the anode surface and on the nature of the organic pollutants, as it appears to be less evident in the presence of anodes with low adsorption capacity and inert surface, while it occurs more frequently at high concentration of organics and aromatic substrates [28].

On the other hand, organics removal via electrochemical reactions can be achieved without electron fouling, by performing the electrolysis at higher anodic potentials in the region of water discharge, owing to the participation of reaction intermediates of oxygen evolution. While this process does not require the addition of oxidation catalysts and does not produce any by-products, it determines a drop in current efficiency caused by the occurrence of secondary reactions of oxygen evolution [28], following reaction **(2.4)**:

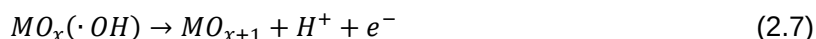


In the first step of the process at higher cell potentials, H₂O in acid solution is discharged at the anode (1.23 V/SHE Standard Hydrogen Electrode), producing adsorbed hydroxyl radicals on the oxide anode surface (MO_x) **(2.5)** which represent the main reaction intermediates for O₂ evolution **(2.6)** [32]:



The following step depends on the nature of the electrode materials:

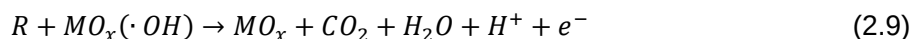
1. At active electrodes, there is a strong affinity between the electrode (MO_x) and the hydroxyl radicals (•OH) [29]. Adsorbed hydroxyl radicals might interact with the oxygen already present in the oxide anode, and the oxygen belonging to the radical itself may translate to the lattice of the anode, forming a higher oxide (MO_{x+1}) [28]:



This chemisorbed oxygen play a mediation role in the selective oxidation of organics on “active” electrodes [28]:



2. At non-active electrodes, where formation of a higher oxide is not an option, hydroxyl radicals (called physisorbed oxygen) might concur to the oxidation of organics, resulting in the complete combustion to CO₂ and water [28], in a reaction occurring very close the electrode surface, due to the short lifespan of hydroxyl radicals [33]:



In general, the hydroxyl radical is more effective for pollutant oxidation than oxygen on the anode lattice [34]. Hence, anodes which are good catalysts for oxygen evolution reactions (called low overvoltage anodes, such as carbon and graphite, 1.7 V/SHE) have an active behaviour, only allowing a partial and selective oxidation of organics (but have low current efficiency for organics oxidation, as most of the current supplied is used to split water), while anodes which don't favour oxygen evolution (called high overvoltage anodes, such as boron doped diamond (BDD) or lead dioxide, respectively 2.3 and 1.9 V/SHE) produce a

complete oxidation of the organics to CO₂ (high current efficiency for organics oxidation) [28], [34].

Figure 2.1 shows a synthesis of the electrochemical oxidation of organic compounds on active and non-active anodes.

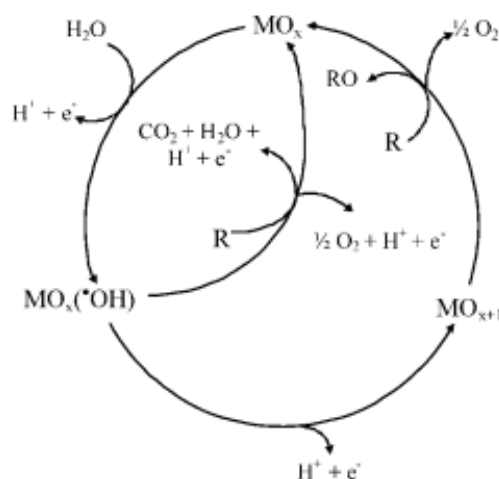


Figure 2.1 - Scheme of the electrochemical oxidation of organic compounds [32]

In some cases (i.e. the removal of heavy metals), the positive ions (M^{n+}) can be removed at the cathode via cathodic deposition **(2.10)** in a phenomenon called electroplating [35]:



In direct electrolysis, before the organics contained in the bulk of wastewater between the electrodes can be oxidised, they must reach the electrode surface and be adsorbed on it. For this reason, mass transfer plays a very important part in the process, as it can often limit the oxidation rate [33]. As already stated, different electrodes' materials determine whether or not hydroxyl radicals are involved in the oxidation of pollutants. In non-active electrodes, where the reaction occurs very close the surface, mass transfer from the water to the electrode surface becomes key to the process, as three stages phases have to be completed [33]:

1. Pollutant transfer from the bulk wastewater to the electrode surface;
2. Anodic reaction (or mediated oxidation via hydroxyl radicals);
3. Oxidised product transfer from the electrode surface to the bulk wastewater.

At this point, if the pollutant does not reach the electrode surface quickly enough, the process becomes mass transfer controlled, and involves the transport of the contaminant by diffusion. The mass transfer rate can thus be modelled as follows **(2.11)** [33]:

$$r = k_m A [(P_{bulk} - P_{electr})] \quad (2.11)$$

where: k_m is the mass transfer coefficient (m s^{-1}), A is the electrode surface (m^2), P_{bulk} and P_{electr} represent the pollutants' concentration in the bulk solution and on the electrode, respectively.

2.5.2 Indirect Electrolysis

Indirect electrolysis actively prevents electron fouling, avoiding a direct electron exchange between organics and the anodic surface. In this case, at potentials far from the oxygen evolution, pollutants are oxidised via electrochemically generated redox reagents, which act as electron carriers between the organics and the electrode [28].

Indirect electrolysis can be achieved through strong oxidising chemicals - such as active chlorine, ozone, hydrogen peroxide, persulfate and percarbonate - or metallic ions - such as Ag^{2+} , Ce^{4+} , Co^{3+} , Fe^{3+} , Mn^{3+} and Ni^{2+} -, which are oxidised on the anode from a stable, low valence state to a reactive high valence state, which, in turn, may attack pollutants and produce hydroxyl free radicals that promote the organics destruction [28], [34].

2.6 Three dimensional electrodes for organics removal

In spite of their advantages, some shortcomings are still limiting the industrial application of electrochemical oxidation techniques, such as the short lifetime of electrode material and low current efficiency achieved. These downsides could be overcome by using a three dimensional electrode (or bed electrode): compared to a conventional electrolytic cell, the addition of granular activated carbon (GAC) or other reactive media in between the electrodes may favour the concentration of pollutants on the adsorbent surface and effectively enhance oxidation, as it eliminates the mass transfer step of the reaction [36]. Furthermore, the large specific area of the particles could provide more reactive sites (for adsorption and even catalytic reactions), determining higher removal efficiency [35].

Although adsorption on GAC is a well-established removal technique, it provides an incomplete removal system, as it only determines a transfer - not a destruction- of the pollutant on its surface. Once the carbon is saturated it is usually landfilled or incinerated, or alternatively it can be regenerated. Regeneration is extensively used, as it is the most environmentally sound and commercially viable option; however, it is a very high energy, high cost process, which could result in material losses of ~5-10% and which would have to be carried out off site [37].

Hence, the technological research is focusing on the implementation of specific 3D electrodes, of which the Arvia Organics Destruction Cell is an example: as the current passes through the bed of media, it determines the oxidation - and consequent desorption - of the adsorbed pollutants, thus providing a simultaneous regeneration of the media and reaching efficiencies up to 80-95% [38].

At appropriate voltage, the bed particles encased between the electrodes will be polarised to form a considerable number of microelectrodes with one anodic and one cathodic surface. While the three-dimensional process spurs from the conventional bi-dimensional electrode process, it has been proven to warranty a COD removal efficiency 10-15% higher than 2D systems [35].

The mechanism for organics removal in 3D electrochemical process is complex, and depends on wastewater matrix, occurring contaminants, electrode and particle materials. The occurring reactions at the anode and cathode are the same as the 2D process (direct and indirect electrolysis), whereas the bed particles located between the electrodes, without direct electric contact, behave as an adsorbent and improve the distribution of ionic charge, which offers more specific degradation processes described below [35].

2.6.1 Adsorption/electrosorption

When an external electrostatic field is applied to the particle electrode surface immersed in an electrolyte, one side of the particle will be negatively polarised, while the other will gather positive charge. The electrolyte's charged ions shift to the opposite side of the charged particle electrodes, determining the occurrence of electrosorption, which, combined with adsorption, allows for the removal of organic substances [35].

2.6.2 Oxidation/catalytic degradation

With the formation of polarised surfaces, every particle acts as a micro electrolytic cell, where direct and indirect electrolysis occurring on the particles' anodic surface determine the abatement of organic substances. However, at the cathodic surface, oxidation occurs via an electro Fenton mechanism [35], [39], as dissolved oxygen is reduced forming hydrogen peroxide **(2.12)**:



These studies suggest that media particles, in particular GAC, could catalyse the transformation from H_2O_2 to hydroxyl radicals, due to the presence of polyaromatic portions and functional groups on the media surface, thus enhancing the concentration of these

reactive oxidants in the 3D system. In fact, at low current density H_2O_2 can react with some metals (i.e. Fe^{2+}) in order to produce hydroxyl radicals [39]:

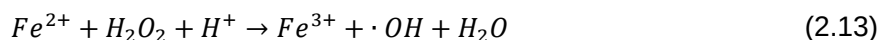


Figure 2.2 shows a complete scheme of the reactions occurring in a 3D electrode.

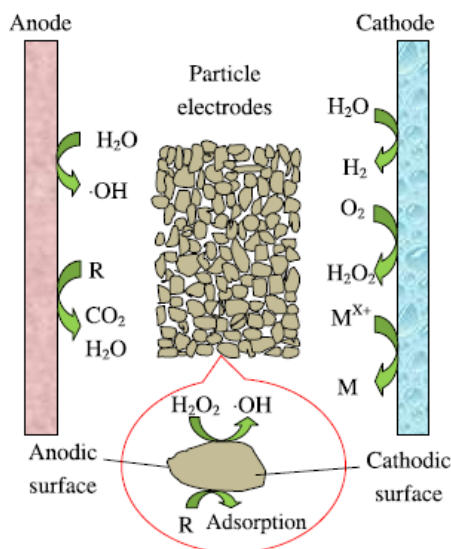


Figure 2.2 – Mechanism scheme of 3D electrode

In summary, depending on the properties of the particle electrodes, some or all of the mechanisms mentioned above occur. The pollutants are effectively degraded by the combination of different mechanisms, and the particle itself undergoes dynamic adsorption, electrochemical oxidation and desorption process, which effectively regenerates the particle electrode [35].

2.7 The ARVIA process

Generally speaking, the particle electrode of a 3D process would mainly have to exhibit good electrical conductivity and offer a good surface area. Granular activated carbon (GAC) is probably the most familiar material due to its superior characteristics, such as large surface area to volume ratio, broad pore structure and excellent adsorption capacity [35]. **Table 2.4** shows the most used particle electrodes materials and their performances.

Table 2.4 – Most used particle electrode materials

Particle material	Characteristics	Role
Granular Activated Carbon (GAC)	Specific surface: ~ 1028 m ² /g Particle sizes: ~ 0.2 mm	Adsorption, catalysis
Metal particles	4 g iron	Electro-Fenton reactions
Carbon Aerogel (CA)	Surface area: ~ 582.7 m ² /g	Adsorption and electrochemical

Particle material	Characteristics	Role
Modified kaolin	Diameter: $\sim 0.2\text{-}0.4\text{ cm}$	oxidation
	Surface area: $\sim 20\text{ m}^2/\text{g}$	Adsorption reaction
	Pore volume: $0.5\text{ cm}^3/\text{g}$	

A new commercial example of 3D electrode for organics removal has been developed at the University of Manchester in 2004 and has later been patented by a spin-out company named Arvia Technology, firstly being used in the removal of oil in the nuclear industry. While a traditional 3D electrode in terms of process, the particle electrode represents the real innovation of this technology: it is called Nyex and it is a non-porous, highly conductive material originated from graphite.

Graphite is a lamellar structure in which hexagonal lattices are layered on top of each other and held together by weak Van der Waals bonds, allowing the layers to be easily separated or to slide past each other. Atoms in the plane are bonded via covalent bonds, with only three of the four available bonding sites effectively used, while the fourth electron is free to migrate in the plane, thus making the material electrically conductive (**Figure 2.3**).

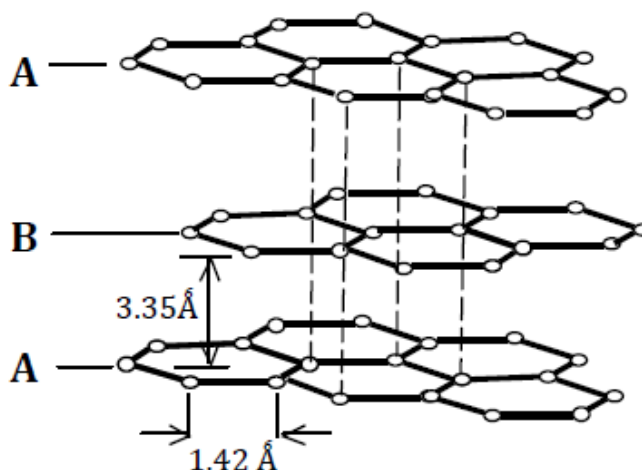


Figure 2.3 - Structure of graphite [40]

Nyex, however, is generated from the modification of graphite by chemical and thermal treatments to enhance conductivity, mass transfer and to add more edges to the basic graphite. This novel media significantly reduces both the adsorption and regeneration times but, due to its reduced specific surface and limited adsorption capacity, requires on site regeneration [41]. As it is graphite based, this material also can be functionalised via intercalation with other compounds, allowing enhancements in the adsorption/oxidation of specific pollutants.

2.8 Adsorption of organics on carbon materials

Adsorption of organics from aqueous solutions on carbon materials is a complex interplay between electrostatic and non-electrostatic interactions and local chemical conditions, which means that a prediction of the adsorption performance of these materials still remains very difficult.

Electrostatic interactions, such as coulombic interactions, are important when dealing with a dissociated or protonated electrolyte in solution and mainly depend on the experimental conditions. Non-electrostatic interactions, which are always attractive interactions, are essentially due to hydrophobic interactions, hydrogen bonding and Van der Waals forces. Other factors affecting the adsorption process are properties of adsorbent and adsorbate, solution chemistry and temperature [40], [42].

2.8.1 Characteristics of the adsorbent

Pore texture, surface chemistry and mineral matter content can affect adsorption on carbonaceous media [42]. Other than surface area and porosity, the adsorption capacity of most carbon materials strongly depends on the accessibility of the organic molecules to the inner surface of the medium, whose resistance to diffusion represents the rate limiting step for porous carbonaceous materials [42]. Conversely, due to its non-porosity, Nyex ensures more rapid kinetics, due to the lack of diffusion into the inner pores [43]

The adsorption capacity of a carbonaceous material is also determined by the chemical nature of its surface. It is a heterogeneous surface, which consist of layers of graphite sheets and their corresponding edges. The latter are much more reactive than the internal atoms of the graphite sheets, and allow for functional groups containing nitrogen, hydrogen, halogens and particularly oxygen to be chemisorbed on them. The surface functional groups can be classified as acidic – i.e. carboxylic, phenols, and basic – i.e. ethers and carbonyls [44]

In the case of adsorption from aqueous phase, the nature of surface functional groups changes the interactions between the solute molecules and the carbon surface [42]. Thus, the presence of acidic or basic groups determines the charge and the hydrophobicity of the graphite layers and helps explaining the different attitude of the adsorbent towards different organics [44].

The presence of an acidic surface oxygen complex affects the surface hydrophobicity, thus impacting the adsorption of those hydrophobic compounds relying on hydrophobic bonding to be adsorbed [40], [42]. In particular, an increase in oxygen content of carbon (and, in

general of acidic surface groups) seems to determine a decrease in its hydrophobicity, as water molecules are bound to the surface oxygen by H-bonds, thus reducing the accessibility of the hydrophobic parts of the adsorbate to the hydrophobic sections of the surface [42]. Widening the studies on the effect of surface oxygen on adsorption, Kwon et al. assert that polar compounds – i.e. acetone [45] – seem to maintain the same adsorption capacity regardless of surface functionalisation with oxygen, whereas non polar adsorbates – i.e. propane [46] – show a decrease in adsorption close to one order of magnitude when the concentration of surface oxygen increases. On the other hand, basic functional groups contribute to enhance the surface hydrophobicity and display a strong affinity for those molecules with a minimal water solubility, such as phenols [44].

Another surface characteristic affecting adsorption is mineral matter content, whose increase determines a decrease in the adsorption capacity, as it can block the pores of the carbon matrix and tends to preferentially adsorb water due to its hydrophilic nature [42].

2.8.2 Characteristics of the adsorbate

Among the characteristics of the adsorbate influencing the process, Moreno-Castilla [42] identifies molecular size, solubility and the nature of the substituent if they are aromatic, which is mostly studied in literature in regards to the interaction between carbon materials and phenolic compounds [44].

Molecular size controls the molecules' accessibility to the pores of the carbonaceous media. Molecules with a suitable size will be adsorbed more favourably, as their dimension will allow more contact sites with the carbon surface, whereas too large molecules will incur difficulties when trying to fit in pores not large enough [42], [44].

As for water solubility, this parameter determines the hydrophobic interactions and it is evident that the more a molecule is soluble in water, the lower its affinity for an adsorptive media will be.

The interaction between functionalised organic groups and graphite surfaces has been studied by several researchers. While most of the studies are focused on aromatic compounds (and phenols in particular), Chen et al. take into account other compounds, asserting that attraction to carbon surfaces increases as nonpolar aliphatic < nonpolar aromatic < nitroaromatics [47]. As for phenolic compounds, Moreno-Castilla proposes three mechanisms to explain their adsorption behaviour on carbon materials, namely: the π - π dispersion interactions, the electron donor–acceptor complex and the solvent effect (H bonds formation) [42].

The π - π dispersion interactions represent the interaction between the aromatic rings in molecules and those on the graphite's basal plane [42]. Again, surface functional groups play an important role in determining the interactions between adsorbent and adsorbate: the presence of basic groups determines an increase in the π - electron density in the graphene layers and an increase in adsorption potential, whereas acidic groups remove electrons from the system, leading to weaker interactions between the π - electron of the compound aromatic's ring and the π - electron of the graphite layer [41], [42].

The electron donor-acceptor mechanism implies that the aromatic rings of the adsorbate act as electron acceptors and the aromatic rings of the carbon surface serve as donors. However, in contrast to this theory, some studies also suggest that graphite surface can behave as amphoteric adsorbents, in which π - π interactions occur between both π donors and acceptors [48];

Finally, in the solvent effect, water molecules can be adsorbed on the surface oxygen groups via H bonds. Once adsorbed on the surface, these molecules act as secondary adsorption centres bonding other water molecules by hydrogen bonds and preventing the migration of organic molecules to a large part of the carbonaceous surface [44].

2.8.3 Solution chemistry and operational parameters

One of the key parameters in describing adsorption is solution's pH, as it regulates the electrostatic interactions between adsorbent and adsorbate and determines the carbon surface charge as well as the dissociation or protonation of the electrolyte via its pK_a [42], [44].

The surface charge of the adsorbent depends on the solution pH and its point of zero charge (pH_{PZC}): when $pH < pH_{PZC}$ the total or external surface charge will be positive on the average, while $pH > pH_{PZC}$ will determine a negative surface charge. The adsorbate will be mainly in protonated form at $pH < pK_a$, while in deprotonated form at $pH > pK_a$. Moreno-Castilla studied the case of phenols, asserting that at pH values below their pK_a , phenols showed a maximal uptake, as they are indissociated and the dispersion interactions were dominant, whereas at $pH > pK_a$ the uptake decreased due to the electrostatic repulsion between the negative surface of the graphite and the formed anions [42].

With regards to the effect of temperature, an increasing uptake of organics is expected to take place when the temperature decreases, as adsorption is a spontaneous process [42].

Finally, when dealing with complex matrixes such as wastewater, another important factor affecting the adsorption process is the presence of a multitude of adsorbates, all competing

for adsorption sites on the carbon surface. For example, natural organic matter (NOM) competes via direct site competition and pore blockage: NOM molecules with similar size to that of target pollutants are mainly responsible for size competition, thus reducing the sites available for adsorption and the adsorption capacity for the target compound [44].

2.9 Parameters influencing 3D electrodes' efficiency

The effectiveness of a 3D electrode depends on a variety of factors, such as wastewater matrix characteristics, operating conditions and employed materials (both for the electrodes and the bed).

2.9.1 Influence of wastewater quality

2.9.1.1 Alkalinity

The hydroxyl radical is non-selective, and can thus be exhausted by the presence of organic or inorganic compounds, other than contaminants of concern. Both carbonates and bicarbonates have the ability to consume hydroxyl radicals, creating carbonate radicals, which can in turn react with other organic and inorganic compounds, at a much slower rate than the one offered by the sole oxidation by $\bullet\text{OH}$. This phenomena is much more prominent in wastewater with medium to high alkalinities ($>100 \text{ mg/L CaCO}_3$), where the concentration of carbonate and bicarbonate ions could be several orders of magnitude higher than the concentration of the choice pollutants [49].

2.9.1.2 Conductivity

Conductivity is a very important parameter in an electrochemical process, as it represents an electrolyte's ability to conduct electricity. In general, wastewaters with high content of inorganic substances (Mg^{2+} , Ca^{2+} , Cl^- , SO_2) have higher ionic strength and conductivity, leading to an increase in the ions' and electrons' mobility. In these conditions, electrochemical processes appear to be practical and cost effective, as energy consumption is reduced with an increase in conductivity [34].

During experiments on 3D electrodes conducted using Na_2SO_4 as electrolyte, Carlesi Jara et al. assert that the organic molecules' mass flow reaching the anodic surface per Ah decreases with the electrolyte conductivity. Furthermore, when the electrolyte displays a poor conductivity in 3D electrodes, the electronic pathway provided by the electrode material appears to be more favourable than the ionic path through the solution [50].

2.9.1.3 pH

The initial pH influences both direct and indirect oxidation and regeneration. Studies on dyes [35] and phenols [51] removal from wastewater suggest that COD removal decreases with increasing pH, especially over pH 6.5 for phenols. In general, Wei et al. [52] suggest that carbonate and bicarbonates may be formed in alkaline solution: their ability to scavenge $\bullet\text{OH}$ radicals (**Section 2.9.1.1**) could determine a deceleration of the oxidation process. For anodic oxidation, the COD removal efficiency decreased with pH increase, potentially due to the enhancement of side reactions of oxygen evolution, which can be more easily controlled and limited in acidic conditions [52]. On the other hand, for indirect oxidation of dyes, the removal efficiency increased with increasing pH, due to the production of H_2O_2 in a more alkaline solution [35].

2.9.1.4 Temperature

Although, many studies have shown that temperature has little impact on electrochemical oxidation with $\bullet\text{OH}$ radicals, the diffusion and oxidation rates would be increased at higher temperatures, and the kinetics of adsorption would be accelerated. In fact, the rise in temperature can produce an acceleration of the molecular motion and enhance the current density at an arbitrary voltage, which could be helpful for the decomposition of the organic matter [53].

2.9.1.5 Initial concentration of pollutants

In general, with the increase of the initial concentration of pollutants in the wastewater matrix, the COD removal efficiency tends to decrease, due to the increase in the adsorption and oxidation loads. Zhang suggests that the particles in the 3D electrode will lose adsorption capacity and catalytic ability, thus decreasing their operating life [35].

2.9.1.6 Natural Organic Matter

NOM comprehends large macromolecular compounds present in water (i.e. humic substances, proteins, lipids, biological debris) and, while not highly reactive, it scavenges hydroxyl radicals, thus limiting the effectiveness of oxidation [49].

In order to find out whether NOM is actually mineralised in anodic oxidation, Park et al. investigated the removal efficiencies' variations of total organic carbon (TOC) and dissolved organic carbon (DOC) at different voltages [54]. The results showed that not only the removals were continuously decreasing with applied voltage but also that, in the case of DOC, negative removals were achieved. These results could be explained by

hypothesising that particulate organic colloids, which can be barely decomposed at lower voltages, are transformed into soluble organics at higher voltages [54].

2.9.2 Influence of operational parameters

2.9.2.1 Current density and cell voltage

Current density and cell voltage are the most important variables in 3D systems, as they influence electrochemical oxidation along with the polarisation behaviour of the particle electrodes. Usually, either current density or voltage are used as a controlling parameter, and usually the treatment performance improves accordingly with their increase, albeit accompanied by an increase in energy consumption [35].

The energy consumption (EC) in an electrochemical cell is calculated with the following equation (2.14) [52]:

$$EC = \frac{UI\Delta t}{3.6V[(COD)_t - (COD)_{t+\Delta t}]} \quad (2.14)$$

where U is the cell voltage (V), $(COD)_t$ and $(COD)_{t+\Delta t}$ are the chemical oxygen demand ($\text{mol O}_2 \text{ m}^{-3}$) at times t and $t+\Delta t$ (s), I is the applied current (A) and V is the volume of the electrolyte (m^3).

Current efficiency is generally defined as “the ratio of the charge used for the oxidation of each compound to the total charge passed through electrolysis” [28]. The instantaneous current efficiency (ICE) can be measured through the values of electrolyte’s COD measured at regular intervals during constant current conditions (2.15):

$$ICE_{COD} = \frac{FV}{8I} \cdot \frac{[(COD)_t - (COD)_{t+\Delta t}]}{\Delta t} \quad (2.15)$$

where F is faraday’s constant (C mol^{-1}), equal to $96,485 \text{ C mol}^{-1}$.

Wei and Guo assert that COD removal is enhanced at higher current densities, especially at the beginning of treatment. However, it is presumed that a high current density would lead to low current efficiency, because of the occurrence of side reactions such as oxygen evolution or solvent breakdown. Furthermore, a high current density could contribute to shorten the electrode lifespan [52].

At the same time, although COD removal has been proven to increase significantly when a higher cell voltage is applied, it is not proportional to the voltage increase, which reflects a drop in current efficiency. This may be caused by an increase in side reactions at higher cell voltage, such as oxygen and hydrogen evolution and heat generation [51].

2.9.2.2 Airflow

Some 3D systems are designed for air sparging and serve two purposes: to promote and speed mass transfer and to supply essential oxygen for electrochemical reactions, e.g. cathodic generation of H_2O_2 . These three-phase (gas, liquid, solid) 3D electrodes can simultaneously employ anodic oxidation, degrading the pollutants to CO_2 and H_2O , and cathodic peroxide generation, which could aid the organics removal by chemical oxidation pathway [51].

While in general, as Xiong suggests, the greater airflow corresponds to higher COD removal efficiency [51], some researchers indicate that the gas bubble formation induced by air could result in shifts in the concentration profiles and lower the conversion efficiencies [35].

2.9.2.3 Treatment time

Treatment time is linked to energy consumption and treatment performance, the optimal one allowing to comply to the consent limits on the effluent discharge with the minimum energy usage. In the case of a continuous flow electrochemical reactor, hydraulic retention time (HRT) is considered to be the most important design parameter [35]. In general, the wastewater's carbon content (COD, TOC) decreases with an increase in HRT, owing to the mineralisation of organic contaminants in the electrochemical cell [52]. A study conducted by Lv et al. on phenols' removal by 3D reactor shows a decrease in concentration with time, with 95% efficiency reached after 30 minutes. However, the removal efficiency did not improve much after the first 10 minutes of treatment, when it was around 90%, but prolonging the treatment time would increase treatment expenses [55].

Treatment time in the 3D reactor also affects particle regeneration efficiency, as studies show that one increases if the other does. However, the treatment time required to guarantee a complete regeneration of the media is also dependent on the current density for current densities lower than 20 mA/cm^2 , whereas no further reduction in treatment time has been observed for current densities higher than 20 mA/cm^2 [37].

2.9.3 Influence of electrode material

In a 3D system, the electrode material is one of the most important factors in determining the efficiency and cost of the process. The anode/cathode materials mostly have to provide good electrocatalytic activity, long service life and stability. Additionally, the particle electrode should have high specific surface, good catalytic activity and stability for the coating substrate (i.e. the pollutants being adsorbed on its surface) [35].

Among the anode materials, graphite, Pt, PbO₂, IrO₂, Sn₂ and conductive diamond films are the most extensively studied in literature. **Table 2.5** gives a comparison of the performance of these materials

Table 2.5 – Electrode materials and their performance (adapted from [29], [34])

Anode	Oxygen evolution potential (V) ^a	Conditions (ICE and current density)	Removal performance (%)	Comments
Pt	1.3 at 0.5 M H ₂ SO ₄	ICE 53% at 8.5 A/m ²	95% removal of ammonia	Selective oxidation is attained, but PtOx can be formed during the process.
IrO ₂	1.6 at 0.5 M H ₂ SO ₄	ICE 54% at 0.6 A/m ² ICE 1.8% at 50 A/m ² for chlorinated phenols	-	Low current efficiency for organics oxidation due to side reactions of O ₂ evolution. Low current efficiencies and high removal efficiencies require longer time.
Graphite	1.7 at 0.5 M H ₂ SO ₄	ICE 70% at 0.03-0.32 A/m ² ICE 6-17% at 10-100 A/m ²	70% removal of phenols, 50% mineralisation with granular graphite	Cheap, large surface area. Low current efficiency for organics oxidation due to side reactions of O ₂ evolution. Electro oxidation at high potentials could cause surface corrosion. Electrodes quite inexpensive and effective. Material subject to electrochemical corrosion and release of Pb ²⁺ can cause water contamination.
PbO ₂	1.9 at 1 M HClO ₄	ICE 15-40% at 80-160 A/m ²	Complete oxidation of aniline to CO ₂	Pure SnO ₂ is a n-type semiconductor. High resistivity at high temperature and cannot be used as electrode material. Conductivity can be improved by doping with B, Bi, F, P and Sb.
SnO ₂ (Ti/SnO ₂ -Sb ₂ O ₅)	1.9 at 0.5 M H ₂ SO ₄	300 A/m ²	Complete removal of phenols	Excellent electrochemical stability. During anodic oxidation, a film of relatively free hydroxyl radicals forms on the surface, representing an "electrode cage" for the process and increasing the efficiencies.
Si/Boron Doped Diamond (BDD)	2.3 at 0.5 M H ₂ SO ₄	33.4-95% depending on pollutant characteristics and oxidation conditions	-	

As listed in **Table 2.5**, the electrode materials can be classified in two groups.

The first one comprises Pt, IrO₂ and graphite, which only allow effective oxidation or organics at low current densities. When current density is high, a decrease in current efficiency is expected due to side reactions of oxygen production. In these active reactors, the hydroxyl radicals formed at high cell potentials interact with the electrode surface forming higher oxides and organics oxidation is carried on only by direct electron transfer

^a Reference electrode SHE (Standard Hydrogen Electrode)

(DET), i.e. chemical oxidation of the pollutant in close proximity to the anode surface, and not by the action of $\bullet\text{OH}$ [33].

The second group includes materials such as BDD on silica substrate or lead dioxide, that allow anodic oxidation to take place at higher current densities with minimal amount of oxygen evolution, leading to an effective and efficient process for a wide variety of organic pollutants [29], [34]. On these electrodes, hydroxyl radicals do not interact with the anodic surface but directly with organics, forming a reaction cage near the electrode surface, because of their very short average lifespan [33].

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3 REMOVAL OF TARGET MICROPOLLUTANTS FROM WASTEWATER USING A PILOT SCALE ORGANIC DESTRUCTION CELL (ODC)

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Abstract

A pilot scale Organic Destruction Cell (ODC), combining adsorption and electrochemical oxidation in a dynamic process, was run for a year in a Water Recycling Centre (WRC) in Cambridgeshire to assess the removal performance of 68 hazardous chemicals – including trace metals, priority hazardous substances and special pollutants, pharmaceuticals and steroids – as requested within the second phase (AMP6, 2015-2020) of the Chemicals Investigation Programme (CIP). Overall, the unit was able to target pharmaceuticals better than any other class of substances, with removals consistently over 50% for the majority of them, being especially effective towards macrolide antibiotics (~ 60-70%) and statins (~70-80%). The majority of determinands (72%) were found at concentration below the set EQSs at discharge, especially auspicious when dilution in receiving water bodies is not a viable option. However, despite evidence of promising performance, the ODC appeared to promote the accumulation of metals (i.e. zinc, nickel) in the final effluent and overall showing quite a weak performance in relation to sanitary determinands. Only a few determinands displayed a correlation between physicochemical properties and removal performance, as it is very difficult to isolate and understand the combined contribution of adsorption and electrochemical oxidation to the removal process. The main operating parameters were identified as current density and effluent flow, albeit an optimisation of these parameters and a study of their influence on performance were not possible due to technical difficulties. The trial also identified the main pre-treatment requirements (i.e. upstream filtration) and evaluated the ODC performance towards future design goals, calculating the technology's reliability, capital and operating expenditures for a full-scale treatment. Although still in the early stages of research and development, overall the unit has the potential to offer a promising alternative to more conventional and established tertiary treatments for micropollutants removal (i.e. AOPs, membranes, GAC), as demonstrated by a multi-criteria analysis (MCA) also presented in this paper.

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3.1 Introduction

Nowadays, more than 700 micropollutants, such as pharmaceuticals, pesticides, personal care products (PCPs) and endocrine disruptive compounds (EDCs), their metabolites and their transformation products, can be detected in the European aquatic environment [1]. These emerging pollutants, whose effects on both human health and aquatic wildlife still remain to be identified with certainty, represent a major challenge the water industry has to face in order to comply to the surface waters' good quality standard, set by the Water Framework Directive (WFD, 2000/60/CE) and by subsequent legislation - such as the Directive on Environmental Quality Standards (2008/105/EC). To face these new regulatory challenges, the UK Water Industry Research (UKWIR), together with the Environment Agency (EA), water utilities and regulators have financed a national programme of investigations into the source, occurrence and removal of emerging pollutants, called Chemicals Investigation Programme (CIP). This programme was updated (CIP2) during AMP6 (Asset Management Plan, 2015-2020) to comprehend more site specific issues, investigate new technologies and possibly set discharge limits for the next AMP [2], [3].

Although some micropollutants could be removed with various degrees of success through a combination of physical, biological or chemical processes within conventional municipal wastewater treatment works (WwTW) [4], final effluents (FE) still represent the ultimate contamination pathway for surface waters, as most traditional technologies cannot guarantee a steady removal for a group of substances which can be substantially different in form and mechanism of action [5]. In addition to source control, another approach to ensure a reduction of micropollutants from WwTWs would be the inclusion of advanced treatments (tertiary treatments). The most widely adopted solutions are adsorption and advanced oxidation processes (AOPs). Both of these processes are regarded as having a high efficiency for organics degradation, with adsorption also allowing for rather simple set-up, along with easiness of operation and control [6]. However, each of these options has its own drawbacks, including the application of chemical dosing for AOPs, the generation of secondary waste streams, high maintenance and energy demands and costs [7].

Adsorption and AOPs are combined within a 3D electrode, in a technology to remove organic micropollutants called Organic Destruction Cell (ODC), patented by Arvia Technology (Runcorn, UK). Compared to a standard electrode, the addition of a granular media contributes to enhance the conductivity and mass transfer or the adsorption of pollutants. The presence of these particles offers more reactive sites for pollutants adsorption or even catalytic reactions, determining a higher removal efficiency [8].

At the core of the ODC is Nyex, a graphite-based, non-porous medium, which can adsorb organic micropollutants on its surface. Simultaneously, a rapid in situ regeneration takes place owing to an electric current passing through the medium, which desorbs and mineralises the pollutants, so that the media can be used again. Adsorption is achieved very rapidly, due to the non-porous nature of Nyex, which consequently leads to reduced residence times. Furthermore, while other AOPs use energy to treat the whole volume of wastewater, the ODC only utilises it in proportion to the effectively treated volume (i.e. the amount of wastewater flowing through the electrodes), potentially determining lower operational costs [7].

According to literature, the organics removal within a 3D electrode depends on the efficiency of both adsorption and anodic oxidation [8]. On one hand, characteristics of the adsorbent (i.e. pore texture, presence of surface functional groups) and of the adsorbate (i.e. molecular size, solubility, presence of aromatic rings), as well as solution chemistry and operational parameters influence the adsorption process on a carbonaceous media [9], [10]. On the other hand, the efficiency of anodic oxidation appears to be strictly linked to wastewater quality (i.e. alkalinity, conductivity, pH, initial pollutants concentration [8], [11]–[14]), to operational parameters (i.e. current density and treatment time [8]), and, mostly, to the electrodes' material, which can make or break the process' feasibility in terms of efficiency and costs [8], [15]–[17].

The aim of this paper is to investigate the efficacy of the ODC for removal of a suite of micropollutants targeted by CIP2, proving that it provides a suitable treatment for these substances and represents a valid alternative to other more conventionally used technologies (i.e. GAC, ozonation, UV/H₂O₂, filtration and MBR). Physicochemical correlations intervening in the removal process will be individuated and a breakdown of the overall efficiency of the process will be provided, in terms of cost assessment, pre-treatment requirements, criticalities emerged during the trial and general robustness of the unit (frequency and nature of unplanned remedial, maintenance and repair).

3.2 Materials and methods

3.2.1 Water recycling centre (WRC)

A water recycling centre (WRC) in Cambridgeshire was chosen to host the Arvia ODC. The WRC receives crude sewage from a catchment with five terminal pumping stations and provides full preliminary, primary, secondary and tertiary treatment. After steps of preliminary screening, grit removal and iron sulphate dosing, the crude sewage is sent to four primary settlement tanks (PSTs). Their outlet is then treated employing eight trickling

filters, followed by three humus tanks and five tertiary nitrifying sand filters. The Arvia unit receives the sand filters' effluent as inlet and discharges into the site's lagoons and in the local watercourse. All flows are pumped to the works and there is no balancing facility. The WRC also includes sludge storage and thickening facilities, where the aerated liquor from the thickening unit is returned to the recirculation pumping tank [18].

