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Removal of pharmaceuticals from WWTP effluent

KWR Watercycle Research Institute

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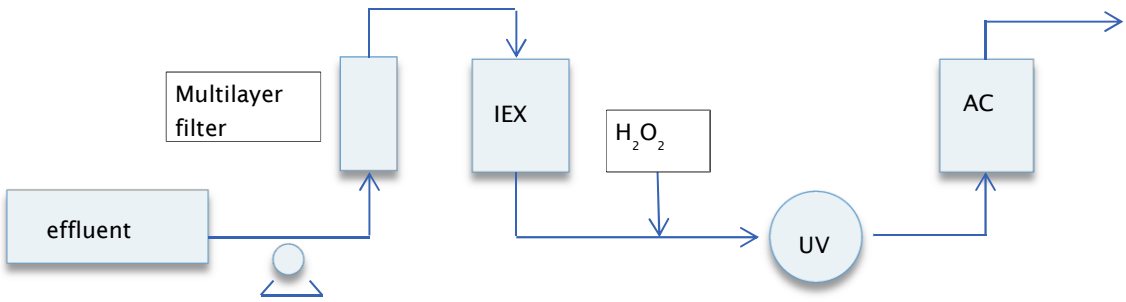
TKI *Managementsamenvatting*

Verwijdering geneesmiddelen uit RWZI-effluent via een twee-traps proces

Auteurs Roberta Hofman-Caris, Wolter Siegers, Jan Hofman

In steeds meer landen wordt onderzoek gedaan naar de verwijdering van geneesmiddelen uit RWZI-effluent, om te voorkomen dat geneesmiddelen, en hun metabolieten, in oppervlaktewater terechtkomen. Geavanceerde oxidatietechnieken worden veel toegepast voor drinkwaterzuivering, maar zijn minder effectief in RWZI-effluent omdat daar veel hogere concentraties slecht biologisch afbreekbaar organisch materiaal voorkomen (gemiddeld 35 mg/L). Door (een deel van) dit materiaal eerst te verwijderen, met behulp van ionenwisseling (IEX) of ozon/biofiltratie, wordt geavanceerde oxidatie veel effectiever en efficiënter. De kosten van het gecombineerde proces liggen daardoor in dezelfde grootte-orde als de kosten voor processen gebaseerd op ozon of actieve kool, maar op deze manier kan een breder scala aan verontreinigingen worden verwijderd.



Schematisch overzicht van additionele zuivering bestaande uit een multilaags filter (voor verwijdering van zwevende stof), IEX, UV/H_2O_2 en Actieve Kool filtratie

Belang: Voorkomen dat geneesmiddelen en hun metabolieten in oppervlaktewater terechtkomen

De meeste RWZI's zijn niet ontworpen voor het verwijderen van geneesmiddelen en hun metabolieten, en kunnen die daarom slechts ten dele (60-70%) verwijderen. Op het ogenblik bevat RWZI-effluent 14-30 µg geneesmiddelen per L. Aangezien het gebruik van geneesmiddelen voortdurend toeneemt (o.a. door de vergrijzing; verwachte toename bijna 40% in 2050), en er door klimaatverandering langere periodes van droogte voorkomen, kan daardoor het gehalte in oppervlaktewater ook toenemen. Dit heeft gevolgen voor het milieu en de drinkwatervoorziening. Daarom wordt het steeds belangrijker om geneesmiddelen uit RWZI-effluent te verwijderen. Momenteel staan er twee hormonen en één geneesmiddel (diclofenac) op de EU-watch list, maar het is de verwachting dat hier in de toekomst meer geneesmiddelen aan zullen worden toegevoegd. Dit zal naar verwachting leiden tot normen voor geneesmiddelen in oppervlaktewater (Kaderrichtlijn Water, en de Environmental Quality Standards Directive (EQSD)).

Aanpak: Eerst verwijderen van organisch materiaal, daarna geavanceerde oxidatie (AOP).

Het onderzoek is uitgevoerd in het kader van de TKI-regeling Topsector Water. Partners waren Waterschapsbedrijf Limburg (WBL), Waterschap

Roer en Overmaas (WRO), Waterleidingmaatschappij Limburg (WML) en KWR Watercycle Research Institute.
Hoewel geavanceerde oxidatie zeer effectief is voor de afbraak van een breed scala aan geneesmiddelen, wordt het proces in effluent verstoord door de aanwezigheid van organisch materiaal (EfOM). Dit organisch materiaal is in dit onderzoek eerst verwijderd met behulp van IEX of ozon/biofiltratie. Vervolgens zijn de geneesmiddelen afgebroken met behulp van verschillende geavanceerde oxidatieprocessen (AOPs) (UV/H_2O_2, UV/O_3, O_3/H_2O_2, $UV/US/H_2O_2$). Nadat het principe op labschaal was uitgetest, zijn pilotexperimenten uitgevoerd op RWZI Panheel. Hierin zijn beide voorbehandelingsprocessen gecombineerd met UV/H_2O_2.

Resultaten: Grote verbetering in efficiëntie AOP.

Uit het onderzoek bleek dat met behulp van IEX vooral humuszuren worden verwijderd, terwijl ozon/biofiltratie met name de hydrofobe fractie van het EfOM verwijdert. Uit het pilot-onderzoek bleek dat het ozon/biofiltratie-proces in potentie erg interessant is, maar nog meer ontwikkeling vraagt dan IEX als voorbehandeling. Gedurende de pilot van ongeveer een half jaar bleek het gecombineerde IEX-UV/H_2O_2 proces zeer stabiel en betrouwbaar te lopen. Door ionenwisseling wordt de kwaliteit van het effluent zodanig verbeterd, dat het energieverbruik van een UV/H_2O_2 proces 84% afneemt. Hierdoor nemen de operationele kosten af, waardoor de totale kosten voor de zuivering in dezelfde grootteorde liggen als de kosten voor processen gebaseerd op ozon of actieve kool. Het voordeel van dit proces is echter dat een breder scala aan geneesmiddelen effectief verwijderd kan worden.

Implementatie: Effectieve en efficiënte verwijdering van geneesmiddelen uit RWZI-effluent.

Het is de verwachting dat er op den duur normen zullen komen voor de aanwezigheid van geneesmiddelen in RWZI-effluent, en dat bestaande RWZI-processen zullen moeten worden uitgebreid. Het hier onderzochte twee-staps proces is een effectieve manier om een heel breed scala aan geneesmiddelen af te breken. Door eerst een deel van het EfOM te verwijderen met behulp van IEX wordt het AOP veel efficiënter, waardoor de kosten van het IEX-UV/H_2O_2 proces vergelijkbaar zijn met kosten van andere aanvullende processen, terwijl het heel breed toepasbaar is. Bovendien is bewezen dat het een bijzonder robuust proces is. Het IEX-UV/H_2O_2 proces is daarmee een interessante optie als aanvulling op een regulier RWZI-proces.

Rapport

Dit onderzoek is beschreven in rapport KWR 2016.064

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Uitgebreide samenvatting

Het gebruik van geneesmiddelen neemt steeds meer toe, en het zuiveringsproces van RWZI's is daarvoor eigenlijk niet ontworpen. Op het ogenblik kan een RWZI ongeveer 60-70% van de geneesmiddelen in het afvalwater verwijderen, waarbij het rendement per geneesmiddel verschilt. Het is de verwachting dat dat in de toekomst niet meer voldoende zal zijn, door toenemende concentraties in het influent. Bovendien wordt verwacht dat er vanuit de EU normen gesteld zullen worden aan de concentraties die geloosd mogen worden op oppervlaktewater (niet voor niets zijn al enkele stoffen op de "Watch List" geplaatst). Technieken die voor de zuivering van drinkwater worden toegepast zijn meestal minder effectief in afvalwater, doordat het gehalte organisch materiaal (EfOM) hierin vrij hoog is. Gangbare technieken, waarnaar in Zwitserland en Duitsland onderzoek wordt gedaan, zijn ozonisatie en actiefkoolfiltratie. Het idee bij dit onderzoek was dat afbraak- of verwijderingstechnieken effectiever worden wanneer het EfOM eerst wordt verwijderd of afgebroken.

De hypothese dat verwijdering van EfOM leidt tot een effectievere verwijdering van geneesmiddelen is in dit TKI-project onderzocht op lab- en pilotschaal. Dit project is uitgevoerd in het kader van de TKI-regeling Topsector Water, in samenwerking met bedrijfsleven (PureBlue Water), onderzoeksinstituut (KWR), Waterschapsbedrijf Limburg, Waterschap Roer en Overmaas en Waterleidingmaatschappij Limburg.

KWR heeft het onderzoek opgezet en samen met PureBlue Water de laboratoriumproeven uitgevoerd. Vervolgens heeft PureBlue Water de proefinstallatie geleverd, waarin het onderzoek is uitgevoerd door PureBlue Water en KWR samen. De ionenwisselaarshars en kennis over ionenwisseling voor zowel het lab- als pilotonderzoek werden geleverd door Lanxess. WBL heeft advies uitgebracht over de uit te voeren pilotproef, en die pilotproef vervolgens gefaciliteerd bij RWZI Panheel. Bovendien heeft WBL, net als WRO, WML, PureBlue Water, en KWR specifieke kennis ingebracht in dit project. KWR heeft de resultaten van de experimenten geanalyseerd en gerapporteerd.

In eerste instantie is geïnventariseerd wat de concentratie en samenstelling van het EfOM is in het effluent van verschillende RWZI's in Nederland. Hierbij is ook gemeten welke geneesmiddelen in het effluent voorkomen, en wat het totale gehalte aan geneesmiddelen is.

Op basis van deze experimenten is besloten het effluent van RWZI Panheel als uitgangsmateriaal te nemen voor laboratoriumexperimenten. Hierop zijn twee verschillende voorbehandelingstechnieken toegepast:

- Ozon/biofiltratie: waarbij vooral het hydrofobe deel van het EfOM bleek te worden afgebroken
- Ionenwisseling (IEX): waarbij met name de negatief geladen humuszuurfractie werd verwijderd

Beide voorbehandelingstechnieken bleken in staat een deel van de geneesmiddelen ook te kunnen verwijderen: ozon/biofiltratie brak vooral "elektronenrijke verbindingen" af (zoals metoprolol en atenolol), terwijl IEX met name negatief geladen moleculen verwijderde (als diatrizoïnezuur en diclofenac).

Als vervolgtechniek voor de zuivering werden hierna op het laboratorium de volgende technieken bestudeerd:

- Filtratie over actieve kool
- UV/waterstofperoxide
- Ozon/waterstofperoxide
- Ozon/UV
- UV/waterstofperoxide/ultrasoon (US)

Hierbij werd gekeken naar de omzetting van geneesmiddelen, en de omzetting of mogelijke vorming van metabolieten.

De verwijdering van een deel van het EfOM bleek relatief weinig effect te hebben op de effectiviteit van filtratie over actieve kool.

Processen gebaseerd op ozon bleken veel geneesmiddelen goed te kunnen afbreken, maar deze processen zijn niet geoptimaliseerd wat betreft ozongehaltes. Aangezien het water in Nederland vaak relatief veel bromide bevat, wordt de toepassing van ozon in de praktijk beperkt door de vorming van het carcinogene bromaat. Voor drinkwater geldt een limiet van 1 μg/L, maar indien ozon wordt gebruikt voor desinfectie is dit 5 μg/L.

Het UV/H_2O_2-proces kan een breed scala aan geneesmiddelen afbreken, maar staat erom bekend dat het vrij veel energie kost. Uit de experimenten bleek dat het energieverbruik van dit proces door de voorbehandeling 84% afnam! Er was een veel lagere UV-dosis nodig om voldoende verwijdering van geneesmiddelen en metabolieten te verkrijgen, maar wanneer een te lage UV-dosis wordt toegepast is het mogelijk dat er transformatieproducten/metabolieten ontstaan of onvoldoende worden afgebroken. Hier moet bij optimalisering van het proces rekening mee gehouden worden. Overigens bleek dat toepassen van ultrasoon tijdens dit proces geen invloed had op de afbraak van medicijnen.

Op basis van de resultaten is besloten een pilot-onderzoek uit te voeren bij RWZI Panheel. Op deze RWZI werd een kleine deelstroom van het effluent behandeld. Aangezien in de pilot werd gewerkt met een vast bed filtratie voor IEX, werd een voorfiltratiestap toegepast om deeltjes te verwijderen werd een voorfiltratiestap toegepast. In het pilotonderzoek werden de volgende combinaties van technieken getest:

- Voorbehandeling met voorfiltratie, ozon/biofiltratie, gevolgd door UV/waterstofperoxide
- Voorbehandeling met voorfiltratie, ionenwisseling, gevolgd door UV/waterstofperoxide
- Behandeling met voorfiltratie, ozon/UV/biofiltratie

Om praktische redenen is voor de ionenwisseling in de pilot gekozen voor een vast bed, waardoor voorfiltratie noodzakelijk was (bij een “fluidized bed” zou dit waarschijnlijk niet nodig zijn). Voorfiltratie vond plaats in een hoogbelast multimediafilter, met een debiet van 1100 tot 1400 L/uur. Met het gefiltreerde effluent werd een tank van 1000 L gevoed, waarmee de vervolgexperimenten werden uitgevoerd. De verblijftijd in de ozon/bioreactor was 9,5 min., het debiet door de ozon/UV(US)/biofiltratie-eenheid bedroeg 250 L/uur . Het debiet in de UV/H_2O_2 reactor werd zodanig ingesteld, dat de gewenste UV-dosis (150 of 300 mJ/cm^2) kon worden bereikt. Deze UV-dosis is erg laag, want bij toepassing van een UV/H_2O_2

proces voor drinkwaterzuivering wordt in de regel een UV-dosis van 500-600 mJ/cm^2 toegepast.

Tijdens het pilotonderzoek deden zich enkele praktische problemen voor met de ozon/biofiltratie-opstelling, waardoor het niet goed mogelijk is betrouwbare conclusies te trekken uit deze serie experimenten. Het IEX-UV/H_2O_2 proces bleek erg robuust, effectief en efficiënt te zijn: vrijwel alle geteste geneesmiddelen werden in hoge mate verwijderd, er is niet aangetoond dat er metabolieten gevormd werden, en het energieverbruik van de UV-reactor lag inderdaad veel lager (meer dan 80%) dan bij onbehandeld RWZI-effluent.

Uit dit onderzoek zijn de volgende conclusies getrokken:

1. RWZI-effluent bevat grote hoeveelheden organisch materiaal (10-20 mg/L) en significante concentraties geneesmiddelen (30-40 µg/L).
2. Ozon/biofiltratie verwijdert vooral de hydrofobe fractie van het EfOM, ionenwisseling verwijdert de negatief geladen humuszuren. Beide technieken kunnen ook een deel van de geneesmiddelen verwijderen, afhankelijk van de aard van die geneesmiddelen (ozonprocessen verwijderen vooral “elektronenrijke” moleculen, terwijl ionenwisseling negatief geladen moleculen verwijdert).
3. UV in combinatie met US levert geen extra verwijdering van geneesmiddelen op.
4. Het ionenwisseling-UV/waterstofperoxide proces is een robuust proces en bijzonder effectief voor de omzetting van een heel breed scala aan geneesmiddelen.
5. Het UV/waterstofperoxide proces is significant effectiever na verwijdering van (een deel van) het EfOM; de energiekosten nemen aanzienlijk af doordat een lagere dosis voldoende is, en minder energie nodig is om die dosis te bereiken (vanwege een hogere UV-transmissie).
6. Dit (totale) proces zal ongeveer € 0,35/m^3 kosten, wat in dezelfde grootteorde is als de kosten voor processen beschreven door STOWA (ozon, snelle zandfiltratie en filtratie over actieve kool).
7. Metabolieten worden ook effectief omgezet; er is geen significante vorming van metabolieten waargenomen tijdens het pilotonderzoek. Wel moet bij de optimalisatie van het proces rekening worden gehouden met een eventuele vorming van metabolieten.
8. Het ozon/biofiltratie proces is veelbelovend, maar er is nog aanvullend onderzoek nodig om het proces optimaal te laten verlopen. Groot voordeel van deze combinatie van technieken is dat er geen reststromen zijn.
9. Behandeling en mogelijkheden voor eventueel hergebruik van het IEX-regeneraat moeten nog onderzoek worden. Dit maakte geen deel uit van het huidige onderzoeksproject.

Dit TKI-onderzoek is gestart op een Technology Readyness Level 2/3, en is wat het IEX-UV/H_2O_2 proces betreft uitgekomen op level 6/7. Punten die nog aandacht behoeven voordat het op grote schaal (niveau 9) kan worden toegepast zijn:

- De noodzaak van een voorfiltratie-stap. Bij toepassing van een “fluidized bed” reactor voor de ionenwisseling is deze stap wellicht overbodig.
- De verwerking en eventueel hergebruik van het IEX-concentraat.
- De bedrijfszekerheid
- Gebruik van chemicaliën en energie over langere termijn, en daarmee de totale kosten van het proces.

- De milieu-impact van het proces (een life cycle analysis)
- Procesregeling en –automatisering.

Abstract

The number and amounts of pharmaceuticals used are increasing, and it is expected that they will continue to increase in next future. WWTPs in general have not been designed to deal with such compounds, as a result of which at present they can only remove 60-70% of the pharmaceuticals. Thus, these pharmaceuticals end up in surface waters, which also are important sources for drinking water production. At the moment there are no standards for the presence of pharmaceuticals in surface water, but as already some compounds have been placed on a EU Watch-list, it is to be expected that in the near future such standards will be set, in order to protect surface waters and sources of drinking water. This, in combination with the expected increase in loads, was the reason to investigate the possibilities to remove pharmaceuticals from WWTP effluent.

From literature it is known that organic material may interfere with treatment methods, aiming at removal of organic micropollutants, like pharmaceuticals. They compete with the micropollutants for adsorption spots, reduce the effectiveness of oxidation techniques, and cause fouling of e.g. membranes.

In this research first the effluent of severals WWTPs throughout the Netherlands has been analyzed. It was found that the composition of the Effluent Organic Matter (EfOM) is more or less comparable, but that there are differences in the concentrations present. A major part of the EfOM consists of humic acids. Furthermore, it was shown that effluent contains 14-30 μg of pharmaceuticals per liter, with an average of about 16 μg/L.

Within the framework of this TKI-project it was studied whether the removal of (part of) the EfOM prior to further treatment aiming at removal or decomposition of the pharmaceuticals would be beneficial for the total process.

In laboratory research two different pre-treatment techniques were studied:

1. Application of an ion exchange resin (IEX), which appeared to mainly remove the humic acid fraction
2. Application of ozone/biofiltration, which mainly removed the hydrophobic fraction of the EfOM

Both pre-treatment techniques were followed by several treatment techniques (three advanced oxidation techniques and one adsorption technique):

1. O_3/H_2O_2
2. O_3/UV
3. UV/H_2O_2
4. UV/US/H_2O_2
5. Filtration over granular activated carbon (GAC)

It was found that pre-treatment was not very beneficial for further treatment with activated carbon. However, it appeared to significantly increase the efficiency of advanced oxidation

processes. It was found that especially in case of a UV/H_2O_2 process a significant decrease in energy demand could be obtained (>80%), and that the majority of pharmaceuticals could be degraded to a high level (>80%) (UV in combination with US didn't result in additional pharmaceutical removal). Based on the results a pilot set-up was designed, which has been built at the WWTP of Panheel.

In the pilot the following processes were studied:

1. Filtration over IEX, followed by UV/H_2O_2
2. O_3/biofiltration, followed by UV/H_2O_2
3. O_3/UV/biofiltration

NB. It was found that the presence of US in the UV reactor didn't result in additional pharmaceutical removal, and thus the UV/US/H_2O_2 process can be considered as a regular UV/H_2O_2 process.

In order to prevent problems with particulate matter in the pilot, the water first was filtrated over a multimedia filter. Furthermore, a GAC filter was applied afterwards, mainly to remove the excess of H_2O_2 used, but also to remove any byproducts that might have been formed, as pharmaceuticals were dosed during testing.

At the start of the pilot investigation some problems occurred with the pumps. As a result of this, the pilot process had to be temporarily stopped. The IEX filtration fully recovered from this downtime, but the O_3/biofiltration process didn't. Therefore, more research will be required to make the O_3/biofiltration process more efficient.

It was found that advanced oxidation of pharmaceuticals performed better after (partial) removal of the EfOM during pre-treatment. Furthermore, best results in this case were obtained for the combination of IEX with UV/H_2O_2. Because of the removal of the humic acid fraction, a low UV-dose (of about 150 mJ/cm^2) appeared to be sufficient. Besides, it was shown that the UV-T of the water was significantly increased , as a result of which less than 20% of the amount of energy was required to obtain the UV-dose desired. Besides, the IEX pre-treatment was proven to be very robust, and it was possible to keep it running for some months without any problems.

Surprisingly, the O_3/biofiltration process with integrated UV seemed to perform less well than the O_3/biofiltration itself. This may be explained from the presence of relatively high concentrations of EfOM during the O_3/biofiltration process, but the results may also have been influenced by the operational problems encountered with the O_3/biofiltration process.

For the IEX/UV-H_2O_2 process cost estimations were made. It was found that the process applied here, consisting of pre-filtration (using a multi-media filter)/IEX/UV-H_2O_2/GAC, was very robust and very effective for the removal of a broad range of pharmaceuticals. The estimated costs are in the same order of magnitude as costs calculated previously for ozone or activated carbon based processes. However, the process described here, will probably be more effective, as is suitable for a broader range of pollutants.

Contents

1 Abbreviations

AC	activated carbon
AOC	assimilable organic carbon
AOP	advanced oxidation process
BB	building blocks
BP	biopolymers
COD	chemical oxygen demand
DOC	dissolved organic carbon
EBCT	empty bed contact time
EC	electric conductivity
GAC	granular activated carbon
EfOM	effluent organic matter
FEEM	fluorescence excitation emission matrix
HOC	hydrophobic organic carbon
HRT	hydraulic retention time
HS	humic substances
IEX	ion exchange
LC-OCD	liquid chromatography-organic carbon detection
LMW-a	low molecular weight acids
LMW-n	low molecular weight neutrals
MBR	membrane bioreactor
NOM	natural organic matter
PAC	powdered activated carbon

PAH	polycyclic aromatic hydrocarbons
PFD	process flow diagram
PRAM	polarity rapid assessment method
SEC	size exclusion chromatorgraphy
SMPs	soluble micriological products
SPE	solid phase extraction
SUVA	specific UV absorption
TOC	total organic carbon
US	Ultrasound
UV	ultraviolet
UV-T	UV-transmission
VUV	vacuum ultra violet
WWTP	wastewater treatment plant
XAD	crosslinked non or low polar aromatic copolymer

2 Introduction

2.1 General

The presence of pharmaceuticals and their metabolites in surface water is a threat to the ecological water quality and to sources of drinking water. Although it is not yet completely clear what the effects of the presence of these compounds are, the subject has aroused interest of politicians. In a recent letter, written by Mrs. W. Mansveld, deputy minister of Infrastructure and Environment (Kenmerk IENM/BSK-2013/63031)[1] it is acknowledged that risks caused by the presence of pharmaceuticals in the environment cannot be excluded, and that it is a social task to decrease the load of pharmaceuticals and other micropollutants in surface water. It is noted that only aiming at a source-oriented approach (efficient use of pharmaceuticals) will not result in a complete solution of the problem, and thus additional measures will be required in the water cycle. Part of dealing with this social task is to discuss with the water sector where and when additional treatment processes will have to be incorporated.

There is a European trend to remove pharmaceuticals in wastewater treatment plants (WWTPs), in order to prevent these compounds from entering the surface water. Some of them have been put on a watch list (EU decision 2015/495) (Barbosa, Moreira et al. 2016). Recently, the Swiss government decided to incorporate an additional treatment process in all WWTPs. Also Germany and France are taking such measures (Mulder, Antakyali et al. 2015). In case this trend will continue, there will be an important demand for effective removal technologies at minimum costs. In the Netherlands there are more than 350 WWTPs, on a European level there are several thousands of WWTPs. Even if additional treatment will only be realized at “large” WWTPs to remove an important part of the load of pharmaceuticals, the potential market is huge. Previous research into this issues within the water cycle of the Dutch province of Limburg in 2011 and 2012 (Hofman, Huiting et al. 2013; Laak, Tolkamp et al. 2013) showed that additional treatment at the WWTP results in an improvement of the surface water quality.

Present techniques to remove micropollutants from wastewater, however, are expensive and have been poorly investigated. Research by Grontmij (Vergouwen, Mulder et al. 2012), commissioned by the parliament, predicts an increase in the costs for wastewater treatment of M€ 560 per year in case all Dutch WWTPs should have to be extended with activated carbon filtration. Application of ozone in combination with activated carbon would even result in a cost increase of M€ 820 per year.

The high costs involved in removing pharmaceuticals from WWTP effluent are caused by the relatively high content of organic matter (COD). This is composed of dissolved, hardly biodegradable components like humic acids. The presence of such compounds results in competition within the additional purification steps. As a result, pharmaceuticals will show a relatively quick breakthrough in activated carbon filters, as the carbon will rapidly become saturated with organic material, and oxidation processes will require high doses to obtain the effect desired. Ion Exchange (IEX) could remove part of the organic material (mainly

[1] http://www.rijksoverheid.nl/documenten-en-publicaties/kamerstukken/2013/06/25/geneesmiddelen-in-drinkwater-en-milieu.html

charged molecules, like humic acids), and thus may improve the effectiveness of downstream treatment processes, like activated carbon or advanced oxidation. Another interesting way to remove (part of) the effluent organic material (EfOM) is pre-treatment with ozone/biofiltration. In this process ozone oxidizes part of the organic compounds, making them better biodegradable in the biofilter.

2.2 Project set-up

In this project it is investigated how part of the EfOM can be removed from the effluent, in order to render subsequent removal of pharmaceuticals, metabolites and other organic micropollutants more effective.

In the first stage of the project WWTP effluents thoughout the country were studied. The concentration and composition of Effluent Organic Matter (EfOM) was determined, and the presence and concentration of a broad range of pharmaceuticals was analyzed. Subsequently, one WWTP (Panheel) was chosen for further experiments.

Then laboratory experiments were carried out, using effluent from this WWTP. In order to remove organic material ion exchange (IEX) and ozone/biofiltration were applied. IEX is based on filtration over columns containing positively charged resins, which can adsorb negatively charged compounds like humic acids. However, some negatively charged pharmaceuticals may be adsorbed too. Suitable ion exchange resins were selected which can remove the disturbing fractions of organic matter. After a while the resin will become fully loaded, but then it can be regenerated by rinsing with an aqueous NaCl solution. In the ozone/biofiltration process organic matter first is partly oxidized by means of ozone, and subsequently the water is fed to a biofilter. As a result of the oxidation process, the organic matter will have become better biodegradable, and thus can (partly) be removed by microorganisms in the biofilter. The advantage of this system is that it doesn't generate a wastestream. In case of IEX a concentrate will be generated, that will have to be treated or disposed of. However, for full scale application of the ozonation process special safety measures will have to be taken.

After pretreatment the water is treated with four different techniques to remove pharmaceuticals:

- Filtration over activated carbon
- Advanced oxidation based on O_3/H_2O_2
- Advanced oxidation based on UV/O_3
- Advanced oxidation based on UV/H_2O_2

KWR had already gained a lot of experience with these techniques in drinking water production, but the matrix in wastewater is much more complex.

Later, at PureBlue Water an additional set of experiments was carried out with water from WWTP Panheel. Part of this water was filtrated over the IEX colum, which also was used in the pilot set-up in Panheel. Both filtrated and non-filtrated water were treated with UV/H_2O_2 or with $UV/US/H_2O_2$.

Based on the results of the laboratory investigation, a pilot set-up was built at WWTP Panheel. Here both pretreatment techniques (IEX and O_3/biofiltration) were applied. In principle fluidized ion exchange (FIX) would be less sensitive to relatively high concentrations of

suspended matter than a fixed bed process, and thus more practical for application at a WWTP. However, as automatic regeneration of a fixed bed column was easier to realize, for this pilot it was chosen to use IEX, preceded by a multilayer filter to remove suspended matter. This multilayer filtration also was applied before the O_3/biofiltration process.

While either IEX or O_3/biofiltration was applied as a pretreatment method, as a downstream technique advanced oxidation by means of UV/H_2O_2 was studied (in fact the UV/US reactor was used, but as laboratory experiments showed that US doesn't interfere with the removal of pharmaceuticals or with the fate of transformation products, this can be considered as a regular UV/H_2O_2 reactor). Furthermore, also experiments were carried out with an integrated O_3/UV/biofiltration process.

In order to remove the excess of H_2O_2 from the UV/H_2O_2 process, and in order to ensure that no pharmaceuticals or byproducts/transformation products would enter the surface water during pilot experiments, the water was filtrated over activated carbon before it was discharged.

2.3 Project partners

The project was carried out within the framework of the Topconsortia for Knowledge & Innovation program of the Dutch ministry of Economic Affairs. Project partners are:

- PureBlue Water: technology supplier. PureBlue Water (formerly known as AWWS) provided knowledge on ozone processes and biofiltration, carried out the ozone and biofiltration experiments in the laboratory phase of the project, supplied the main part of the pilot plant, and was involved in the operation of the pilot plant at WWTP Panheel.
- Waterschapsbedrijf Limburg (WBL): end user. WBL provided knowledge on WWTPs, facilitated the pilot plant at WWTP Panheel, and supported its operation.
- Waterschap Roer en Overmaas (WRO): end user. WRO provided knowledge on WWTP processes.
- Waterleidingmaatschappij Limburg (WML). WML provided knowledge on water treatment.
- KWR Watercycle Research Institute: research institution. KWR provided knowledge, carried out part of the laboratory and pilot experiments, provided part of the pilot set-up, carried out the analyses, and was responsible for dissemination of the knowledge acquired.

The IEX resins were kindly supplied by Lanxess.

2.4 Choice of pharmaceuticals

Previous research (ter Laak, Kooij et al. 2014) showed that the type and concentrations of pharmaceuticals in surface water strongly depend on consumption patterns in the catchment areas of the rivers. Furthermore, it is known that there are national differences in preferred prescription of pharmaceuticals, and that pharmaceuticals can be degraded in WWTPs or in surface water to various extends. As a result, the type and concentrations of pharmaceuticals in surface water will show local variations.

In recent years attention has been paid to the occurrence and treatment of organic micropollutants. In international (European) projects different lists of pharmaceuticals were applied, depending on the countries involved. For the Dutch situation KWR has applied a

mixture of over 40 pharmaceuticals (and some metabolites), the choice of which depended on the following criteria:

- Presence in wastewater and/or surface water
- Broad range in properties (sensitivity towards e.g. oxidation and photolysis, adsorption properties)
- Availability and possibilities for analysis

In European projects like TAPES (Transnational Action Program on Emerging Substances) and DEMEAU (Demonstration of promising technologies to address emerging pollutants in water and wastewater) and Dutch projects, like PACAS (Powdered Activated Carbon in Activated Sludge) different extensive lists of organic micropollutants were applied. In many cases a short list was decided on, containing compounds which were studied by most partners. In an overview is given of some of these short lists containing pharmaceuticals, and which of these compounds are also used in the present investigation.

Table 2-1: Overview of pharmaceuticals studied in various (international) projects

Compound	Demeau	Swiss government, 1st list	Swiss government, 2nd list	TAPES	PACAS	This investigation
10,11-transdiol carbamazepine					x	x
Acetyl sulfamethoxazole					x	x
Amisulpride			x			
Azitromycin						
Bezafibrate	x					x
Candesartam			x			
Carbamazepine	x	x		x	x	x
Citalopram			x			
Clarithromycine			x		x	
Diatrizoate (or amidotrizoic acid)				x	x	x
Diclofenac	x	x	X	x	x	x
Erythromycin					x	x
Guanylureum					x	x
Ibuprofen					x	x
Iohexol					x	
Iomeprol					x	
Iopamidol					x	
Iopromide	x				x	
Iotalamic acid					x	
Irbesartam			x			
Hydrochloro thiazide			x			
Hydroxy-ibuprofen					x	
Metformin					x	x

Metoprolol	x		x	x	x	x
phenazone	x					x
primidone	x					
Sotalol					x	x
sulfamethoxazole	x	x		x	x	x
trimethoprim	x				x	x
Venlafaxine			x			x

N.B. In some cases not only pharmaceuticals but also other organic micropollutants, like benzotriazole and mecoprop, are included in the lists. However, these compounds are no pharmaceuticals, and therefore weren't included in this overview.

In recent years a lot of research into water treatment, both for wastewater and drinking water, has been done using atrazine as a reference compound. It is known that it is relatively difficult to remove this compound from water, and thus it was assumed that sufficient removal of atrazine would automatically imply sufficient removal of other organic micropollutants too. However, at the moment it is known that there are large differences in the behavior of different organic compounds in various treatment processes, and that removal of a certain compound does not mean that other compounds will be removed too. Furthermore, the use of atrazine is not allowed anymore. As a result another reference compound or set of reference compounds will be required.

As there are large differences in behavior of different compounds, it probably will be better to use a set of organic micropollutants as a reference. This set may depend on local conditions, as the occurrence of compounds also may depend on local conditions. Apart from occurrence, behavior in treatment processes and possitilities to analyze the compounds also will have to be taken into account. In this research a relatively extensive list of compounds is presented, which may be used to establish a short reference list. The exact composition of the short list, however, will be a strategic/political choice, which will have to be made by waterboards, drinking water companies and/or politics.

2.5 How to read the report

Chapter 3 gives an overview of recent literature on the characterization of organic material in effluent, and removal technologies for pharmaceuticals and other organic micropollutants.

Chapter 4 shows the composition of six WWTP effluents throughout the whole country. The concentrations and compositions of organic material in the effluent of six WWTPs was determined, not only based on BOD and COD, as is usual practice, but also by means of a chemical characterization. Furthermore, concentrations of pharmaceuticals and some of their (known) metabolites in these effluents were measured.

Chapters 5 and 6 deal with the small scale laboratory experiments that were carried out with WWTP effluent from WWTP Panheel. Chapter 4 gives the experimental details, chapter 5 the results and discussion. As a pre-treatment to remove (part of) the EfOM, IEX and ozone/biofiltration were applied. Subsequent treatment techniques studied were filtration over activated carbon, O_3/H_2O_2, O_3/UV and UV/H_2O_2. Based on the results obtained the pilot study was designed.

Chapters 7 and 8 show the set-up and the results of the pilot study respectively. This pilot study consisted of two possible pre-treatment steps (IEX and O_3/biofiltration) and UV/H_2O_2 as

a subsequent treatment for the removal of micropollutants. Besides, O_3/UV/biofiltration was studied as a separate, one-step, treatment process.

In chapter 9 all results are discussed, and a cost estimation is made for an extension of WWTP Panheel, including filtration/IEX/UV-H_2O_2/activated carbon. It is shown that this process is very effective and robust, and that the total costs are in the same order of magnitude as costs estimated for other processes, like filtration over activated carbon or ozonation.

Finally, conclusions and recommendations can be found in chapter 10.

3 Literature study

3.1 Introduction

In recent years it became clear that surface water contains more and increasing concentrations of pharmaceuticals (Rivera-Utrilla, Sánchez-Polo et al. 2013); (Luo, Guo et al. 2014);(Lekkerkerker-Teunissen, Knol et al. 2013);(Lindberg, Östman et al. 2014). It is expected that in the near future the presence of pharmaceuticals in surface water will increase as a result of increasing use of pharmaceuticals (e.g. as a result of aging; an increase of almost 40% is expected in 2050) (Van Der Aa, Kommer et al. 2011), and climate change (the influence of river discharge etc.) (Wuijts, Bak-Eijsberg et al. 2012). Awareness that pharmaceuticals occur in surface water, and thus also in sources for drinking water, is growing in various organizations, like hospitals and nursing homes, and in politics. The European Committee compiled a list of compounds which will have to be treated with priority within Europe (the "Water Framework Directive (WFD) List" 2000/60/EC, and the EQSD 2008/105/EC), and set environmental quality standards for these compounds. This list does not contain any pharmaceuticals, but recently a "watch list" was added with compounds which may be added to the list, including the pharmaceuticals 17-alpha-ethinylestradiol (EE2), 17-beta-estradiol (E2), and diclofenac (Barbosa, Moreira et al. 2016). According to the WFD all surface water within the EU member states will have to meet the environmental quality standards for pharmaceuticals that are considered priority compounds by 2021[2]. More and more initiatives are taken to study the extent of the problem, its effects, and techniques that can be applied to decrease or solve the problem. An example is the PILLS project (http://www.pills-project.eu/) , in which an international partnership of water boards, research institutes and hospitals cooperated to develop and test several installations to treat hospital wastewater. After the successful closure of the project, is was succeeded by the present project "noPILLS" (http://www.no-pills.eu/).

After use, pharmaceuticals are excreted via urine and feces, and via wastewater end up in WWTPs. These, however, have not been designed to remove such compounds (Michael, Rizzo et al. 2013; Luo, Guo et al. 2014). In general WWTP processes consist of a physico-chemical treatment, followed by biological treatment to remove organic material (COD), nitrogen and phosphate. Both do not focus on the removal of pharmaceuticals, and, according to some authors, the presence of pharmaceuticals may even be disadvantageous for the micro organisms which take care of the biological treatment of the water (Rivera-Utrilla, Sánchez-Polo et al. 2013). However, according to the STOWA report "Zorg-deel C" (Vergouwen, Pieters et al. 2011) for some compounds (like Dipyridamol, Bezafibrate, Cyclofosfamide, Ibuprofen, Levetiracetam, Fenazon and Quetiapine) the removal percentage in a WWTP can be higher than 80 %.

This literature study focusses on recent literature (after about 2010) on the removal of pharmaceuticals from WWTP effluent, and the role of (natural) organic material and possible inorganic compounds within these processes.

[2] http://www.rijkswaterstaat.nl/water/wetten_en_regelgeving/natuur_en_milieuwetten/kaderrichtlijn_water http://www.rivm.nl/Onderwerpen/K/Kaderrichtlijn_Water_KRW

3.2 Characterization of effluent organic material (EfOM)

The composition of effluent organic material (EfOM) can be characterized in various ways. In principle EfOM consists of a combination of natural organic material (NOM), originating from drinking water, which is the main component of wastewater, soluble microbiological products (SMPs) and micropollutants (Shon, Vigneswaran et al. 2008). In general EfOM consists for about 50% of proteins, 40% of carbohydrates, 10% fats and oils, and traces (≤μg/L) of organic micropollutants. It is also possible to make a classification based on particle size:

- Particulate organic carbon (> 0,45 μm)
- Dissolved organic carbon (< 0,45 μm). This also contains cell fragments and macromolecules.

SMPs end up in the water during the biological treatment, and originate either from the conversion of organic compounds by micro organisms, or from dead micro organisms. The SMPs contain humic acids, polysaccharides, proteins, amino acids, antibiotics, extra cellular enzymes, parts of the micro organisms themselves, and conversion products (Azami, Sarrafzadeh et al. 2012; Xie, Ni et al. 2013).

A common method to characterize organic material is by means of LC-OCD techniques (Huber, Balz et al. 2011). In this case the following classification is applied:

- Biopolymers (BP) with molecular weight (MW) >> 20.000
- Humic substances (HS) with MW ≈ 1000
- "Building blocks" (BB) with MW ≈ 300-500. (These are natural conversion products of humic substances)
- Neutral components with MW < 350
- Acidic components (LMW-acids) with MW < 350

Size exclusion Chromatography (SEC) often also is applied to determine the molecular weight distribution of the material.

Assimilable organic carbon (AOC) is a mixture of various fractions of organic material, which differ per type of water (Grefte 2013; Grefte, Rietveld et al. 2014). Grefte concluded that per type of water a specific linear relation can be observed between the average AOC concentration and the concentration of LMW-acids.

Important parameters in the characterization of EfOM and NOM are the aromaticity and the hydrophobicity of the material. Both variables are related. Often, the specific absorption at 254 nm (SUVA) is used for characterization. However, size distribution and SUVA are not necessarily related. Thus, coagulation largely affects the SUVA value, but may hardly affect the molecular weight of the DOC.

Fluorescence (FEEM) too is applied to characterize dissolved organic material from a biological treatment process (Rosario-Ortiz, Snyder et al. 2007). Rosario-Ortiz c.s. studied a method to determine the polarity of various EfOM fractions by means of the "polarity rapid assessment method" (PRAM). In this method water is extracted by means of various adsorbents (solid phase extraction, SPE). Apart from the hydrophobic surface of the material (and its aromatic character), also the molecular weight and molecular weight distribution play an important role. Column materials used for this technique are e.g. C_2, C_8 and C_{18},

which show an increasing capacity for hydrophobic components. The most important parameter to characterize the various fractions is the difference in hydrophobic surface of the various components. Furthermore, dipole interactions and hydrogen bridging are used for characterization, for example by applying anion exchangers with NH_2 (a weak anion exchanger) and SAZ (a strong anion exchanger). This method is affected by the pH and ionic strength (Rosario-Ortiz, Snyder et al. 2007; Rosario-Ortiz, Snyder et al. 2007; Rosario-Ortiz, Mezyk et al. 2008; Rosario-Ortiz, Mezyk et al. 2008; Rosario-Ortiz, Wert et al. 2010).

The PRAM method differs from the commonly applied extraction using a XAD resin, as in the XAD method a low pH is applied and separation of the fractions is carried out in series instead of in a parallel execution. In XAD different fractions can be isolated and analyzed. Thus it is possible to determine a mass balance based on the XAD method, whereas this cannot be done using the PRAM results (Rosario-Ortiz, Snyder et al. 2007).

3.3 Effect of EfOM and inorganic components on wastewater treatment processes.

Several treatment techniques are known, which in principle could be applied to remove organic micropollutants, like pharmaceuticals, from wastewater. However, the presence of EfOM and possibly inorganic components may negatively influence this. This paragraph gives a short overview.

3.3.1 Biological processes

Biological processes often cannot or only to a limited extend decompose organic micropollutants (although there are some examples of pharmaceuticals that can be decomposed to a relatively large extend (Vergouwen, Pieters et al. 2011). This certainly is the case for poly cyclic aromatic hydrocarbons (PAHs) (Rubio-Clemente, Torres-Palma et al. 2014), not only because of their low biodegradability, but also because they often are toxic to microorganisms.

3.3.2 Adsorption on activated carbon

Activated carbon often is applied in drinking water treatment. Sometimes powdered activated carbon (PAC) is applied, but in most cases granular activated carbon (GAC) is used. PAC is used only once, whereas GAC is regenerated after use. After some time the carbon surface is covered with all kinds of compounds, decreasing the adsorption capacity. GAC then has to be regenerated, which is a relatively expensive process. Adsorption often is based on hydrophobic interactions (like π-π interactions with aromatic compounds), but also electrostatic interactions and hydrogen bridging can occur (Rivera-Utrilla, Sánchez-Polo et al. 2013). The presence of EfOM in many cases is very disadvantageous for the application of adsorption techniques. The organic compounds compete with the organic micropollutants that will have to be removed, occupying adsorption spots at the carbon surface. Mainly HS and BB are known for this effect. As EfOM occurs in concentrations in the range of mg/L, whereas micropollutants only occur in the range of μg/L, the micropollutants are at a disadvantage. If relatively large molecules will have been adsorbed at the carbon surface, smaller organic micropollutants cannot be adsorbed anymore, and thus the total adsorption capacity is drastically decreased. Furthermore, especially compounds with a high molecular weight (like BP and HS) may block pores, as a result of which the activated carbon surface cannot be reached by micropollutants anymore (Quinlivan, Li et al. 2005; Hu, Martin et al. 2014). As a result of this so called “pore blocking” both adsorption capacity as well as adsorption rate will decrease. The effect can be decreased by adjusting the pore size distribution. Low molecular weight compounds, especially low molecular weight acids, hardly affect the adsorption process. Apart from the direct interaction between organic

micropollutants and EfOM on one hand, and the carbon surface on the other, also factors like ion strength, and pH play an important role in the adsorption process, as they may influence both the surface charge of the carbon and the configuration of the organic compounds.

3.3.3 Membrane filtration

Fouling is one of the problems that may occur when membrane filtration is applied as a treatment technique (another problem is dealing with the formed concentrate). Fouling may occur by microorganisms ("biofouling"), by dissolved organic carbon (DOC), organic colloidal particles and by inorganic compounds ("scaling") (Verliefde, Cornelissen et al. 2009; Farias, Howe et al. 2013).

In most cases the membrane surface carries a negative electrical charge (Bellona, Drewes et al. 2004). The polarity of the EfOM therefore is an important parameter which influences the effectivity of membrane filtration (Rosario-Ortiz, Snyder et al. 2007). According to Azami et al. (Azami, Sarrafzadeh et al. 2012) SMPs play an important role in membrane fouling. These SMPs can interact with the membrane surface, as was concluded from ζ-potential measurements. Furthermore, these compounds may act as a kind of binder for suspended flocs. Polymers, excreted by microorganisms, and proteins also may cause fouling of membranes (Farias, Howe et al. 2013).

3.3.4 (Advanced) oxidation processes (AOPs)

Oxidation processes are more and more applied to remove organic micropollutants from e.g. drinking water or wastewater. Organic and inorganic compounds in wastewater often negatively affect such processes by means of competition (Oller, Malato et al. 2011). In literature, various (advanced) oxidation processes for treatment of wastewater or drinking water are described, like processes based on ozone, on UV-irradiation, and Fenton processes (Velo-Gala, López-Peñalver et al. 2014). Such processes can also convert PAHs, although pH and temperature may affect the conversion (Rubio-Clemente, Torres-Palma et al. 2014). These authors give an overview of the costs that are involved with different types of processes.

An important disadvantage of oxidation processes, that requires special attention for implementation of such processes, is the possible formation of byproducts. In principle compounds can be mineralized (converted into CO_2 and H_2O), but in most cases this would require enormous amounts of energy. Thus, the oxidation is stopped before the mineralization level is reached. It then is assumed that smaller, partly converted, molecules are better biodegradable. It was shown that often this indeed is the case, but in some cases it has been shown that the byproducts formed may even be more toxic than the parent compounds (Oller, Malato et al. 2011). A famous example is tramadol, the metabolite of which is much more toxic than the parent compound itself.

The position of the oxidation process within the total treatment also may play an important role. Placing before the biological treatment step has the advantage that organic micropollutants, that are harmful to the microorganisms, can be removed before they can cause any harm to the microorganisms, and that better biodegradable compounds will be added to the microorganisms (Oller, Malato et al. 2011; Rivera-Utrilla, Sánchez-Polo et al. 2013). In general the micropollutant concentrations will be so low, that a negative effect on microorganisms is not to be expected. However, illegal discharge of chemicals from laboratories in which pharmaceuticals of abuse are synthesized may cause significantly

higher concentrations in the wastewater. If the AOP is placed before the biological treatment care will have to be taken that no byproducts are formed which may be harmful to microorganisms, and that the nutritive value of the converted compounds still will be high enough for the biodegradation. This may be regulated by adjusting the oxidation time. Another important aspect is that the oxidator itself (e.g. ozone or hydrogen peroxide) may be harmful for microorganisms, and therefore contact between the oxidator and the microorganisms will have to be prevented. In literature only limited information can be found on (advanced) oxidation processes combined with biological processes (Oller, Malato et al. 2011).

Worldwide processes based on ozone are most frequently applied to purify drinking water and wastewater. Either only ozone, or ozone combined with UV-irradiation or H_2O_2 are applied. As the composition of wastewater strongly differs from the composition of drinking water, process conditions will depend on the type of water. For wastewater treatment much higher ozone concentrations or UV doses are required than for drinking water production. In the Netherlands the application of ozone for drinking water production is limited, as the sources of drinking water contain relatively high bromide contents. Upon contact with ozone bromide is converted into the toxic bromate.

Switzerland recently decided to extend most of the WWTPs with an ozone process, in order to remove micropollutants like pharmaceuticals from the major part of the countries wastewater. At EAWAG a lot of research is done for this (Michael, Rizzo et al. 2013), partly within the framework of the European DEMEAU-project[3]. Besides that research is done into the effect of ozone treatment on the composition of hospital wastewater (Kovalova, Siegrist et al. 2013). These authors estimate the costs of wastewater treatment in Switzerland are about €1,70/m^3, which will increase up to €1,80/m^3 if an additional ozone process step will be implemented. In case organic material is present in the water, like clearly is the case for wastewater and WWTP effluent, part of the ozone will react with this material, increasing the ozone demand, or reducing the conversion of the micropollutants. The latter also is negatively affected by the presence of radical scavengers like carbonate and hydrogen carbonate (Rosario-Ortiz, Mezyk et al. 2008). In the Netherlands, (Mulder, Antakyali et al. 2015) have given an overview of estimated costs for the removal of pharmaceuticals from wastewater by means of ozonation/sand filtration (€0,16 - €0,22/m^3, depending on the capacity of the WWTP), powdered activated carbon (PAC)/sand filtration (€0,16 - €0,22/m^3) or filtration over granular activated carbon (GAC) (€0,16 - €0,22/m^3), based on research in Germany and Switzerland.

UV processes too are often applied for the conversion of organic micropollutants. Depending on the wavelength used organic compounds may absorb UV irradiation, and as a result decompose. The use of UV irradiation to generate radicals offers the possibility to decompose a much wider range of organic micropollutants. A common method is the combination of UV with H_2O_2, in which hydroxyl radicals are formed which are very effective oxidants for a large amount of organic compounds. Photocatalysis, in which UV irradiation generates radicals at the surface of e.g. TiO_2, also often is described in literature (Rivera-Utrilla, Sánchez-Polo et al. 2013; Choi, Lee et al. 2014; Mohapatra, Brar et al. 2014). However, although such processes have extensively been studied at a laboratory scale, hardly any full scale applications are known. Probably this is related to the fact that intensive contact between the reactive catalyst surface, the irradiation and the micropollutants is required,

[3] http://demeau-fp7.eu/

which is relatively difficult to realize on a large scale. In principle there are two possible solutions:

1. Using small (nano) particles. This has the advantage of a large surface area, but the disadvantage that the particles will have to be totally removed afterwards.
2. Applying TiO_2 coated reactors or reactor parts, for which both a high active surface area and a good fixation to the surface will be required.

It was found that the presence of nitrate and humic acids is disadvantageous for the conversion of organic micropollutants by means of advanced oxidation. This is caused by the fact that these compounds too can absorb UV irradiation, and may generate radicals, but may also scavenge radicals (Rosario-Ortiz, Snyder et al. 2007; Rosario-Ortiz, Wert et al. 2010; Rivera-Utrilla, Sánchez-Polo et al. 2013). Thus a higher UV dose, implicating a larger energy demand, will be required to degrade the organic micropollutants. How important this effect is will not only depend on the EfOM concentration, but also on its composition.

Azimi, Allen et al. (2014) describe the favorable effect of the presence of polyphosphate on UV disinfection. As polyphosphate under the influence of UV irradiation can form hydroxyl radicals, and during biological treatment processes accumulates in the form of flocs, inactivation of microorganisms within the flocs is stimulated. The authors even suggest that an AOP based on the combination of polyphosphate with UV may be possible. Brame, Long et al. (2014), however, regard the presence of phosphate, like that of organic material, as unfavorable for advanced oxidation processes. The advantage of hydroxyl radicals is that they unselectively react with all kinds of compounds, which, however, also makes them liable to scavenging. Therefore the authors state that NOM has a much larger negative effect on processes based on hydroxyl radicals, than on oxidation processes based on singlet oxygen, which is a much more specific oxidator. Phosphate might reduce the effectiveness of hydroxyl radicals at least with a factor 2. For their experiments they applied a background phosphate concentration of 60-3000 mg PO_4^{3-}/L. This is very high, as the Dutch effluent on the average contains 1 mg P/L or 3 mg PO_4^{3-}/L[4]. According to Keen, McKay et al. (2014) up to 95% of the capture and scavenging of hydroxyl radicals in effluent can be attributed to the presence of organic material. Thus, the influence of carbonate and hydrogen carbonate ions in this water is negligible. Nitrate reacts slowly with hydroxyl radicals, but nitrite, on the contrary, may be a disturbing factor. Nitrite can be formed from nitrate under the influence of UV irradiation (ca. 200 nm).

The role of metals during (advanced) oxidation processes seems to have received little attention thus far. It appears that some metals can dissolve as a result of oxidation (Gagnon, Turcotte et al. 2014). UV processes are believed to mainly oxidize zinc, whereas ozone more strongly affects cadmium and cupper. Often metals are removed in wastewater treatment, but in case only a physico-chemical treatment is applied significant amounts of metals may be released (in the Netherlands this doesn't happen, as here metals are removed together with the sludge). Often the metals are present in the form of complexes and thus don't affect biological processes. By UV irradiation (even caused by sunlight) or ozone treatment, however, they may be released and in that case can influence organisms (not only microorganisms, as the authors specifically studied the influence on mussels).

[4] http://statline.cbs.nl/StatWeb/publication/?DM=SLNL&PA=70152ned&D1=0-35,39,43&D2=0,3,6,12,17&D3=a&D4=l&VW=T

During processes based on US high-frequency sound, with a frequency between 2 and 10 MHz, or low-frequency sound, with a frequency between 20 and 100 kHz, is applied (Tijani, Fatoba et al. 2014). This causes caviation in the water: bubbles are formed which implode, causing local temperatures between 3000 and 5000 K and pressures between 500 and 10,000 atm. Under these circumstances water decomposes, resulting in the formation of hydroxyl radicals. However, also oxygen can be degraded. Organic micropollutants thus can be decomposed.

Chlorination of wastewater in order to obtain disinfection before discharge is not applied within the EU. In the VS a sanitation step is required before effluent discharge, and in most cases chlorine is applied. Chlorine compounds can react with organic micropollutants and with EfOM, resulting in the formation of chlorine-containing disinfection byproducts, which may harm public health (Rivera-Utrilla, Sánchez-Polo et al. 2013). Especially chlorine dioxide is a strong oxidator, which can react with various organic compounds. Especially if a compound contains functional groups with a high electron density (like tertiary amines and fenoxides) such reactions may occur. Also for the application of e.g. (advanced) oxidation processes this will have to be taken into account (Liu, Zhang et al. 2012; Rivera-Utrilla, Sánchez-Polo et al. 2013).

3.4 Removal of EfOM and other components

From the previous paragraph it can be concluded that the presence of EfOM may negatively affect the effectiveness of processes to remove organic micropollutants like pharmaceuticals from wastewater. EfOM competes with pharmaceuticals, causes fouling of membranes and adsorbents, and results in a relatively high chemical (like O_3 and H_2O_2) and energy (UV) demand. It is to be expected that treatment processes may become notably more efficient if first EfOM and possibly some inorganic components could be removed. For this project recent literature was consulted to find techniques that can remove EfOM, and to predict the effect of application of such techniques on the total treatment process.

The large influence of EfOM on techniques that can be applied to degrade organic micropollutants can be explained from the fact that EfOM too consists of organic molecules. This, on the other hand, also implies that the techniques mentioned before may be used as a kind of pre-treatment for the degradation of EfOM. Kovalova, Siegrist et al. (2013) studied membrane bioreactors (MBRs) as a pre-treatment of hospital wastewater. The organic micropollutants subsequently were removed by means of advanced oxidation. They also published a cost estimate for several processes. In the Netherlands the Reinier de Graaf hospital in Delft applies the “Pharmafilter concept”, in which all wastewater is treated by means of a MBR-O_3-ACF (activated carbon filtration step) process. The solid fraction is separated and fermented. The liquid fraction first is treated in the MBR in order to remove mainly organic material (COD). By means of membrane filtration the active sludge is isolated, and then ozone is applied to oxidize organic compounds in the water. Finally water is filtrated over activated carbon to remove the final traces of pollutants.

As described in the previous paragraph, EfOM can be converted by means of oxidation, e.g. by ozone. Gerrity, Gamage et al. (2011) determined that a O_3/H_2O_2 process in itself can be very effective in the conversion of EfOM, thus significantly changing the effluent character. Increasing DOC values result in increasing amounts of ozone, a higher degradation rate of the ozone and more scavenging of hydroxyl radicals (Wert, Gonzales et al. 2011). Conversion of organic micropollutants in the presence of other organic compounds thus requires a relatively high ozone dose. Grefte en Wert c.s. determined that the reaction of ozone with

NOM (and also with EfOM) depends on the composition of organic material. Ozone mainly reacts with humic acids and building blocks (Grefte 2013; Grefte, Rietveld et al. 2014). In case many humic acids are present, addition of ozone results in the formation of mainly low molecular acids and aldehydes. According to Rosario-Ortiz, Mezyk et al. (2008) the reaction rate constant of EfOM with hydroxyl radicals does not change by reaction with ozone. The EfOM character changes, but as this results in the formation of more reactive groups which may react with hydroxyl radicals, this has no net effect on the reaction with ·OH.

HS may effectively be removed by means of anion exchange. For an identical ozone dose per DOC this results in a lower ozone use, higher disinfection capacity, and more bromate formation. Thus, less biodegradable organic material is formed, which results in a higher biological stability of the treated water. Also Hu, Martin et al. (2014) conclude that anion exchange is an effective way to remove HS and BB, and that also a significant part of the LMW acids 96.5%) is removed. Concentrations of LMW neutral compounds do not change when anion exchange is applied (Hu, Martin et al. 2014). According to Sjoerdsma, Laarman et al. (2014) humic acids isolated in this way may be applied for soil improvement, after salts will have been removed. This possibility also is investigated by PWN Technologies.
Wert, Gonzales et al. (2011) added iron(III) chloride in order to coagulate organic compounds in wastewater, thus removing them before oxidation by ozone. This mainly is effective for compounds with a relatively high molecular weight. This is reflected in both a change in SUVA and in DOC concentrations. It suggests that especially aromatic compounds can be removed by means of coagulation. Thus, application of coagulation before ozone oxidation will mainly affect the first phase of the oxidation process, as ozone also prefers to react with aromatic compounds. Parameters which help determine the effectiveness of coagulation are pH, alkalinity, temperature, and the presence of divalent cations and anions like hydrogen carbonate, chloride and sulphate (Luo, Guo et al. 2014).