The site has a capacity of approximately 11,450 m³/d as Full Flow to Treatment (FFT) and serves a population of 15,274. The site needs to comply with consents on BOD, TSS, NH₄-N, phosphorus, set by the Water Resources Act (WRA) of 1991, as well as iron and copper, as a result of the Habitats Directive (93/43/CEE). The limits are shown in **Table 3.1**.

Table 3.1 - WRC current effluent consent limits (Anglian Water)

DWF (Dry Weather Flow) (m ³ /d)	FFT (m ³ /d)	BOD (mg/L)	TSS (mg/L)	NH ₄ ⁺ -N (mg/L)	P (mg/L)	Fe (mg/L)	Cu (µg/L)
4,200	11,405	11	20	5	1	3	80

The consented trade effluents in the WRC catchment may contribute up to 4% of the total average daily flow and are thus considered not significant when compared to the domestic load entering the works.

3.2.2 Pilot plant configuration and Organics Destruction Cell (ODC)

The pilot plant was installed in a 6 m long container. As shown in **Figure 3.1**, the system comprises the following components:

- A buffer/balancing tank (Tank T1), fed by a centrifugal booster pump and with 2000 L capacity, which is used as a flow equaliser in case of flow drops or interruptions of supply from the sand filters and which is maintained in a state of constant overflow;
- A main treatment tank (Tank T2), which contains the Nyex bed and the electrodes and where the anodic oxidation takes place, fed by centrifugal booster pump after the balancing tank;
- An outflow/backwash tank (Tank T3), with 1000 L capacity, fed by gravity from Tank T2 and constantly kept in overflow.

The feed for Tank T1 is interlocked with the effluent flow of the five nitrifying sand filters (NSF) upstream of the pilot. Whenever either the NSF effluent flow drops below 30 L/s, a loss of power occurs or the sand filters are in recirculation mode, the interlock is interrupted and the system is left to be fed with the additional volume collected in Tank T1 until the interlock is restored.

Two parallel 100 µm True Sense Judo Inline Backwashing filters supplied by GE (General Electric Company) were installed between T1 and T2 in order to control and eliminate the solids' load accessing to the process tank.

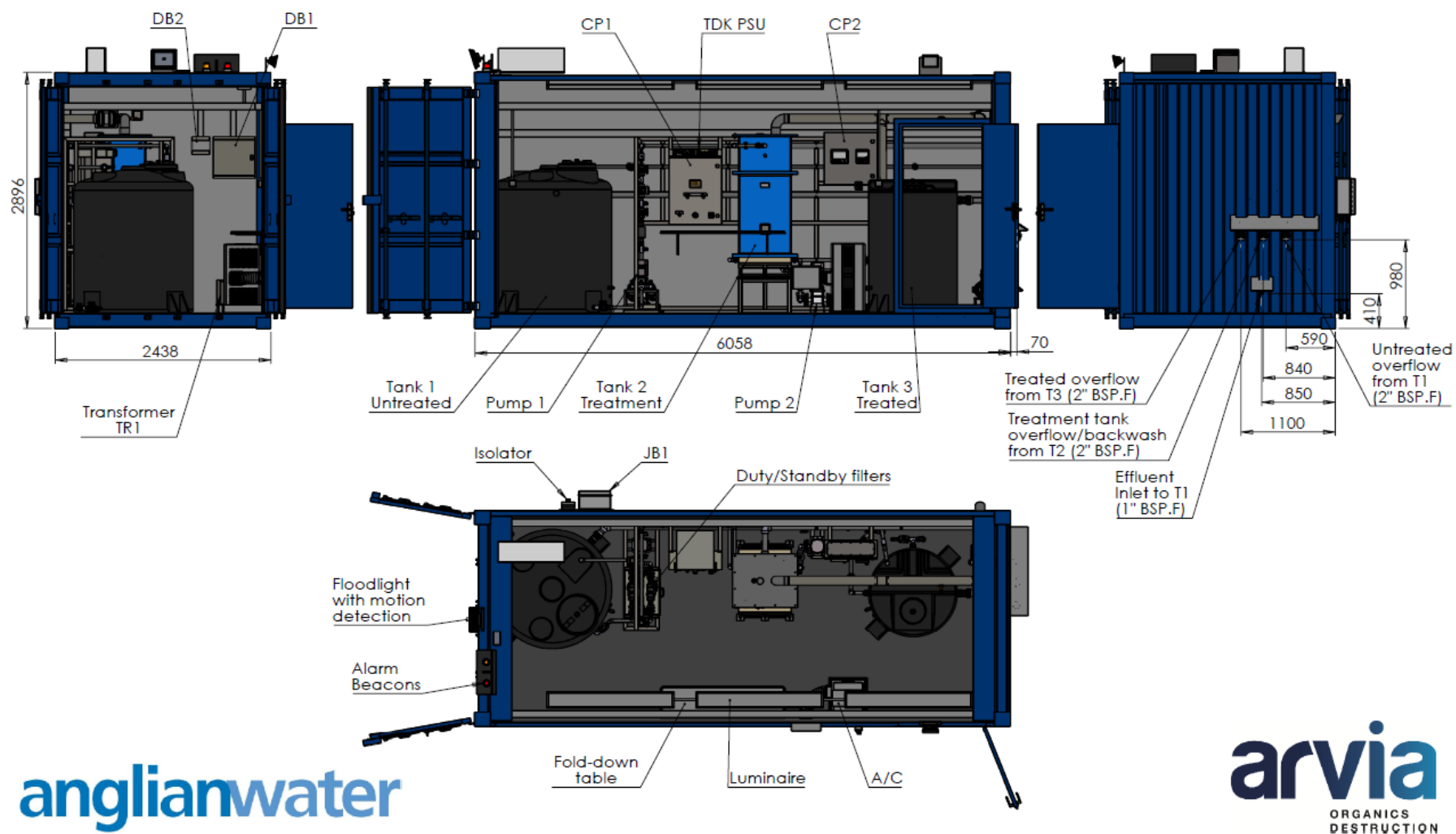


Figure 3.1 - Schematics of the Arvia pilot plan (as provided by Arvia Technology)

Tank T2 (**Figure 3.2**) consists of four parallel organic destruction cells (ODC 4-50), fed from tank T1. The influent enters the top of the tank and flows in a downward direction. Each cell has an active area of 50×50 cm and a width of 10 cm, for a total active volume of 25 L, so that the combined active volume is 100 L. Each cell is equally divided into an anodic and a cathodic compartment by a $400 \mu\text{m}$ membrane of modified polyethylene with 56% porosity, which allows ionic exchange. Both cathode and anode are made of carbon, which can be used as electrode material at low current densities (up to 10 mA/cm^2) and presents limited side reactions of oxygen evolution, without losing effectiveness in organics' removal [16]. The electrodes' polarity switched every 30 minutes. Based on previous in-house trials, Arvia advised that the applied current density be at 4 mA/cm^2 with a total current intensity of 10 A. These conditions were kept throughout the trial due to time constraints that did not allow a more through optimisation to be carried out.

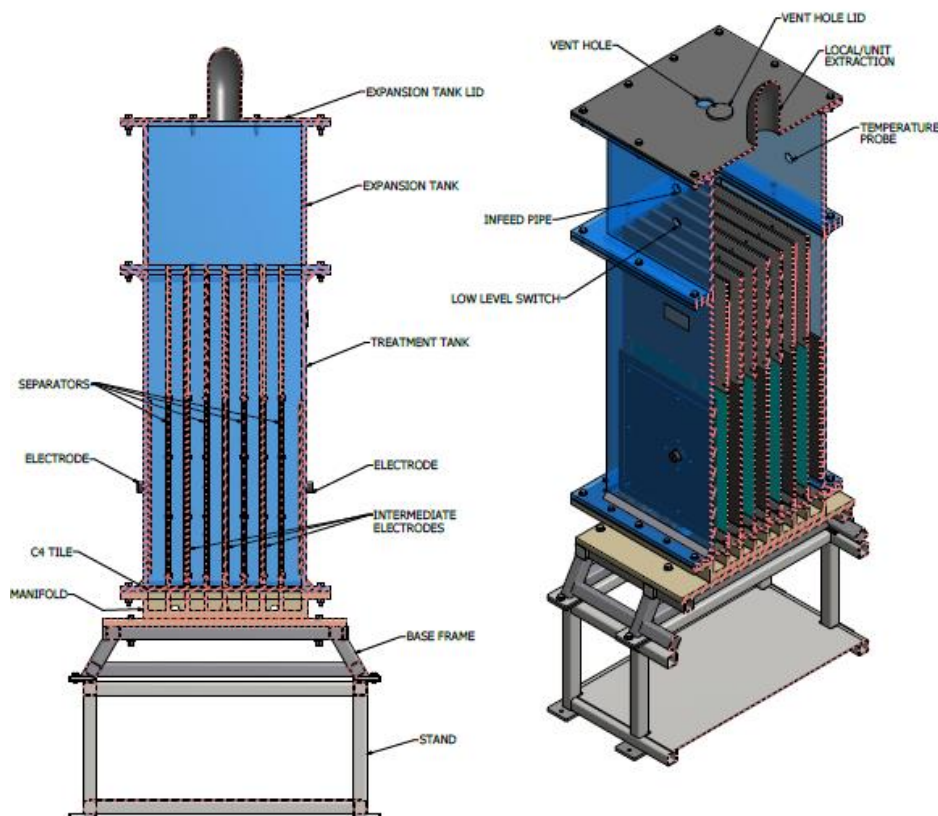


Figure 3.2 - ODC 4-50 design schematics (as provided by Arvia Technology)

Tank 2 inlet flow was maintained between 200-250 L/h, at least 10% higher than the outlet to maintain the tank in constant overflow. The effluent flow had to be kept as constant as possible at 200 L/h for the whole duration of the trial, so that the hydraulic retention time (HRT) for the process amounted to 30 minutes. Owing to the formation of gas bubbles in

the plenum chamber at the tank's bottom which were blocking the water's exit point, the effluent flow frequently dropped below 200 L/h if the pilot was left unattended for a few days. To restore the original effluent flow, a backwash process could be activated by using the treated effluent from T3, which was then recirculated to T2. Expanding the Nyex bed and removing any impurities adsorbed onto the granules, the backwash flow entered T2 from the bottom through the plenum chamber between 800 L/h and 1,700 L/h.

The bed in between the electrodes consisted of ~96 kg of dry Nyex 2180, a non-porous, highly conductive medium, whose main properties are listed in **Table 3.2**.

Table 3.2 - Nyex 2180 properties (supplied by Arvia Technology)

Property	Value
Bed voids volume (porosity) (%)	47
BET surface area (m ² /g)	0.8
Density (g/cm ³)	2.2
Particle diameter range	150 µm to 2.8 mm

The unit's performances could be optimised by adjusting both the flow from the process tank and the current density. Nevertheless, because of technical issues limiting the outflow stability, the pilot was run at 200 L/h and 4 mA/cm² (10 A) for the whole duration of the trial.

During the whole duration of the trial, gaseous hydrogen production at the cathode had to be monitored with fixed and portable hydrogen monitors. The ODC 4-50 produces gaseous hydrogen at the cathode, and according to **(3.1)**, two moles of electrons are needed to form a mole of hydrogen.



3.2.3 Onsite sampling

3.2.3.1 CIP2 determinands analysed

CIP2 revised and further extended the list of substances originally targeted in the Chemicals Investigation Programme, to include priority substances, substances pending review to be classified as priority substances and other substances of specific concern. This project aims at investigating the fate of all the substances listed by CIP2, for a total of 68 determinands:

- **Metals:** nickel, lead, copper, zinc, cadmium, mercury, iron, aluminium, chromium, both dissolved and total fraction;

- **Priority substances:** “penta” congeners 28, 47, 99, 100, 153 and 154 (BDEs), di (2-ethylhexyl) phthalate (DEHP), nonylphenol, nonylphenol with 1, 2 and 3 ethoxylate units, tributyltin compounds (TBT), octylphenols (4-(1,1',3,3'- tetramethylbutyl)-phenol), hexabromocyclododecane, benzo(a)pyrene;
- **Special pollutants:** Perfluorooctane sulfonic acid (PFOS), perfluorooctanoic acid (PFOA), fluoranthene, triclosan, cypermethrin;
- **Steroids:** oestrone (E1), 17 β -oestradiol (E2), 17 α -ethinyloestradiol (EE2);
- **Pharmaceuticals:** diclofenac, ibuprofen, atorvastatin, para and ortho hydroxy atorvastatin, propranolol, atenolol, erythromycin, norerythromycin, azithromycin, clarithromycin, ciprofloxacin, metformin, ranitidine, carbamazepine, 10,11-epoxy carbamazepine, sertraline, norsetraline, fluoxetine, tamoxifen, trixylenyl phosphate, 1,2,3 benzotriazole (tautomers 1H and 2H), tolytriazole (4, 5 methyl benzotriazole).
- **Sanitary determinands:** total suspended solids, ammoniacal nitrogen, total oxidised nitrogen, biochemical oxygen demand, chemical oxygen demand, total phosphorus, soluble reactive phosphate, total organic carbon, dissolved organic carbon, calcium, pH, alkalinity and sulphide.

The determinands' physico-chemical properties are reported in **Appendix A**.

3.2.3.2 Sampling procedure

A sampling campaign was conducted from March to September 2016 according to the guidelines provided by CIP2 [19]. The sampling campaign was originally designed to collect samples on a "stratified random" basis, where the fifteen sampling events were spaced into equal intervals, but are randomly placed into each interval. Four samples (each one comprising of 18 different bottles) were collected for each event: one sample and one duplicate for both the ODC influent and effluent. However, due to maintenance issues, no samples were collected in April

In a sampling event, samples were separated by 4h or longer, trying when possible to avoid a fixed period between them: this allowed the inclusion of any potential variability in concentration experienced within the day. Samples were collected largely during working hours (Mon-Fri, 10 am to 3.30 pm), with 10% of the samples taken out of working hours. The outcome of analysis for all the 60 samples (30 influent, 30 effluent) collected during the trial was submitted to the Atkins-led CIP2 technical group and later included in a report, collecting data from all the trials conducted by water utilities on national scale.

Samples for aluminium, metals and DOC had to be filtered on site through 0.45 μ m. Sulphides were fixed on site, adding to the samples 2 ml of sodium carbonate and 2 mL of

zinc acetate in that order. A summary of the bottles used for each one of the determinands is presented in **Appendix B**. Samples were kept in a fridge until transportation and then stored in a cold room (4°C) until analysed by Anglian Water Central Laboratories (Huntingdon, Cambridgeshire).

3.2.3.3 Sampling schedule

The sampling dates, times and conditions of each sample are reported in **Appendix C**. The average daily flows from the nitrifying sand filters (unit's feed flow) during the sampling period are presented in **Figure 3.3**, with the red bars marking days when a sample was collected.

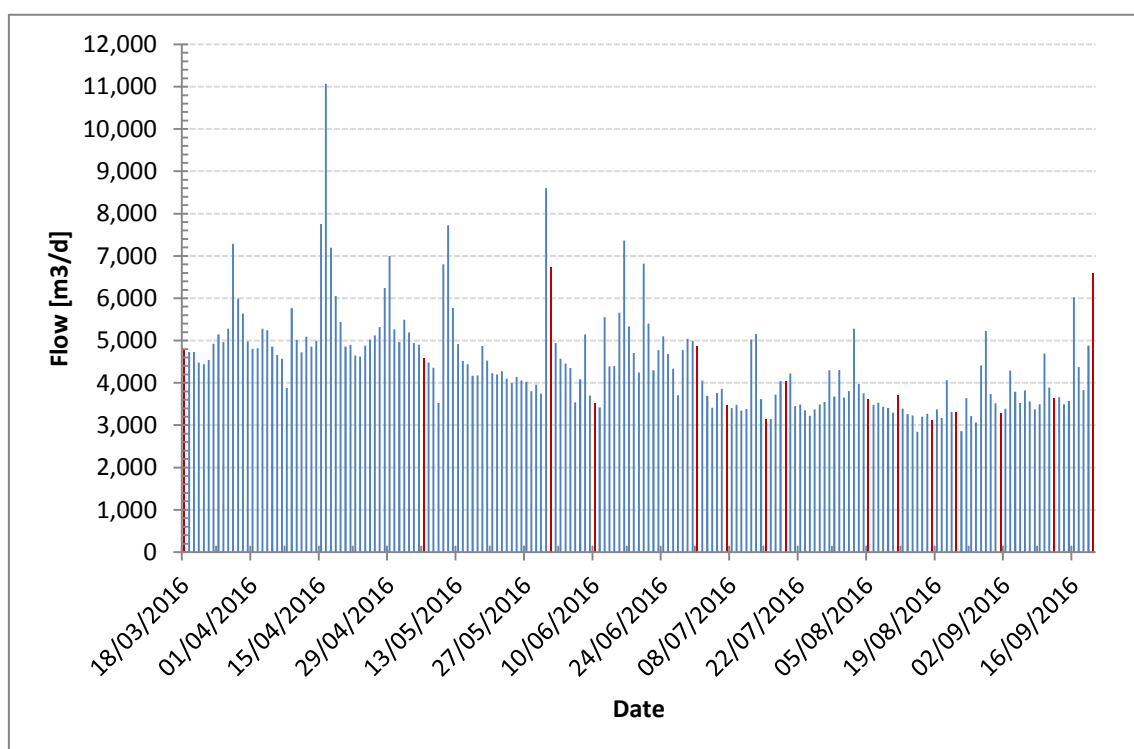


Figure 3.3 - Average daily flow from nitrifying sand filters during sampling period (data adapted from AW telemetry system)

3.2.4 Analytical methods

Hazardous substances quantifications were conducted according to the CIP2 guidelines by Anglian Water Central Laboratories. A summary of the methods used for each analyte of interest can be found in **Table 3.3**.

Table 3.3 - Summary of analytical methods used by Anglian Water Central Laboratories

Nickel total, Lead Total, Copper total, Zinc total, Cadmium total, Chromium total, Aluminium total and Iron total

Samples are acidified with 1% v/v nitric acid and digested at 180°C for a minimum of 8 hours, before analysis by inductively coupled plasma-mass spectrometry (ICP-MS)

Nickel dissolved, Lead dissolved, Copper dissolved, Zinc dissolved, Cadmium dissolved, Chromium dissolved, Aluminium dissolved and Iron dissolved

Samples are acidified with 1% v/v nitric acid and digested at 180°C for a minimum of 8 hours, before analysis by inductively coupled plasma-mass spectrometry (ICP-MS)

Mercury dissolved and Mercury total

Samples preserved with 1 mg/L Au, 1% v/v nitric acid and 1% hydrochloric acid, before analysis by inductively coupled plasma-mass spectrometry (ICP-MS)

PBDEs, PAHs, Octylphenol, Nonylphenols

Liquid-liquid extraction into hexane by rolling overnight. Concentration on air line. Analysed by gas chromatography- tandem mass spectrometry (GC-MS/MS), operating in MRM mode. Injection using solvent evaporation mode.

Cypermethrin

Liquid-liquid extraction into hexane by rolling overnight. Concentration on air line. Analysed by gas chromatography- tandem mass spectrometry (GC-MS/MS), operating in MRM mode. Injection using solvent evaporation mode.

DEHP

Liquid-liquid extraction into dichloromethane by rolling overnight. Analysed by gas chromatography-mass spectrometry (GC-MS) in SIM mode. Hot spitless injection.

Pharmaceuticals/Triazoles/TXP and ethoxylates

Direct aqueous injection methods. Samples and standards are pH adjusted where required, an internal standard added, analysed by liquid chromatography- tandem mass spectrometry (LC-MS/MS) operating in MRM mode.

Steroids

Solid phase extraction, followed by normal phase clean up using fraction collection. Concentration on an air line, residue re-dissolved in mobile phase. Analysed by liquid chromatography- tandem mass spectrometry (LC-MS/MS) operating in MRM mode.

TBT

Liquid-liquid extraction into a mixture of ethyl acetate-hexane by rolling overnight. Concentration on an air line, residue re-dissolved in acetonitrile. Analysed by liquid chromatography- tandem mass spectrometry (LC-MS/MS) operating in MRM mode.

Hexabromocyclododecane

Liquid-liquid extraction into hexane by rolling overnight. Concentration on an air line, residue re-dissolved in mobile phase. Analysed by liquid chromatography- tandem mass spectrometry (LC-MS/MS) operating in MRM mode.

PFOS/PFOA and Triclosan

Solid phase extraction, followed by concentration on an air line. Residue re-dissolved in mobile phase. Analysed by liquid chromatography- tandem mass spectrometry (LC-MS/MS) operating in MRM mode.

3.2.5 Data handling and analysis

During the sampling campaign, 55 metals, priority substances, steroids and pharmaceuticals were quantified in 60 samples, in addition to 13 other sanitary parameters (including pH and alkalinity), as listed in **Section 3.2.3.1**. Together with data on influent and effluent flow, temperature, turbidity, conductivity and voltage for each sample, they made up for more than 5,000 data points.

Appendix D shows the LOD values for Anglian Water Central Laboratories (reporting limits) and those dictated by the Programme. The Quality Assurance and Quality Control (QA/QC) Directive (2009/90/EC) recommends that determinations falling below LOD should be substituted with half the LOD value, as long as this is more or less as low as the CIP requirement. Since the reporting limits as provided by Anglian Water laboratory were lower than LODs, these, and not LODs, were used for the analysis. This method allowed the data set to be reduced and a few determinands to be discarded on the basis that their influent and effluent values were consistently (equal to or more than 90% of data) under their reporting limit. These determinands are: cadmium, mercury, chromium, BDEs, nonylphenol (technical), nonylphenol monoethoxylate, octylphenols, cypermethrin, sulphide, tamoxifen and trixylenyl phosphate.

Given the size of the data set, the first step involved checking the presence of outliers, in order to remove inconsistent data and possibly reduce the number of determinands to analyse. For statistical analysis purpose, after the data had been log-transformed, values falling outside the 1.5-interquartile range (IQR) threshold were rejected. Out of a total of 4,680 determinations for influent and effluent concentrations, only 3.65% of values were deemed an outlier and disallowed.

Because in some cases the measured concentrations were close to the LOD, error quantification had to be taken into account, so that any hypothesis about their elimination efficiency appears to be arguable. Nonetheless, average removal was calculated for each of the compounds from the influent and effluent concentration of all the determinands, for a total of 30 different removal data throughout the sampling campaign. The reported removals were determined as an average of these values. Maximum, minimum, 25th and 75th percentile and standard deviation were also calculated. Box plots of influent and effluent concentration for the determinands (minus the disallowed ones) are presented in **Appendix E**.

Principal components analysis (PCA) was used as an exploratory tool for the study hazardous substances' removal and was conducted with the Statistica software, developed by StatSoft and commercialised by Dell. The PCA included structural (i.e. composing elements, functional groups, presence of aromatic rings, double and triple bonds) and physical properties (molecular weight, water solubility, Log k_{ow} , Log k_{oc}).

A multi-criteria analysis (MCA) was carried out following the principal hierarchy analysis (PHA) method, established in the early 70s at the University of Pennsylvania (US) [20].

3.3 Results

3.3.1 Hydrogen production at the cathode

The hydrogen production at the cathode is summarised in **Table 3.4**. The total H₂ produced in T2 amounts to 0.017 m³ H₂/h in the worst-case scenario, which assumes a 100% reduction of water at the cathode.

Table 3.4 - Hydrogen production at the cathode

Parameter	Units	Value	Notes
Cell surface	cm ²	2,500	Each cell has 50 × 50 cm dimensions
Current density applied to T2	mA/ cm ²	4.00	
Current intensity to T2	A	10.00	
Charge passed through Nyex	C/s	10.00	
Amount of electrons passed per second in each cell	mol e ⁻ /(s cell)	1.04×10 ⁻⁴	Faraday constant (charge of a mol of electrons) 96,485 C/ mol e ⁻
Amount of H ₂ produced per second in each cell	mol H ₂ /(s cell)	5.18×10 ⁻⁵	2 mol of electrons are needed to form a mole of hydrogen.
Total amount of H ₂ produced in T2	mol H ₂ /s	2.07×10 ⁻⁴	The ODC 4-50 is composed of 4 cells
Total H ₂ produced in T2	L H ₂ /h	16.72	Considering standard conditions, a mole of gas occupies 22.4 L
	m ³ H ₂ /h	0.017	

3.3.2 WRC historical data

Historical data on consented standard sanitary parameters (BOD, TSS, NH₄-N⁺, phosphorus and iron) from samples collected in the WRC during routine checks in 2015 (crude sewage and final effluent) was analysed to provide a baseline of the site's efficiency before the Arvia pilot plant was installed on site. These values are presented in **Table 3.5**.

Table 3.5 - Standard sanitary and consented parameters at the inlet and outlet of the WRC, over the period 1st January 2015 to 31st December 2015.

	Unit	No of samples	WRC inlet (crude sewage Mean ± SE Min, Max)	WRC discharge (Mean ± SE Min, Max)	% removal ¹
Biochemical Oxygen Demand (BOD ₅)	mg/L O	12	290.33 ± 19.01 193.00, 414.00	4.19 ± 0.49 2.12, 6.85	98.6
Chemical Oxygen Demand (COD)	mg/L O	12	700.33 ± 35.32 448.00, 874.00	36.61 ± 3.39 19.2, 56.2	94.8
Ammonia Total	mg/L N	12	41.08 ± 2.29 25.20, 51.30	²	-

¹ Removal throughout the WRC was calculated with the averages for inlet and final effluent.

² Ammonia values were not available for the final effluent.

	Unit	No of samples	WRC inlet (crude sewage Mean $\pm$ SE Min, Max)	WRC discharge (Mean $\pm$ SE Min, Max)	% removal ¹
Total Suspended Solids (TSS)	mg/L	12	331.08 $\pm$ 22.85 184.00, 435.00	6.83 $\pm$ 1.18 (1.00, 16.00)	97.9
Orthophosphate Total	mg/L P	12	5.76 $\pm$ 0.37 3.84, 9.00	0.44 $\pm$ 0.11 (0.12, 1.21)	92.3
Phosphorus Total	mg/L P	12	9.06 $\pm$ 0.40 6.19, 11.10	0.66 $\pm$ 0.14 (0.26, 1.69)	92.7
Iron	mg/L Fe	12	0.41 $\pm$ 0.04 0.21, 0.66	0.34 $\pm$ 0.04 (0.16, 0.53)	16.3
Turbidity (tube test)	mg/L	15	100	10	90.0

Removal rates were above 90% for all the consented parameters, with the sole exception of iron, whose achieved removal was about 16% owing to the dosing of ferric sulphide in the works. All parameters met the regulatory consents for the site (11 mg/L BOD₅, 20 mg/L TSS, 1 mg/L total P and 3 mg/L Fe, as seen in **Table 3.1**).

3.3.3 Conventional wastewater parameters

For each sample, standard sanitary and wastewater parameters at the inlet and outlet of the Arvia unit were assessed (**Table 3.6**).

Table 3.6 – Quantification of standard sanitary parameters, ODC 4-50

Compounds	Unit	ODC influent (NSF Effluent, Mean $\pm$ SE Min, Max)	ODC effluent (Mean $\pm$ SE Min, Max)	% removal (Mean $\pm$ SE Min, Max)
TSS	mg/L	2.93 $\pm$ 0.50 1.00, 11.00	1.97 $\pm$ 0.25 1.00, 6.00	-44.2 $\pm$ 26.6 -500.0, 90.9
Ammoniacal Nitrogen	mg/L	1.25 $\pm$ 0.19 0.231, 4.33	1.47 $\pm$ 0.20 0.35, 4.20	-115.9 $\pm$ 53.9 1250.6, 61.4
Total Oxidised Nitrogen	mg/L	34.16 $\pm$ 0.89 26.40, 45.80	27.95 $\pm$ 1.14 18.30, 42.90	18.0 $\pm$ 2.7 -17.0, 41.6
BOD ₅	mg/L	1.87 $\pm$ 0.23 1.00, 4.94	2.79 $\pm$ 0.12 2.06, 4.54	-84.6 $\pm$ 18.2 252.0, 50.5
COD	mg/L	25.77 $\pm$ 0.95 17.20, 36.50	27.88 $\pm$ 0.92 20.90, 44.00	-9.4 $\pm$ 4.3 -51.9, 27.4
Total Phosphorus	mg/L	0.202 $\pm$ 0.010 0.137, 0.294	0.241 $\pm$ 0.027 0.134, 0.830	-7.4 $\pm$ 4.3 -68.3, 32.4
TOC	mg/L	9.83 $\pm$ 0.29 7.03, 14.00	11.39 $\pm$ 0.22 9.26, 14.00	-19.3 $\pm$ 3.2 -57.0, 3.8
DOC	mg/L	9.36 $\pm$ 0.24 7.10, 12.10	11.16 $\pm$ 0.32 8.34, 16.30	-16.8 $\pm$ 2.7 -51.6, 5.1
Calcium	mg/L	121.42 $\pm$ 1.13 111.00, 132.00	117.19 $\pm$ 1.69 98.60, 134.00	1.8 $\pm$ 0.7 -4.7, 1.9
pH	-	7.13 $\pm$ 0.02 6.87, 7.39	6.59 $\pm$ 0.02 6.36, 6.83	6.7 $\pm$ 0.7 -8.9, 12.8

Compounds	Unit	ODC influent (NSF Effluent, Mean $\pm$ SE Min, Max)	ODC effluent (Mean $\pm$ SE Min, Max)	% removal (Mean $\pm$ SE Min, Max)
Alkalinity	mg CaCO ₃ /L	98.80 $\pm$ 3.03 70.00, 135.00	113.5 $\pm$ 3.87 75.00, 160.00	-10.7 $\pm$ 3.9 -48.0, 60.0

Most sanitary parameters, with the exception of TSS, total oxidised nitrogen (NO₂ and NO₃) calcium and pH, showed an increase in concentration after the Arvia process. Nonetheless, all the values for sanitary determinands are lower at discharge than the site's historical data (Table 3.5). All the consented parameters are within the site's limits.

3.3.4 Trace metals

Table 3.7 summarizes the concentrations for the metals included in the CIP programme, with the exception of cadmium, mercury and chromium, which could not be detected in the influent and effluent in at least 90% of the total samples.

Table 3.7 - Quantification of metals, ODC 4-50.

Compounds	Unit	ODC influent (NSF Effluent, Mean $\pm$ SE Min, Max)	ODC effluent (Mean $\pm$ SE Min, Max)	% removal (Mean $\pm$ SE Min, Max) ³
Nickel (dissolved)	µg/L	8.44 $\pm$ 0.18 (6.52, 9.96)	12.77 $\pm$ 0.31 9.81, 16.30	-49.0 $\pm$ 3.8 -90.9, -16.2
Nickel (total)	µg/L	8.49 $\pm$ 0.18 (5.69, 6.981)	12.11 $\pm$ 0.34 7.94, 15.90	-42.5 $\pm$ 4.1 -110.9, -6.7
Lead (dissolved)	µg/L	0.07 $\pm$ 0.01 (0.05, 0.18)	0.05 $\pm$ 0.00	14.5 $\pm$ 5.2 0.0, 67.9
Lead (total)	µg/L	0.16 $\pm$ 0.01 (0.10, 0.26)	0.09 $\pm$ 0.01 0.05, 0.20	46.9 $\pm$ 5.4 -25.0, 77.5
Copper (dissolved)	µg/L	5.40 $\pm$ 0.27 (2.86, 8.28)	10.96 $\pm$ 0.52 7.59, 18.00	-118.0 $\pm$ 16.3 -421.7, -32.2
Copper (total)	µg/L	6.88 $\pm$ 0.38 3.34, 12.40	11.81 $\pm$ 0.57 7.22, 18.60	-84.8 $\pm$ 13.7 -350.4, -6.3
Zinc (dissolved)	µg/L	16.32 $\pm$ 0.81 8.07, 28.60	28.20 $\pm$ 1.02 18.10, 40.90	-85.6 $\pm$ 11.4 -217.1, 14.9
Zinc (total)	µg/L	149.90 $\pm$ 42.91 10.50, 1020.00	269.08 $\pm$ 48.98 16.00, 1220.00	-1049.6 $\pm$ 408.4 -11519.0, 89.7
Iron (dissolved)	µg/L	143.15 $\pm$ 8.14 63.80, 234.00	113.90 $\pm$ 7.05 53.70, 232.00	13.1 $\pm$ 5.7 -88.1, 50.6
Iron (total)	µg/L	344.52 $\pm$ 16.24 183.00, 561.00	158.41 $\pm$ 9.99 85.60, 309.00	52.8 $\pm$ 2.6 15.7, 72.0
Aluminium (dissolved)	µg/L	4.73 $\pm$ 0.49 3.32, 14.70	10.65 $\pm$ 0.68 7.40, 19.10	-184.6 $\pm$ 28.6 -476.2, 49.0

³ The percentage removal is calculated as average of the removal values for each coupled influent and effluent sample collected (30 in total), and not as an average of the mean influent and effluent values presented in Table 3.7. The same is valid for Table 3.8.

Compounds	Unit	ODC influent (NSF Effluent, Mean $\pm$ SE Min, Max)	ODC effluent (Mean $\pm$ SE Min, Max)	% removal (Mean $\pm$ SE Min, Max) ³
Aluminium (total)	$\mu\text{g/L}$	7.34 $\pm$ 0.77 3.32, 21.40	9.53 $\pm$ 0.82 6.70, 20.90	-102.1 $\pm$ 30.6 -530.5, 57.8
Aluminium (reactive)	$\mu\text{g/L}$	6.13 $\pm$ 0.84 2.00, 22.00	11.92 $\pm$ 0.89 6.00, 22.00	-175.1 $\pm$ 37.7 -600.0, 22.2

Zinc and iron had the overall highest average concentration detected in the influent, with 50% and 42% of the total present in the dissolved phase, respectively, which became 25% and 75% in the effluent. Copper and nickel also seemed to occur predominantly in the dissolved phase, with the latter dissolved in the influent at 98% of the total. In general, most of the metals displayed an increase in the dissolved fraction from influent to effluent, as when the organic pollutants break down during oxidation, they potentially release metals in the dissolved phase, thus also determining an increase the total fraction.

For some of the samples observed, effluent concentrations of total zinc were two or even three orders of magnitude higher than those found in the influent. However, since concentrations of the same order of magnitude were detected in a number of influent samples as well, it was hypothesised that spikes in zinc concentration could have occurred within the WRC: while undetected when sampling the influent, they could have emerged when the effluent sample was taken, as some time passed between the two samples. This is further corroborated by the presence in the area of a few traders specialised in machinery washing (printing machines, heat exchangers) and circuit printing, which have been issued zinc consents and therefore possibly release Zn in their wastewater.

Despite its main purpose being organics' oxidation, the ODC 4-50, due to its electrochemical nature, could potentially achieve metal reduction in the effluent cations' adsorption on the cathode, as detailed in **Section 2.5.1**. However, an accumulation was observed for the majority of metal determinands, especially for zinc, with the only exception of lead and iron. Despite the concentration increase in the final effluent, metals subjected to consent were still within the limits dictated by the Habitat Directive (3 mg/L Fe and 80 $\mu\text{g/L}$ Cu).

3.3.5 Hazardous substances

Table 3.8 displays the occurrence of hazardous substances (priority substances, special pollutants, steroids and pharmaceuticals) in both influent and effluent samples collected during the trial. **Figure 3.4** offers a representation of removal efficiencies achieved during treatment with the ODC 4-50.

Preliminary investigation of the WRC influent showed that almost all of the determinands were detected in the influent, with the exception of BDEs, nonylphenol monoethoxylate, octylphenols, tamoxifen and trixylenyl phosphate. These compounds, together with nonylphenol (technical) and cypermethrin, were eliminated from the analysis as they were not detected in either the ODC influent or effluent with enough frequency to allow a study of their removal and behaviour.

Table 3.8 – Quantification of hazardous substances, ODC 4-50

Compounds	Unit	ODC influent (NSF Effluent, Mean $\pm$ SE Min, Max)	ODC effluent (Mean $\pm$ SE Min, Max)	% removal (Mean $\pm$ SE Min, Max)
Priority substances/Special pollutants				
Diethylexyl-phtalate (DEHP)	$\mu\text{g/L}$	0.457 ± 0.076 0.100, 1.530	0.356 ± 0.061 0.100, 1.290	11.3 ± 7.3 -73.3, 85.4
Perfluorooctane sulhonic acid (PFOS)	ng/L	34.400 ± 2.131 16.000, 74.000	27.620 ± 1.512 12.100, 42.400	16.3 ± 3.2 -44.4, 39.7
Perfluorooctanoic acid (PFOA)	ng/L	6.531 ± 0.42 2.450, 14.500	6.192 ± 0.346 2.330, 10.500	3.7 ± 5.3 -119.7, 51.2
Hexabromocyclododecane (HBDD)	ng/L	4.685 ± 0.251 3.070, 8.970	1.764 ± 0.200 0.890, 5.670	67.5 ± 1.4 49.0, 82.1
Nonylphenol diethoxylate (NOP2)	$\mu\text{g/L}$	0.049 ± 0.006 0.025, 0.140	0.025 ± 0.000	20.2 ± 6.0 0.0, 75.0
Nonylphenol triethoxylate (NOP3)	$\mu\text{g/L}$	0.043 ± 0.005 0.025, 0.140	0.025 ± 0.000	17.3 ± 5.2 0.0, 64.3
Tribuytin compounds (TBT)	ng/L	0.145 ± 0.015 0.100, 0.357	0.100 ± 0.000	13.0 ± 4.8 0.0, 72.0
Fluoranthene (FLU)	ng/L	2.430 ± 0.087 1.610, 3.900	0.450 ± 0.000	81.5 ± 0.7 72.0, 88.5
Benzo(a)pyrene (BAP)	ng/L	0.683 ± 0.128 0.187, 2.470	0.150 ± 0.022 0.090, 0.520	64.6 ± 4.2 -8.6, 91.8
Triclosan (Tricl)	$\mu\text{g/L}$	0.0740 ± 0.001 0.0580, 0.0900	0.0234 ± 0.001 0.0130, 0.0380	69.6 ± 1.5 58.2, 81.4
Steroids				
Oestrone (E1)	ng/L	1.95 ± 0.19 0.37, 4.34	0.65 ± 0.09 0.18, 1.84	61.7 ± 5.3 -44.9, 88.6
17 β -estradiol (E2)	ng/L	0.96 ± 0.02 0.15, 0.37	0.43 ± 0.02 0.15, 0.43	14.0 ± 19.1 -300.0, 85.0
17 α -ehtinyl estradiol (EE2)	ng/L	0.20 ± 0.01 0.08, 0.35	0.04 ± 0.01 0.02, 0.11	79.0 ± 3.2 33.3, 95.7
Pharmaceuticals				
Diclofenac (DCF)	$\mu\text{g/L}$	0.354 ± 0.019 0.194, 0.535	0.103 ± 0.011 0.032, 0.249	69.6 ± 3.3 6.0, 92.1
Ibuprofen (IBPF)	$\mu\text{g/L}$	0.442 ± 0.058 0.046, 1.380	0.213 ± 0.028 0.026, 0.633	39.8 ± 13.2 -310.9, 81.2
Atorvastatin (ATOV)	$\mu\text{g/L}$	0.177 ± 0.009 0.092, 0.260	0.052 ± 0.009 0.005, 0.183	70.3 ± 4.5 12.0, 97.29

Compounds	Unit	ODC influent (NSF Effluent, Mean $\pm$ SE Min, Max)	ODC effluent (Mean $\pm$ SE Min, Max)	% removal (Mean $\pm$ SE Min, Max)
Ortho-hydroxy-atorvastatin (ATOVo)	$\mu\text{g/L}$	0.162 ± 0.009 0.090, 0.271	0.032 ± 0.006 0.005, 0.128	80.4 ± 3.3 31.6, 97.3
Para-hydroxy-atorvastatin (ATOVp)	$\mu\text{g/L}$	0.232 ± 0.012 0.143, 0.371	0.067 ± 0.013 0.244, 0.005	72.8 ± 4.3 14.4, 97.5
Propranolol (PRPL)	$\mu\text{g/L}$	0.242 ± 0.007 0.173, 0.342	0.089 ± 0.005 0.048, 0.163	63.6 ± 2.3 31.1, 80.1
Atenolol (ATNL)	$\mu\text{g/L}$	0.455 ± 0.014 0.296, 0.561	0.238 ± 0.018 0.097, 0.469	43.1 ± 4.5 -33.3, 70.5
Erythromycin (ERMY)	$\mu\text{g/L}$	0.485 ± 0.021 0.253, 0.774	0.214 ± 0.020 0.070, 0.410	55.2 ± 4.5 -21.8, 82.0
Norerythromycin (ERMYn)	$\mu\text{g/L}$	0.041 ± 0.002 0.023, 0.067	0.080 ± 0.003 0.055, 0.137	-104.1 ± 10.4 -280.6, -43.1
Azithromycin (AZMY)	$\mu\text{g/L}$	0.180 ± 0.009 0.106, 0.294	0.074 ± 0.008 0.022, 0.177	59.9 ± 3.4 16.3, 79.2
Clarithromycin (CLMY)	$\mu\text{g/L}$	0.507 ± 0.033 0.211, 0.873	0.200 ± 0.021 0.056, 0.531	59.4 ± 3.7 -8.5, 80.5
Ciprofloxacin (CIPR)	$\mu\text{g/L}$	0.318 ± 0.019 0.189, 0.571	0.082 ± 0.008 0.032, 0.181	75.0 ± 1.2 52.0, 93.2
Metformin (METF)	$\mu\text{g/L}$	3.619 ± 0.120 2.510, 4.780	2.781 ± 0.202 1.430, 5.540	27.3 ± 5.3 -91.9, 55.6
Ranitidine (RNTD)	$\mu\text{g/L}$	1.063 ± 0.030 0.703, 1.310	0.226 ± 0.021 0.074, 0.480	79.0 ± 2.1 52.0, 93.2
Carbamazepine (CBAZ)	$\mu\text{g/L}$	0.714 ± 0.029 0.362, 0.947	0.423 ± 0.012 0.316, 0.575	41.7 ± 2.7 9.5, 60.3
10,11-epoxy- carbamazepine (CBAZe)	$\mu\text{g/L}$	0.073 ± 0.003 0.044, 0.098	0.061 ± 0.002 0.047, 0.079	14.1 ± 3.3 -50.0, 39.7
Sertraline (SERT)	$\mu\text{g/L}$	0.039 ± 0.001 0.027, 0.060	0.015 ± 0.001 0.005, 0.031	64.6 ± 2.5 44.4, 86.5
Norsertaline (SERTn)	$\mu\text{g/L}$	0.025 ± 0.001 0.015, 0.044	0.011 ± 0.001 0.005, 0.028	60.5 ± 3.4 17.2, 80.8
Fluoxetine (FLXT)	$\mu\text{g/L}$	0.055 ± 0.001 0.043, 0.068	0.026 ± 0.002 0.012, 0.047	53.1 ± 2.6 17.8, 73.5
1,2,3 benzotriazole (BZT)	$\mu\text{g/L}$	2.387 ± 0.161 1.050, 4.060	2.217 ± 0.109 1.360, 3.390	2.5 ± 2.8 -35.2, 36.0
Tolytriazole (4,5 methyl benzotriazole) (TZT)	$\mu\text{g/L}$	1.044 ± 0.033 0.662, 1.380	0.890 ± 0.021 0.736, 1.220	15.5 ± 3.3 -39.9, 37.0

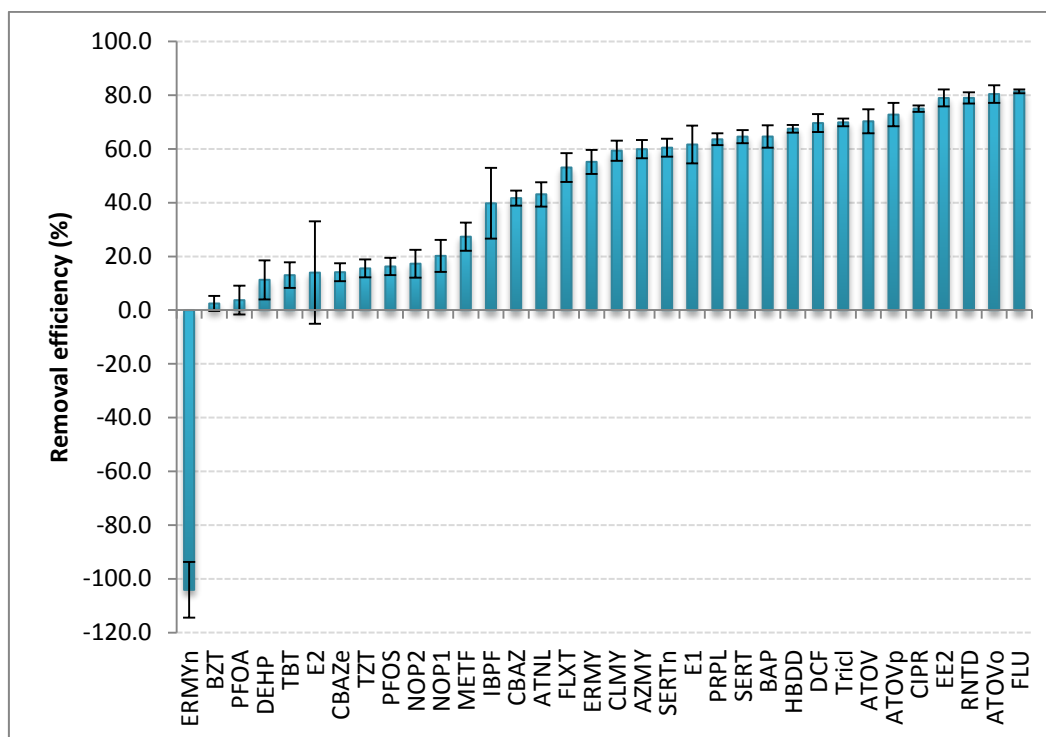


Figure 3.4 – Removals of selected micropollutants in ODC 4-50. Error bars represent the standard error of the data.

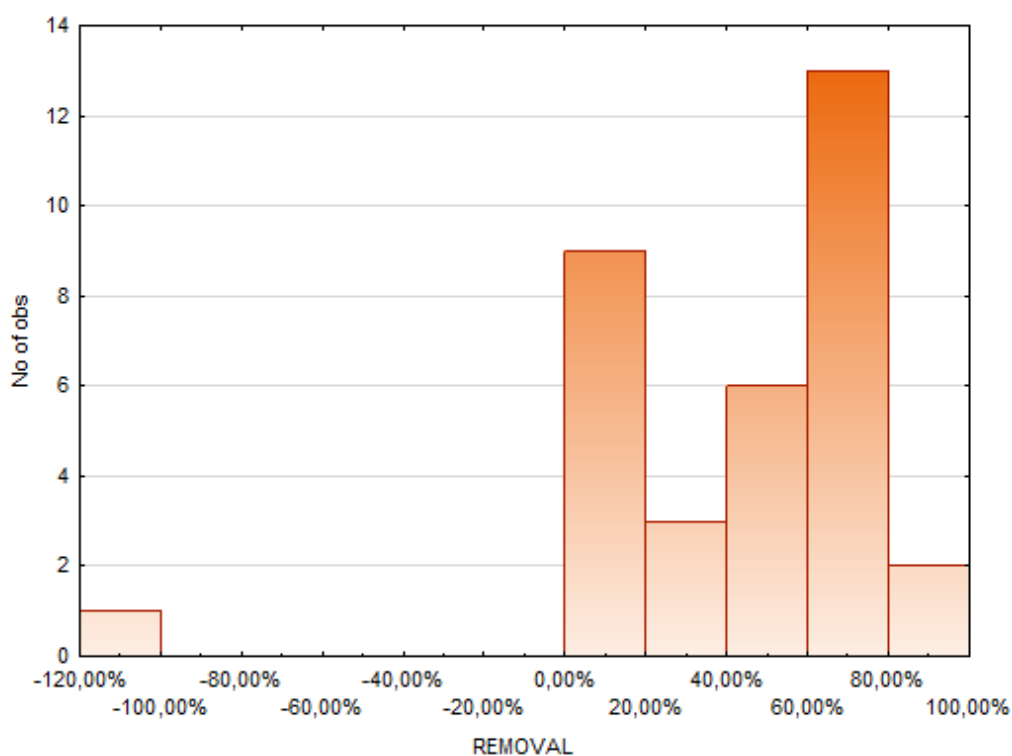


Figure 3.5 - Histogram of relative removal frequency

Figure 3.5 offers a breakdown of the removal efficiency into different classes of frequency.

The highest influent concentrations were measured for metformin, ranitidine, benzotriazole and tolytriazole (all over 1 µg/L), whereas for the majority of other hazardous substances the concentration values range between 0.1-1 µg/L. Oestrogens, perfluorinated carboxylic acids (PFOS, PFOA), HBCDD and PAHs are detected at concentrations in the order of ng/L.

Overall, pharmaceuticals represent the better performing class of contaminants, with removal of the majority of these chemicals over 50%, with the exception of a few substances, such as ibuprofen, carbamazepine and metformin, which are generally regarded as highly mobile and recalcitrant and reach a removal between 25% and 40% in the ODC. Three out of the five compounds with removal > 75% are pharmaceuticals (ortho-hydroxy-atorvastatin, ciprofloxacin and ranitidine), while the other two are 17 α -ethinyloestradiol (oestrogen) and fluoranthene (PAH). On the other hand, priority substances comprise the majority of the 20-40% class, together with the pharmaceuticals 10,11 epoxy-carbamazepine, benzotriazole, tolytriazole and the steroid 17 β -oestrone.

Oestrogens E1 and EE2 achieved a removal of ~61% and ~79%, respectively. These results are especially auspicious because their concentration values at discharge after the Arvia process are consistently under Environmental Quality Standards.

Only two determinands, fluoranthene and ortho-hydroxy-atorvastatin achieved a removal superior to 80%, whereas structurally similar compounds, benzo(a)pyrene for the former, ATOV and ATOVp for the latter, were removed with lower efficiency (~65% BAP, ~70% ATOV and ATOVp). Norerythromycin increased in the effluent, thus determining a negative value of removal, possibly due to the oxidation of its parent compound, erythromycin.

3.4 Discussion

3.4.1 Removal of sanitary determinands and trace metals

Some sanitary parameters and trace metals presented negative removals after the Arvia process. Removals are calculated as the difference between influent and effluent concentrations so the following reasons can explain such results. For sanitarities and most metals, influent and effluent concentrations in the ODC are always quite close in value, with an overlap in standard deviations for many of the considered samples, thus possibly accounting for negative removal values. Moreover, while the samples were taken trying to respect the unit's retention time at 200 L/h (30 minutes), given the difficulties in keeping the effluent flow constant for the duration of the trial, there is no guarantee that this actually happened and that the time to percolate the bed of Nyex was effectively taken into account.

An explanation valid for TOC and DOC is that particulate organic colloids, which can be barely decomposed at lower voltages, are transformed into soluble organics at voltages close to the ODC 4-50 operating parameters [13].

According to Dr. Nkrumah-Amoako from Arvia Technology (K. Nkrumah-Amoako 2017, personal communication, 10th March), another possible explanation is the adsorption/desorption equilibrium of some determinands, which may mean they can be desorbed from the Nyex before they are oxidised by the applied electrical current.

Total suspended solids (TSS) constantly caused issue during the trial, mostly because of their influence on effectiveness of the medium. Owing to various causes (i.e. failures within the WRC, treatment issues in the upstream sand filters, weather conditions), TSS built up in the balancing tank and were transferred to T2, where they could coat the medium, thus decreasing the number of accessible sites for adsorption. While on average the TSS in the effluent were lower than in the influent, negative removals were found in a considerable number of TSS samples, possibly due to build up in the effluent pipes.

As for metals, despite literature suggesting that TSS could be used as a proxy of metal concentration (in particular for Cu, Zn, Ni, Pb in their dissolved and total speciation) [3], [21], no noteworthy correlation was detected within the sampled data, thus discarding the hypothesis that an increase in metals' concentration in the effluent could be linked to an increase or build up in TSS, as detailed above.

These negative results could be caused by electroplating possibly occurring within the ODC 4-50, a phenomenon which uses electric current to reduce the dissolved metal cations, so that they adsorb on the cathode to form a thin metal coating. As the electrodes in the ODC 4-50 switch their polarity every 30 minutes, once the cathode changes to anode, the cations could be desorbed and re-released in dissolved phase into the treated effluent, thus also justifying the metals' increase both in the total and in the dissolved phase (S. Usmani 2016, personal communication, 12th April). However, Arvia Technology have conducted analysis on the ODC 4-50 and have discarded the possibility of leachate formation for any of the treated metals, thus rejecting this as an interpretation for their negative removal (K. Nkrumah-Amoako 2017, personal communication, 10th March).

3.4.2 Removal of hazardous substances

The most important pathways of removal for organic compounds during wastewater treatment are: biotransformation/biodegradation, volatilisation and abiotic degradation (adsorption). Due to their low values of Henry's coefficient K_H (ranging from 10^{-29} for erythromycin and 10^{-2} for perfluorinated carboxylic acids), the fraction removed by

volatilisation could be effectively discounted. The impact of biodegradation could not be distinguished from the abiotic mechanisms occurring in the ODC 4-50, as measurements of Dissolved Oxygen (DO) and microbial activity were not taken throughout the trial. However, no other removal mechanism is anticipated in the ODC 4-50 besides adsorption and electrochemical oxidation (K. Nkrumah-Amoako 2017, personal communication, 10th March). The latter could be a result of either direct electron transfer (DET) between the organics and the anode's surface, or more commonly, of hydroxyl radical oxidation, when $\bullet$ OH radicals intervene in the oxidation at higher anodic potentials.

As a general rule for a 3D electrode, a compound's removal efficiency depends on the relative kinetics of adsorption and electrochemical oxidation. For DET oxidation, adsorption onto Nyex is a pre-requisite for treatment, and thus a substance's affinity for adsorption will govern its overall removal ability. This seems to be less significant for hydroxyl radical oxidation: in this case the removal rates are also affected by a compound's oxidation potential, i.e. the voltage threshold at which the organics oxidation reaction is dominant over the oxygen evolution reaction; of out two determinands with similar adsorptive abilities, the one with the more favourable oxidation potential at the operating voltage will be treated to a greater extent than the other one. However, it is extremely difficult to isolate these various steps in the process, as they are part of a dynamic equilibrium (K. Nkrumah-Amoako 2017, personal communication, 10th March).

3.4.3 Principal component analysis (PCA)

Principal component analysis (PCA) was performed to identify patterns in the behaviour of the hazardous substances and to ascertain which variables drive such trends. As a general rule, corroborated by literature [22], a group of substances with similar characteristics will behave consistently towards a single treatment method.

Figure 3.6 shows the factor plot of the hazardous substances analysed.

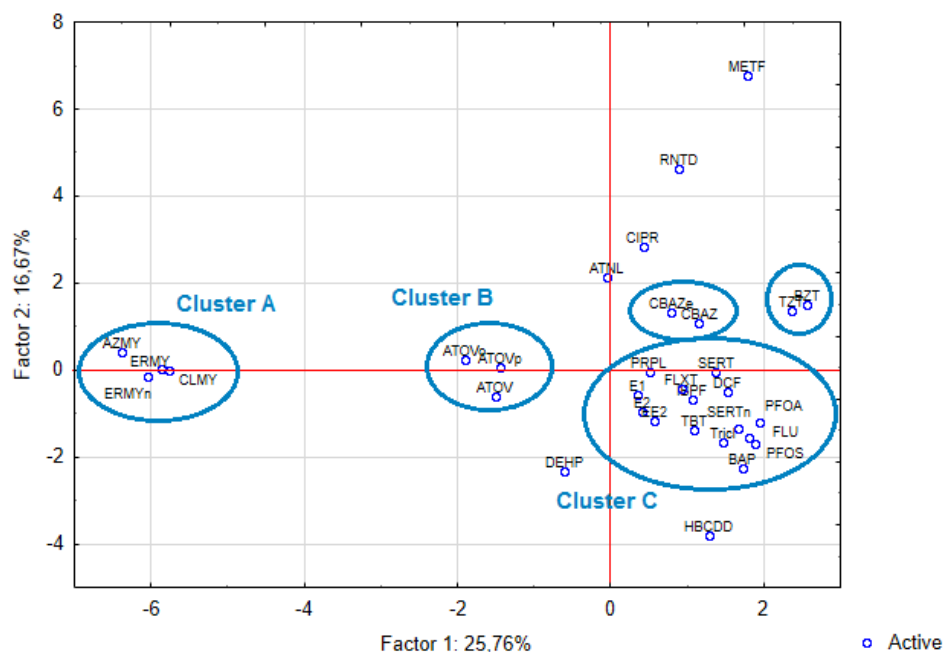


Figure 3.6 - Factor plot for hazardous substances based on their physico-chemical properties

Three distinct clusters can be singled out: cluster A includes macrolides antibiotics (AZMY, ERM, ERMyn and CLMY), cluster B groups statins (ATOV, ATOVo and ATOVp) while cluster C is a mixture of different classes of pharmaceuticals, along with steroids and other compounds of interest. Similar substances, such as CBAZ and CBAZe, BZT and TZT are also grouped together, while a few of the determinands appear to be isolated from the others.

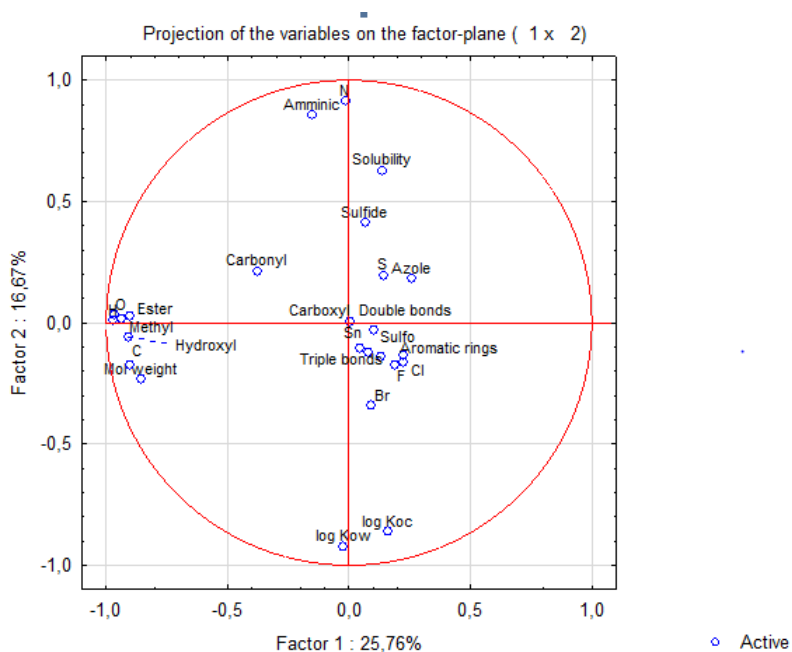


Figure 3.7 - Loading plot for hazardous substances

With the exception of norerythromycin in cluster A, whose concentration increased in the effluent possibly due to the formation of conjugates from erythromycin's oxidation, compounds in clusters A and B presented similar removal rates (60-70% for group A and 70-80% for group B). This finding was further corroborated when correlations between determinands were investigated, as each substance showed a positive linear correlation with other substances in the same cluster, with statins ($ATOVo/ATOVo$ $R^2 = 0.9220$; $ATOVo/ATOVp$ $R^2 = 0.9684$; $ATOVo/ATOVp$ $R^2 = 0.9293$) slightly better correlated than macrolides ($ERMY/AZMY$ $R^2 = 0.9010$; $ERMY/CLMY$ $R^2 = 0.9184$; $AZMY/CLMY$ $R^2 = 0.8526$). These determinands linearly correlated both intra-cluster and inter-cluster, with a maximum $R^2=0.9311$ for $ATOVo/AZMY$ and a minimum $R^2 = 0.7706$ for $ATOVo/CLMY$.

As the loading plot in **Figure 3.7** shows, both the clusters A and B (i.e. macrolides and statins, respectively) seem to be influenced by their molecular weight: substances with the highest molecular weight and size seem to display similar removal behaviour (~500 g/mol for statins and ~700 g/mol for macrolides). At the same time, the hazardous substances included in these two clusters are rich in esters, methyl and hydroxyl groups.

Generally, aromatic compounds have more affinity for adsorption on carbonaceous media than aliphatics, because of the interactions between the graphite's basal planes and the adsorbate's aromatic rings [23]. Furthermore, studies assert that interactions between aromatic adsorbates and their adsorbent increase with increasing aromatic rings in adsorbate molecules [24]. Although macrolides' possess a high number of aromatic rings compared to most of the other determinands, the presence of rings does not appear to be a principal component explaining why these compounds are clustered and similarly removed. On the other hand, PAHs such as fluoranthene and benzo(a)pyrene are grouped together within cluster C on account of their aromaticity. However, despite benzo(a)pyrene having more aromatic rings than fluoranthene, the latter shows a higher percentage of removal in the effluent, suggesting that other factors other than aromaticity could be responsible for these results.

In addition to PAHs, cluster C includes a variety of different substances which, although similar for structure and properties (i.e. presence of double bonds, aromatic rings, halogen atoms) did not achieve comparable removals. Within this cluster, chlorinated compounds (DCF, Tricl, SERT, SERTn) were removed in the range 60-69%, whereas no similarity was found in the degradation of brominated or fluorinated substances. Steroids, though similar in structure and physical properties, and thusly grouped in this cluster, represent the class of compounds with the more marked variability in removal, ranging from 79% for EE2 to 14% for E1.

As **Figure 3.6** shows, carbamazepine and carbamazepine epoxide are grouped together on account of their similar physicochemical properties. However, they show a significant difference in removal. CBAZe is, in fact, one of the main intermediates of carbamazepine metabolism, so that a decrease in carbamazepine concentration due to oxidative degradation may lead to an increase in CBAZe concentration.

As for standalone compounds, ciprofloxacin and ranitidine stand out. Both have a similarly high water solubility and are removed with efficiency above 75%. This suggests that their removal could be mainly due to oxidative process, as opposed to the adsorption on carbonaceous media, which loses efficiency for soluble adsorbates.

While clusters A and B seem to confirm the theoretical assumption of this principal components analysis, evidence suggests that due to the diversity and high variability of these substances' properties, a behavioural prediction based solely on these characteristics could lead to conflicting outcomes [22]. These results may indicate that other factors, aside from those considered in this study, are responsible for the determinands' degradation, i.e. synergic or inhibiting reactions established with other compounds, owing to their concomitant presence in the same wastewater matrix. Moreover, as stated in **Section 3.4.1**, the ODC 4-50 is based on a synergic and dynamic combination of adsorption and electrochemical oxidation, thus making it is extremely difficult to isolate the contribution of each of the processes to the removal of a specific substance, or class of substances.

3.4.4 EQS exceedance and required dilution

As described in **Section** Error! Reference source not found., many determinands from the CIP2 list are removed to a good extent by the ODC 4-50. However, some chemicals need to be prioritised for further consideration, as their concentrations in the final effluent still exceed the dictated environmental quality standards (EQS) or, for steroids and pharmaceuticals, predicted no effect concentration (PNEC), even after undergoing tertiary treatment.

An EQS is defined as *“the concentration of a particular pollutant or group of pollutants in water, sediment or biota, which should not be exceeded in order to protect human health and the environment”*. Predicted No Effect Concentration is established in the Registration, Evaluation, Authorisation and Restriction of Chemicals Regulation (REACH, EC/1907/2006) as *“the concentration of a substance in any environment below which adverse effects will most likely not occur during long term or short term exposure”*.

In this study, hazardous chemicals subject to attention are dissolved nickel, copper and zinc, perfluorooctane sulfonic acid, perfluorooctanoic acid, diclofenac, ibuprofen, clarithromycin, benzotriazole and tolytriazole. These substances were singled out by dividing the final effluent concentration of each sample by their EQS/PNEC. Values > 1 at a frequency of > 50% were classified as chemicals of concern, and their average concentration divided by their EQS or PNEC value in order to determine a dilution factor [2].

Table 3.9 displays the frequency at which these chemicals surpassed their EQS or PNEC and the dilution potentially required to reinstate them under the consented limits.

Table 3.9 – Percentage of samples exceeding the EQS or PNEC and required dilution. PNECs are indicated in red.

Substance	EQS or PNEC (µg/L)	Samples exceeding EQS/PNEC (%)	Required dilution		
			1:10 or less	1:10 – 1:50	> 1:100
Nickel (dissolved)	4.00	100	Yes		
Copper (dissolved)	1.00	100		Yes	
Zinc (dissolved)	12.90	100	Yes		
Perfluorooctane sulfonic acid (PFOS)	0.00065	100		Yes	
Perfluorooctanoic acid (PFOA)	0.00065	100	Yes		
Diclofenac (DCF)	0.05	77	Yes		
Ibuprofen (IBPF)	0.01	100		Yes	
Clarithromycin (CLMY)	0.13	70	Yes		
1,2,3 Benzotriazole (BZT)	0.02	96			Yes
Tolytriazole (4,5 methyl BZT) (TZT)	0.02	100		Yes	

As seen in **Table 3.9**, many chemicals would require a dilution ratio between 1:10 and 1:50, which increases to 1:100 in the case of BTZ. According to Comber et al. [25], out of 3,704 WwTWs for which estimated river flow data was available within 1 km to the discharge point, about 28% of the works had a dilution of less than 1:10 compared to measured WRCs flows.

This estimation, as well as the possibility that contaminants might already be present upstream from the discharge point in the receiving water body, weakens the practicability of dilution. In a small site such as the studied WRC, where the receiving stream does not have a significant flow, dilution does not appear to be a realistic option, as it is estimated to be 1:3.

3.4.5 Reliability of the technology

The performance of Arvia ODC 4-50 was assessed using key performance indicators (KPIs), in order to evaluate the frequency and nature of unplanned remedial, maintenance and repair.

The total duration of the trial was 186 days, for 40 of which the pilot plant was stopped waiting for maintenance. Therefore, considering that the process was halted immediately after collecting the first trial sample and restarted only on the 28th of April, the actual operating time is estimated to 3,504 h. **Table 3.10** presents the estimated maintenance times for each pilot component, accounting for all the events occurred from April 28th to September 20th 2016, as per the trial log book.

Table 3.10 – Estimated maintenance time for Arvia ODC 4-50 components

Component	Total time (h)	Fraction of total maintenance time (%)
Filters	11.25	35
Pumps	9	28
Tank T1	9	28
Probes (pH, conductivity, turbidity)	3	9
Total	32.25	100

Maintenance efficiency (3.2), effectiveness (3.3) and percentage of remedial work needed were calculated, considering the operating time as the amount of hours the process run during the trial

$$\text{Maintenance efficiency} = \frac{\text{Maintenance man hours}}{\text{Operating time}} \times 100 = 0.9\% \quad (3.2)$$

A low value of maintenance efficiency indicates that the current practices and mechanisms are effective and the operating conditions are all within the expected range [26].

Assuming as down time the hours the unit was not functioning to its full potential due to maintenance or unplanned stops to the process, estimated at ~118 h, the maintenance effectiveness is calculated as follows:

$$\text{Maintenance effectiveness} = \frac{\text{Operating time}}{\text{Operating time} + \text{down time}} \times 100 = 97\% \quad (3.3)$$

According to literature [26], a maintenance effectiveness over 95% is a key indicator of good performance of maintenance practices. However, a large part of maintenance time was spent for unplanned remedial of previously completed maintenance work, for a rework percentage of ~41%.

Another important KPI to take into account is the mean time between failures (MTBF), where a failure is identified as an alarm occurring to any part of the pilot plant, as indicated in **Table 3.11**, as per the trial log book.

Table 3.11 - Failure occurrences during the trial

Component	Alarms (failure events)	Fraction (%)
Filters	11	35
Hydrogen monitor	9	29
Low level alarm	7	23
General alarm	4	13
Total	31	100

Considering the operating time of 146 days, the mean time between failure events was estimated to be ~ 113 h.

3.4.6 Overall performance and criticalities

Overall, the ODC run without major problems for the most part of the trial, delivering micropollutants removal and maintaining all the consented parameters for the site below the limit.

The performance was hindered by a few design and conceptual issues, which should be addressed further and more satisfactorily in view of future application goals. These issues were mainly an underestimation of the TSS presence in the influent and the formation of gas bubbles in the plenum chamber.

As for suspended solids, which clogged the media and determined the effluent flow to constantly drop, it is advised that the unit be preceded upstream by a tighter pre-treatment system, possibly pile cloth filtration to diminish or block the TSS build up in the influent pipework and process tank. Provided a suitable flow equalisation is reached upstream, it is suggested that the balancing tank T1 might be eliminated, as it facilitates accumulation of solids in the system.

A newly designed backwash system will also contribute to solve the TSS issue, so that the backwashing flow is evenly distributed in the tank and does not short circuit and follow preferential paths in the media, thus decreasing the backwash efficiency in removing impurities from Nyex. For simplicity of maintenance and operation, the backwash process will need to be automated. This system will also aim at impeding the settling of gas bubbles formed on the plenum chamber, which block the effluent from flowing to T3 by gravity.

3.5 Cost assessment

In order to evaluate the Arvia ODC performance towards future design goals, and to assess its application as a control measure for hazardous substances on a national level, capital expenditure (CAPEX) and operating expenditure (OPEX) were estimated for full scale plants (ODC 22-100, 22 cells per module, with electrodes of 100 × 100 cm). Each plant serves a different range of population equivalent (from 500 to 500,000 PE, according to the CIP2 guidelines for options appraisal analysis) and treats a proportional flow.

All the calculations are based on data supplied by Arvia Technology. This assessment only represents a best estimate of the costs for a unit at full scale. At this stage, the supplier cannot confidently assess to what extent these figures will be accurate for future costs appraisals, as this is technology has never been scaled up to more than 10-20,000 PE and this trial represents the first of its kind.

Assuming a water consumption of 228 L/d per person, **Table 3.12** presents the dry weather flow (DWF) for each PE case and estimates the average DWF (using an averaging factor of 1.3) and the peak flow, which is assumed to be 3 times the DWF for PE < 10,000 and 6 times the DWF for PE ≥ 10,000. The modules are designed to support a peak flow.

Table 3.12 - Design parameters for ODC 22-100 at different population equivalent

ITEM	PE					
	500	2,000	10,000	25,000	100,000	500,000
Dry weather flow (DWF) (m ³ /d)	114	456	2,280	5,700	22,800	114,000
Average DWF (m ³ /d)	148	593	2,964	7,410	29,640	148,200
Peak flow (m ³ /d)	684	2,736	6,840	17,100	68,400	342,000
Number of modules	3	11	26	65	216	1,080

Table 3.13 shows the inputs employed for calculating the CAPEX and OPEX of a full scale plant designed for different PE conditions, as provided by Arvia Technology.

Table 3.13 - Arvia inputs for CAPEX and OPEX calculations

ITEM	PE					
	500	2,000	10,000	25,000	100,000	500,000
Cost of cell (£)	53,000	202,800	453,188	610,875	1,149,125	4,437,000
Project engineering (£)	28,800	28,800	48,000	72,000	96,000	144,000
Arvia MEICA (£)	17,100	45,600	67,830	121,125	178,125	570,000
Backwash pump power requirement (kWh)	0.507	4.032	13.44	40.32	134.4	800
Feed pump power requirement (kW)	0.507	4.032	13.44	40.32	134.4	800
Electrochemical oxidation power requirement (kW)	2.89	10.59	25.03	62.56	207.90	1039.50

ITEM	PE					
	500	2,000	10,000	25,000	100,000	500,000
Testing and commissioning (£)	5,000	10,000	25,000	37,500	50,000	62,500

Capital expenditure takes into account civil construction costs, including a concrete base for the modules, MEICA (Mechanical, Electric, Instrumentation, Control and Automation) costs, testing and commissioning expenses (**Table 3.14**). The cell cost includes costs of electrodes, membranes and Nyex.

Table 3.14 - Capital expenditure (CAPEX) summary

ITEM	PE					
	500	2,000	10,000	25,000	100,000	500,000
Arvia civil costs (£)						
Arvia civil costs	3,886	15,545	29,148	48,580	129,545	485,795
Sub-total	3,886	15,545	29,148	48,580	129,545	485,795
Arvia MEICA costs (£)						
Arvia cell cost	53,000	202,800	453,188	610,875	1,149,125	4,437,000
Arvia MEICA costs	17,100	45,600	67,830	121,125	178,125	570,000
Project management	4,800	4,800	8,000	12,000	16,000	24,000
Design engineering	9,600	9,600	16,000	24,000	32,000	48,000
Sub-total	84,500	262,800	545,018	768,000	1,375,250	5,079,000
Testing and commissioning (£)						
Testing and commissioning	5,000	5,000	25,000	37,500	50,000	62,500
Process engineering	14,400	14,400	24,000	36,000	48,000	72,000
Sub-total	19,400	19,400	49,000	73,500	98,000	134,500
TOTAL CAPEX (£)	108,000	298,000	624,000	891,000	1,603,000	5,700,000

OPEX for each year of operation includes staff, maintenance and energy costs, as seen in **Table 3.15**.

In accordance with the cost models used for CIP2, operational and maintenance labour are calculated respectively as 5% and 2.5% of an annual working leave per site, estimated at £35,000. The power requirements for pumps are based on the pumps' ratings (**Table 3.13**), assuming the booster feed pump works continuously while the backwash pumps works only for 20 minutes a day for the whole year. The energy consumption required for electrochemical oxidation is calculated on the assumptions that power costs £0.11/kWh and that each module consumes 0.14 kWh/m³, running at 26.5 V, 6.25 A, 600 L/h for 50% of the time for the year (K. Nkrumah-Amoako 2017, personal communication, 21st April).