NOM can also be photolysed, resulting in the conversion of mainly aromatic hydrocarbons. High molecular weight organic material is converted into LMW acids. This, amongst others, results in a more aliphatic NOM character, with more carboxyl and carbonyl groups, making the material more hydrophilic (Liu, Zhang et al. 2012).

Especially in combination with the presence of chlorine UV irradiation may result in changes in the composition of e.g. NOM. There are two types of mercury UV lamps that often are applied: Low Pressure (LP) and Medium Pressure (MP). The main difference is that LP lamps emit only one wavelength (253,7 nm), whereas MP lamps emit radiation over a range of 200-300 nm. As a result, MP lamps cause much more photolysis of organic compounds than LP lamps do. The presence of nitrate in the water may be important, as at a wavelength of about 200 nm nitrate may generate radicals, which can react with NOM or EfOM (Oller, Malato et al. 2011). Vacuum UV (VUV) can also convert organic material (Ratpukdi, Siripattanakul et al. 2010). Absorption of VUV by water molecules results in the formation of hydroxyl radicals, which in turn can convert organic compounds. This radical formation, however, only can take place in the direct vicinity of the VUV lamp, and therefore large scale application of this technology is still difficult to realize. Combining VUV with ozone results in an effective advanced oxidation process for the degradation of NOM, in which not only high but also low molecular weight material is converted. As high molecular weight NOM in general contains aromatic compounds, it will contain a higher number of reactive groups. In principle NOM can be mineralized (i.e. converted into CO_2 and H_2O), but at lower doses already a sufficient increase in biodegradability can be obtained.

An inverse process can also be imagined, in which an MBR is applied in order to reduce the amounts of polysaccharides and proteins, thus reducing membrane fouling. For carbohydrates this strategy will be less efficient, but by increasing the residence time in the bioreactor here too the concentration can be decreased. It seems that it is not molecular weight but rather the character of the organic compounds (like hydrophobicity) which plays a role in membrane fouling. Residence time in general hardly affects the concentrations of inorganic compounds, like sodium, calcium, chlorine, sulphate, hydrogen carbonate and nitrate. These compounds, however, can effectively be removed by means of reverse osmosis.

4 Composition of various effluents

4.1 Introduction

At the WWTPs Dokhaven (Rotterdam), Eindhoven, Utrecht, Panheel, Roermond and Garmerwolde samples were taken for analysis of both EfOM and organic micropollutants like pharmaceuticals and their metabolites. Panheel and Roermond are considered as possibles sites for pilot research, Eindhoven and Utrecht apply conventional aerobic treatment processes, Garmerwolde and Dokhave apply a two step installation, in which the COD is decreased in the first step by means of coagulation). KWR possesses an analytical method which can be used to determine a wide range of commonly observed pharmaceuticals in one step. Using a mixture of these pharmaceuticals much experience was obtained in other research projects. Therefore, it was decided to use this analytical to determine the concentrations of these compounds in the effluents studied, and to apply the mixture during experiments. For more details on the analytical method and the mixture used see (Wols, Hofman-Caris et al. 2013).

In Garmerwolde apart from the common wastewater treatment also the Nereda process is applied. In the Nereda process effluent only pH, electrical conductivity and chemical oxygen demand (COD) were determined. All other analyses were performed using the total effluent, i.e. a combination of the common and the Nereda effluent.

4.2 Sampling procedure

The following sampling procedure was applied:

- At all sites once samples were taken during a weekday under dry weather conditions
- 24 hour flow proportional samples of the effluent were taken
- Samples were taken by a WWTP employee
- Sample volume: 2 x 5 L
- Part of the samples was used for analysis, the rest of the samples was frozen (without previous filtration), and later used for e.g. adsorption experiments

4.3 Composition of Effluent Organic Matter

Using an LC-OCD method (Huber, Balz et al. 2011) the DOC-Labor Dr. Huber characterized the EfOM in different effluents. In general the following fractions were observed (

Table 4-1):

Table 4-1: Different fractions in EfOM

Fraction	Description	Molecular mass
DOC	Total dissolved organic carbon	
HOC	Hydrophobic fraction DOC	
CDOC	Hydrophilic fraction DOC	
Biopolymers (BP)	Part of CDOC	>> 20.000
Humic acids (HA)	Part of CDOC	Ca. 1000
Building blocks (of humic acids) (BB)	Part of CDOC	300-500
Low molecular weight neutrals (LMWn)	Part of CDOC	< 350
Low molecular weight acids (LMWa)	Part of CDOC	< 350

Furthermore, SUVA (specific UV absorption, which is a measure for the concentration of aromatic compounds), the chemical oxygen demand (COD) and the electric conductivity (EC) of the samples were determined (Table 4-2). Besides, the concentration of inorganic colloids (negatively charged inorganic poly electrolytes, polyhydroxides and oxihydrates of Fe, Al, S or Si) was determined. The complete DOC Labor report is shown in Appendix I. An overview of the absolute and relative concentrations of the various EfOM fractions is shown in Figure 4-1 and Figure 4-2.

Table 4-2: Composition of various effluents

Sample	pH	EGV	COD	DOC	HOC	BP	HA	BB	LMWn	LMWa	SUVA
		µS/cm	mg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	l/mg.m
Dokhaven	7,6	901	25,3	10653	1376	698	4637	2011	1932	0	3,05
Eindhoven	7,26	529	24,6	9654	1121	750	4045	1995	1743	0	3,15
Utrecht	7,28	672	25	10276	1110	865	3575	2092	2415	218	2,71
Garmerwolde	7,46	1138	44,1	18299	1826	1128	8513	3256	3262	314	2,97
Panheel	7,56	991	40,2	14282	1090	2595	4821	2443	3143	190	2,47
Roermond	7,87	1500	50,1	21430	1093	1544	7865	7031	3897	0	3,39
Nereda	7,18	990	61,9	--	--	--	--	--	--	--	--
average	7,5	955	34,9	14099	1269	1263	5576	3138	2732	120,3	3,0

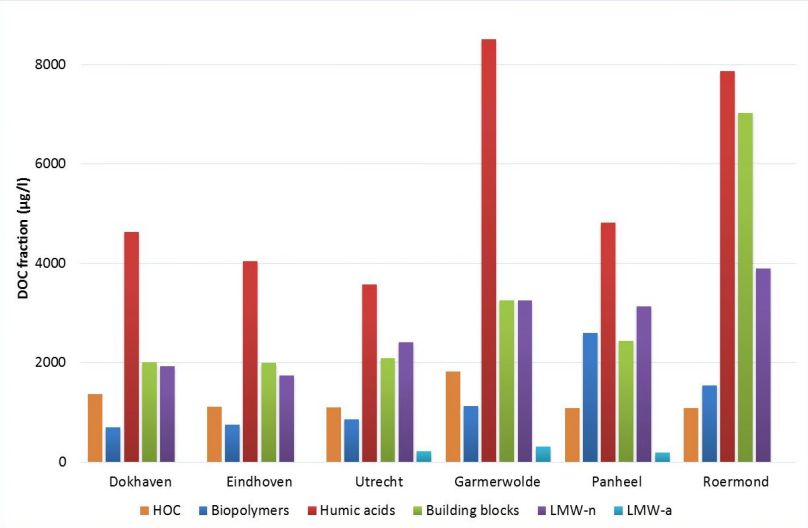


Figure 4-1: concentrations of various EfOM fractions (µg/l)

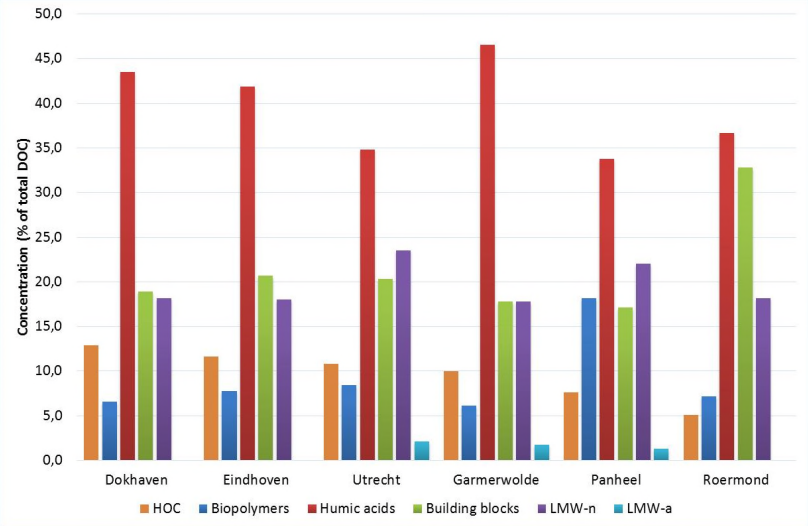


Figure 4-2: concentrations of various EfOM fractions as a percentage of total DOC

From the above it can be concluded that the Garmerwolde and Roermond effluents contain high EfOM concentrations compared with other effluents, and that in the Roermond effluent a relatively high biopolymer content can be observed. The other fractions can be observed in comparable magnitudes. On the average the effluents contain about:

- 40% humic acids (HA)
- 20% building blocks (BB)
- 20% neutral components
- 10% biopolymers (with a relatively high nitrogen content)
- 10% hydrophobic components

This average composition is in accordance with what was described in literature. (see chapter 3).

The COD value is determined by the concentration and type of the EfOM. This clearly is shown in Figure 4-3. A linear relation can be observed between the DOC content and the COD. The graph does not exactly pass the origin, which is caused by the presence of nitrogen containing compounds. Within the EfOM mainly humic acids determine the COD value (they also represent the main fraction within the EfOM). HOC, biopolymers and building blocks hardly affect the COD value.

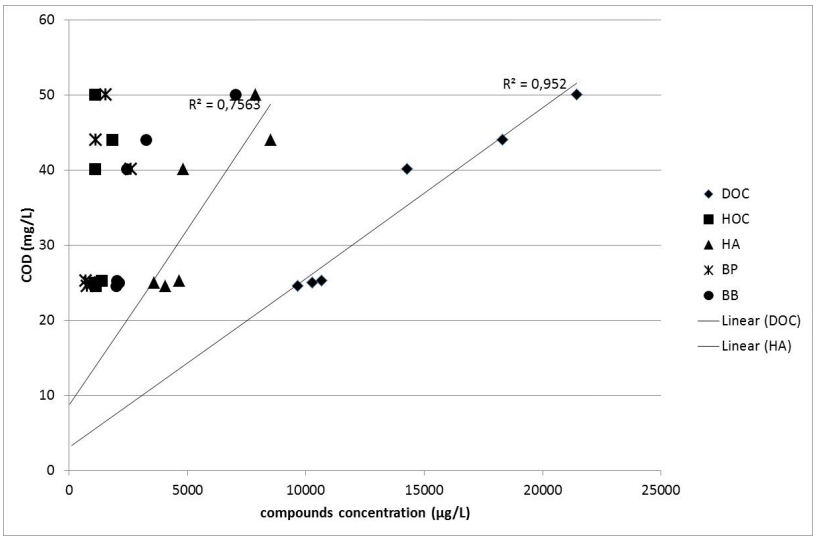


Figure 4-3: Relation between COD and EfOM-composition.

In **Error! Reference source not found.** the COD value of different effluents is compared. It is noted that especially the Garmerwolde, Panheel and Roer mond effluents show a significantly higher COD value than the Dutch average, whereas the other effluents show a value below the average. This may be biased by the fact that this is a kind of snapshot: it cannot be excluded that the year average values show a different picture.

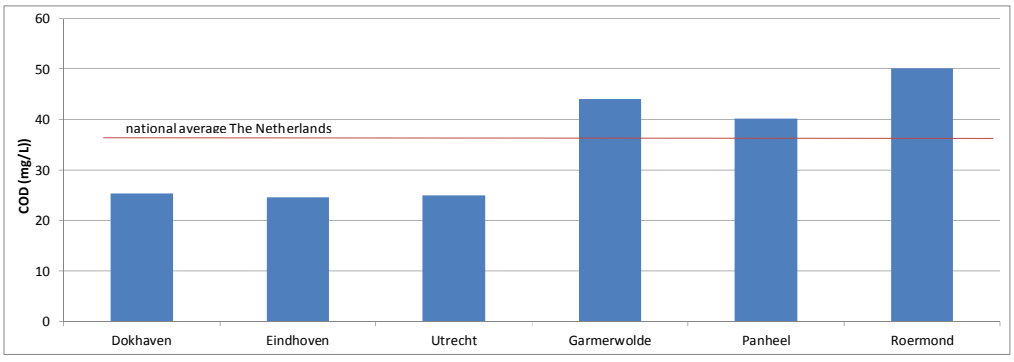


Figure 4-4: COD-values in the effluents analyzed.

The SUVA value is a measure of het aromatic content of het water. Figure 3-5 compares the SUVA values of het different effluents studied.

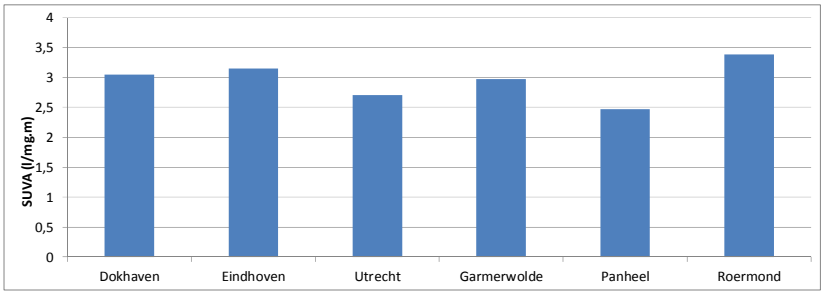


Figure 4-5: SUVA-values of the different effluents.

For all samples the SUVA-value seems to be about 3 L/mg.m. The SUVA of the Panheel sample seems to be rather low, whereas the SUVA of the water in Roermond seems to be relatively high. The SUVA value cannot directly be related to a certain EfOM fraction, as can be concluded from Figure 4-6.

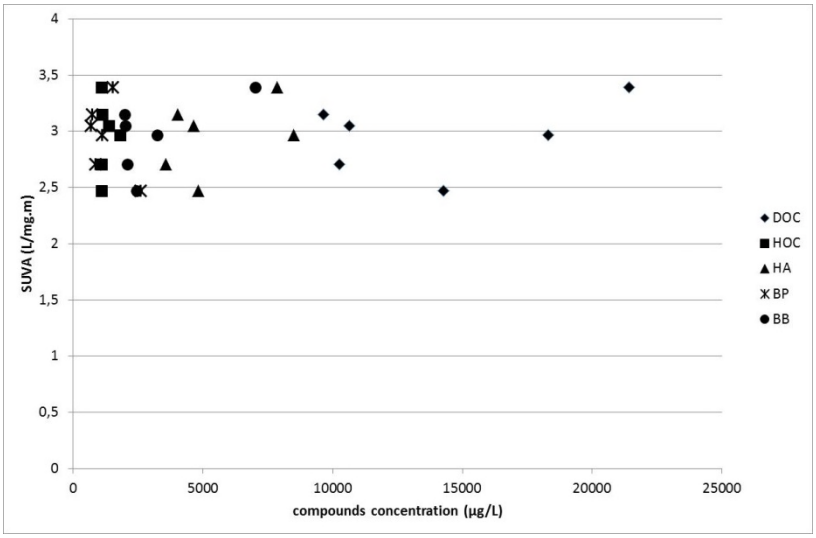


Figure 4-6: SUVA-values versus EfOM concentrations in different EfOM-fractions.

The conductivity of het effluent probably mainly is determined by the presence of inorganic components (like salts) in the water. Figure 4-7 shows that there are relatively large differences in electric conductivity, the conductivity in the Roermond effluent being the highest. Although conductivity seems to increase linearly with the DOC content, it cannot be related to the composition of the DOC. Probably this is related with the fact that a high DOC concentration often is accompanied by high concentrations of inorganic acids.

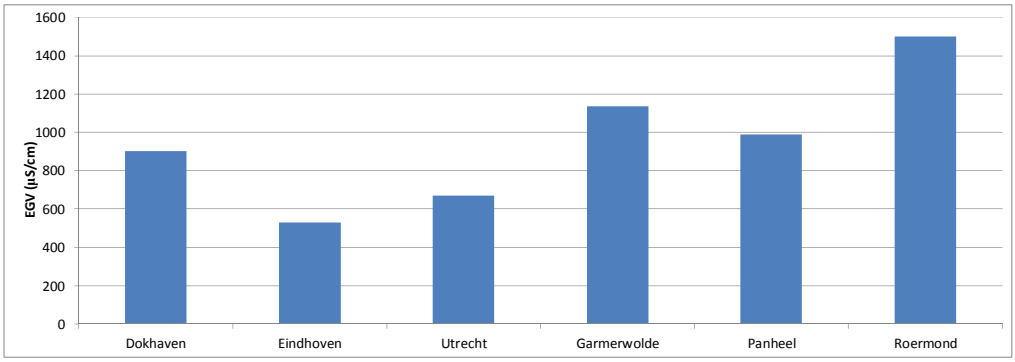


Figure 4-7: Electric conductivity of the effluents.

4.4 Concentrations of pharmaceuticals and their metabolites

The concentrations of common pharmaceuticals and their metabolites was determined in the effluents. The results are shown in Figure 4-8.

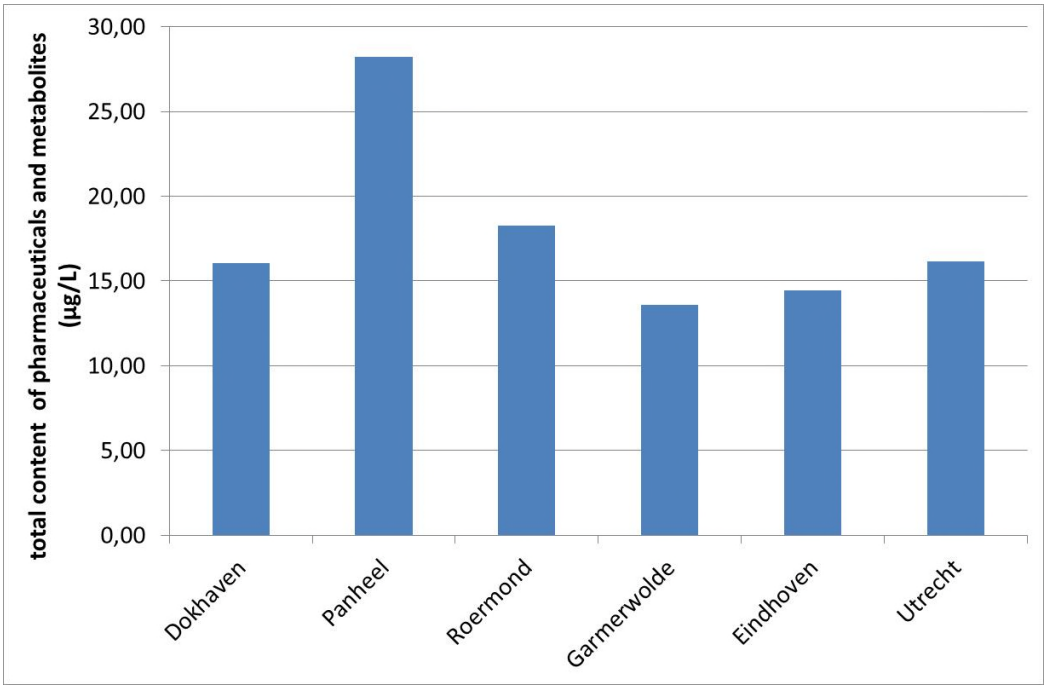


Figure 4-8: Total content of pharmaceuticals and their metabolites in the effluents

From these data it can be concluded that the effluents studied contain 14-28 µg/L pharmaceuticals and their metabolites, the average of most WWTPs being about 16 µg/L. Only in the Panheel effluent the concentration appears to be significantly higher (ca. 28 µg/L).

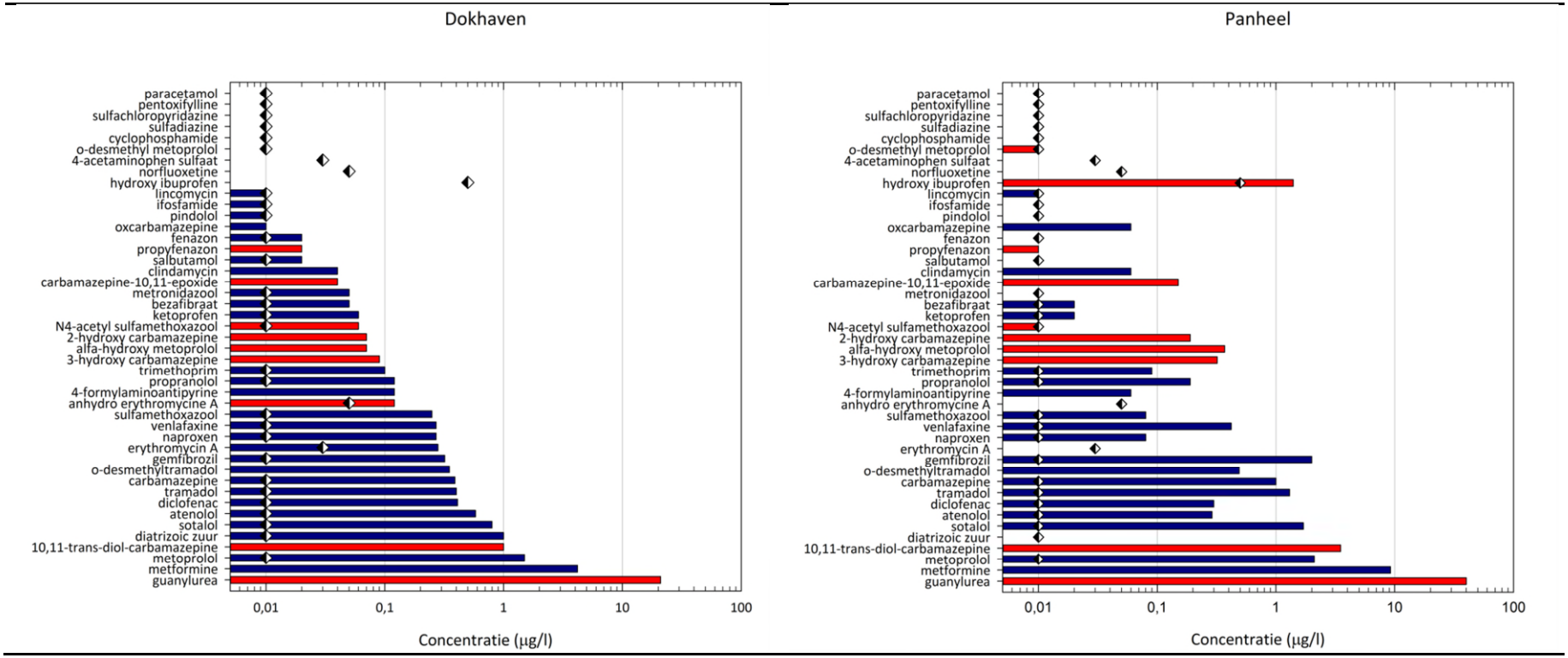
Each effluent was investigated for 62 common pharmaceuticals and their metabolites. 16 of these compounds couldn't be detected in any of these effluents, indicating that they are not

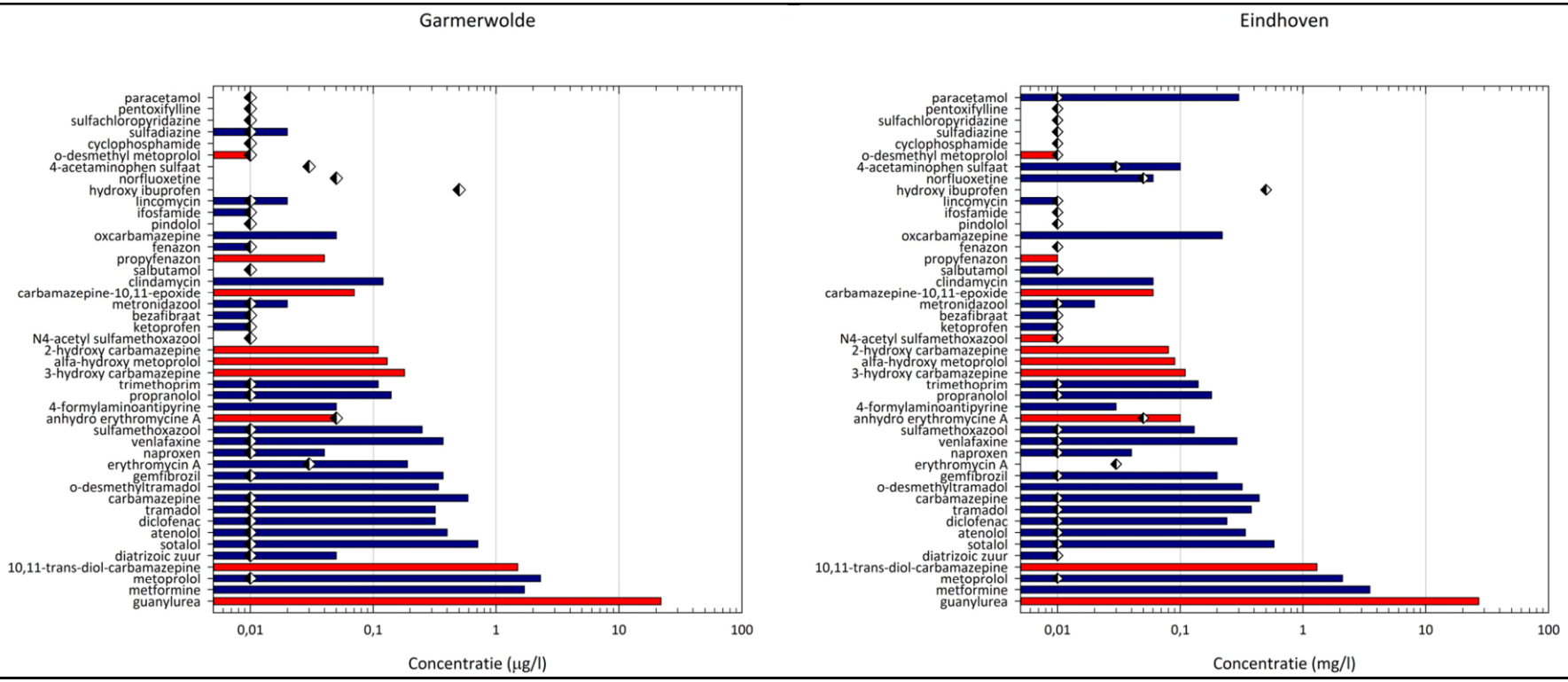
present or present at concentrations below the reporting limit. An overview of these metabolites, containing the corresponding reporting limits, is shown in Table 4-3.

TABLE 4-3. COMPOUNDS WHICH WERE ANALYZED BUT COULD NOT BE DETECTED ABOVE THE REPORTING LIMIT.

Compound	Reporting limit (µg/L)
Dimethylaminophenazon	0,01
AMPH	0,01
Clofibric acid	0,01
Salicylic acid	5,0
Acetyl sulfadiazine	0,01
O-Desmethyl naproxen	0,05
Cortisone	0,03
Cortisol	0,03
Clenbuterol	0,01
Terbutaline	0,01
Sulfachloropyridazine	0,01
Prednisolone	0,05
Pindolol	0,01
Penicillin V	0,01
Paroxetine	0,01
Niacin	0,01

An overview of the concentrations per pharmaceutical and/or metabolite measured is shown in Figure 4-9.


Dokhaven
Panheel
paracetamol
pentoxifylline
sulfachloropyridazine
sulfadiazine
cyclophosphamide
o-desmethyl metoprolol
4-acetaminophen sulfaat
norfluoxetine
hydroxy ibuprofen
lincomycin
ifosfamide
pindolol
oxcarbamazepine
fenazon
propyfenazon
salbutamol
clindamycin
carbamazepine-10,11-epoxide
metronidazool
bezafibraat
ketoprofen
N4-acetyl sulfamethoxazool
2-hydroxy carbamazepine
alfa-hydroxy metoprolol
3-hydroxy carbamazepine
trimethoprim
propranolol
4-formylaminoantipyrine
anhydro erythromycine A
sulfamethoxazool
venlafaxine
naproxen
erythromycin A
gemfibrozil
o-desmethyltramadol
carbamazepine
tramadol
diclofenac
atenolol
sotalol
diatrizoic zuur
10,11-trans-diol-carbamazepine
metoprolol
metformine
guanylurea
0,01
0,1
1
10
100
Concentratie (µg/l)


Garmerwolde
paracetamol
pentoxifylline
sulfachloropyridazine
sulfadiazine
cyclophosphamide
o-desmethyl metoprolol
4-acetaminophen sulfaat
norfluoxetine
hydroxy ibuprofen
lincomycin
ifosfamide
pindolol
oxcarbamazepine
fenazon
propyfenazon
salbutamol
clindamycin
carbamazepine-10,11-epoxide
metronidazool
bezafibraat
ketoprofen
N4-acetyl sulfamethoxazool
2-hydroxy carbamazepine
alfa-hydroxy metoprolol
3-hydroxy carbamazepine
trimethoprim
propranolol
4-formylaminoantipyrine
anhydro erythromycine A
sulfamethoxazool
venlafaxine
naproxen
erythromycin A
gemfibrozil
o-desmethyltramadol
carbamazepine
tramadol
diclofenac
atenolol
sotalol
diatrizoic zuur
10,11-trans-diol-carbamazepine
metoprolol
metformine
guanylurea
0,01
0,1
1
10
100
Concentratie (µg/l)
Eindhoven
paracetamol
pentoxifylline
sulfachloropyridazine
sulfadiazine
cyclophosphamide
o-desmethyl metoprolol
4-acetaminophen sulfaat
norfluoxetine
hydroxy ibuprofen
lincomycin
ifosfamide
pindolol
oxcarbamazepine
fenazon
propyfenazon
salbutamol
clindamycin
carbamazepine-10,11-epoxide
metronidazool
bezafibraat
ketoprofen
N4-acetyl sulfamethoxazool
2-hydroxy carbamazepine
alfa-hydroxy metoprolol
3-hydroxy carbamazepine
trimethoprim
propranolol
4-formylaminoantipyrine
anhydro erythromycine A
sulfamethoxazool
venlafaxine
naproxen
erythromycin A
gemfibrozil
o-desmethyltramadol
carbamazepine
tramadol
diclofenac
atenolol
sotalol
diatrizoic zuur
10,11-trans-diol-carbamazepine
metoprolol
metformine
guanylurea
0,01
0,1
1
10
100
Concentratie (mg/l)

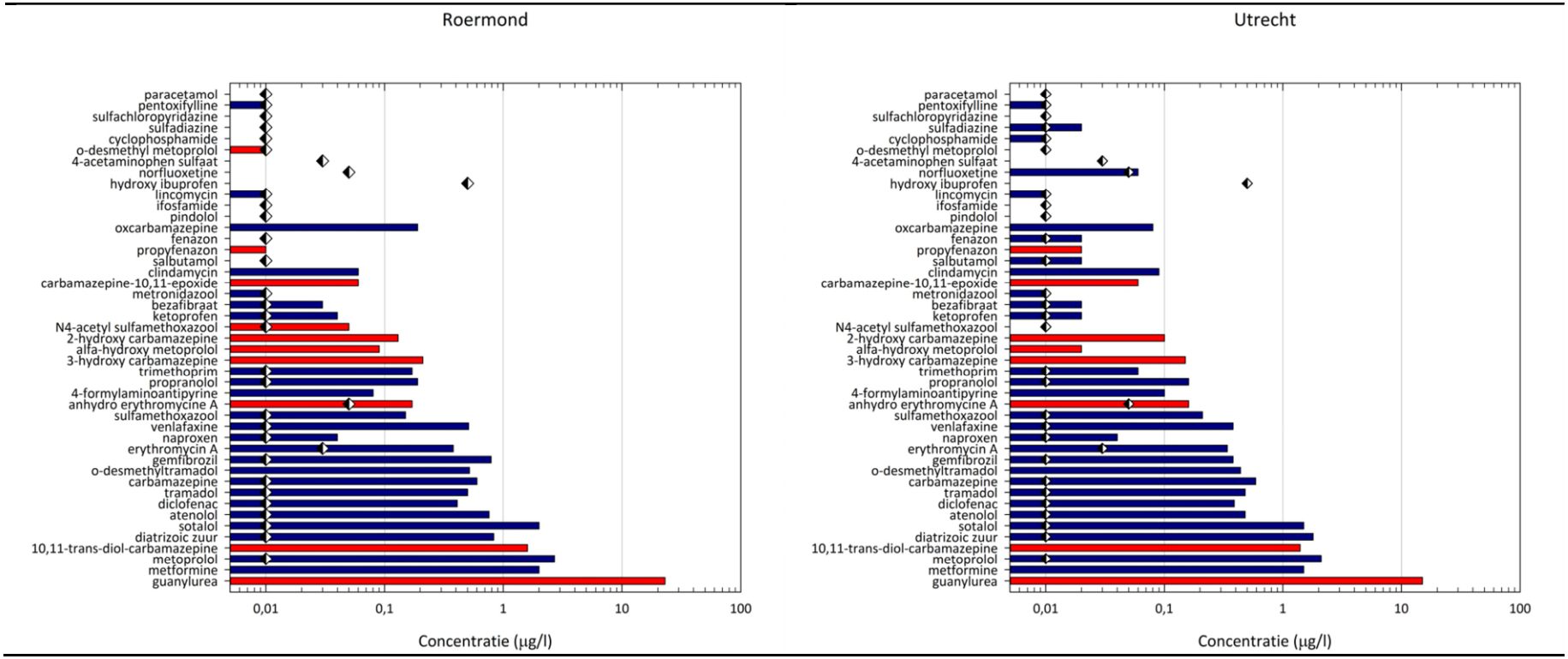


Figure 4-9. Overview of the pharmaceuticals and metabolites measured in the effluents. Blue bars: pharmaceuticals; red bars: conversion products ◆ reporting limit (LOQ)

From the overview it can be concluded that especially Metformin and its metabolite Guanylurea appear in high concentrations. This was expected, based on the use of Metformin, an antidiabetic which is administered in relatively high doses. It is known that in WWTPs metformin can be converted into Guanylurea. Furthermore Carbamazepine and its conversion products can be observed in relatively high concentrations in the effluents. Besides, it can be concluded that in general the concentrations of various compounds are comparable at the different locations, apart from a few exceptions (like Hydroxyl-ibuprofen in Panheel and Paracetamol in Eindhoven). It should, however, be noted that this too is a snapshot of the situation, and the average concentrations may differ from the values measured.

4.5 Discussion on the composition of effluents

It is known that surface waters, depending on circumstances like precipitation and temperature, for a substantial part may consist of effluent. From the analyses shown in paragraph 4.4 it can be seen that the concentrations of pharmaceuticals and their metabolites in all effluents studied are relatively high. This shows that WWTPs with their present treatment processes are not able to remove such pollutants from the water to a sufficient level, and that an additional treatment step will be required. In principle several techniques can be applied, like filtration of activated carbon or advanced oxidation. However, research has shown that the effectiveness and efficiency of such processes strongly depends on the presence of EfOM, which occurs in high concentrations in effluent. It is likely that the removal of EfOM will result in a better yield of a subsequent process step to remove organic micropollutants from the water. From the data in paragraph 4.3 it appears that the most important fraction within the EfOM are the humic acids, which largely contribute to the COD of the samples. This implies that they will probably also strongly affect the conversion of organic micropollutants by advanced oxidation. Besides, as a result of their relatively high molecular mass these compounds will compete strongly with e.g. pharmaceuticals in adsorption on activated carbon. Removal of this fraction probably will be the most effective way to improve the removal or conversion of organic micropollutants. Because of their high molecular mass, filtration over activated carbon may be applied for this purpose, but as it mainly are acidic compounds, ion exchange processes also can be considered.

4.6 Overview of selection of processes for the removal of EfOM and pharmaceuticals

Based on literature and the composition of the EfOM measured, two techniques were selected for pretreatment of the effluent:

1. IEX: this adsorbs the negatively charged part of the EfOM, so it is expected that mainly humic acids will be removed.
2. O_3/biofiltration: with this technique organic compounds are partly oxidized, making them better biodegradable. The microorganisms present in the filter bed will subsequently remove part of the EfOM.

For this part of the study effluent from WWTP Roermond and WWTP Panheel was used. It was decided to continu experiments with effluent from WWTP Panheel.

Based on experience with drinking water treatment and a literature search, the following techniques were selected for the subsequent treatment of the effluent:

- Filtration over activated carbon
- O_3/H_2O_2 (advanced oxidation)
- UV/O_3 (advanced oxidation)
- UV/H_2O_2 (advanced oxidation)

It is known that these techniques can be very effective in the removal of organic micropollutants like pharmaceuticals, but that the process is hindered by the presence of organic matter.

First at laboratory scale the effect of pretreatment on EfOM concentration and composition have been investigated. Furthermore, it has been checked what the influence of the pretreatment on the pharmaceuticals is. Then, the pretreated water has been treated by any of the four mentioned techniques, and the effect of the pretreatment on the effectivity of the processes has been studied. Based on the laboratory results obtained some processes were chosen for investigation at a pilot scale at WWTP Panheel.

5 Laboratory research: materials and methods

5.1 Experimental set-up of laboratory research

For the laboratory research two types of pretreatment (IEX and O_3/biofiltration), and five different treatment methods (filtration over AC, O_3/H_2O_2, UV/H_2O_2, UV/US/H_2O_2 and UV/O_3) were tested on effluent (mainly from WWTP Panheel, although some experiments were carried out with effluent from WWTP Roermond).

In order to study which combination of processes would be most feasible for testing in a pilot set-up, the following processes were tested at the laboratory:

- Effect of IEX pre-treatment on pharmaceuticals
- Effect of O_3/biofiltration pre-treatment on pharmaceuticals (with two different normal filtration periods)
- Effect of IEX pre-treatment on UV/H_2O_2 processes (collimated beam)
- Effect of IEX pre-treatment on filtration over activated carbon
- Effect of O_3/H_2O_2 treatment on effluent.
  Starting COD 44 mg/L. 36 mg H_2O_2/L. Ozone doses 0, 12.5, 31.2, and 62.4 mg/L. Spiking of pharmaceuticals by KWR.
- Effect of IEX on O_3/H_2O_2 processes
  Starting COD 25 mg/L. 36 mg H_2O_2/L. Ozone doses 0, 12.5, 31.2, and 62.4 mg/L. Spiking of pharmaceuticals by KWR.
- Effect of O_3/biofiltration pre-treatment on O_3/H_2O_2 processes.
  Starting COD 29 mg/L. 36 mg H_2O_2/L. Ozone doses 0, 12.5, 31.2, and 62.4 mg/L. Spiking of pharmaceuticals by PureBlue Water (82 ml of solution to 70 L of effluent). Period of biofiltration too short.
- Effect of O_3/biofiltration pre-treatment on O_3/UV processes.
  Starting COD 29 mg/L. Ozone doses 0, 12.5, 31.2, and 62.4 mg/L. Spiking of pharmaceuticals by PureBlue Water (82 ml of solution to 70 L of effluent). Period of biofiltration too short. UV dose increasing during experiments from 120 to 150 mJ/cm^2.
- Effect of O_3/biofiltration pre-treatment on O_3/UV processes.
  Starting COD 29 mg/L. Ozone doses 0, 12.5, 31.2, and 62.4 mg/L. Spiking of pharmaceuticals by PureBlue Water (49 ml of solution to 49 L of effluent). Normal period of biofiltration. UV dose increasing during experiments from 120 to 150 mJ/cm^2.
- Effect of US in UV/H_2O_2 process. Two UV doses (150 and 300 mJ/cm^2) were applied, 10 mg H_2O_2/L and in some experiments 30 W US. The US deviced had been integrated into the flow-through UV reactor.The experiments were carried out at PureBlue Water.

In the following paragraphs all experiments mentioned above will be described in detail.

5.2 Pre-treatment by means of ion exchange (IEX)

5.2.1 Batch experiments

The removal of EfOM from effluent was tested using two types of resins produced by Lanxess. The first resin (Lewatit® A 8071) is a strongly basic anion exchange resin consisting of an Acryl-divinyl benzene copolymer, which is suitable for removal of EfOM from surface water. The second resin (Lewatit® S 6368 A) is a strongly basic polystyrene ion exchange resin, which is often used in food industry to remove color from fruit juice. Both resins were used in a chloride-form (see specifications in Appendix III).

On September 18th 2014 the effluents of WWTP Panheel and WWTP Roermond were sampled (24 hour flow proportional sample from 17-9-2014 9.00 o'clock until 18-9-2014 8.59 o'clock). The adsorption of EfOM fractions on both resins was investigated in batch experiments, by adding one liter of water to a certain amount (100 g/L) of resin. Subsequently, the bottles were continuously stirred during seven days at 20 ˚C. Then they were analyzed for TOC (dosage 20 and 500 mg resin/L) and LC-OCD (blank and 100 mg resin/L), by DOC-Labor dr. Huber.

5.2.2 Column experiments

After the batch tests, water was pretreated for further investigation of the effect of pre-treatment on the removal or organic micropollutants (pharmaceuticals). For this part of the project column experiments were carried out.

In order to test the removal of EfOM from effluent and to prepare water for further laboratory testing, on October 28th 2014 samples were taken from the effluent basin of WWTP Panheel. These samples were treated with either ion exchange (via a column, no batch tests) or by means of the ozone-biofiltration process. The effluent and the treated water were analyzed by means of LC-OCD.

TABLE 5-1. INDICATOR OF EFLLUENT TREATMENT

Treatment	
Ion exchange	
- Type of resin	Lewatit® S 6368 A
- Volume of resin	10 L
- Water flow	10 BV/min
- Filtrated water volume	300 L
Ozone/biofiltration	
- Ozone dose	0,15 – 0,30 – 0,50 g O_3/g CZV
- Contact time biofiltration	15 – 30 min
- Treated water volume	83 L per batch

5.3 Pre-treatment by means of IEX

On September 18th 2014 PureBlue Water also took a sample from the Roermond effluent. As a much larger volume was required (1 m^3) in this case a grab sample was taken. For each experiment part was filtrated over Lewatit S6368A, according to Table 5-1.

5.4 Pre-treatment by means of ozone-biofiltration

From the grab sample for each experiment a 2 L sample of the water was treated in a small pilot set-up applying ozonation and biofiltration (using a biofilm on a carrier) separately. The idea is that a low ozone dose can be applied, degrading non-biodegradable compounds into biodegradable molecules, which are bound and converted by means of fixed bed biofiltration. The settings are shown in Appendix IV.

The ozone doses applied were 0, 0.15, 0.3 and 0.5 g O_3/g COD.

Biofiltration was carried out in a fixed bed with active aeration. It contains a fixed carrier with a biofilm, which had been used before. The carrier is based on lignite coke. Two different residence times were applied in the bioreactor for the effluent research: 15 and 30 minutes (see Table 5-1).

After this experiment 1 m^3 of water from WWTP Panheel was taken. The residence time within the bioreactor was shortened in order to obtain conditions which can be applied in a full scale wastewater treatment installation. However, as in the first experiments of this series the ozone concentration could not be decreased far enough, the residence time had to be decreased to 4 minutes. This appeared to be too short, resulting in a limited removal of EfOM. Therefore this pre-treatment was repeated later with a longer residence time. So, this type of pre-treatment for the laboratory samples of Panheel was carried out twice:

- First pre-treatment: ozone dose 13 mg/L, residence time 4.2 minutes (which in fact appeared to be too short)
- Second pre-treatment: ozone dose 10 mg/L, residence time 6 minutes

5.5 Dosing of pharmaceuticals

A mixture of pharmaceuticals (including caffeine as a reference compound) was added to the water samples before ozone/biofiltration or IEX for experiments (See Appendix V). For some compounds metabolites are known, which may be observed in wastewater. Besides, such compounds might also be formed during oxidation processes. Therefore, their presence in water, before and after treatment, was also measured, although these compounds have not been dosed to the water. The compounds were measured before and after the pre-treatment step, and after advanced oxidation. In case after treatment the limit of detection was reached, this limit was used as the final concentration. As a result of this, the removal and conversion data reported refer to the minimum removal and conversion.

5.6 Collimated beam experiments

In order to be able to carry out UV/H_2O_2 experiments under well-defined conditions, the experiments were carried out in a collimated beam set-up.

The UV dose is defined as the energy (or the amount of photons) absorbed by an irradiated object during a certain period per area or volume. In UV installations for water treatment, water flows along the lamps (or quartz sleeves). The UV dose then is determined by the lamp intensity and the residence time of a particle or microorganism in the reactor. This residence time in turn depends on the flow profile and the reactor geometry, which is difficult to characterize. Because of this reason often a collimated beam set up is used in laboratories, as it can be operated under standard, well defined, conditions.

A collimated beam set up offers the possibility to determine the effect of the UV dose on the inactivation of microorganisms and the conversion of chemical compounds under controlled and ideal conditions at laboratory scale. In the KWR installation dose-effect relations can be measured. The set up can be equipped with various types of UV lamps, like low pressure (LP) and medium pressure (MP) mercury lamps. In this way the dose-effect relation of a specific lamp can be determined (Harmsen 2004). The collimated beam set up is schematically shown in Figure 5-1.

The lamp ('beamer' in Figure 5-1) is placed in a box made of stainless steel. The irradiation enters a wooden box through a hole. By means of a collimator, formed by adjustable plates, a parallel UV bundle hits the water sample. As the plates are removed or adjusted, the bundle can be adjusted, obtaining an optimal uniform irradiation of the sample surface. Furthermore, the sample is stirred during the irradiation.

By means of an automatic shutter, the UV irradiation is interrupted after a certain irradiation time. The required irradiation time is calculated based on specific conditions (for example UV_{254nm} (LP-lamp) or $UV_{200-300\ nm}$ (DBD- or MP-lamp), the UV-intensity of the lamp, sample volume, petri factor) using published calculation sheets (Bolton and Linden 2003). If disinfection tests are carried out, a correction is made for the (DNA) absorption curve in the calculation of the irradiation time. During UV/H_2O_2 tests, such a correction is not made.

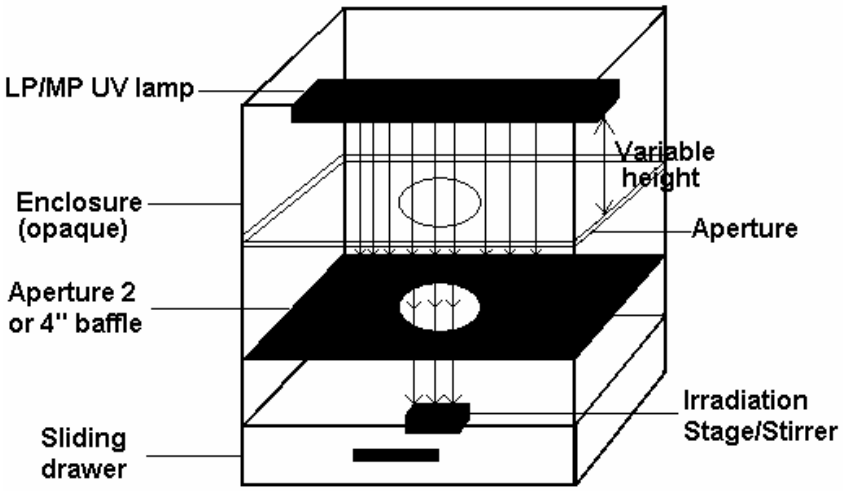


Figure 5-1: Schematic picture of a collimated beam installation

The UV dose (mJ/cm^2) has been defined as the product of the irradiation time (t in seconds) and the irradiation intensity (wavelength dependent UV output of the lamp) in mW/cm^2. A detailed description of the calculation of UV doses can be found in report BTO 2004.014 "Protocol Collimated Beam UV" (Harmsen 2004) and in the article "Standardization of Methods for Fluence (UV Dose) Determination in Bench-scale UV Experiments" (Bolton and Linden 2003).

The lamp intensity (= irradiation intensity) is measured using an IL 1700 Research Radiometer and a SED sensor. This sensor detects UV-light between 185 and 310 nm. This equals the wavelength range that is applied for disinfection of microorganisms and conversion of organic micropollutants. Besides, the sensor has been equipped with a filter (the "wide-eye diffuser" (W)). This diffuser ensures that the light, entering the sensor under various corners, attributes equally to the total intensity measured.

10 mg/L H_2O_2 (JT Baker; Baker analyzed; casnr. 7722-84-1) was added to the solution. All solutions were treated with a low pressure UV lamp (Philips PLL60W). The distance between the lamp and the irradiated surface was 30 cm. The solutions were treated using different UV-doses of 0, 300, and 600 mJ/cm^2 respectively (N.B. for removal of organic micropollutants from drinking water in general a UV-dose of 500-700 mJ/cm^2 is applied). Each time 100 ml solution was irradiated. All samples were treated in an order chosen at random.

5.7 O_3/H_2O_2 experiments

In a pre-treated solution, containing pharmaceuticals, 36 mg H_2O_2/L was dissolved. Subsequently, ozone was added in a concentration of 12.5, 31.2 or 62.4 mg/L to a batch reactor. Experiments were carried out in batch mode. 70 L of water was added to the ozone reactor after which ozone dosing started. H_2O_2 (36 mg/L) was added instantaneously at the start of the experiment. Subsequently samples were taken after 10, 20 and 50 minutes.

5.8 O_3/UV experiments

Ozone was added to pre-treated water in a concentration of 12.5, 31.2 or 62.4 mg/L (see section 5.7). This was fed to a flow through UV-reactor, equipped with a 90 W LP-UV lamp, and the applied dose was 120-150 mJ/cm^2. The increase in UV-dose was caused by the increase in UV-Transmission (UV-T) during the experiment, caused by the O_3/UV process. The flow through UV-reactor had been equipped with a US device (30W), which also was operated during the experiments. However, later experiments with UV/H_2O_2 processes showed that this US device, at the low power applied, did not affect the experimental results.

5.9 Filtration over activated carbon

Batch experiments were carried out using granulated activated carbon (GAC). For this purpose 30, 60, 120, 250, 500 or 1000 mg PAC was added to 1 L of solution, containing pharmaceuticals (with or without pre-treatment). After stirring for 34 days, the samples were analyzed, determining the amounts of pharmaceuticals that had been adsorbed.

5.10 Effect of US

Effluent of RWZI Panheel was used, and part was filtrated over an IEX column. The untreated water was spiked by KWR with pharmaceuticals, and was treated with UV/H_2O_2 at 150 mJ/cm^2 (10 mg H_2O_2 /L), and with the same process in combination with US (30 W). The filtrated water was treated with UV/H_2O_2, both at 150 and at 300 mJ/cm2 (10 mg H2O2/L), with and without 30 W US. The US device had been integrated into the flow through UV reactor of PureBlue Water.

6 Laboratory research: Results and discussions

Two different pre-treatment techniques were applied:

- IEX (column filtration)
- O_3/biofiltration.

Afterwards, four different techniques were applied for the removal of pharmaceuticals from the WWTP effluent:

- UV/H_2O_2
- O_3/H_2O_2
- UV/O_3
- Filtration over activated carbon

Furthermore, the effect of the pre-treatment itself on the pharmaceutical content was studied. In the next paragraphs the results obtained are shown.

6.1 Pre-treatment by means of IEX: effect on EfOM in Roermond and Panheel

It is expected that IEX will remove negatively charged compounds, i.e. humic acids, from the EfOM. This was checked in batch experiments by determining the TOC value of water samples to which a certain amount of resin had been added. The results are shown Table 6-1 and Figure 6-1.

TABLE 6-1. TOC (mg/L) IN EFFLUENT AFTER ADSORPTION EXPERIMENT WITH ANION EXCHANGE RESIN (BLANK AND 100 mg/L RESIN MEASURED BY MEANS OF LC-OCD, 20 AND 500 mg/L MEASURED VIA TOC (LAM-068)

Resin dose (mg/L)	Roermond S 6368 A	Roermond A 8071	Panheel S 6368 A	Panheel A 8071
0; Blank	28,9	28,9	15,9	15,9
20	28	29	16	16
100	23,0	25,4	12,3	13,9
500	20	24	9,4	11

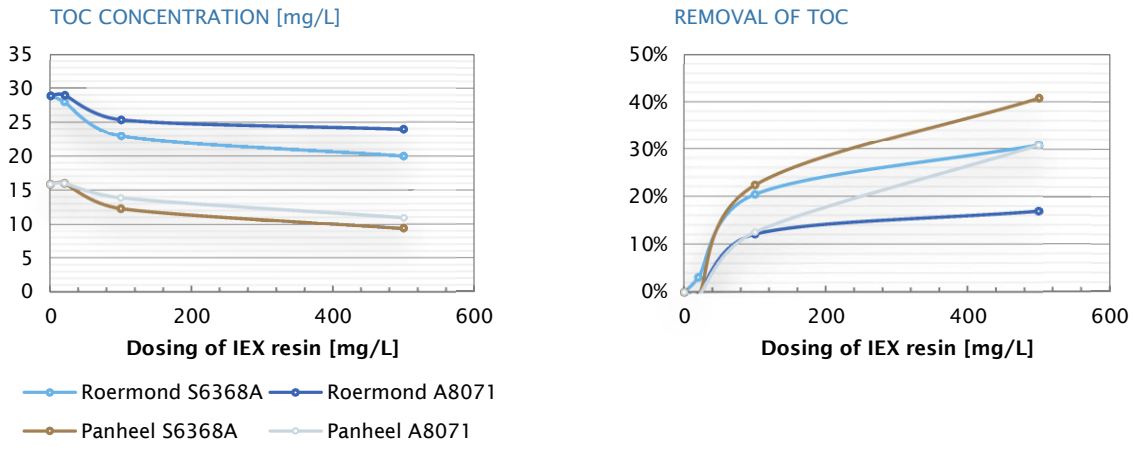


Figure 6-1. TOC-concentrations (left) and removal (right) at different resin concentrations.

It was also studied which part of the EfOM was preferably removed by IEX in batch experiments (Figure 6-2).

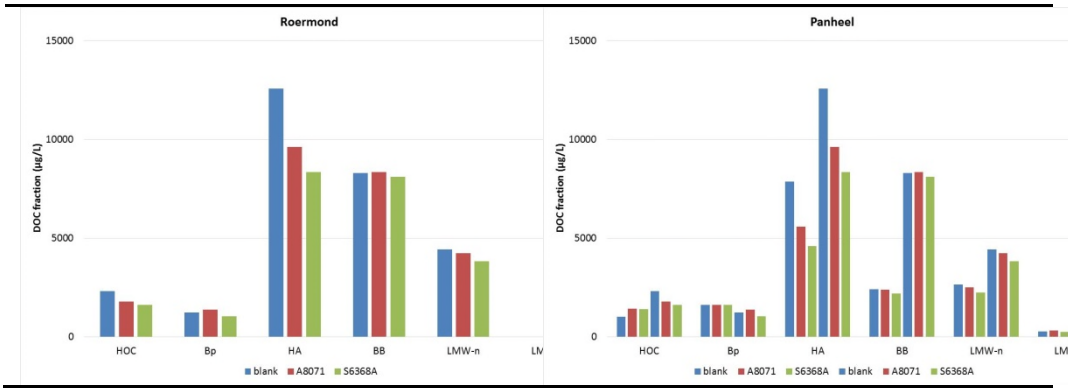


Figure 6-2. Removal of EfOM-fractions from effluent by ionexchange resins Lewatit® A 8071 and Lewatit® S 6368 A. Left: Effluent Roermond; Right: Effluent Panheel.

In Figure 6-1 the reduction of the TOC concentration by adsorption on ion exchange resins is shown. From the left graphs it can be concluded that TOC-concentrations in the Roermond effluent are higher than in the Panheel effluent, which is in accordance with previous measurements (see chapter 4). Furthermore, it seems that the styrene resin gives a better removal of TOC than the acrylic resin used.

It is notable that the adsorption does not increase linearly with increasing resin dose, but seems to flatten at higher resin dosage. In such a batch experiment extra addition of resin thus will not result in a further decrease in TOC concentration. This effect seems to be stronger for the Roermond effluent than for the Panheel effluent. From the right graph in Figure 6-1it can be observed that for both resins TOC removal seems to flatten more strongly in the Roermond effluent than in the Panheel effluent.

Figure 6-2 shows the removal of different DOC fractions. For every fraction the effluent concentration (blank) is shown and the concentrations after adsorption using either ion exchange resin A 8071 or S 6368 A. The results show that the resins mainly remove humic acids. Besides, a small decrease in the amount of neutral compounds can be seen and, when the styrene resin is used, a small decrease in the amount of building blocks is observed.

From the measurements it can be concluded that application of ion exchange can remove part of the humic compounds present in the effluent.

N.B. The resins can be regenerated, using an aqueous NaCl solution preferably at high pH. The concentrate that is obtained has to be disposed of. What the options for disposal or treatment of the concentrate are, and what the costs involved will be, has not been part of this investigation.