Table 3.15 - Yearly operating expenditure (OPEX) summary

ITEM	PE					
	500	2,000	10,000	25,000	100,000	500,000
Staff cost (£/y)						
Operational labour	1,750	1,750	3,500	3,500	7,000	7,000
Maintenance labour	875	875	1,750	1,750	3,500	3,500

ITEM	PE					
	500	2,000	10,000	25,000	100,000	500,000
Sub-total	2,625	2,625	5,250	5,250	10,500	10,500
Maintenance cost (£/y)						
Civil maintenance	39	155	291	486	1,295	4,858
MEICA maintenance spares	428	1,140	1,696	3,028	4,453	14,250
Annual Nyex top up	257	1,026	2,565	6,413	21,375	106,875
Annual ODC spares	684	2,736	6,840	17,100	57,000	285,000
Sub-total	1,407	5,057	11,392	27,027	84,124	410,983
Energy cost (£/y)						
Backwash pumps	7	53	178	534	1,781	10,600
Infeed pumps	489	3,885	12,951	38,852	129,508	770,880
Electrochemical oxidation cost	2,403	9,612	24,030	60,074	200,248	1,001,241
Sub-total	2,898	13,551	37,159	99,461	331,537	1,782,721
TOTAL OPEX per year (£/y)⁴	7,000	22,000	54,000	132,000	427,000	2,205,000
TOTAL OPEX per treated m³ (£/m³)	0.028	0.022	0.022	0.021	0.017	0.018

The total expenditure (TOTEX) per treated m³ provides a key performance indicator allowing a comparison between the Arvia ODC and any other technology for micropollutants treatment. The calculation is conducted employing a peak flow and assuming an asset life of 10 years. As **Table 3.16** highlights, the technology would consistently become more cost effective when PE and treated volumes increase, as the capital investment would have less of a bearing upon the overall cost.

Table 3.16 – Total expenditure (TOTEX) for asset life and treated volumes

	PE					
	500	2,000	10,000	25,000	100,000	500,000
CAPEX (£)	108,000	298,000	624,000	891,000	1,603,000	5,700,000
OPEX for asset life (£)	70,000	220,000	540,000	1,320,000	4,270,000	22,050,000
TOTEX for asset life (£)	178,000	518,000	1,164,000	2,211,000	5,873,000	27,750,000
TOTEX per treated m³ (£/m³)	0.071	0.052	0.047	0.035	0.024	0.022

3.6 Multi-criteria analysis for options appraisal

In order to reach a conclusion on whether the Arvia ODC represents a viable technology for micropollutants removal, a multi-criteria analysis (MCA) was performed, against alternative commercial technologies for treating final effluent. This analysis represents a best estimate of the ODC performance at full scale; albeit a subjective tool by definition, the MCA was based on a combination of information obtained from literature and from Arvia Technology, together with evidence from the pilot trial conducted, in order to mitigate its bias.

⁴ The OPEX cost is rounded up to the third digit.

The chosen method for the analysis was the analytical hierarchy process (AHP). In using this method to model a problem, a network structure representing that problem is needed, as well as pairwise comparisons to establish relationships within the structure. In general, from an overall objective, the method descends down to criteria for assessment and to further sub-criteria, until the alternatives from which the choice has to be made are reached [20]. **Figure 3.8** shows the network structure used as basis for this assessment of the ODC.

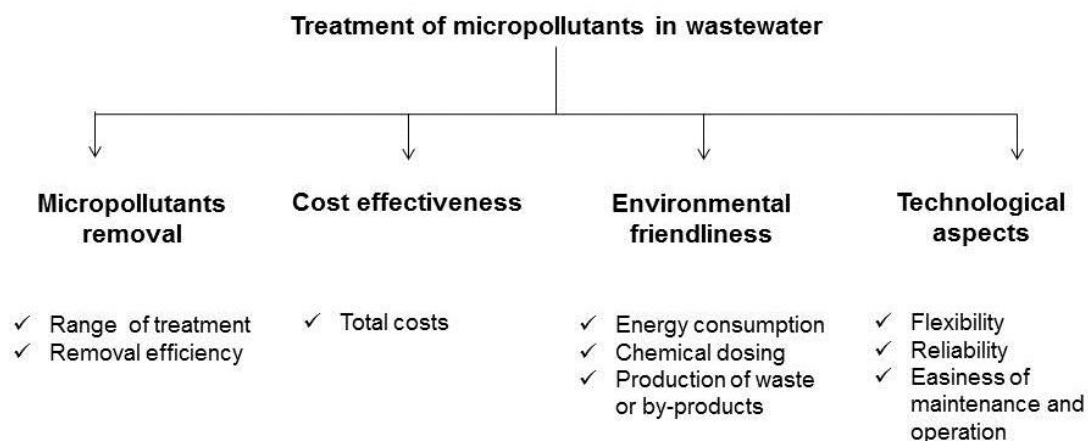


Figure 3.8 - AHP network structure for technologies appraisal, including four criteria and nine sub-criteria

According to this network, a good technology for micropollutants removal from wastewater should be able to achieve a removal over 70% for as many pollutants as possible and to treat a wider range of substances; it should be cheaper, consume less energy, require less maintenance and be easily adaptable to unforeseen circumstances, easier to maintain and operate; it should not necessitate chemical dosing or produce waste and by-products.

The organics destruction cell was compared to five of the most frequently used tertiary treatments, as found in literature: adsorption on GAC [22], [27], [28], advanced oxidation processes [22], [28], such as ozonation and UV/H₂O₂ oxidation, membrane bioreactor (MBR) [22], [29] and membrane filtration.

3.6.1 Weighting of criteria

In order to assign relative importance to criteria in the technologies' appraisal, each sub-criterion was weighted against the others, following the scale presented in **Table 3.17**.

Table 3.17 - Weighting scale for AHP (adapted from [20])

Score	Definition	Explanation
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Score	Definition	Explanation
1	Equal importance	Two activities contribute equally to the objective
3	Moderate importance of one over the other	One activity is moderately favoured over the other
5	Essential or strong importance	One activity is strongly favoured over the other
7	Very strong importance	An activity is very strongly favoured to contribute to the objective
9	Extreme importance	The evidence favouring one activity over the other is of the highest possible level of affirmation

When compromise between the options is needed, even numbers can be used up to 8. Moreover, if activity i (row) has one of the above numbers assigned to it when compared to activity j (column), then j has the reciprocal value when compared to i [20]. A matrix for each criterion was formed, for a total of four, with sub-criteria composing rows and columns. For each row, the geometric mean and its percentage fraction were calculated, the latter indicating the weight of that specific sub-criterion against the others.

In this analysis, the weights' allocation was based on the premise that, when choosing to install a technology at full scale within CIP2, the removal of micropollutants (RM) would have to be prioritised, followed by cost effectiveness (CE), environmental friendliness (EF) and technological aspects (TA). The matrix of weights below (**W**) shows the applied weights for each sub-criterion (i), whereas the columns (j) indicate the criterion, in order of priority. The breakdown of weights assigned for each criterion is attached in **Appendix F**.

$$W = \begin{bmatrix} \text{Range of treatment} \\ \text{Micropollutants removal} \\ \text{Total costs} \\ \text{Energy consumption} \\ \text{Chemical use} \\ \text{By products and waste production} \\ \text{Flexibility} \\ \text{Reliability} \\ \text{Easiness of maintenance/operation} \end{bmatrix} = \begin{bmatrix} \text{RM} & \text{CE} & \text{EF} & \text{TA} \\ 0.30 & 0.21 & 0.11 & 0.06 \\ 0.30 & 0.21 & 0.11 & 0.06 \\ 0.15 & 0.31 & 0.06 & 0.04 \\ 0.09 & 0.08 & 0.22 & 0.04 \\ 0.05 & 0.05 & 0.22 & 0.06 \\ 0.05 & 0.05 & 0.22 & 0.06 \\ 0.02 & 0.02 & 0.02 & 0.23 \\ 0.02 & 0.02 & 0.02 & 0.23 \\ 0.02 & 0.02 & 0.02 & 0.23 \end{bmatrix}$$

3.6.2 Pairwise technology comparison

The next step in the MCA was to set up matrices of paired comparisons for the chosen technologies with respect to the network's sub-criteria. There are nine matrices, one for each sub-criterion, as shown in **Appendix F**. For each matrix, a [1,6] vector with relative scores is originated, by weighting the geometric mean of each alternative against their total score. The comparison scores followed the rules set in **Table 3.17**.

Range of treatment (RT)

A literature review assessed which and how many hazardous substances in the CIP2 suite each technology had been trialled for either at full or pilot scale. The ones with the best

range appeared to be the ODC 4-50 and GAC which, according to literature [22], [27], [30], have been trialled for the highest and most diverse (i.e. belonging to a variety of classes) number of substances included in CIP2. MBR [22], AOPs [22] and membrane filtration [22] follow and the resulting vector is presented below.

$$RT = \begin{bmatrix} ODC \\ GAC \\ O_3 \\ UV H_2O_2 \\ MBR \\ Membrane filtration \end{bmatrix} = \begin{bmatrix} 0.48 \\ 0.23 \\ 0.09 \\ 0.09 \\ 0.07 \\ 0.03 \end{bmatrix}$$

Micropollutants removal (MPR)

For this sub-criterion, the highest score was assigned to that technology which, according to literature, was able to remove the highest absolute number of pollutants with efficiency over 70%. The highest score was thus assigned to GAC [22], [27], [30] and MBR [22], followed by ODC, AOPs [22] and membrane filtration [22].

$$MPR = \begin{bmatrix} ODC \\ GAC \\ O_3 \\ UV H_2O_2 \\ MBR \\ Membrane filtration \end{bmatrix} = \begin{bmatrix} 0.14 \\ 0.24 \\ 0.08 \\ 0.08 \\ 0.24 \\ 0.04 \end{bmatrix}$$

Total costs (TC)

In order to compare the economic feasibility, the total costs for a full scale plant of 100,000 PE were appraised, based on literature [22],[31],[32]. As Wahlberg [31] presents the costs in SEK, the conversion rate to GBP is assumed to be 0.086 SEK/GBP, the annual average of the 2016 currency conversion.

$$TC = \begin{bmatrix} ODC 4 - 50 \\ GAC \\ O_3 \\ UV H_2O_2 \\ MBR \\ Membrane filtration \end{bmatrix} = \begin{bmatrix} 0.50 \\ 0.09 \\ 0.28 \\ 0.15 \\ 0.03 \\ 0.04 \end{bmatrix}$$

Energy consumption (EC)

The energy consumption is calculated as kWh/treated m³. AOPs are the most energy consumptive processes, followed by MBR and membrane filtration (a combination of micro and nano-filtration consumes 5.70 kWh/m³ [33]). The ODC 4-50 uses less energy, with an estimated 0.14 kWh/m³ for a unit running in standard conditions (26.5 V, 6.25 A, 600 L/h). The scores are distributed based on data presented in **Section 3.5** for the ODC 4-50, whereas values for the other technologies were found in literature [33].

$$EC = \begin{bmatrix} ODC \\ GAC \\ O_3 \\ UV H_2O_2 \\ MBR \\ Membrane filtration \end{bmatrix} = \begin{bmatrix} 0.49 \\ 0.28 \\ 0.03 \\ 0.03 \\ 0.16 \\ 0.09 \end{bmatrix}$$

Chemical use (CU)

The ODC together with GAC [22] and UV/H₂O₂ [22] do not necessitate the dosing of chemicals, whereas the handling of O₃ could raise fire and toxicity risks and both MBR and membrane processes use chemicals for the membrane's cleaning process.

$$CU = \begin{bmatrix} ODC \\ GAC \\ O_3 \\ UV H_2O_2 \\ MBR \\ Membrane filtration \end{bmatrix} = \begin{bmatrix} 0.27 \\ 0.27 \\ 0.06 \\ 0.27 \\ 0.04 \\ 0.04 \end{bmatrix}$$

Production of waste or by-products (PWB)

According to Arvia Technology, the ODC does not produce any by-products and only requires to waste the media fraction which does not cover the electrodes (which, consequently, is not regenerated) (K.Nkrumah Amoako 2017, personal communication, 2nd May). The same could be said for GAC [22], which however contributes to waste production in the form of spent GAC requiring regeneration or replacement. On the contrary, while AOPs do not produce any waste, they potentially form by-products such as bromate, carboxyls, aldehydes and ketones and residual peroxide in the case of UV/H₂O₂. Membrane processes and MBR require treatment of the concentrate [22], and MBRs release by-products due to the use of chloramine to clean the membrane.

$$PWB = \begin{bmatrix} ODC \\ GAC \\ O_3 \\ UV H_2O_2 \\ MBR \\ Membrane filtration \end{bmatrix} = \begin{bmatrix} 0.31 \\ 0.11 \\ 0.04 \\ 0.04 \\ 0.10 \\ 0.25 \end{bmatrix}$$

Flexibility (F)

Flexibility is intended as the ability of a technology to suit different installation and operation conditions without having to be modified. GAC is highly flexible, as it can be applied where needed, but also needs some pre-treatment of the inlet [22], while MBRs can accommodate a wide range of influent fluctuations, but have so far only been applied to small scale WwTWs [22]. AOPs require complicated additional equipment during installation, and the treatment itself can be greatly affected by factors such as COD, BOD, TSS or water with low UV transmission [22]. Membrane filtration has to be subjected to intense pre-treatment and is greatly influenced by membrane lifetime. The ODC's performance seems to be similarly impacted by the influent quality. However, the unit's

modular structure and range and compactness make it very flexible for different uses and installations.

$$F = \begin{bmatrix} ODC \\ GAC \\ O_3 \\ UV H_2O_2 \\ MBR \\ Membrane filtration \end{bmatrix} = \begin{bmatrix} 0.17 \\ 0.35 \\ 0.03 \\ 0.03 \\ 0.35 \\ 0.09 \end{bmatrix}$$

Reliability (R)

Reliability is here intended as the ability of a technology to be dependent and perform according to its original specifications. While membrane based systems consistently deliver high quality effluents [22], ODC and GAC's performance shows a lower efficiency in presence of TSS (as seen in **Section 3.4.1**) and DOC [22], respectively. The ODC's performance in particular, despite achieving an acceptable performance in terms of reliability (**Section 3.4.5**), was subjected to issues which could have been avoidable had the unit been in a further stage of development. As for AOPs, they are hindered by the formation of by-products, and in the case of ozonation by the presence of potential ozone scavengers [22].

$$R = \begin{bmatrix} ODC 4 - 50 \\ GAC \\ O_3 \\ UV H_2O_2 \\ MBR \\ Membrane filtration \end{bmatrix} = \begin{bmatrix} 0.13 \\ 0.13 \\ 0.04 \\ 0.04 \\ 0.30 \\ 0.30 \end{bmatrix}$$

Easiness of maintenance and operation (EMO)

Compared to the other carbon based technology, GAC [22], the ODC is quite easy to maintain and operate, as does not need regeneration of adsorbents, but only an occasional media augmentation, which does not require long stops in operation or excessive resources (in terms of staff, OPEX etc.). AOP technologies are very difficult to operate and maintain, as they need professional and trained staff, constant reagent dosing and high quality construction materials [22]. Likewise, membrane technologies require highly trained staff and, as membranes can be subjected to severe fouling, they need frequent and intensive cleaning [22].

$$EMO = \begin{bmatrix} ODC 4 - 50 \\ GAC \\ O_3 \\ UV H_2O_2 \\ MBR \\ Membrane filtration \end{bmatrix} = \begin{bmatrix} 0.54 \\ 0.32 \\ 0.03 \\ 0.10 \\ 0.06 \\ 0.06 \end{bmatrix}$$

Each one of these sub-criteria vectors, in order, form the matrix of choices **C**, presented below:

$$C = \begin{bmatrix} ODC\ 4 - 50 \\ GAC \\ O_3 \\ UV\ H_2O_2 \\ MBR \\ Membrane\ filtration \end{bmatrix} = \begin{bmatrix} RT & MPR & TC & EC & CU & PWB & F & R & EMO \\ 0.48 & 0.14 & 0.50 & 0.49 & 0.27 & 0.31 & 0.17 & 0.13 & 0.54 \\ 0.23 & 0.24 & 0.09 & 0.28 & 0.27 & 0.11 & 0.35 & 0.13 & 0.32 \\ 0.09 & 0.08 & 0.28 & 0.03 & 0.06 & 0.04 & 0.03 & 0.04 & 0.03 \\ 0.09 & 0.08 & 0.15 & 0.03 & 0.27 & 0.04 & 0.03 & 0.04 & 0.10 \\ 0.07 & 0.24 & 0.03 & 0.16 & 0.04 & 0.10 & 0.35 & 0.30 & 0.06 \\ 0.03 & 0.04 & 0.04 & 0.09 & 0.04 & 0.25 & 0.09 & 0.30 & 0.06 \end{bmatrix}$$

Multiplying matrices **W** [4×9] and **C** [9×6], the final matrix **T** [4×6] represents the total scores assigned to each technology in regards to each main criterion considered in the analysis.

$$T = W \times C = \begin{bmatrix} ODC\ 4 - 50 \\ GAC \\ O_3 \\ UV\ H_2O_2 \\ MBR \\ Membrane\ filtration \end{bmatrix} = \begin{bmatrix} RM & CE & EF & TA \\ 0.36 & 0.39 & 0.35 & 0.31 \\ 0.22 & 0.19 & 0.22 & 0.25 \\ 0.10 & 0.13 & 0.07 & 0.05 \\ 0.10 & 0.11 & 0.11 & 0.08 \\ 0.13 & 0.11 & 0.12 & 0.20 \\ 0.06 & 0.06 & 0.10 & 0.13 \end{bmatrix}$$

According to this multi-criteria analysis, the Organic Destruction Cell could, when scaled up for future application, lead on other technologies for tertiary treatment, presenting itself as a valid alternative for micropollutants removal from wastewater on every account.

3.7 Conclusions

The study of the Arvia ODC 4-50 was aimed at assessing a pilot scale version of the technology, evaluating its performance for organic micropollutants removal and appraising its viability as a future option for full scale employment in treatment plants.

This technology combines adsorption on a graphite medium and electrochemical oxidation. Other degradation mechanisms (i.e. volatilisation or biodegradation) are not likely to influence the final removal outcome. Although the main removal processes responsible for organics degradation are straightforward and have been investigated before in literature, their combined approach makes it extremely difficult to understand to what extent adsorption and oxidation singularly contribute to the degradation of a specific substance or a class of substances.

Arvia ODC 4-50 performed favourably for the removal of specific classes of organic pharmaceuticals, such as statins (70-80%) and macrolides antibiotics (60-70%), as well as for chlorinated substances, polycyclic aromatic compounds and water soluble hazardous

substances with water solubility in the order of 10^4 mg/L, such as ciprofloxacin and ranitidine. No consistent removals were observed for steroids, which ranged from 13% to 79%, whereas most sanitary determinands and metals analysed were accumulated in the unit, with effluent concentrations exceeding the influent ones. Furthermore, when the treated final effluent was compared to the EQSs set for CIP2 determinands, without accounting for dilution effects and for the quality of the receiving water body, the majority of the determinands (72%) were found below those set quality criteria.

Although lower than alternative treatment technologies such as GAC or ozonation, energy consumption, normalised at 0.14 kWh/m^3 of treated final effluent, still represents the major contributing factor to estimated operational costs (1.1 pence/m^3) and it steadily increases with the population served. The process requires no chemical usage and therefore produces less sludge; hence the technology may offer lower operational carbon usage than other advanced oxidation processes; at the same time gas emissions including hydrogen and the greenhouse gas CO_2 are produced, albeit their exact quantification and effect on the total carbon footprint still requires further research. In fact, there are currently no full-scale installations of the Arvia ODC elsewhere, so that a precise and sensible quantification of costings and carbon footprint is not possible.

Promising performance notwithstanding, the ODC is currently still at the early stages of development, without any full-scale application. Improved solids capture is required upstream of the process to avoid clogging the bed of media and an improved flow balancing method and backwash system need to be implemented.

3.8 References

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4 PERFORMANCE OF A LABORATORY SCALE ORGANIC DESTRUCTION CELL (ODC) FOR THE REMOVAL OF CARBAMAZEPINE

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Abstract

Among the emerging contaminants targeted in the UKWIR Chemicals Investigation Programme (CIP2), carbamazepine (CBZ) is reportedly one of the hardest pharmaceuticals to treat in conventional wastewater treatment works (WWTWs), due to its extreme persistence at low concentrations. As a result of this ineffective removal, carbamazepine can bypass WWTWs and is among the most frequently reported pollutants in surface water. Being a good indicator of anthropogenic activity, CBZ was singled out for a bench scale trial of an Organic Destruction Cell (ODC), an electrolytic cell combining adsorption on a reactive media and oxidation. Although isolating the contribution of each of these removal mechanisms is quite challenging, due to the dynamic nature of the process, steady removals were achieved once the media was saturated, when electrochemical oxidation was enhanced and the two processes occurred simultaneously.

The main aim of this trial was to assess the unit's performance for the removal of carbamazepine in a more controlled matrix (spiked tap water) than real wastewater, thus allowing to investigate how its degradation could be enhanced by optimising the operating conditions, namely current density and effluent flow and, by proxy, retention time in the unit. Overall, baseline conditions for both effluent flow (5 L/h) and current density (4 mA/cm², for a total of 1.6 A) were found to be the most conducive for carbamazepine removal (~78% on average), as this combination seemed to simultaneously guarantee a sufficient retention time for carbamazepine adsorption and an efficient oxidation by means of •OH radicals. Experimental evidence also showed that slight alterations of pH and temperature in the water matrix did not significantly influence the removal performance, whereas an energy appraisal of the performance highlighted abnormally elevated values of cell voltage (almost double the expected ones for any current density applied), possibly caused by increased resistance within the ODC.

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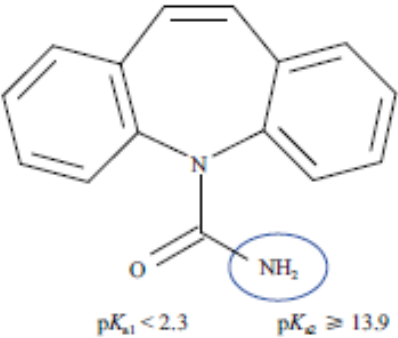
4.1 Introduction

Over the last few decades there has been increasing pressure to reduce levels of pollution in water bodies in the UK and Europe, in a drive to meet good ecological status set out by the Water Framework Directive (WFD, 2000/60/CE). Wastewater final effluents (FE) have especially been identified as one of the key point sources of pollution in the environment. In many cases current wastewater treatment works (WwTWs) are not specifically designed to treat certain classes of substances, which can bypass the treatment works and be discharged with the FE, thus posing a potential threat to the aquatic wildlife and to the quality of drinking water [1]–[3].

Micropollutants typically range from a few ng/L to several µg/L and consist of a wide array of *“synthetic or naturally occurring chemicals that are not commonly monitored in the environment, but which have the potential to enter the environment and cause known or suspected adverse ecological and (or) human health effects”* [4]. Micropollutants include pharmaceuticals, personal care products, steroid hormones, industrial chemicals and many other compounds [3]. Their presence in the aquatic environment has been raising concern worldwide, owing to their potential toxicological threat to living organisms. As the vast majority of micropollutants are used daily in households, workplaces, or the urban environment, their release into the aquatic environment has likely occurred for a long time, but they are only now being routinely detected owing to novel and improved detection methods. In other cases, synthesis of new industrial chemicals or changes in use and disposal of the existing ones may have led to the creation of new sources of pollution [4], [5]. Legislation such as the WFD and its daughter directives have begun to raise public awareness on the presence of trace contaminants in the aquatic environment.

Carbamazepine (CBAZ) is a widely prescribed anticonvulsant drug, whose main properties are summarised in **Table 4.1**. When ingested, approximately 72% of the administered dose is absorbed, while the rest is discharged through faeces. CBAZ is reportedly one of the hardest pharmaceuticals to treat in conventional WwTWs, with average removals being at around 32% [6]. Carbamazepine can bypass WwTWs and is widely detected in downstream water bodies, being among the most frequently reported micropollutants in surface waters [6]. Moreover, only slight changes in concentration are detectable during soil passage to the underground aquifers. These persistency characteristics qualify carbamazepine as a suitable marker for anthropogenic influences on the aquatic environment [7], [8].

Table 4.1 - Physicochemical properties for carbamazepine (CBAZ)¹

Carbamazepine (CBAZ)		
 $pK_{a1} < 2.3$ $pK_{a2} \geq 13.9$	CAS number:	298-46-4
	Molecular formula:	C ₁₅ H ₁₂ N ₂ O
	Molecular weight	236.28
	Water solubility (mg/L):	1.12 × 10 ²
	Henry's law constant (atm m ³ /mol)	1.08 × 10 ⁻¹⁰
	Log K _{ow}	2.45
	Log K _{oc}	2.23 ²
	pK _a :	Neutral

Due to its poor removal in WwTWs, a range of single treatments, or a combination of them, has been employed to remove CBAZ from wastewater, including electrochemical oxidation [9], advanced oxidation processes (AOPs) [10], membrane processes [9] and adsorption [6].

Adsorption has always been considered a valid process for removal of organic compounds from wastewater, as it can achieve very low discharge consents. Granular activated carbon (GAC) is probably the most familiar and widely employed material, owing to its large surface area to volume ratio, broad pore structure and excellent adsorption capacity [11], which guarantee high loading of pollutants on the adsorbent [12]. However, once the carbonaceous material has been exhausted, it needs regeneration, which is a very costly process in terms of energy consumption and material losses [13]. To address this issue, adsorption and AOPs are combined within a 3D electrode patented by Arvia Technology (Cheshire, UK) and called Organic Destruction Cell (ODC). The ODC achieves removal of micropollutants and consists of an electrolytic cell with a bed of carbonaceous medium interposed between the electrodes. Compared to a standard electrode, the addition of a granular media contributes to enhance the conductivity and mass transfer of the adsorption of pollutants. The presence of this medium offers more reactive sites for pollutants adsorption or even catalytic reactions, determining a higher removal efficiency [11].

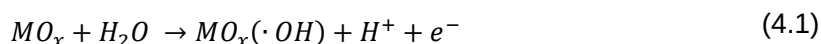
At the heart of the ODC is Nyex, a non-porous, highly conducting carbonaceous material. Nyex delivers a comparatively smaller adsorption capacity than GAC, when employed for compounds such as phenol, chloro-phenol, atrazine, acid violet 17 [14]. However, in terms of performance, this medium has two main advantages when compared to GAC: its high

¹ SRC Physprop database <http://esc.syrres.com/fatepointer/webprop.asp?CAS=298464>

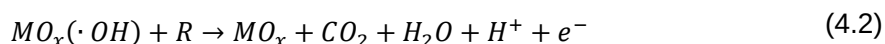
² EPIWEB 4.1

conductivity allows to obtain organics destruction at low cell voltages and an almost complete material regeneration, whereas its non-porous nature reduces the adsorption rates and the time to achieve regeneration [13].

Anodic oxidation in a 3D electrode is a combination of two processes. One is direct electron transfer (DET), where organics contained in the bulk of wastewater are electrolysed after adsorption on the anode surface [15]. The second is oxidation via the hydroxyl radical, which is able to react efficiently and non-selectively with several types of organics. Hydroxyl radicals result from the oxidation of water, thus organic compounds can be completely degraded by reaction with adsorbed $\bullet\text{OH}$ radicals. After the $\bullet\text{OH}$ radicals are formed by anodic discharge of the water, they adsorb on the electrode's active sites (MO_x) (4.1):



The adsorbed hydroxyl radical oxidises the organic pollutants (4.2):



where R represent the organic pollutants.

This study investigates the performance and the optimal operating conditions of a bench scale ODC for the removal of carbamazepine from the aqueous media. The objective was to replicate at a smaller scale the conditions of a pilot scale ODC situated in a Water Recycling Centre (WRC) in Cambridgeshire, in order to better understand its performance and its effectiveness under more controlled circumstances. The main parameters being assessed are matrix related (i.e. pH and temperature) and operational, namely effluent flow and current density.

4.2 Materials and methods

4.2.1 Adsorbent

The material used in the laboratory scale ODC is a granular, highly conductive and non-porous media called Nyex 2180, supplied by Arvia Technology in the form of a dry powder. It is mainly comprised of carbon (~99%), with maximum ash and moisture contents being 1 and 0.5%, respectively. Other properties are presented in **Table 4.2**.

Table 4.2 - Nyex 2180 properties (supplied by Arvia Technology)

Property	Value
Bed voids volume (porosity) (%)	47

Property	Value
BET surface area (m ² /g)	0.8
Density (g/cm ³)	2.2
Particle diameter range	150 μ m to 2.8 mm

4.2.2 Organic Destruction Cell (ODC)

The chosen organic destruction cell was the ODC 1-20, so called because it only consists of a single electrochemical cell with 20 $\times$ 20 cm electrodes. The cell was equally divided into an anodic and a cathodic compartment by a 400 μ m membrane of modified polyethylene with 56% porosity, which allowed ionic exchange. Each compartment of the cell contained 1.3 kg of Nyex.

While oxidation processes occurred at the anode, gaseous hydrogen was produced at the cathode. Both electrodes were made of carbon. This material can be used as electrode material at low current densities and presents limited side reactions of oxygen evolution without losing effectiveness in removal of organics [16]. Both electrodes had an active area of 400 cm² and, given a 5 cm width, the cell total active volume was 2 L. The unit was fed from a 1000 L intermediate bulk container (IBC), holding tap water fortified with CBAZ, and its effluent was collected into a 200 L plastic tank. The experimental set up can be seen in **Figure 4.1**, while **Figure 4.2** shows a close up of the ODC 1-20.

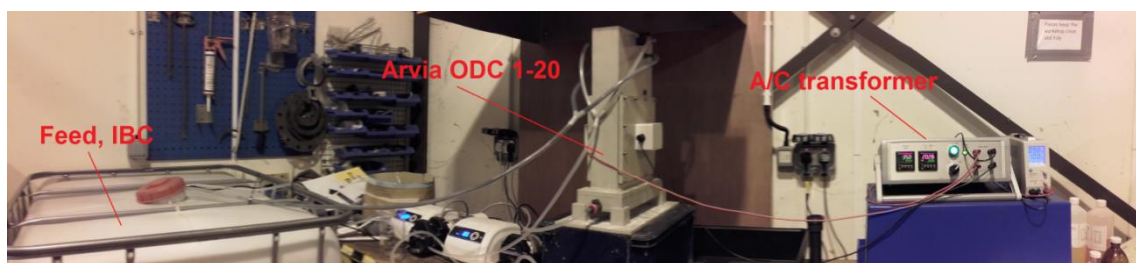


Figure 4.1 - Arvia ODC 1-20 set up

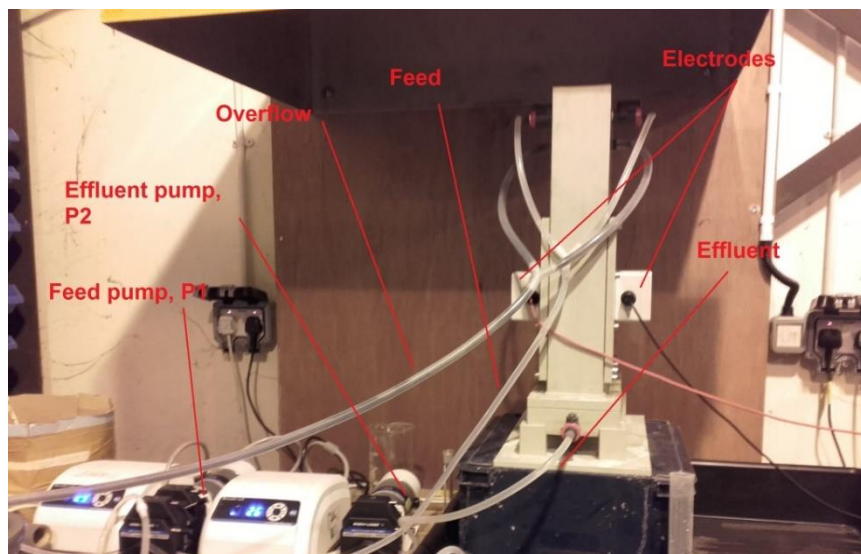


Figure 4.2 - Arvia ODC 1-20 close up

4.2.3 Spiking

A stock solution of carbamazepine from Qm_x Laboratories (Thaxted, UK) (99.5% purity) was prepared as follows: 0.01 ± 0.0001 g of powder was added to 100 mL of PLC Gradient Grade methanol and dissolved. Subsequently, this solution was mixed in a glass beaker containing methanol (MeOH) to make 1L of stock solution, with a nominal concentration of 10 mg/L. To reach the target concentration of 1 μ g/L for the influent, 100 mL of stock solution were dosed into the IBC containing 1000 L of water.

4.2.4 Operating conditions and sampling procedure

The ODC 1-20 was used to examine the removal of CBAZ under different conditions of effluent flow and current density. During the first three weeks, current density was maintained at a baseline of 4 mA/cm², while the flow was varied between 5, 2.5 and 10 L/h during the first, second and third week, respectively. Flow values were chosen to fit within the unit design parameters, in order to test the removal efficiency at different retention times. For the next two weeks, with a flow kept at 5 L/h, the current density was changed between a 2.5 mA/cm², i.e. the minimum current density to guarantee a treatment, and 5 mA/cm², i.e. the maximum current density applicable without damaging the electrodes. Arvia Technology advised the operation within this current density range, based on previous work at bench scale conducted in-house. The unit was fed at a flow 10% higher than the effluent flow, in order to keep the ODC 1-20 in constant overflow, according to guidelines provided by Arvia Technology. **Table 4.3** summarises the combination of conditions tested for each week of the trial.

Table 4.3 - Experimental conditions of current density and effluent flow for the trial

	Week 1	Week 2	Week 3	Week 4	Week 5
Current density (mA/cm²)	4.0	4.0	4.0	2.5	5.0
Effluent flow (L/h)	5.0	2.5	10	5.0	5.0

Each week, the ODC 1-20 was run continuously for a period of 96 h. Influent samples were collected from the bottom tap of the IBC at 0 and 96 h. Effluent was sampled at 0, 2, 6, 24, 28, 48, 72 and 96 h. All the samples were taken in duplicates, for a total of 20 samples per week. Once collected in a 250 mL clear bottle, the samples were stored in a fridge at 4°C before being sent for analysis at an external laboratory, ALS Environmental Ltd (Coventry, UK). The analytical method for carbamazepine is summarised in **Table 4.4**.

Table 4.4 – Carbamazepine analytical method

	Limit of detection (µg/L) ³	Reporting limit (µg/L)	Uncertainty of measurement (%) ⁴
<u>Carbamazepine</u> Solid phase extraction (SPE) from the aqueous matrix and elution from SPE cartridges with MeOH. Concentration of the extract using nitrogen, and quantification by high resolution, accurate mass (HRAM) liquid chromatography- mass spectrometry (LC-MS) with a gradient elution.	0.000048	0.001	31.7

During the trial, gaseous hydrogen production was estimated. The electrolytic cell produces gaseous hydrogen at the cathode, and according to (4.3), two moles of electrons are needed to form a mole of hydrogen:



4.2.5 Data handling and analysis

A total of 100 samples were collected during the ODC 1-20 experimental run, as described in **Section** Error! Reference source not found.. In addition, pH, temperature and voltage data for each sampling event were registered.

The influent's concentration of carbamazepine was assumed to be constant during each weekly run of the unit: under this hypothesis, only one value for influent concentration was used as an average of the four samples collected. Effluent concentrations of

³ Limit of detection is defined as 4.65× within batch standard deviation of blank matrix.

⁴ Uncertainty of measurement stated calculation is sum of Bias and 2× Relative Standard deviation of spiked standard in treated effluent sample.

carbamazepine (0, 2, 6 h etc.) were calculated as an average of the two duplicates taken at that time.

For each set of flow and current density conditions, the removal was estimated as a difference between the average influent and the average value of the effluent for each sampling event, returning a total of 8 values (0, 2, 6, 24, 28, 48, 72, 96 h).

4.3 Results

4.3.1 Hydrogen production

As previously mentioned, the total cathodic production of hydrogen at different current densities is shown in **Table 4.5**.

Table 4.5 - Total volume of H₂ produced at the cathode at different current densities

	2.5 mA/cm ²	4 mA/cm ²	5 mA/cm ²
Cell surface (cm ²)	400		
Current intensity (A)	1	1.6	2
Charge passed through Nyex (C/s)	1	1.6	2
Moles of electrons passed through Nyex (mol e ⁻ /s) ⁵	1.4*10 ⁻⁵	1.66*10 ⁻⁵	2.07*10 ⁻⁵
Total moles of H ₂ produced in a cell (mol H ₂ /s)	5.18*10 ⁻⁶	8.29*10 ⁻⁶	1.04*10 ⁻⁵
Total volume of H ₂ produced (L/h) ⁶	0.42	0.67	0.84

4.3.2 Treatment of carbamazepine in tap water matrix

4.3.2.1 pH and temperature

Two measurements of pH and temperature (for both the sample and its duplicate) were taken at each sampling event during the trial, and then averaged. Their values are presented in **Table 4.6** for the whole five weeks of trial. pH did not display a wide range of variability, settling at values close to neutrality, whereas temperature ranged from 5 °C in week 2 to almost 14 °C in week 5.

Table 4.6 - pH and temperature values registered during the trial

Time (h)	Week 1		Week 2		Week 3		Week 4		Week 5	
	pH	Temp (°C)	pH	Temp (°C)	pH	Temp (°C)	pH	Temp (°C)	pH	Temp (°C)
0	8.5	7.0	7.3	5.0	6.9	7.5	7.3	6.1	7.6	6.8

⁵ Faraday constant, F=96,485 C/mol e⁻

⁶ Considering standard conditions, a mole of gas occupies 22.4 L

Time (h)	Week 1		Week 2		Week 3		Week 4		Week 5	
	pH	Temp (°C)	pH	Temp (°C)	pH	Temp (°C)	pH	Temp (°C)	pH	Temp (°C)
2	7.8	8.7	7.0	7.7	7.1	8.6	7.3	7.8	7.2	10.0
6	7.7	8.9	6.9	9.7	7.1	8.6	7.2	8.8	7.2	11.1
24	7.7	7.8	6.9	7.7	7.2	8.3	7.2	8.4	7.2	9.2
28	7.7	8.4	6.9	10.3	7.2	8.4	7.2	8.5	7.1	11.4
48	7.8	6.3	6.9	7.8	7.3	9.7	7.3	8.5	7.1	12.0
72	7.5	7.2	6.8	6.2	7.3	11.3	7.3	7.6	7.1	12.6
96	7.4	6.1	7.0	6.2	7.3	11.4	7.3	7.3	7.1	13.5

4.3.2.2 Effluent flow and current density

During the first three weeks, the current density was maintained at a baseline 4 mA/cm² while changing the flow through the unit. Altering the effluent flow determines a variation in the retention time at which the unit operates. **Table 4.7** shows the retention time for each flow condition investigated in the trials: hydraulic retention time (HRT) is the ratio between active volume of the cell and effluent flow, whereas empty bed contact time (EBCT) takes into account the bed porosity and indicates the time needed for water to percolate through the media bed (see **Table 4.2** for Nyex porosity).

Table 4.7 - Treatment time for varying flow conditions

	Week 1	Week 2	Week 3
Current intensity (A)	1.60	1.60	1.60
Flow (L/h)	5	2.5	10
HRT (min)	24	48	12
EBCT (min)	27	54	13

The effluent concentrations for carbamazepine at each different flow condition are presented in **Figure 4.3**, **Figure 4.4** and **Figure 4.5**, which represent the combination of conditions for weeks one, two and three, respectively. Error bars represent the standard deviation of the data. In the three plots CBAZ concentration showed a rapid decrease from initial values during the first 2 to 6 h and reached quite high removal percentages (75-90%).

Subsequently, CBAZ concentrations in the effluent increased, levelling off at 0.4 µg/L by the end of the test. It is speculated that this behaviour could be due to the two processes associated with the ODC. The swift decrease in concentration may coincide with an initial phase where adsorption is the dominant removal mechanism. After that, once the media bed is saturated, electrochemical oxidation is the more active removal mechanism and concentration slightly increases as a result of the combination of adsorption and oxidation (K. Nkrumah-Amoako 2017, personal communication, 18st April).

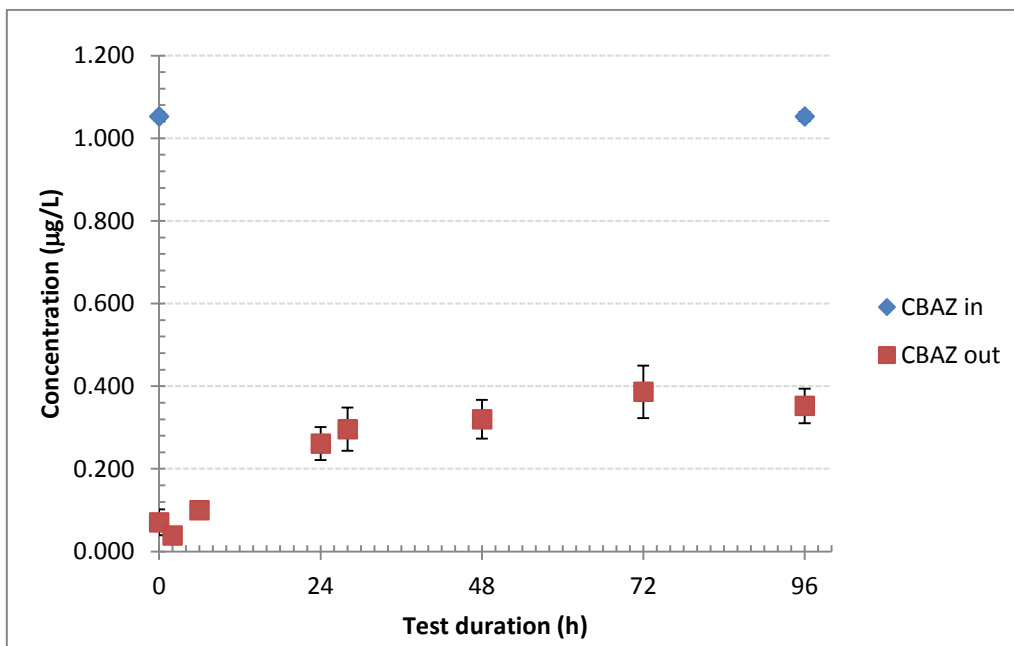


Figure 4.3 - Effluent concentrations of carbamazepine for week 1 (5 L/h, 4 mA/cm²)

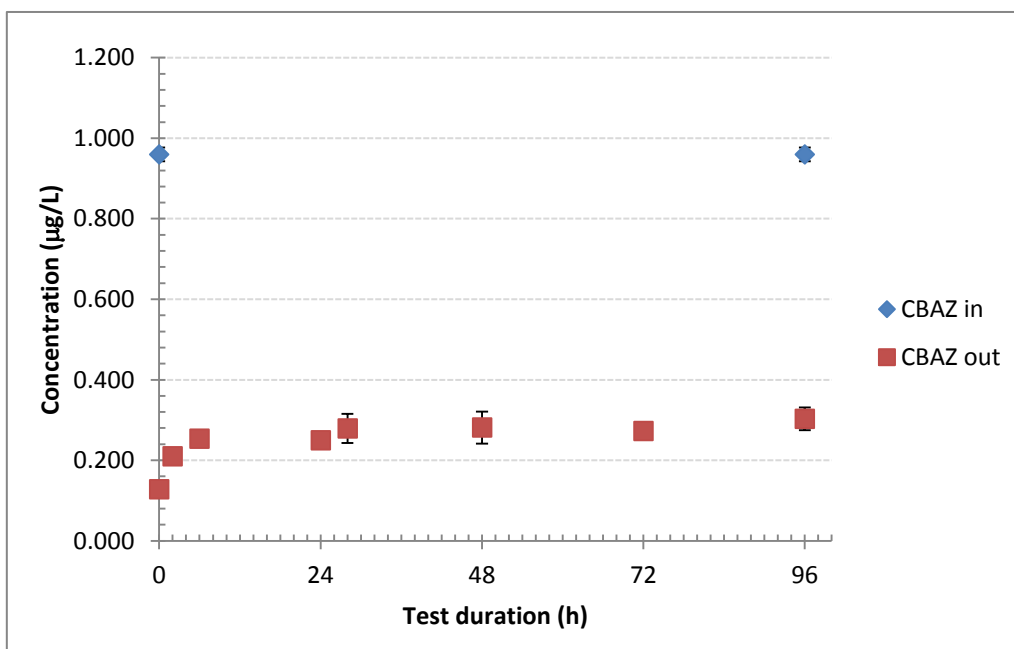


Figure 4.4 - Effluent concentration of carbamazepine for week 2 (2.5 L/h, 4 mA/cm²)

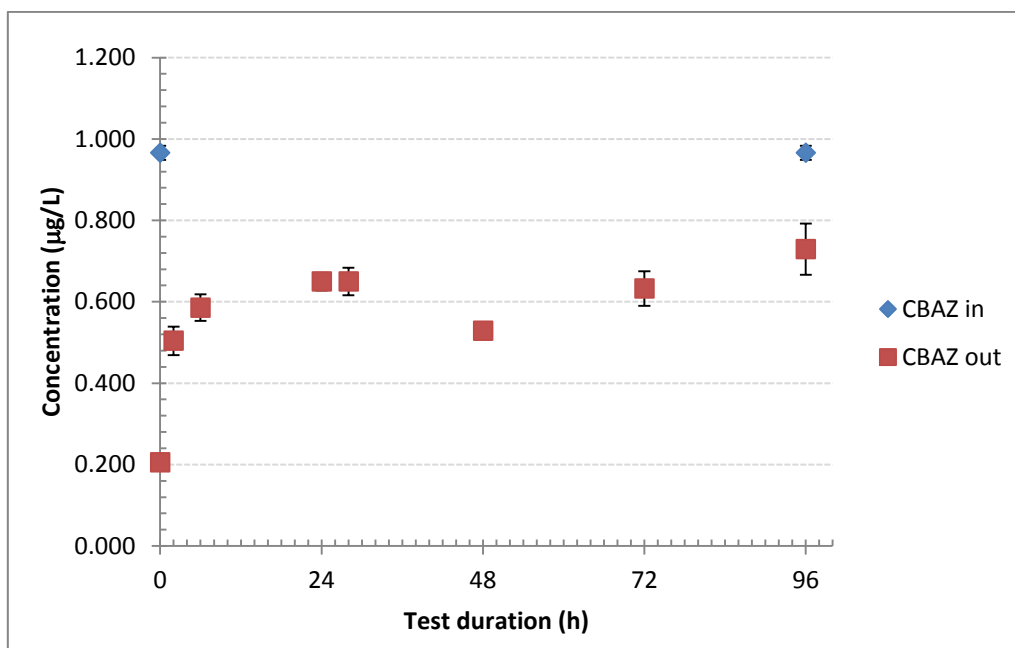


Figure 4.5 - Effluent concentration of carbamazepine for week 3 (10 L/h, 4 mA/cm²)

During the fourth and fifth week, a flow of 5 L/h was kept while the current density was changed between a lower value of 2.5 mA/cm² (week 4) and a higher one of 5 mA/cm² (week 5). Results from week 1 at 4 mA/cm² were used as baseline. Considering an electrode area of 400 cm², the current intensity passed through the media was 1.6 for week 1, 1.0 A for week 4 and 2.0 A for week 5.

Effluent concentrations for weeks 4 and 5 are plotted in **Figure 4.6** and **Figure 4.7**, whereas **Figure 4.3** represents the baseline conditions. Error bars correspond to the standard deviation of each time point. During week 4, at the lower current density, carbamazepine was removed up to ~75% in the first 24 h, but the concentration increased again, reaching a plateau. As for the higher current, the removal did not change significantly for the whole 96 h and reached values ~53%.

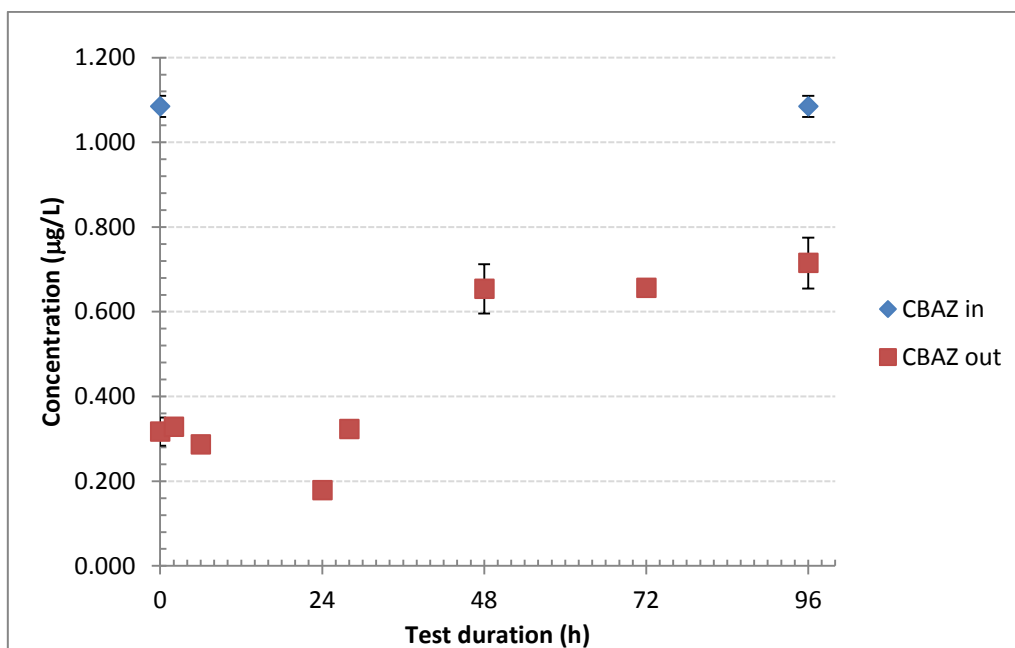


Figure 4.6 - Effluent concentration of carbamazepine for week 4 (5 L/h, 2.5 mA/cm²)

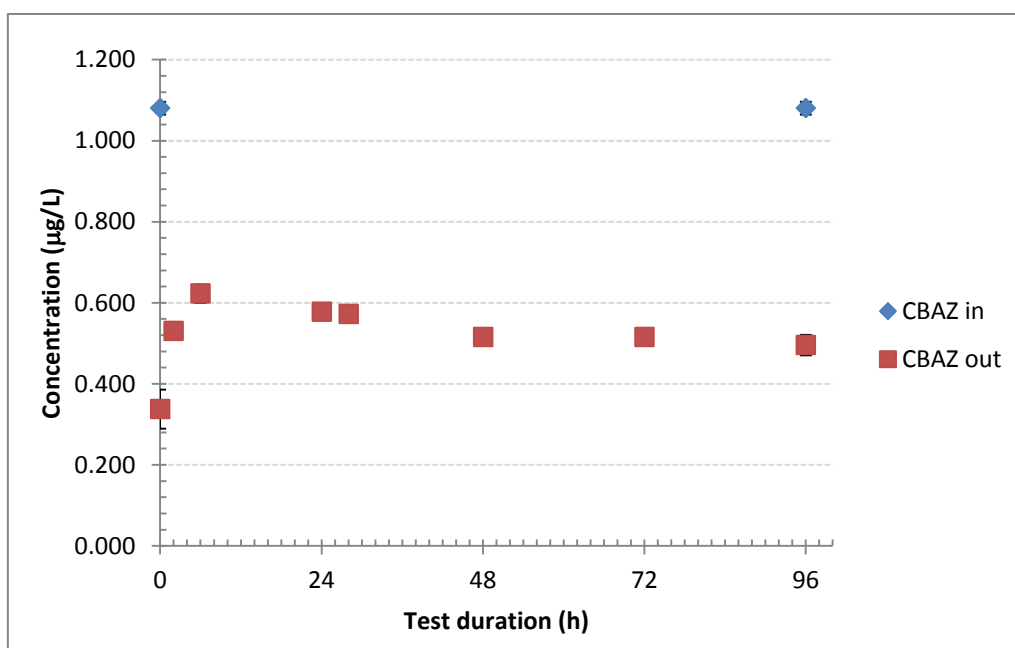


Figure 4.7 - Effluent concentration of carbamazepine for week 5 (5 L/h, 5 mA/cm²)

Figure 4.8 shows the applied cell potentials. The first three weeks displayed similar values, as the current density was maintained constant throughout. Moreover, when the applied current density was increased in week five, the voltages also increased to values up to ~17 V. Although these recordings are consistent as expected (they increase or decrease with the applied current density), they are higher than those initially estimated for those current densities: the manufacturer advised that the standard voltage at 5 mA/cm² should be

around ~7/8 V (see **Section 4.3.3**) (K. Nkrumah-Amoako 2017, personal communication, 17th February).

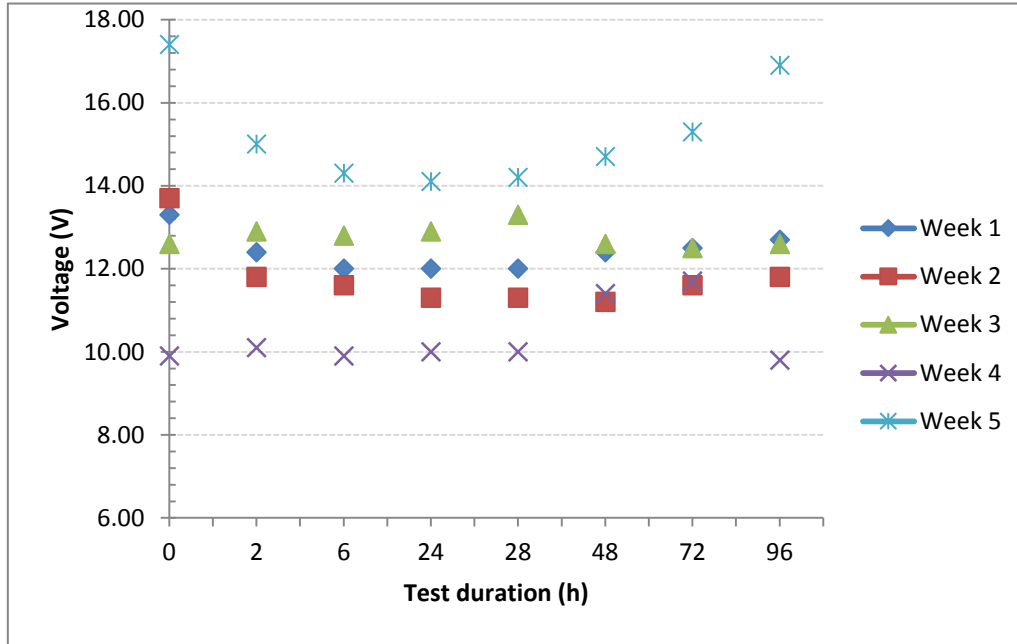


Figure 4.8 - Applied cell potential for each week of trial

4.3.3 Specific energy consumption

Since the main use of energy within the process is due to electrochemical regeneration, the main requirement for the process is based on regeneration energy expressed in kWh/m³ [17]. The specific energy consumption (EC, kWh/m³) in an electrolytic cell was calculated with the following equation (4.4) [18]:

$$EC = \frac{UI\Delta t}{V} \quad (4.4)$$

where U is the average cell voltage throughout the trial (V), Δt (h) is the test duration, I is the applied current (A) and V is the volume of electrolyte treated during the trial (m³).

Based on (4.4), when the current intensity is maintained constant, the energy consumption is a function of voltage and effluent flow, whereas it is a function of voltage and current density at constant flow. Considering this relation and the fact that the average applied cell voltage reached higher values than expected, the energy consumption mostly increased on account of voltage, no matter which conditions of current density and flow the unit was run at.

In fact, the applied voltage values registered during the trial were almost double than those expected if the unit was run without any interference. **Table 4.8** shows the actual and estimated (K. Nkrumah-Amoako 2017, personal communication, 3rd May) amount of energy consumed each week to treat a particular volume of water during the 96h trial.

Table 4.8 - Average energy consumption per volume of treated effluent, actual and estimated values

	Week 1	Week 2	Week 3	Week 4	Week 5
Current intensity (A)	1.6	1.6	1.6	1.0	2.0
Average voltage (V)	12.3	11.6	12.7	10.2	15.3
Total treated flow (m³)	0.48	0.24	0.96	0.48	0.48
Average carbamazepine removal (%)	78	74	42	60	52
Average energy consumption (kWh/ m³)	3.9	7.4	2.0	2.0	6.1
Estimated voltage (V)	6.5	6.5	6.5	6.0	7.0
Estimated average energy consumption (kWh/ m³)	2.1	4.2	1.0	1.2	2.8

In fact, the applied voltage values registered during the trial were almost double than those expected if the unit was run without any interference. **Table 4.8** also shows the forecasted values for energy consumption with the expected voltages (K. Nkrumah-Amoako 2017, personal communication, 3rd May).

4.4 Discussion

4.4.1 Removal as function of pH and temperature

Along with operating conditions such as effluent flow (treatment time) and current density, literature suggests other factors affecting the performance of a 3D electrode are related to the matrix, namely pH [11], [19] and temperature [20].

Figure 4.9 displays removals achieved as a function of the pH conditions during the experimental trial.

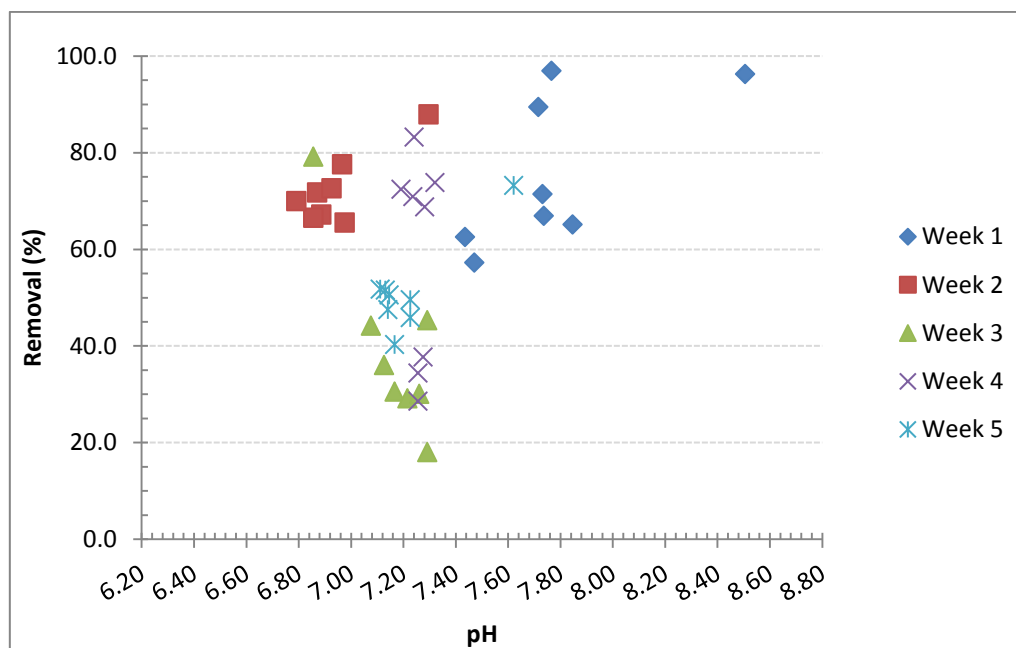


Figure 4.9 - Removal as function of pH for each trial week

Zhang et al. [11] reported that during anodic oxidation the removal efficiency of organics increases with an increase in pH, possibly owing to an enhancement in side reactions of oxygen evolution. With regards to adsorption, adsorbate will be mainly in protonated form at $\text{pH} < \text{pK}_{\text{a}}$, while in deprotonated form at $\text{pH} > \text{pK}_{\text{a}}$.

Oleszczuck et al. [21] suggested that at 5-7 pH carbamazepine is in protonated form, thus electrostatic interactions occur between CBAZ and a graphite based surface (multi-walled nanotubes), and adsorption is enhanced at these pH. Nevertheless, carbamazepine has two different dissociation constants ($\text{pK}_{\text{a}1} < 2.3$ and $\text{pK}_{\text{a}2} \geq 13.9$) and therefore is entirely present in neutral form at the pH range of 1.9-11.9. This suggests that its removal behaviour within this pH range is not correlated to effluent pH [22]. **Figure 4.9** clearly shows the lack of correlation between pH and CBAZ removal efficiency at the range of pH investigated in this study.

As for temperature, kinetic evidence suggests that diffusion and oxidation rates would be increased at higher temperatures and that adsorption should also quicken. A rise in temperature can produce an acceleration in the molecular motion and enhance the current density at an arbitrary voltage, which could be beneficial for the organics decomposition [20]. However, since the trial was conducted for five consecutive weeks, the explored range of temperature was not wide enough to cause any significant change in treatment performance, as no correlation is shown between temperature and removal values (Error! Reference source not found.).

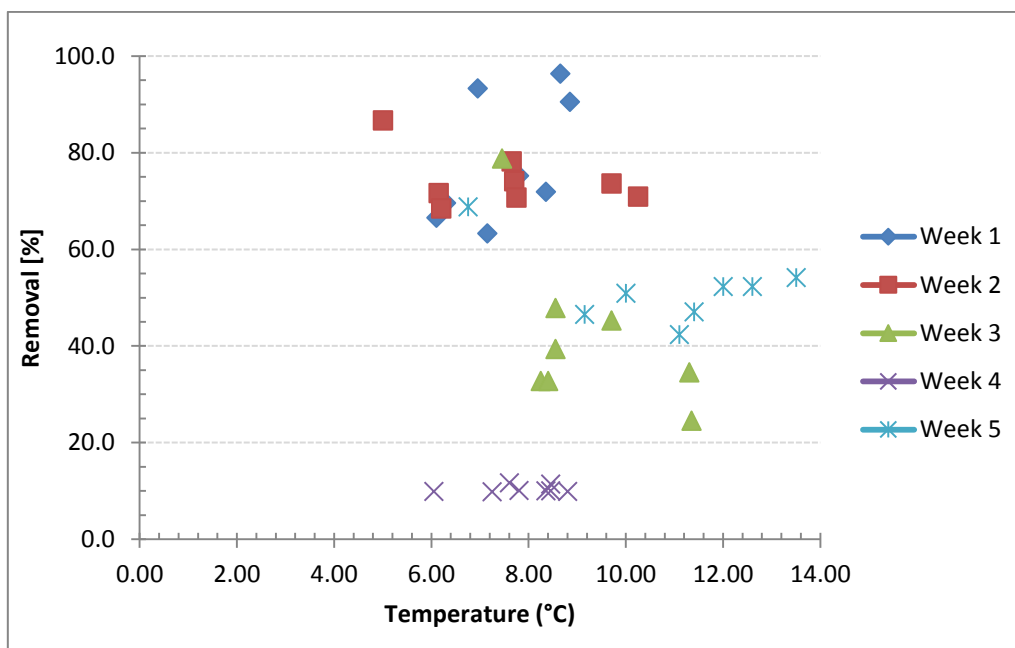


Figure 4.10 - Removal as function of temperature for each trial week

4.4.2 Removal as function of effluent flow

Effluent flow is inversely proportional to retention time, which according to literature [9], [23], is one of the most influent parameters for electrochemical oxidation of carbamazepine. The main advantage of decreasing the flow rate is the enhanced treatment capacity: the water's carbon content decreases with an increase in HRT, owing to the organic mineralisation occurring within the cell [18].

Figure 4.11 provides a comparison between the achieved removal rates at different effluent flows.

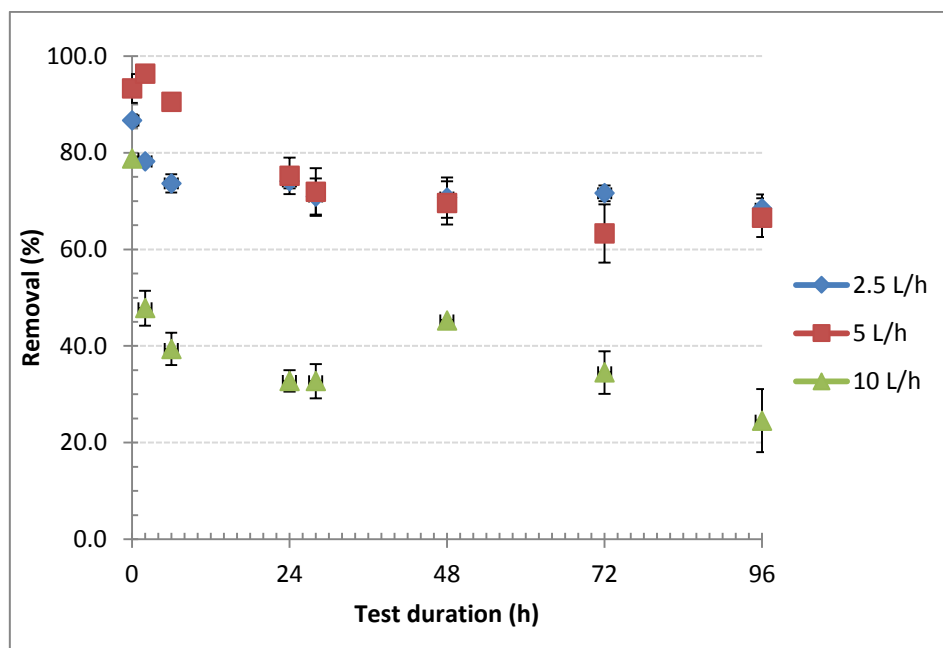


Figure 4.11 - Comparison of CBAZ removals at different flow conditions

At a flow rate of 10 L/h, the removal efficiency appears rather poor. In fact, running at higher flow rates might compromise treatment for those compounds which do not adsorb readily into Nyex, so that the system is limited by the achieved adsorption [17]. Carbamazepine, which is soluble in water and has a low octanol-water coefficient, might not have enough time to be fully adsorbed on the media, thus bypassing the stage of accumulation on Nyex. Hence, the only fraction treated would be that remaining in the bulk of water.

After 96 h CBAZ presented a slightly higher removal at a flow rate of 2.5 L/h than at 5 L/h, but their average values were still comparable, despite the higher retention time guaranteed when running the unit at 2.5 L/h. This occurrence might indicate the existence of a critical retention time after which any additional time CBAZ is retained in the unit does not contribute to improve the removal efficiency. As the treatment performance is similar after 24 minutes (5 L/h) and 48 minutes (2.5 L/h), running the ODC at 5 L/h would allow to treat a bigger volume of water while achieving a comparable removal efficiency.

4.4.3 Removal as function of current densities

Current density has been proven to be the most important parameter regulating the performance of a 3D electrode [23]. It influences the electrochemical oxidation as well as the polarisation of particle electrodes (medium's granules), which can behave as microelectrodes and enhance oxidation of organic at appropriate current densities [11].

Figure 4.12 shows the evolution of CBAZ removal as a function of applied current densities. At 4 mA/cm², which in the ODC 1-20 corresponds to a current intensity of ~1.6 A, the removal is higher than that achieved at current density 2.5 mA/cm² (~1.0 A). Higher applied currents lead to an increase in the hydroxyl radicals generation from water oxidation in the 3D electrode, which are able to react continuously with refractory contaminants and enhance treatment [23], [24].

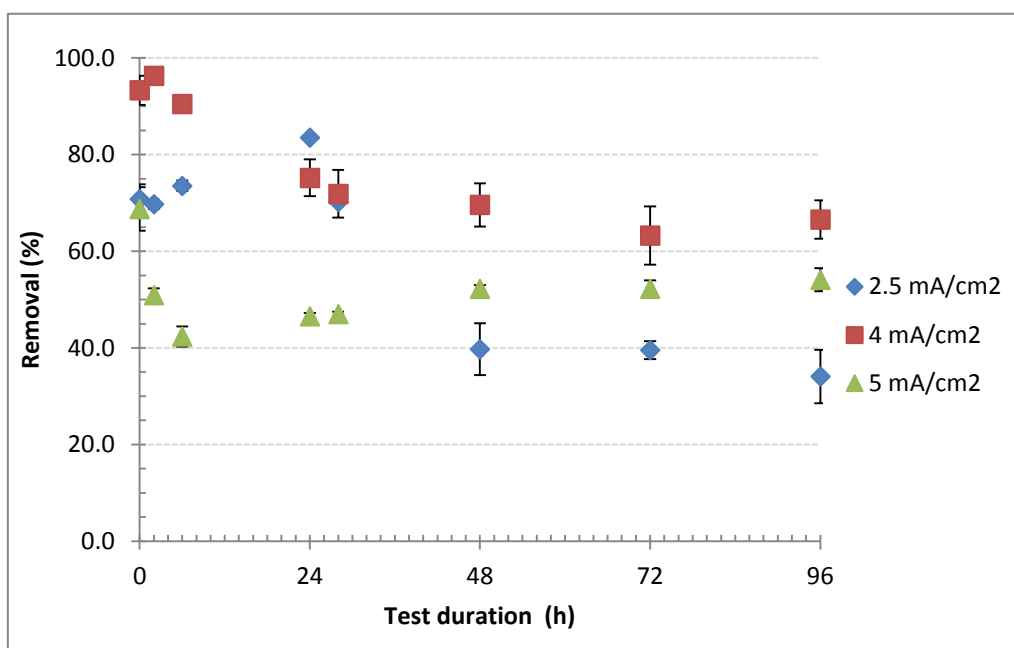


Figure 4.12 - Comparison of carbamazepine removal for different current densities

This explanation is not applicable to a higher current density of 5 mA/cm². During week 5, an increase in cell potential was experienced in the ODC 1-20 (see **Figure 4.8**). An additional resistance to electrons' movement in the electrolyte, such as membrane's fouling or formation of gas bubbles is likely to be responsible for this abnormal voltage increase and for the diminished removal of CBAZ.

High current densities (and consequently increased cell potentials) can increase the energy consumption, due to heat generation and to the occurrence of side reactions of oxygen and hydrogen evolution [19], [25], and they can also reduce the anode's lifetime due to corrosion. Studies conducted on COD removal with 3D electrodes suggest an increase in organics removal when a higher cell voltage is applied [19]. However, a continuous increase in the parameter did not lead to a considerable enhancement of removal efficiency [11]. This removal was not proportional to the voltage increase and operating at high voltages led to a drop in current efficiency, possibly due to side reactions [19].

4.5 Conclusions

A laboratory scale unit of the Arvia Organics Destruction Cell (ODC) was tested in a five week-long trial. The objective was to evaluate its removal performance against operational and matrix related parameters for the treatment of carbamazepine, a very recalcitrant pollutant commonly found in the final effluent of conventional WwTWs.

Current density and effluent flow are the main operating parameters appraised. When the applied current density is increased, more $\bullet\text{OH}$ radicals are formed and react with organic contaminants to enhance their oxidation. However, when the unit was operated at the highest current density (5 mA/cm^2), removals did not increase when compared to the other conditions evaluated. Resistance to the electrons and hydroxyl radical movement through the membrane and the formation of gas bubbles at the bottom of the cell determined an increase in voltage and a drop in current efficiency. This upsurge in applied voltage also determined higher than expected values of energy consumption throughout the trial.

When effluent flow was increased (and conversely treatment time was shortened) the organics degradation was negatively affected and adsorption seemed to assume a critical role in the process: if the organic pollutants are not retained in the unit for a period of time enough to guarantee their adsorption on the media, they are likely washed out with the effluent, thus hindering the removal performance. Overall, baseline conditions for both current density and effluent flow (4 mA/cm^2 and 5 L/h) were the most conducive to the elimination of CBAZ ($\sim 78\%$ on average).

Operational parameters strongly influenced CBAZ degradation and could generally be optimised with success to improve the level of treatment, whereas parameters related to the water matrix showed no correlation with the overall ODC performance. In regards to maintenance issues, the possible membrane fouling and the formation of gas bubbles occurring in the unit's plenum chamber would need to be addressed in further stages of development of the ODC 1-20, as they can have a negative effect on the unit's performance and cause an increase in energy consumption.

4.6 References

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5 CONCLUSIONS

5.1 Overall discussion

The performance of the Arvia Organic Destruction Cell (ODC), a technology combining adsorption and electrochemical oxidation for the removal of organic micropollutants was investigated both at pilot scale and at bench scale.

The pilot scale study was carried on in a water recycling centre in Cambridgeshire with ODC 4-50:

- After 15 sampling events over a six months period, pharmaceuticals appeared to be generally treated more efficiently than other classes of substances, with removal over 50% for the majority of them. Steroids and priority substances/special pollutants showed a less consistent behaviour, with removal ranging from 14% to 80% for steroids and between 4-70% for priority substances. In the case of sanitary determinands, the removal values were often negative (signifying an accumulation in the final effluent), as influent and effluent concentrations in the ODC were always quite close in value, with an overlap in standard deviations for many of the considered samples. Most metals also showed were accumulated due to unforeseen occurrences which took place during the trial, such as concentration spikes in the works and electroplating.
- The study shows that some classes of substances sharing similar physicochemical properties display comparable removals. In the case of statins and macrolide antibiotics, degradation appeared to be driven mainly by parameters such as molecular weight, as molecules with high molecular weight seemed to be better adsorbed on the media (60-70% for macrolides, 70-80% for statins). Chlorinated substances had similar removal rates, in the range of 60-69%. Although many of the investigated physicochemical properties are generally connected with adsorption performance, an appraisal of this mechanism's contribution to the overall removal of a particular substance appears quite challenging: in fact, adsorption and electrochemical oxidation are deeply interlaced within the Arvia ODC's dynamic process, thus not allowing for a clear separation of the two processes.
- A total number of ten determinands (nickel, copper, zinc, PFOS, PFOA, diclofenac, ibuprofen, clarithromycin, benzotriazole and tolytriazole) will need to be prioritised for further consideration, as their discharge concentration exceeds the mandated EQS for discharge in surface waters. Considering that relying on dilution in the

receiving water body is not always a feasible option, measures to reduce their concentration will have to be put in place.

- A best estimate for a full scale version of the Arvia ODC was appraised with a multi-criteria analysis in terms of micropollutants removal performance, cost effectiveness, environmental friendliness and other technological aspects and proved to represent a viable alternative to conventional treatment (AOPs, membrane technologies, GAC).
- While quite promising in terms of micropollutants removal, the Arvia ODC is still in the early development stages, as it has no full-scale installations yet. The unit's design needs to include more effective pre-treatment stages and its resilience needs to be improved to cope with unexpected operational occurrences such as high TSS feed loads, feed buffering and instrumentation malfunctioning. Moreover, further investigation on the Arvia ODC carbon and environmental (i.e. production of by-products) footprint will have to be continued.

In addition to the pilot variant of the Arvia ODC, a laboratory scale unit (ODC 1-20), was tested for the removal of carbamazepine in more controlled feed conditions.