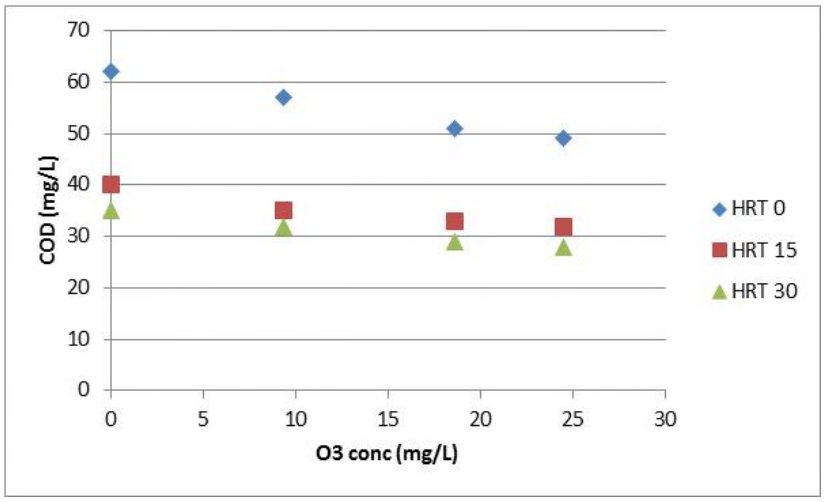
6.2 Pre-treatment by means of ozone-biofiltration: effect on EfOM in Roermond

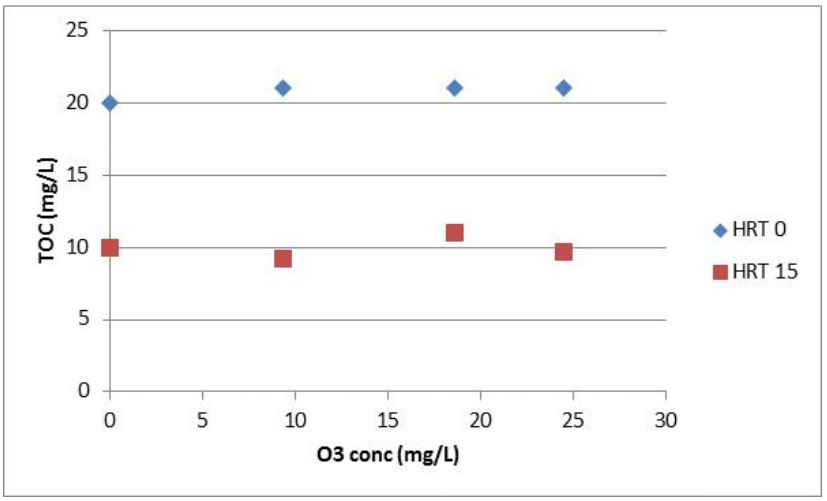
The results obtained with ozonation-biofiltration of the Roermond effluent are shown in Table 6-2.

Table 6-2: Results of pre-treatment by means of ozone and biofiltration. UV-transmission (UV-T) at 254 nm. HRT = hydraulic retention time in the bioreactor

Ozone (mg O_3/L)	COD after O_3 (mg/L)	COD HRT 15 (mg/L)	COD HRT 30 (mg/L)	TOC after O_3 (mg C/L)	TOC HRT 15 (mg C/L)	UV-T O_3 (%)	UV-T HRT 15 (%)	UV-T HRT 30 (%)
0	62	40	35	20	10	22.7	40.8	47.5
9.3	57	35	32	21	9.5	28.9	40.4	47.8
18.6	51	33	29	21	11	34.2	48.4	51.2
24.5	49	32	28	21	9.7	38.1	52	56.6

Table 6-2 shows that an increasing ozone dose results in a further decrease in COD, and an increase in UV-T. During the experiments, the color of the water was visually diminished. TOC stays constant at increasing ozone doses, as the ozone does not mineralize the components, but merely oxidizes them into smaller molecules. This, however, may make the compounds better biodegradable, which is reflected in the COD, TOC and UV-T values after 15 or 30 minutes biodegradation. Increasing the residence time in the biofiltration process step results in a decrease in both COD and TOC of the water, and an increase in UV-T. This graphically shown in Figure 6-3. However, it can be noticed that the difference between a HRT of 15 and 30 minutes is relatively small.





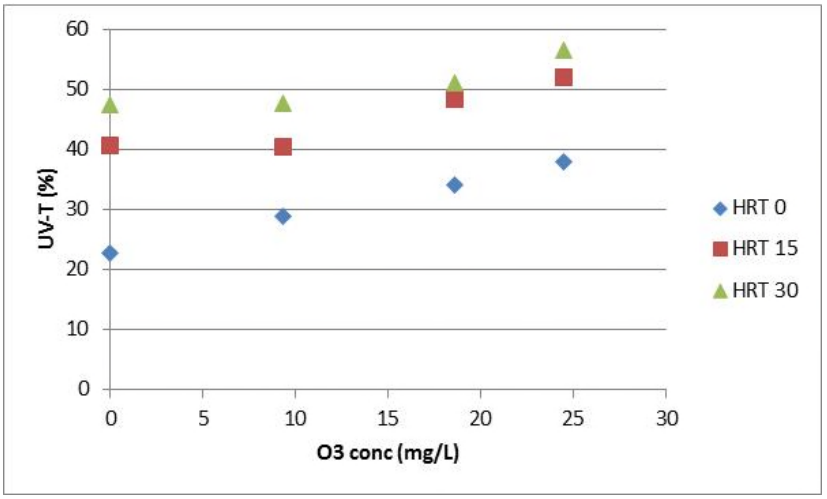


Figure 6-3: Effect of ozonisation and biodegradation on several parameters (COD, TOC and UV-T).

As the difference between 15.3 and 24.5 mg O_3/L also was relatively small, for pre-treatment an ozone dose of 15.3 (i.e. 0.3 g O_3/g COD) was chosen for further research. The effect on the composition of the organic matter, measured by means of LC-OCD, is shown in Figure 6-4.

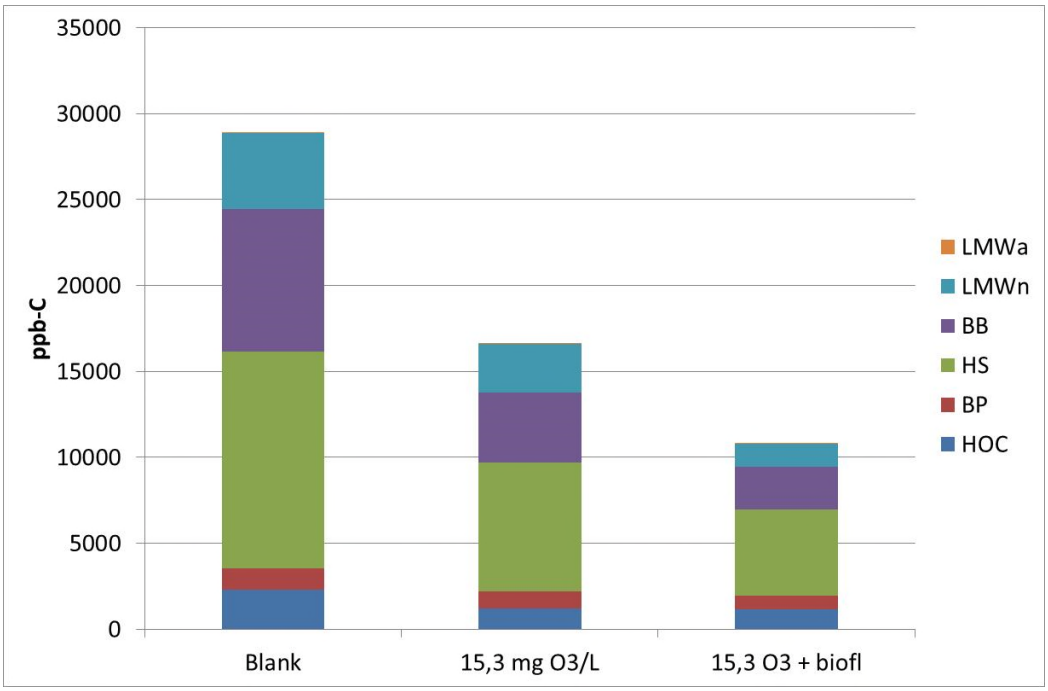


Figure 6-4: Effect of pre-treatment by means of ozone or ozone/biofiltration on the LC-OCD composition of the organic matter in the water sample of Roermond.

It can be noticed that the HOC content is decreased by oxidation by ozone, but the remaining HOC is hardly affected by the biofiltration. However, the fractions of HS, BB and LMWn decrease during O_3 treatment, and more during biofiltration. LMW neutrals show 75% removal, humic substances 60% and biopolymers only 30%. This confirms the assumption that smaller molecules are better biodegradable.

6.3 IEX in column tests and O_3/biofiltration; effect on EfOM in Panheel

Although in batch tests the resin showed a leveling off of the EfOM removal, this effect could not be observed in the column test, that was carried out before further testing for the removal of pharmaceuticals. This may be explained by kinetic and diffusion effects and/or by filtration of EfOM adsorbed at particles, which did not occur during the batch experiment. The results can be seen in Figure 6-5, which shows the DOC composition of untreated and treated water from WWTP Panheel. Obviously, the fraction of humic substances was removed completely by the IEX. Furthermore, circa 50% of HOC, 60% of the building blocks, and 25% of the biopolymers was removed.

Two pre-treatment experiments were carried out using the O_3/biofiltration process. In the first experiment the residence time in the bioreactor probably was too short, in the second experiment the “normal” residence time was applied. These results too are shown in Figure 6-5. The incomplete pre-treatment with O_3 and biofiltration seems to result in a small change in DOC composition. About 20-25% of the humic substances, biopolymers and LMW neutrals

were removed. This resulted in an increase in the amounts of biopolymers and low molecular weight acids. When a full biofiltration process was conducted, all hydrophobic compounds were removed. Besides, significant amounts of humic substances (± 40%), biopolymers (± 50%), and building blocks (± 20%) were removed. However, the total removal of DOC by O_3/biofiltration in both cases turned out to be lower than after IEX treatment.

As different fractions seem to be removed by both pre-treatment techniques, it is very interesting to check the effect of these techniques on the subsequent removal of pharmaceuticals. Therefore, it was decided to apply and compare both types of pre-treatment.

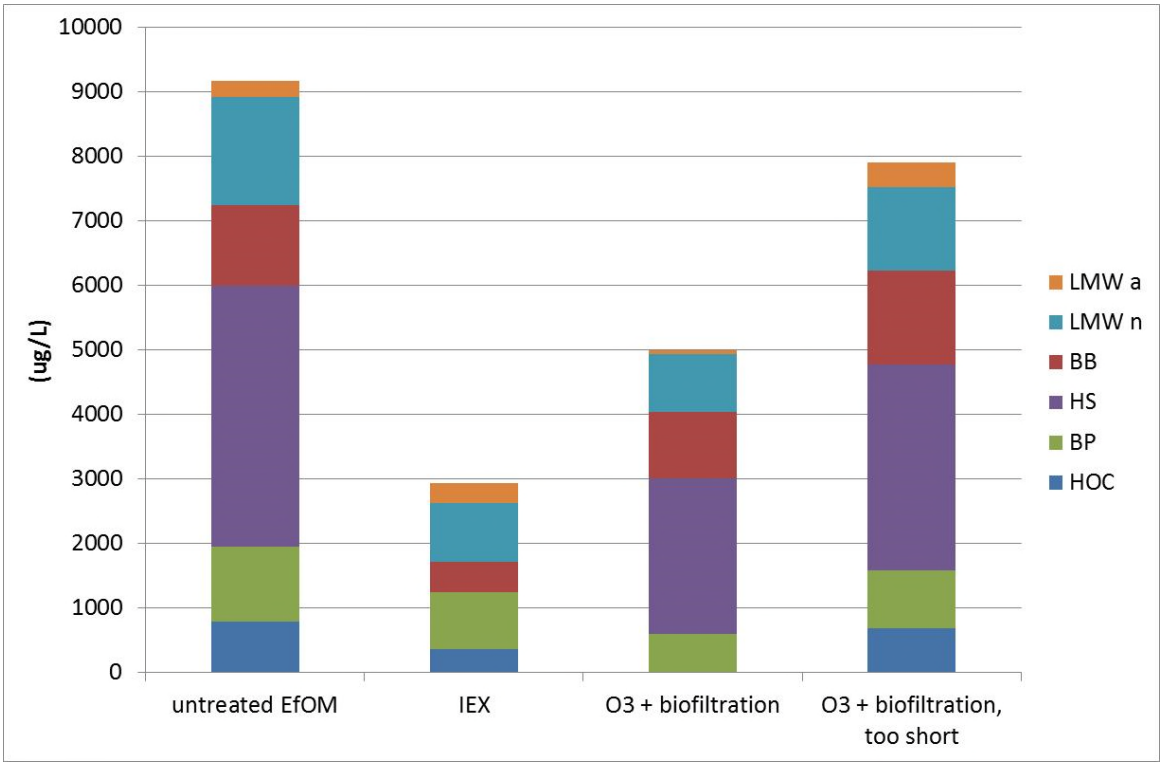


Figure 6-5: Effect of pre-treatment by means of IEX (column tests) or O_3/biofiltration on the composition of the DOC in the effluent of WWTP Panheel.

6.4 Removal of pharmaceuticals during pre-treatment

After the batch tests further tests were started to remove pharmaceuticals. These tests were carried out in two phases. The first phase aimed at EfOM removal, whereas the second test aimed at the subsequent removal of pharmaceuticals.

As pharmaceuticals also are organic compounds, it is to be expected that the pre-treatment method, aiming at decreasing the EfOM content, will also (partly) remove pharmaceuticals. This was tested with the WWTP Panheel effluent. The results are shown in Figure 6-6. Obviously, for some pharmaceuticals IEX is a rather efficient removal method, which

probably is caused by the negative charge the compounds carry at about neutral pH (Table 12-2 Appendix IV). For carbamazepine, which is supposed to be neutral, still a high removal can be found, whereas for ketoprofen, with a negative charge, rather low removal is observed. At the moment there is no explanation for this behavior. As expected, O_3/biofiltration is much more effective for the removal of pharmaceuticals than IEX, as most compounds are more or less sensitive towards ozonation (this is most effective with electron rich compounds). The very high oxidation by ozonation probably was caused by the relatively high ozone concentrations applied.

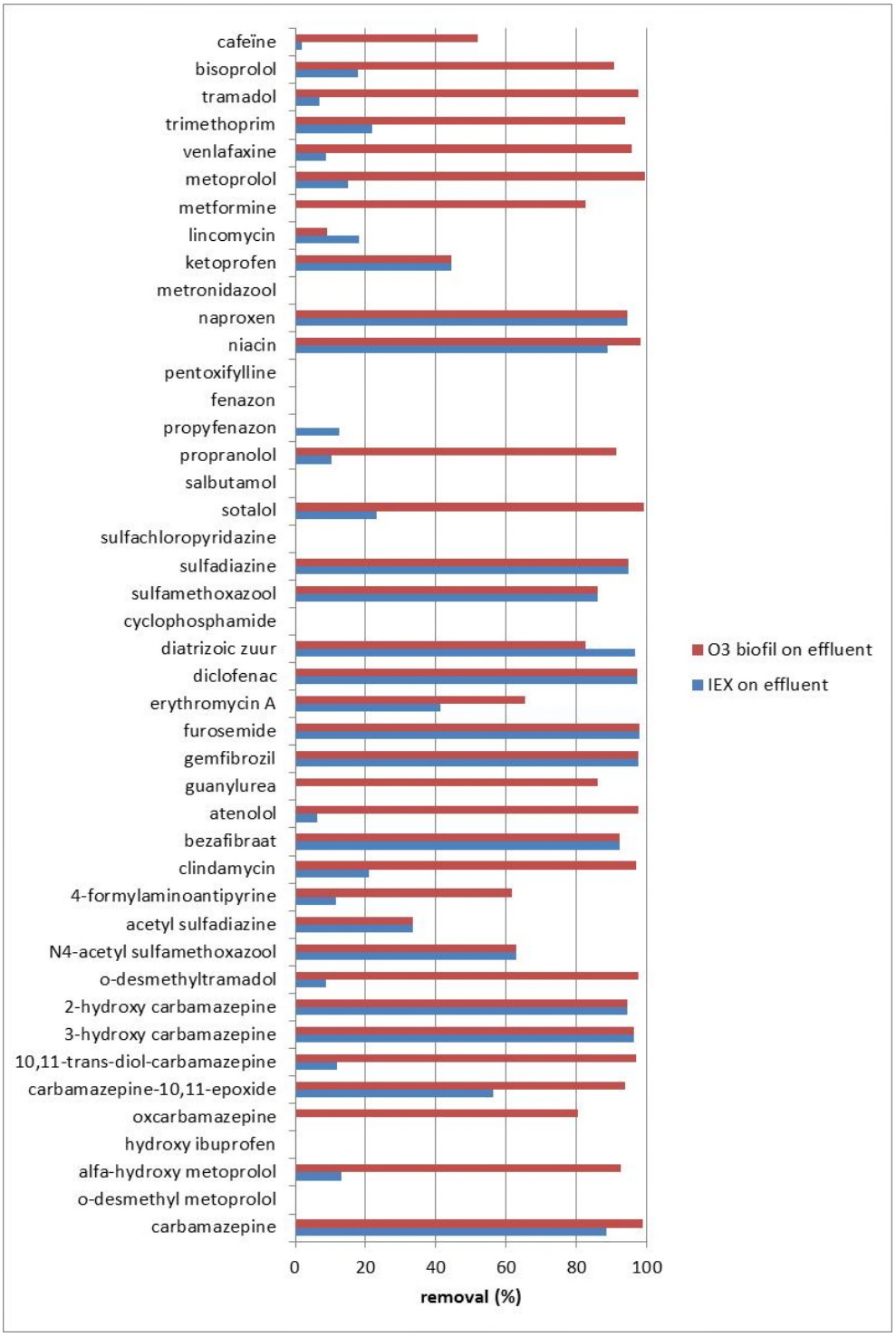


Figure 6-6: Removal of pharmaceuticals from the WWTP Panheel effluent by IEX or O_3/biofiltration pre-treatment

6.5 Removal of pharmaceuticals by the UV/H_2O_2 and O_3/H_2O_2 without pre-treatment

As a check the removal of pharmaceuticals in water that had not been pretreated was compared, using two oxidation techniques: UV/H_2O_2 and O_3/H_2O_2. The results are shown in Figure 6-7. Two different UV doses were tested: 300 and 600 mJ/cm^2 respectively.

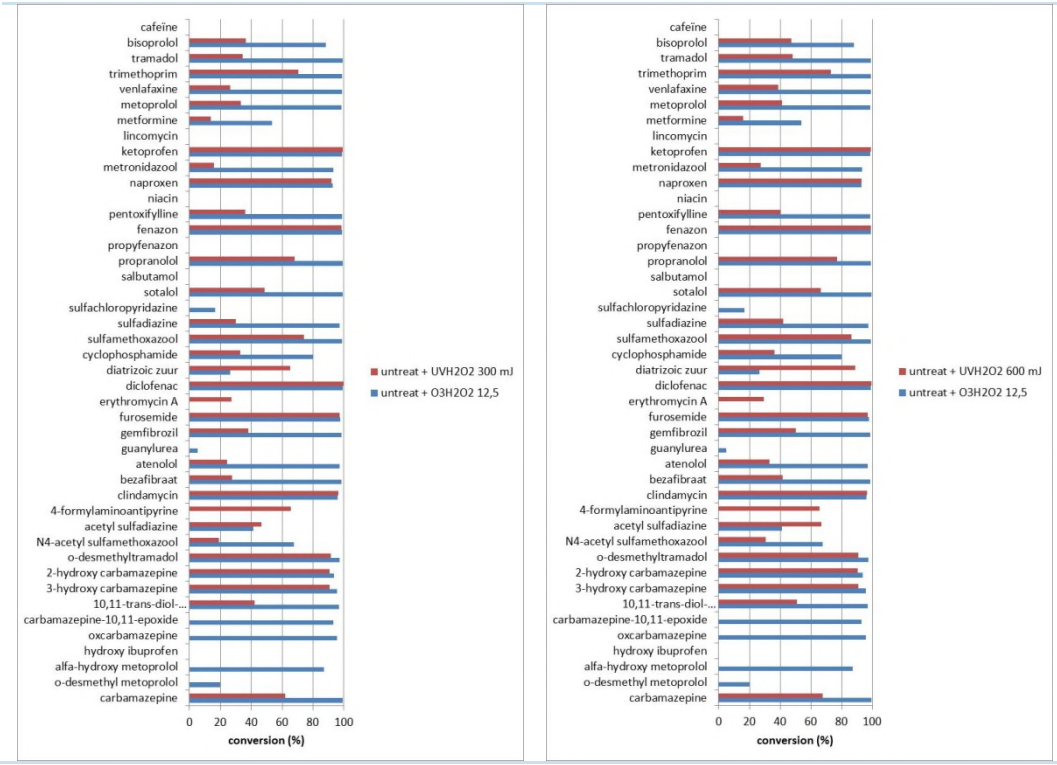


Figure 6-7: comparison of conversion of pharmaceuticals in non-pretreated water using UV/H_2O_2 versus O_3/H_2O_2. 12,5 mg O_3 in combination with 36 mg H_2O_2 per liter. UV dose 300 (left) or 600 (right) mJ/cm^2, in combination with 10 mg H_2O_2/L.

It is clear that the O_3/H_2O_2 treatment is more effective than the UV/H_2O_2 treatment, but this may be caused by the relatively high H_2O_2 concentration used in the O_3/H_2O_2 process (36 mg/L, whereas only 10 mg/L is used in the UV/H_2O_2 process). Furthermore, the conversion increases with increasing UV dose, as is to be expected. As the energy demand of a UV process in general is relatively high, without pre-treatment the O_3/H_2O_2 process seems to be more efficient than the UV/H_2O_2 treatment. However, for a fair comparison the energy required for the production of O_3 and H_2O_2 also should be taken into account, and their concentrations applied would have to be optimized.

6.6 Removal of pharmaceuticals by the UV/H_2O_2 process after IEX pre-treatment

The pretreated material was treated in a collimated beam set-up, applying three different U-doses: 0, 300 and 600 mJ/cm^2. 10 mg H_2O_2/L was added to the solution, in order to obtain an AOP. The results are shown in Figure 6-8.

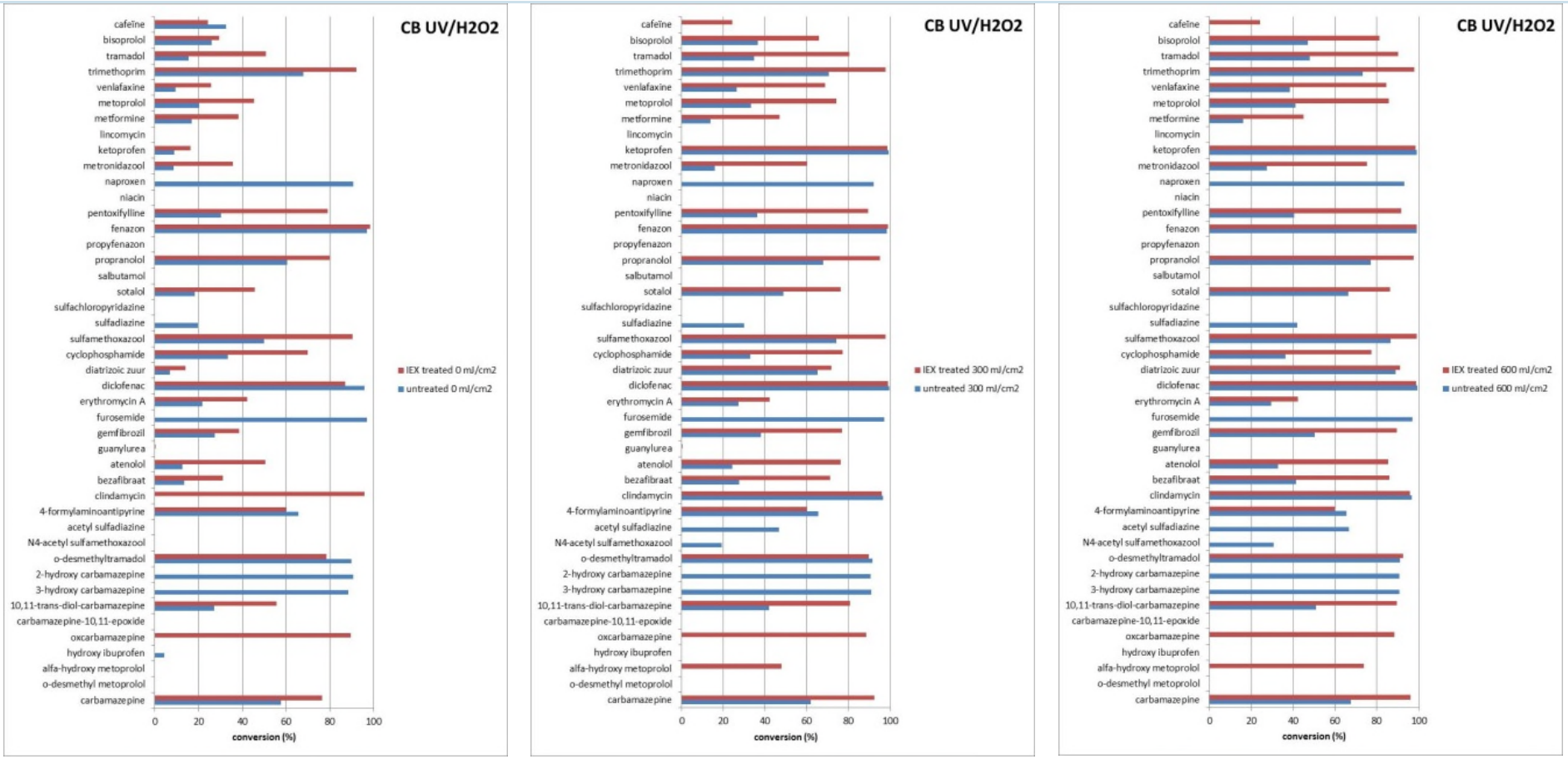


Figure 6-8: Conversion in UV/H_2O_2 processes at different UV-doses. IEX pretreated samples. 10 mg H_2O_2/L

Samples that had been pre-treated with IEX are presented by the red bars. In some cases, like for naproxen, sulfadiazine and furosemide no red bars can be observed in Figure 6-8). According to Appendix V these compounds carry a negative charge under the circumstances applied, and obviously already were removed to a high extend by only IEX. For other compounds removal by IEX may have resulted in a relatively low concentration at the start of the UV experiment. As a result, the maximum conversion by the UV/H_2O_2 process that could be reached will have been relatively low, as beneath the reporting limit the reporting limit itself was used as the minimum concentration (e.g. if the actual concentration i the influent of the UV-reactor had already been decreased to 0.02 μg/L, with a reporting limit of 0.01 μg/L the highest conversion that can be calculated is only 50%, although the real conversion may have been significantly higher) .

UV-dose = 0 mJ/cm^2 represents the conversion caused by only H_2O_2. It can be seen that for some pharmaceuticals (like naproxen, fenazon, diclofenac, furosemide and clindamycin) only addition of H_2O_2 may already result in a significant conversion of the compounds. Furthermore, it can be concluded that in general high conversions are obtained, that increase with increasing UV dose. However, after IEX pre-treatment a high conversion already can be obtained at a lower UV-dose, than in case no pre-treatment was applied. This suggests that competition by EfOM, or more specifically, by humic substances, decreases the efficiency of the UV/H_2O_2 process.

An additional advantage of the IEX pre-treatment is that the UV-transmission (UV-T) is increased from 38% to 69%, which results in a decrease to an about three times lower energy demand for the UV-process.

Thus, it can be concluded that the UV/H_2O_2 process becomes far more efficient after the IEX pre-treatment, as a significantly lower energy dose is required, and that the energy requirement to reach this dose is only 30% of the energy demand for the same dose in untreated water.

Although in principle mineralization can be obtained applying advanced oxidation (converting organic compounds into CO_2 and H_2O), in most cases oxidation is not carried out to that level. It has been shown that a lower degree of oxidation results in the formation of lower molecular weight compounds, which in general are better biodegradable than their parent compounds. However, it cannot be totally excluded that in this way byproducts are formed, and in some cases they may even be more harmful than their parent compounds. Therefore, in this research it also was investigated what happens to known conversion products of some of the pharmaceuticals. These don't necessarily represent all possible transformation products of the pharmaceuticals added, neither is it clear whether they will be formed by AOPs. However, they may already have been present in the effluent, and it cannot be excluded that they are formed during photolysis or oxidation. Thus, these experiments give an idea about the formation and possible degradation of metabolites/transformation products. The results are shown in Figure 6-9.

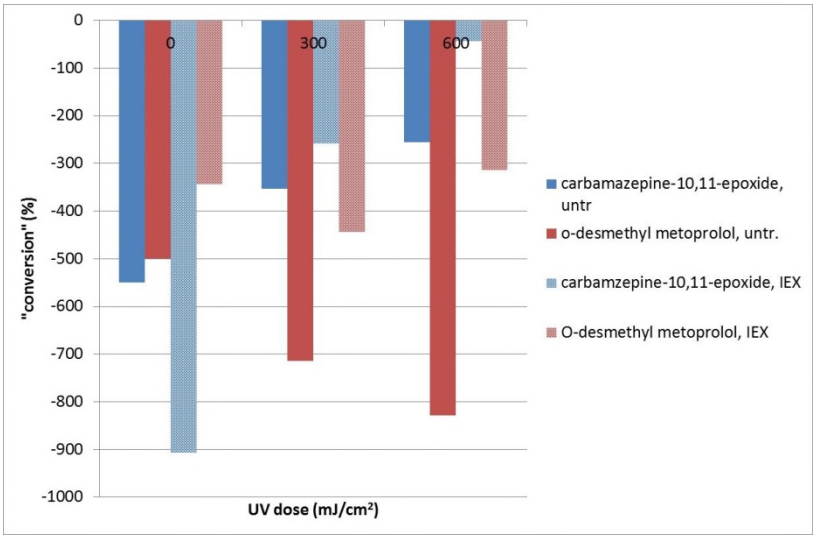


Figure 6-9: Formation of conversion products of carbamazepine and metoprolol during UV/H_2O_2 process in untreated and IEX pre-treated effluent.

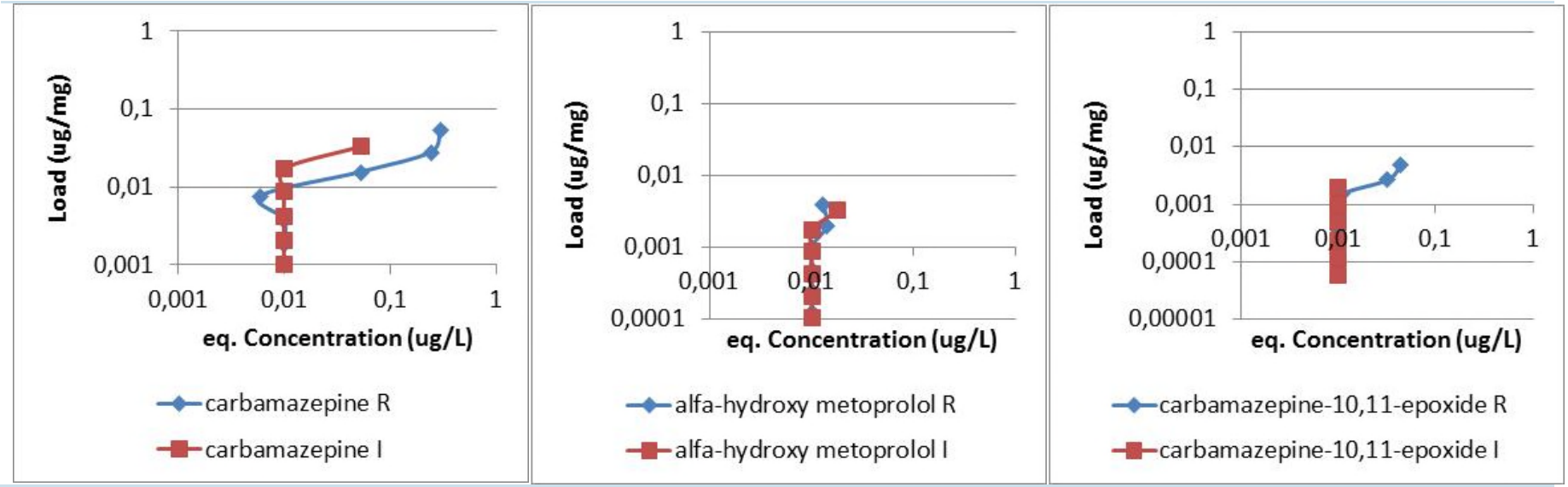
According to Figure 6-9 Carbamazepine-10,11-epoxide and O-desmethyl Metoprolol can already be formed by addition of H_2O_2. In that case pre-treatment by IEX seems to increase the Carbamazepine-10,11-epoxide formation, which may be explained from the higher H_2O_2 concentration available for reaction with carbamazepine (as there is less EfOM present to react with). For O-desmethyl metoprolol the formation increases with increasing UV dose. However, it seems to decrease after IEX pre-treatment, suggesting that maybe organic radicals, formed in a reaction of organic material (humic substances) with H_2O_2 are involved in its formation, resulting in a lower formation in the absence of EfOM. Another explanation is that degradation of the formed product is more efficient under these circumstances.

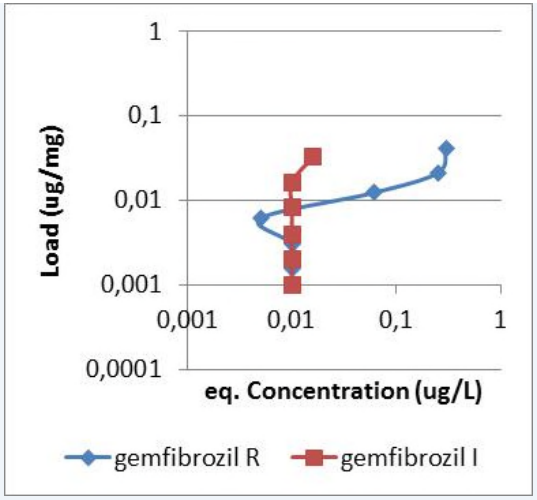
In untreated water the Carbamazepine-10,11-epoxide concentration decreases with increasing UV dose, indicating that the byproduct formed is degraded during the UV/H_2O_2 process. This effect is stronger in the pretreated water, reflecting the improved performance of the AOP in the absence of humic acids/EfOM.

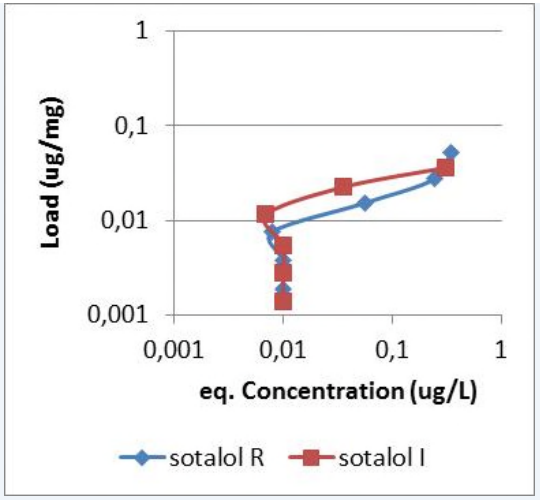
It can be concluded that the UV/H_2O_2 process becomes much more efficient after IEX pre-treatment, as a result of which the energy demand of the process is significantly decreased. However, as byproducts may be formed during the process, it will have to be determined which UV-dose is the optimum dose, as a lower dose requires less energy, but may result in a higher byproduct formation. On the other hand: in order to remove the excess H_2O_2 in general a UV/H_2O_2 process is followed by a filtration step, e.g. applying activated carbon. Most probably, the small amounts of byproducts formed during the advanced oxidation process will be removed in that step. This, however, will have to be confirmed by futher research.

6.7 Removal of pharmaceuticals by filtration over activated carbon after IEX pre-treatment

The effect of IEX pre-treatment, removing the humic substances from the water, on AC filtration were studied by determining adsorption curves on PAC. The results are shown in Figure 6-10.


Load (ug/mg)
1
0,1
0,01
0,001
0,001
0,01
0,1
1
eq. Concentration (ug/L)
carbamazepine R
carbamazepine I
Load (ug/mg)
1
0,1
0,01
0,001
0,0001
0,001
0,01
0,1
1
eq. Concentration (ug/L)
alfa-hydroxy metoprolol R
alfa-hydroxy metoprolol I
Load (ug/mg)
1
0,1
0,01
0,001
0,0001
0,00001
0,001
0,01
0,1
1
eq. Concentration (ug/L)
carbamazepine-10,11-epoxide R
carbamazepine-10,11-epoxide I


Load (ug/mg)
1
0,1
0,01
0,001
0,0001
0,001
0,01
0,1
1
eq. Concentration (ug/L)
gemfibrozil R
gemfibrozil I


Load (ug/mg)
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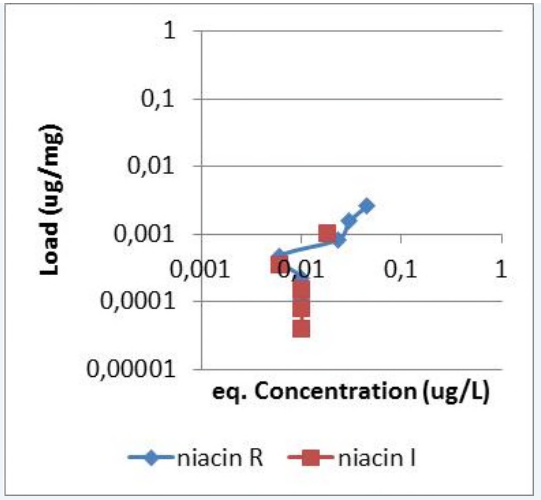
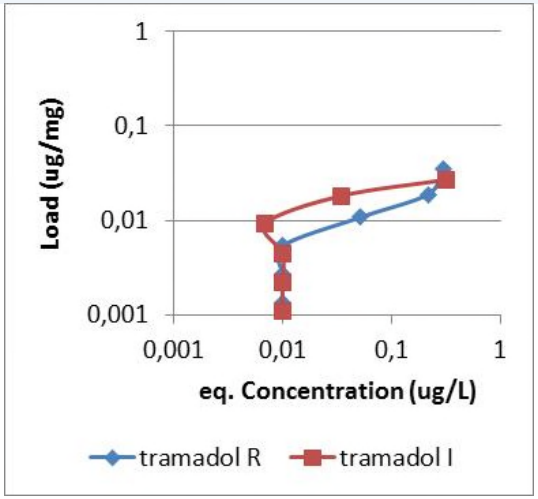
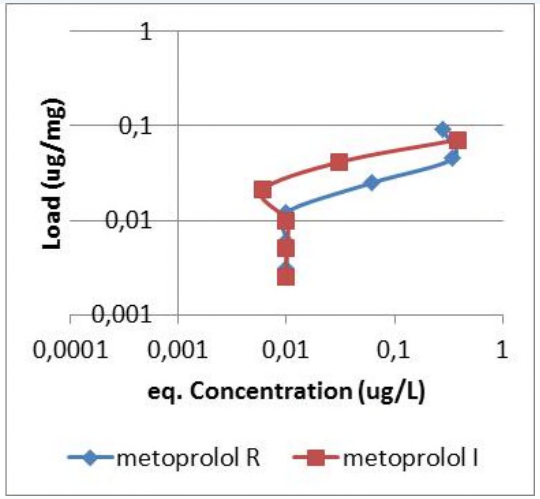
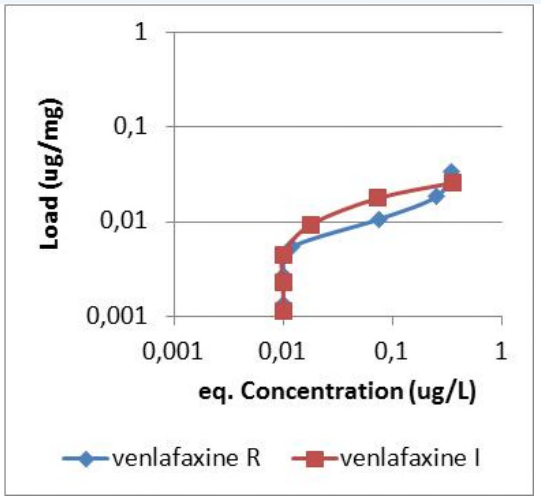
0,01
0,001
0,001
0,01
0,1
1
eq. Concentration (ug/L)
sotalol R
sotalol I


Load (ug/mg)
1
0,1
0,01
0,001
0,0001
0,00001
0,001
0,01
0,1
1
eq. Concentration (ug/L)
niacin R
niacin I


Load (ug/mg)
1
0,1
0,01
0,001
0,001
0,01
0,1
1
eq. Concentration (ug/L)
tramadol R
tramadol I


Load (ug/mg)
1
0,1
0,01
0,001
0,0001
0,001
0,01
0,1
1
eq. Concentration (ug/L)
metoprolol R
metoprolol I


Load (ug/mg)
1
0,1
0,01
0,001
0,001
0,01
0,1
1
eq. Concentration (ug/L)
venlafaxine R
venlafaxine I

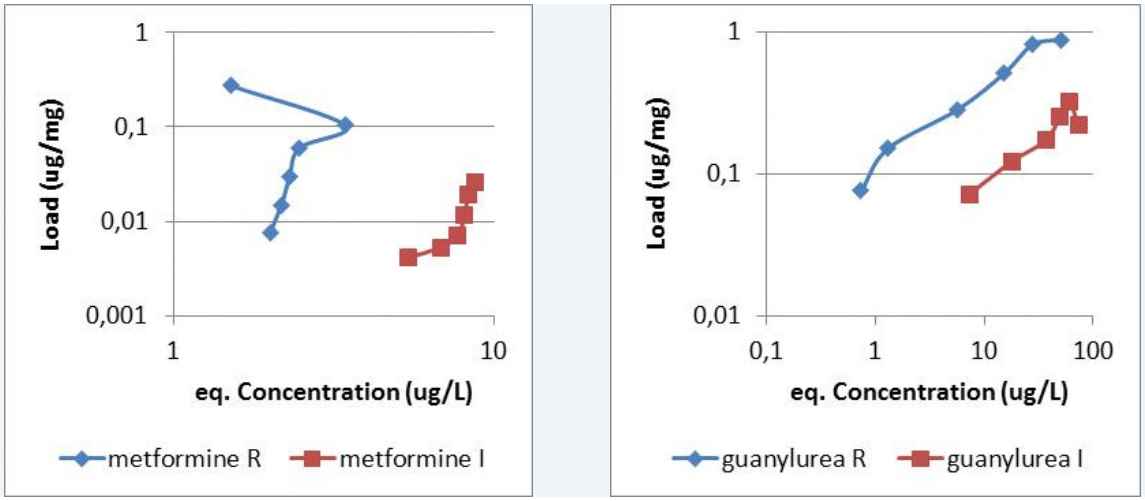


Figure 6-10:AC adsorption curves for several pharmaceuticals. R = untreated water, I = IEX treated water.

In many cases it was found that the major part of the pharmaceuticals analyzed had been adsorbed at the AC to such an extend, that the aqueous concentration was lower than the reporting limit. This explains why for carbamazepine, alfa-hydroxy metoprolol, carbamazepine-10,11-epoxide, gemfibruzil, sotalol, niacin, tramadol, metoprolol, and venlafaxine several data are shown on a vertical line (the reporting limit). The real concentrations will been lower than 0.01.

It was found that for most pharmaceuticals a maximum load of the carbon is achieved. In those cases where it could be measured, it seems that after IEX pre-treatment this maximum load for most pharmaceuticals seems to be slightly higher than without pre-treatment, indicating some competition of humic substances at the surface adsorption sites. The difference is rather small. However, surprisingly for metformin and its metabolite Guanylurea opposite effects seem to be found. This may be explained from some kind of complex formation between metformin or Guanylurea with humic substances, the complex being adsorbed better than the single pharmaceutical.

6.8 Removal of pharmaceuticals by means of O_3/H_2O_2 after pre-treatment

Experiments with O_3/H_2O_2 processes with a H_2O_2 concentration of 36 mg/L and varying O_3 concentrations (0, 12.5, 31.2, and 62.4 mg/L) were carried out, using untreated, IEX-treated and O_3-biofiltration treated effluent. For the latter experiment samples with the short biofiltration residence time were used, which still contained a significant amount of hydrophobic compounds.

The results of the O_3/H_2O_2 application to IEX pretreated water are shown in Figure 6-12.

As shown in paragraph 6.6, addition of 10 mg H_2O_2/L already results in a significant conversion of the pharmaceuticals. This explains why in general in these O_3/H_2O_2 processes conversions are very high, as here a concentration of 36 mg H_2O_2/L was applied. In literature in general a ratio of O_3:H_2O_2 of about 2 is applied, here the ratio was varied from 0.3 to 1.8. For compounds which show a relatively low conversion, the conversion increases when the water has been pretreated by means of IEX, i.e. when the humic substances have been removed. Furthermore it can be seen that in some cases, like for niacin, an increasing ozone concentration results in a higher conversion. However, for most compounds a very high conversion already is obtained at an ozone dose of 12.5 mg/L, probably (partly) due to oxidation by H_2O_2.

A similar experiment was carried out using water that had been pretreated by means of O_3 and biofiltration, but with the short residence time in the bioreactor. These results are shown in Figure 6-13. Again, as a result of the relatively high H_2O_2 concentration, conversions in general are high. In some cases it seems that the pre-treatment gives a higher conversion, e.g. for metformin, and for some compounds, like niacin, it seems that increasing the ozone concentration may also result in some improvement. However, there also are some compounds that seem to be better degraded without a pre-treatment. Maybe this involves the contribution of organic radicals, formed from reactions with EfOM.

Figure 6-14 compares the effects of the IEX and Ozone/biofiltration (short residence time) pre-treatment for the O_3/H_2O_2 AOP, using three different ozone doses (H_2O_2 concentration 36 mg/L). Although in general most conversions are very high, it seems that after IEX pre-treatment more compounds can almost fully be degraded than after O_3/biofiltration pre-treatment. This is related to the analysis. As in the O_3/biofiltration step some compounds

already had been degraded to a relatively high level, further degradation to a concentration below the reporting limit results in a relatively low maximum conversion calculated, although in fact the conversion might have been higher.

Metabolites were also measured, as shown in Figure 6-11. Contrarily to Figure 6-9, these metabolites do not seem to be formed here, but are degraded.

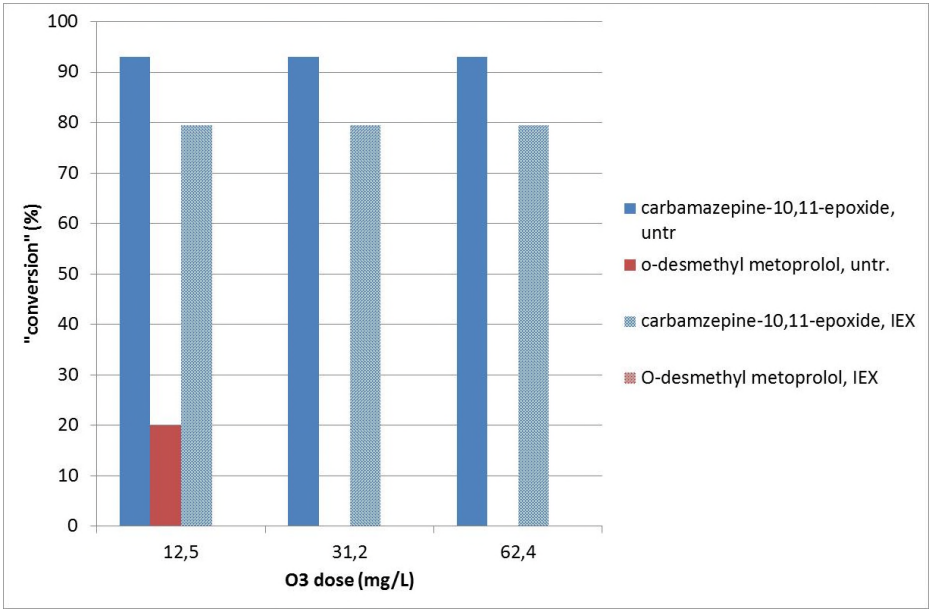


Figure 6-11: Conversion of metabolites in the O_3/H_2O_2 process.

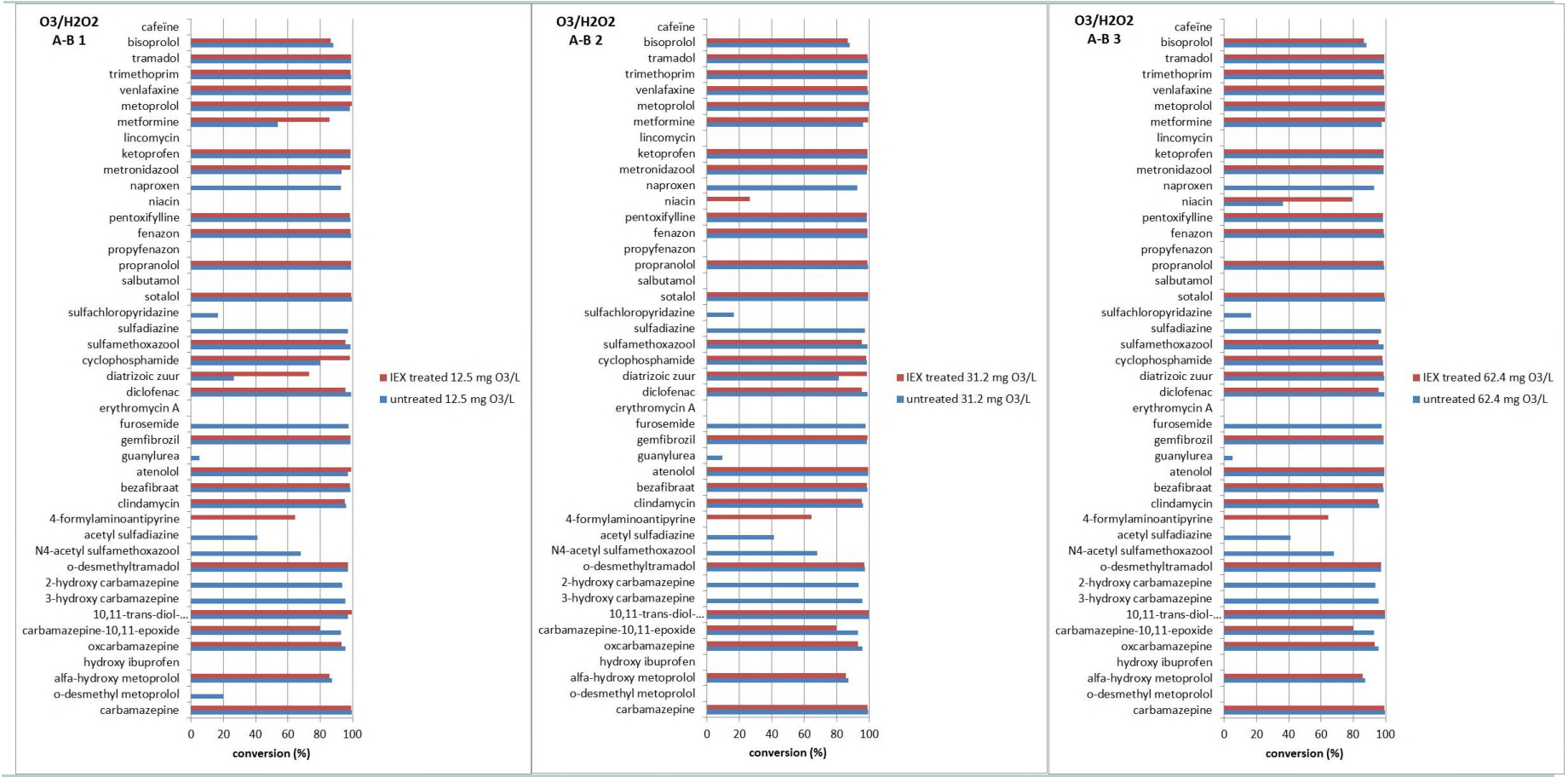


Figure 6-12: conversion of pharmaceuticals by means of O_3/H_2O_2 processes. 36 mg H_2O_2/L. Effect of ozone concentration and of IEX pre-treatment.

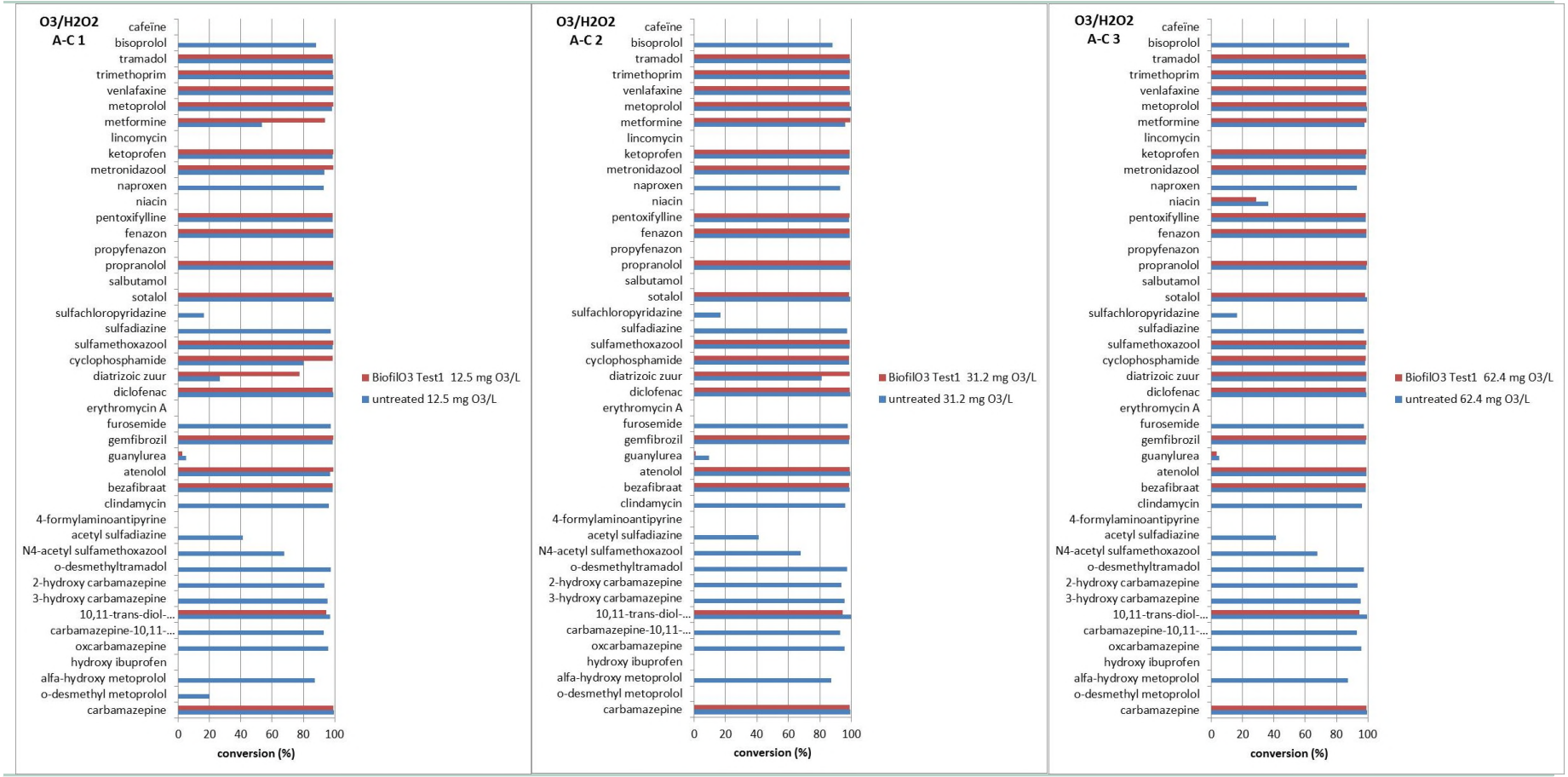


Figure 6-13: conversion of pharmaceuticals by means of O_3/H_2O_2 processes. 36 mg H_2O_2/L. Effect of ozone concentration and of O_3/biofiltration pre-treatment (short residence time).