- The unit's performance was not particularly impacted by changes in the physical properties of the water feed namely pH and temperature. However, this might change when considering compounds other than carbamazepine and when extending the trial's time frame to include seasonality.
- The main optimisable parameters for the Arvia ODC are effluent flow and current density. The study explored the impact of their variation on the unit's overall performance. While an increase in current density and a decrease in flow (higher retention time) generally determine the best performance when considered separately, the best overall removal for carbamazepine (~78%) was reached at intermediate values for the ranges of flow and current density explored (5 L/h, 4 mA/cm²).
- The removal of CBAZ in the bench unit is higher than the average one obtained in the pilot plant (~42%, **Section 3.3.5**), which operates with the same current density (but current intensity of 10 A) and higher retention time (~30min). This could be due to the hindering action of a real wastewater matrix and the simultaneous presence of other micropollutants, with whom carbamazepine could interact.
- The energetic performance of the unit was hindered by the abnormally elevated values of applied cell voltage. In order to guarantee a more efficient use of energy

and current, the unit's design should be modified to resolve the formation of gas bubbles in the plenum chamber, which obstruct the movement of the electrons.

- While the performance in terms of carbamazepine removal in the bench unit appears to be quite promising in controlled conditions, this evaluation does not take into account the formation of by-products or CBAZ metabolites, which should therefore be closely monitored in any further assessment of the ODC

5.2 Further considerations and future work

As the second phase of the Chemicals Investigation Programme reached an end in March 2017, gathering data on source, removal and occurrence of micropollutants in the final effluent and assessing the performance of both full and pilot scale technologies for their removal, the water industry and regulators will be called to act on CIP's recommendations for chemical compliance in the future. In particular, it is assumed that the work conducted under the CIP umbrella will represent the starting point for the Environment Agency to set new consent limits for some of the priority substances and to define which WwTWs could potentially be subjected to them.

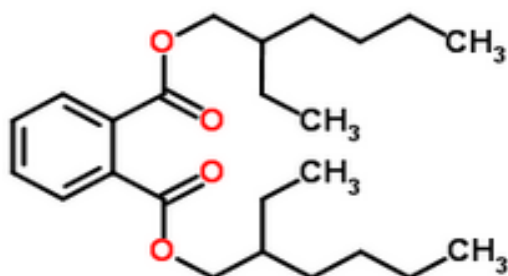
The Arvia ODC trial has highlighted a few issues worth considering when planning additional work on emerging contaminants for the rest of AMP6 and for AMP7:

- While removal represents a functional parameter to quantify the effectiveness of a technology, current legislation aims to achieve good final effluent quality in terms of concentrations. Further work should gravitate towards those technologies and schemes that guarantee results in relation to lowering the concentrations below the set EQS, as dilution of the FE before the receiving water body does not always constitute a feasible option.
- Although the Arvia ODC has been proved to perform satisfactorily for a wide range of micropollutants belonging to different classes, it is not applicable with the same degree of success for the removal of all the determinands included in the CIP list. Their variability in physicochemical properties and concentration makes sure that single contaminants/class of substances will need to be addressed individually and specific planning will need to be put in place for each one of them.
- Hence, it is paramount that, in light of the Environment Agency's decision on consents and sites, an options appraisal on each technology is conducted, to highlight whether a particular technology could be effective in specific conditions. These could include site configuration, costs, effectiveness towards the targeted pollutants, range of residual removal to be achieved to reach the EQS etc.

- Micropollutants can be more easily removed at source than in the final effluent, when the wastewater has not been diluted with wastewater of different origin. For this reason, together with an end of pipe strategy, a wider, catchment-based strategy will need to be implemented at source in order to reduce the load of micropollutants released into the sewers and reaching the water treatment works.

Appendix A CIP2 suite structure and physicochemical properties¹

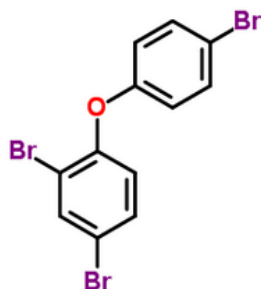
Diethylexyl-phthalate (DEHP)



CAS number:	11-87-7
Molecular formula:	C ₂₄ H ₃₈ O ₄
Molecular weight	390.56
Water solubility (mg/L):	2.70 × 10 ⁻¹
Henry's law constant (atm m ³ /mol)	2.70 × 10 ⁻⁷
Log K _{ow}	7.60
Log K _{oc}	5.00
pK _a :	-

Plasticiser. Poorly water soluble, non volatile. High potential for accumulation. Mainly from anthropogenic source.

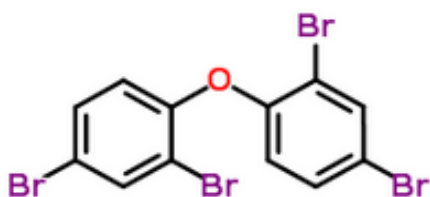
BDE 28



CAS number:	41318-75-6
Molecular formula:	C ₁₂ H ₇ Br ₃ O
Molecular weight	406.89
Water solubility (mg/L):	2.64 × 10 ⁻²
Henry's law constant (atm m ³ /mol)	2.03 × 10 ⁻⁵
Log K _{ow}	5.88
Log K _{oc}	4.23
pK _a :	-
pK _a :	-

Polybrominated diphenyl ether. Persistent, bioaccumulative.

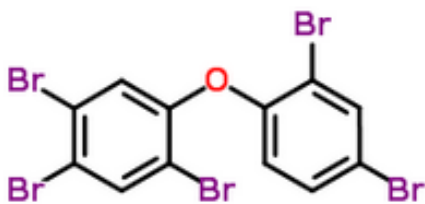
BDE 47



CAS number:	5436-43-1
Molecular formula:	C ₁₂ H ₆ Br ₄ O
Molecular weight	485.69
Water solubility (mg/L):	1.46 × 10 ⁻³
Henry's law constant (atm m ³ /mol)	8.48 × 10 ⁻⁶
Log K _{ow}	6.77
Log K _{oc}	4.73
pK _a :	-
pK _a :	-

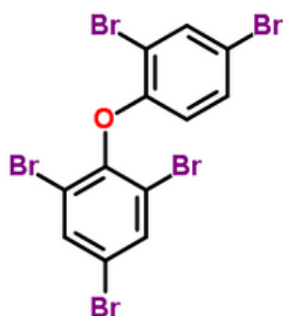
Polybrominated diphenyl ether. Persistent, bioaccumulative.

¹ Sources: www.chemspider.com; www.drugbank.ca; www.pubchem.ncbi.nlm.nih.gov; EPIWEB v4.11 (USEPA).

BDE 99

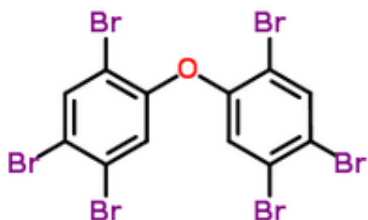
CAS number:	60348-60-9
Molecular formula:	C ₁₂ H ₅ Br ₅ O
Molecular weight	564.59
Water solubility (mg/L):	1.33 × 10 ⁻²
Henry's law constant (atm m ³ /mol)	9.00 × 10 ⁻⁷
Log K _{OW}	6.84
Log K _{OC}	4.76
pK _a :	-

Polybrominated diphenyl ether. Persistent, bioaccumulative.

BDE 100

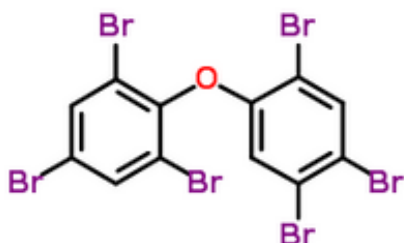
CAS number:	189084-64-8
Molecular formula:	C ₁₂ H ₅ Br ₅ O
Molecular weight	564.59
Water solubility (mg/L):	-
Henry's law constant (atm m ³ /mol)	-
Log K _{OW}	8.03
Log K _{OC}	5.23
pK _a :	-

Polybrominated diphenyl ether. Persistent, bioaccumulative.

BDE 153

CAS number:	68631-49-2
Molecular formula:	C ₁₂ H ₄ Br ₆ O
Molecular weight	643.58
Water solubility (mg/L):	-
Henry's law constant (atm m ³ /mol)	-
Log K _{OW}	7.62
Log K _{OC}	5.60
pK _a :	-

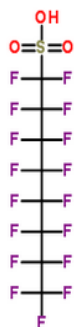
Polybrominated diphenyl ether. Persistent, bioaccumulative.

BDE 154

CAS number:	207122-15-4
Molecular formula:	C ₁₂ H ₄ Br ₆ O
Molecular weight	643.58
Water solubility (mg/L):	-
Henry's law constant (atm m ³ /mol)	-
Log K _{OW}	8.83
Log K _{OC}	5.59
pK _a :	-

Polybrominated diphenyl ether. Persistent, bioaccumulative.

Perfluorooctane sulfonic acid (PFOS)



CAS number:	1763-23-1
Molecular formula:	$C_8H_{17}SO_3$
Molecular weight	500.13
Water solubility (mg/L):	1.04×10^{-1}
Henry's law constant (atm m ³ /mol)	1.10×10^{-2}
Log K _{ow}	4.49
Log K _{oc}	3.41
pK _a :	0.14

Perfluorinated carboxylic acid. Head polar, tail strongly hydrophobic. Very persistent in the environment, very stable due to C-F bonds.

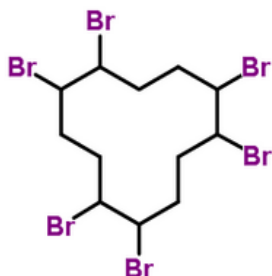
Perfluorooctanoic acid (PFOA)



CAS number:	335-67-1
Molecular formula:	$C_8H_{15}O_2$
Molecular weight	414.07
Water solubility (mg/L):	4.81×10^{-1}
Henry's law constant (atm m ³ /mol)	9.00×10^{-2}
Log K _{ow}	4.81
Log K _{oc}	2.82
pK _a :	2.80

Perfluorinated carboxylic acid. Head polar, tail strongly hydrophobic. Very persistent in the environment, very stable due to C-F bonds.

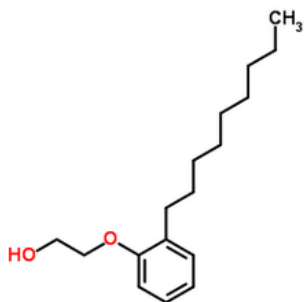
Hexabromocyclododecane (HBCDD)



CAS number:	3 different isomers
Molecular formula:	$C_{12}H_6Br_6$
Molecular weight	641.70
Water solubility (mg/L):	2.09×10^{-5}
Henry's law constant (atm m ³ /mol)	6.43×10^{-11}
Log K _{ow}	7.74
Log K _{oc}	6.72
pK _a :	-

Cyclo-alkane. Flame retardant. Persistent, bioaccumulative.

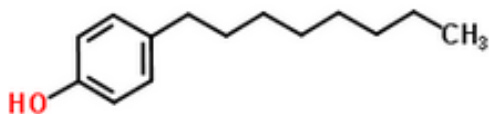
Nonylphenol monoethoxylate (NOP1)



CAS number:	3 different isomers
Molecular formula:	$C_{12}H_{26}O_2$
Molecular weight	641.70
Water solubility (mg/L):	2.09×10^{-5}
Henry's law constant (atm m ³ /mol)	6.43×10^{-11}
Log K _{ow}	5.58
Log K _{oc}	3.45
pK _a :	-

Cyclo-alkane. Flame retardant. Persistent, bioaccumulative.

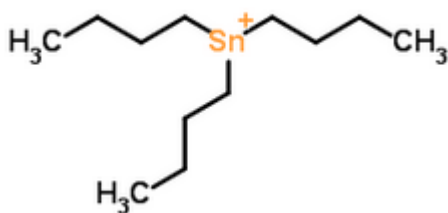
Octylphenols ((4-(1,1',3,3'-tetramethylbutyl)-phenol) (OCT)



CAS number:	1086-26-4***à
Molecular formula:	
Molecular weight	
Water solubility (mg/L):	
Henry's law constant (atm m ³ /mol)	
Log K _{ow}	
Log K _{oc}	
pK _a :	

Quite stable in water. Can be produced from the breakdown of alkylphenol ethoxylates.

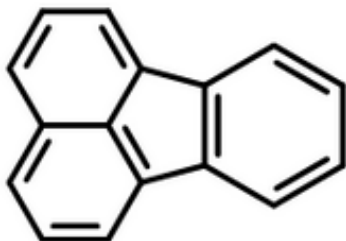
Tributyltin compounds (TBT)



CAS number:	36643-28-4
Molecular formula:	C ₁₂ H ₇ Sn
Molecular weight	291.07
Water solubility (mg/L):	4.36
Henry's law constant (atm m ³ /mol)	6.43
Log K _{ow}	4.10
Log K _{oc}	3.56
pK _a :	-

Adheres to sediments due to low specific gravity and low solubility. Component of antifouling paint.

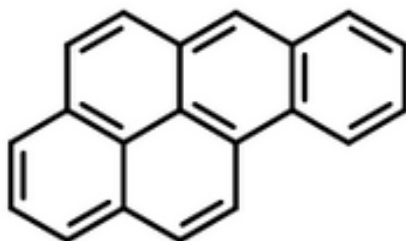
Fluoranthene (FLU)



CAS number:	260-44-0
Molecular formula:	C ₁₆ H ₁₀
Molecular weight	202.26
Water solubility (mg/L):	1.30 × 10 ⁻¹
Henry's law constant (atm m ³ /mol)	8.86 × 10 ⁻⁶
Log K _{ow}	5.16
Log K _{oc}	4.48
pK _a :	-

Polycyclic aromatic compound. High water solubility, difficult to remove from water.

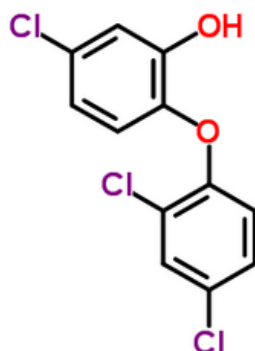
Benzo(a)pyrene (BAP)



CAS number:	50-32-8
Molecular formula:	C ₂₀ H ₁₂
Molecular weight	252.32
Water solubility (mg/L):	1.62 × 10 ⁻³
Henry's law constant (atm m ³ /mol)	4.57 × 10 ⁻⁷
Log K _{ow}	6.13
Log K _{oc}	5.32
pK _a :	-

Product of incomplete combustion. Highly carcinogenic, strongly adsorbs on organic matter.

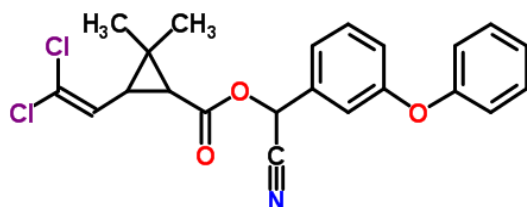
Triclosan (Tricl)



CAS number:	50-32-8
Molecular formula:	C ₁₂ H ₇ Cl ₃ O ₂
Molecular weight	289.55
Water solubility (mg/L):	4.62
Henry's law constant (atm m ³ /mol)	4.99 × 10 ⁻⁹
Log K _{ow}	4.76
Log K _{oc}	3.93
pK _a :	7.90

Antibacterial agent. Possible cause of antimicrobial resistance.

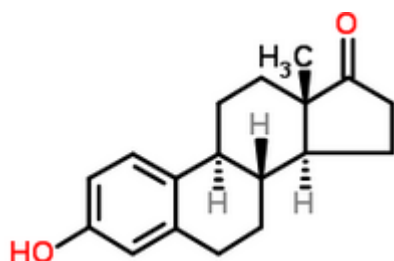
Cypermethrin (CYP)



CAS number:	52315-07-8***
Molecular formula:	C ₂₂ H ₁₉ Cl ₂ NO ₃
Molecular weight	416.30
Water solubility (mg/L):	1.15 × 10 ⁻¹
Henry's law constant (atm m ³ /mol)	7.89 × 10 ⁻⁷
Log K _{ow}	6.60
Log K _{oc}	5.15
pK _a :	8.30

Pesticide. Used to control ectoparasites.

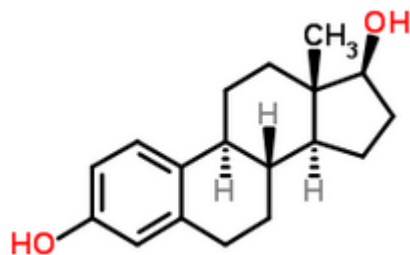
Oestrone (E1)



CAS number:	53-16-7
Molecular formula:	C ₁₈ H ₂₂ O ₂
Molecular weight	270.37
Water solubility (mg/L):	3.00 × 10 ⁻²
Henry's law constant (atm m ³ /mol)	3.80 × 10 ⁻¹⁰
Log K _{ow}	3.13
Log K _{oc}	3.02
pK _a :	10.33

Naturally occurring estrogen.

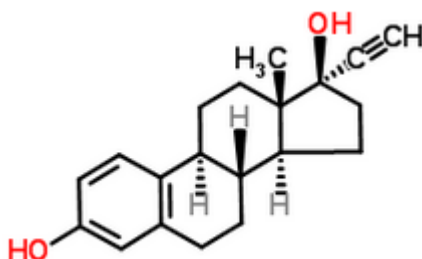
17β-oestradiol (E2)



CAS number:	50-28-2
Molecular formula:	C ₁₈ H ₂₄ O ₂
Molecular weight	272.39
Water solubility (mg/L):	3.60
Henry's law constant (atm m ³ /mol)	3.64 × 10 ⁻¹¹
Log K _{ow}	4.01
Log K _{oc}	2.90
pK _a :	10.33

Naturally occurring estrogen.

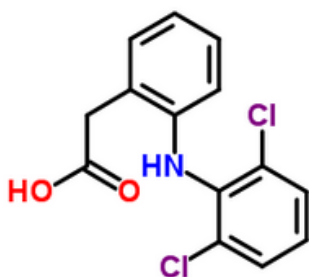
17 α -ethynylestradiol (EE2)



CAS number:	57-63-6
Molecular formula:	C ₁₈ H ₂₄ O ₂
Molecular weight	296.41
Water solubility (mg/L):	1.13 × 10 ⁻¹
Henry's law constant (atm m ³ /mol)	7.94 × 10 ⁻¹²
Log K _{ow}	3.67
Log K _{oc}	2.71
pK _a :	10.33

Semisintetic alkylated estradiol. Often used as the estrogenic component in oral contraceptives.

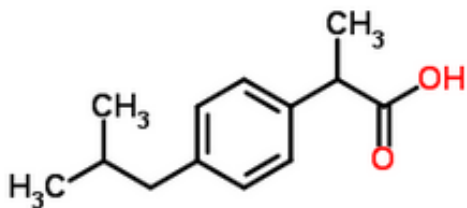
Diclofenac (DCF)



CAS number:	15307-86-5
Molecular formula:	C ₁₄ H ₁₁ Cl ₂ NO ₂
Molecular weight	296.15
Water solubility (mg/L):	2.37
Henry's law constant (atm m ³ /mol)	4.73 × 10 ⁻¹²
Log K _{ow}	4.51
Log K _{oc}	2.61
pK _a :	4.15

Anti-inflammatory agent with antipyretic and analgesic actions.

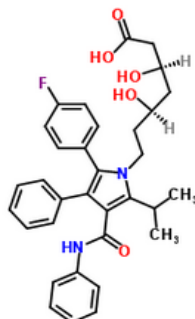
Ibuprofen (IBPF)



CAS number:	15687-27-1
Molecular formula:	C ₁₃ H ₁₈ O ₂
Molecular weight	206.29
Water solubility (mg/L):	2.10 × 10 ⁻¹
Henry's law constant (atm m ³ /mol)	1.52 × 10 ⁻⁷
Log K _{ow}	3.97
Log K _{oc}	2.35
pK _a :	4.91

Anti-inflammatory agent . Widespread diffusion. High mobility in aquatic environment.

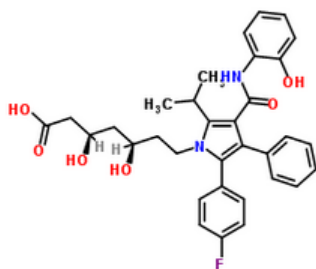
Atorvastatin (ATOV)



CAS number:	134523-00-5
Molecular formula:	C ₃₃ H ₃₅ FN ₂ O ₅
Molecular weight	558.66
Water solubility (mg/L):	1.12 × 10 ⁻³
Henry's law constant (atm m ³ /mol)	2.41 × 10 ⁻²³
Log K _{ow}	6.36
Log K _{oc}	2.60
pK _a :	4.33

Anti-cholesteremic agent, synthetic lipid lowering agent.

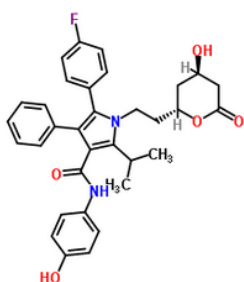
Ortho-hydroxy-atorvastatin (ATOVo)



CAS number:	214217-86-4
Molecular formula:	C ₃₃ H ₃₅ FN ₂ O ₅
Molecular weight	574.64
Water solubility (mg/L):	-
Henry's law constant (atm m ³ /mol)	-
Log K _{ow}	4.13
Log K _{oc}	2.31
pK _a :	-

Anti-cholesteremic agent, synthetic lipid lowering agent.

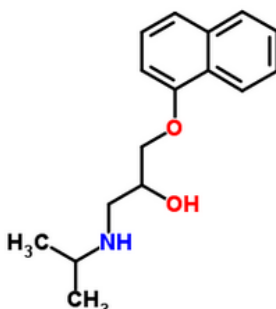
Para-hydroxy-atorvastatin (ATOVP)



CAS number:	163217-70-7
Molecular formula:	C ₃₃ H ₃₅ FN ₂ O ₅
Molecular weight	556.24
Water solubility (mg/L):	-
Henry's law constant (atm m ³ /mol)	-
Log K _{ow}	3.55
Log K _{oc}	3.54
pK _a :	-

Anti-cholesteremic agent, synthetic lipid lowering agent.

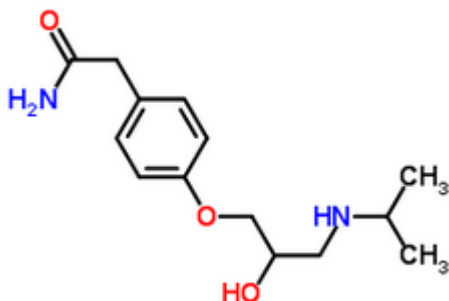
Propranolol (PRPL)



CAS number:	525-66-6
Molecular formula:	C ₁₆ H ₂₁ NO ₂
Molecular weight	259.35
Water solubility (mg/L):	6.17 × 10 ¹
Henry's law constant (atm m ³ /mol)	7.98 × 10 ⁻¹³
Log K _{ow}	3.48
Log K _{oc}	2.45
pK _a :	9.42

β-blocker, anti-hypertensive. High solubility in water.

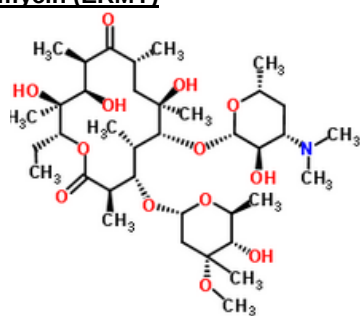
Atenolol (ATNL)



CAS number:	29122-68-7
Molecular formula:	C ₁₄ H ₂₂ N ₂ O ₃
Molecular weight	266.34
Water solubility (mg/L):	13.3 × 10 ⁴
Henry's law constant (atm m ³ /mol)	1.37 × 10 ⁻¹⁸
Log K _{ow}	0.16
Log K _{oc}	0.61
pK _a :	9.60

β-blocker, anti-hypertensive. Very high solubility in water.

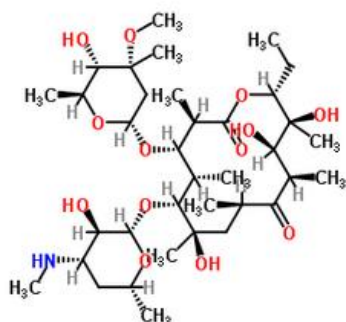
Erythromycin (ERMY)



Broad spectrum antibiotic with antibacterial activity.

CAS number:	114-07-8
Molecular formula:	C ₃₇ H ₆₇ NO ₁₃
Molecular weight	733.95
Water solubility (mg/L):	5.17 × 10 ⁻¹
Henry's law constant (atm m ³ / mol)	5.42 × 10 ⁻²⁹
Log K _{ow}	3.06
Log K _{oc}	2.75
pK _a :	8.88

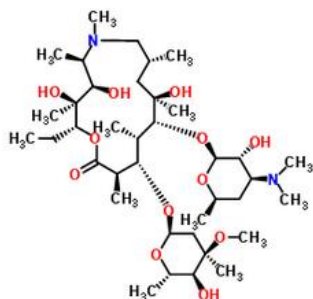
Norerythromycin (ERMYn)



Broad spectrum antibiotic with antibacterial activity. Metabolite of erythromycin.

CAS number:	992-62-1
Molecular formula:	C ₃₆ H ₆₅ NO ₁₃
Molecular weight	719.92
Water solubility (mg/L):	3.40
Henry's law constant (atm m ³ / mol)	2.47 × 10 ⁻²⁹
Log K _{ow}	2.21
Log K _{oc}	2.77
pK _a :	-

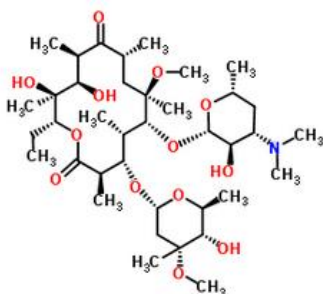
Azithromycin (AZMY)



Semi synthetic antibiotic derived from erythromycin.

CAS number:	83905-01-5
Molecular formula:	C ₃₈ H ₇₂ N ₂ O ₁₂
Molecular weight	749.00
Water solubility (mg/L):	6.24 × 10 ⁻²
Henry's law constant (atm m ³ / mol)	5.30 × 10 ⁻²⁹
Log K _{ow}	4.02
Log K _{oc}	1.68
pK _a :	8.74

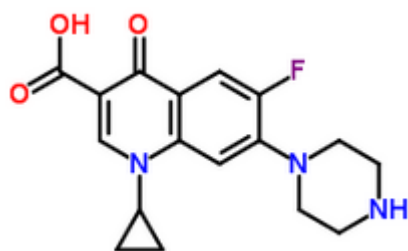
Clarithromycin (CLMY)



Semi synthetic antibiotic derived from erythromycin.

CAS number:	81103-11-9
Molecular formula:	C ₃₈ H ₆₉ NO ₁₃
Molecular weight	747.97
Water solubility (mg/L):	3.42 × 10 ⁻¹
Henry's law constant (atm m ³ / mol)	1.73 × 10 ⁻²⁹
Log K _{ow}	3.16
Log K _{oc}	1.37
pK _a :	8.99

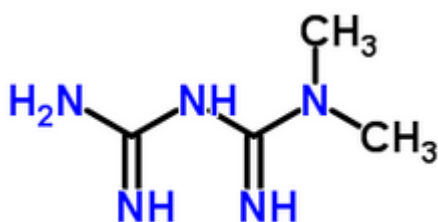
Ciprofloxacin (CIPR)



CAS number:	85721-33-1
Molecular formula:	C ₁₇ H ₁₈ FN ₃ O ₃
Molecular weight	331.35
Water solubility (mg/L):	3.00 × 10 ⁴
Henry's law constant (atm m ³ /mol)	5.09 × 10 ⁻¹⁹
Log K _{ow}	0.28
Log K _{oc}	-
pK _a :	6.09

Broad spectrum antibiotic.

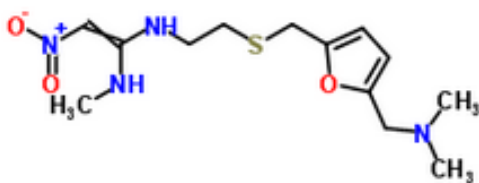
Metformin (METF)



CAS number:	657-54-9
Molecular formula:	C ₄ H ₁₁ N ₅
Molecular weight	129.17
Water solubility (mg/L):	1.00 × 10 ⁶
Henry's law constant (atm m ³ /mol)	7.64 × 10 ⁻¹⁶
Log K _{ow}	-2.64
Log K _{oc}	-0.67
pK _a :	12.40

Anti-hyperglycaemic agent, which is not metabolised by the human body and excreted unchanged.. Potential endocrine disruptor.

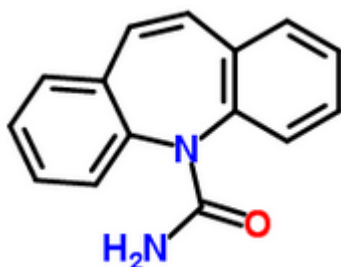
Ranitidine (RNTD)



CAS number:	66357-35-5
Molecular formula:	C ₁₃ H ₂₂ N ₄ O ₃ S
Molecular weight	314.14
Water solubility (mg/L):	2.47 × 10 ⁴
Henry's law constant (atm m ³ /mol)	3.42 × 10 ⁻¹⁵
Log K _{ow}	0.27
Log K _{oc}	1.14
pK _a :	8.08

Gastric secretion blocker.

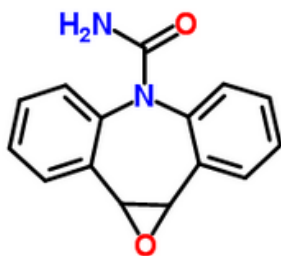
Carbamazepine (CBAZ)



CAS number:	298-46-4
Molecular formula:	C ₁₅ H ₁₂ N ₂ O
Molecular weight	236.28
Water solubility (mg/L):	1.12 × 10 ²
Henry's law constant (atm m ³ /mol)	1.08 × 10 ⁻¹⁰
Log K _{ow}	2.45
Log K _{oc}	2.23
pK _a :	13.90

Anticonvulsant.

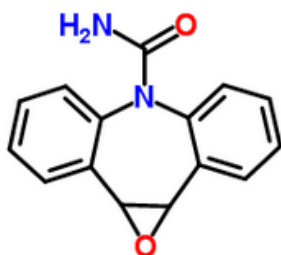
10,11-epoxy-carbamazepine (CBAZe)



Anticonvulsant. Carbamazepine metabolite.

CAS number:	36507-30-9
Molecular formula:	C ₁₅ H ₁₂ N ₂ O ₂
Molecular weight	252.09
Water solubility (mg/L):	2.77 × 10 ²
Henry's law constant (atm m ³ /mol)	9.14 × 10 ⁻¹¹
Log K _{ow}	0.95
Log K _{oc}	2.59
pK _a :	-

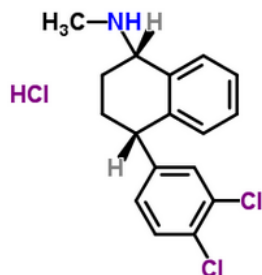
10,11-epoxy-carbamazepine (CBAZe)



Anticonvulsant. Carbamazepine metabolite.

CAS number:	36507-30-9
Molecular formula:	C ₁₅ H ₁₂ N ₂ O ₂
Molecular weight	252.09
Water solubility (mg/L):	2.77 × 10 ²
Henry's law constant (atm m ³ /mol)	9.14 × 10 ⁻¹¹
Log K _{ow}	0.95
Log K _{oc}	2.59
pK _a :	-

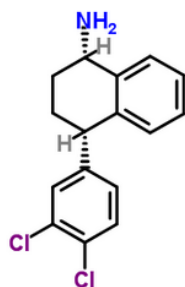
Sertraline (SERT)



Antidepressant.

CAS number:	79559-97-0
Molecular formula:	C ₁₇ H ₁₈ Cl ₃ N
Molecular weight	342.69
Water solubility (mg/L):	9.38 × 10 ¹
Henry's law constant (atm m ³ /mol)	3.90 × 10 ⁻¹⁵
Log K _{ow}	2.18
Log K _{oc}	2.09
pK _a :	-

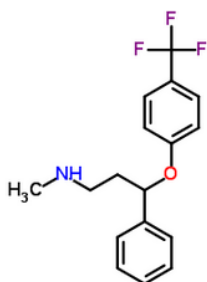
Norsertraline (SERTn)



Antidepressant. Metabolite of sertraline.

CAS number:	79559-97-0
Molecular formula:	C ₁₆ H ₁₅ Cl ₂ N
Molecular weight	292.20
Water solubility (mg/L):	1.06 × 10 ¹
Henry's law constant (atm m ³ /mol)	2.32 × 10 ⁻⁸
Log K _{ow}	4.82
Log K _{oc}	5.37
pK _a :	-

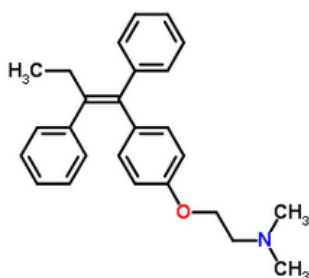
Fluoxetine (FLXT)



Antidepressant.

CAS number:	54910-89-3
Molecular formula:	C ₁₇ H ₁₈ F ₃ NO
Molecular weight	309.33
Water solubility (mg/L):	6.03 × 10 ¹
Henry's law constant (atm m ³ /mol)	8.90 × 10 ⁻⁸
Log K _{OW}	4.05
Log K _{OC}	3.05
pK _a :	9.06

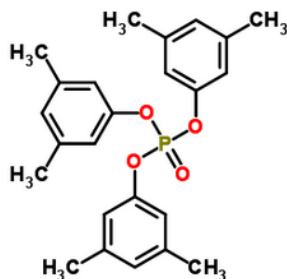
Tamoxifen (TMXF)



Selective oestrogen receptor. Can inhibit oestrogenic activity.

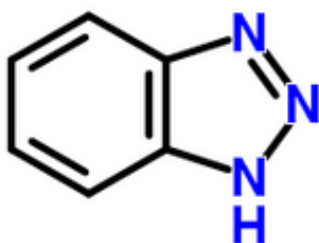
CAS number:	10540-29-1
Molecular formula:	C ₂₆ H ₂₉ NO
Molecular weight	371.53
Water solubility (mg/L):	1.94 × 10 ⁻¹
Henry's law constant (atm m ³ /mol)	4.49 × 10 ⁻¹⁰
Log K _{OW}	6.30
Log K _{OC}	4.40
pK _a :	8.87

Trixylenyl-phosphate (TXP)



CAS number:	25155-23-1
Molecular formula:	C ₂₄ H ₂₇ O ₄ P
Molecular weight	410.45
Water solubility (mg/L):	8.90 × 10 ⁻¹
Henry's law constant (atm m ³ /mol)	7.19 × 10 ⁻⁸
Log K _{OW}	7.98
Log K _{OC}	5.11
pK _a :	-

1,2,3 benzotriazole (BZT)



Anticorrosive agent.

CAS number:	95-14-7 (1H) 116421-31-9 (2H)
Molecular formula:	C ₆ H ₅ N ₃
Molecular weight	119.13
Water solubility (mg/L):	1.98 × 10 ⁴
Henry's law constant (atm m ³ /mol)	1.47 × 10 ⁻⁷
Log K _{OW}	1.44
Log K _{OC}	1.76
pK _a :	8.37

Tolytriazole (4,5 metyl BZT)



Anticorrosive agent.

CAS number:	29385-43-1
Molecular formula:	C ₇ H ₇ N ₃
Molecular weight	133.15
Water solubility (mg/L):	3.07 × 10 ³
Henry's law constant (atm m ³ /mol)	1.62 × 10 ⁻⁷
Log K _{OW}	1.71
Log K _{OC}	1.94
pK _a :	-

Appendix B Summary of sampling bottles

Name	Description	Determinands
C1	1 L amber glass, containing copper nitrate and 30% hydrochloric acid	Steroids
C2	0.5 L amber glass	PBDE
C3	0.5 L amber glass	Cypermethrin
C4	1 L amber glass, pre-cleaned	Tributyltin compounds
C5	0.5 L amber glass, pre-cleaned	PFOS
C6	0.5 L amber glass, containing copper nitrate and 30% hydrochloric acid	Ethoxylathes
C7	40 mL amber vial	Trixylenyl phosphate
C8	0.5 L amber glass	Positive pharmaceuticals
C9	0.5 L amber glass, containing acetic acid	Negative pharmaceuticals
D1	HDPE, red cap	Total metals
D2	300 mL glass, red cap	Total Mercury
D3	300 mL glass, blue cap	Dissolved Mercury
DT	330 mL plastic	DOC
FA	125 mL white plastic	Dissolved metals
SA	1 L plastic	Sanitary determinands
U	125 mL white plastic	Sulphide
WH	330 mL plastic	TOC
AL	125 mL white plastic	Dissolved aluminium

Appendix C Sampling dates, times and conditions (March – September 2016)

Sample	Date	Time	Out of working hours (Y/N)	Inlet flow (L/h)	Outlet flow (L/h)	Volts (V)	Conductivity T1 (µS/m)	pH T1	Turbidity T1 (FNU)	Conductivity T2 (µS/m)	pH T2	Turbidity T2 (FNU)	Temp T1 (°C)	Temp T2 (°C)	Temp T3 (°C)
1	18 th March	10:40	N	300	185	29.3	1159.8	7.01	9.8	1183.5	6.35	2.4	10.2	10.3	10.7
1a	18 th March	15:30	Y	300	200	29.4	1160.5	6.98	8.9	1173.6	6.46	2.3	10.5	10.7	11.4
2	6 th May	10:20	N	300	205	21.2	1092.9	6.91	49.9	1137.3	6.35	2.3	14.2	14.5	14.7
2a	6 th May	16:40	Y	300	200	28.0	1067.1	6.86	56.5	1117.8	6.22	2.8	15.3	15.9	15.5
3	1 st June	11:15	N	115	100	29.2	156.0	6.87	7.1	1041.1	6.21	1.5	14.5	15.8	16.0
3a	1 st June	16:00	Y	195-215	105	27.0	841.0	7.12	6.1	997.5	6.24	2.5	14.6	15.9	16.9
4	10 th June	10:30	N	255	205	22.6	1095.3	6.65	4.5	1105.7	6.03	1.6	18.0	19.4	20.0
4a	10 th June	15:00	N	255	190	25.7	1092.4	6.67	4.8	1155.9	5.98	1.6	18.8	19.4	20.3
5	1 st July	10:45	N	240	200	25.5	980.3	6.83	8.7	981.7	6.10	17.9	18.1	20.0	20.6
5a	1 st July	15:35	Y	250	200	20.0	988.3	6.87	8.6	979.1	6.16	18.9	18.4	20.2	20.7
6	7 th July	11:05	N	235	200	24.0	1023.2	6.81	13.7	1033.4	6.10	45.5	18.3	19.7	20.6
6a	7 th July	15:20	N	245	205	20.0	1017.5	6.78	18.0	1030.2	6.11	45.4	19.0	20.5	20.9
7	15 th July	10:30	N	245	205	28.3	902.4	7.02	5.5	1015.7	6.7	2.6	18.1	19.4	19.4
7a	15 th July	16:15	Y	245	200	27.7	1022.3	6.96	5.8	1027.8	6.10	2.6	18.8	19.9	20.3
8	19 th July	11:20	N	245	200	25.9	1039.0	6.93	36.6	1073.5	6.19	3.7	21.3	22.4	23.2
8a	19 th July	15:35	Y	235	200	22.3	1012.8	6.84	45.0	1031.6	6.04	3.7	22.1	23.8	23.9

Sample	Date	Time	Out of working hours (Y/N)	Inlet flow (L/h)	Outlet flow (L/h)	Volts (V)	Conductivity T1 (μS/m)	pH T1	Turbidity T1 (FNU)	Conductivity T2 (μS/m)	pH T2	Turbidity T2 (FNU)	Temp T1 (°C)	Temp T2 (°C)	Temp T3 (°C)
9	5 th August	11:15	N	250	195	28.5	1013.2	6.86	7.8	1026.6	6.00	3.7	19.2	21.4	22.0
9a	5 th August	16:00	Y	245	205	28.3	992.4	6.84	8.0	1023.2	6.10	2.7	20.0	22.3	22.3
10	11 th August	10:30	N	265	210	26.6	1074.2	7.02	7.5	1106.1	6.05	2.7	17.9	19.5	19.6
10a	11 th August	15:20	N	230	210	25.7	1038.9	6.95	7.8	1088.9	6.06	2.6	18.5	19.9	19.9
11	18 th August	10:20	N	245	200	24.5	1085.5	6.92	72.8	1116.4	6.07	1.7	19.6	21.2	21.5
11a	18 th August	15:00	N	250	200	24.5	1085.5	6.96	61.9	1073.5	6.11	1.7	19.7	21.5	21.7
12	23 rd August	9:30	Y	235	205	24.8	981.9	6.97	112.6	1005.5	6.01	2.6	19.6	21.2	21.9
12a	23 rd August	15:35	Y	245	210	26.9	969.2	6.98	5.1	988.6	6.01	2.6	20.9	22.6	22.7
13	1 st September	10:45	N	230	200	27.1	97	7.08	7.8	1070.5	6.11	3.7	20.1	21.8	21.9
13a	1 st September	15:45	Y	225	210	-	986.7	7.07	7.7	1054.3	6.12	4.6	20.8	22.5	22.6
14	12 th September	9:55	Y	210	205	22.9	973.5	6.61	7.6	1002.9	5.83	2.6	18.9	20.1	20.5
14a	12 th September	14:00	N	240	205	26.0	975.3	6.66	7.8	975.9	5.97	2.6	19.6	20.7	21.1
15	20 th September	10:10	N	220	205	31.5	711.7	6.76	11.6	943.7	5.92	3.6	19.1	20.6	20.9
15a	20 th September	14:40	N	245	205	30.6	711.5	6.89	10.8	841.9	6.00	2.6	19.4	20.3	21.2

Appendix D Limits of Detection (LOD), reporting limits and EQSs for CIP2 suite

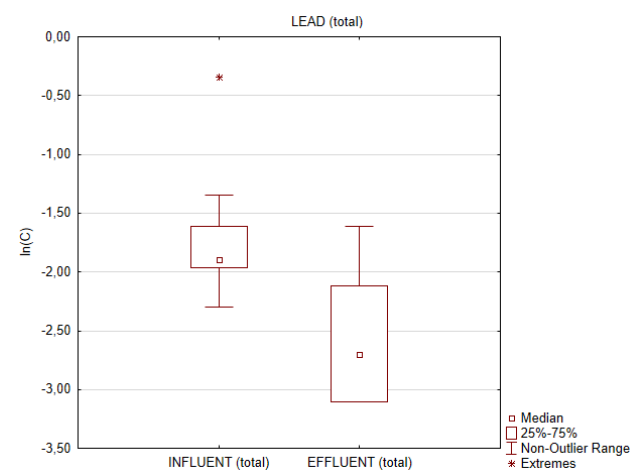
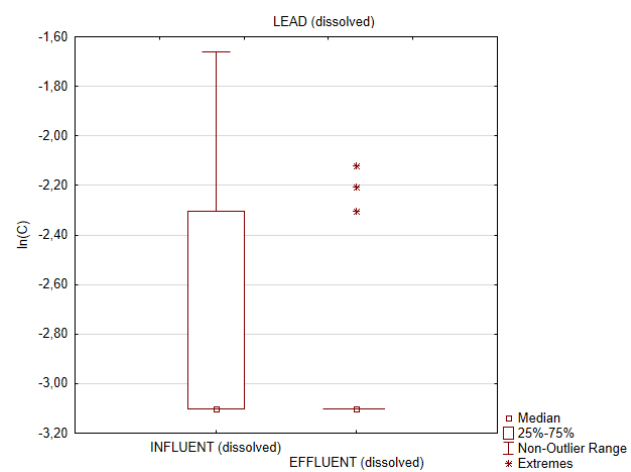
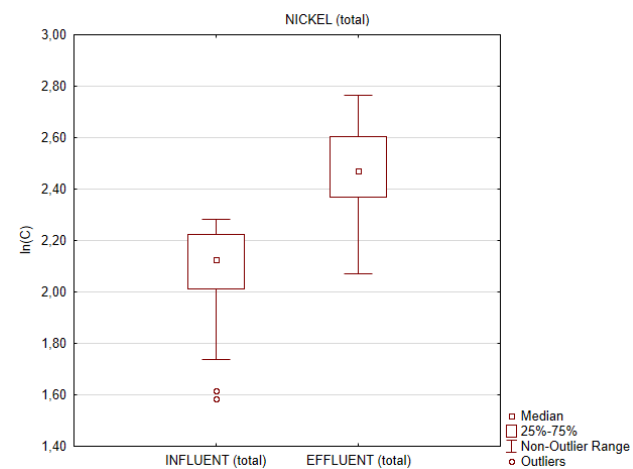
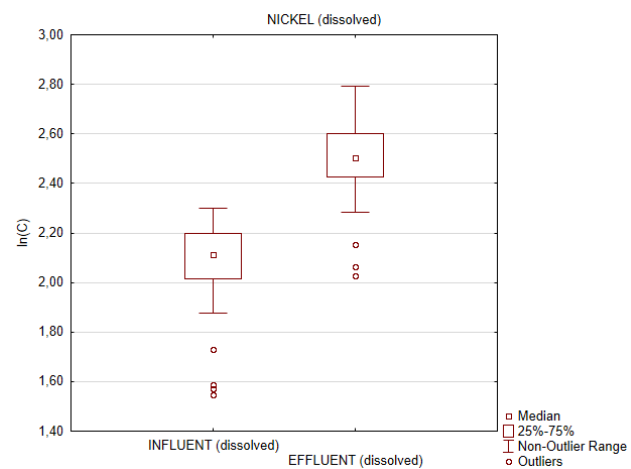
Determinand	CAS number	LOD (µg/L)	Reporting limit ¹ (µg/L)	AA-EQS ² (µg/L)
Nickel (dissolved)	7440-02-0	0.5	0.41	4
Nickel (total)		0.5	0.04	
Lead (dissolved)		0.2	0.09	1.2
Lead (total)	7439-92-1	0.2	0.09	
Copper (dissolved)		0.3	1.33	1
Copper (total)	7440-50-8	0.3	1.33	
Zinc (dissolved)		0.5	2.61	12.9
Zinc (total)	7440-66-6	0.5	2.61	
Cadmium (dissolved)		0.04	0.06	0.08
Cadmium (total)	7440-43-9	0.04	0.06	
Mercury (dissolved)		0.001	0.03	
Mercury (total)	7439-97-6	0.001	0.03	
Iron (dissolved)		50	45.91	1000
Iron (total)	7439-89-6	50	45.91	730
Aluminium (dissolved)		50	6.63	
Aluminium (total)	7429-90-5	50	6.63	
Aluminium (reactive)		4	4.	50
Chromium (dissolved)		0.5	0.52	3.4
Chromium (total)	7440-47-3	0.5	0.52	
Diethylexylphtalate	117-81-7	0.3	0.2	1.3
BDE 28	41318-75-6	0.0005	0.0005	0.0005
BDE 47	5436-43-1	0.0005	0.0005	0.0005
BDE 99	60348-60-9	0.0005	0.0005	0.0005
BDE 100	189084-64-8	0.0005	0.0005	0.0005
BDE 153	68631-49-2	0.0005	0.0005	0.0005
BDE 154	207122-15-4	0.0005	0.0005	0.0005
Perfluorooctane sulfonic acid	1763-23-1	0.00065	0.00009	0.00065
Perfluorooctanoic acid	335-67-1	0.00065	0.00009	0.00065
Hexabromocyclododecane	*	0.0016	0.00020	0.0016
Nonylphenol (technical)	25154-52-3 **	0.1	0.1	0.3
Nonylphenol monoethoxylate		0.1	0.05	0.3
Nonylphenol diethoxylate		0.1	0.05	0.3
Nonylphenol triethoxylate		0.1	0.05	0.3
Octylphenols	1806-26-4 ***	0.1	0.1	0.1
Tributyltin compounds	36643-28-4	0.0002	0.00020	0.0002
Fluoranthene	206-44-0	0.0063	0.00090	0.0063
Benzo(a)pyrene	50-32-8	0.00017	0.00017	0.00017
Triclosan	3380-34-5	0.1	0.01	0.1
Cypermethrin	52315-07-8 ****	0.00008	0.00008	0.00008
Total Suspended Solids (mg/L)		2	2	
Ammoniacal nitrogen (mg/L)		0.1	0.231	
Total oxidised nitrogen (mg/L)		5	0.354	
BOD (mg/L)		1	0.24	
COD (mg/L)		5	11.5	
Total phosphorus (mg/L)		0.01	12.69	
Soluble reactive phosphate		0.01	0.104	0.067
TOC (mg/L)		0.5	0.93	
DOC (mg/L)		0.5	0.93	

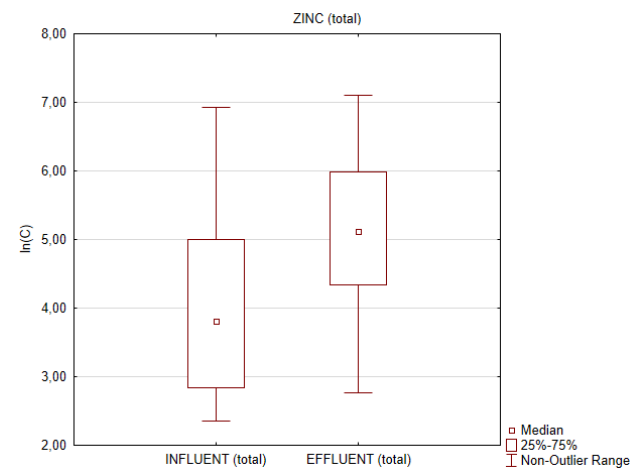
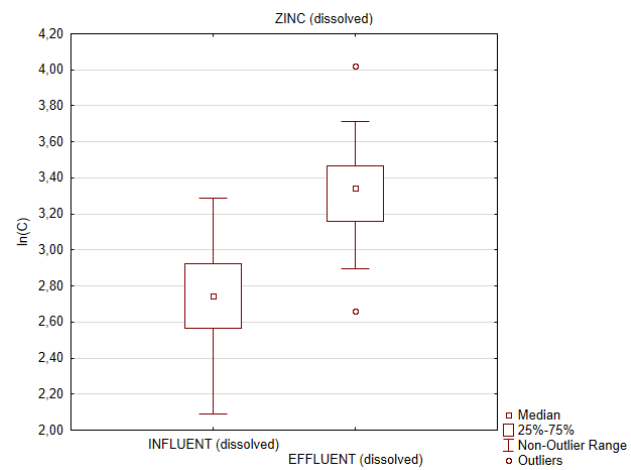
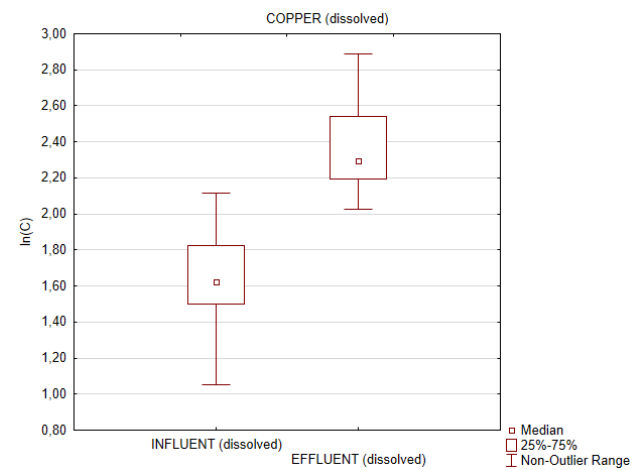
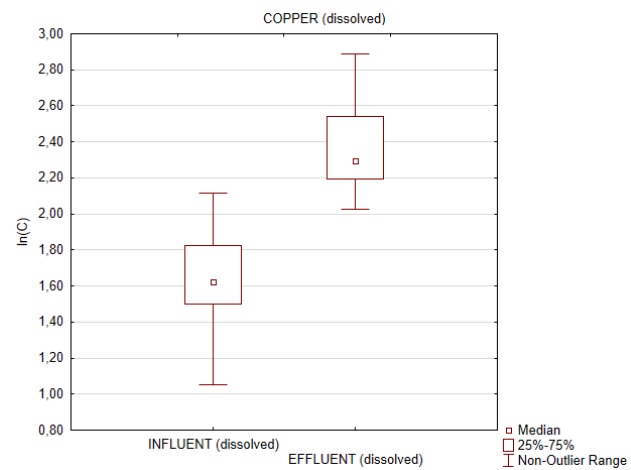
¹ As provided by Anglian Water central laboratories, Huntington.

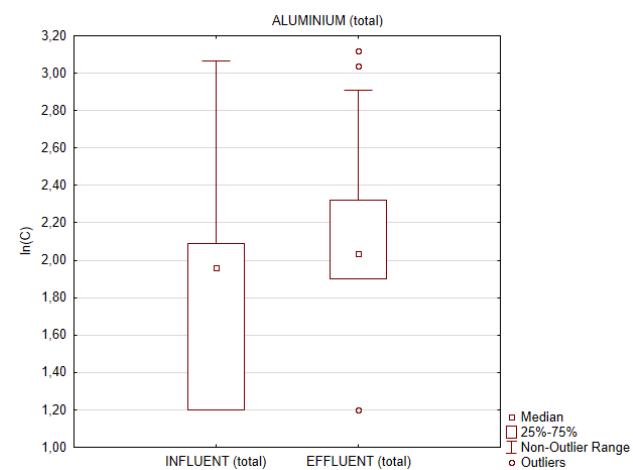
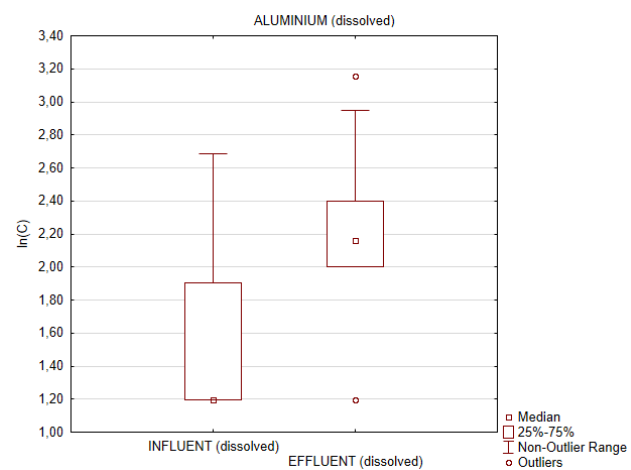
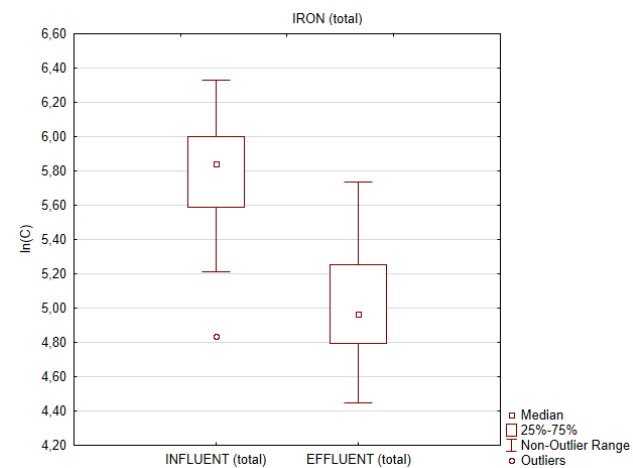
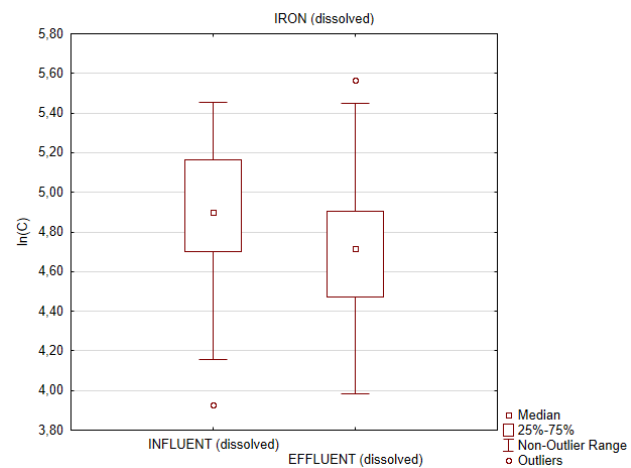
² Pharmaceuticals refer to PNEC (Predicted No Effect Concentration).

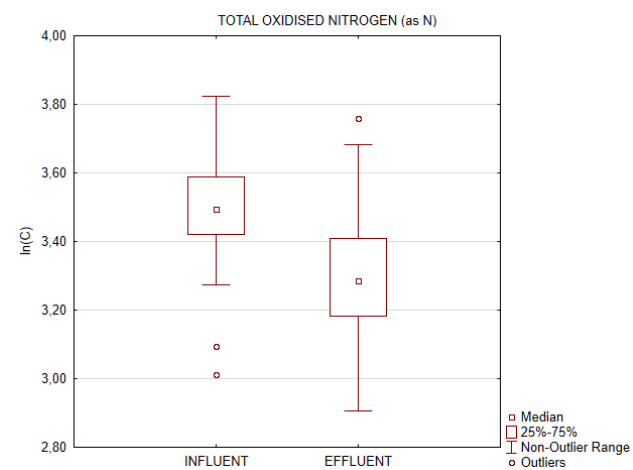
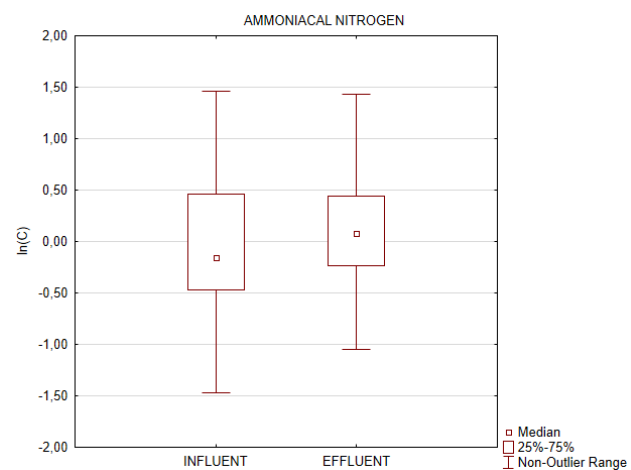
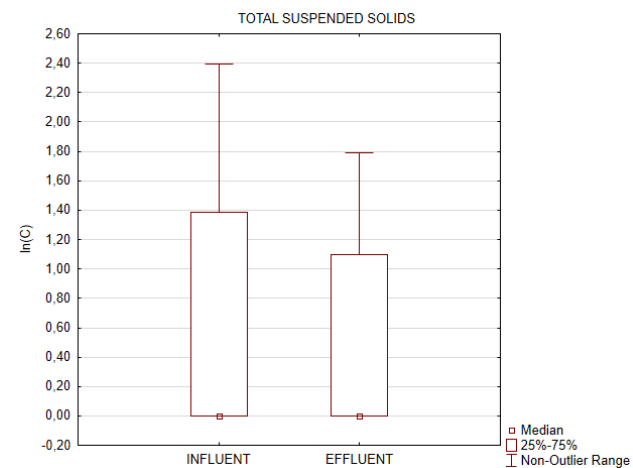
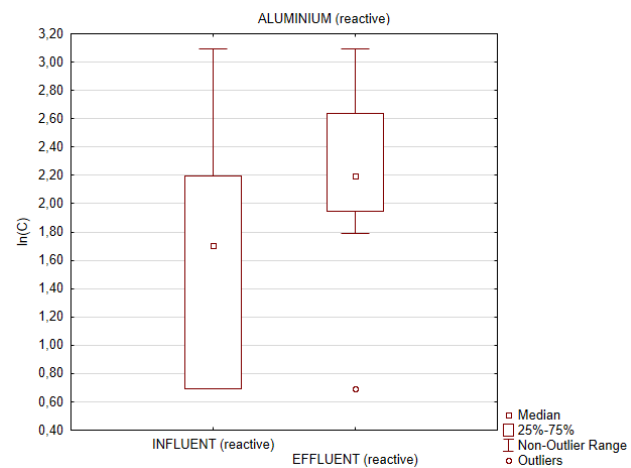
Determinand	CAS number	LOD (µg/L)	Reporting limit ¹ (µg/L)	AA-EQS ² (µg/L)
pH				
Calcium (mg/L)		5	0.13	0.1
Sulphide (mg/L)		0.01	0.02	0.0002
Oestrone	53-16-7	0.001	0.00003	0.003
17b-oestradiol	50-28-2	0.0003	0.00003	0.001
17a-ethinyloestradiol	57-63-6	0.00003	0.00003	0.0001
Diclofenac	15307-86-5	0.01	0.010	0.05
Ibuprofen	15687-27-1	0.01	0.010	0.01
Atrovastatin	134523-00-5	0.01	0.01	1.7
Ortho-hydroxy-atorvastatin	214217-86-4	0.01	0.01	1.7
Para-hydroxy-atorvastatin	163217-70-7	0.01	0.01	1.7
Propranolol	525-66-6	0.01	0.01	0.1
Atenolol	29122-68-7	0.01	0.01	148
Erythromycin	114-07-8	0.1	0.01	0.2
Norerythromycin	299409-85-1	0.1	0.01	0.2
Azithromycin	83905-01-5	0.005	0.005	0.09
Clarithromycin	81103-11-9	0.01	0.01	0.13
Ciprofloxacin	85721-33-1	0.01	0.01	0.089
Metformin	657-24-9	0.1	0.01	13.45
Ranitidine	66357-35-5	0.1	0.01	0.31
Carbamazepine	298-46-4	0.1	0.01	2.5
10,11 epoxy-carbamazepine	36507-30-9	0.1	0.01	2.5
Sertraline	79559-97-0	0.01	0.01	0.121
Norsetraline	87857-41-8	0.01	0.01	0.121
Fluoxetine	54910-89-3	0.01	0.01	0.047
Tamoxifen	10540-29-1	0.005	0.005	0.49
Trixylenyl phosphate	25155-23-1	0.01	0.01	0.1
Benzotriazole	95-14-7	0.002	0.002	0.02
Tolyriazole	29385-43-1	0.002	0.002	0.02

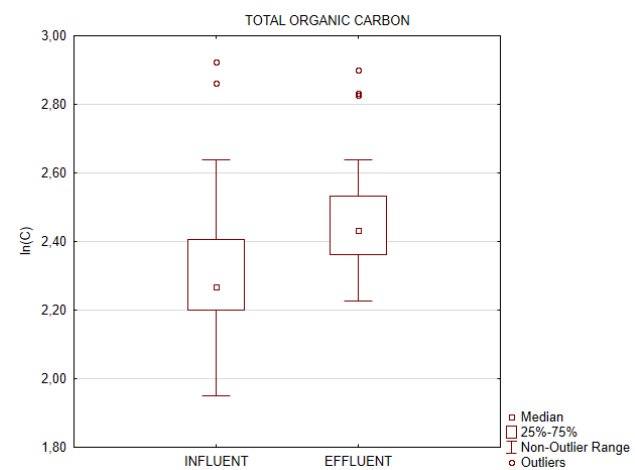
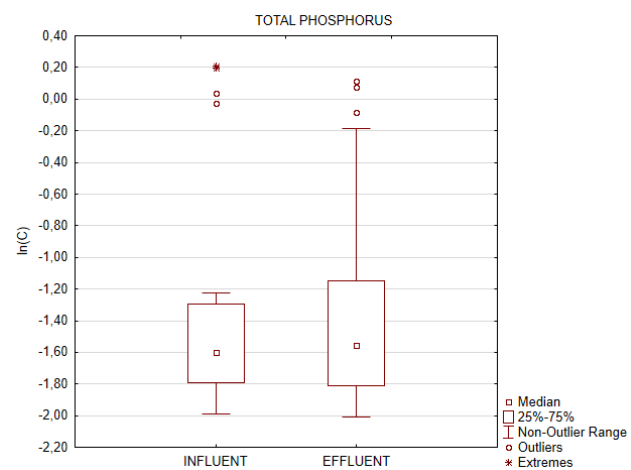
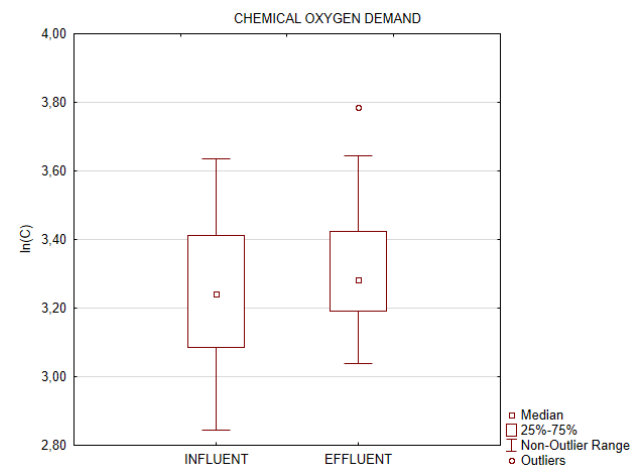
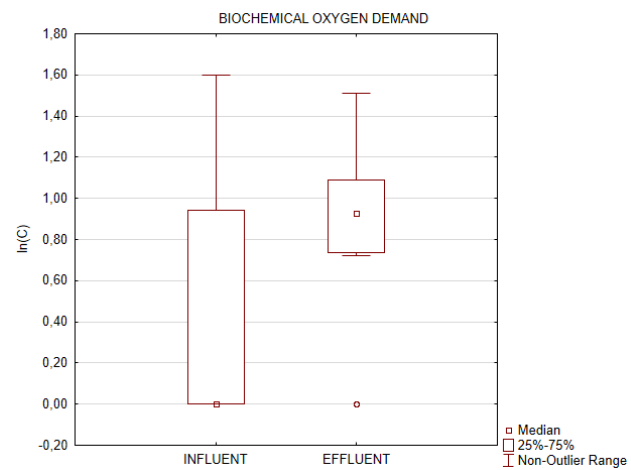
Appendix E Box plots of influent and effluent concentrations

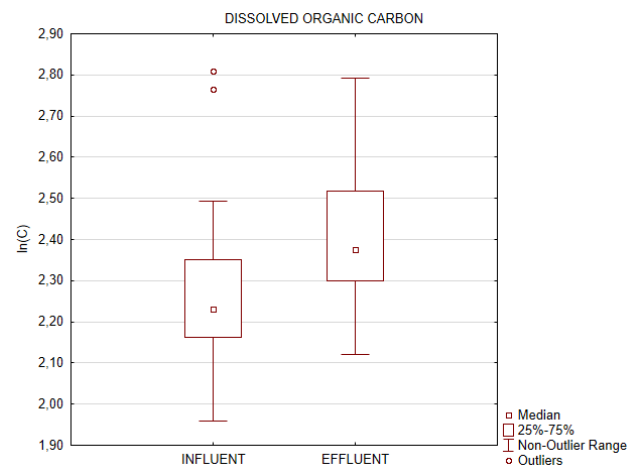




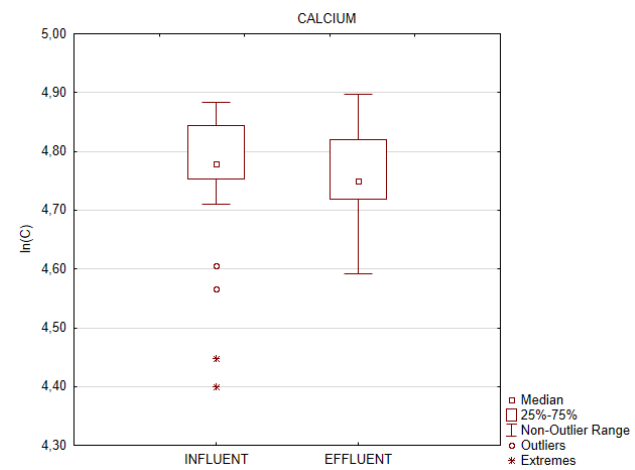




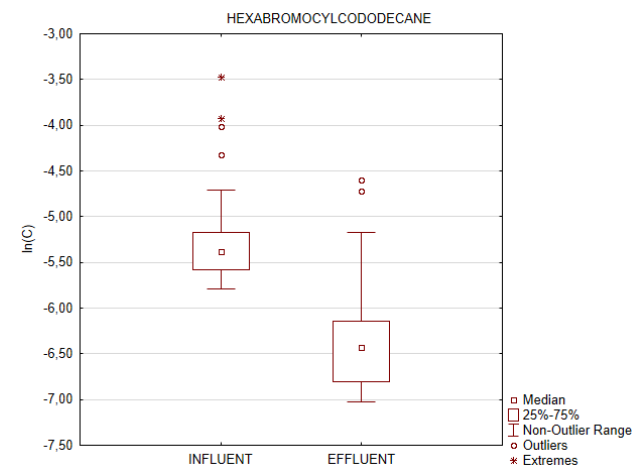
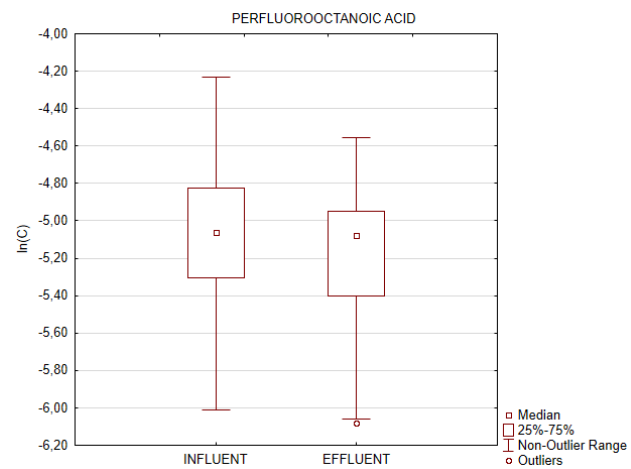
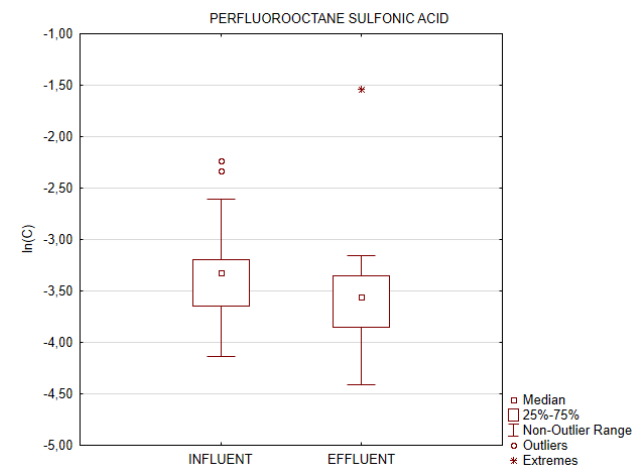
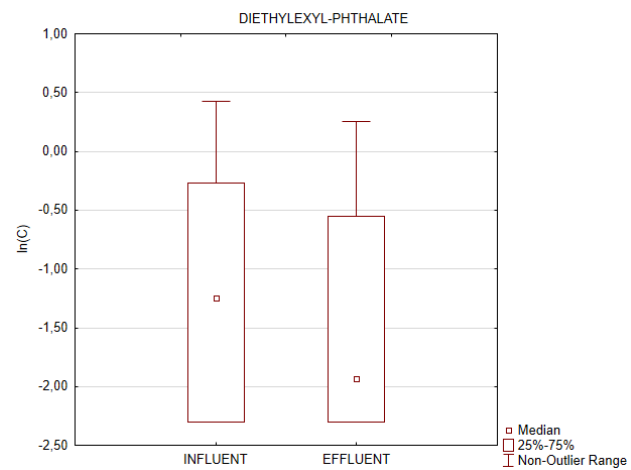


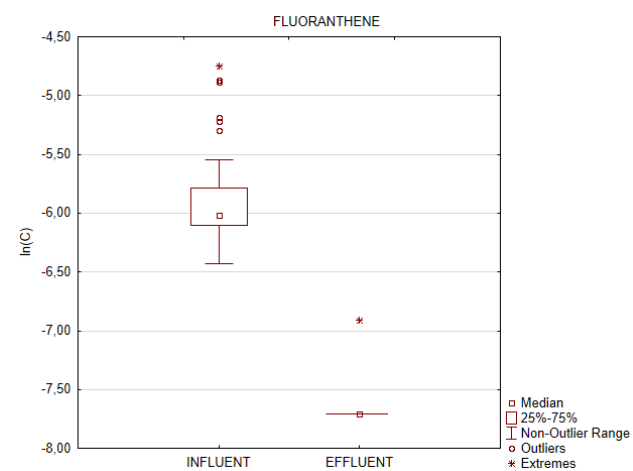
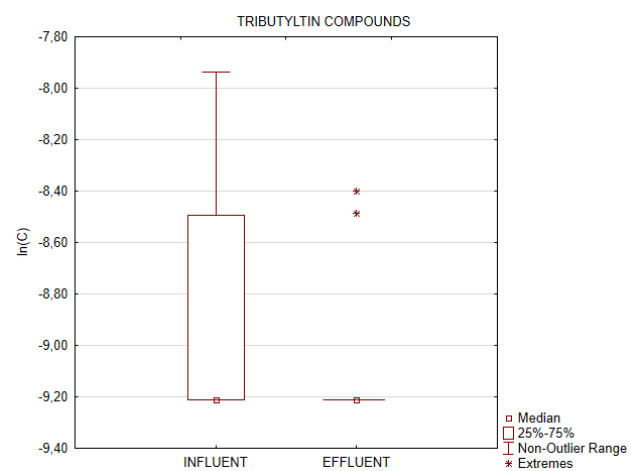
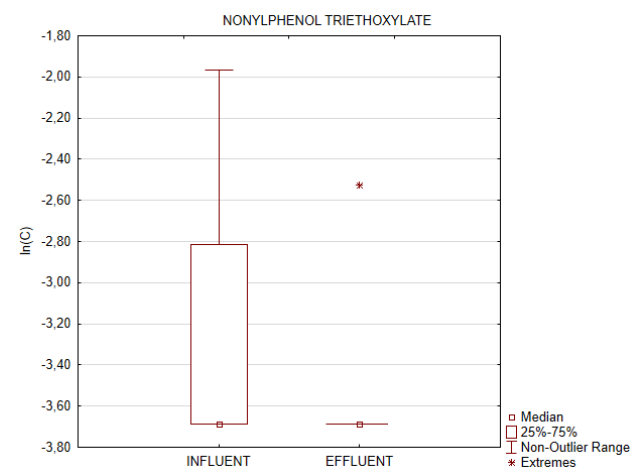
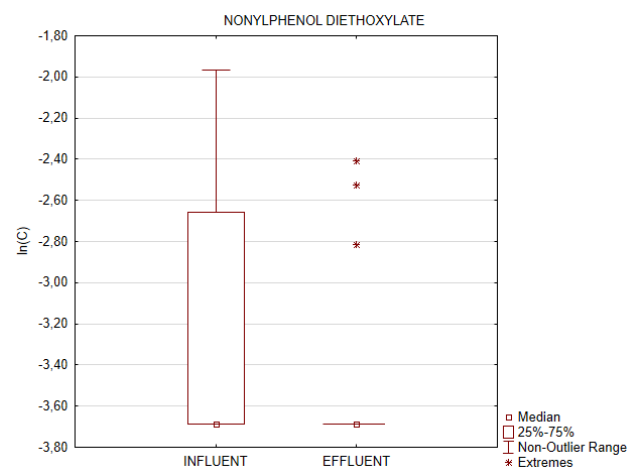