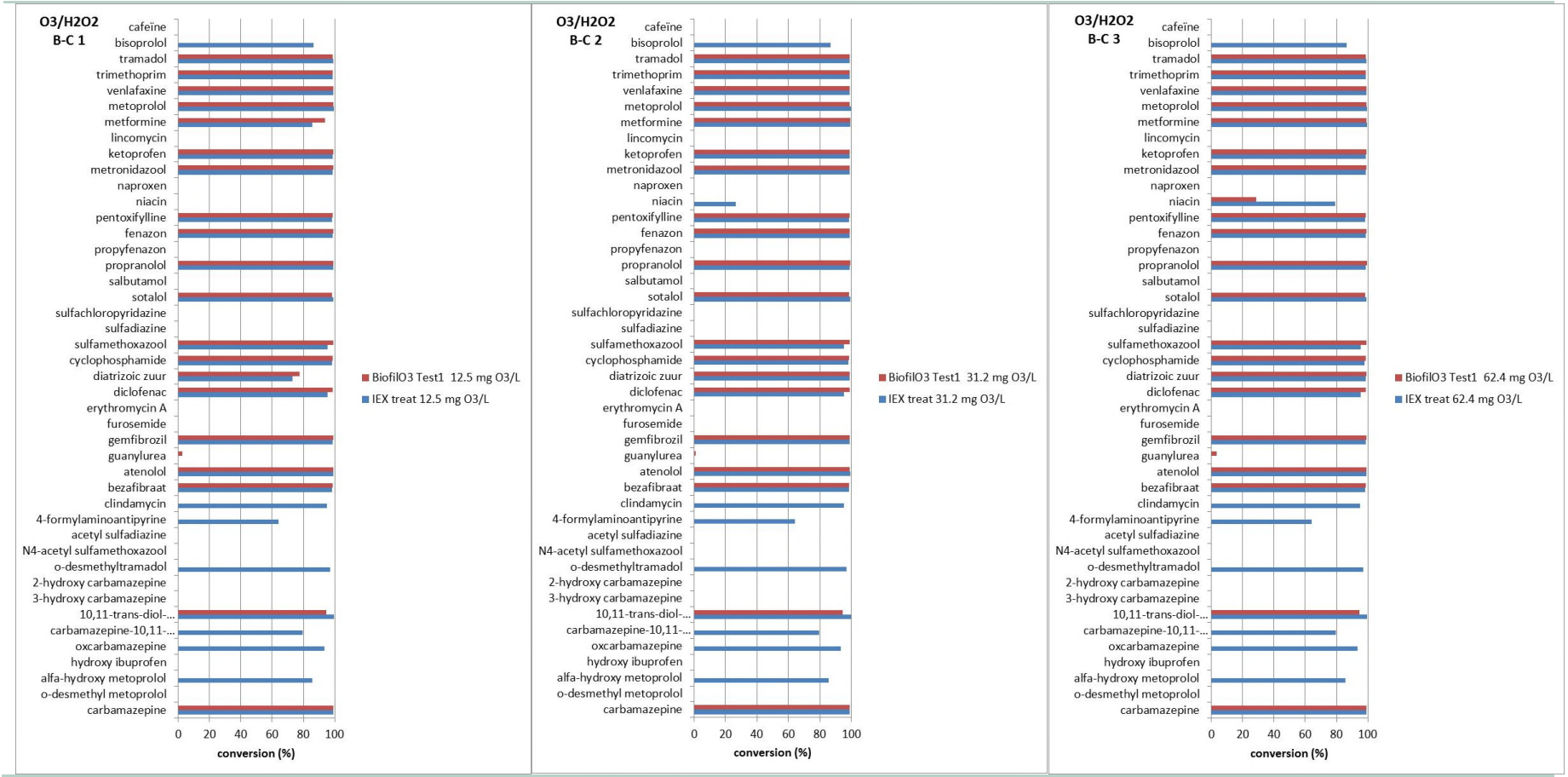
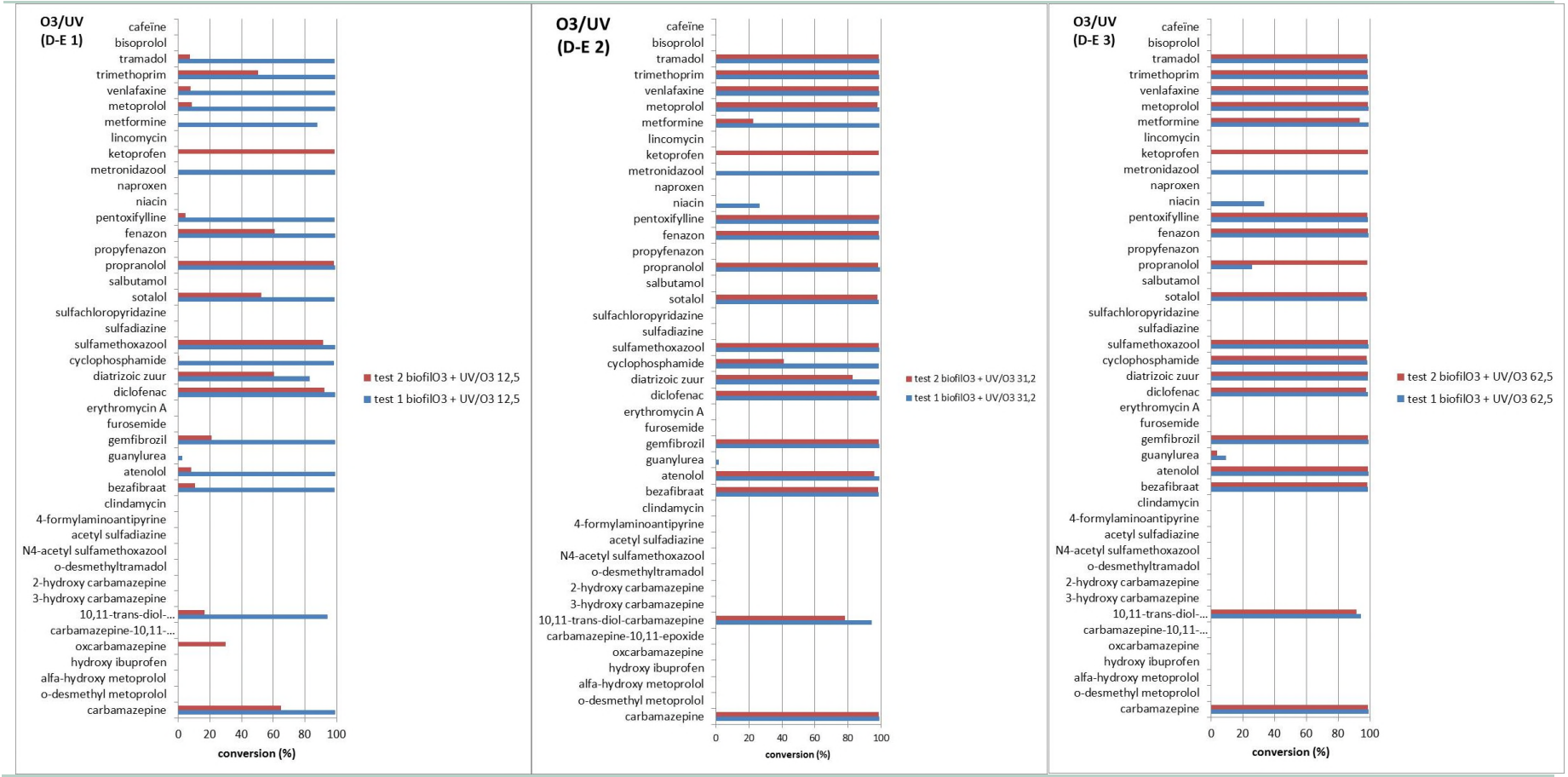


Figure 6-14: conversion of pharmaceuticals by means of O_3/H_2O_2 processes. 36 mg H_2O_2/L. Effect of IEX pre-treatment versus O_3/biofiltration pre-treatment (short residence time)



.Figure 6-15: conversion of pharmaceuticals by means of O_3/UV processes. Effect of residence time in O_3/biofiltration pre-treatment (test 1 4 minutes, test 2 6 minutes)

6.9 Effect of residence time in the O_3/biofiltration pre-treatment

As mentioned before, at first a pre-treatment was carried out in which the residence time in the biofiltration reactor in fact appeared to have been too short, as a result of which the EfOM composition and concentration appeared to have hardly been affected. The effect of this on the pre-treatment and the subsequent treatment with O_3/UV is shown in Figure 6-16. It seems that the shorter residence time has a positive effect on the subsequent conversion of pharmaceuticals. There are two possible explanations for this fact:

- HOC forms radicals under the influence of O_3/UV, which are involved in the conversion of some pharmaceuticals.
- In the first O_3/biofiltration test, with the 4 min. residence time in the biofilter, the O_3 concentration was 13 mg/L. Therefore, this test may have been more effective than the other tes (6 min. residence time in the biofilter), with an ozone concentration of 10 mg/L. At higher ozone concentrations the effect will not be visible anymore.

6.10 Effect of O_3/H_2O_2 versus O_3/UV in pharmaceutical conversion

Water, that had been pretreated with O_3/biofiltration (short residence time), afterwards was treated both with O_3/H_2O_2 and with O_3/UV. The results are shown in Figure 6-16. In general both techniques seem to give similar results. Conversions are high, and may even increase a little when the ozone concentration is increased. It is unclear why at the highest ozone dose in O_3/UV the conversion of propranolol decreases: maybe this is an experimental error.

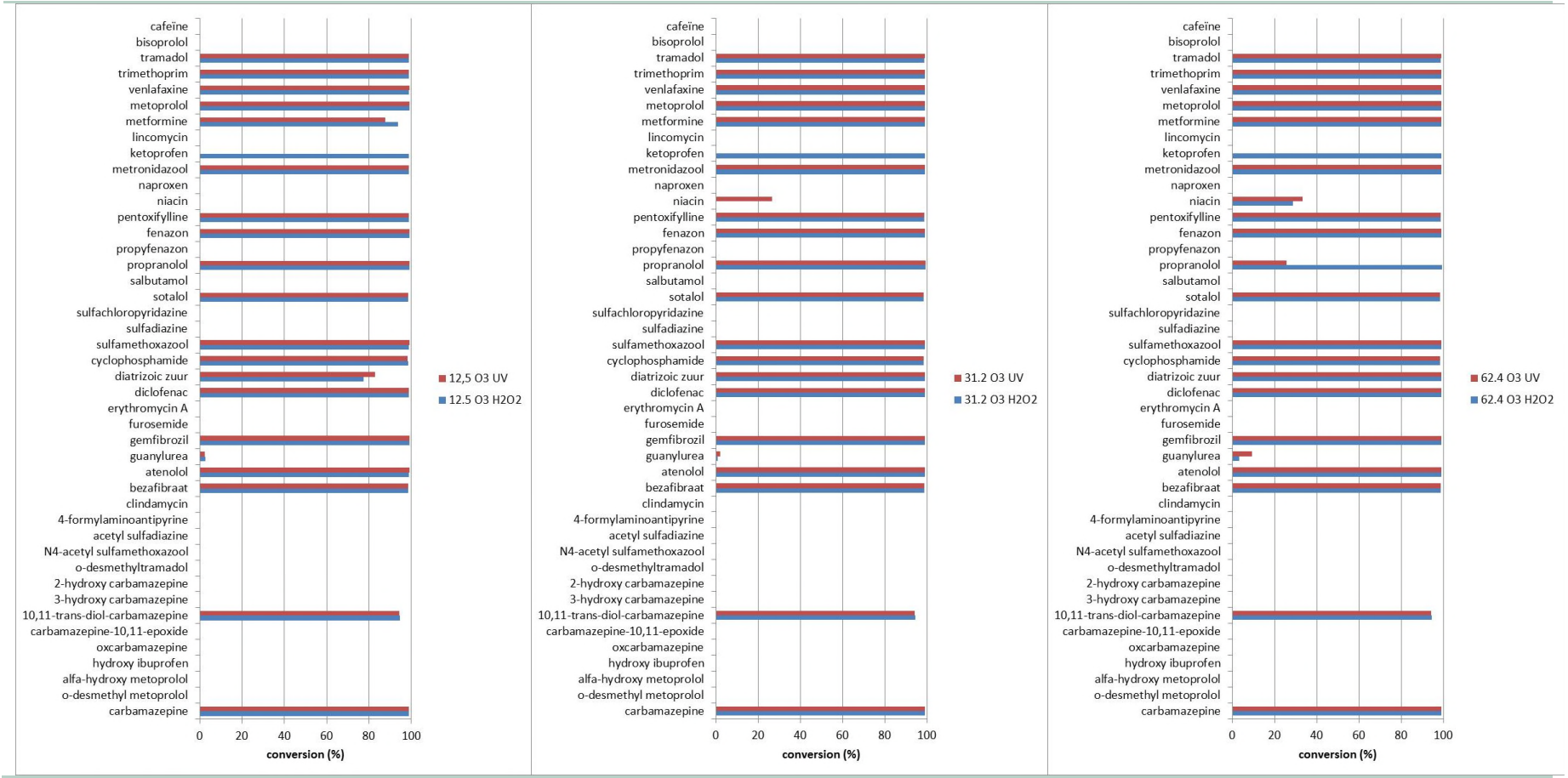


Figure 6-16: Comparison of O_3/H_2O_2 and O_3/UV technique in water pretreated by means of O_3/biofiltration (short residence time).UV dose 120-150 mJ/cm², H_2O_2 concentration 36 mg/L.

Also in this case the fate of metabolites was studied, as shown in Figure 6-17.

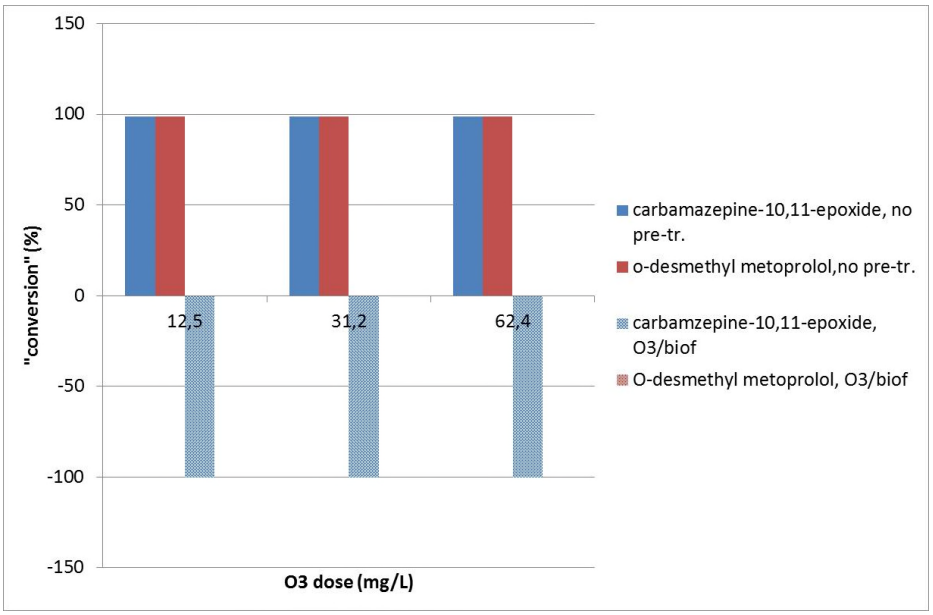


Figure 6-17:Conversion of metabolites in the O_3/UV process without pre-treatment and after O_3/biofiltration pretreatment. O-desmethyl metoprolol could not be detected after pre-treatment followed by O_3/UV, although it was present after only O_3/UV

It seems that the UV process is responsible for the formation of especially carbamazepine-10,11-epoxide. In this case the formation is less than in Figure 6-9, as a lower UV dose was applied (130 mJ/cm^2 versus 300 mJ/cm^2). O-desmethyl metoprolol could not be observed after the combined O_3/biofiltration-UV/O_3 process.

6.11 Effect of US in a UV/H_2O_2 process

These experiments were carried out in November 2016. Effluent from WWTP Panheel was taken, and analyzed (see Figure 6-18). From this figure it can be observed that the EfOM content of the effluent in Nov. 2014 was significantly lower than in Jan. 2016. In Nov. 2016 the total EfOM content was lower than in Jan. 2016, but higher than during the laboratory experiments in Nov. 2014. This difference mainly is caused by the presence of building blocks (+55%) and biopolymers (+33%), and partly by the humic substances and low molecular weight neutrals (both 24%). However, the EfOM contained 41% less low molecular weight acids and 10% less HOC.

In all cases the IEX removes the total HS fraction from the EfOM.

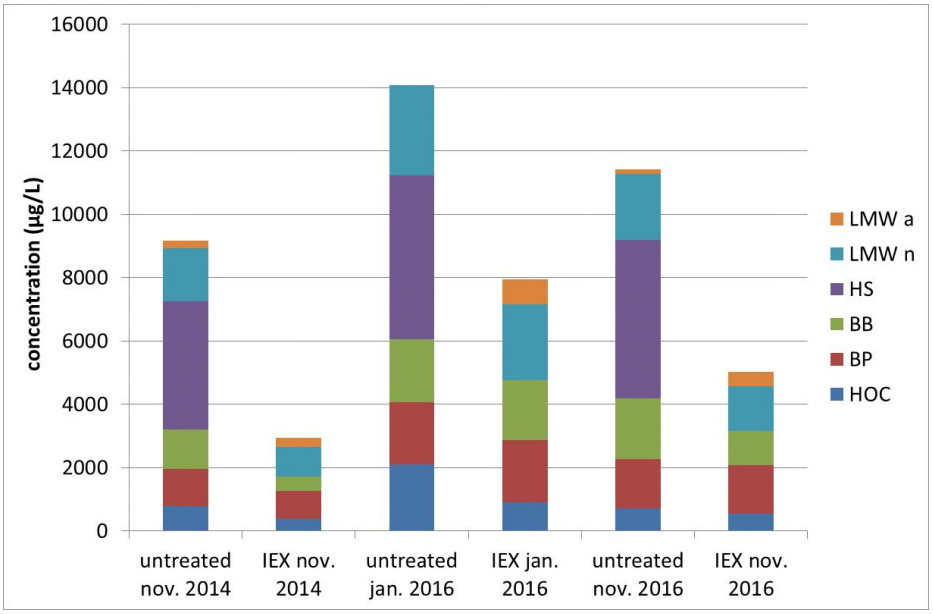


Figure 6-18: Effect of IEX filtration on composition of effluent of Panheel

Apart from the EfOM composition, also the pharmaceutical content of the effluent was analyzed. The results, and comparison with previous effluent samples used in this project, are shown in Figure 6-19. The presence of (known) metabolites is shown in Figure 6-20. Although guanylurea is a metabolite of metformin, it is shown in Figure 6-19, as it occurs in very high concentrations.

It can be concluded that the concentrations of pharmaceuticals and metabolites in the effluent, especially in 2016, are similar (the concentrations in Nov. 2014 seem to be a little higher).

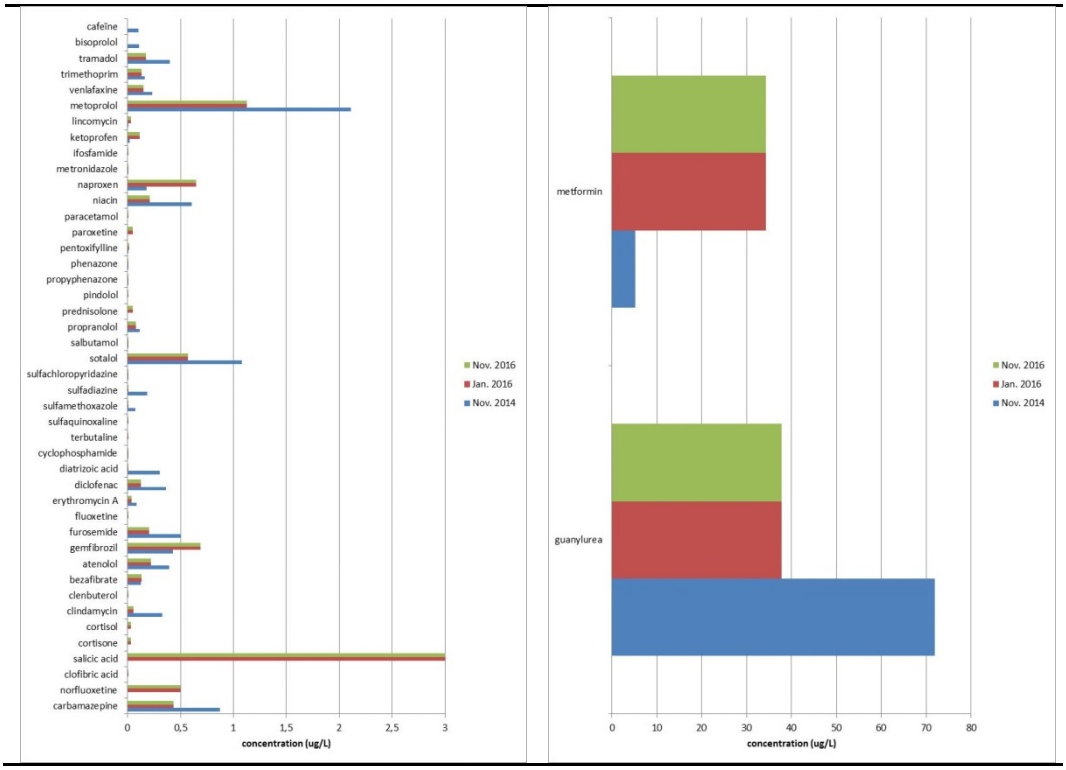


Figure 6-19: pharmaceutical content of effluent of WWTP Panheel.As the metformin and guanylurea contents are much higher than the concentrations of the other pharmaceuticals, these compounds are shown separatedly in the right graph.

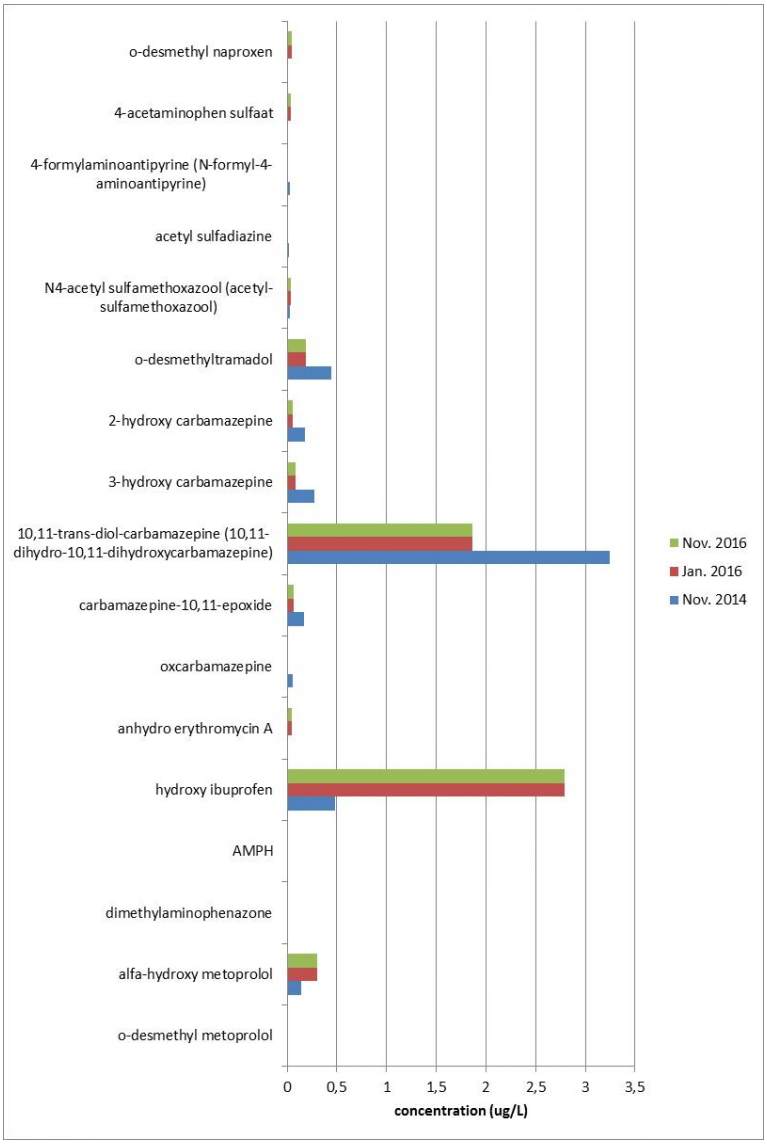


Figure 6-20: known metabolites of pharmaceuticals in the effluent of WWTP Panheel.

The results for the removal of pharmaceuticals are shown in Figure 6-21, Figure 6-22 and Figure 6-23 .

For the untreated effluent the difference with and without US application (at 30 W) is negligible. Also for the IEX treated effluent the differences with and without US appear to be negligible. Thus, the UV/US/H_2O_2 process applied here can be considered as a regular UV/H_2O_2 process. As in other experiments, it can be seen that the charged pharmaceuticals are (partly) removed by IEX. Furthermore, it can be concluded that for the majority of pharmaceuticals the UV/H_2O_2 process appears to be very effective, causing high removal. This removal is significantly higher after IEX treatment, indicating that the HS fraction of the EfOM is a fraction which significantly interferes with the AOP.

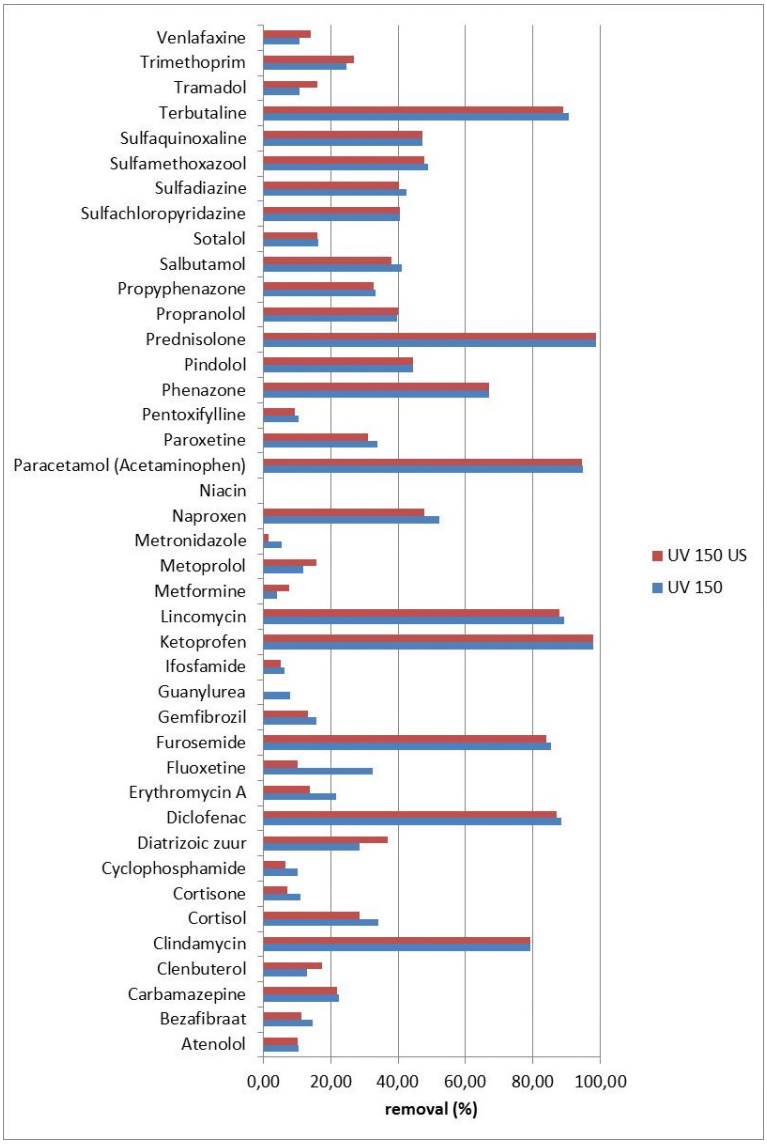


Figure 6-21: removal of pharmaceuticals by a UV/H_2O_2 process (150 mJ/cm2; 10 mg H_2O_2/L) with and without US in effluent of WWTP Panheel (no IEX).

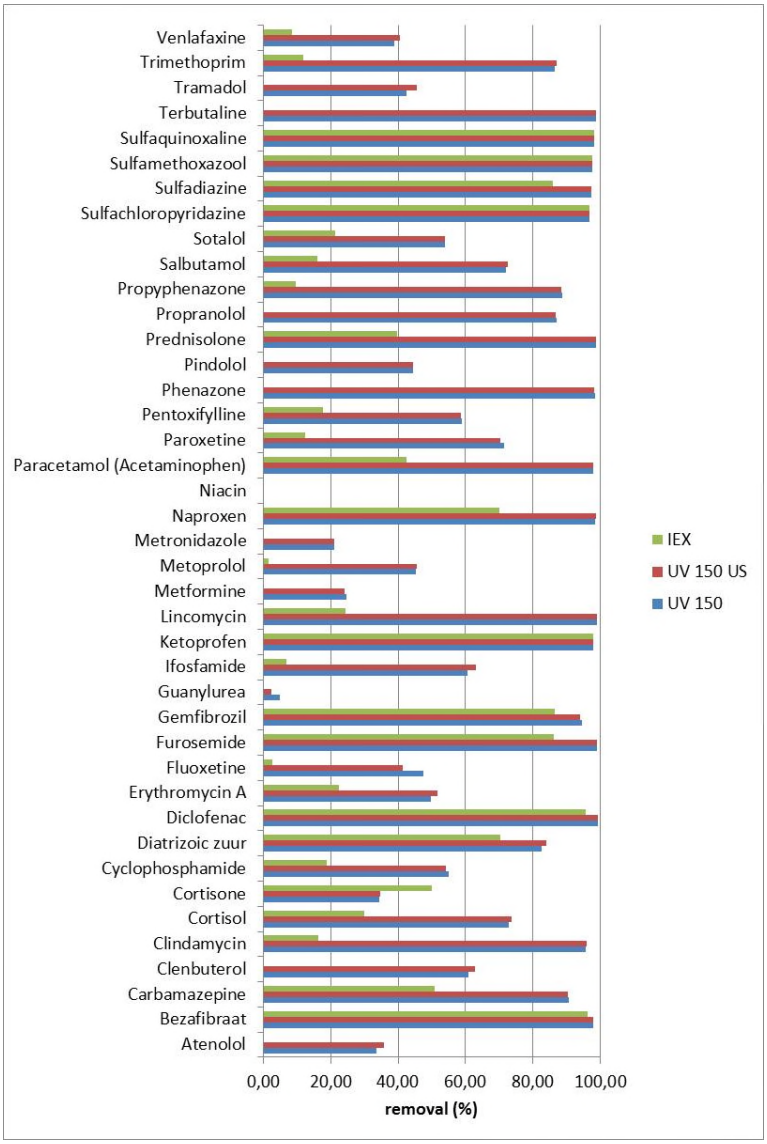


Figure 6-22: removal of pharmaceuticals by IEX, followed by a UV/H_2O_2 process (150 mJ/cm²; 10 mg H_2O_2/L) with and without US.

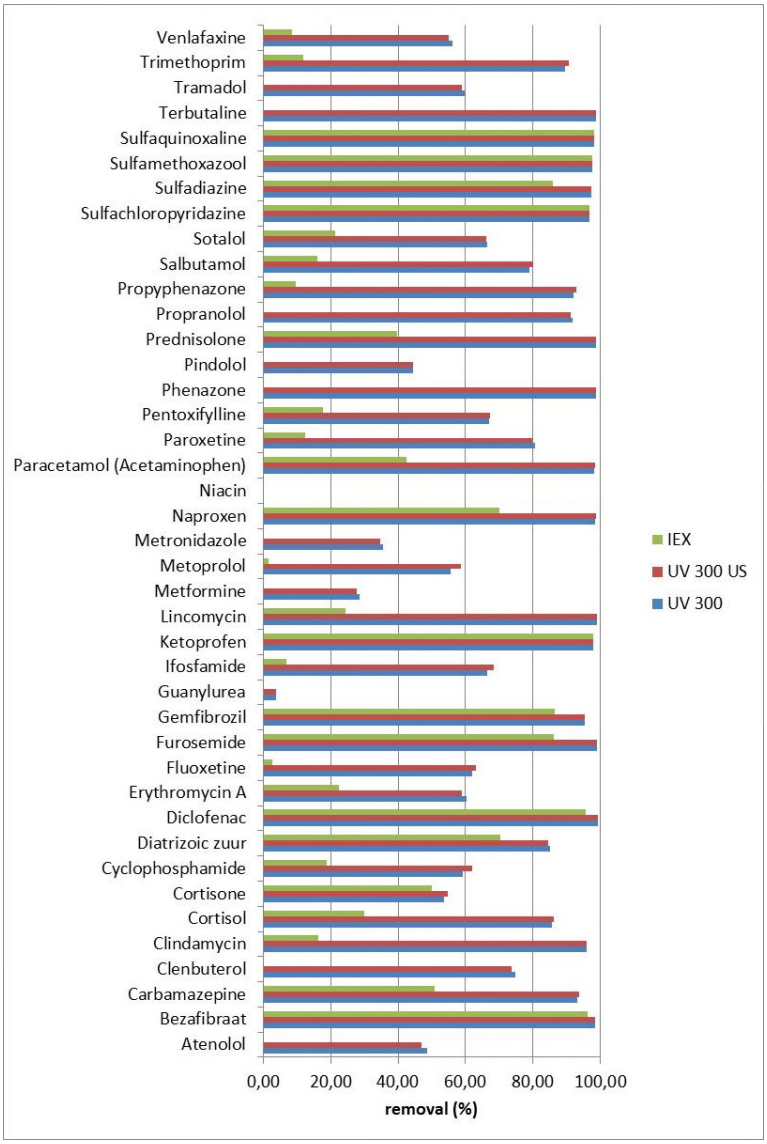


Figure 6-23: removal of pharmaceuticals by IEX, followed by a UV/H_2O_2 process (300 mJ/cm²; 10 mg H_2O_2/L) with and without US.

For the AOP itself (after the IEX) it seems that 150 mJ/cm² is high enough to obtain a good removal of the pharmaceuticals. Increasing the UV dose to 300 mJ/cm² hardly improves the removal (see Figure 6-24). This is remarkable, as in drinking water production UV doses of about 500 mJ/cm² are common for UV/H_2O_2 processes. This also points to the fact that HS in water has a large impact on the effectiveness of the UV/H_2O_2 process. The presence of US (in this reactor) doesn't affect the results.

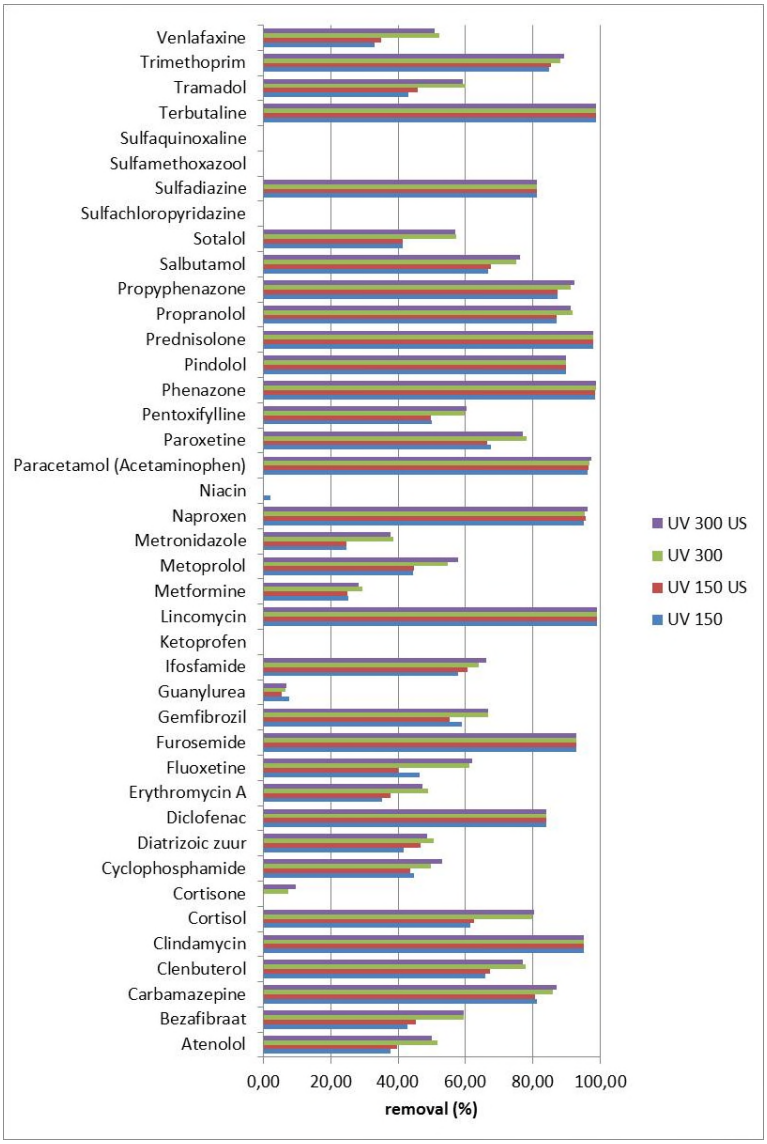


Figure 6-24: Effectiveness of AOP (UV/H_2O_2) after IEX (removal based on the concentrations obtained after IEX).

During these experiments also the fate of (known) metabolites has been determined. The results are shown in Figure 6-25. It can be seen that here too no significant difference can be observed with or without US. Furthermore, most metabolites are at least partly removed by the AOP, and this process is more effective after IEX pretreatment.

The same UV-reactor as described here, equipped with the 30 W US device, has been applied during the O_3/UV laboratory experiments, carried out at PureBlue Water, and during the pilot experiments (UV/H_2O_2 and O_3/UV/biofiltration). However, as the US device doesn't seem to affect the results obtained, the UV-reactor can be considered a regular UV-reactor, and the processes studied during the experiments can be regarded as processes without US.

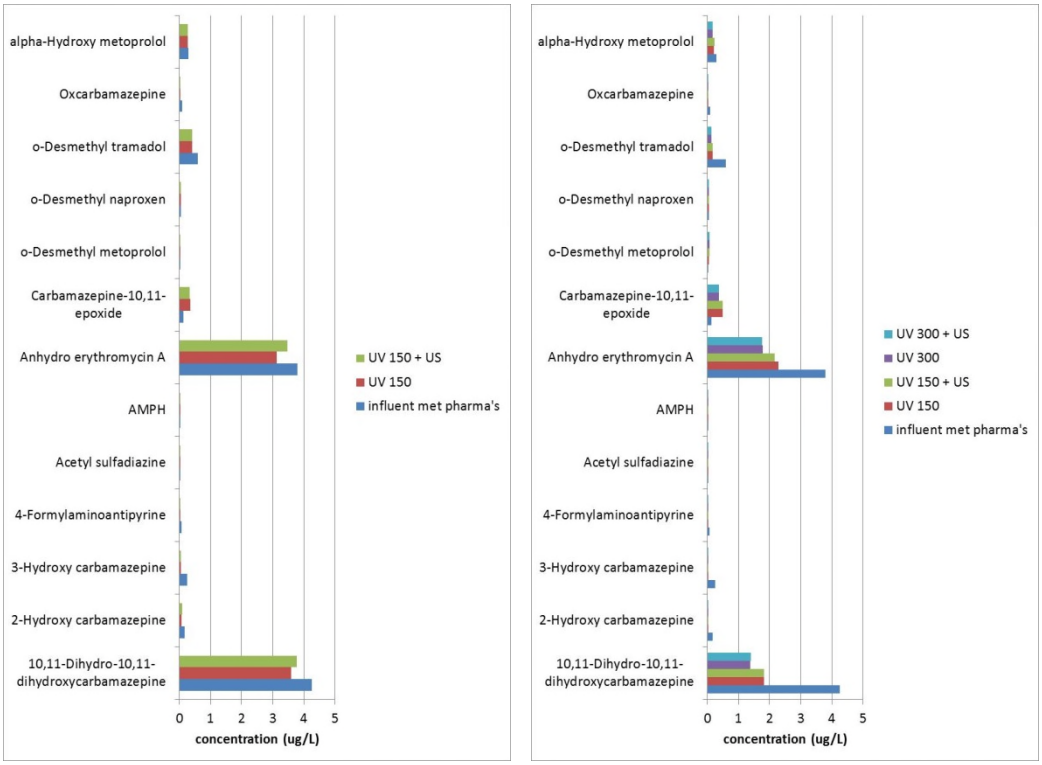


Figure 6-25: fate of metabolites during UV/US/H_2O_2 experiments. Left figure: without IEX pretreatment; right figure: with IEX pretreatment.

6.12 Follow-up in pilot research

In the previous sections it was shown that removal of at least part of the EfOM increases the efficiency of a subsequent treatment process to remove organic micropollutants like pharmaceuticals. The effect of an improvement in UV-T on the energy demand of a UV/H_2O_2 process is shown in Table 6-3. Obviously, it may not only be technically but also economically advantageous to pre-treat the effluent before the removal of pharmaceuticals.

Table 6-3: Effect of pre-treatment on UV-T and thus on the energy requirement of a subsequent UV/H_2O_2 process.

Type of water	UV-T (%)	Relative energy consumption UV/H_2O_2 process
Panheel Effluent	38	100 %
After O_3/bio-filtration	69	38 %
After IEX	85	16 %

Based on the experimental results shown in the previous sections, it was decided to build a pilot plant at the WWTP in Panheel, to test the long time performance of a process, consisting of pre-treatment followed by AOP. This pilot plant contained two parallel pre-treatment processes: ion exchange and O_3/biofiltration. In principle for ion exchange a fluidized bed reactor could be applied, which is less sensitive towards particulate matter (although it still may be a problem if fouling occurs). However, it was found that operation and automatic regeneration of the column filtration for this pilot would be significantly easier using a fixed bed reactor (IEX). Therefore, it was decided to equip the pilot with a multilayer pre-filtration step, in order to prevent fouling of the plant with particulate matter from the WWTP effluent. As a treatment process for the removal of pharmaceuticals, a UV/H_2O_2 process was installed. A final filtration over activated carbon was necessary in order to remove the excess of H_2O_2, and also, to remove possible residuals of the pharmaceuticals, as in the pilot additional pharmaceuticals were dosed to the effluent.

Furthermore, the O_3/biofiltration set-up was equipped with a LP UV-lamp, so that also the effects of an O_3/UV/biofiltration process could be studied.

7 Pilot research: materials and methods

7.1 Set-up at WWTP Panheel (WBL)

The pilot, situated at the Panheel WWTP (WBL), consisted of:

1. Filtration set-up to remove particles and suspended solids: combination of a fixed bed of four different layers (anthracite, sand and two finer materials for finer filtration) The filtration velocity was 25 m^3/m^2.h., fed by the effluent of the WWTP. The flow was set to 1.100 to 1.400 L/h continuously. The filtration set-up is backwashed with filtrated water (influent over a 150 μm filter) after reaching a maximum backpressure setpoint.
2. 1.000 L vessel to store the filtrated water of (1), called pretreated influent water, continuously flowing over near the WWTP effluent sampling point.
3. A-IEX (Anion Ion Exchange) unit, consisting of 2 IEX vessels containing 25 L of Lanxess type Lewatit S 6368 A to remove humic acids from the pretreated influent water. The IEX treated water is, in case of dosage of the pharmaceuticals, fed to the UV/H_2O_2set-up (5), otherwise the IEX effluent is discarded near the WWTP effluent sampling point. Every 7.000 L of pretreated influent water, the IEX of the used IEX vessel is regenerated with 5 kg of NaCl (Broxo) as 50 L of 10% (w/w) NaCl. After flushing the bed to remove the salty water, the IEX is ready to be used again.
4. The O_3-Biofiltration and O_3-UV-Biofiltration set-up consisted of a Primozone ozone generator (type GM-1), able to produce a maximum of 50 g/h of ozone. During the different tests the ozone concentrations were varied. During standard operation, a steady dose of 7 g O_3/h was dosed. The UV system was a Lazur M3 system, consisting of a low pressure amalgam lamp of 70 W. Although the UV reactor was equipped with a 30 W US device, experiments have shown that this will probably not have affected the results obtained (see section 6.11). The biofiltration reactor consisted of a 80 L vessel containing a special biofilm carrier material with very large surface, enabling a biofilm to grow inside the reactor. Water contact times varied between different experiments from 5 to 12 min. The O_3-biofiltration and O_3/UV biofiltration reactor were fed continuously using a pump controlled by a flow meter, so the flow into the reactor could be set to a fixed value (which could differ during different tests).
5. A UV/H_2O_2set-up was operated discontinuously and only during the spiking of pharmaceuticals. Influent of the UV/H_2O_2 system was collected into the influent vessel of 200 L. A selected amount of hydrogen peroxide was dosed manually into the vessel. The UV system also consisted of a low pressure Amalgam lamp of 70 W. Although the UV reactor was equipped with a 30 W US device, experiments have shown that this will probably not have affected the results obtained (see section 6.11).During different tests, UV254 absorption was measured and the dose of 150 or 300 mJ/cm^2 was set with a flow controlling system.
6. The ACF (Activated Carbon Filtration) unit consisting of 2 columns filled with Norit activated carbon (type PK 1-3) to treat the pilot effluent water used during the dosage of the pharmaceuticals. The ACF is used as an extra barrier in case of

leaching of pharmaceuticals or their metabolites/transformation products during treatment by IEX-UV/H_2O_2 or O_3-Biofiltration- UV/H_2O_2. The ACF is not used in this research to study the effects of ACF for the removal of pharmaceuticals.

The whole set-up was positioned in a trailer, which was parked at the WWTP. In Figure 7-1 some photographs of the pilot situated in Panheel are shown, in the 0 the PFD of the pilot is given.

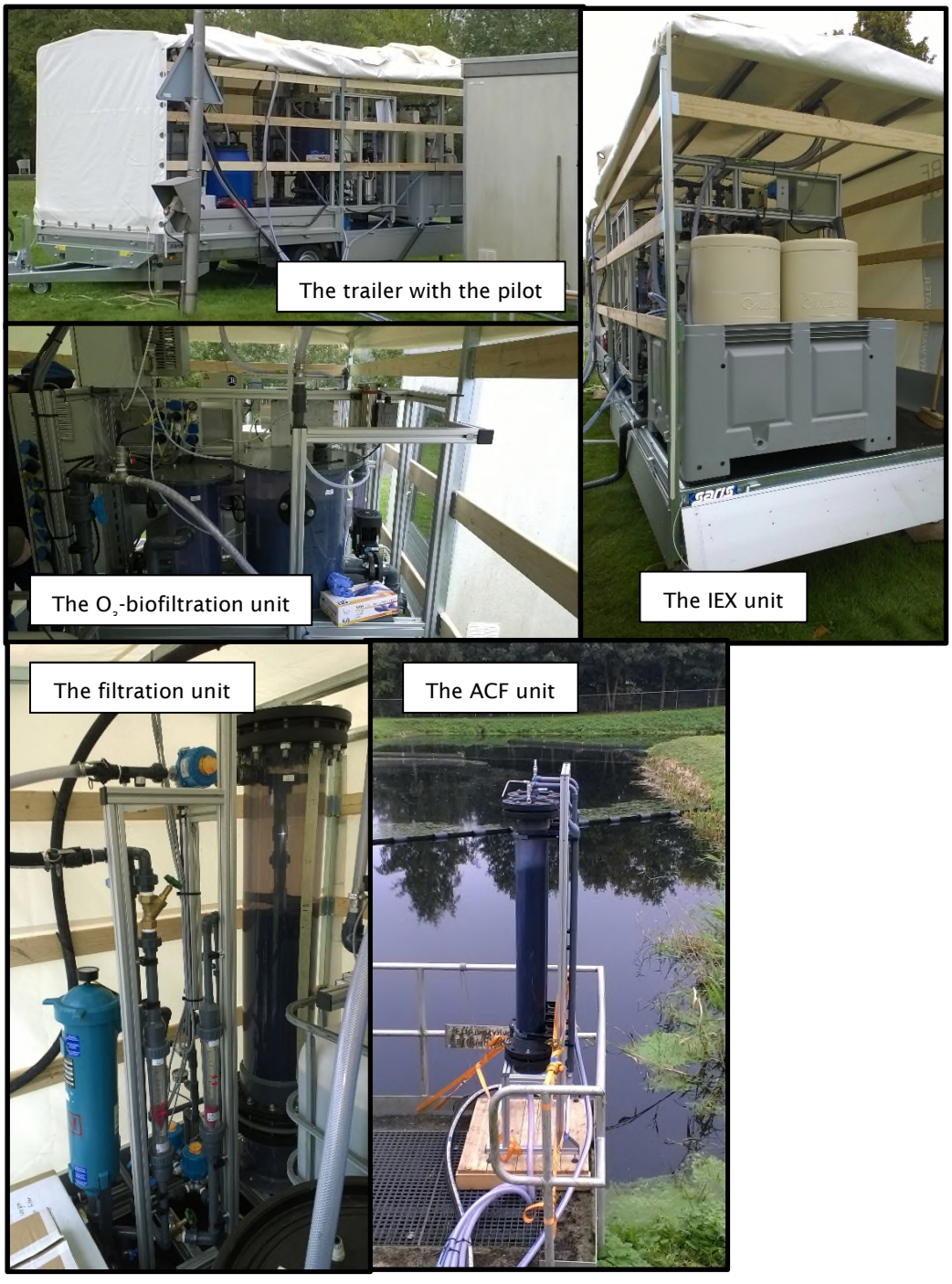


Figure 7-1 Photographs of the pilot at Panheel

7.2 General operation

The pilot has been running from October 19th 2015 until the end of February 2016. The first weeks were used for start-up and building up the treatment process for the IEX and O_3-Biofiltration processes. Especially the Biofiltration needed sufficient time in order to let the micro-organisms grow enough to reach a desired or optimal removal of organic carbon. Also the IEX process was used and regenerated during a certain period to evaluate performance of the removal of organic carbon (humic acids) and to determine whether the filtration and regeneration process could be run stabe. After this period the dosing experiments with pharmaceuticals were started.

After the first series of dosing experiments, on November 27th, some problems occurred with the pump. As a result of this the biofiltration process had to be temporarily stopped, and restarted after the pump had been repaired. It was left running for some time before the next experiments were carried out, in order to give the biomass some time to recover. The second series of dosing experiments took place on December 17th. However, experimental data of the EfOM composition showed that the O_3/biofiltration process did not seem to have recovered its full effectiveness after the downtime.

7.3 Dosing experiments

At November 27th and December 17th 2015 dosing experiments with a cocktail of pharmaceuticals were carried out as given in the lists below. In

Table 7-1 the list of dosed pharmaceuticals is given, Table 7-2 gives an overview of some known metabolites of the pharmaceuticals applied, that were analyzed. These metabolites, which partly will have been present in the effluent already, were also analyzed, although they had not been dosed. In this way it is possible to check whether such metabolites too can be removed, or whether they may be formed during the oxidation process.

All samples were taken in duplicate, all experiments were performed in duplicate using the same batch of pretreated influent water containing the dosed pharmaceuticals. In total two batches of pretreated influent water containing the pharmaceuticals were used for the experiments. The experimental procedure was as follows:

1. The 1.000 L vessel with prefiltered effluent is filled, after this the filtration unit is stopped during the dosing experiments;
2. 1 L of the 1-5 mg/L cocktail with pharmaceuticals is dosed to the 1.000 L vessel to obtain a concentration of 1-5 µg/L of pharmaceuticals, and mixed well by recirculating the water by means of the pump. A duplicate sample is taken for the analyses;
3. Application of the IEX-UV/H_2O_2 process:
    a. 100 L of water passes the IEX column (contact time set at 2 min.) filling a 200 L vessel to rinse the tubing and vessel with pharmaceuticals containing water;
    b. After discarding the water via the ACF unit, the 200 L vessel is completely filled with 200 L IEX effluent (ct 2 min). A duplicate sample is taken for the analyses;
    c. 10 mg/L H_2O_2 is dosed to the 200 L and mixed well;
    d. After 2 min. warming-up of the UV lamp, water passes the UV/ H_2O_2 unit with a defined flow to reach the desired UV-dose (0, 150 or 300 mJ/cm^2). The dose is calculated using UV-T data, and realized by means of the flow through the reactor. Duplicate samples are taken for the analyses.
    e. The water passes the ACF unit before it is returned to WWTP effluent.
4. Application of the O_3-Biofiltration-UV/H_2O_2 process:
    a. 200 L of water passes the O_3-Biofiltration unit (contact time 9.5 min) filling a 200 L vessel to rinse the tubing and vessel with pharmaceuticals containing water;
    b. After discarding the water via the ACF unit, the 200 L vessel is completely filled with 200 L O_3-Biofiltration, contact time 9.5 min. The Empty Bed Contact Time (EBCT) is 19 min., but as the 80 L biofiltration vessel had been filled for 50%, the real contact time is 9.5 min. A duplicate sample is taken for the analyses;
    c. 10 mg/L H_2O_2 is dosed to the 200 L and mixed well;
    d. After 15 min warming-up of the UV lamp, water passes the UV/ H_2O_2 unit with a defined flow to reach the desired UV-dose (0, 150 or 300 mJ/cm^2). The dose is calculated using UV-T data, and realized by means of the flow through the reactor. Duplicate samples are taken for the analyses.
    e. The water passes the ACF unit before it is returned to WWTP effluent.
5. Application of the O_3-UV-Biofiltration process:
    a. The pharmaceuticals containing solution passes the 80 L O_3-UV-Biofiltration unit with a flow of 250 L/h (contact time 20 min) during warming-up of the UV-lamp;

b. 150 L of water is used for the O_3-UV-Biofiltration process with a defined flow to reach the desired UV-dose. A duplicate sample is taken for the analyses;
c. The water passes the ACF unit before it is returned to WWTP effluent.

Table 7-1 Cocktail of pharmaceuticals dosed to the effluent of WWTP Panheel

Pharmaceutical	CAS no.	Gross formula	Concentration (µg/L)
Atenolol	29122-68-7	C14H22N2O3	1
Bezafibraat	41859-67-0	C19H20ClNO4	1
Carbamazepine	298-46-4	C15H12N2O	1
Clenbuterol	37148-27-9	C12H18Cl2N2O	1
Clindamycin	18323-44-9	C18H33ClN2O5S	1
Cortisol	50-23-7	C21H30O5	1
Cortisone	53-06-5	C21H28O5	1
Cyclophosphamide	50-18-0	C7H15Cl2N2O2P	1
Diatrizoic zuur	117-96-4	C11H9I3N2O4	1
Diclofenac	15307-86-5	C14H11Cl2NO2	1
Erythromycin A	59319-72-1	C37H67NO13	1
Fluoxetine	59333-67-4	C17H18F3NO	1
Furosemide	54-31-9	C12H11ClN2O5S	1
Gemfibrozil	25812-30-0	C15H22O3	1
Guanylurea	141-83-3	C2H6N4O	5
Ifosfamide	3778-73-2	C7H15Cl2N2O2P	1
Ketoprofen	22071-15-4	C16H14O3	1
Lincomycin	859-18-7	C18H34N2O6S	1
Metformine	657-24-9	C4H11N5	5
Metoprolol	37350-58-6	C15H25NO3	1
Metronidazool	443-48-1	C6H9N3O3	1
Naproxen	22204-53-1	C14H14O3	1
Niacin	59-67-6	C6H5NO2	1
Paracetamol	103-90-2	C8H9NO2	1
Paroxetine	61869-08-7	C19H20FNO3	1
Penicillin V	132-98-9	C16H18N2O5S	1
Pentoxifylline	6493-05-6	C13H18N4O3	1
Phenazone	60-80-0	C11H12N2O	1
Propyphenazone	479-92-5	C14H18N2O	1
Pindolol	13523-86-9	C14H20N2O2	1
Prednisolone	50-24-8	C21H28O5	1
Propranolol	525-66-6	C16H21NO2	1
Salbutamol	18559-94-9	C13H21NO3	1
Sotalol	3930-20-9	C12H20N2O3S	1
Sulfachloropyridazine	80-32-0	C10H9ClN4O2S	1
Sulfadiazine	68-35-9	C10H10N4O2S	1
Sulfamethoxazool	723-46-6	C10H11N3O3S	1
Sulfaquinoxalin	59-40-5	C14H12N4O2S	1
Terbutaline	23031-32-5	C12H19NO3	1
Tramadol	27203-92-5	C16H25NO2	1
Trimethoprim	738-70-5	C14H18N4O3	1
Venlafaxine	93413-69-5	C17H27NO2	1

Table 7-2 Possible metabolites of the pharmaceuticals measured in the effluent of WWTP Panheel. The presence of these metabolites was analyzed, the metabolites had not been dosed to the pilot reactors.

Metabolite	CAS no.	Gross formula	Metabolite of
Salicylzuur	69-72-7	C7H6O3	Acetylsalicylzuur
2-hydroxy carbamazepine	68011-66-5	C15H12N2O2	Carbamazepine
3-hydroxy carbamazepine	68011-67-6	C15H12N2O2	Carbamazepine
10,11-trans-diol-carbamazepine	35079-97-1	C15H14N2O3	Carbamazepine
Carbamazepine-10,11-epoxide	36507-30-9	C15H12N2O2	Carbamazepine
Oxcarbamazepine	28721-07-5	C15H12N2O2	Carbamazepine
Clofibrinezuur	882-09-7	C10H11ClO3	Clofibraat
Anhydro-erythromycin A	23893-13-2	C37H65NO12	Erythromycin A
Norfluoxetine	83891-03-6	C16H16F3NO	Fluoxetine
Hydroxy ibuprofen	51146-55-5	C13H18O3	Ibuprofen
AMPH	38604-70-5	C9H12N2O	Metamizole
Dimethylaminophenazon	58-15-1	C13H17N3O	Metamizole
α-Hydroxy metoprolol	56392-16-6	C15H25NO4	Metropolol
O-Desmethyl metoprolol	62572-94-5	C14H23NO3	Metropolol
O-Desmethyl Naproxen	123050-98-6	C13H12O3	Naproxen
4-Acetaminophen sulfaat	32113-41-0	C8H9NO5S	paracetamol
4-Formylaminoantipyrine	1672-58-8	C12H13N3O2	Phenazone
Acetyl sulfadiazine	127-74-2	C12H12N4O3S	Sulfadiazine
N4-acetyl sulfamethoxazool	21312-10-7	C12H13N3O4S	Sulfamethoxazool
O-Desmethyltramadol	73986-53-5	C15H23NO2	Tramadol

In Table 7-3 details are given about the measurements and experiments that were performed at the pilot.

Table 7-3 Plan of measurements and experiments at the pilot at WWTP Panheel

Parameters	**IEX**	**Ozone-biofiltration**	**UV/H_2O_2**	**ACF**	**Frequency**
UV absorption	yes	yes	yes	no	Every week
LC-OCD and COD	yes	yes	yes	no	During dosing experiments
Pharmaceuticals	yes	yes	yes	no	During dosing experiments
Ozone dosing	no	yes	no	no	Every week
UV dosing	no	no	yes	no	During dosing experiments
pH	yes	yes	yes	no	During dosing experiments
WWTP effluent	no	no	no	no	During dosing experiments
Installation parameters					
Pressure	no	no	no	no	Every 2 weeks
Flow	yes	yes	yes	no	Every week
Temperature (WBL)	yes	yes	yes	no	During dosing experiments
Time after regeneration	yes	no	no	no	Every 2 weeks
Chemicals IEX	yes	no	no	no	Every 2 weeks
During dosing of pharmaceuticals					
	Experiments				
	Exp 1, 2	Exp 3, 4			
IEX (750 L/h, 1 setting)	2 min ct	2 min ct			
UV-H_2O_2 (2 settings, 10 mg/L H_2O_2)	150 J/cm²	300 mJ/cm²			
	Exp 5, 6	Exp 7, 8	Exp 9, 10	Exp 11,12	Exp 13, 14	Exp 15, 16
Ozone-biofiltration / UV-H_2O_2 (2 settings, 10 mg/L H_2O_2)	12 mg/L 150 mJ/cm²	12 mg/L 300 mJ/cm²	18 mg/L 150 mJ/cm²	18 mg/L 300 mJ/cm2	23 mg/L 150 mJ/cm²	23 mg/L 300 mJ/cm²
	Exp 17		Exp 18			
Ozone-UV / biofiltration	18 mg/L ozone	150 mJ/cm² UV	23 mg/L ozone	150 mJ/cm² UV		

7.4 Pilot performance

At the pilot at Panheel the filtration, IEX and O_3-Biofiltration treatments were most of the time constantly in use, while during the dosing of the pharmaceuticals also the UV/H_2O_2 and ACF treatments were used. The filtration, IEX and O_3-Biofiltration treatment performances were monitored during the total period for several parameters.

7.4.1 filtration treatment

In Figure 7-2 part of the logged flows of the filtration treatment and ozone-biofiltration are shown, the IEX flow could not be logged. In Figure 7-3 the pressure behavior of the filtration treatment is shown. As can be seen in Figure 7-2, some disturbances occurred during the pilot like a major breakdown of the pump of the pretreated influent which fed the ozone-biofiltration and IEX system. Between 3-12 and 8-12 the main pilot pump was replaced, and during this period the ozone-biofiltration and IEX units were stopped. From 8-12-15 the pilot has been running continuously almost without any significant problems. The pressure buildup and backwashes of the filtration unit are shown in the pressure figures (Figure 7-3).

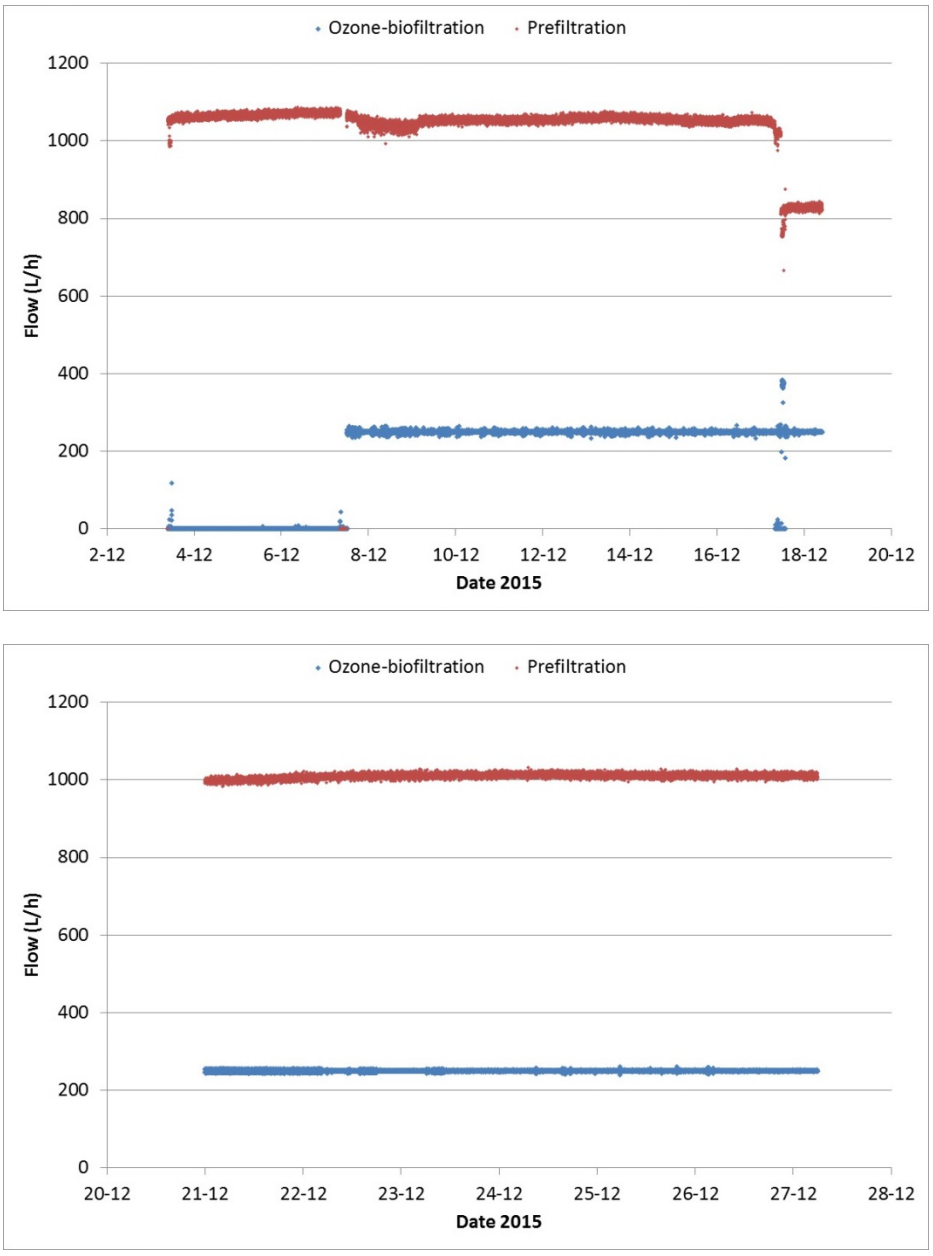


Figure 7-2: Flows of the filtration and ozone-biofiltration at the pilot of Panheel from 2-12 until 27-12-2015)

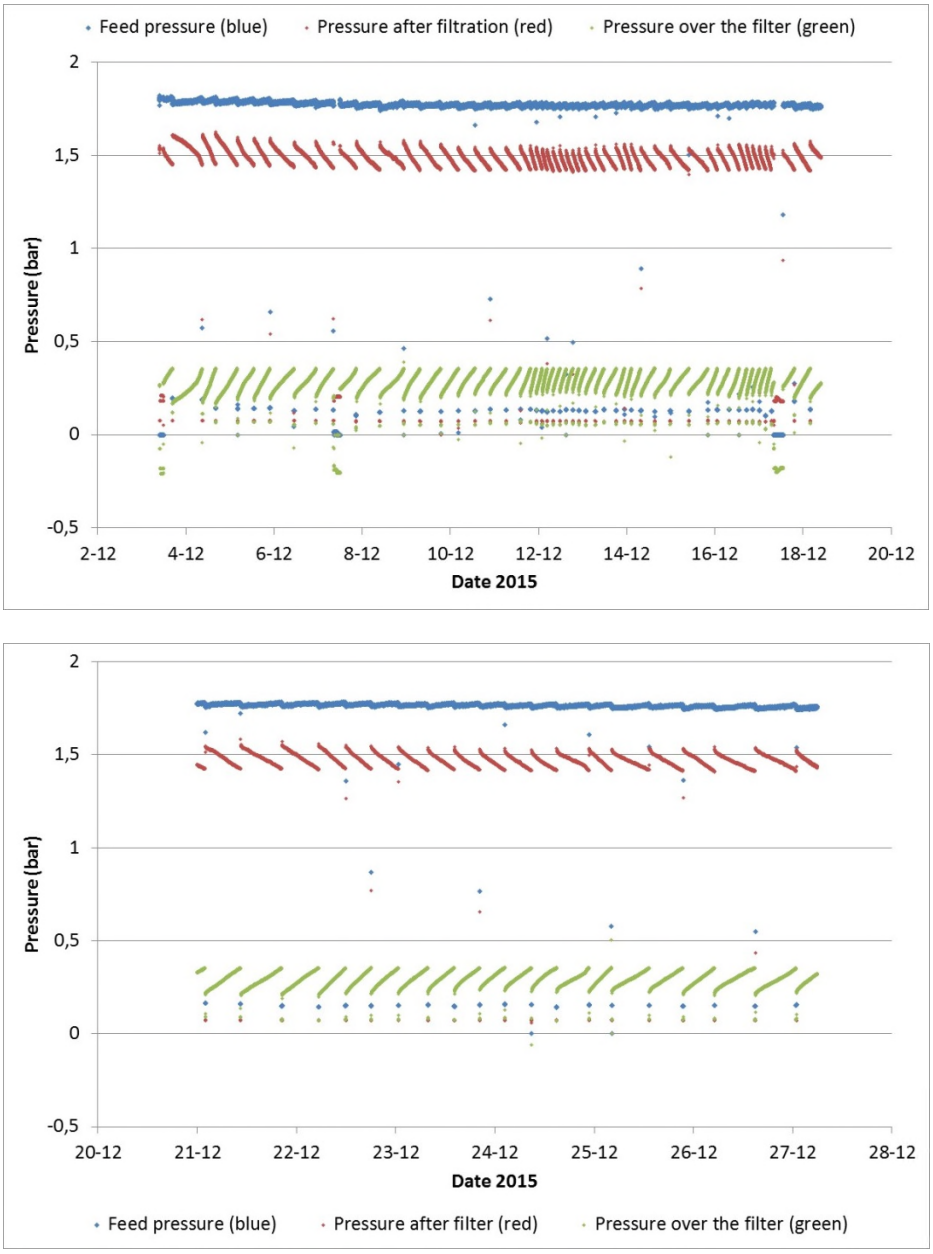


Figure 7-3: Pressure development of the filtration at the pilot of Panheel from 2-12 till 27-12-2015

7.4.2 Anion-IEX treatment

The regeneration of the IEX unit showed some startup difficulties due to a low feed pressure. To overcome this problem, the feed pressure was increased from 0,8 to about 1,4 bar (see Figure 7-5, improvement of IEX regeneration). To get an idea of the performance of the Anion IEX treatment, during the whole period several samples were taken to measure the UV-T (254 nm) of the IEX effluent in relation to the UV-T of the pre-treated influent water. UV-T values give an indication of the removal of organic carbon (especially humic acids), although measuring DOC or TOC gives more reliable results. UV-T, however, could be measured on-site and was necessary for calculating the UV/H_2O_2 experimental circumstances. Extra LC-OCD samples were taken to measure organic carbon fractions, like humic acids, in more

detail. In Figure 7-4 the UV-T and removal of the IEX at different treated volumes of water is given. At every 7.000 L the IEX resin is backwashed, regenerated with 2 bedvolumes of 10 % NaCl and flushed at ambient temperature according to the recommendations of the supplier (Lanxess, see also Appendix III). Increasing the temperature and/or the addition of NaOH could improve the regeneration, however this seemed not to be necessary for the application of this pilot. After each regeneration the process was repeated.

In Figure 7-4 three UV-T lines are shown. The data of the first weeks are not shown, as in this period the regeneration performed insufficiently. The higher the UV-T value, the better the expected performance of the UV/H_2O_2 treatment for the oxidation of the pharmaceuticals in the water. When the regeneration was less than optimum, the UV-T results were affected by about 10-15 %. The UV-T of the effluent decreased from 90 to about 80 % by the treatment of 7.000 L of pretreated influent water. The influent UV-T is normally about 60 %, but showed some dips to 40 and 50 % (at 950 and 5.000 L), which directly influenced the IEX effluent UV-T value, but appeared to hardly affect the UV-T increase. The removal efficiency of the IEX treatment (= UV-T increase by the IEX treatment) was about 20 to 40 %. This is in good accordance with removal of the humic acid fraction (as this will be the main fraction removed, according to laboratory experiments), which accounts for about 30-35% of the total DOC (see Figure 4-2).

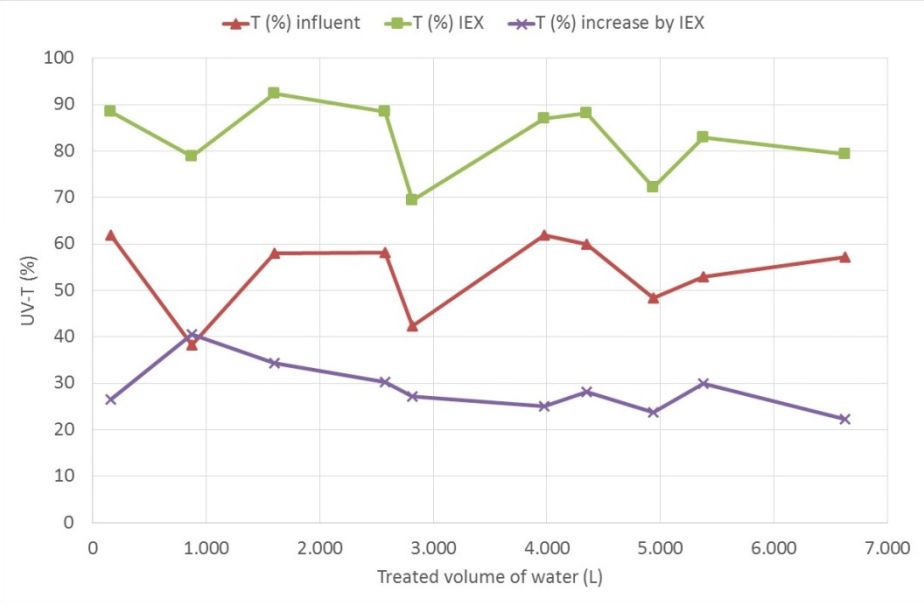


Figure 7-4: UV-T measurements of the IEX treatment (red: influent; green: IEX effluent excluding less performed regeneration; purple: IEX-effluent minus influent, giving the increase of UV-T by the IEX treatment)

7.4.3 ozone-biofiltration treatment

In order to obtain information about the performance of the O_3-Biofiltration treatment, during the experimental period several samples were taken to measure the UV-T (254 nm) of the O_3-Biofiltration effluent in relation to the UV-T of the pre-treated influent water. In Figure 7-5 the UV-T values of the influent, O_3-Biofiltration effluent and IEX effluent (including the poor regeneration data) in time are shown. It should be taken into consideration as well that the shown IEX values cannot be corrected for the treated volume: when samples are taken

just after regeneration the UV-T is expected to be higher than the UV-T of a sample taken just before regeneration.

As can be seen, after 2-12-2015 the O_3-Biofiltration UV-T decreased in time. This probably can be explained by effects of the breakdown of the pump used to feed the O_3-Biofiltration and IEX units with pre-filtrated effluent. From 3-12 to 8-12 both treatments were stopped and restarted at 8-12. After this period, the O_3-Biofiltration UV-T did not increase to the original values. This might be caused by a higher ozone dose at the biofiltration during the period of breakdown of the pump and the manual stop of the pilot, however this effect could only be assumed. Also the formation of preference channels in the biofiltration bed is assumed, because the biofiltration bed was not backwashed regularly during this pilot. The removal efficiency of the O_3-Biofiltration decreased from about 20 to about 5 % in time. The IEX performance seemed not to be influenced by the stopping period of the pilot. For the flow during the pilot, see Figure 7-2, UV-T is a measure for the removal of organic carbon (especially humic acids), but by measuring DOC or TOC more reliable results can be obtained. UV-T however, could be measured on-site, which was necessary for calculating the UV/H_2O_2 circumstances. Extra LC-OCD samples were taken to measure organic carbon fractions, like humic acids, more in detail.

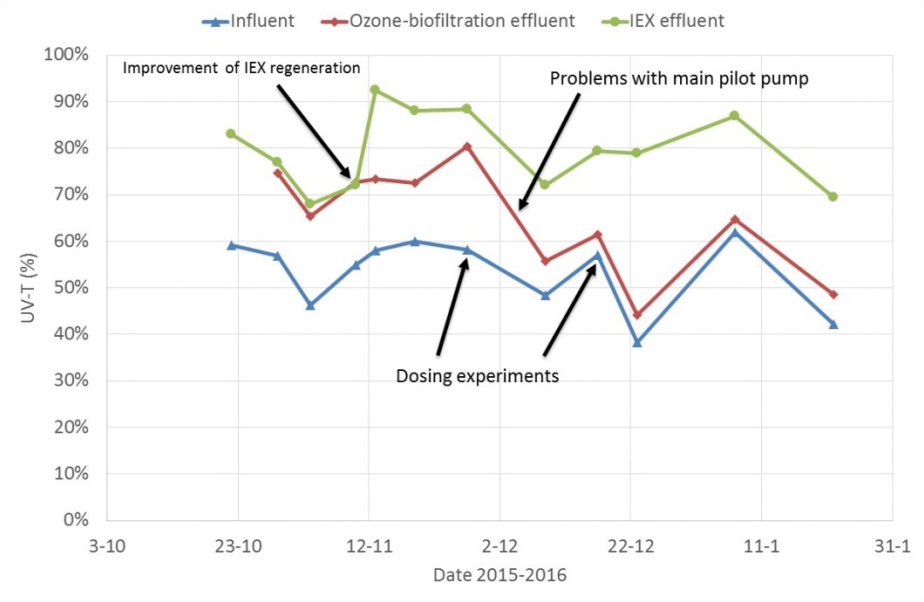


Figure 7-5: UV-T (%) values of the influent, ozone-biofiltration and IEX in time

7.5 Water characterisation

7.5.1 Effluent measurements

The influent of the pilot was the effluent of the WWTP. During the dosing experiments the WWTP effluent was measured by taking 24 h samples, which were analyzed by WBL, giving the results shown in Table 7-4.

Table 7-4 Analytical measurements of the WWTP effluent (influent of the pilot) during the days of the dosing experiments and statistical analytical values of 2015

Date	Flow	N_{tot}	BOD	COD	SS *	P	PO_4	NH_4	N-Kj	NO_2	sNO_3NO_2 **
2015	m^3/h	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L	mg/L
27-11	4816	27,1	2,2	30	2,2	3,4	3,7	4	5,1	0,94	22
17-12	11317	17,7	5,1	31	4,5	1,6	1,6	5,4	6,7	2,7	11
Statistical values of the year 2015											
Average	8499	27,2	4,3	81,8	5,8	4,3	4,1	8,6	11,2	1,6	16,0
Minimum:	4260	10,4	1,3	17,0	2,2	0,98	0,96	0,05	1,6	0,0	0,1
Maximum:	16499	44,0	9,0	75,0	15	7,5	7,3	24	29	8,0	40,0

* SS = suspended solids

** sNO_3NO_2 = sum of nitrate-N and nitrite-N, normally nitrate-N forms the major part

7.5.2 LC-OCD measurements

Although UV-T data give an idea about the performance of the pre-treatment processes, more detailed information can obtained from LC-OCD analyses.

In Figure 7-6 the effect is shown of the ozone/biofiltration process on the composition of the EfOM. It can be seen that in November the effect is almost negligible. In December the amount of hydrophobic material is decreased, which is in accordance with the previous laboratory experiments, but the overall difference is small. Oppositely to what would have been expected, the removal of EfOM at a higher ozone dose (23 mg/L) seems to be lower than at a lower ozone dose (18 mg/L). So far it is unclear what caused this difference. In time it was noticed that there was an ozone smell in the trailer, indicating that there was an ozone leakage. As a result of this, the effective ozone doses may have been lower than had been calculated. It is unknown when this leakage started, and whether it may have affected the ozone doses during our experiments.

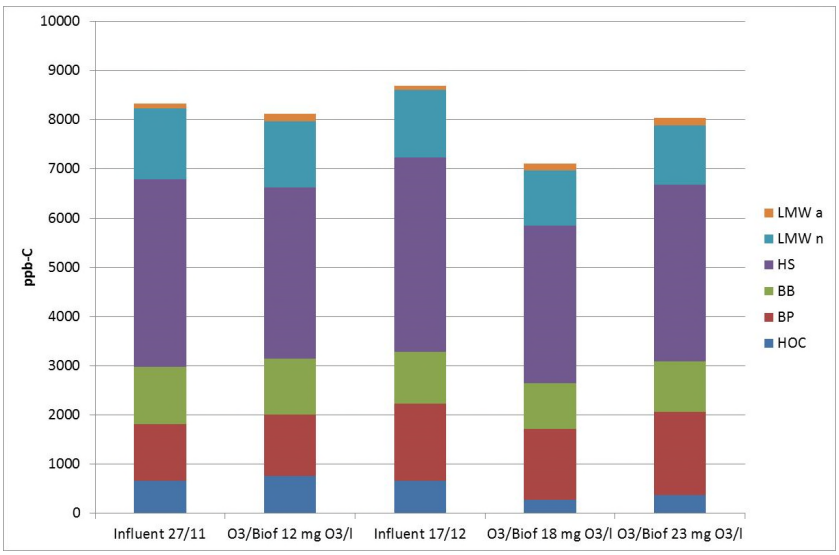


Figure 7-6: Effect of ozone/biofiltration on the EfOM composition in November and December 2015.

In Figure 7-7 the results are shown of the LC-OCD analyses of samples taken during the pilot in January 2016. In 0 the full report of the LC-OCD analyses is given. The organic carbon content measured in January 2016 was relatively high (~12 mg C/L) compared with earlier measurements (~10 mg C/L). The pre-filtration treatment (not used at the laboratory tests) did not reduce the LC-OCD fractions. When compared with the laboratory tests, the O_3-Biofiltration treatment specifically showed a much poorer performance. The main reduction was found for the hydrophobic part and some LMW acids were formed during the ozonation step, but not removed during the biofiltration treatment. The IEX treatment removed all humic substances as expected, and released LMW acids. Also a major hydrophobic part of het EfOM was removed.

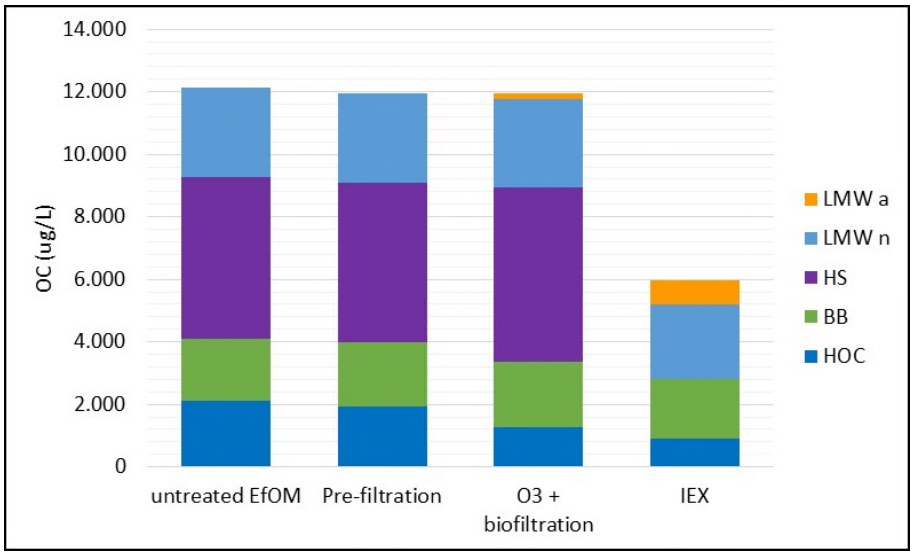


Figure 7-7 LC-OCD measurements of the pilot streams during the pilot in January 2016 (HOC Hydrophobic Organic Carbon; BB: Building Blocks; HS: Humic Substances; LMW n: Low Molecular Weight neutrals; a: acids)

It is possible that the problems with the pumps at the start of the pilot investigation may have been responsible for the relatively low efficiency of the O_3/biofiltration process, as previous laboratory experiments did show the removal of the whole HOC fraction and some other compounds (see section 5.3). However, from the pilot investigation it can be concluded that the removal of EfOM by means of the O_3/biofiltration pre-treatment at the moment isn't yet a robust process, and would require more attention in a subsequent investigation. On the other hand, removal of mainly humic acids by means of IEX indeed appears to be a very effective way to decrease the EfOM content of the water before advanced oxidation, in accordance with previous laboratory experiments (see section 5.2).

The effect of the pre-treatment process on possible bromate formation also was tested. The influent concentration of bromide appeared to be 50 μg/L (sample taken at 17-12- 2015). This is a common value for wastewater, as from previous research it is known that the effluent in Tilburg contains 50-150 μg/L, in Eindhoven 90-150 μg/L, and in Leiden <10 μg/L (Mulder, Antakyali et al. 2015). The corresponding bromate concentrations were measured in the influent, after addition of 18 mg O_3/L or 23 mg O_3/L, after O_3/UV/biofiltration (18 and 23 mg O_3/L), and after UV/H_2O_2, but in all cases appeared to be < 0.5 μg/L. This seems to indicate that no significant bromate was formed during the process. However, as the ozone-

EfOM results also were unexpected, it is possible that the ozone dose has been lower than the measurements had indicated, as a result of which the bromate formation also may have been limited.

7.6 Removal of pharmaceuticals

In Table 7-5 the settings of the pilot are given during the dosing experiments at 27-11-2015 and 17-12-2015.

Table 7-5 Settings of the pilot during 2 dosing dates

27-11-2015	**Time**	**UV-T (%)**	**pH**	**EGV (µS/cm)**	**Flow (L/h)**	**UV-dose (mJ/cm²)**	**V flush (L)**	**V batch (L)**
Influent start	08:30	58,1	6,26	682	1.200	0	0	0
Ozone-biofiltration start	08:30	80,4	6,39	657	250	0	0	0
Influent exp 1-8	10:30	59,2	6,1	661	1.200	-	-	-
IEX exp 1,3 effl	10:40	86,8	6,26	725	750	-	-	-
UV/H2O2 exp 1,3	11:15	86,7	5,7	723	1000/500	150/300	100	200
IEX exp 2,4 effl	11:45	86,8	5,59	724	750	-	-	-
UV/H2O2 exp 2,4	12:06	86,7	5,79	785	1000/500	150/300	0	200
O_3-BF 12 mg/L exp 5-8	14:00	63,7	6,45	642	375	-	-	-
O_3-BF / UV/H2O2 exp 5-8	14:15	65,1	6,33	641	830/415	150/300	200	180
17-12-2015	**Time**	**UV-T (%)**	**pH**	**EGV (µS/cm)**	**Flow (L/h)**	**UV-dose (mJ/cm²)**	**V flush (L)**	**V batch (L)**
Influent start	08:00	57,1	6,41	432	-	-	-	-
IEX effluent start	08:00	79,4	6,41	437	-	-	-	-
Ozone-biofiltration start	08:00	61,4	6,14	437	-	-	-	-
Influent exp 9-18	09:30	55,3	5,98	427	-	-	-	
O_3-BF 18 mg/L exp 9-12	10:45	65,9	6,28	429	840/420	150/300	200	200
O3-UV-BF exp 17 18 mg/L O3	11:30	61,4	6,33	423	249	150	-	-
O_3-BF 23 mg/L exp 13-16	12:30	66,3	6,28	421	840/420	150/300	200	200
O3-UV-BF exp 18 23 mg/L O3	13:30	61,4	6,3	418	375	150	-	-

8 Pilot research: results and discussion

8.1 Removal of pharmaceuticals by IEX or O_3/biofiltration pre-treatment

As pharmaceuticals are organic compounds, like EfOM, it is likely to assume that part of the pharmaceuticals added will already be removed by the pre-treatment method itself. This effect is shown in Figure 8-1. For the O_3/biofiltration pre-treatment three different ozone concentrations were applied: 12, 18 and 23 mg/L.

As expected, IEX can remove the negatively charged compounds. In this respect there is a rather good accordance between the laboratory data shown in Figure 6-6, and these data, and besides it seems to correspond well to the charges of the compounds as shown in Table 12-2. During the pilot experiments on 27-11-2015 (when the effect of IEX and 12 mg O_3/L was measured) pH was 8.4, and on 17-12-2015 (when 18 and 23 mg O_3/L were tested) it was 7.7, whereas during the laboratory experiments a pH of about 7.5 was measured. This may account for the differences observed between Figure 6-6 and Figure 8-1: for ketoprofen a higher removal was observed, whereas for niacin, sulfadiazine, diatrizoic acid, and gemfibrozil a lower removal was found. For carbamazepine the difference is the largest: in the laboratory experiments it was removed to >80%, whereas in the pilot a removal of about 25% was observed, which is more in line with the fact that it should not carry an electrostatic charge at this pH.

Again, the removal by means of ozone/biofiltration is more effective than by means of IEX, as had been expected (see also section6.4). It can also be noticed that increasing the ozone concentration often results in a higher removal of the pharmaceuticals. For some compounds >80% or even >90% removal can be obtained in this way. Thus, ozone/biofiltration at relatively high ozone concentrations can rather be considered as a “treatment method” than as a “pre-treatment method”. Possibly, this method in itself would be sufficient for removal of pharmaceuticals from WWTP effluent. However, more research is required to turn this into a sufficiently robust process for continuous operation.

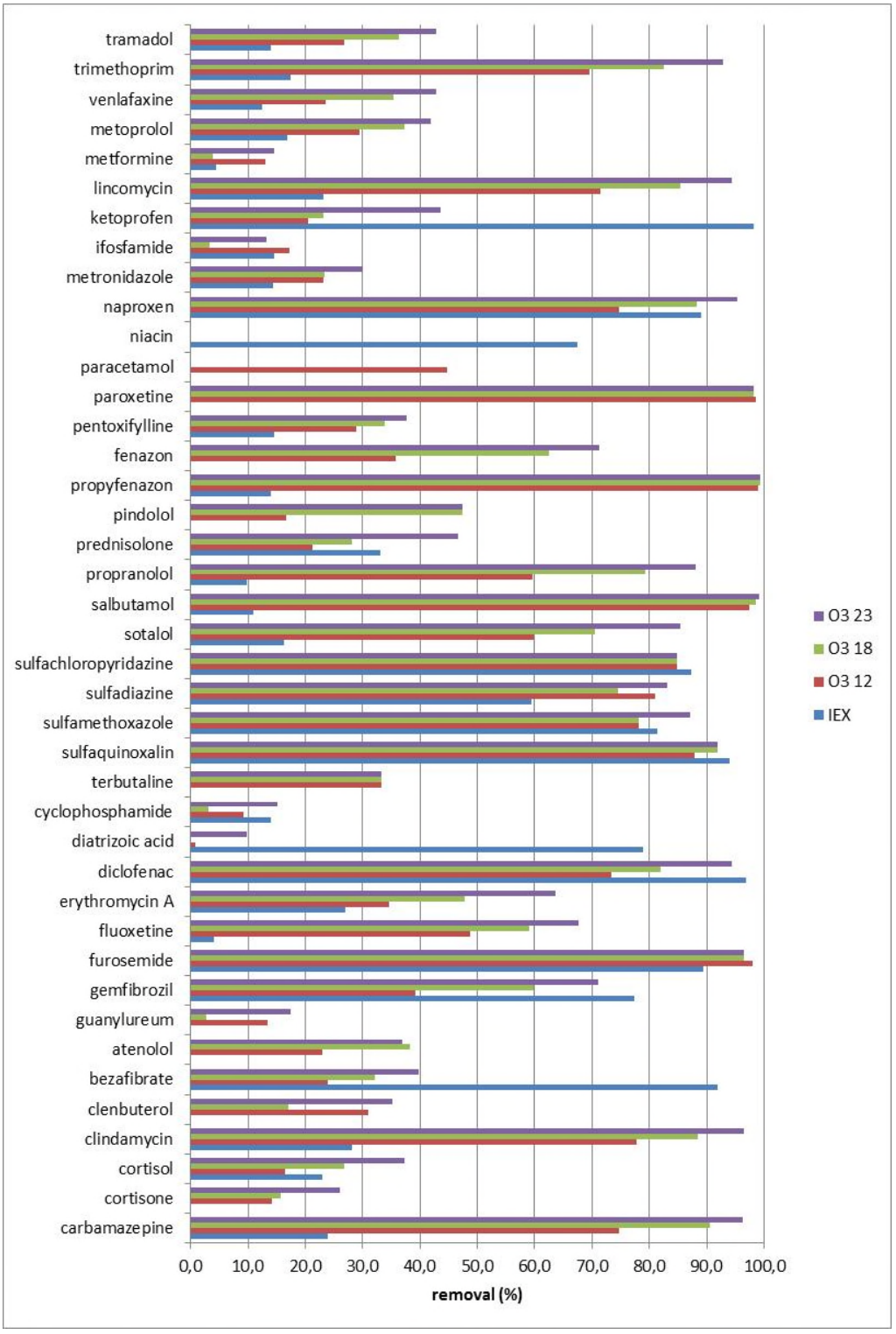


Figure 8-1: Effect of pre-treatment method on removal/conversion of pharmaceuticals

8.2 Effect of pre-treatment on the subsequent UV/H_2O_2 process

8.2.1 Effect of IEX pre-treatment on the UV/H_2O_2 process.

The effect of the IEX pre-treatment on the UV/H_2O_2 process is shown in Figure 8-2. As expected, most pharmaceuticals can be effectively removed by the UV/H_2O_2 process, and in cases where the degradation grade is not very high, this can be improved by increasing the UV dose. Only for metformin and guanylurea the process seems to be less effective, as had been expected. If we just consider the effect of the pre-treatment on the compound conversion in the UV/H_2O_2 process, Figure 8-3 is obtained. This graph, however, may distort the results. If a compound already was removed to a large extent by IEX, its influent concentration in the UV reactor already was relatively low. As a result the maximum conversion that could be calculated, assuming the limit of detection as the lowest possible concentration, will be relatively low. This effect e.g. can be observed for ketoprofen, sulfachloropyridazin, sulfaquinoxalin, sulfamethoxazole, diclofenac and furosemide.

For terbutalin some strange results can be observed. Its concentration in the IEX influent, after addition of the mixture of pharmaceuticals, seemed to be too low (0.015 μg/L), whereas after IEX treatment is seemed to be 0.96 and 0.88 μg/L, which is more likely considering the fact that about 1 μg/L had been added. Moreover, as the charge of the molecule at this pH is +1(Table 12-2), it is very unlikely that it would interact with the IEX resin used. It therefore seems that in the analysis of the IEX influent sample something went wrong, as a result of which the removal data in Figure 8-2 for terbutalin are not reliable. However, the data shown in Figure 8-3 seem to be more reliable.

Also for pindolol some remarkable results are obtained, as in this case the concentration in the IEX influent seems to be lower than the concentration after IEX, although both concentrations (0.16 μg/L before IEX and 0.23 μg/L after IEX) are much lower than the 1 μg/L that should have been added. After UV/H_2O_2 treatment the concentration seemed to be below the limit of detection, but as the analytical data don't seem to be very reliable, no conclusions should be drawn for this compound.

Another compound for which it is known that analysis sometimes seems to give unexpected results, is niacin. Analytical uncertainties in this case probably also explain the remarkable results, that can be observed in Figure 8-2 and Figure 8-3. Niacin is supposed to be negatively charged at neutral pH, and thus could be adsorbed by IEX. This is in accordance with the data for IEX in Figure 8-1 and Figure 8-2. However, it is extremely unlikely that the concentrations of niacin would increase during UV/H_2O_2 treatment. Therefore, no conclusions should be drawn for this compound on the efficiency of the UV/H_2O_2 process.

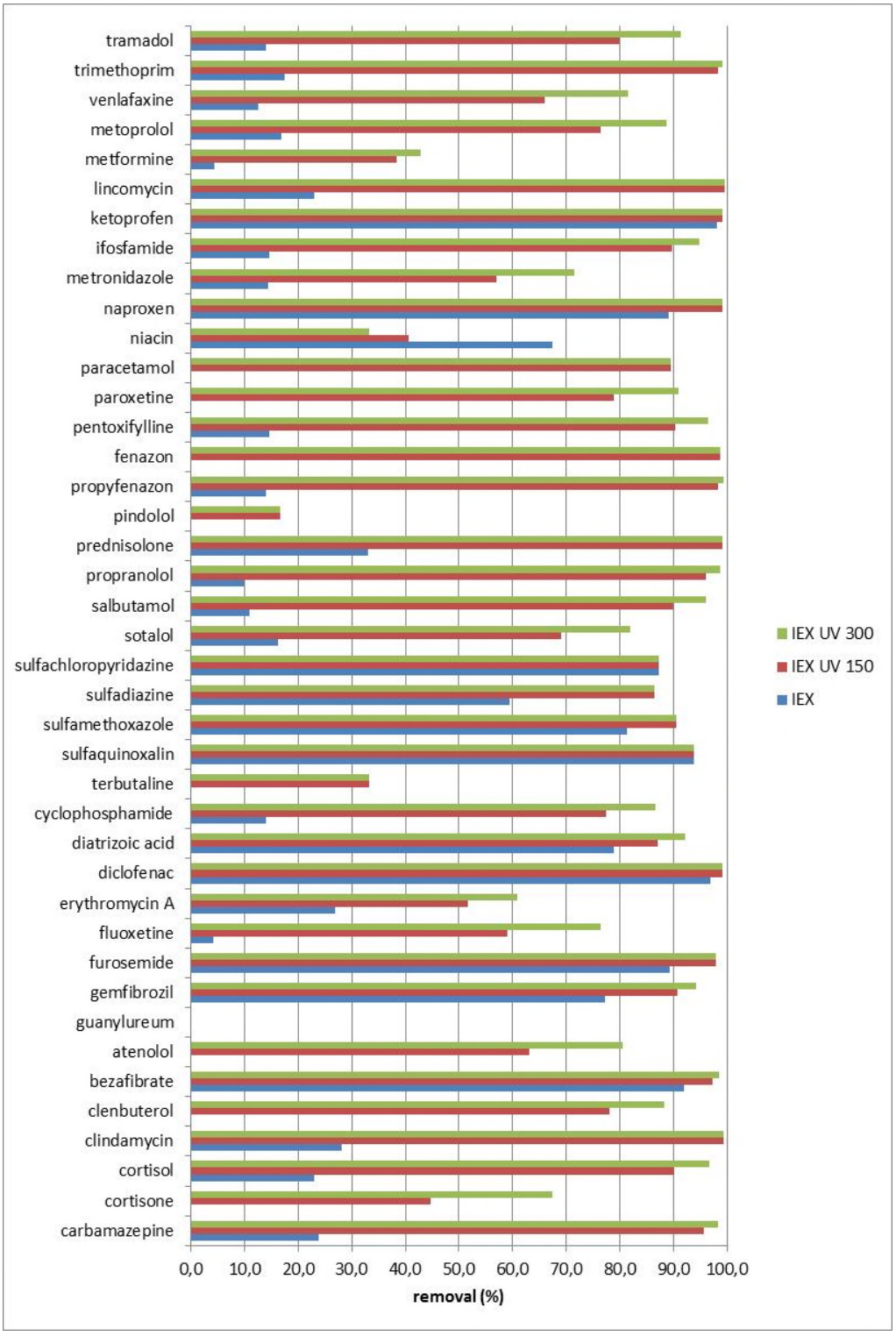


Figure 8-2: Total removal of pharmaceuticals by means of IEX, possibly followed by UV/H_2O_2 treatment, applying a UV dose of 150 or 300 mJ/cm².

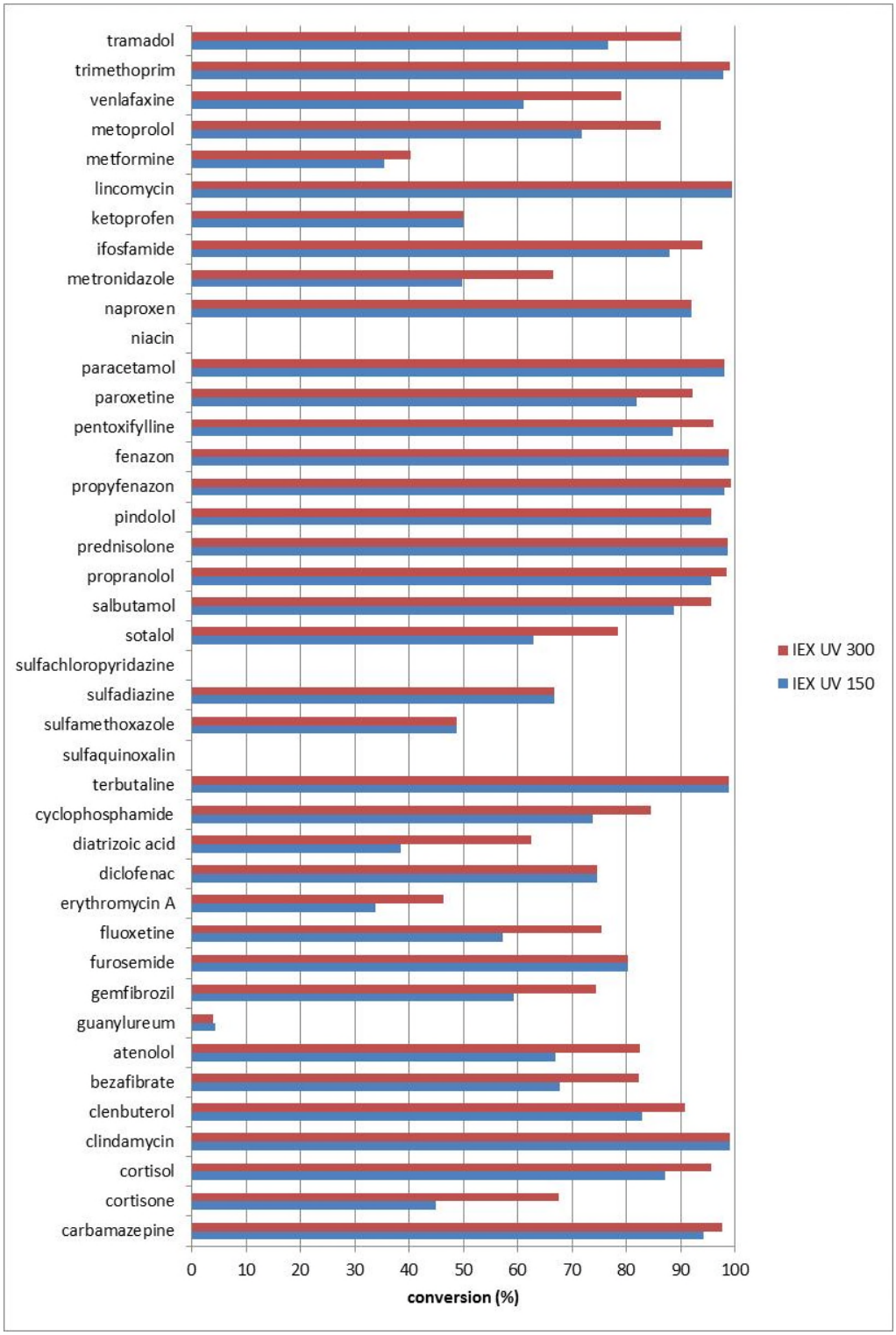


Figure 8-3: Effect of IEX pre-treatment on the conversion in the UV/H_2O_2 reactor.

In general it can be seen that after IEX a very good removal of most pharmaceuticals can be obtained by means of UV/H_2O_2. For most compounds an increase in UV dose from 150 to

300 mJ/cm^2 results in a (small) increase in conversion, as a result of which for the majority of compounds a conversion ≥ 80% can be obtained. Only for metformin and its metabolite Guanylureum the UV/H_2O_2 process is less effective, as was expected based on previous experiences in drinking water treatment. This can be contributed to the molecular structure of these compounds, which makes them less sensitive towards photolysis and oxidation. For trimethoprim, lincomycin, naproxen, paracetamol, fenazon, propyfenazon, prednisolone, sulfadiazine, clindamycin and carbamazepine almost complete removal can be obtained even at 150 mJ/cm^2, which is a very low UV-dose for such processes (in drinking water production in general UV-doses of about 500-700 mJ/cm^2 are applied for advanced oxidation processes). Therefore, it can be concluded IEX pre-treatment effectively improves the UV water quality, as a result of which the UV/H_2O_2 process can be run very efficiently.

8.2.2 Effect of ozone/biofiltration pre-treatment on the UV/H_2O_2 process

On 27-12-2015 experiments were carried out, in which a pre-treatment of the water with O_3/biofiltration at an ozone dose of 12 mg/L was applied. On 17-12-2015 similar experiments were carried out at ozone doses of 18 and 23 mg/L.

The results of the experiments with an ozone dose of 12 mg/L are shown in Figure 8-4 and Figure 8-5. In general the results are comparable to the results described with IEX pre-treatment in section 8.2. In general the conversion of the compounds increases with increasing UV dose. For paroxetine, propyfenazon, salbutamol, sulfachloropyridazine, sulfadiazine, sulfamethoxazole, sulfaquinoxalin and furosemide the removal by the pre-treatment already exceeded 80%. This explains why for paroxetine, propyfenazon, salbutamol, and furosemide the oxidation by means of UV/H_2O_2 does not seem to be very effective: as already the major part of the compounds had been removed before the UV/H_2O_2 process, the calculation of the real removal by oxidation was hindered by the limit of detection. For sulfachloropyridazine, sulfadiazine, sulfamethoxazole and sulfaquinoxalin the removal by means of UV/H_2O_2 at a UV dose of 150 mJ/cm^2 was not calculated due to concentrations below the limit of detection, as a result of which here the effect of an increase in UV dose still can be observed.

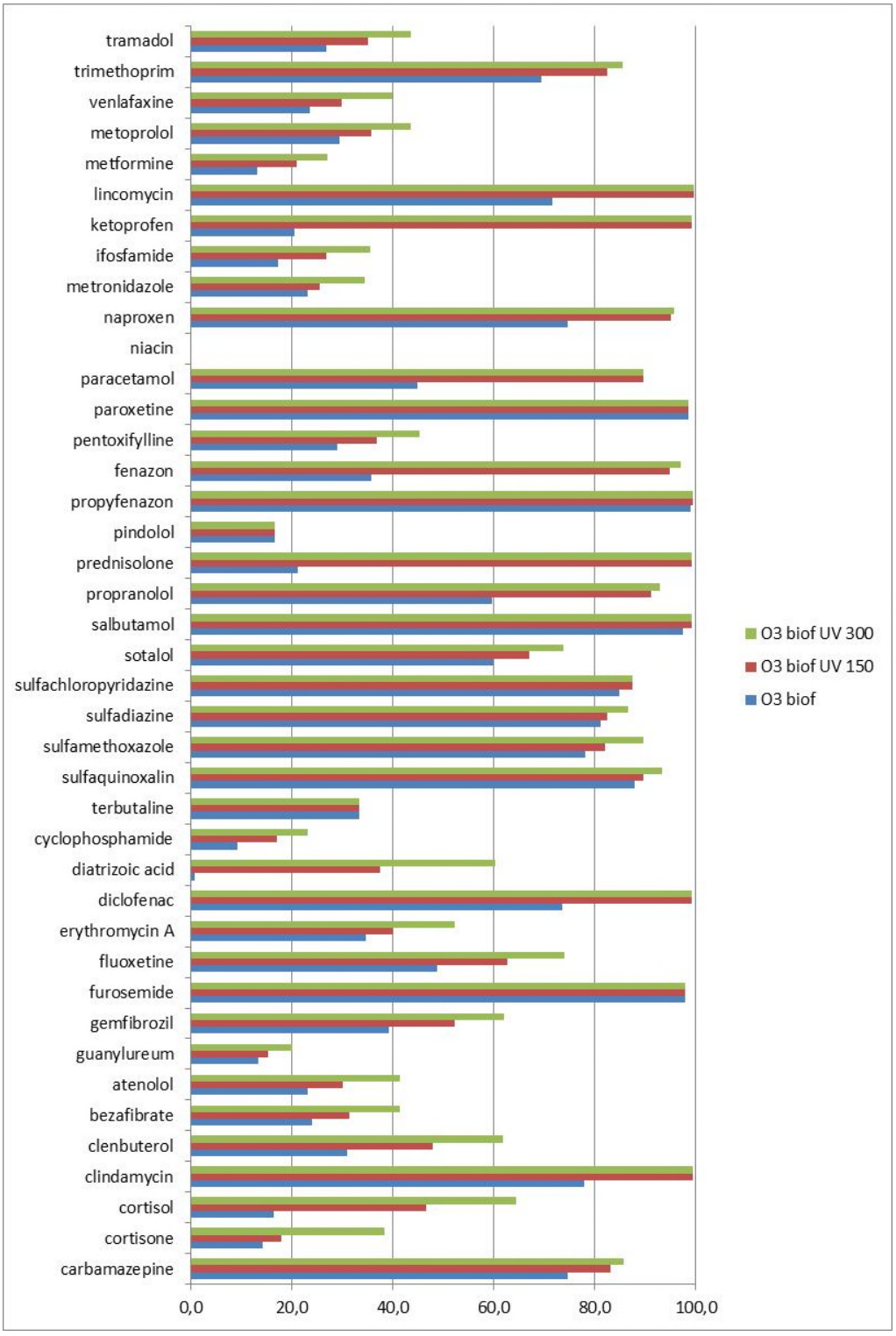


Figure 8-4: Total removal (%) of pharmaceuticals by means of O_3/biofiltration (12 mg O_3/L), possibly followed by UV/H_2O_2 treatment, applying a UV dose of 150 or 300 mJ/cm^2.

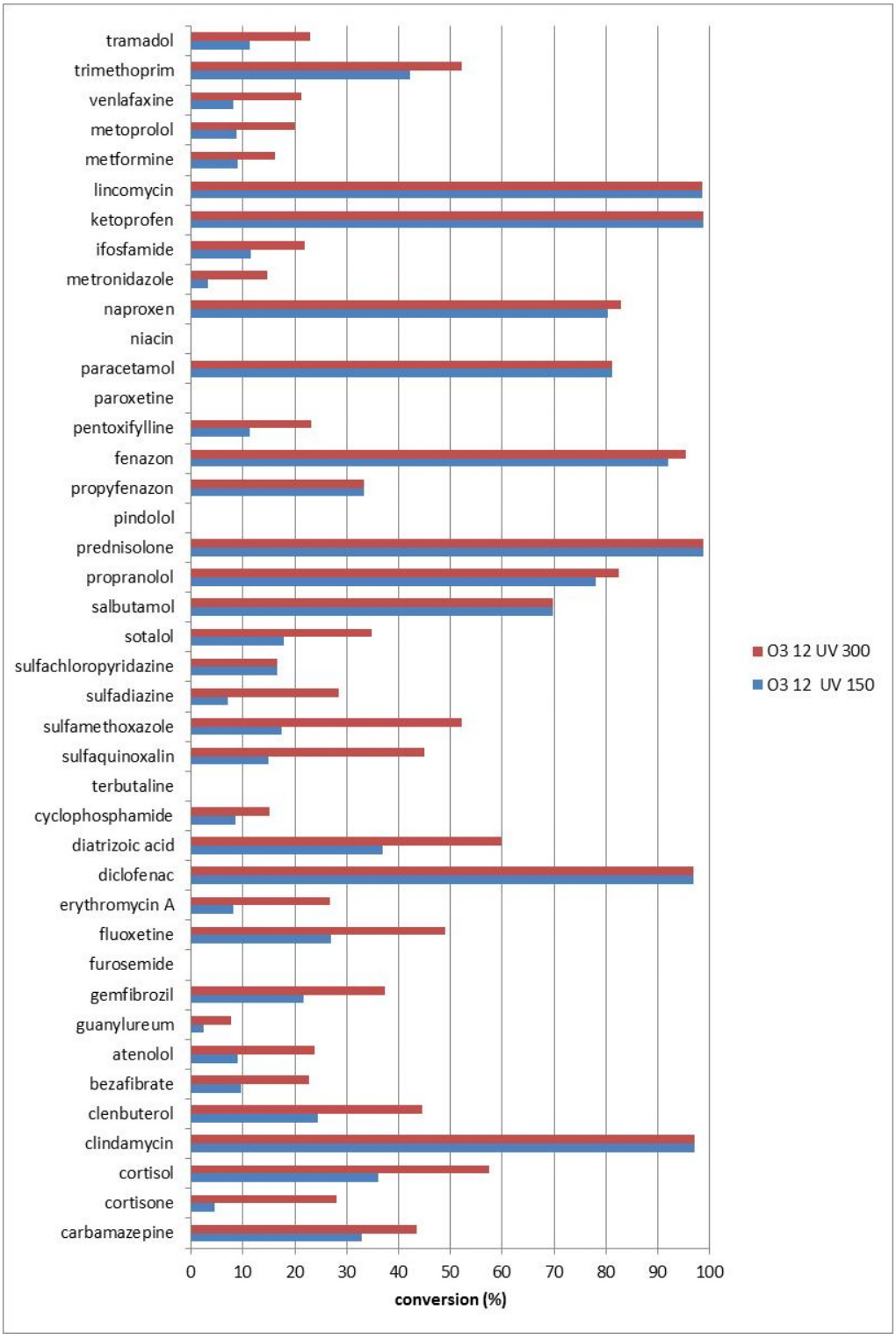


Figure 8-5: Effect of O_3/biofiltration pre-treatment (12 mg O_3/L) on the conversion in the UV/H_2O_2 reactor.

Results obtained with higher ozone doses are shown in Figure 8-6 - Figure 8-9 . As was the case for pre-treatment with 12 mg O_3/L, here too the pre-treatment may already remove the

compounds for ≥ 80%, as a result of which the effectiveness of the UV/H_2O_2 process cannot be calculated very well, due to the limit of detection of the pharmaceuticals.

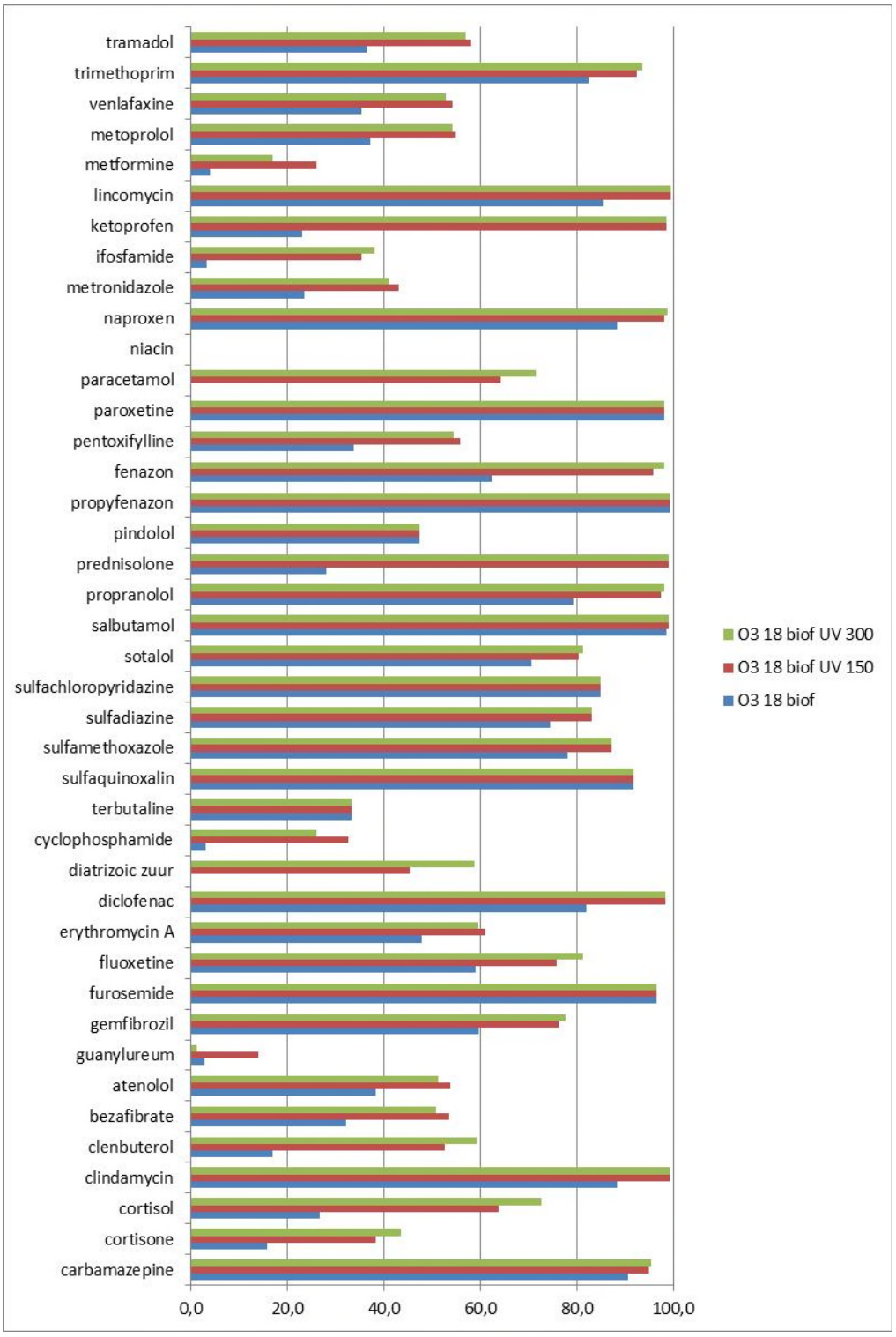


Figure 8-6: Total removal (%) of pharmaceuticals by means of O_3/biofiltration (18 mg O_3/L), possibly followed by UV/H_2O_2 treatment, applying a UV dose of 150 or 300 mJ/cm².