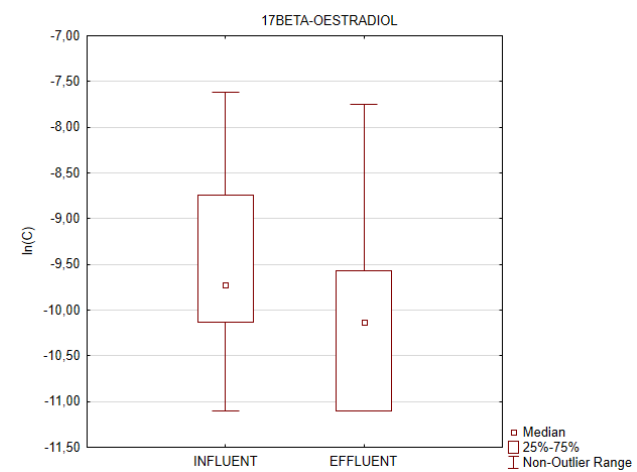
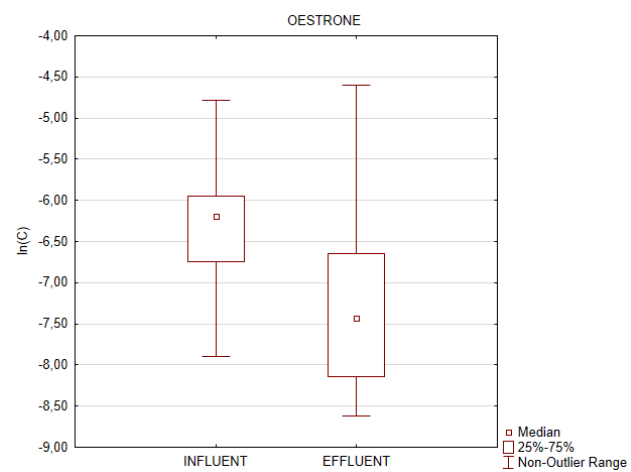
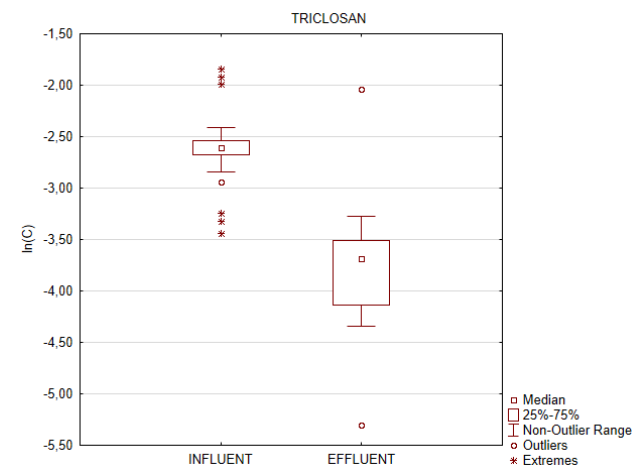
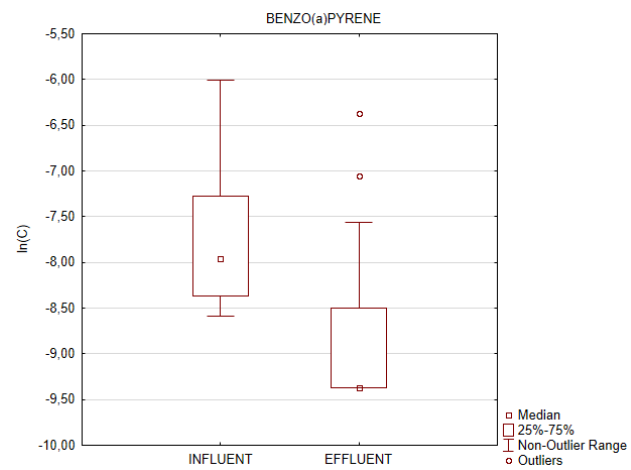
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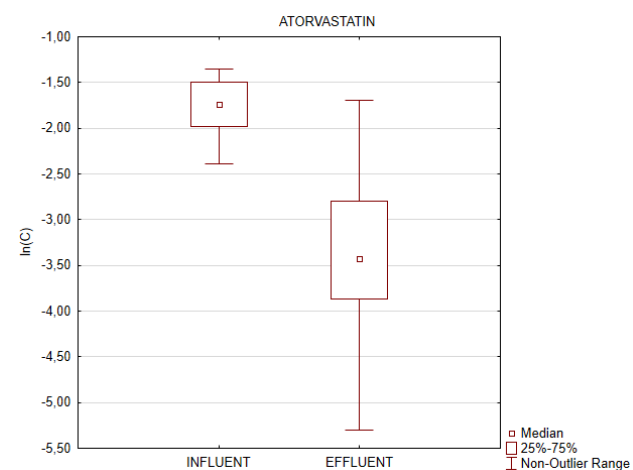
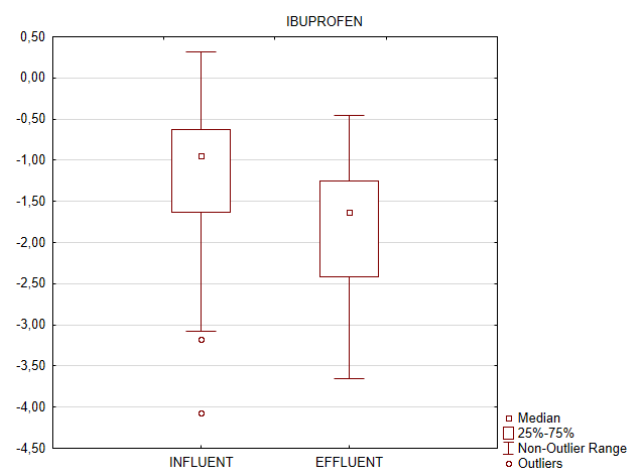
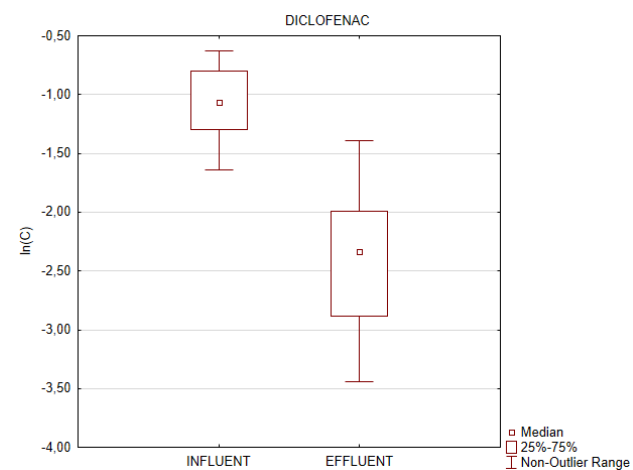
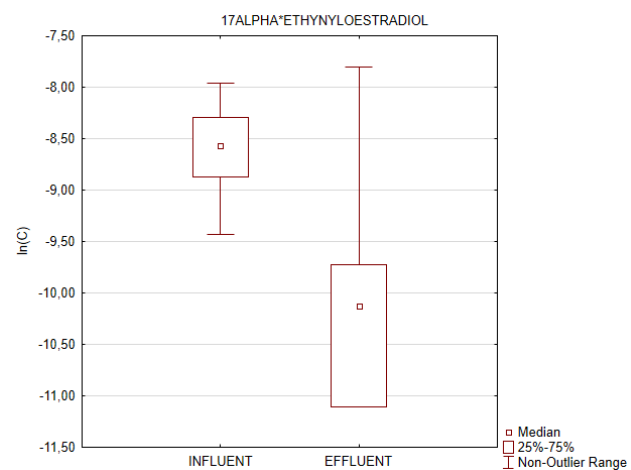


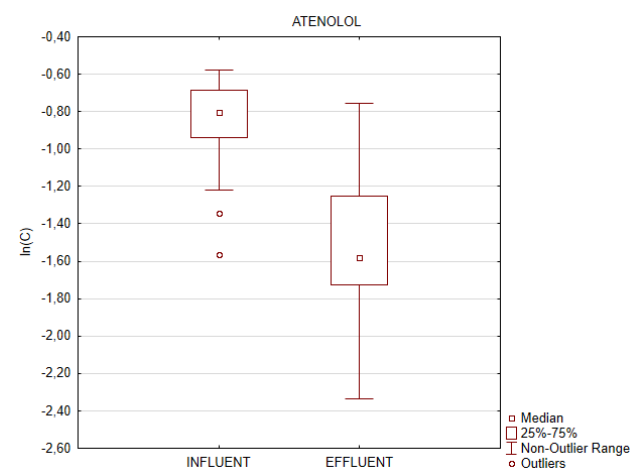
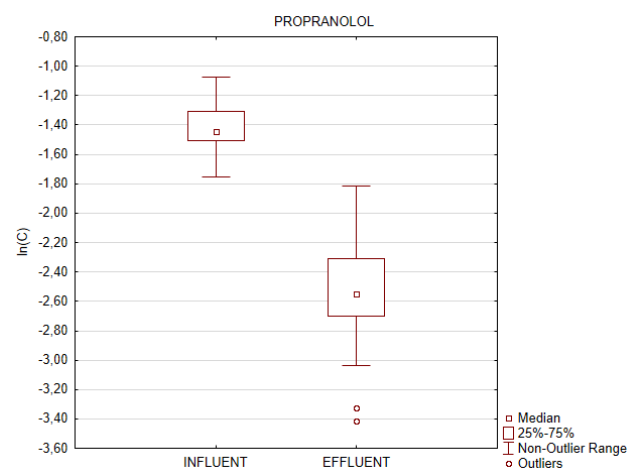
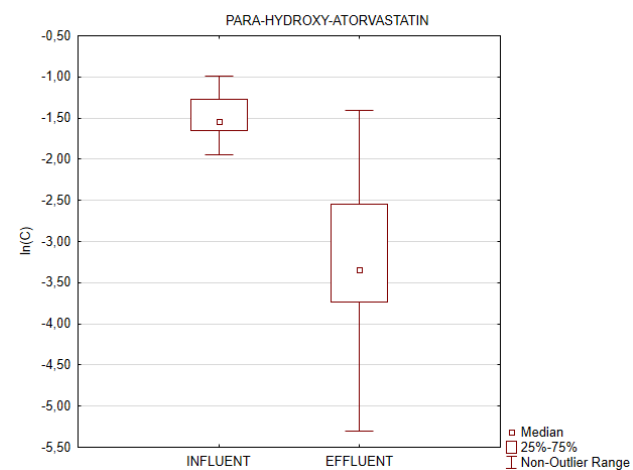
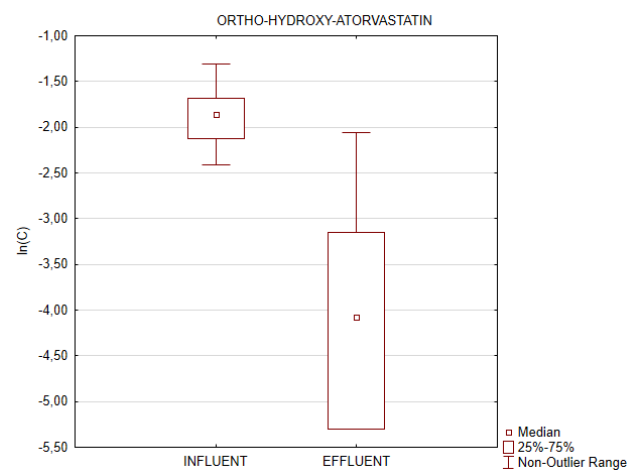
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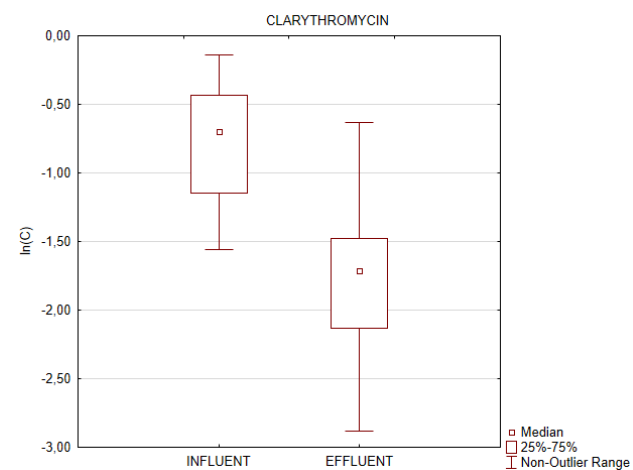
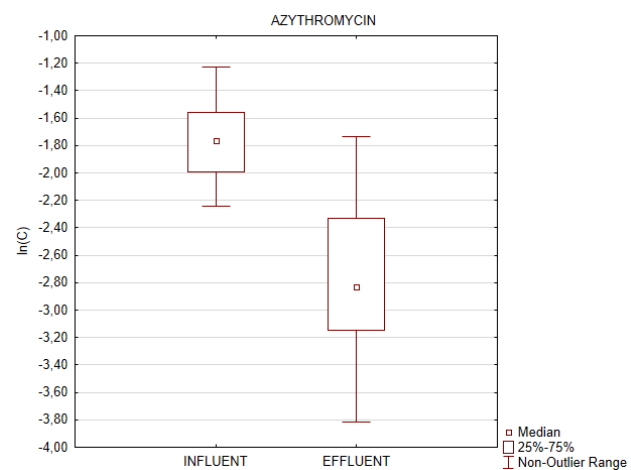
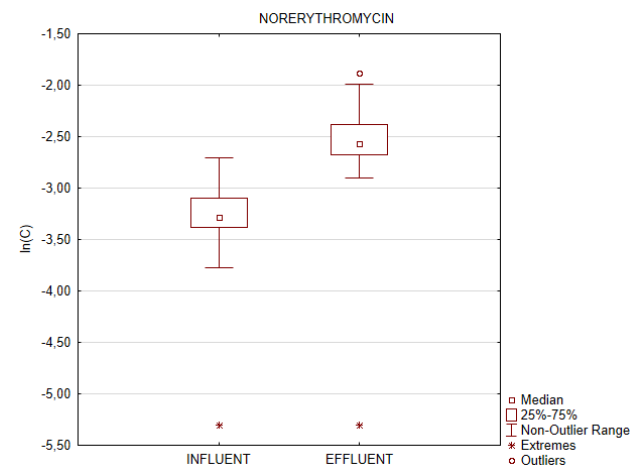
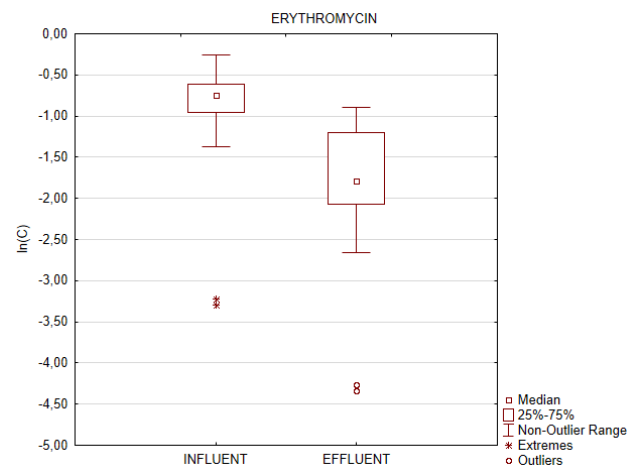


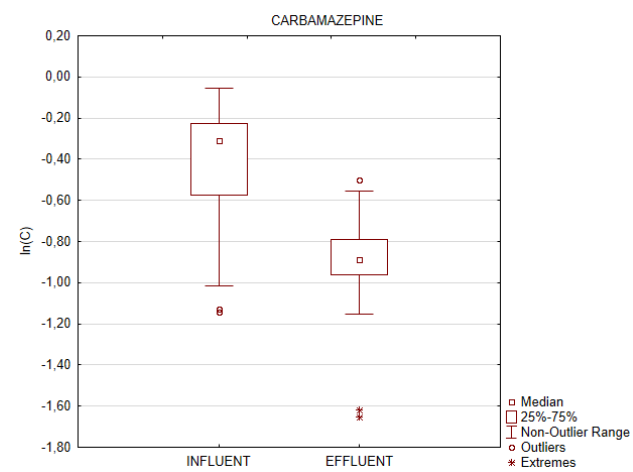
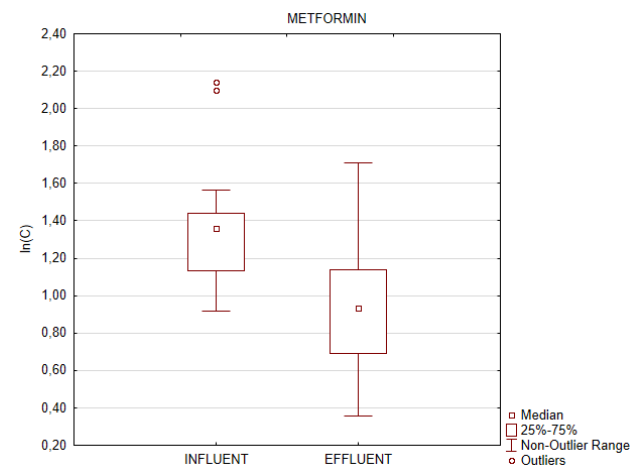
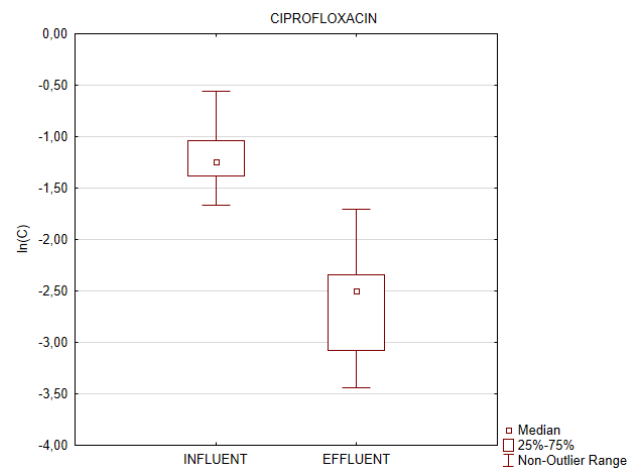


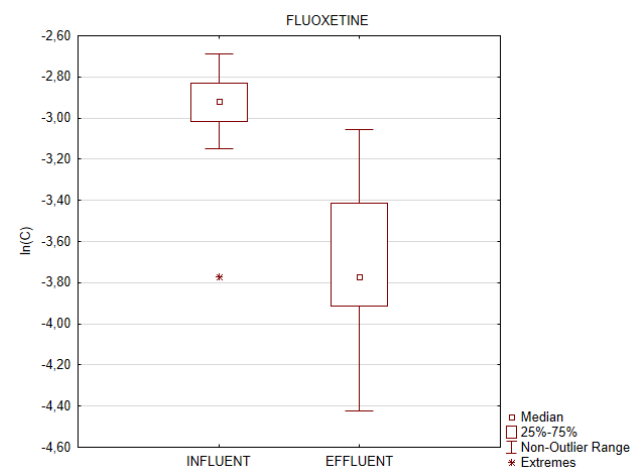
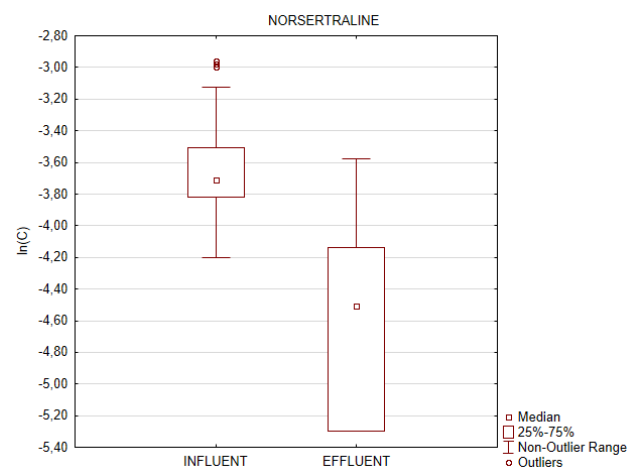
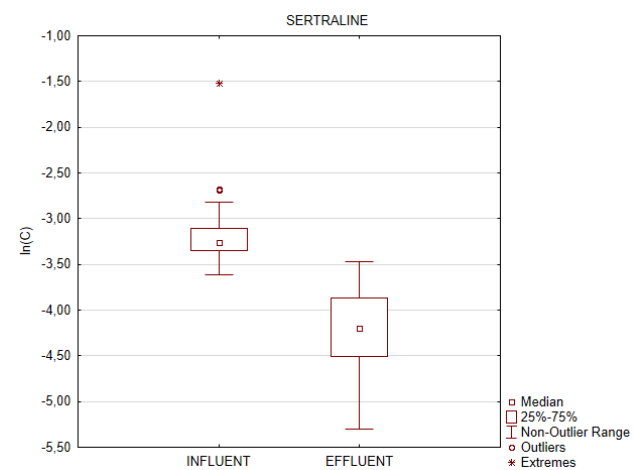
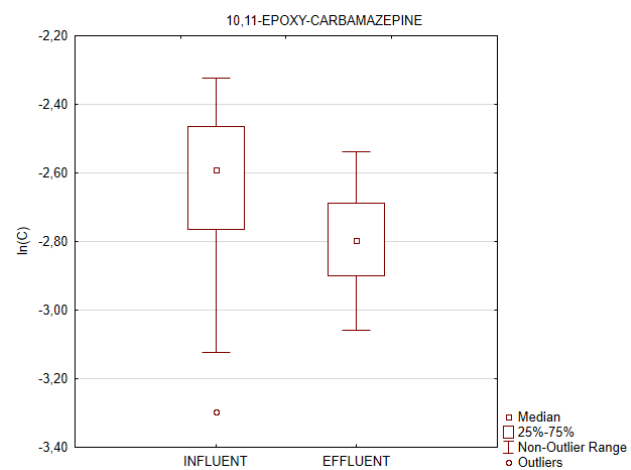


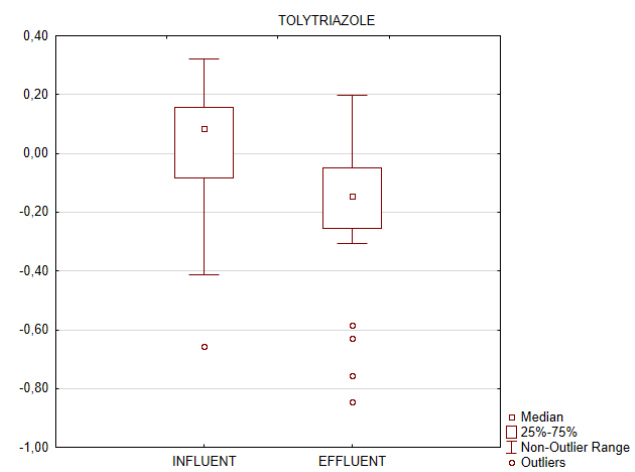
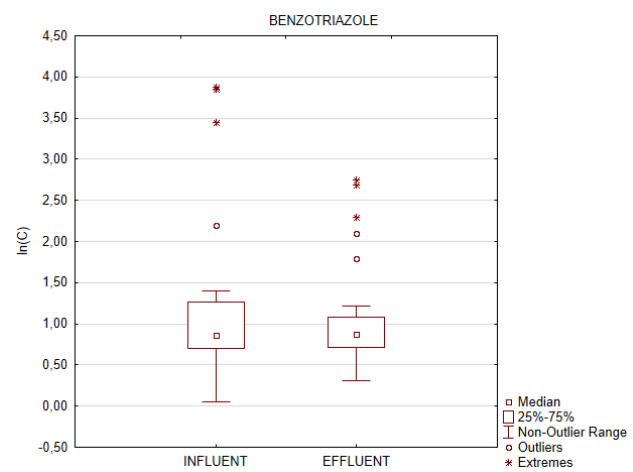












Appendix F Multi-criteria analysis (MCA)

F.1 Weighting of criteria

How important is sub-criteria A (rows, *i*) relative to sub-criteria B (columns, *j*)?

Equally important	1
Moderately important	3
Essentially or strongly more important	5
Very strongly more important	7
Extremely more important	9

Removal of pollutants	Range of treatment	Removal efficiency	Total costs	Energy consumption	Chemical dosing	By products/waste production	Flexibility	Reliability	Easiness of maintenance/operation	Geom. mean	Weight
Range of treatment	1.00	1.00	5.00	5.00	7.00	7.00	9.00	9.00	9.00	4.58	0.30
Removal efficiency	1.00	1.00	5.00	5.00	7.00	7.00	9.00	9.00	9.00	4.58	0.30
Total costs	0.20	0.25	1.00	3.00	5.00	5.00	7.00	7.00	7.00	2.22	0.15
Energy consumption	0.20	0.25	0.33	1.00	3.00	3.00	5.00	5.00	5.00	1.38	0.09
Chemical dosing	0.14	0.17	0.20	0.33	1.00	1.00	3.00	3.00	3.00	0.70	0.05
By products/waste production	0.14	0.17	0.20	0.33	1.00	1.00	3.00	3.00	3.00	0.70	0.05
Flexibility	0.11	0.13	0.14	0.20	0.33	0.33	1.00	1.00	1.00	0.33	0.02
Reliability	0.11	0.13	0.14	0.20	0.33	0.33	1.00	1.00	1.00	0.33	0.02
Easiness of maintenance/operation	0.11	0.13	0.14	0.20	0.33	0.33	1.00	1.00	1.00	0.33	0.02

Cost effectiveness	Range of treatment	Removal efficiency	Total costs	Energy consumption	Chemical dosing	By products/waste production	Flexibility	Reliability	Easiness of maintenance/operation	Geom. mean	Weight
Range of treatment	1.00	1.00	0.33	5.00	6.00	6.00	7.00	7.00	7.00	3.01	0.21
Removal efficiency	1.00	1.00	0.33	5.00	6.00	6.00	7.00	7.00	7.00	3.01	0.21
Total costs	3.00	3.00	1.00	4.00	6.00	6.00	8.00	8.00	8.00	4.43	0.31
Energy consumption	0.20	0.20	0.25	1.00	2.00	2.00	5.00	5.00	5.00	1.20	0.08
Chemical dosing	0.17	0.17	0.17	0.50	1.00	1.00	3.00	3.00	3.00	0.73	0.05
By products/waste production	0.17	0.17	0.17	0.50	1.00	1.00	3.00	3.00	3.00	0.73	0.05
Flexibility	0.14	0.14	0.13	0.20	0.33	0.33	1.00	1.00	1.00	0.34	0.02
Reliability	0.14	0.14	0.13	0.20	0.33	0.33	1.00	1.00	1.00	0.34	0.02
Easiness of maintenance/operation	0.14	0.14	0.13	0.20	0.33	0.33	1.00	1.00	1.00	0.34	0.02

Environmental friendliness	Range of treatment	Removal efficiency	Total costs	Energy consumption	Chemical dosing	By products/waste production	Flexibility	Reliability	Easiness of maintenance/operation	Geom. mean	Weight
Range of treatment	1.00	1.00	4.00	0.33	0.33	0.33	6.00	6.00	6.00	1.47	0.11
Removal efficiency	1.00	1.00	4.00	0.33	0.33	0.33	6.00	6.00	6.00	1.47	0.11
Total costs	0.25	0.25	1.00	0.20	0.20	0.20	5.00	5.00	5.00	0.73	0.06
Energy consumption	3.00	3.00	5.00	1.00	1.00	1.00	7.00	7.00	7.00	2.92	0.22
Chemical dosing	3.00	3.00	5.00	1.00	1.00	1.00	7.00	7.00	7.00	2.92	0.22
By products/waste production	3.00	3.00	5.00	1.00	1.00	1.00	7.00	7.00	7.00	2.92	0.22
Flexibility	0.17	0.17	0.20	0.14	0.14	0.14	1.00	1.00	1.00	0.29	0.02
Reliability	0.17	0.17	0.20	0.14	0.14	0.14	1.00	1.00	1.00	0.29	0.02
Easiness of maintenance/operation	0.17	0.17	0.20	0.14	0.14	0.14	1.00	1.00	1.00	0.29	0.02

Technological aspects	Range of treatment	Removal efficiency	Total costs	Energy consumption	Chemical dosing	By products/waste production	Flexibility	Reliability	Easiness of maintenance/operation	Geom. mean	Weight
Range of treatment	1.00	1.00	1.00	1.00	1.00	1.00	0.33	0.33	0.33	0.69	0.06
Removal efficiency	1.00	1.00	1.00	1.00	1.00	1.00	0.33	0.33	0.33	0.69	0.06
Total costs	1.00	1.00	1.00	1.00	0.33	0.33	0.25	0.25	0.25	0.49	0.04
Energy consumption	1.00	1.00	1.00	1.00	0.33	0.33	0.20	0.20	0.20	0.46	0.04
Chemical dosing	1.00	1.00	3.00	3.00	1.00	1.00	0.17	0.17	0.17	0.70	0.06
By products/waste production	1.00	1.00	3.00	3.00	1.00	1.00	0.17	0.17	0.17	0.70	0.06
Flexibility	3.00	3.00	4.00	5.00	6.00	6.00	1.00	1.00	1.00	2.65	0.23
Reliability	3.00	3.00	4.00	5.00	6.00	6.00	1.00	1.00	1.00	2.65	0.23
Easiness of maintenance/operation	3.00	3.00	4.00	5.00	6.00	6.00	1.00	1.00	1.00	2.65	0.23

F.2 Pairwise technology comparison

How much better is technology A (rows, i) compared to technology B (columns, j)?

Equally good	1
Moderately better	3
Strongly advantageous	5
Very strongly advantageous	7
Overwhelmingly better	9

Range of treatment (RT)	Arvia ODC	Activated carbon	Ozonation/ ozone based AOP	UV/H2O2 AOP	Membrane bioreactor	Membrane process	Score	Ratio
Arvia ODC	1.00	4.00	7.00	7.00	5.00	6.00	4.25	0.48
Activated carbon	0.25	1.00	5.00	5.00	3.00	4.00	2.05	0.23
Ozonation/ ozone based AOP	0.14	0.20	1.00	1.00	2.00	4.00	0.78	0.09
UV/H2O2 AOP	0.14	0.25	1.00	1.00	2.00	4.00	0.81	0.09
Membrane bioreactor	0.20	0.33	0.50	0.50	1.00	3.00	0.61	0.07
Membrane process	0.17	0.20	0.25	0.25	0.33	1.00	0.30	0.03

Micropollutants removal (MPR)	Arvia ODC	Activated carbon	Ozonation/ ozone based AOP	UV/H2O2 AOP	Membrane bioreactor	Membrane process	Score	Ratio
Arvia ODC	1.00	0.50	2.00	2.00	0.50	4.00	1.26	0.14
Activated carbon	2.00	1.00	3.00	3.00	1.00	5.00	2.12	0.24
Ozonation/ ozone based AOP	0.50	0.33	1.00	1.00	0.33	3.00	0.74	0.08
UV/H2O2 AOP	0.50	0.33	1.00	1.00	0.33	3.00	0.74	0.08
Membrane bioreactor	2.00	1.00	3.00	3.00	1.00	5.00	2.12	0.24
Membrane process	0.25	0.20	0.33	0.33	0.20	1.00	0.32	0.04

Total costs (TC)	Arvia ODC	GAC	Ozonation/ ozone based AOP	UV/H2O2 AOP	Membrane bioreactor	Membrane process	Score	Ratio
Arvia ODC	1.00	7.00	3.00	5.00	9.00	8.00	4.43	0.50
GAC	0.14	1.00	0.20	0.33	5.00	4.00	0.76	0.09
Ozonation/ozone based AOP	0.33	5.00	1.00	3.00	7.00	6.00	2.44	0.28
UV/H2O2 AOP	0.20	3.00	0.33	1.00	6.00	5.00	1.35	0.15
Membrane bioreactor	0.11	0.17	0.14	0.17	1.00	0.50	0.25	0.03
Membrane process	0.13	0.20	0.17	0.20	2.00	1.00	0.34	0.04

Energy consumption (EC)	Arvia ODC	GAC	Ozonation/ ozone based AOP	UV/H2O2 AOP	Membrane bioreactor	Membrane process	Score	Ratio
Arvia ODC	1.00	3.00	9.00	9.00	4.00	7.00	4.35	0.49
GAC	0.33	1.00	6.00	6.00	4.00	5.00	2.49	0.28
Ozonation/ozone based AOP	0.11	0.17	1.00	1.00	0.14	0.20	0.28	0.03
UV/H2O2 AOP	0.11	0.17	1.00	1.00	0.14	0.20	0.28	0.03
Membrane bioreactor	0.25	0.25	7.00	7.00	1.00	3.00	1.45	0.16
Membrane process	0.14	0.20	5.00	5.00	0.33	1.00	0.79	0.09

Chemical use (CU)	Arvia ODC	GAC	Ozonation/ ozone based AOP	UV/H2O2 AOP	Membrane bioreactor	Membrane process	Score	Ratio
Arvia ODC	1.00	1.00	7.00	1.00	5.00	5.00	2.37	0.27
GAC	1.00	1.00	7.00	1.00	5.00	5.00	2.37	0.27
Ozonation/ozone based AOP	0.14	0.14	1.00	0.14	3.00	3.00	0.55	0.06
UV/H2O2 AOP	1.00	1.00	7.00	1.00	5.00	5.00	2.37	0.27
Membrane bioreactor	0.20	0.20	0.33	0.20	1.00	1.00	0.37	0.04
Membrane process	0.20	0.20	0.33	0.20	1.00	1.00	0.37	0.04

Production of waste and by-products (BWP)	Arvia ODC	GAC	Ozonation/ ozone based AOP	UV/H2O2 AOP	Membrane bioreactor	Membrane process	Score	Ratio
Arvia ODC	1.00	3.00	5.00	5.00	3.00	2.00	2.77	0.31
GAC	0.33	1.00	4.00	4.00	1.00	0.33	1.10	0.13
Ozonation/ozone based AOP	0.20	0.25	1.00	1.00	0.33	0.20	0.39	0.04
UV/H2O2 AOP	0.20	0.25	1.00	1.00	0.33	0.20	0.39	0.04
Membrane bioreactor	0.33	1.00	3.00	3.00	1.00	0.33	1.00	0.11
Membrane process	0.50	3.00	5.00	5.00	3.00	1.00	2.20	0.25

Flexibility (F)	Arvia ODC	GAC	Ozonation/ ozone based AOP	UV/H2O2 AOP	Membrane bioreactor	Membrane process	Score	Ratio
Arvia ODC	1.00	0.33	5.00	5.00	0.33	4.00	1.49	0.17
GAC	3.00	1.00	7.00	7.00	1.00	6.00	3.10	0.35
Ozonation/ozone based AOP	0.20	0.14	1.00	1.00	0.14	0.17	0.30	0.03
UV/H2O2 AOP	0.20	0.14	1.00	1.00	0.14	0.17	0.30	0.03
Membrane bioreactor	3.00	1.00	7.00	7.00	1.00	6.00	3.10	0.35
Membrane process	0.25	0.17	6.00	6.00	0.17	1.00	0.79	0.09

Reliability (R)	Arvia ODC	GAC	Ozonation/ ozone based AOP	UV/H2O2 AOP	Membrane bioreactor	Membrane process	Score	Ratio
Arvia ODC	1.00	1.00	5.00	5.00	0.33	0.33	1.19	0.13
GAC	1.00	1.00	5.00	5.00	0.33	0.33	1.19	0.13
Ozonation/ozone based AOP	0.20	0.25	1.00	1.00	0.17	0.17	0.33	0.04
UV/H2O2 AOP	0.20	0.25	1.00	1.00	0.17	0.17	0.33	0.04
Membrane bioreactor	3.00	3.00	6.00	6.00	1.00	1.00	2.62	0.30
Membrane process	3.00	3.00	6.00	6.00	1.00	1.00	2.62	0.30

Easiness of maintenance and operation (EMO)	Arvia ODC	GAC	Ozonation/ ozone based AOP	UV/H2O2 AOP	Membrane bioreactor	Membrane process	Score	
Arvia ODC	1.00	3.00	9.00	7.00	8.00	8.00	4.79	0.54
GAC	0.33	1.00	7.00	8.00	5.00	5.00	2.79	0.32
Ozonation/ozone based AOP	0.11	0.11	1.00	0.33	0.25	0.25	0.25	0.03
UV/H2O2 AOP	0.14	0.14	3.00	1.00	3.00	3.00	0.91	0.10
Membrane bioreactor	0.13	0.13	4.00	0.33	1.00	1.00	0.52	0.06
Membrane process	0.13	0.13	4.00	0.33	1.00	1.00	0.52	0.06