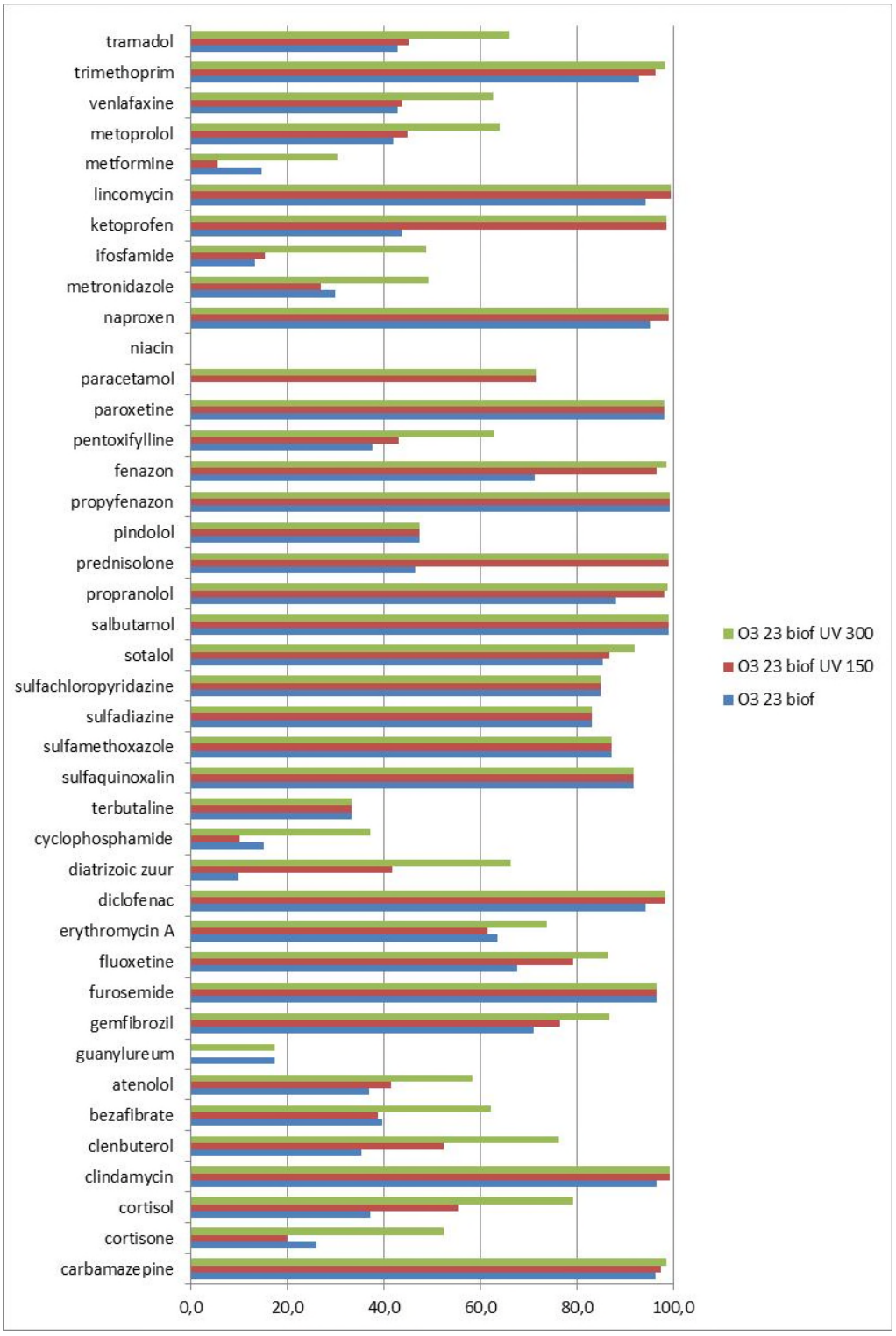


Figure 8-7: Total removal (%) of pharmaceuticals by means of O_3/biofiltration (23 mg O_3/L), possibly followed by UV/H_2O_2 treatment, applying a UV dose of 150 or 300 mJ/cm^2.

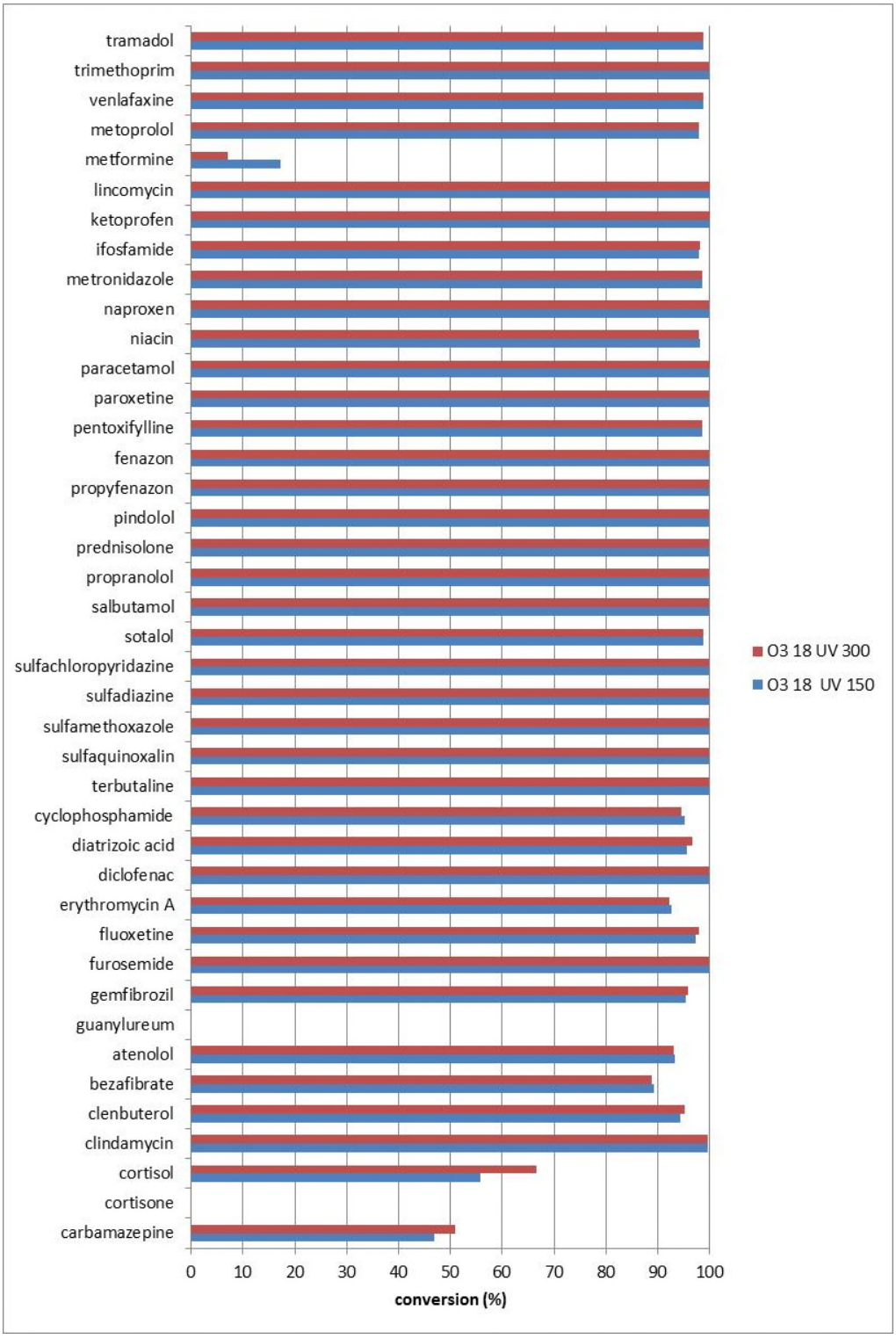


Figure 8-8: Effect of O_3/biofiltration pre-treatment (18 mg O_3/L) on the conversion in the UV/H_2O_2 reactor.

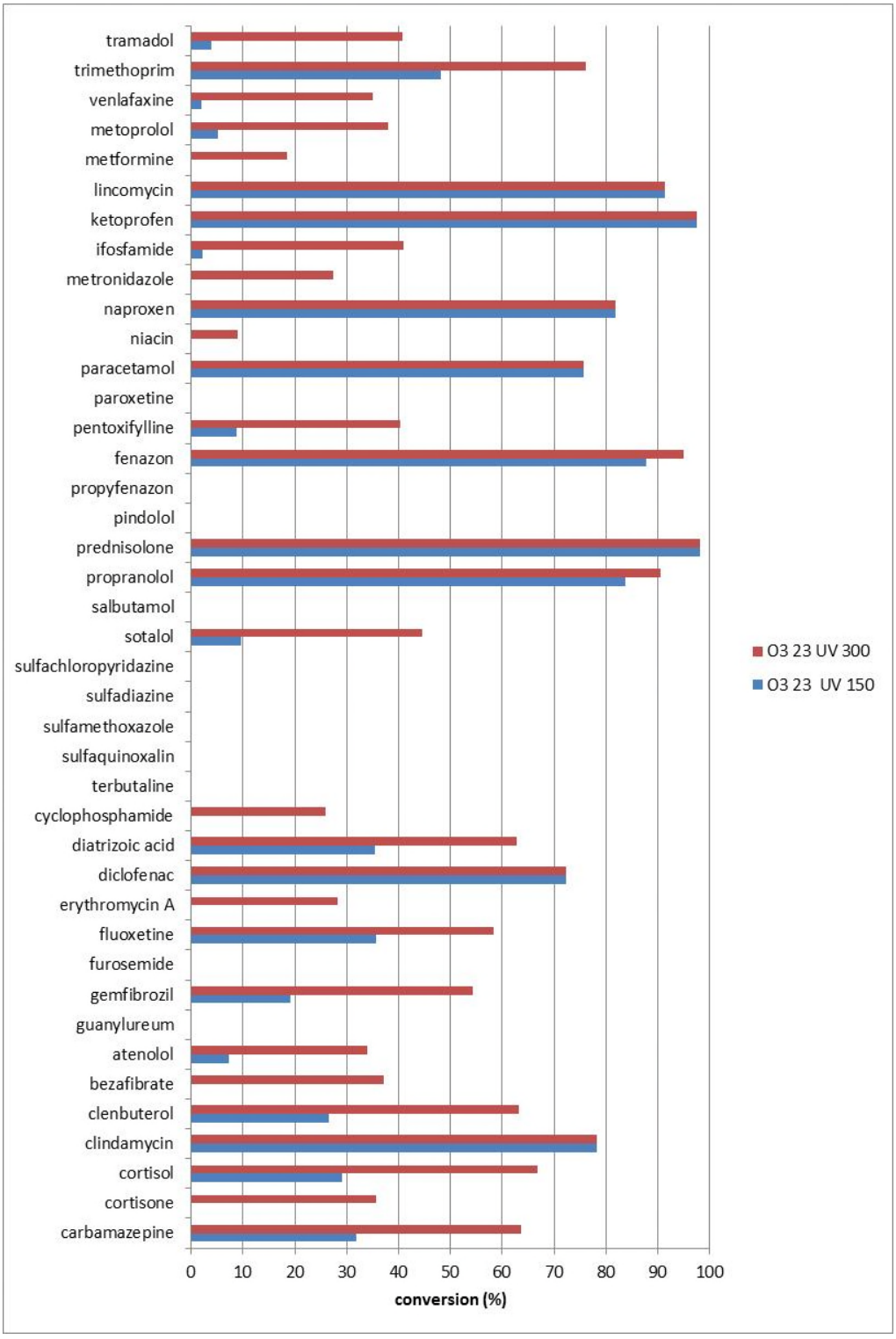


Figure 8-9: Effect of O_3/biofiltration pre-treatment (23 mg O_3/L) on the conversion in the UV/H_2O_2 reactor.

At 18 mg O_3/L this is the case for the same compounds as described above, but lincomycin, trimethoprim, naproxen, diclofenac, clindamycin and carbamazepine now also belong to this group. With 23 mg O_3/L propranolol and sotalol have to be added to this group. For sulfaquinoxalin there seems to be no improvement of the removal by applying UV/H_2O_2 after O_3/biofiltration at concentrations of 18 and 23 mg O_3/L (at 12 mg/L there still was some effect of a higher UV dose, but now removal doesn't further improve). Thus, it may be concluded that at higher ozone concentrations the O_3/biofiltration process can be considered as treatment rather than pre-treatment.

8.2.3 Comparison of pre-treatment methods for UV/H_2O_2 process.

A comparison of the different pre-treatment processes (IEX and O_3/biofiltration at three different ozone doses) is given in Figure 8-10 and Figure 8-11. Here the total removal is shown, as this gives the fairest comparison (without effects of reaching the limit of detection already in the pre-treatment process). For this comparison the lowest ozone dose was taken, as at higher ozone doses large part of the pharmaceuticals already may have been removed, and besides that at the higher ozone doses we sometimes obtained unexpected results (it is possible that the ozone doses calculated are less reliable, as explained before). Furthermore, the results at 150 mJ/cm^2 are shown. At 150 mJ/cm^2 it clearly can be seen that the combination of IEX and UV/H_2O_2 is most effective for the removal of the majority of compounds. At a higher UV dose of 300 mJ/cm^2 the situation for some compounds is improved, but still in general the IEX/UV/H_2O_2 combination gives the best results. This may indicate that the humic acids in the EfOM have a large influence on the effectiveness of the UV/H_2O_2 process, as these compounds are very effectively removed by IEX, and much less by O_3/biofiltration. Thus, it can be concluded that probably IEX is the most efficient pre-treatment process for UV/H_2O_2 processes in a complex matrix, like a WWTP effluent. However, during regeneration of the IEX resin a concentrate is formed, which contains high concentrations of salt and humic acids. In principle these can be separated, after which the salt may be reused for regeneration purposes, and the humic acids might be used as soil conditioner. It has to be investigated whether the presence of some organic micropollutants (e.g. pharmaceuticals) would hinder this application. The costs involved with handling of the concentrate have not been studied within the framework of this project (also see chapter 9).

However, this study also shows that by increasing the O_3 dose, the O_3/biofiltration process in itself may be a good alternative to the combined IEX/UV/H_2O_2 process. This process doesn't have the disadvantage of a concentrate being formed, as has the IEX process.

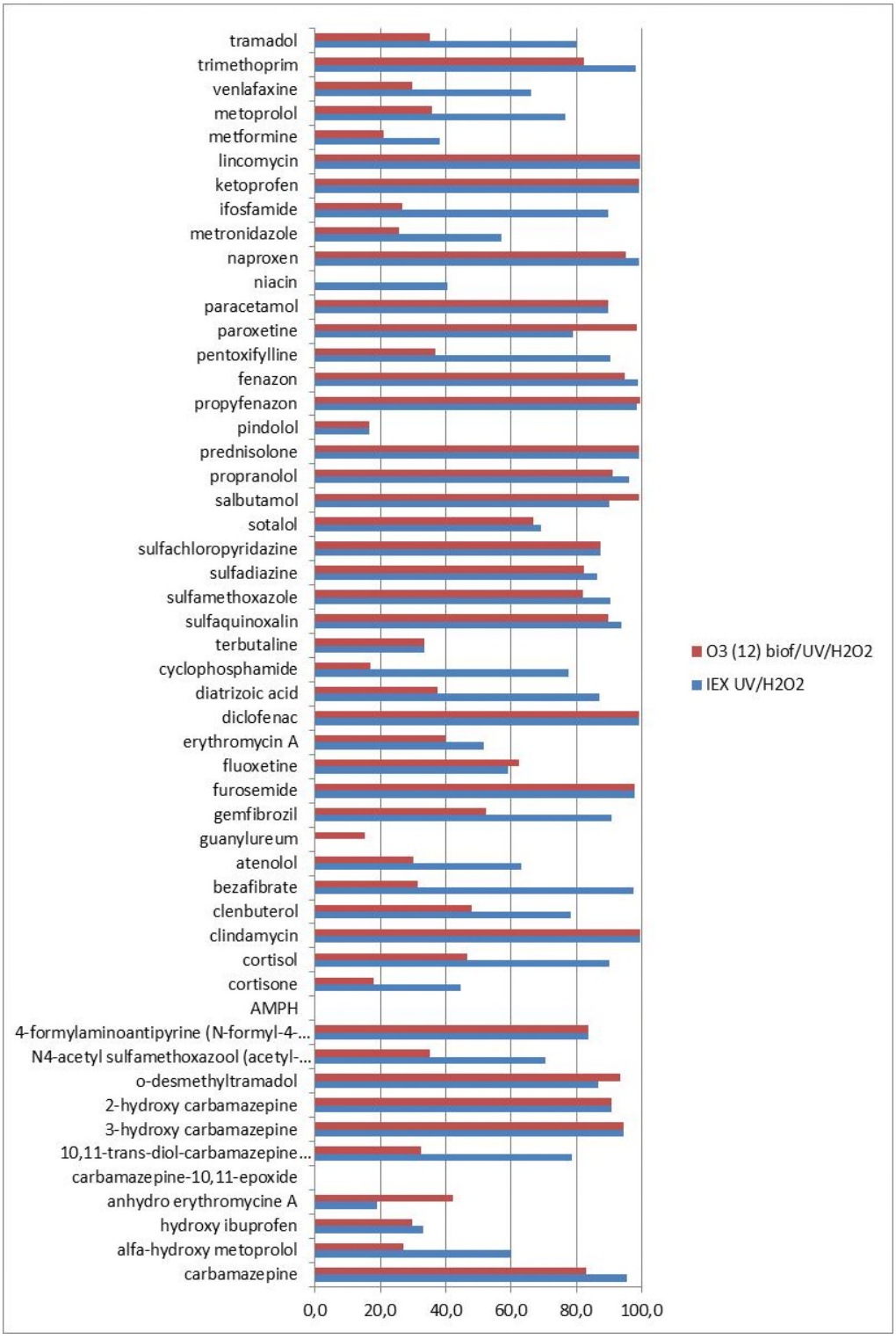


Figure 8-10: Comparison of total removal (%) by UV/H_2O_2 at 150 mJ/cm² after different pre-treatment processes.

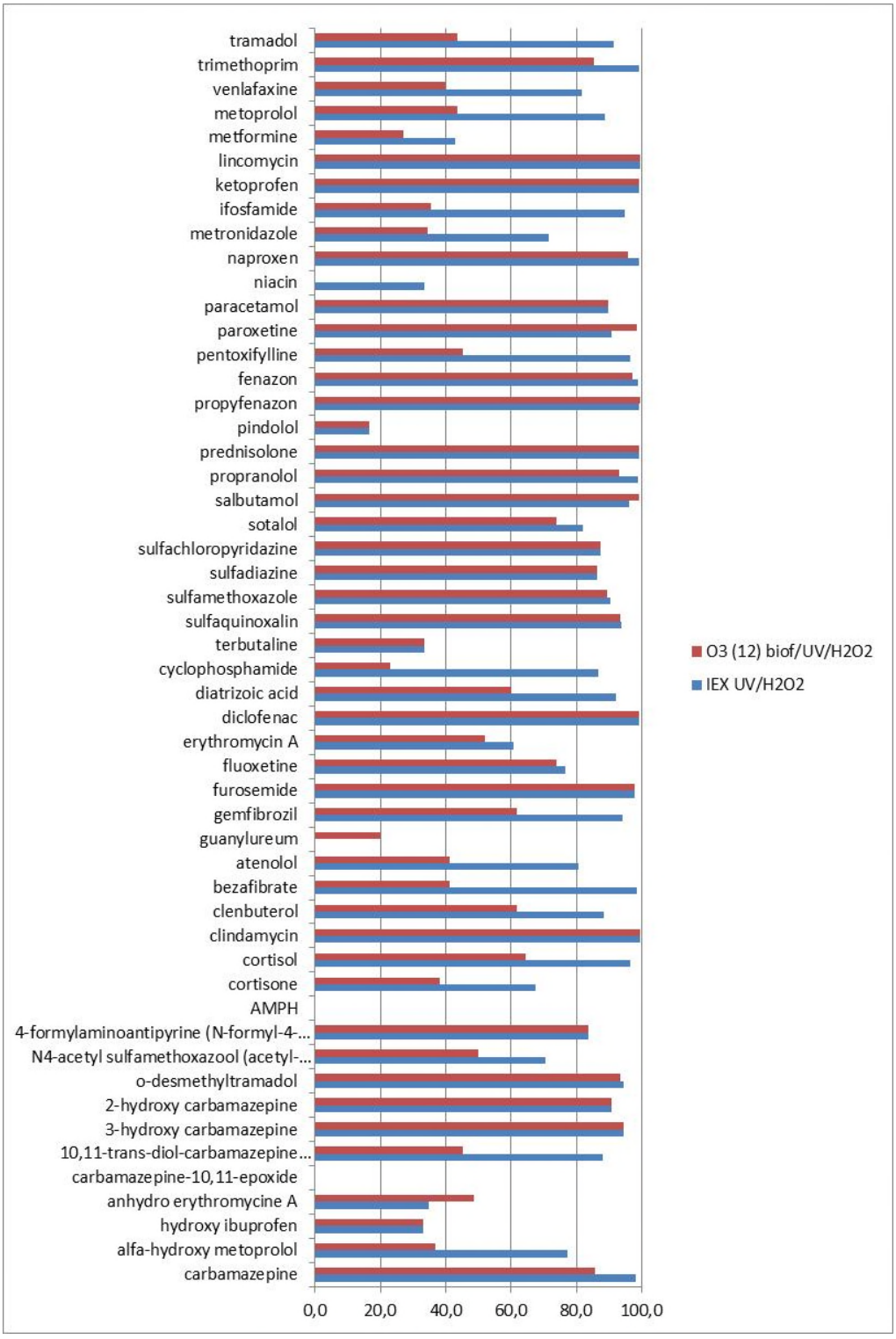


Figure 8-11: Comparison of total removal (%) by UV/H_2O_2 at 300 mJ/cm² after different pre-treatment processes.

8.3 O_3/UV/biofiltration processes

O_3/UV processes are considered as advanced oxidation processes (see also section 3.3.4). In the pilot the possibilities of such processes were studied by combining the O_3/biofiltration process with a UV reactor. First ozone is added to the water, which then passes through the UV-reactor. Finally, the water is filtered over the biofilter. The results obtained are shown in Figure 8-12.

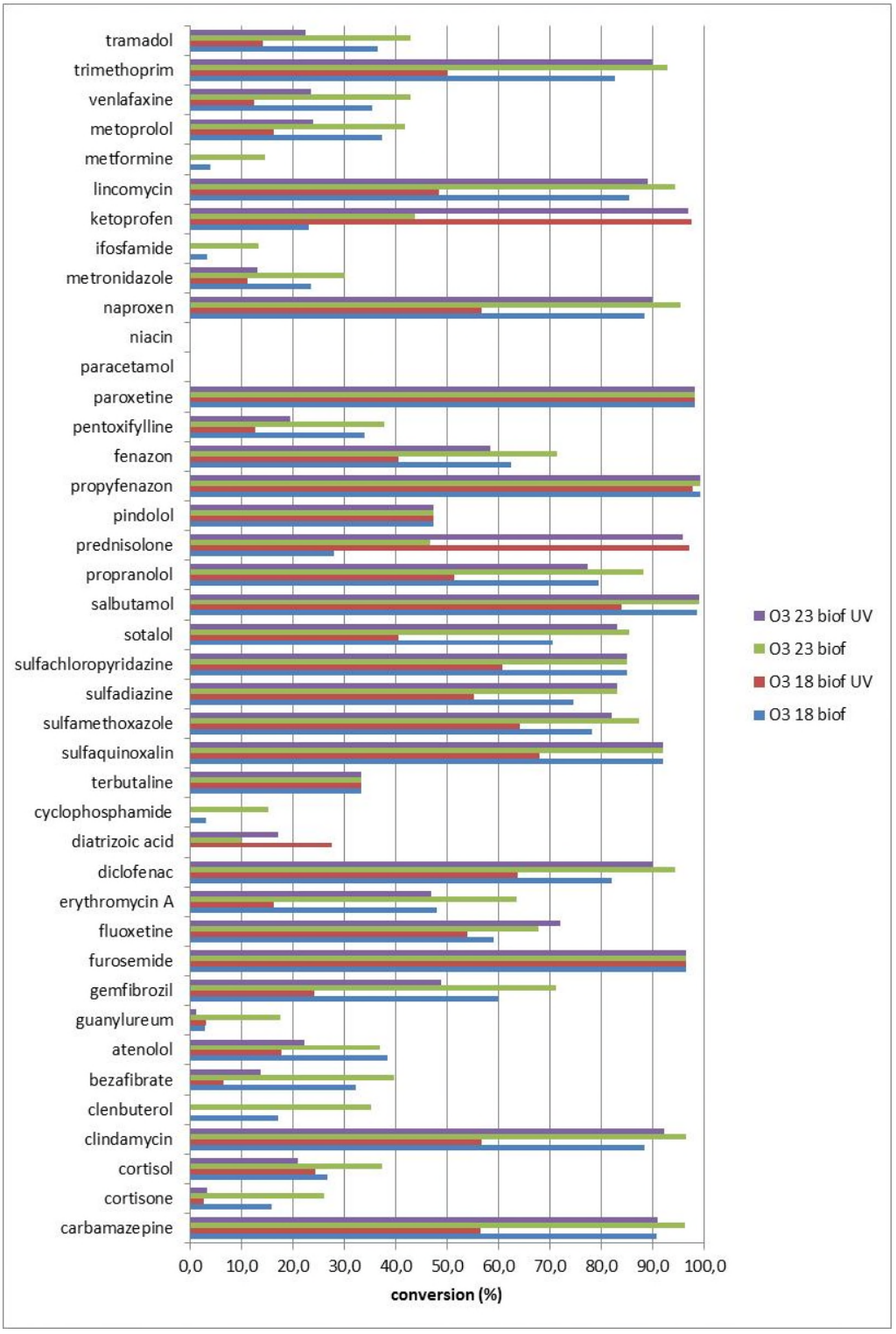


Figure 8-12: Conversion of pharmaceuticals by means of O_3/biofiltration or O_3/UV/biofiltration

Previous experiments revealed that increasing the ozone dose results in a higher conversion of pharmaceuticals, and this can also be observed in Figure 8-12, both for the process

without and the process with the UV reactor. However, surprisingly it seems that using the UV lamp decreases the conversion grade of the compounds. As the experiments were carried out at the same day, using the same water, it is not likely that the ozone concentrations would have differed with and without UV. In principle UV should enhance the decomposition of ozone, so it would be expected that more reactions would have taken place. However, obviously, the ozone and biofiltration are less effective for pharmaceutical degradation in case UV is applied, so it may be argued that instead more EfOM may have been converted in this way. Samples of the O_3/biofiltration pre-treatment (Figure 7-6) show that in this case there hardly has been any conversion of the EfOM. Thus the samples will still have contained high EfOM levels, which may have preferably reacted in the O_3/UV process.

8.4 Comparison of reactors by means of E_{EO} values

It is known that the relatively high energy use of a UV/H_2O_2 process is its main disadvantage. This energy use depends on several parameters:

- Type of component
- Water matrix
- Reactor geometry

As a result, it is very difficult to compare different reactors and/or processes. For this purpose in literature the E_{EO} value is applied, i.e. electrical energy per order, defined as:

$$E_{EO} = \frac{P}{F * \lg \frac{c_i}{c_e}}$$

In which P is the electrical power (kW), F is the flow (m^3/hour), c_i is the concentration in the influent and c_e is the concentration of the effluent. The unit of E_{EO} = kWh/m^3order.

This value shows the energy required to degrade 90% of a certain compound in a certain water type and in a certain UV reactor. It can be applied to compare the effectiveness of the UV/H_2O_2 process for different organic micropollutants, for different water matrices, or for various reactor types/geometries.

E_{EO} values were used to compare the effect of IEX filtration, removing the humic acid fraction, and O_3/biofiltration (mainly removing the hydrophobic part of the EfOM) on the efficiency of the subsequent UV/H_2O_2 process. In order to obtain a fair comparison, only the energy requirement of the UV process was compared, using the pharmaceutical concentrations after pre-treatment as the influent concentrations. For E_{EO} calculations only data obtained at 150 mJ/cm^2 UV dose and at 12 mg O_3/L were used (Figure 8-13). The reason is that if already near complete oxidation is already obtained at 150 mJ/cm^2, increasing the dose to 300 mJ/cm^2 will result in twice the energy demand, whereas the conversion calculated will hardly increase. Besides, at a higher UV dose and/or O_3 concentration the difference often is less clear: if already a high conversion is obtained during (pre-)treatment, the improvement will be limited due to the fact that the concentration will reach the limit of detection. In order to avoid this problem, in Figure 8-14 the E_{EO} values are only shown for compounds which had been removed for less than 80% by means of either IEX or O_3/biofiltration.

The results show that IEX pre-treatment, or in other words removal of humic acids, results in a significantly lower E_{EO} value than removal of mainly the hydrophobic fraction by

O_3/biofiltration. Differences in E_{EO} values between different compounds can be attributed to the sensitivity of the compounds towards the UV/H_2O_2 process, which is due to the molecular structure of the compounds.

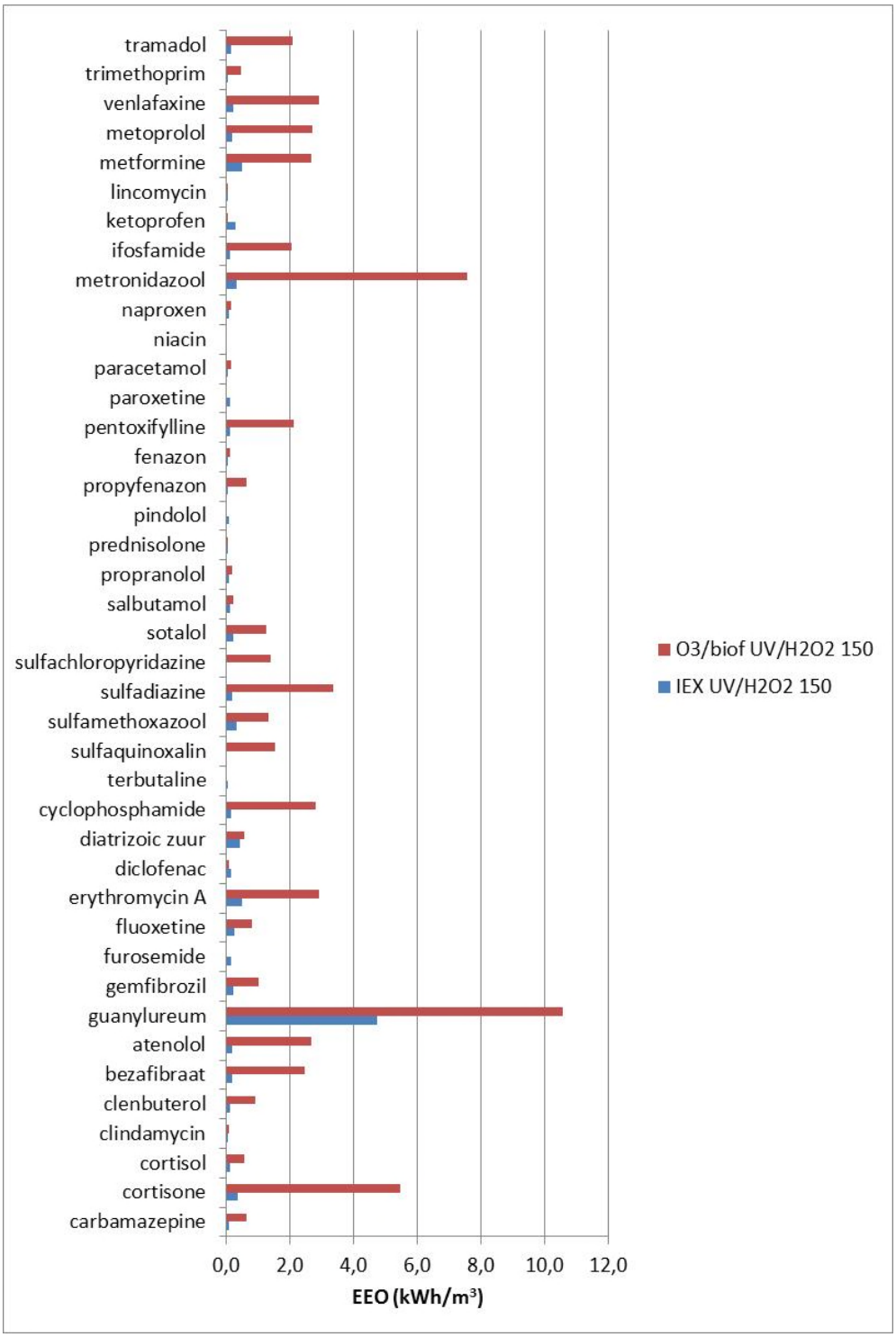


Figure 8-13: E_{EO} values calculated for the UV/H_2O_2 process (at a UV dose of 150 mJ/cm²) after pre-treatment with either O_3/biofiltration (at an ozone dose of 12 mg/L) or IEX.

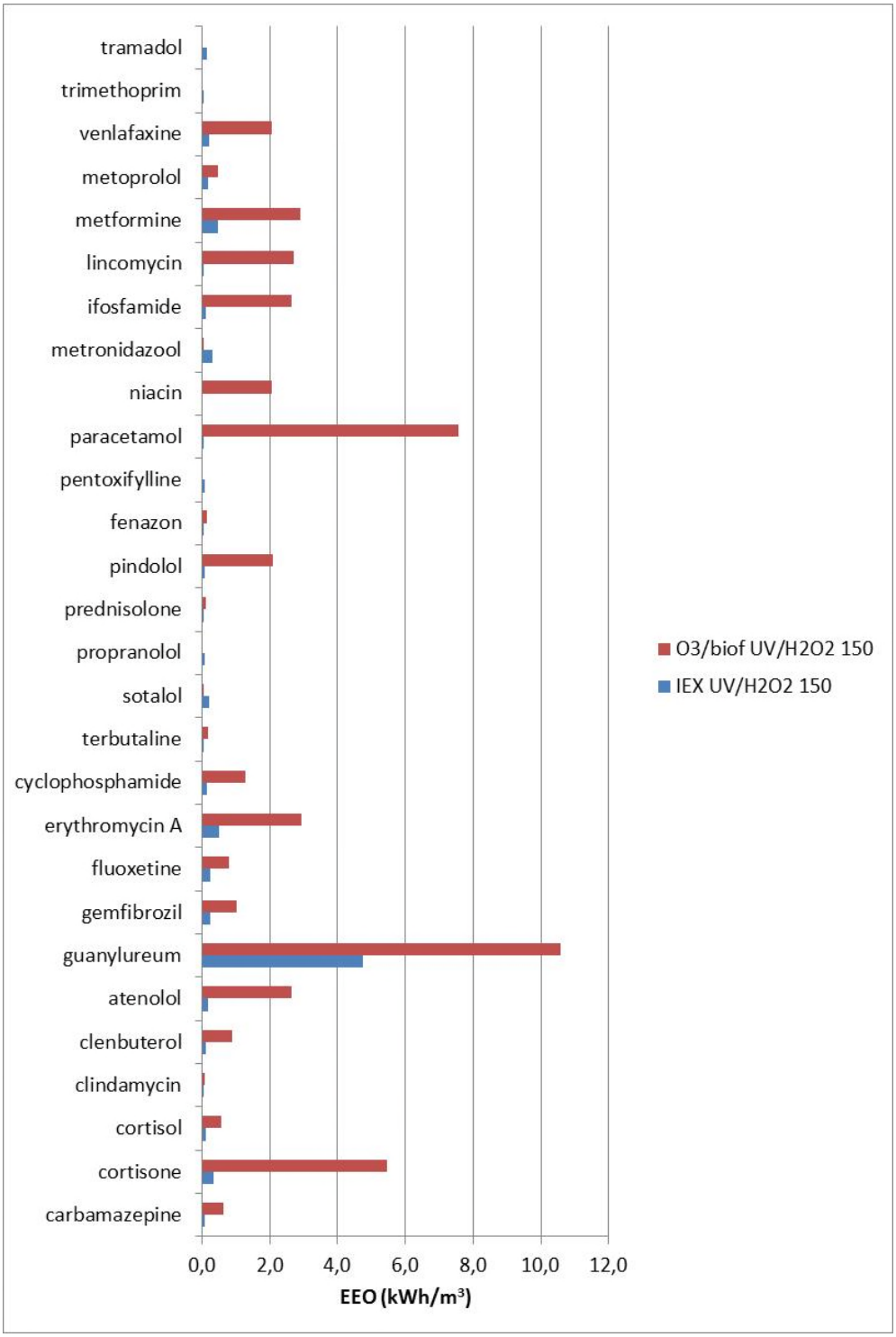


Figure 8-14: E_{EO} values calculated for the UV/H_2O_2 process (at a UV dose of 150 mJ/cm²) after pre-treatment with either O_3/biofiltration (at an ozone dose of 12 mg/L) or IEX. Only compounds taken into account which showed less than 80% removal by means of the pre-treatment method itself.

Furthermore, a comparison was made for O_3/biofiltration processes with additional UV/H_2O_2 process and with integrated UV. For the integrated UV process first ozone is added, and then

the water passes a UV-reactor. UV in combination with ozone also results in the formation of hydroxyl ions, and thus can be considered as an advanced oxidation process. As integrated UV is applied before biofiltration, for the E_{EO} calculations the original pharmaceutical concentration after dosing of the pharmaceuticals has been applied, in order to obtain a fair comparison, as for both types of processes the same ozone generation and biofiltration were applied. In Figure 8-15 the data are shown for compounds that are removed to <80% by means of O_3/biofiltration itself (at a concentration of 23 mg O_3/L). Figure 8-16 shows the E_{EO} data for the compounds that already can be removed to >80% by O_3/biofiltration (although at lower concentrations a smaller number of compounds is removed to that extend).

In comparing the O_3/biofiltration process at different ozone concentrations, followed by a UV/H_2O_2 process, it is to be expected that the E_{EO} values will decrease as the ozone concentrations increase from 12 to 18 and 23 mg/L (although of course more energy will be required for the ozone generation). This is due to the fact that at higher ozone concentrations more organic compounds will be converted (and UV-T will be increased), and thus less energy will be required for the removal of micropollutants. For many compounds indeed a decrease in E_{EO} can be observed when the ozone concentration is increased from 12 to 18 mg/L. However, for terbutaline about the same E_{EO} is calculated. This cannot be attributed to a high conversion by ozone/biofiltration itself, as the conversion of terbutaline here was about 35% (see Figure 8-1). Obviously, terbutaline is not very sensitive towards oxidation by ozone.

Furthermore, it can be observed that for some compounds (pindolol, terbutaline, erythromycin, fluoxetine and clenbuterol) the green bars (23 mg O_3/L) are identical to the red (18 mg/L) bars, and for some other compounds are higher than the red bars or even significantly higher than the blue (12 mg/L) bars (see metformin, ifosfamide, and cyclofosphamide). For cortisone the E_{EO} at 23 mg/L about equals the E_{EO} value at 12 mg/L. During the testing period it was noticed that some ozone leakage did occur, as a result of which the ozone concentrations in December may have been lower than 18 or 23 mg/L. From Figure 8-1, however, it can be concluded that at least the O_3 concentrations increased when they theoretically were increased from 12 to 18 and 23 mg/L, as in this order also the removal of pharmaceuticals took place. On the other hand, the small effect of the ozone/biofiltration process on the EfOM composition also was rather remarkable, indicating that something strange might have happened here. This may also account for the effects that can be observed here.

For compounds that are removed to a high extent by O_3/biofiltration (Figure 8-16) such "strange" effects cannot be observed, but here the E_{EO} calculations may be less reliable, as conversions already could have been high before the water entered the UV reactor.

In Figure 8-15 and Figure 8-16 also the effect of the integrated UV reactor on E_{EO} values is shown. Two conclusions can be drawn from these data:

1. At a higher ozone concentration the E_{EO} value decreases, as is to be expected, as more radicals will be formed at higher ozone concentrations.
2. The E_{EO} values of the integrated UV reactor are higher than of the external UV reactor. In both cases an advanced oxidation process is expected to take place. However, the main difference is that in case of the external UV/H_2O_2 process the UV is applied after part of the EfOM has been removed, whereas in the integrated UV/O_3 process the EfOM still is present (biofiltration will take place later in the process).

Obviously, the presence of the EfOM interferes with the removal of the pharmaceuticals, resulting in higher E_{EO} values.

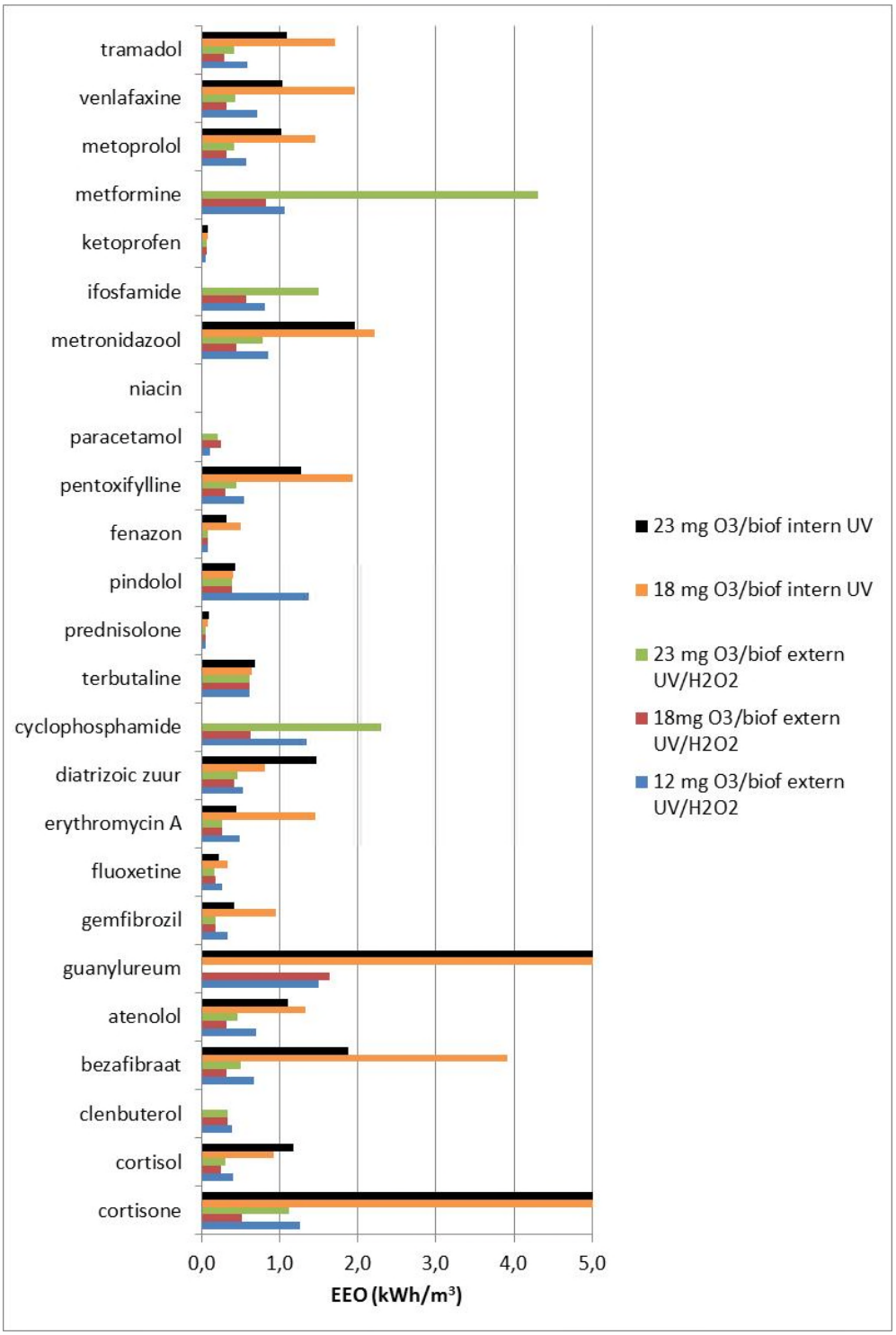


Figure 8-15: Comparison of the O_3/biofiltration process followed by UV/H_2O_2 and the O_3/biofiltration process with integrated UV irradiation. Compounds which show >80% removal by O_3/biofiltration itself have been left out of this graph.

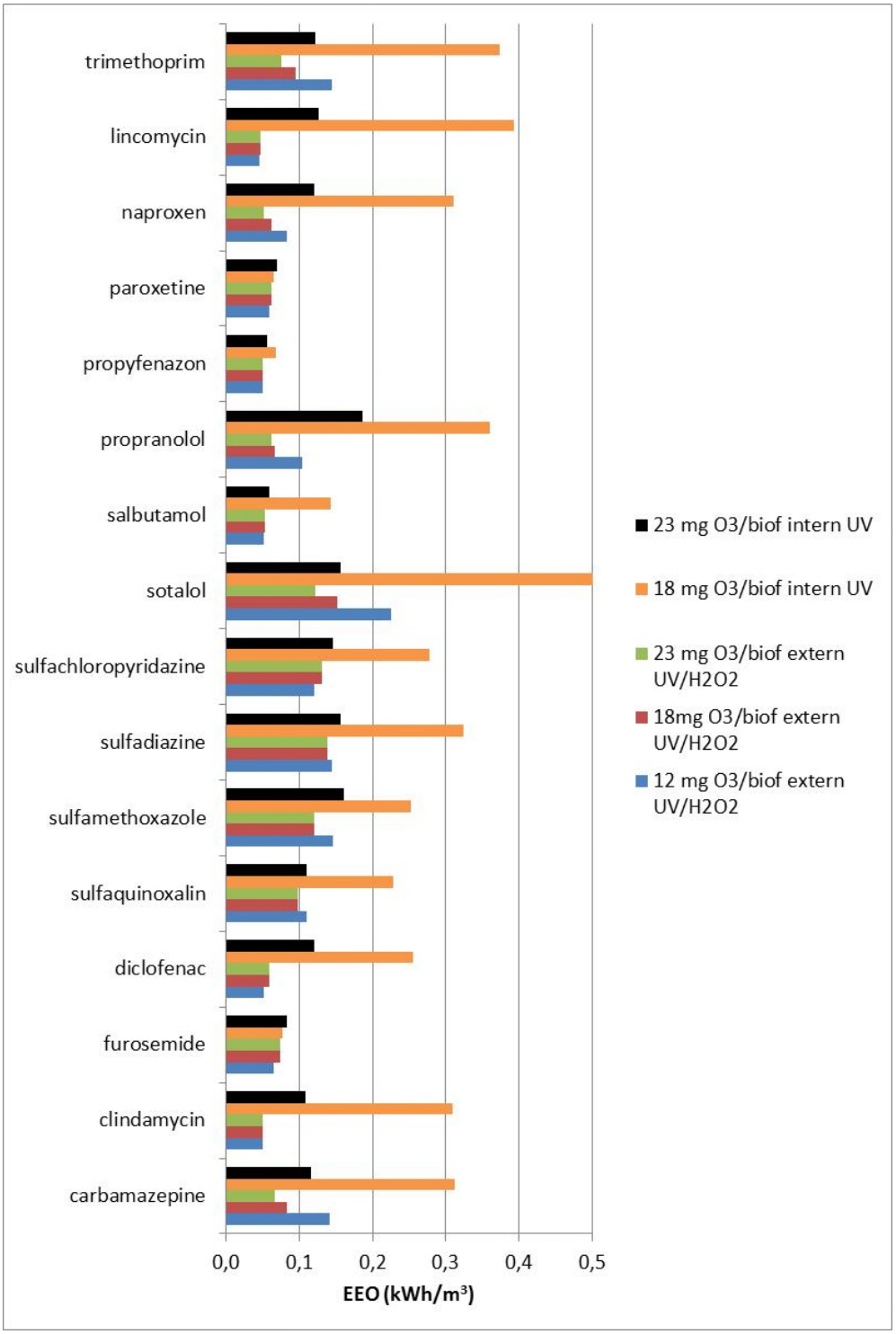


Figure 8-16: Comparison of the O_3/biofiltration process followed by UV/H_2O_2 and the O_3/biofiltration process with integrated UV irradiation, showing the results for compounds which show >80% removal for O_3/biofiltration at a concentration of 23 mg O_3/L or less.

The data from Figure 8-15 are not really clear. It is to be expected that the E_{EO} value will decrease with increasing ozone concentration, as this should result in a better conversion.

However, indeed it is found that for 12 mg O_3 a higher E_{EO} is calculated than for 18 mg O_3, but surprisingly often, e.g. for tramadol and venlafaxine, at 23 mg O_3 a higher E_{EO} is found. However, this is not the case with diatrizoic acid and fluoxetine.

For the integrated UV reactor it is to be expected too that the E_{EO} at 18 mg O_3 should be higher than at 23 mg O_3, but surprisingly this is not the case for terbutaline, diatrizoic acid and cortisol.

Overall, the results obtained with O_3/(UV/)biofiltration are very difficult to explain. However, during these experiments it was also observed that some leakage of ozone may have occurred, as a result of which the ozone concentrations may have differed from the desired concentrations. Furthermore, the intermission of the process at the beginning of the project, and the fact that no backwashing has been applied, may have affected the performance of the biofilter. Therefore, it is very difficult to exactly understand what may have caused the remarkable results obtained. Further research into the ozone/biofiltration (and possibly also into the ozone/UV/biofiltration) process would be required to be able to explain the results obtained, and to determine the full possibilities of this technology.

8.5 Fate of metabolites in the pilot set-up

Metabolites of pharmaceuticals can be formed in the human body, but also later, e.g. during the wastewater treatment process. A well-known example is the conversion of metformin into guanylureum by microorganisms, present in wastewater sludge. Similarly, it is likely that during biofiltration and advanced oxidation not all compounds will be mineralized into CO_2 and H_2O, and that transformation products will be formed. As the conversion processes are very complicated, especially in case many different compounds and EfOM are involved, it is not certain which compounds may be present. However, there are some known metabolites of the pharmaceuticals we studied, for which detection is possible together with the analysis of the mother compounds. Although these metabolites have not been dosed to the system, they were analyzed during the experiments. They may have been present in the WWTP effluent, but may also have been formed during pilot treatment. Thus, through detections information can be obtained on the possible formation of metabolites, and possibly some other transformation products (also see Figure 6-9, Figure 6-11 and Figure 6-17).

As the treated WWTP effluent contains some pharmaceuticals, the presence of metabolites was also determined in this water, before further pilot treatment. The results are shown in Figure 8-17. The effect of the pre-treatment process is also shown here. Experiments with IEX or with 12 mg O_3/L were carried out in Nov. 2015, the other experiments took place in Dec. 2105.

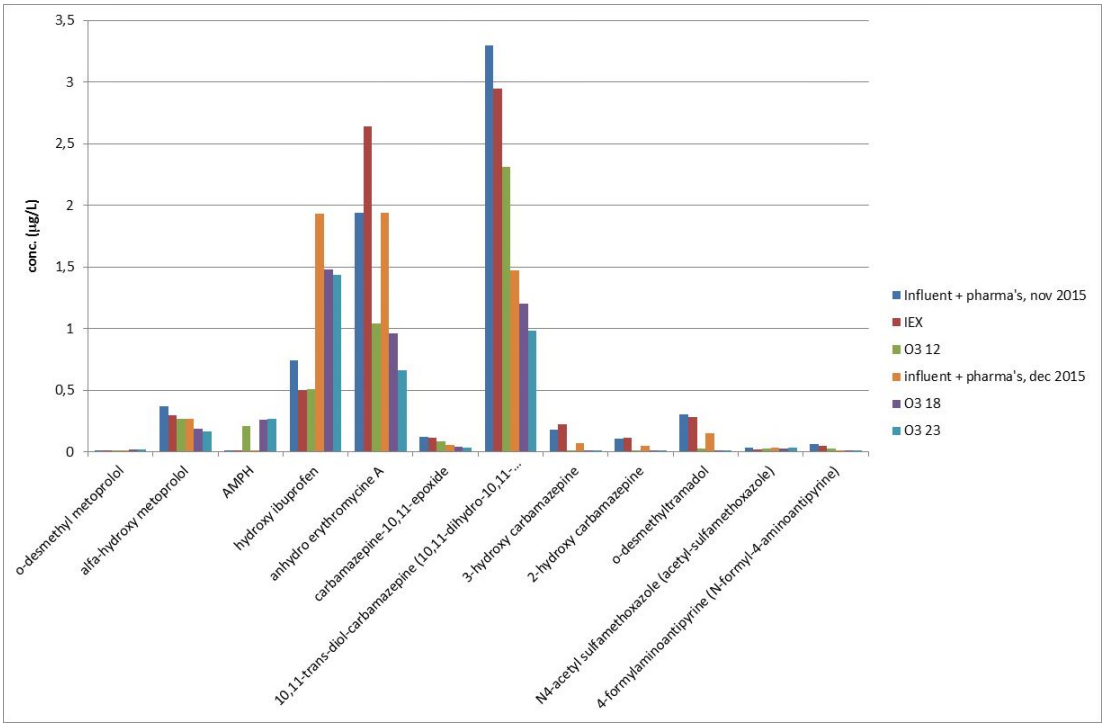


Figure 8-17: Presence of known metabolites in wastewater and after pre-treatment of the water with either IEX or O_3/biofiltration. Experiments with IEX and an ozone concentration of 12 mg/L were carried out in Nov. 2015, experiments with 18 and 23 mg O_3/L were carried out in Dec. 2015.

It can be concluded that some metabolites clearly are present in the influent of the pilot set-up, especially hydroxyl ibuprofen, anhydro eruthromycine A and 10,11-trans-diolcarbamazepine. Guanylurea is present in relatively high concentrations, and during the dosing experiments was dosed to the water, so this compound is taken into account in the previous sections.

As expected, IEX removes part of the metabolites, probably the ones that carry a negative charge at this pH. Remarkably, for 3-hydroxy-carbamazepine the concentration seems to increase a little, but as the concentrations are relatively low, this probably can be attributed to experimental uncertainties.

O_3/biofiltration is able to remove more metabolites than IEX, and in general metabolite concentrations don't seem to increase by the treatment. An increase in ozone dose results in a decrease in metabolite concentrations, indicating that these metabolites are being degraded rather than being formed. However, for AMPH there seems to be an increase in concentration after O_3/biofiltration, in both test series studied. AMPH is a metabolite of metamizole, which had not been dosed to the system, and could not be analyzed by the present method used. It therefore cannot be excluded that metamizole may have been present in the effluent and was converted into AMPH during O_3/biofiltration.

In Figure 8-18 the presence of metabolites after IEX filtration and after subsequent oxidation with UV/H_2O_2 at two different UV doses is shown. It can be concluded that the advanced oxidation process is very effective in removing the metabolites, and that no net formation of

these metabolites can be observed. Increasing the UV dose in general results in a lower concentration of these metabolites.

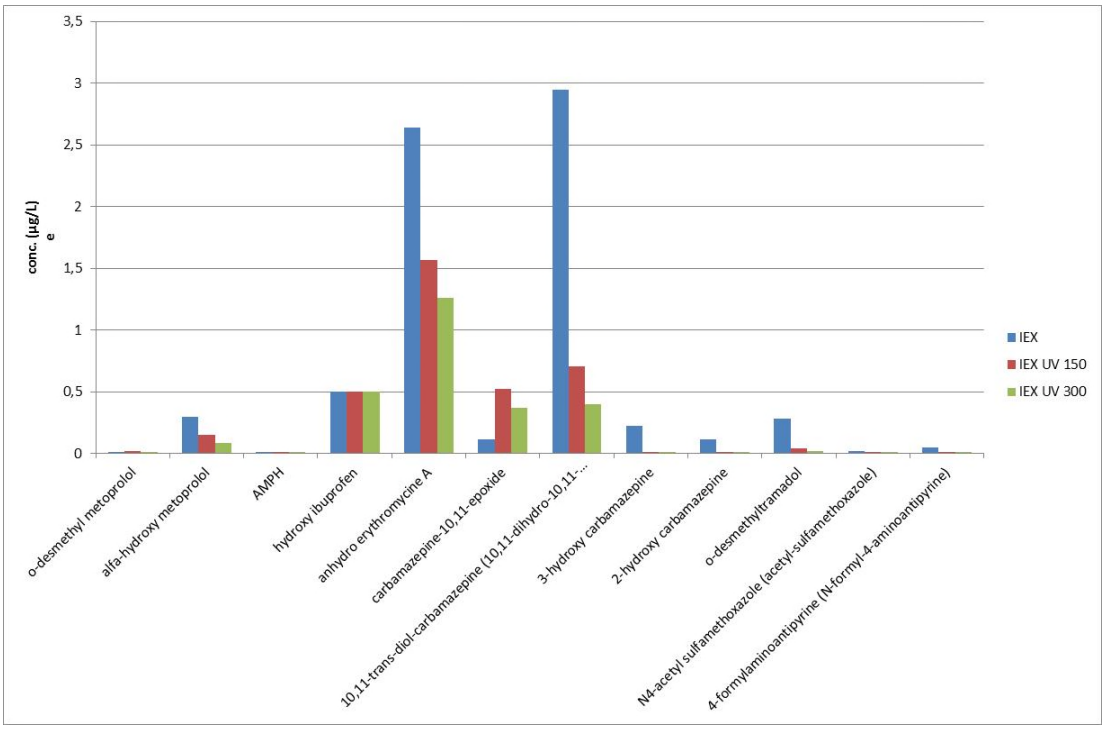


Figure 8-18: Presence of metabolites after IEX and after subsequent treatment with UV/H_2O_2 at a UV dose of 150 or 300 mJ/cm² and 10 mg H_2O_2/L.

The results after pre-treatment with O_3/biofiltration at 12 mg O_3/L are shown in Figure 8-19. Here too the concentration of metabolites seems to decrease with increasing UV dose, although the differences for some compounds (alpha-hydroxy metoprolol and carbamazepine 10,11-epoxide) are small. For anhydro erythromycin A it seems that at a "low" UV dose of 150 mJ/cm² some additional material is formed, which is removed at higher concentrations.

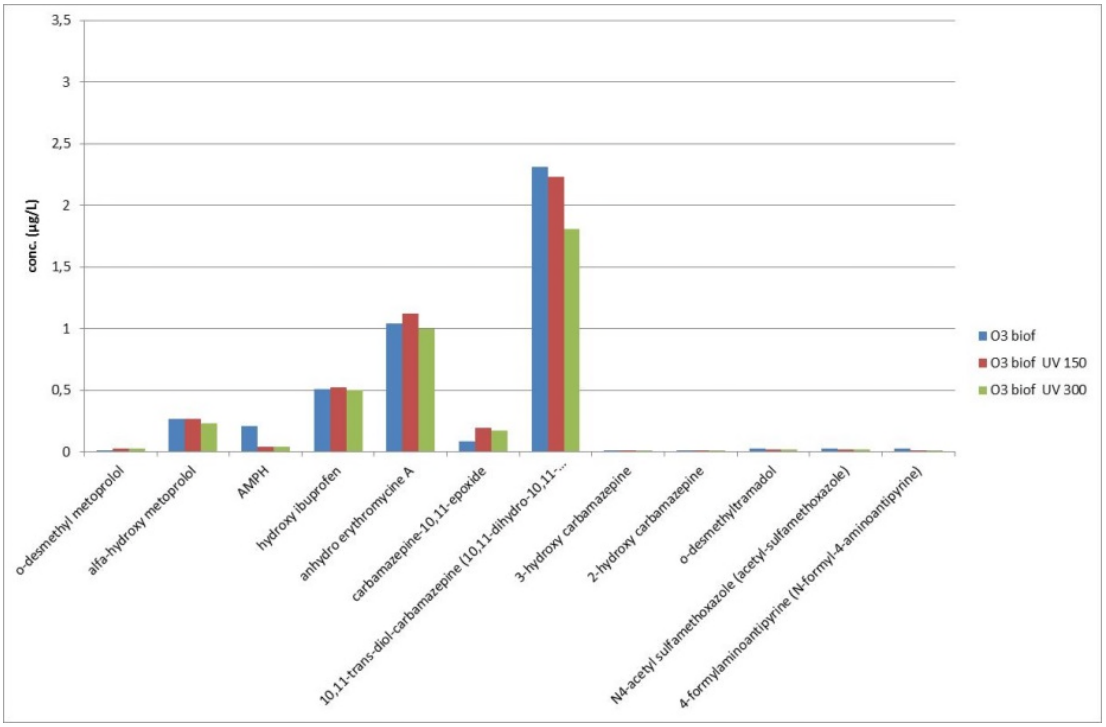


Figure 8-19: Presence of metabolites after O_3/biofiltration (12 mg O_3/L), and after subsequent treatment with UV/H_2O_2 at a UV dose of 150 or 300 mJ/cm² and 10 mg H_2O_2/L.

At higher ozone concentrations comparable results can be obtained (Figure 8-20 and Figure 8-21), although after pre-treatment at 23 mg O_3/L it seems that the formation of anhydro erythromycin A increases at 150 mJ/cm². At the moment it is not clear what causes this effect, but as there were some more remarkable results for these two experiments with higher ozone doses, and the ozone doses do not seem to have been fully clear, it is difficult to determine the cause.

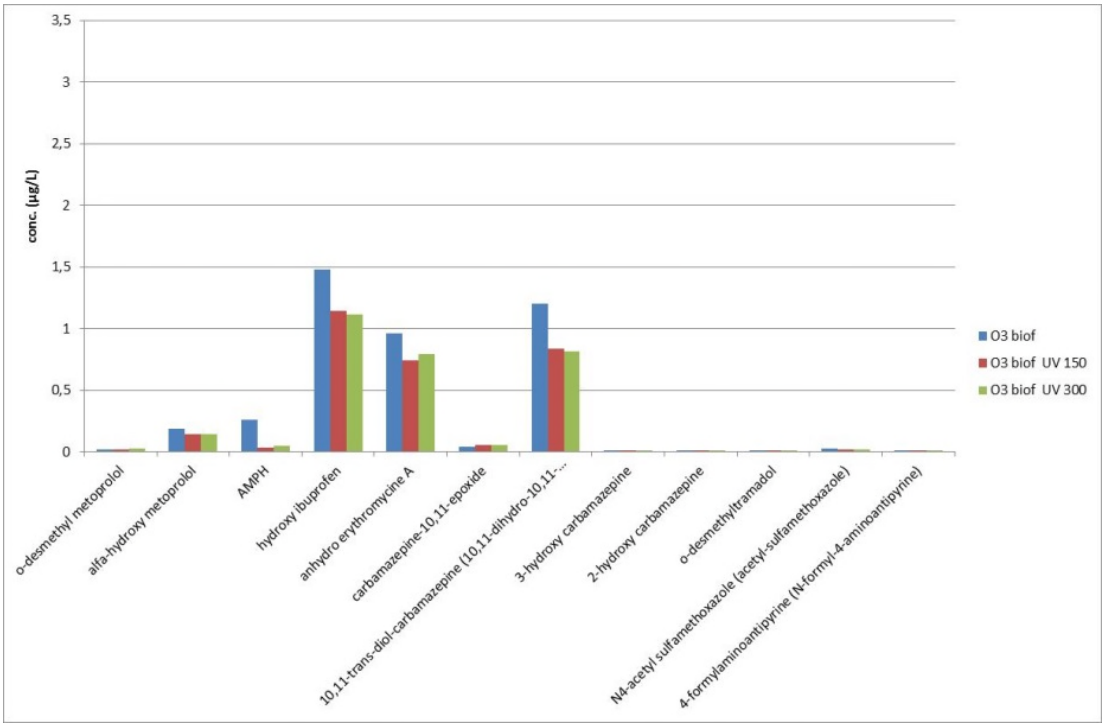


Figure 8-20: Presence of metabolites after O_3/biofiltration (18 mg O_3/L), and after subsequent treatment with UV/H_2O_2 at a UV dose of 150 or 300 mJ/cm² and 10 mg H_2O_2/L.

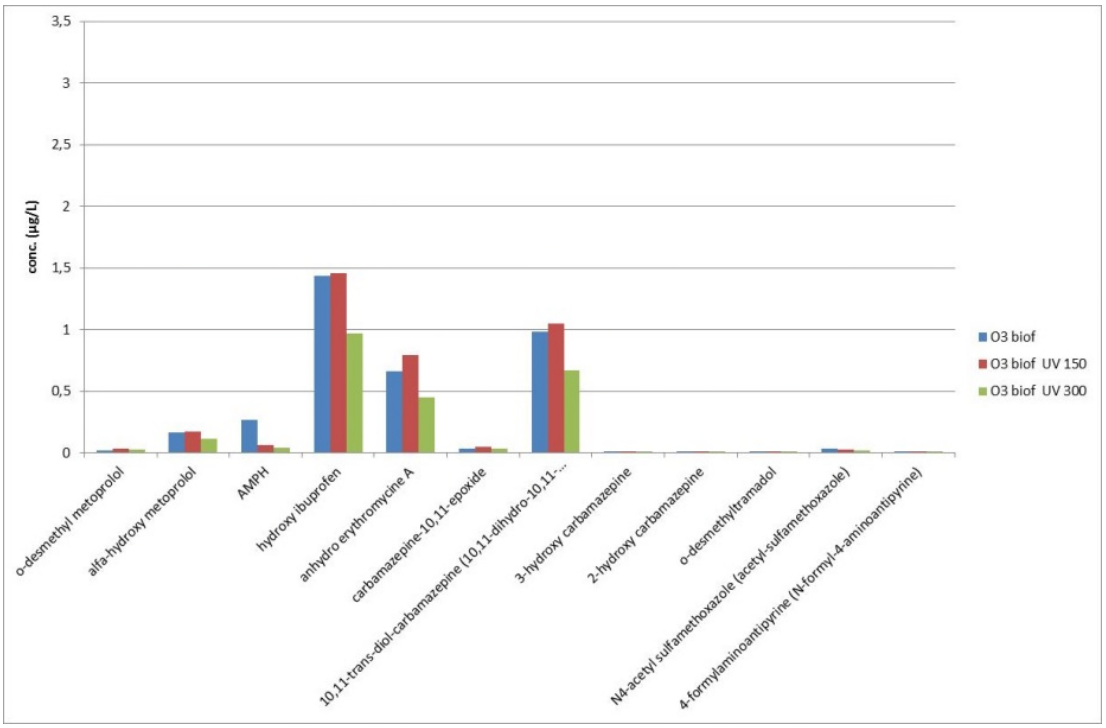


Figure 8-21: Presence of metabolites after O_3/biofiltration (23 mg O_3/L), and after subsequent treatment with UV/H_2O_2 at a UV dose of 150 or 300 mJ/cm² and 10 mg H_2O_2/L.

A comparison of the effect of adding an integrated UV reactor to the O_3/biofiltration system is shown in Figure 8-22.It seems that the concentration of metabolites was higher before dosage of the pharmaceuticals than after. We don't have an explanation for this effect.

It can be noticed that at higher ozone concentrations the concentrations of metabolites in general seem to be lower, both with and without integrated UV lamp. However, it can also be concluded that with the integrated UV system the concentration of metabolites seems to be higher than without the UV reactor. Obviously, degradation of the pharmaceuticals is more efficient without the UV reactor. This may be due to the presence of EfOM during the O_3/UV AOP, which may make this process less effective (as also mentioned in section8.4.

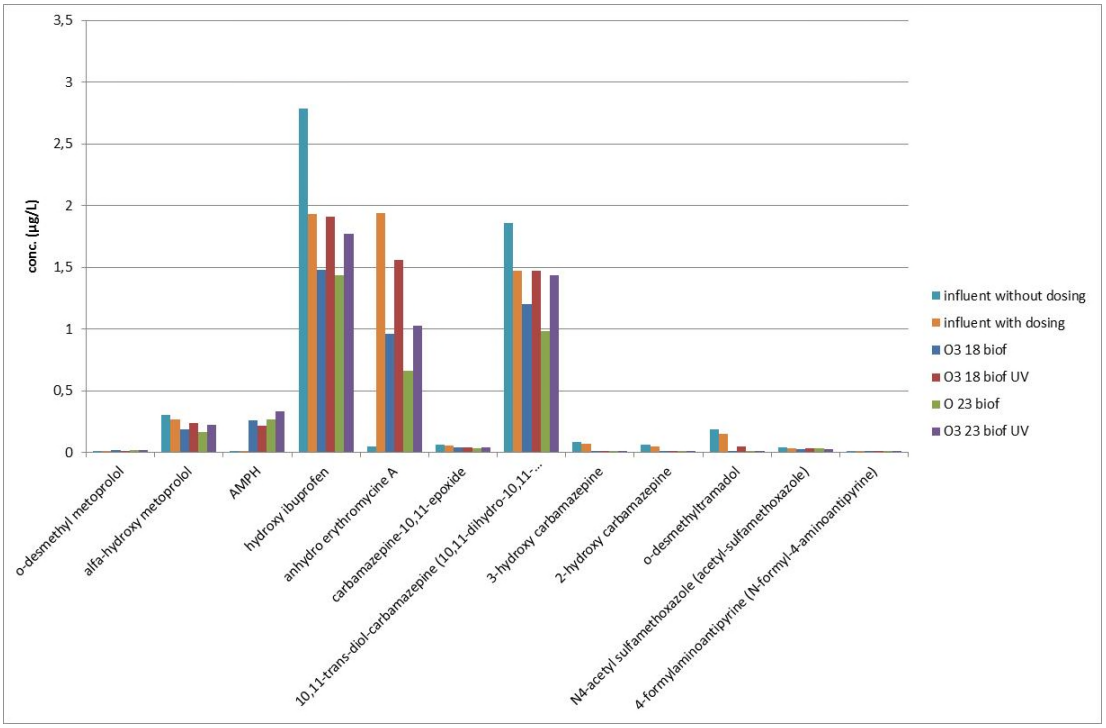


Figure 8-22: Effect of O_3/biofiltration with and without integrated UV reactor on the fate of metabolites.

As the conditions of the O_3/biofiltration and O_3/UV/biofiltration processes are not totally clear, more research would be required in order to be able to fully explain the results obtained, and to determine the possibilities of this technology in wastewater treatment.

9 Discussion and cost estimation

9.1 Possibilities for application

From this research it clearly can be concluded that conventional wastewater treatment cannot remove all pharmaceuticals present in wastewater. As expectations are that in the coming years the amounts and concentrations of pharmaceuticals will increase, it is clear that, no measures being taken, concentrations in WWTP effluent, and thus in surface water, will also increase. This may harm both the aquatic environment and the production of safe drinking water. Therefore, it is necessary to study the possibilities for additional removal steps within the wastewater treatment process. Research into this field already is being done in e.g. Switzerland (using ozone based processes) and Germany (mainly focusing on activated carbon), but the present report shows some possibilities for pharmaceutical removal in WWTPs by means of advanced oxidation in the Netherlands.

From both the laboratory and the pilot results it can be concluded that the presence of EfOM hinders the efficient removal of pharmaceuticals (and other organic micropollutants). The hypothesis that removal of (part of) the EfOM results in a more efficient advanced oxidation process for organic micropollutants was confirmed in this project. According to laboratory results, for pre-treatment two different methods can be applied:

- Removal of the hydrophobic fraction by means of ozone/biofiltration
- Removal of the humic acids by means of ion exchange.

In principle removal of EfOM by means of filtration over activated carbon also can be applied, but in laboratory experiments this didn't give very good results. This is due to the fact that after some time the activated carbon will become loaded and compounds will break through, and because some, relatively small compounds, eventually may be exchanged for larger molecules. Besides, it was shown that for some compounds, like metformin and guanylurea, adsorption on activated carbon will improve in the presence of EfOM, possibly due to the formation of complexes, which are more easy to adsorb.

The pilot experiments showed that UV/H_2O_2, preceded by IEX is a robust process for wastewater treatment. The IEX filtration and regeneration process ran without problems during the pilot period, and the subsequent UV/H_2O_2 process became significantly more efficient by this pre-treatment step. A "problem" which has not yet been addressed, is the treatment of the concentrate that is formed during regeneration of the IEX column. This concentrate contains high concentrations of salt and EfOM (mainly humic acids). In principle it will be possible to separate the EfOM and the salt, and the EfOM might be used as e.g. a fertilizer. However, our experiments have also shown that the concentrate may contain (charged) pharmaceuticals, and it should be studied whether this may interfere with the reuse of the material.

9.2 Comparison with the "conventional" approach

The results obtained with the ozone/biofiltration process are not unambiguous. This probably is due to some practical problems during the pilot investigation period, which may have affected the performance of the technique. However, some results indicate that removal

of the humic acid fraction gives the best improvement of the subsequent UV/H_2O_2 technique for removal of organic micropollutants. The combination of IEX and UV/H_2O_2 results in a very efficient process, with a high removal of a broad range of organic micropollutants, even at low UV doses. A dose of 150 mJ/cm^2 in many cases may be sufficient, whereas in general for application of advanced oxidation in drinking water production doses in the order of magnitude of 500-700 mJ/cm^2 are required. Besides, as a result of the removal of part of the EfOM, the UV-T of the water is significantly increased, as a result of which the amount of energy required to obtain the desired dose, is relatively low. Thus, the total process may be more efficient than application of one single process.

In other countries the problem of the presence of pharmaceuticals in wastewater also has been noticed, and measures are being taken to solve it. In Switzerland it has been decided to add ozonization to the main conventional WWTP's. However, as wastewater contains high concentrations of EfOM, relatively high concentrations of ozone will be required. In the Netherlands, where bromide concentrations in water in general are higher than in Switzerland (on the average already ca. 120 μg/L in the Rhine and ca. 70 μg/L in the Meuse, where they enter the country (Mulder, Antakyali et al. 2015)), this would result in a significant increase in the bromate content of surface water (even though wastewater doesn't only contain used drinking water). This is an unwanted side effect, as bromate is considered carcinogenic. In Germany processes based on activated carbon filtration are being studied for the removal of pharmaceuticals from wastewater. As EfOM in general consists of relatively large organic molecules, this material will be a serious competitor for adsorption sites at the carbon surface. As a result, the regeneration frequency of the activated carbon probably will have to be relatively high, involving relatively high costs.

Therefore, we think that a two-step process, IEX followed by advanced oxidation, may be technically and economically worthwhile considering. Due to the removal of the humic acids and the related improvement in UV-T value, the energy demand of the UV-process will decrease with over 80% (see Table 6-3)

In principle the ozone/biofiltration process also may be a very interesting and elegant process, either as a pre-treatment step or as a single process. Relatively low ozone concentrations may be applied, as total oxidation of EfOM (and organic micropollutants) will not be required. Partial degradation may turn organic compounds into better biodegradable compounds, which subsequently can be removed by means of biofiltration. This process will probably not give problems with the formation of a concentrate or with expensive regeneration. However, the pilot experiments have shown that at the moment the process still has to become more robust, as disturbances can still significantly affect the performance. Probably, such problems can be solved, but more research will be required to make the process robust enough for application in full scale wastewater treatment.

9.3 Practical implementation

In the present pilot research the following process steps were applied:

- Pumping phase: as most existing WWTPs discharge directly into surface water using gravity as a driving force, application of an additional treatment step will involve an additional pumping phase. However, in case a new WWTP is built, this may not be necessary.
- Multi phase filtration: this filtration step was added in order to remove suspended solids from the water, as a fixed bed IEX was applied. However, in case a fluidized

bed IEX would be applied, this filtration may be unnecessary. For the O_3/biofiltration process this also may be unnecessary.

- IEX pretreatment or O_3/biofiltration
- UV/H_2O_2 reactor. UV-T can be measured before this reactor, in order to determine the required UV-settings.
- Activated carbon: the main purpose of this process step was the removal of the excess of H_2O_2. It can also remove possible byproducts, formed during the oxidation process. However, it will depend on circumstances whether this will be necessary. It also will have to be investigated whether this filtration is necessary after O_3/UV,biofiltration.

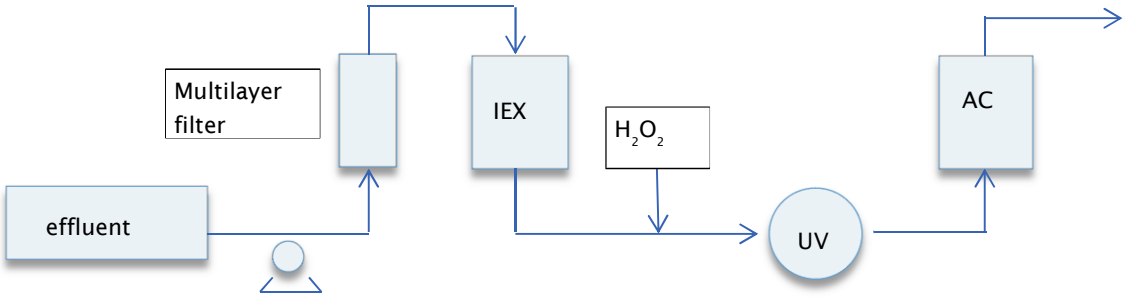


Figure 9-1: Schematic overview of an additional treatment step consisting of a multi layer filter, IEX, UV/H_2O_2 and filtration over AC.

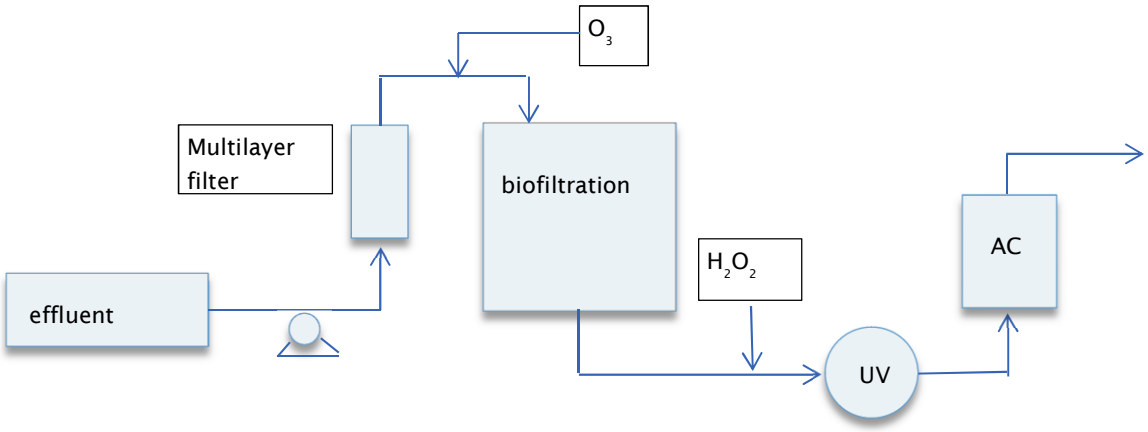


Figure 9-2: Schematic overview of an additional treatment step consisting of a multi layer filter, ozone/biofiltration, UV/H_2O_2 and filtration over AC.

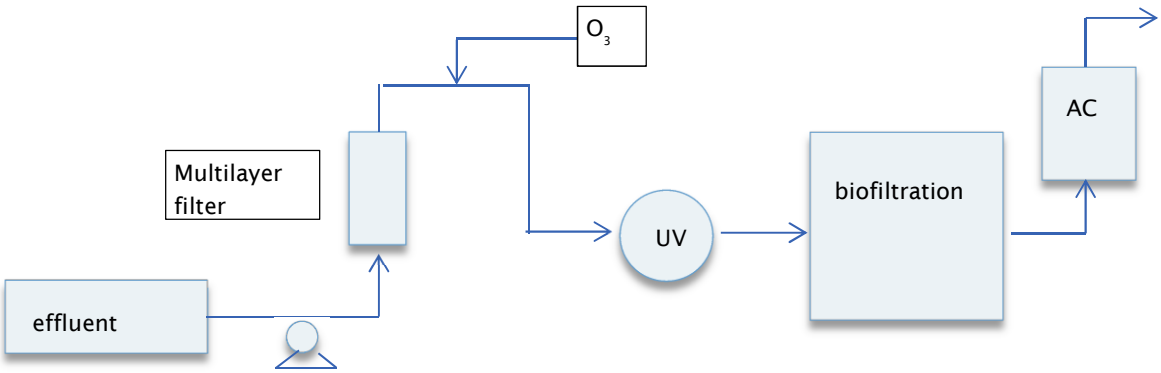


Figure 9-3: Schematic overview of an additional treatment step consisting of a multi layer filter, ozone/UV/biofiltration and filtration over AC.

9.4 Cost estimations

From the results described above it can be concluded that the pre-treatment indeed may affect the effectiveness of the subsequent treatment by means of advanced oxidation or adsorption. As the differences observed for activated carbon with and without pre-treatment by means of IEX were relatively small, and as for metformin and guanylurea even opposite results were obtained, it was decided that in a subsequent pilot investigation focus would be on advanced oxidation processes.

Whether a double treatment (IEX followed by advanced oxidation) would be a realistic part of a treatment process not only depends on how far organic micropollutants can be removed, but also on the costs involved, and the amounts of chemicals and energy required in the additional processes. Based on laboratory results it was tried to compose an overview of all advantages and disadvantages of the treatment techniques suggested, and to estimate the costs involved when a certain treatment would be implemented at full scale.

Table 9-1: advantages and disadvantages of several treatment techniques.

Proces	Advantages	Disadvantages/ points of attention
IEX filtration	Removal of a significant part of the EfOM, which interferes with e.g. AOP or adsorption. It gives a higher UV-transmission, as a result of which UV processes require less energy.	NaCl is required for regeneration of the resin. Formation of humic rich salty concentrate, that has to be dealt with
O_3/biofiltration	Simple and relatively cheap process Improvement of biological water quality	Separate room required for ozone generators, oxygen, cryogenic tank. Rinsing of filters Possibility of introducing

		microorganisms into rest of process? Robustness: this still needs improvement.
Adsorption over Activated Carbon	Removal of contaminants	Activated carbon regularly has to be regenerated, which involves transport costs and a high energy demand for the thermal regeneration itself.
UV/H_2O_2	Conversion of contaminants Very effective for several types of contaminants.	Relatively high energy demand of the UV process. Order of magnitude of 0.4 kWh/m³ Formation of byproducts, that may be harmful, and possibly will have to be removed Storage and dosing of H_2O_2
O_3/H_2O_2	Conversion of contaminants Very effective for several types of contaminants. Low energy demand.	Formation of byproducts, that may be harmful, and possibly will have to be removed Ozone production requires cryogenic storage tank for oxygen, and about 0.05 kWh/m³ Storage and dosing of H_2O_2 Separate room required for ozone generators, oxygen, cryogenic tank.
UV/O_3	Conversion of contaminants Very effective for several types of contaminants.	Relatively high energy demand of the UV process. Formation of byproducts, that may be harmful, and possibly will have to be removed Ozone production requires cryogenic storage tank for oxygen, and about 0.05 kWh/m³ Separate room required for ozone generators, oxygen, cryogenic tank.

NB. It was established that the phosphate and oxygen content of the WWTP effluent is high enough for subsequent biofiltration.

For the costs the total investment costs (M€), the operational costs (€/m³), and the yearly operating costs (M€/year) were calculated for the Panheel WWTP, based on a total capacity of 1,825 Mm³/year (information from Panheel; Hofman et al., 2013). The costs were

calculated using the CoP Cost Calculator of RHDHV. The accuracy of the calculations is about 30%. An extensive overview of all calculations can be found in (Hofman et al., 2013). For a full scale application a buffer basin with a pumping phase and rapid sand filtration would be required, which is included in the cost estimation.

The Opex cost calculation for the in situ generation of ozone results in a price of €2,5/kg (including the generation of ozone from pure oxygen, the energy for the ozone generator, cooling of the generator and pumping energy for dissolution of ozone in water. This means that for a concentration of 12,5 mg O_3/L the costs would be about €0.0315/m^3.

Biofiltration does not require high operational costs, as the ozonation process automatically introduces oxygen into the reactor and causes recirculation. Possibly, an additional blower (2.2kW) can be installed in order to obtain a good distribution of the water over the filter bed. For a bioreactor with a flow of 100 m^3/hour (15 m^3 reactor, height 3 m, diameter 2.5 m) and an air flow of 100 Nm^3/hour the energy requirement for 100 m^3/hour would be 2kW/hour, which results in additional costs of about 0.002 €/m^3 .

As the O_3/biofiltration pre-treatment did not function optimally, it will be difficult to estimate the costs for processes based on this pre-treatment. An estimation of costs involved in ozone based advanced oxidation processes by PureBlue Water is given in Table 9-2.

Table 9-2: Cost estimation for AOPs based on ozone (PureBlue Water)

Ozone dose	Costs (€/m^3)
12.5 mg/L	0.03
31.2 mg/L	0.08
62.4 mg/L	0.16

It will be interesting to further study ozone/biofiltration, either as a pre-treatment for e.g. an AOP like UV/H_2O_2, or as a full treatment, in order to obtain more information on the possibilities, advantages and challenges of this technology.

Applying the same cost calculation as in Hofman et al. (2013) cost estimations were made for the following process steps, shown in Table 9-3.

Table 9-3: Cost estimation for the additional treatment of Panheel WWTP effluent, including different processes.

pre-treatment		Costs pre-treatment (€/m³)	Treatment		Costs treatment (€/m³)	Total costs (€/m³)
O_3/biofiltration	O_3 12,5 mg/L + biofiltration 15 min.	0.032 + 0.002	UV/H_2O_2	UV 300 mJ/cm² 10 mg H_2O_2/L	0.069 0.013	0.116
O_3/biofiltration	O_3 12,5 mg/L + biofiltration 15 min.	0.032 + 0.002	O_3/H_2O_2	31 mg O_3/L 36 mg H_2O_2/L	0.078 0.039	0.151
O_3/biofiltration	O_3 12,5 mg/L + biofiltration 15 min.	0.032 + 0.002	O_3/UV	31 mg O_3/L UV 130 mJ/cm²	0.078 0.050	0.162
IEX	IEX	0.111	UV/H_2O_2	UV 300 mJ/cm² 10 mg H_2O_2/L	0.069 0.013	0.193
IEX	IEX	0.111	O_3/H_2O_2	31 mg O_3/L 36 mg H_2O_2/L	0.078 0.039	0.228
IEX	IEX	0.111	O_3/UV	31 mg O_3 UV 130 mJ/cm²	0.078 0.050	0.239

Based on the results of the pilot plant, it was decided to make full cost calculations for a process consisting of additional IEX + UV/H_2O_2 + ACF, and to compare these results with previous results for additional ACF, IEX + ACF, and IEX + UV/H_2O_2.

As some pressure will be required for the filtration steps, additional costs were included for this (consisting of a pumping reservoir and a low pressure pump). Furthermore, rapid sand filtration was added to account for the fact that a filtration was carried out before the IEX process, in order to prevent problems in case the effluent should contain particles. In case FIX could be used, the total costs of this combination may be lower, as FIX is supposed to be less sensitive to the presence of particles. However, as contamination of the FIX resin also may cause problems, it can be argued that even in that case an additional filtration step, previous to the FIX column, would be advisable.

Thus, for the total cost calculation, for each process the following costs have to be added:

- Pumping reservoir: 0.005 €/m³
- Low pressure pump: 0.027 €/m³
- Rapid sand filtration: 0.066 €/m³

These costs will be identical for every combination of additional treatment techniques. Furthermore, based on the calculation model, on a yearly base the costs for the operator will

be about 0.01M€, and for the administration 0.002M€ (taking into account a production of 1825 Mm^3/year.

ACF was added to the UV/H_2O_2 process in order to remove the excess of H_2O_2. For this process a contact time of 10 minutes was assumed, and furthermore it was assumed that reactivation should take place after 24 months (maybe even a longer period would be possible, as the main purpose of this filtration step is the removal of H_2O_2, and not the adsorption of compounds). Besides, the electrical energy required for the UV process was taken as 90 Wh/m^3, as was the case in the pilot plant. The total calculations, and comparisons to previous results, are shown in Appendix VIII. In Table 9-4 an overview of the total costs is shown:

Table 9-4: Estimation of investment and operating costs for several scenarios, applied to WWTP Panheel.

Process		Investment costs (M€)	Total operating costs (M€/year)	(€/m^3)	(€/IE)
1	Effluent + ACF*)	4,17	0,615	0,337	24,6
2	Effluent + IEX + ACF*)	5,97	0,763	0,418	30,5
3	Effluent + IEX + UV/H_2O_2	3,72	0,542	0,297	21,7
4	Effluent + IEX + UV/H_2O_2 + ACF	4,76	0,613	0,343	25,0

*)Hofman et al., 2013.

It can be concluded that the process based on IEX and UV/H_2O_2 (with rapid sand filtration previous to IEX and AC filtration afterwards) is about as expensive as activated carbon based processes, or possibly even cheaper than those processes.

In a recent STOWA-report (Mulder, Antakyali et al. 2015) an overview of results obtained in Germany and Switzerland was given. For a WWTP of about the size of Panheel (20.000 IE; Panheel has 25.000 IE) the results shown in Table 9-5 were calculated.

Table 9-5: Cost estimation for different processes according to (Mulder, Antakyali et al. 2015); assuming a DOC content of 11 mg/L.

Process	Costs (€/m^3)
O_3 + rapid sand filtration	0.26 ± 0.05
PAC*) + rapid sand filtration	0.30 ± 0.04
GAC **)+ rapid sand filtration	0.33 ± 0.05

*) 12 mg/L, contact time 35 min.

**) empty bed contact time 30 min., life time 6 months (8,800 bed volumes). It was assumed that the quality of the GAC after regeneration would not be sufficient for efficient removal of pharmaceuticals, and thus it was assumed that after 6 months the carbon would have to be replaced with fresh carbon.

The deviations mentioned in Table 9-5 depend on the DOC content of the water, which was taken as 11 mg/L as an average, but could vary from 7-15 mg/L. For Panheel, the DOC content is about 15 mg/L, as a result of which costs would be at the upper level, so 0.30-0.40 €/m^3. This is in the same range as the predicted costs for out process which is ca. 0.34 €/m^3.

The IEX/UV/H_2O_2 process studied in this project is very robust, and shows a very good removal for a broad range of organic micropollutants, including compounds which are very difficult to remove by means of activated carbon (like small, hydrophilic, and/or charged compounds).

In the STOWA report the formation of reaction products by ozone is mentioned as a risk for oxidation processes. It is known that ozone is very efficient for the oxidation of electron rich compounds, but is less effective for other organic micropollutants. The UV/H_2O_2 process described has a high efficiency for a much broader range of compounds. However, in case transformation products and/or metabolites would be formed (which could not be concluded from the pilot experiments), they would be removed by the subsequent activated carbon filtration. Furthermore, it has been shown that even in the ozone/biofiltration pre-treatment no bromate formation could be detected, which is a serious disadvantage of ozone processes, in case bromide is present.

Thus, it can be concluded that the filtration/IEX/UV-H_2O_2/ACF process is a very robust process, which will cost not more than filtration over activated carbon, but will be more effective for the removal of pharmaceuticals and other organic micropollutants.

The costs of IEX concentrate treatment have not been included yet, but these will be the same for scenarios 2-4 in Table 9-4. As the concentrate will contain large amount of humic acids, it may be possible to separate salt and the organic fraction. Possibly, the organic fraction may be used as a kind of fertilizer. However, this also will depend on the concentrations (and types) of organic micropollutants present in the concentrate.

9.5 Optimization of the treatment process; technology readiness level

In terms of "technology readiness level" ( ) it can be stated that research started at level TRL 2/3: for the individual process steps applicability had been proven under certain conditions, but the combination of techniques and water matrix had not yet been studied. Furthermore, it was experimentally shown that WWTP effluent contains significant amounts of EfOM and pharmaceuticals. At the moment we are at level TLR 6/7 for the IEX-UV/H_2O_2 process.

Table 9-6: Definitions of Technology Readiness Levels (TRLs)

Level	description
TRL 1	basic principles observed
TRL 2	technology concept formulated
TRL 3	experimental proof of concept
TRL 4	technology validated in lab
TRL 5	technology validated in relevant environment (industrially relevant environment in the case of key enabling technologies)
TRL 6	technology demonstrated in relevant environment (industrially relevant environment in the case of key enabling technologies)
TRL 7	system prototype demonstration in operational environment
TRL 8	system complete and qualified
TRL 9	actual system proven in operational environment (competitive manufacturing in the case of key enabling technologies; or in space)

In case IEX followed by UV/H_2O_2 is implemented as an additional treatment step in wastewater treatment, some extra aspects will have to be taken into account:

- A pumping phase may be required.
- In this project prefiltration was applied as for IEX a fixed bed colum was used. However, it will have to be investigated whether this also will be necessary if a fluidized bed will be applied.
- For optimization not only the degradation of pharmaceuticals should be taken into account, but also the possible formation of transformation products and metabolites, as mentioned in chapter 6. When the UV dose is decreased, care should be taken that this will not result in the formation of unwanted products. Furthermore, the fate of metabolites, already present in the effluent, in the treatment process also should be taken into account. As the conversion of compounds and formation of transformation products is a rather complicated process, it will be difficult to predict and analyze which transformation products may be formed. Bioassays may be useful to determine possible effects.
- The IEX resin will have to be regenerated regularly. This results in the formation of a concentrated NaCl solution, containing at least EfOM, but possibly also some pharmaceuticals. The treatment of this concentrate also will have to be taken into account. There are techniques to separate organic matter and salt, after which the salt can be reused, and the organic matter e.g. may be used in agricultural applications. However, it will have to be investigated whether the organic matter contains some pharmaceuticals, and if so, what kind and what concentration ranges (it is possible that some pharmaceuticals, present at the resin, may not be released upon regeneration; this will depend on resin and compound properties). Further research into this matter will be required.
- A continuous process should be run for several months, applying both IEX and UV/H_2O_2,in order to establish the operational reliability, and to measure the use of chemicals, the energy demand, and the removal of pharmaceuticals and metabolites. This will result in a better cost estimation for the total process.
- Process control and automization will have to be developed.
- Possibly a life cycle analysis will be useful.

The results obtained from the ozone/biofiltration and ozone/UV/biofiltration processes are not yet well understood. This may be due to some technical problems that occurred with this set-up. More research will be required. The main advantage of the principle is that no waste will be created, contrarily to e.g the IEX process, which will always generate a concentrate. Therefore, it is worthwhile to further investigate the the possibilities of this technology. Here too research started at TRL 2/3, and at the moment it is considered to be at TRL 4/5.

10 Conclusions and recommendations

10.1 Conclusions

The following conclusions can be drawn from the project, described in this report:

1. WWTP effluent contains relatively large amounts of organic matter.
2. WWTP effluent contains significant concentrations of pharmaceuticals. As it is expected that the use of pharmaceuticals will increase in near future, it is possible that these compounds eventually may affect the aquatic environment and possibly also drinking water production. It therefore is to be expected that standards may be set in (near) future. A first step in this direction is the placement of some compounds like diclofenac on the European Watch List.
3. According to literature, the organic matter in effluent may hinder further removal of organic micropollutants by means of adsorption, oxidation processes or membrane filtration.
4. A significant part of the EfOM consists of humic acids. Laboratory research alsow shows that ion exchange is a very effective technique to remove the humic acid fraction of EfOM, whereas O_3/biofiltration seems to mainly remove the hydrophobic fraction.
5. It was shown that both pre-treatment methods may already remove part of the pharmaceuticals. IEX is most effective for negatively charged compounds, whereas O_3/biofiltration is most effective for electron rich molecules.
6. Laboratory research also shows that previous removal of (part of) the EfOM makes a subsequent advanced oxidation process (O_3/H_2O_2, O_3/UV, or UV/H_2O_2) (much) more efficient.
7. The presence of a 30 W US device inside the flow through UV reactor, used in the O_3/UV experiments and during the UV/H_2O_2 pilot experiments, probably has not affected the results obtained. The UV/US reactor can be considered as a regular UV-reactor.
8. The influence of pre-treatment on adsorption on GAC appeared to be relatively small, and seemed even to be negative for some compounds (metformin and guanylurea).
9. In the pilot set-up it was found that filtration over IEX columns was very robust, and could be performed over a longer period of time without any problems. Regeneration of the IEX resin could be carried out automatically.
10. In the pilot set-up the O_3/biofiltration process appeared to give some problems in continuous operation. This should require more attention.
11. The IEX/UV-H_2O_2 process is a very robust barrier for pharmaceuticals. As the UV-T is significantly increased by the IEX filtration, a relatively low UV dose will be sufficient to obtain high conversion of pharmaceuticals in the AOP. Besides, a low amount of energy will be required to reach this UV dose, as a result of which the UV/H_2O_2 process requires less than 20% of the amount of energy than in case of no pre-treatment. Therefore, this process is very efficient.

12. The total costs of a treatment based on filtration/IEX/UV-H_2O_2/ACF are in the same order of magnitude as costs for filtration over activated carbon or ozonisation. However, the process studied here is much more effective for a broad range of organic micropollutants, including also charged, small and hydrophilic compounds which are not easy to remove by means of activated carbon. Also in comparison with ozon this process can degrade a broader range of compounds. For the cost estimations an additional pumping phase and a filtration step before the IEX were taken into account.

10.2 Recommendations

- WWTP effluent at the moment already contains significant concentrations of various pharmaceuticals. As it is expected that this will increase in near future, it is worthwhile to further study what is the best way to deal with these compounds. Another issue that should be addressed is the optimum location for additional treatment.
- In order to remove pharmaceuticals and other organic micropollutants from WWTP effluent the combination of filtration/IEX/UV-H_2O_2/ACF is very effective. This process can be applied at about similar costs as alternative processes which have been suggested, but are less efficient for a broad range of compounds. It should be tested whether this can be applied at more WWTPs.
- Research should be done into the treatment possibilities for concentrate of IEX processes.
- More attention should be paid to the possibilities of an O_3/biofiltration process. At the moment the process seems to be less robust than IEX or IEX/UV-H_2O_2, but if this can be improved, it may be a very effective pre-treatment method, or even can be considered as a treatment method (instead of e.g. filtration activated carbon). The main advantage is that no concentrate will be formed.

11 Acknowledgement

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Appendix I

Report DOC-Labor

Effluent samples of different WWTP's

LC-OCD Analyses of RWZI sec. Effluent Samples

Your project-ID / our project ID: **B14060046WS / KWR_15 / A4138**
Project Partner / contact: **Wolter Siegers / Wolter.Siegers@kwrwater.nl**
 # and type of samples: **6 / (water)**
Measuring conditions: **column: 50714 / 015** **flows: 1.0 / Ø / Ø** **buffer: STD**

Sampling date:	**2014 - Jun – 11-17**	**STD ☐**	**MC ☐**
Incoming date:	**2014 - Jun - 24**	**report:**	**☐ Y ☐ N**
Measuring date:	**2014 - Jun – 24-26**	**data processing:**	**Dipl.-Ing. A. Balz**
Date of Report:	**2014 - Jun - 26**	**report:**	**Dr. S. Huber**

***Disclaimer*: We guarantee the correctness of analytical data according to the actual state or standard of science and technology. All interpretations are based on the assumption that samples are representative for a situation under investigation. We do not take responsibility for any action that is taken on the basis of our reports, irrespective of whether such action has been recommended by us or not. Reports are treated confidentially and are exclusive property of customer. Anonymized data may be used for scientific purposes if no additional agreements are made.**

Technical note: LC-OCD stands for "Liquid Chromatography - Organic Carbon Detection". Separation is based on size-exclusion chromatography (SEC) followed by multidetection with organic carbon (OCD), UV-absorbance at 254 nm (UVD) and organic bound nitrogen (OND). All concentration values refer to mass of organic bound carbon (OC). As a "rule-of-thumb" compound mass is about twice (for acids threefold) the value of OC. Chromatograms are processed on the basis of area integration using the program ChromCALC. In many samples the acid fraction contains low-molecular mass humic acids which are subtracted by ChromRES on the basis of SAC/OC ratio for HS. Thus, despite the visible presence of an acid peak there may no LMW acids be present.

SUMMARIC PARAMETERS:

***DOC (Dissolved OC)*:** Determined in the column bypass after in-line 0.45 µm filtration.

***HOC (Hydrophobic OC)*:** Difference DOC minus CDOC, thus all OC retained on the column is defined as „hydrophobic". This could be natural hydrocarbons or sparingly soluble "humins" of the humic substances family.

INORGANIC COLLOIDS (respond only in UV-Chromatograms): Negatively charged **inorganic** polyelectrolytes, polyhydroxides and oxidhydrates of Fe, Al, S or Si are detected by UV light-scattering (Raleigh-effect).

***CDOC (Chromatographic DOC)*:** This is the OC value obtained by area integration of the total chromatogram. Chromatographic subfractions of CDOC are:

***ROM = Refractory Organic Matter*:**
A: Humics (HS): In LC-OCD measurements there is a tight definition for HS based on retention time, peak shape and SAC. Calibration on the basis of "Suwannee River" Standard IHSS-FA and IHSS-HA. In addition, statistical data are given, like number-averaged molecular mass (Mn) and aromaticity (SAC/OC).
B: Building Blocks (BB): The HS-fraction is accompanied by shoulders, shape, concentration and UV-activity varies. This are sub-units of HS with molecular weights of 300-450 g/mol. Building Blocks are considered to be natural breakdown products of humics. They cannot be removed in flocculation processes.

***BOM = Biogenic Organic Matter*:**
C: Biopolymers (BP): This fraction is very high in molecular weight (100.000 - 2 Mio. g/mol), hydrophilic, not UV-absorbing. BP are typically polysaccharides but may also contain proteinic matter (this is quantified on basis of OND). BP exist only in surface waters.
D: LMW Organic Acids (OA): In this fraction all aliphatic, low-molecular weight (LMW) organic acids co-elute due to an ion chromatographic effect. A small amount of HS may fall into this fraction and is subtracted on the basis of SAC/OC ratios.
E: LMW Neutrals (NEU): Low-molecular weight (LMW weakly or uncharged hydrophilic or slightly hydrophobic ("amphiphilic") compounds appear in this fraction. This includes alcohols, aldehydes, ketones and amino acids. The hydrophobic character increases with retention time, e. g. pentanol appears at 120 min, octanol at 240 min. NEU may be in part refractory.

***SOM = Synthetic Organic Matter*:**
With LC-OCD all water-soluble synthetic organic compounds can be quantified and identified (after comparison with model compound) down to the low ppb-range. However, chromatographic resolution in SEC is moderate (about 15000 theoretical plates/metre). Typical examples for SOM are flocculant polymers, antiscalants, organic additives like amines, resin leaching products like polysulfonic acids (PSS) or trimethyl amine (TMA).

***Inorganic Colloids* (only visible in UV-detection):** Inorganic colloidal or particulate matter eluting slightly before the biopolymer fraction becomes visible by Raleigh light scattering. This material could be iron oxid hydrates or colloidal sulfur.

***SUVA (SAC/DOC)*:** Additional parameter derived from the ratio of DOC and SAC.

Results

Table 1

Project: KWR_15	DOC	HOC*	CDOC	Approx. Molecular Weights in g/mol: >>20.000				~1000 (see separate HS-Diagram)						300-500	<350	<350		
	Dissolved	Hydrophob.	Hydrophil.	BIO-polymers	DON (Norg)	N/C	% Proteins in BIOpol.**	Humic Subst. (HS)	DON (Norg)	N/C	Aromaticity (SUVA-HS)	Mol-Weight (Mn)	Position in HS diagram	Building Blocks	LMW Neutrals	LMW Acids	Inorg. Colloid.	SUVA
	ppb-C	ppb-C	ppb-C	ppb-C	ppb-N	µg/µg	% BIOpol.	ppb-C	ppb-N	µg/µg	L/(mg*m)	g/mol	–	ppb-C	ppb-C	ppb-C	SAC (m^{-1})	(SAC/DOC) L/(mg*m)
	% DOC	% DOC	% DOC	% DOC	–	–	–	% DOC	–	–	–	–	–	% DOC	% DOC	% DOC	–	–
Effluent Dokhaven	10653	1376	9277	698	90	0,13	39	4637	282	0,04	3,77	565	A	2011	1932	n.q.	0,10	3,05
11/12-06-14	100%	12,9%	87,1%	6,6%	–	–	–	43,5%	–	–	–	–	–	18,9%	18,1%	–	–	–
Effluent Eindhoven	9654	1121	8533	750	93	0,12	37	4045	143	0,04	3,60	469	B	1995	1743	n.q.	0,20	3,15
12/13-06-14	100%	11,6%	88,4%	7,8%	–	–	–	41,9%	–	–	–	–	–	20,7%	18,1%	–	–	–
Effluent Utrecht	10276	1110	9166	865	108	0,12	37	3575	150	0,04	2,99	445	C	2092	2415	218	0,15	2,71
12/13-06-14	100%	10,8%	89,2%	8,4%	–	–	–	34,8%	–	–	–	–	–	20,4%	23,5%	2,1%	–	–
Effluent Nereda+bestaand	18299	1826	16473	1128	149	0,13	40	8513	375	0,04	3,51	523	D	3256	3262	314	0,29	2,97
12/13-06-14	100%	10,0%	90,0%	6,2%	–	–	–	46,5%	–	–	–	–	–	17,8%	17,8%	1,7%	–	–
Effluent Panheel	14282	1090	13192	2595	291	0,11	34	4821	277	0,06	3,05	512	E	2443	3143	190	0,51	2,47
17-06-14	100%	7,6%	92,4%	18,2%	–	–	–	33,8%	–	–	–	–	–	17,1%	22,0%	1,3%	–	–
Effluent Roermond	21430	1093	20337	1544	201	0,13	39	7865	373	0,05	3,21	469	F	7031	3897	n.q.	0,38	3,39
17-06-14	100%	5,1%	94,9%	7,2%	–	–	–	36,7%	–	–	–	–	–	32,8%	18,2%	–	–	–

LMW = low-molecular weight
DON = Dissolved organic nitrogen
n.q. = not quantifiable (< 1ppb; signal-to-noise ratio)
n.m. = not measured

*:Grey colour in HOC: Significance unclear
**:under the presumption that all org. N in the BIOpolymer fraction originates from proteins
**: pale green: cross sensitivity inferred

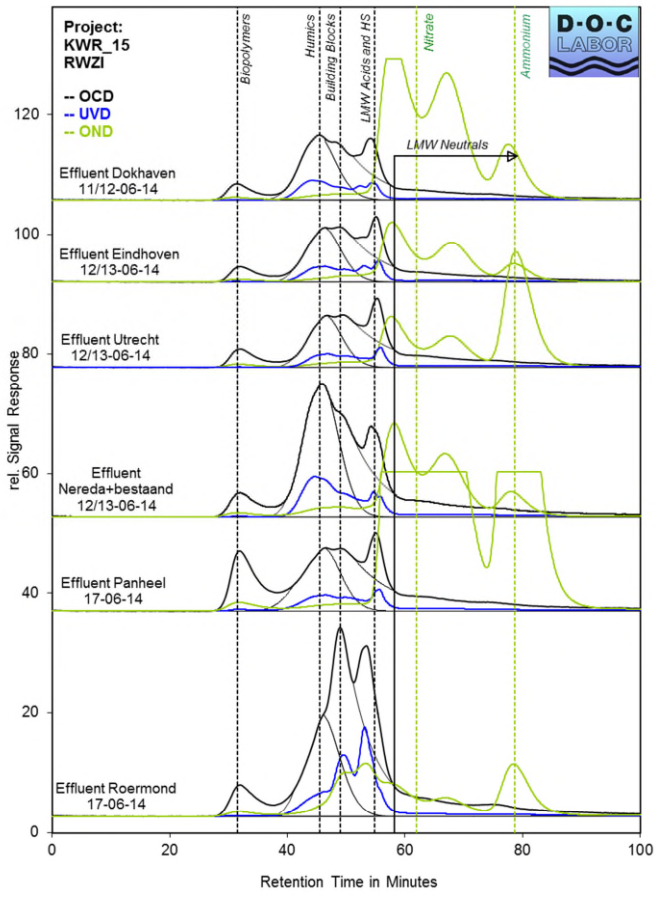


Fig. 1: LC-OCD chromatograms

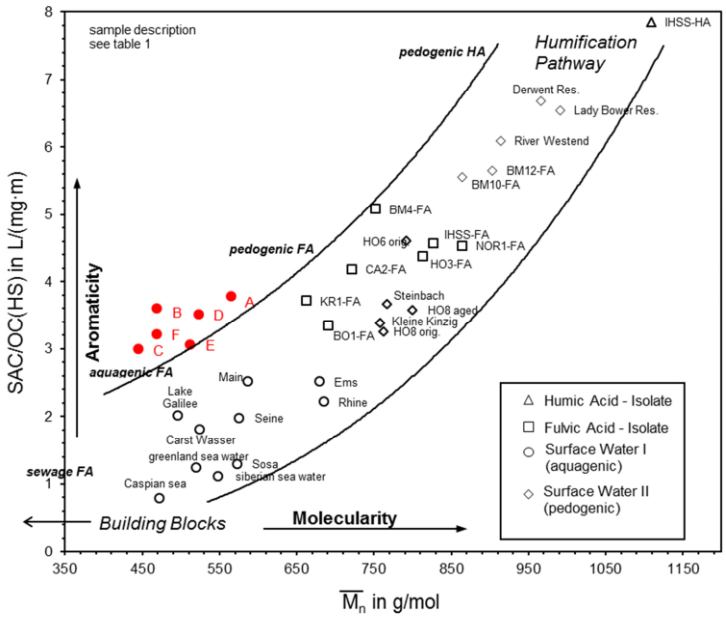


Fig. 2: Humic substances diagramm

Effluent samples of the pilot at Panheel January 2016

Results

LMW = low-molecular weight
DON = Dissolved organic nitrogen
n.q. = not quantifiable (< 1ppb; signal-to-noise ratio)
n.m. = not measured

*:Grey colour in HOC: Significance unclear
**:under the presumption that all org. N in the BIOpolymer fraction originates from proteins
***: pale green: cross sensitivity inferred

Table 1

D-O-C LABOR	DOC	HOC*	CDOC	Approx. Molecular Weights in g/mol: >>20.000				~1000 (see separate HS-Diagram)						300-500	<350	<350		
				BIO-polymers	DON (Norg)	N/C	% Proteins in BIOpol.**	Humic Subst. (HS)	DON (Norg)	N/C	Aromaticity (SUVA-HS)	Mol-Weight (Mn)	Position in HS diagram	Building Blocks	LMW Neutrals	LMW Acids	Inorg. Colloid.	SUVA
Project: kwr_27	Dissolved	Hydrophob.	Hydrophil.														SAC	(SAC/DOC)
	ppb-C	ppb-C	ppb-C	ppb-C	ppb-N	µg/µg	% BIOpol.	ppb-C	ppb-N	µg/µg	L/(mg*m)	g/mol	--	ppb-C	ppb-C	ppb-C	(m^{-1})	L/(mg*m)
	% DOC	% DOC	% DOC	% DOC	--	--	--	% DOC	--	--	--	--	--	% DOC	% DOC	% DOC	--	--
INFL voor Filtrate	14097	2108	11989	1953	194	0,10	30	5167	297	0,06	2,73	531	A	1995	2874	n.q.	0,62	2,53
22 JAN 2016	100%	15,0%	85,0%	13,9%	--	--	--	36,6%	--	--	--	--	--	14,1%	20,4%	--	--	--
NA Filtrate	13861	1935	11926	1921	202	0,11	32	5105	279	0,05	2,94	524	B	2042	2859	n.q.	0,39	2,53
22 JAN 2016	100%	14,0%	86,0%	13,9%	--	--	--	36,8%	--	--	--	--	--	14,7%	20,6%	--	--	--
NA O3, Biof	14030	1276	12754	2093	216	0,10	31	5605	329	0,06	2,83	531	C	2069	2832	154	0,28	2,12
22 JAN 2016	100%	9,1%	90,9%	14,9%	--	--	--	40,0%	--	--	--	--	--	14,7%	20,2%	1,1%	--	--
NA IEX	7937	909	7028	1960	205	0,10	31	n.q.	n.q.	--	--	--	--	1898	2379	792	0,13	1,42
22 JAN 2016	100%	11,5%	88,5%	24,7%	--	--	--	--	--	--	--	--	--	23,9%	30,0%	10,0%	--	--

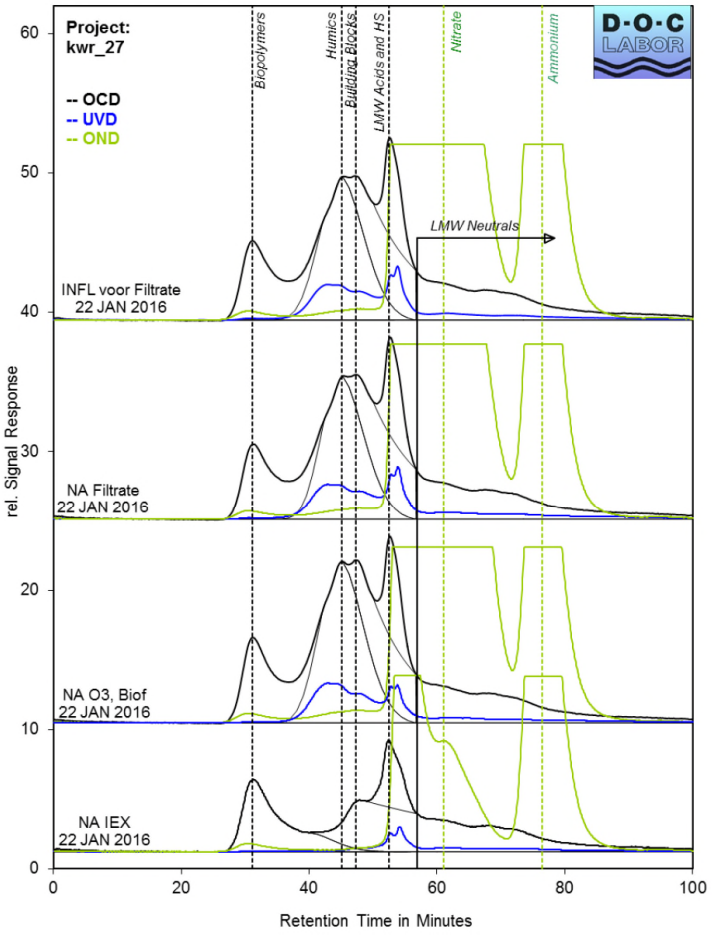


Fig. 1: LC-OCD Chromatograms

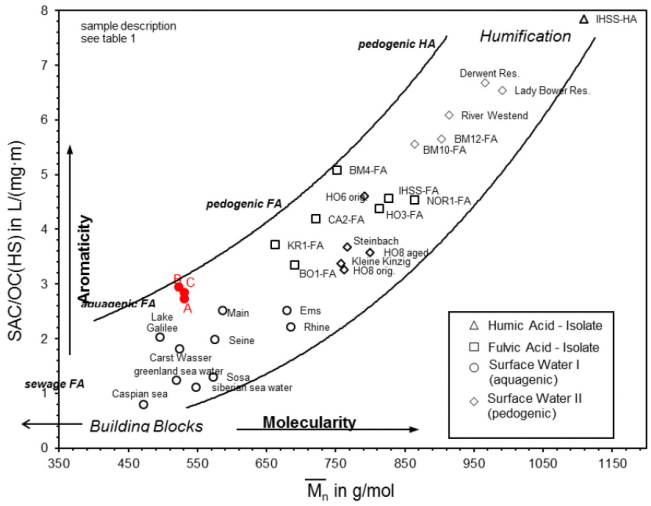


Fig. 2: HS-Diagram(s)

Appendix II

Data of sampling characterizing effluent

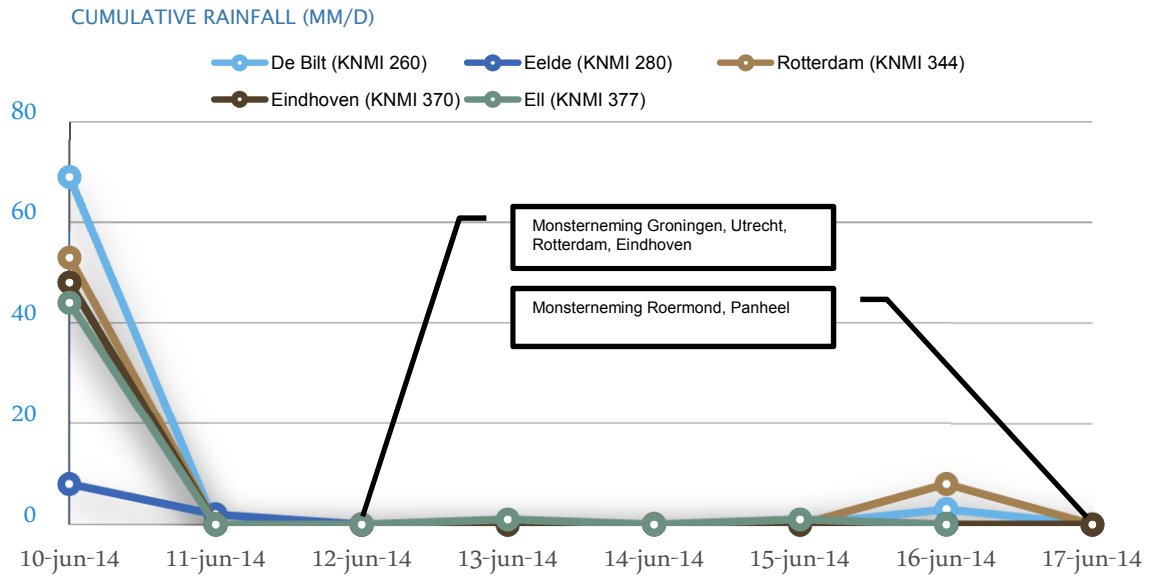


Figure12-1: cumulative rainfall at some locations during sampling

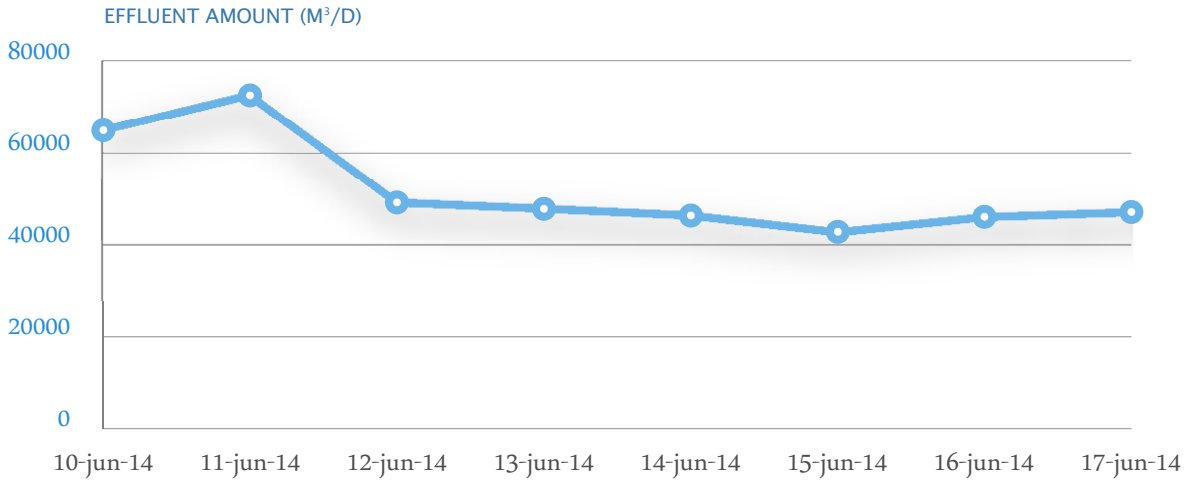


Figure12-2: Effluent amount at WWTP Utrecht

Appendix III

Specifications of the used Lewatit® anion exchangers and regeneration calculations

Spec sheet S 6863 A (Chloride)

PRODUCT INFORMATION
LEWATIT® S 6368 A

Lewatit®

Lewatit® S 6368 A is a Food grade, strongly basic macroporous anion exchange resin (type I) with beads of uniform size (monodisperse) based on polystyrene.

Lewatit® S 6368 A is suitable for:

in the hydroxide form:

» removal of acid and simultaneous decolorisation of solutions of organic substances. e.g. sugar, gelatine, glycerine, grape must, whey, fruit concentrates etc.

in the chloride form:

» decolorisation of sugar syrup (beet or cane), glycerine, grape must, fruit juices.

The macroporous structure ensures very good adsorption of organic substances (e.g. colorants) and partial adsorption of organic acids and mineral acids. The substances are easy to be desorbed by regeneration with caustic soda solution (OH^- form) or alkalized brine solution (Cl^- form).

When using **Lewatit® S 6368 A** to treat potable water and the aqueous solutions listed above, special care should be given to the initial cycles of the new resin. Please refer to the recommended start-up conditions available on request.

The special properties of this product can only be fully utilized if the technology and process used correspond to the current state-of-the-art. Further advice in this matter can be obtained from Lanxess, Business Unit Ion Exchange Resins.

PRODUCT INFORMATION LEWATIT® S 6368 A

Lewatit®

General Description

Ionic form as shipped	chloride
Functional group	quaternary amine, type I
Matrix	crosslinked polystyrene
Structure	macroporous
Appearance	beige, opaque

Physical and Chemical Properties

		metric units	
Uniformity Coefficient*		max.	1.1
Mean bead size*		mm	0.62 (+/- 0.05)
Bulk density	(+/- 5 %)	g/l	640
Density		approx. g/ml	1.06
Water retention		wt. %	60 - 65
Total capacity*		min. eq/l	1.0
Volume change	Cl --> OH	max.	20
Stability	at pH-range		0 - 14
Storability	of the product	max. years	2
Storability	temperature range	°C	-20 - +40

* Specification values subjected to continuous monitoring.

PRODUCT INFORMATION LEWATIT® S 6368 A

Lewatit®

Recommended Operating Conditions*

		metric units		
Operating temperature		max. °C	70 (OH) / 85 (Cl)	
Operating pH-range			0 - 12	
Bed depth		min. mm	800	
Specific pressure drop	at viscosity 1 mPa*s	approx. kPa*h/m²	0.8	
Pressure drop		max. kPa	300	
Linear velocity	backwash (20 °C)	approx. m/h	4 - 5	
Freeboard	backwash (extern / intern)	vol. %	80 - 100	
Regenerant			NaOH	NaCl/ NaOH
Counter current regeneration	level	approx. g/l	60-80	200/20
Counter current regeneration	concentration	wt. %	4	10/1
Co current regeneration	level	approx. g/l	60-80	200/20
Co current regeneration	concentration	approx. wt. %	4	10/1
Linear velocity	regeneration	approx. m/h	5	
Linear velocity	rinsing	approx. m/h	5	
Rinse water requirement	slow / fast	approx. BV	4	

* The recommended operating conditions refer to the use of the product under normal operating conditions. It is based on tests in pilot plants and data obtained from industrial applications. However, additional data are needed to calculate the resin volumes required for ion exchange units. These data are to be found in our Technical Information Sheets.

Spec sheet A 8071

PRODUCT INFORMATION LEWATIT® A 8071

Lewatit

Lewatit® A 8071 is a strongly basic, gelular anion exchange resin (type I) based on an acryl-divinylbenzene copolymer of special bead size distribution.
Due to its acrylic structure **Lewatit® A 8071** stands for effective adsorption and desorption of naturally occuring organic substances. Its very high total capacity and outstanding mechanical stability together with the excellent resistance to osmotic shock makes it unique for all demineralization applications especially if a low silica leakage is required.

Lewatit® A 8071 is especially suitable for:

- demineralizing water later used for industrial steam generation operated with co- or counter-current systems such as Lewatit® Liftbed System or Lewatit® Rinsebed System
- the removal of organic matter, especially from surface water
- the extension of life time of acid baths in the finishing industry (acid retardation process)

The special properties of this product can only be fully utilized if the technology and process used correspond to the current state-of-the -art. Further advice in this matter can be obtained from Lanxess, Business Unit Ion Exchange Resins.

PRODUCT INFORMATION LEWATIT® A 8071

Lewatit

General Description

Ionic form as shipped	Cl^-
Functional group	Quaternary amine, type I
Matrix	Crosslinked polyacrylamide
Structure	Gel type beads
Appearance	White, translucent

Physical and Chemical Properties

		metric units	
Uniformity Coefficient*		max.	1.8
Bead size*	> 90 %	mm	0.4 - 1.6
Effective size*		mm	0.55 (+/- 0.05)
Bulk density	(+/- 5 %)	g/l	730
Density		approx. g/ml	1.09
Water retention		wt. %	57 - 64
Total capacity*		min. eq/l	1.25
Volume change	Cl^- --> OH^-	max. vol. %	25
Stability	at pH-range		0 - 14
Storability	of the product	max. years	2
Storability	temperature range	°C	-20 - 40

* Specification values subjected to continuous monitoring.

PRODUCT INFORMATION
LEWATIT® A 8071

Lewatit®

Recommended Operating Conditions*

		metric units	
Operating temperature		max. °C	30
Operating pH-range			0 - 14
Bed depth		min. mm	800
Specific pressure drop	(15 °C)	approx. kPa*h/m²	1.1
Pressure drop		max. kPa	150
Linear velocity	operation	max. m/h	50
Linear velocity	backwash (20 °C)	approx. m/h	9
Bed expansion	(20 °C, per m/h)	approx. vol. %	11
Freeboard	backwash (extern / intern)	vol. %	100
Regenerant			NaOH
Counter current regeneration	level	approx. g/l	70
WS-System	concentration	approx. wt. %	2 - 4
Linear velocity	regeneration	approx. m/h	5
Linear velocity	rinsing	approx. m/h	5
Rinse water requirement	slow / fast	approx. BV	6
Co current regeneration	level	approx. g/l	100
Co current regeneration	concentration	approx. wt. %	4
Rinse water requirement	slow / fast	approx. BV	10

* The recommended operating conditions refer to the use of the product under normal operating conditions. It is based on tests in pilot plants and data obtained from industrial applications. However, additional data are needed to calculate the resin volumes required for ion exchange units. These data are to be found in our Technical Information Sheets.

PRODUCT INFORMATION
LEWATIT® A 8071

Lewatit®

Additional Information & Regulations

Safety precautions
Strong oxidants, e.g. nitric acid, can cause violent reactions if they come into contact with ion exchange resins.

Toxicity
The safety data sheet must be observed. It contains additional data on product description, transport, storage, handling, safety and ecology.

Disposal
In the European Community Ion exchange resins have to be disposed, according to the European waste nomenclature which can be accessed on the internet-site of the European Union.

Storage
It is recommended to store ion exchange resins at temperatures above the freezing point of water under roof in dry conditions without exposure to direct sunlight. If resin should become frozen, it should not be mechanically handled and left to thaw out gradually at ambient temperature. It must be completely thawed before handling or use. No attempt should be made to accelerate the thawing process.

Scavenger calculation S 6863 A (Chloride)

Scavenger calculation

Resin type :	**Lewatit S 6368 A**	
		Organics expressed in
Organics content	10,000 ppm	TOC
Flow	0,75 m³/h	
Specific load	30,00 BV/h	(to be adapted if necessary)
Resin volume	0,03 m³	
KMnO4 resin capacity	25 g/l	(to be adapted if necessary)
Bed height	520 mm	
Free board	80 %	
Surface area	0,048 m²	
Inside diameter	247 mm	
Cylindrical height	936 mm	
Standardized diameter	200 mm	300 mm
Corresponding area	0,031 m²	0,071 m²
Corresponding bed height	796 mm	354 mm
Linear velocity	15,7 m/h	
KMnO4 capacity of 0,03 m³ resin	0,63 kg	
Volume per cycle	11,90 m³	
Cycle time	15,8 hours	
% of efficiency = 80,00 %		
Leakage	2,000 ppm	TOC
Regeneration @ 35-45°C		
Volume = 2 BV	0,05 m³	
NaCl @ 10 %	5,00 kg	
NaOH @ 1 %	0,50 kg	
Displacement = 2 BV	0,05 m³	
Rinse = 5 BV	0,13 m³	

Scavenger calculation

Resin type :	**Lewatit S 6368 A**		
		Organics expressed in	
Organics content	10,000 ppm	TOC	
Flow	0,38 m³/h		
Specific load	15,00 BV/h	(to be adapted if necessary)	
Resin volume	0,03 m³		
KMnO4 resin capacity	25 g/l	(to be adapted if necessary)	
Bed height	520 mm		
Free board	80 %		
Surface area	0,048 m²		
Inside diameter	247 mm		
Cylindrical height	936 mm		
Standardized diameter	200 mm	300 mm	
Corresponding area	0,031 m²	0,071 m²	
Corresponding bed height	796 mm	354 mm	
Linear velocity	7,8 m/h		
KMnO4 capacity of 0,03 m³ resin	0,63 kg		
Volume per cycle	11,90 m³		
Cycle time	31,6 hours		
% of efficiency = 80,00 %			
Leakage	2,000 ppm	TOC	
Regeneration @ 35-45°C			
Volume = 2 BV	0,05 m³		
NaCl @ 10 %	5,00 kg		
NaOH @ 1 %	0,50 kg		
Displacement = 2 BV	0,05 m³		
Rinse = 5 BV	0,13 m³		

Appendix IV

Settings of the ozone/biofiltration process as pre-treatment in laboratory experiments

Experiments were carried out in a laboratory scale AOP reactor. The ozone dose applied was 7 g/h, the O_2/O_3 mixture was added by means of a pump and a venture. The pump flow was 1500 L/h and the pressure applied was 1 bar. The total volume at the start of the experiments was 83 L, the COD was 62 mg/L.

Table 12-1: Settings of the ozone reactor

Ozone dose (g O_3/gCOD)	Total volume (liter)	Total load (gCOD)	Sampling time (h:mm:ss)
0	83	5.15	0:00:00
0.15	83	5.15	0:06:37
0.3	63	3.91	0:10:03
0.5	43	2.67	0:11:26

The blank sample was taken before the test. For every sample a volume of 20 L was taken for analysis and further treatment by biofiltration.

Appendix V

Data of the used pharmaceuticals and of metabolites analyzed.

Table 12-2: Data of pharmaceuticals used ((Lee, Lee et al. 2013); www.drugbank.ca/pharmaceuticals;(Lemer 1975); http://web.squ.edu.om/med-Lib/MED_CD/E_CDs/A%20Practical%20Guide%20to%20Contemporary%20Pharmacy%20Practice/pdf/pKa-table.pdf); www.chemspider.com; www.chemicalize.org

Pharmaceutical	MW	log K_{ow}	log $D_{pH\ 7.4}$	pKa	charge @ pH 7
Acetyl sulphadiazine	292.3	0.4	-0.7	**6.1**	**-1**
alfa-hydroxy metoprolol					
Aminophenazone (aminopyrine)	231.1	1.0	0.8	**5**	**0**
Bezafibrate	361.8	4.3	0.7	**3.4**	**-1**
bisoprolol	325.4	1.9	0.1	**9.67**	**1**
				14.09	
caffeine	194.2	-0.1	0.3	**-0.92**	**0**
Carbamazepine	236.1	2.5	2.7	-	**0**
Carbamazepine-10,11-epoxide	252.3	0.95	1.3	**3.65**	**0**
				5.13	
clindamycin	425.0	2.2	1.1	**12.16**	**0**
cyclophosphamide	260	0.63	0.2	**0, 12.8**	**0**
Diatrizoic acid	614	1.37	-2.7	**2.17**	**-1**
Diclofenac	295.0	4.5	1.0	**4.2**	**-1**
erythromycin	733	3.06	2.08		**0**
Furosemide	330.7	2.0	-0.8	**4.25**	**-1**
Gemfibrozil	250.2	4.8	1.8	**4.5**	**-1**
guanylurea	102.1	-3.6	-1.8		
hydroxy ibuprofen	223.3	2.3	-0.5	**4.63**	**-1**
Ketoprofen	254.3	3.1	-0.3	**4.3**	**-1**
lincomycin	406.5	0.6	-0.9	**12.37**	**1**
				13.56	
				14.54	
				15.11	
Metformin	129.1	-1.4	-3.8	**12.3**	**1**
metronidazool	171.2	-0.02	0.1	**2.57**	**0**
Metoprolol	267.2	1.9	-0.1	**9.5**	**1**
N-4-acetyl-sulphamethoxazole	295.3	1.2	0.4	**5.88**	**-1**

Naproxen	230.1	3.2	0.5	**4.2**	**-1**
Niacin (vitamine B3, nicotinic acid)	123.1	0.4	-2.9	**2.8, 4.2**	**-1**
O-desmethyl-metoprolol	253	1.28	-0.8	**9.7**	**1**
o-desmethyltramadol					
oxcarbamazepine	252.3	1.1	1.9	**12.92**	**0**
				15.96	
pentoxifylline	278.3	0.3	0.5	**19.64**	**0**
Phenazone	188.1	0.4	0.3	**1.4**	**0**
Propranolol	259.3	3.5	1.3	**9.6**	**1**
propyphenazone	230	1.94	1.74	**-0.24**	**0**
Salbutamol	239.3	0.6	-1.9	**9.3**	**1**
Sotalol	272.1	0.2	-1.6	**9**	**1**
sulfachloropyridazine	284.7	0.3	-0.8	**2.02**	**0**
				6.60	
Sulfadiazine	250.1	-0.1	-0.7	**2.0, 7.0**	**-0.5**
Sulfamethoxazole	253.1	0.9	-0.2	**1.8, 5.6**	**-1**
Terbutalin	225.3	0.9	-1.6	**9.76**	**+1**
Tramadol	263.4	2.5	0.5	**9.23**	**1**
				13.8	
Trimethoprim	290.1	0.9	0.6	**7.2**	**0.5**
venlafaxine	277.4	3.3	1.4	**8.91**	**1**
				14.42	
2-hydroxy-carbamazepine				**9.3**	
3-hydroxy-carbamazepine				**9.46**	
4-formylaminoantipyrine					
10,11-trans-diol-carbamazepine					

Appendix VI

Experimental laboratory data.

Table 12-3: Analytical results obtained for laboratory experiments

Description of sample	carbamazepine	o-desmethyl metoprolol	alfa-hydroxy metoprolol	Dimethyl-aminophenazon	AMPH	hydroxy ibuprofen	norfluoxetine
untreated Effluent	0.871	0.007	0.137	< 0.01	< 0.01	0.481	< 0.50
Effluent + IEX	0.101	0.007	0.119	< 0.01	< 0.01	< 0.50	< 0.50
Effluent + dosed pharmas	1.93	0.007	0.132	< 0.01	< 0.01	< 0.50	< 0.50
Effluent + dosed pharmas LP 10 mg H_2O_2/l 0 mJ/cm^2	0.815	0.042	0.200	< 0.01	< 0.01	0.478	< 0.50
Effluent + dosed pharmas LP 10 mg H_2O_2/l 300 mJ/cm^2	0.736	0.057	0.171	< 0.01	< 0.01	< 0.50	< 0.50
Effluent + dosed pharmas LP 10 mg H_2O_2/l 600 mJ/cm^2	0.626	0.065	0.136	< 0.01	< 0.01	< 0.50	< 0.50
Effluent + dosed pharmas +IEX	1.04	0.007	0.115	< 0.01	< 0.01	< 0.50	< 0.50
Effluent + dosed pharmas +IEX LP 10 mg H_2O_2/l 0 mJ/cm^2	0.244	0.031	0.139	< 0.01	< 0.01	< 0.50	< 0.50
Effluent + dosed pharmas +IEX LP 10 mg H_2O_2/l 300 mJ/cm^2	0.081	0.038	0.060	< 0.01	< 0.01	< 0.50	< 0.50
Effluent + dosed pharmas	0.041	0.029	0.030	< 0.01	< 0.01	< 0.50	< 0.50

+IEX							
LP 10 mg H_2O_2/l 600 mJ/cm^2							
Effluent + pharmas	0.300	< 0.01	0.013	< 0.01	< 0.01	< 0.50	< 0.50
30 mg AC/L							
Effluent + pharmas	0.244	< 0.01	0.014	< 0.01	< 0.01	< 0.50	< 0.50
60 mg AC/L							
Effluent + pharmas	0.053	< 0.01	< 0.01	< 0.01	< 0.01	< 0.50	< 0.50
120 mg AC/L							
Effluent + pharmas	0.006	< 0.01	< 0.01	< 0.01	< 0.01	< 0.50	< 0.50
250 mg AC/L							
Effluent + pharmas	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.50	< 0.50
500 mg AC/L							
Effluent + pharmas	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.50	< 0.50
1000 mg AC/L							
Effluent + pharmas + IEX	0.053	< 0.01	0.018	< 0.01	< 0.01	< 0.50	< 0.50
30 mg AC/L							
Effluent + pharmas + IEX	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.50	< 0.50
60 mg AC/L							
Effluent + pharmas + IEX	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.50	< 0.50
120 mg AC/L							
Effluent + pharmas + IEX	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.50	< 0.50
250 mg AC/L							
Effluent + pharmas + IEX	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.50	< 0.50
500 mg AC/L							
Effluent + pharmas + IEX	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.50	< 0.50
1000 mg AC/L							
Effluent + pharmas	1.64	< 0.01	0.078	< 0.01	< 0.01	< 0.50	< 0.50
0 mg O_3/L, 36 mg H_2O_2/L							
Effluent + pharmas	< 0.01	0.008	< 0.01	< 0.01	< 0.01	< 0.50	< 0.50
12.5 mg O_3/L, 36 mg H_2O_2/L							
Effluent + pharmas	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.50	< 0.50

31.2 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.50	< 0.50
62.4 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas + IEX	0.935	< 0.01	0.069	< 0.01	< 0.01	< 0.50	< 0.50
0 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas + IEX	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.50	< 0.50
12.5 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas + IEX	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.50	< 0.50
31.2 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas + IEX	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.50	< 0.50
62.4 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas O_3/biofiltration (too short period)	0.953	< 0.01	< 0.01	< 0.01	< 0.01	< 0.50	< 0.50
0 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas O_3/biofiltration (too short period)	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.50	< 0.50
12.5 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas O_3/biofiltration (too short period)	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.50	< 0.50
31.2 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas O_3/biofiltration (too short period)	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.50	< 0.50
62.4 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas O_3/biofiltration (too short period)	0.963	< 0.01	< 0.01	< 0.01	< 0.01	< 0.50	< 0.50

0 mg O_3/L, UV 120-150 mJ/cm^2							
Effluent + pharmas	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.50	< 0.50
O_3/biofiltration (too short period)							
12.5 mg O_3/L, UV 120-150 mJ/cm^2							
Effluent + pharmas	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.50	< 0.50
O_3/biofiltration (too short period)							
31.2 mg O_3/L, UV 120-150 mJ/cm^2							
Effluent + pharmas	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.50	< 0.50
O_3/biofiltration (too short period)							
62.4 mg O_3/L, UV 120-150 mJ/cm^2							
Effluent + pharmas	0.720	< 0.01	< 0.01	< 0.01	< 0.01	< 0.50	< 0.50
O_3/biofiltration							
0 mg O_3/L, UV 120-150 mJ/cm^2							
Effluent + pharmas	0.253	< 0.01	< 0.01	< 0.01	< 0.01	< 0.50	< 0.50
O_3/biofiltration							
12.5 mg O_3/L, UV 120-150 mJ/cm^2							
Effluent + pharmas	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.50	< 0.50
O_3/biofiltration							
31.2 mg O_3/L, UV 120-150 mJ/cm^2							
Effluent + pharmas	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.50	< 0.50

O_3/biofiltration 62.4 mg O_3/L, UV 120-150 mJ/cm^2							
	anhydro erythromycine A	clofibrinezuur	Oxcarbamaze-pine	carbamazepine-10,11-epoxide	10,11-trans-diol-carbamaze-pine (10,11-dihydro-10,11-dihydroxycarbamazepine)	3-hydroxy carbama-zepine	2-hydroxy carbamaze-pine
untreated Effluent	< 0.05	< 0.01	0.051	0.165	3.25	0.272	0.182
Effluent + IEX	< 0.05	< 0.01	0.072	0.072	2.86	< 0.01	< 0.01
Effluent + dosed pharmas	< 0.05	< 0.01	< 0.01	0.191	3.48	0.087	0.181
Effluent + dosed pharmas LP 10 mg H_2O_2/l 0 mJ/cm^2	< 0.05	< 0.01	< 0.01	1.24	2.54	0.010	0.017
Effluent + dosed pharmas LP 10 mg H_2O_2/l 300 mJ/cm^2	< 0.05	< 0.01	< 0.01	0.867	2.02	0.008	0.017
Effluent + dosed pharmas LP 10 mg H_2O_2/l 600 mJ/cm^2	< 0.05	< 0.01	< 0.01	0.679	1.71	0.008	0.017
Effluent + dosed pharmas +IEX	< 0.05	< 0.01	0.086	0.069	2.59	< 0.01	< 0.01
Effluent + dosed pharmas +IEX LP 10 mg H_2O_2/l 0 mJ/cm^2	< 0.05	< 0.01	0.009	0.694	1.15	< 0.01	< 0.01
Effluent + dosed pharmas +IEX LP 10 mg H_2O_2/l 300 mJ/cm^2	< 0.05	< 0.01	< 0.01	0.247	0.503	< 0.01	< 0.01
Effluent + dosed pharmas +IEX LP 10 mg H_2O_2/l 600 mJ/cm^2	< 0.05	< 0.01	< 0.01	0.099	0.273	< 0.01	< 0.01
Effluent + pharmas	< 0.05	< 0.01	0.053	0.044	1.16	0.036	0.025

30 mg AC/L Effluent + pharmas	< 0.05	< 0.01	0.020	0.032	0.841	0.036	0.028
60 mg AC/L Effluent + pharmas	< 0.05	< 0.01	< 0.01	0.011	0.264	0.006	0.005
120 mg AC/L Effluent + pharmas	< 0.05	< 0.01	< 0.01	< 0.01	0.038	< 0.01	< 0.01
250 mg AC/L Effluent + pharmas	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
500 mg AC/L Effluent + pharmas	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
1000 mg AC/L Effluent + pharmas + IEX	< 0.05	< 0.01	< 0.01	< 0.01	0.387	< 0.01	< 0.01
30 mg AC/L Effluent + pharmas + IEX	< 0.05	< 0.01	< 0.01	< 0.01	0.039	< 0.01	< 0.01
60 mg AC/L Effluent + pharmas + IEX	< 0.05	< 0.01	< 0.01	< 0.01	0.007	< 0.01	< 0.01
120 mg AC/L Effluent + pharmas + IEX	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
250 mg AC/L Effluent + pharmas + IEX	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
500 mg AC/L Effluent + pharmas + IEX	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
1000 mg AC/L Effluent + pharmas	< 0.05	< 0.01	0.235	0.142	2.87	0.228	0.155
0 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas	< 0.05	< 0.01	0.010	< 0.01	0.087	< 0.01	< 0.01
12.5 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
31.2 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
62.4 mg O_3/L, 36 mg H_2O_2/L							

Effluent + pharmas + IEX 0 mg O_3/L, 36 mg H_2O_2/L	< 0.05	< 0.01	0.147	0.049	2.33	< 0.01	< 0.01
Effluent + pharmas + IEX 12.5 mg O_3/L, 36 mg H_2O_2/L	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Effluent + pharmas + IEX 31.2 mg O_3/L, 36 mg H_2O_2/L	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Effluent + pharmas + IEX 62.4 mg O_3/L, 36 mg H_2O_2/L	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Effluent + pharmas O_3/biofiltration (too short period) 0 mg O_3/L, 36 mg H_2O_2/L	< 0.05	< 0.01	0.010	< 0.01	0.180	< 0.01	< 0.01
Effluent + pharmas O_3/biofiltration (too short period) 12.5 mg O_3/L, 36 mg H_2O_2/L	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Effluent + pharmas O_3/biofiltration (too short period) 31.2 mg O_3/L, 36 mg H_2O_2/L	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Effluent + pharmas O_3/biofiltration (too short period) 62.4 mg O_3/L, 36 mg H_2O_2/L	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Effluent + pharmas O_3/biofiltration (too short period) 0 mg O_3/L, UV 120-150 mJ/cm^2	< 0.05	< 0.01	< 0.01	0.009	0.171	< 0.01	< 0.01
Effluent + pharmas	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01

O_3/biofiltration (too short period) 12.5 mg O_3/L, UV 120-150 mJ/cm^2 Effluent + pharmas	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
O_3/biofiltration (too short period) 31.2 mg O_3/L, UV 120-150 mJ/cm^2 Effluent + pharmas	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
O_3/biofiltration (too short period) 62.4 mg O_3/L, UV 120-150 mJ/cm^2 Effluent + pharmas	< 0.05	< 0.01	< 0.01	0.005	0.119	< 0.01	< 0.01
O_3/biofiltration 0 mg O_3/L, UV 120-150 mJ/cm^2 Effluent + pharmas	< 0.05	< 0.01	0.007	< 0.01	0.099	< 0.01	< 0.01
O_3/biofiltration 12.5 mg O_3/L, UV 120-150 mJ/cm^2 Effluent + pharmas	< 0.05	< 0.01	< 0.01	< 0.01	0.026	< 0.01	< 0.01
O_3/biofiltration 31.2 mg O_3/L, UV 120-150 mJ/cm^2 Effluent + pharmas	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
O_3/biofiltration 62.4 mg O_3/L, UV 120-150 mJ/cm^2							

	salicylzuur	o-desmethyltramadol	N4-acetyl sulfamethoxazole (acetyl-sulfame-thoxazole	acetyl sulfadiazine	4-formylamino-antipyrine (N-formyl-4-aminoanti-pyrine)	4-acetami-nophen sulfaat	o-desmethyl naproxen
untreated Effluent	< 5.0	0.439	0.027	0.015	0.026	< 0.03	< 0.05
Effluent + IEX	< 5.0	0.400	< 0.01	< 0.01	0.023	< 0.03	< 0.05
Effluent + dosed pharmas	< 5.0	0.428	0.026	0.015	0.029	< 0.03	< 0.05
Effluent + dosed pharmas LP 10 mg H_2O_2/l 0 mJ/cm^2	< 5.0	0.043	0.030	0.019	< 0.01	< 0.03	< 0.05
Effluent + dosed pharmas LP 10 mg H_2O_2/l 300 mJ/cm^2	< 5.0	0.037	0.021	0.008	< 0.01	< 0.03	< 0.05
Effluent + dosed pharmas LP 10 mg H_2O_2/l 600 mJ/cm^2	< 5.0	0.039	0.018	0.005	< 0.01	< 0.03	< 0.05
Effluent + dosed pharmas +IEX	< 5.0	0.394	< 0.01	< 0.01	0.025	< 0.03	< 0.05
Effluent + dosed pharmas +IEX LP 10 mg H_2O_2/l 0 mJ/cm^2	< 5.0	0.085	< 0.01	< 0.01	< 0.01	< 0.03	< 0.05
Effluent + dosed pharmas +IEX LP 10 mg H_2O_2/l 300 mJ/cm^2	< 5.0	0.041	< 0.01	< 0.01	< 0.01	< 0.03	< 0.05
Effluent + dosed pharmas +IEX LP 10 mg H_2O_2/l 600 mJ/cm^2	< 5.0	0.029	< 0.01	< 0.01	< 0.01	< 0.03	< 0.05
Effluent + pharmas 30 mg AC/L	< 5.0	0.102	0.010	0.008	0.014	< 0.03	< 0.05
Effluent + pharmas 60 mg AC/L	< 5.0	0.062	< 0.01	< 0.01	0.008	< 0.03	< 0.05
Effluent + pharmas 120 mg AC/L	< 5.0	0.012	< 0.01	< 0.01	< 0.01	< 0.03	< 0.05
Effluent + pharmas	< 5.0	< 0.01	< 0.01	< 0.01	< 0.01	< 0.03	< 0.05

250 mg AC/L Effluent + pharmas	< 5.0	< 0.01	< 0.01	< 0.01	< 0.01	< 0.03	< 0.05
500 mg AC/L Effluent + pharmas	< 5.0	< 0.01	< 0.01	< 0.01	< 0.01	< 0.03	< 0.05
1000 mg AC/L Effluent + pharmas + IEX	< 5.0	0.098	< 0.01	< 0.01	< 0.01	< 0.03	< 0.05
30 mg AC/L Effluent + pharmas + IEX	< 5.0	< 0.01	< 0.01	< 0.01	< 0.01	< 0.03	< 0.05
60 mg AC/L Effluent + pharmas + IEX	< 5.0	< 0.01	< 0.01	< 0.01	< 0.01	< 0.03	< 0.05
120 mg AC/L Effluent + pharmas + IEX	< 5.0	< 0.01	< 0.01	< 0.01	< 0.01	< 0.03	< 0.05
250 mg AC/L Effluent + pharmas + IEX	< 5.0	< 0.01	< 0.01	< 0.01	< 0.01	< 0.03	< 0.05
500 mg AC/L Effluent + pharmas + IEX	< 5.0	< 0.01	< 0.01	< 0.01	< 0.01	< 0.03	< 0.05
1000 mg AC/L Effluent + pharmas + IEX	< 5.0	0.369	0.031	0.017	< 0.01	< 0.03	0.070
250 mg AC/L Effluent + pharmas + IEX	< 5.0	< 0.01	< 0.01	< 0.01	< 0.01	< 0.03	< 0.05
500 mg AC/L Effluent + pharmas + IEX	< 5.0	< 0.01	< 0.01	< 0.01	< 0.01	< 0.03	< 0.05
1000 mg AC/L Effluent + pharmas	< 5.0	< 0.01	< 0.01	< 0.01	< 0.01	< 0.03	< 0.05
0 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas	< 5.0	0.337	< 0.01	< 0.01	0.028	< 0.03	< 0.05
12.5 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas	< 5.0	< 0.01	< 0.01	< 0.01	< 0.01	< 0.03	< 0.05
31.2 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas + IEX	< 5.0	< 0.01	< 0.01	< 0.01	< 0.01	< 0.03	< 0.05
31.2 mg O_3/L, 36 mg H_2O_2/L							

Effluent + pharmas + IEX 62.4 mg O_3/L, 36 mg H_2O_2/L	< 5.0	< 0.01	< 0.01	< 0.01	< 0.01	< 0.03	< 0.05
Effluent + pharmas O_3/biofiltration (too short period) 0 mg O_3/L, 36 mg H_2O_2/L	< 5.0	< 0.01	< 0.01	< 0.01	< 0.01	< 0.03	< 0.05
Effluent + pharmas O_3/biofiltration (too short period) 12.5 mg O_3/L, 36 mg H_2O_2/L	< 5.0	< 0.01	< 0.01	< 0.01	< 0.01	< 0.03	< 0.05
Effluent + pharmas O_3/biofiltration (too short period) 31.2 mg O_3/L, 36 mg H_2O_2/L	< 5.0	< 0.01	< 0.01	< 0.01	< 0.01	< 0.03	< 0.05
Effluent + pharmas O_3/biofiltration (too short period) 62.4 mg O_3/L, 36 mg H_2O_2/L	< 5.0	< 0.01	< 0.01	< 0.01	< 0.01	< 0.03	< 0.05
Effluent + pharmas O_3/biofiltration (too short period) 0 mg O_3/L, UV 120-150 mJ/cm^2	< 5.0	< 0.01	< 0.01	< 0.01	< 0.01	< 0.03	< 0.05
Effluent + pharmas O_3/biofiltration (too short period) 12.5 mg O_3/L, UV 120-150 mJ/cm^2	< 5.0	< 0.01	< 0.01	< 0.01	< 0.01	< 0.03	< 0.05
Effluent + pharmas O_3/biofiltration (too short	< 5.0	< 0.01	< 0.01	< 0.01	< 0.01	< 0.03	< 0.05

period)							
31.2 mg O_3/L, UV 120-150 mJ/cm^2							
Effluent + pharmas	< 5.0	< 0.01	< 0.01	< 0.01	< 0.01	< 0.03	< 0.05
O_3/biofiltration (too short period)							
62.4 mg O_3/L, UV 120-150 mJ/cm^2							
Effluent + pharmas	< 5.0	< 0.01	< 0.01	< 0.01	< 0.01	< 0.03	< 0.05
O_3/biofiltration							
0 mg O_3/L, UV 120-150 mJ/cm^2							
Effluent + pharmas	< 5.0	< 0.01	< 0.01	< 0.01	< 0.01	< 0.03	< 0.05
O_3/biofiltration							
12.5 mg O_3/L, UV 120-150 mJ/cm^2							
Effluent + pharmas	< 5.0	< 0.01	< 0.01	< 0.01	< 0.01	< 0.03	< 0.05
O_3/biofiltration							
31.2 mg O_3/L, UV 120-150 mJ/cm^2							
Effluent + pharmas	< 5.0	< 0.01	< 0.01	< 0.01	< 0.01	< 0.03	< 0.05
O_3/biofiltration							
62.4 mg O_3/L, UV 120-150 mJ/cm^2							

	cortisone	cortisol	clindamycin	clenbuterol	bezafibrate	atenolol	guanylureum
untreated Effluent	< 0.03	< 0.03	0.327	< 0.01	0.127	0.396	71.9
Effluent + IEX	< 0.03	< 0.03	0.258	< 0.01	< 0.01	0.371	76.3
Effluent + dosed pharmas	< 0.03	< 0.03	0.291	< 0.01	1.06	1.36	77.0
Effluent + dosed pharmas LP 10 mg H_2O_2/l 0 mJ/cm^2	< 0.03	< 0.03	0.291	< 0.01	0.916	1.19	80.1

Effluent + dosed pharmas LP 10 mg H_2O_2/l 300 mJ/cm^2	< 0.03	< 0.03	< 0.01	< 0.01	0.767	1.03	80.5
Effluent + dosed pharmas LP 10 mg H_2O_2/l 600 mJ/cm^2	< 0.03	< 0.03	< 0.01	< 0.01	0.621	0.913	81.4
Effluent + dosed pharmas +IEX	< 0.03	< 0.03	0.244	< 0.01	0.751	1.30	79.6
Effluent + dosed pharmas +IEX LP 10 mg H_2O_2/l 0 mJ/cm^2	< 0.03	< 0.03	< 0.01	< 0.01	0.518	0.642	79.3
Effluent + dosed pharmas +IEX LP 10 mg H_2O_2/l 300 mJ/cm^2	< 0.03	< 0.03	< 0.01	< 0.01	0.216	0.308	79.5
Effluent + dosed pharmas +IEX LP 10 mg H_2O_2/l 600 mJ/cm^2	< 0.03	< 0.03	< 0.01	< 0.01	0.105	0.190	80.1
Effluent + pharmas 30 mg AC/L	< 0.03	< 0.03	0.082	< 0.01	0.131	0.232	50.5
Effluent + pharmas 60 mg AC/L	< 0.03	< 0.03	0.062	< 0.01	0.115	0.186	27.9
Effluent + pharmas 120 mg AC/L	< 0.03	< 0.03	0.016	< 0.01	0.024	0.048	15.3
Effluent + pharmas 250 mg AC/L	< 0.03	< 0.03	< 0.01	< 0.01	< 0.01	0.008	5.72
Effluent + pharmas 500 mg AC/L	< 0.03	< 0.03	< 0.01	< 0.01	< 0.01	< 0.01	1.31
Effluent + pharmas 1000 mg AC/L	< 0.03	< 0.03	< 0.01	< 0.01	< 0.01	< 0.01	0.745
Effluent + pharmas + IEX 30 mg AC/L	< 0.03	< 0.03	0.058	< 0.01	0.026	0.277	73.0
Effluent + pharmas + IEX 60 mg AC/L	< 0.03	< 0.03	< 0.01	< 0.01	< 0.01	0.026	60.0
Effluent + pharmas + IEX	< 0.03	< 0.03	< 0.01	< 0.01	< 0.01	0.006	49.3

120 mg AC/L Effluent + pharmas + IEX	< 0.03	< 0.03	< 0.01	< 0.01	< 0.01	< 0.01	36.5
250 mg AC/L Effluent + pharmas + IEX	< 0.03	< 0.03	< 0.01	< 0.01	< 0.01	< 0.01	18.0
500 mg AC/L Effluent + pharmas + IEX	< 0.03	< 0.03	< 0.01	< 0.01	< 0.01	< 0.01	7.32
1000 mg AC/L Effluent + pharmas	< 0.03	< 0.03	0.259	< 0.01	0.789	1.24	86.3
0 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas	< 0.03	< 0.03	< 0.01	< 0.01	0.011	0.037	81.9
12.5 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas	< 0.03	< 0.03	< 0.01	< 0.01	< 0.01	< 0.01	78.1
31.2 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas	< 0.03	< 0.03	< 0.01	< 0.01	< 0.01	< 0.01	82.0
62.4 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas + IEX	< 0.03	< 0.03	0.208	< 0.01	0.604	1.13	74.2
0 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas + IEX	< 0.03	< 0.03	< 0.01	< 0.01	< 0.01	< 0.01	77.4
12.5 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas + IEX	< 0.03	< 0.03	< 0.01	< 0.01	< 0.01	< 0.01	80.2
31.2 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas + IEX	< 0.03	< 0.03	< 0.01	< 0.01	< 0.01	< 0.01	82.1
62.4 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas	< 0.03	< 0.03	< 0.01	< 0.01	0.704	0.931	23.7
O_3/biofiltration (too short period) 0 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas	< 0.03	< 0.03	< 0.01	< 0.01	< 0.01	< 0.01	23.1
O_3/biofiltration (too short period)							

12.5 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas O_3/biofiltration (too short period)	< 0.03	< 0.03	< 0.01	< 0.01	< 0.01	< 0.01	23.5
31.2 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas O_3/biofiltration (too short period)	< 0.03	< 0.03	< 0.01	< 0.01	< 0.01	< 0.01	22.9
62.4 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas O_3/biofiltration (too short period)	< 0.03	< 0.03	< 0.01	< 0.01	0.698	0.975	20.3
0 mg O_3/L, UV 120-150 mJ/cm^2 Effluent + pharmas O_3/biofiltration (too short period)	< 0.03	< 0.03	< 0.01	< 0.01	< 0.01	< 0.01	19.8
12.5 mg O_3/L, UV 120-150 mJ/cm^2 Effluent + pharmas O_3/biofiltration (too short period)	< 0.03	< 0.03	< 0.01	< 0.01	< 0.01	< 0.01	19.9
31.2 mg O_3/L, UV 120-150 mJ/cm^2 Effluent + pharmas O_3/biofiltration (too short period)	< 0.03	< 0.03	< 0.01	< 0.01	< 0.01	< 0.01	18.4
62.4 mg O_3/L, UV 120-150 mJ/cm^2 Effluent + pharmas	< 0.03	< 0.03	< 0.01	< 0.01	0.568	0.689	12.8

O_3/biofiltration 0 mg O_3/L, UV 120-150 mJ/cm^2 Effluent + pharmas	< 0.03	< 0.03	< 0.01	< 0.01	0.508	0.631	13.2
O_3/biofiltration 12.5 mg O_3/L, UV 120-150 mJ/cm^2 Effluent + pharmas	< 0.03	< 0.03	< 0.01	< 0.01	< 0.01	0.029	12.8
O_3/biofiltration 31.2 mg O_3/L, UV 120-150 mJ/cm^2 Effluent + pharmas	< 0.03	< 0.03	< 0.01	< 0.01	< 0.01	< 0.01	12.3
O_3/biofiltration 62.4 mg O_3/L, UV 120-150 mJ/cm^2							

	gemfibrozil	furosemide	fluoxetine	erythromycin A	diclofenac	diatrizoic acid	Cyclophos-phamide
untreated Effluent	0.427	0.508	< 0.01	0.087	0.362	0.302	< 0.01
Effluent + IEX	< 0.01	< 0.01	< 0.01	0.051	< 0.01	< 0.01	< 0.01
Effluent + dosed pharmas	1.53	0.335	< 0.01	0.092	1.44	1.17	0.793
Effluent + dosed pharmas LP 10 mg H_2O_2/l 0 mJ/cm^2	1.11	< 0.01	< 0.01	0.072	0.062	1.09	0.529
Effluent + dosed pharmas LP 10 mg H_2O_2/l 300 mJ/cm^2	0.950	< 0.01	< 0.01	0.067	0.006	0.409	0.532
Effluent + dosed pharmas LP 10 mg H_2O_2/l 600 mJ/cm^2	0.761	< 0.01	< 0.01	0.065	< 0.01	0.130	0.505
Effluent + dosed pharmas +IEX	0.994	< 0.01	< 0.01	0.052	0.841	0.826	0.625
Effluent + dosed pharmas +IEX LP 10 mg H_2O_2/l 0 mJ/cm^2	0.611	< 0.01	< 0.01	< 0.03	0.110	0.711	0.189

Effluent + dosed pharmas +IEX	0.229	< 0.01	< 0.01	< 0.03	< 0.01	0.234	0.143
LP 10 mg H_2O_2/l 300 mJ/cm^2 Effluent + dosed pharmas +IEX	0.103	< 0.01	< 0.01	< 0.03	< 0.01	0.073	0.141
LP 10 mg H_2O_2/l 600 mJ/cm^2 Effluent + pharmas 30 mg AC/L	0.301	< 0.01	< 0.01	< 0.03	0.409	1.00	0.222
Effluent + pharmas 60 mg AC/L	0.254	< 0.01	< 0.01	< 0.03	0.280	0.756	0.165
Effluent + pharmas 120 mg AC/L	0.061	< 0.01	< 0.01	< 0.03	0.066	0.491	0.063
Effluent + pharmas 250 mg AC/L	0.005	< 0.01	< 0.01	< 0.03	0.005	0.180	0.014
Effluent + pharmas 500 mg AC/L	< 0.01	< 0.01	< 0.01	< 0.03	< 0.01	< 0.01	< 0.01
Effluent + pharmas 1000 mg AC/L	< 0.01	< 0.01	< 0.01	< 0.03	< 0.01	< 0.01	< 0.01
Effluent + pharmas + IEX 30 mg AC/L	0.016	< 0.01	< 0.01	< 0.03	0.011	0.274	0.083
Effluent + pharmas + IEX 60 mg AC/L	< 0.01	< 0.01	< 0.01	< 0.03	< 0.01	0.039	0.012
Effluent + pharmas + IEX 120 mg AC/L	< 0.01	< 0.01	< 0.01	< 0.03	< 0.01	< 0.01	< 0.01
Effluent + pharmas + IEX 250 mg AC/L	< 0.01	< 0.01	< 0.01	< 0.03	< 0.01	< 0.01	< 0.01
Effluent + pharmas + IEX 500 mg AC/L	< 0.01	< 0.01	< 0.01	< 0.03	< 0.01	< 0.01	< 0.01
Effluent + pharmas + IEX 1000 mg AC/L	< 0.01	< 0.01	< 0.01	< 0.03	< 0.01	< 0.01	< 0.01
Effluent + pharmas 0 mg O_3/L, 36 mg H_2O_2/L	0.724	0.422	< 0.01	< 0.03	1.11	1.09	0.598

Effluent + pharmas 12.5 mg O_3/L, 36 mg H_2O_2/L	< 0.01	< 0.01	< 0.01	< 0.03	< 0.01	0.801	0.119
Effluent + pharmas 31.2 mg O_3/L, 36 mg H_2O_2/L	< 0.01	< 0.01	< 0.01	< 0.03	< 0.01	0.205	< 0.01
Effluent + pharmas 62.4 mg O_3/L, 36 mg H_2O_2/L	< 0.01	< 0.01	< 0.01	< 0.03	< 0.01	< 0.01	< 0.01
Effluent + pharmas + IEX 0 mg O_3/L, 36 mg H_2O_2/L	0.828	< 0.01	< 0.01	< 0.03	0.219	0.769	0.498
Effluent + pharmas + IEX 12.5 mg O_3/L, 36 mg H_2O_2/L	< 0.01	< 0.01	< 0.01	< 0.03	< 0.01	0.208	0.009
Effluent + pharmas + IEX 31.2 mg O_3/L, 36 mg H_2O_2/L	< 0.01	< 0.01	< 0.01	< 0.03	< 0.01	< 0.01	< 0.01
Effluent + pharmas + IEX 62.4 mg O_3/L, 36 mg H_2O_2/L	< 0.01	< 0.01	< 0.01	< 0.03	< 0.01	< 0.01	< 0.01
Effluent + pharmas O_3/biofiltration (too short period) 0 mg O_3/L, 36 mg H_2O_2/L	1.05	< 0.01	< 0.01	< 0.03	0.886	0.925	0.660
Effluent + pharmas O_3/biofiltration (too short period) 12.5 mg O_3/L, 36 mg H_2O_2/L	< 0.01	< 0.01	< 0.01	< 0.03	< 0.01	0.209	< 0.01
Effluent + pharmas O_3/biofiltration (too short period) 31.2 mg O_3/L, 36 mg H_2O_2/L	< 0.01	< 0.01	< 0.01	< 0.03	< 0.01	< 0.01	< 0.01
Effluent + pharmas O_3/biofiltration (too short period) 62.4 mg O_3/L, 36 mg H_2O_2/L	< 0.01	< 0.01	< 0.01	< 0.03	< 0.01	< 0.01	< 0.01

Effluent + pharmas O_3/biofiltration (too short period) 0 mg O_3/L, UV 120-150 mJ/cm^2	1.04	< 0.01	< 0.01	< 0.03	0.904	0.908	0.647
Effluent + pharmas O_3/biofiltration (too short period) 12.5 mg O_3/L, UV 120-150 mJ/cm^2	< 0.01	< 0.01	< 0.01	< 0.03	< 0.01	0.155	0.011
Effluent + pharmas O_3/biofiltration (too short period) 31.2 mg O_3/L, UV 120-150 mJ/cm^2	< 0.01	< 0.01	< 0.01	< 0.03	< 0.01	< 0.01	< 0.01
Effluent + pharmas O_3/biofiltration (too short period) 62.4 mg O_3/L, UV 120-150 mJ/cm^2	< 0.01	< 0.01	< 0.01	< 0.03	< 0.01	< 0.01	< 0.01
Effluent + pharmas O_3/biofiltration 0 mg O_3/L, UV 120-150 mJ/cm^2	0.779	< 0.01	< 0.01	< 0.03	0.417	0.721	0.463
Effluent + pharmas O_3/biofiltration 12.5 mg O_3/L, UV 120-150 mJ/cm^2	0.614	< 0.01	< 0.01	< 0.03	0.032	0.285	0.460
Effluent + pharmas O_3/biofiltration	< 0.01	< 0.01	< 0.01	< 0.03	< 0.01	0.123	0.272

31.2 mg O_3/L, UV 120-150 mJ/cm^2 Effluent + pharmas O_3/biofiltration 62.4 mg O_3/L, UV 120-150 mJ/cm^2	< 0.01	< 0.01	< 0.01	< 0.03	< 0.01	< 0.01	< 0.01
	terbutaline	sulfaquinoxalin	Sulfame-thoxazole	sulfadiazine	Sulfachloro-pyridazine	sotalol	salbutamol
untreated Effluent	< 0.01	< 0.01	0.071	0.187	0.006	1.08	0.008
Effluent + IEX	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.830	0.011
Effluent + dosed pharmas	< 0.01	< 0.01	0.410	0.167	0.005	1.90	< 0.01
Effluent + dosed pharmas LP 10 mg H_2O_2/l 0 mJ/cm^2	< 0.01	< 0.01	0.205	0.134	0.005	1.55	< 0.01
Effluent + dosed pharmas LP 10 mg H_2O_2/l 300 mJ/cm^2	< 0.01	< 0.01	0.106	0.117	< 0.01	0.973	< 0.01
Effluent + dosed pharmas LP 10 mg H_2O_2/l 600 mJ/cm^2	< 0.01	< 0.01	0.055	0.097	< 0.01	0.639	< 0.01
Effluent + dosed pharmas +IEX	< 0.01	< 0.01	0.594	< 0.01	< 0.01	1.39	< 0.01
Effluent + dosed pharmas +IEX LP 10 mg H_2O_2/l 0 mJ/cm^2	< 0.01	< 0.01	0.057	< 0.01	< 0.01	0.757	< 0.01
Effluent + dosed pharmas +IEX LP 10 mg H_2O_2/l 300 mJ/cm^2	< 0.01	< 0.01	0.013	< 0.01	< 0.01	0.330	< 0.01
Effluent + dosed pharmas +IEX LP 10 mg H_2O_2/l 600 mJ/cm^2	< 0.01	< 0.01	0.006	< 0.01	< 0.01	0.191	< 0.01
Effluent + pharmas 30 mg AC/L	< 0.01	< 0.01	0.294	0.140	0.005	0.346	< 0.01
Effluent + pharmas	< 0.01	< 0.01	0.151	0.093	< 0.01	0.247	< 0.01

60 mg AC/L Effluent + pharmas	< 0.01	< 0.01	0.037	0.028	< 0.01	0.057	< 0.01
120 mg AC/L Effluent + pharmas	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.008	< 0.01
250 mg AC/L Effluent + pharmas	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
500 mg AC/L Effluent + pharmas	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
1000 mg AC/L Effluent + pharmas + IEX	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.307	< 0.01
30 mg AC/L Effluent + pharmas + IEX	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.036	< 0.01
60 mg AC/L Effluent + pharmas + IEX	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.007	< 0.01
120 mg AC/L Effluent + pharmas + IEX	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
250 mg AC/L Effluent + pharmas + IEX	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
500 mg AC/L Effluent + pharmas + IEX	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
1000 mg AC/L Effluent + pharmas	< 0.01	< 0.01	0.877	0.365	0.012	1.57	< 0.01
0 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
12.5 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
31.2 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
62.4 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas + IEX	< 0.01	< 0.01	0.216	< 0.01	< 0.01	1.17	< 0.01
0 mg O_3/L, 36 mg H_2O_2/L							

Effluent + pharmas + IEX 12.5 mg O_3/L, 36 mg H_2O_2/L	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Effluent + pharmas + IEX 31.2 mg O_3/L, 36 mg H_2O_2/L	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Effluent + pharmas + IEX 62.4 mg O_3/L, 36 mg H_2O_2/L	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Effluent + pharmas O_3/biofiltration (too short period) 0 mg O_3/L, 36 mg H_2O_2/L	< 0.01	< 0.01	0.953	< 0.01	< 0.01	0.632	< 0.01
Effluent + pharmas O_3/biofiltration (too short period) 12.5 mg O_3/L, 36 mg H_2O_2/L	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Effluent + pharmas O_3/biofiltration (too short period) 31.2 mg O_3/L, 36 mg H_2O_2/L	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Effluent + pharmas O_3/biofiltration (too short period) 62.4 mg O_3/L, 36 mg H_2O_2/L	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Effluent + pharmas O_3/biofiltration (too short period) 0 mg O_3/L, UV 120-150 mJ/cm^2	< 0.01	< 0.01	0.984	< 0.01	< 0.01	0.645	< 0.01
Effluent + pharmas O_3/biofiltration (too short period)	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01

12.5 mg O_3/L, UV 120-150 mJ/cm^2							
Effluent + pharmas	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
O_3/biofiltration (too short period)							
31.2 mg O_3/L, UV 120-150 mJ/cm^2							
Effluent + pharmas	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
O_3/biofiltration (too short period)							
62.4 mg O_3/L, UV 120-150 mJ/cm^2							
Effluent + pharmas	< 0.01	< 0.01	0.700	< 0.01	< 0.01	0.450	< 0.01
O_3/biofiltration							
0 mg O_3/L, UV 120-150 mJ/cm^2							
Effluent + pharmas	< 0.01	< 0.01	0.060	< 0.01	< 0.01	0.214	< 0.01
O_3/biofiltration							
12.5 mg O_3/L, UV 120-150 mJ/cm^2							
Effluent + pharmas	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
O_3/biofiltration							
31.2 mg O_3/L, UV 120-150 mJ/cm^2							
Effluent + pharmas	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
O_3/biofiltration							
62.4 mg O_3/L, UV 120-150 mJ/cm^2							
	propranolol	prednisolone	pindolol	propyfenazon	fenazon	Pentoxi-fylline	paroxetine
untreated Effluent	0.116	< 0.05	< 0.01	0.008	< 0.01	< 0.01	< 0.05

Effluent + IEX	0.104	< 0.05	< 0.01	0.007	< 0.01	< 0.01	< 0.05
Effluent + dosed pharmas	1.17	< 0.05	< 0.01	0.009	1.01	0.820	< 0.05
Effluent + dosed pharmas LP 10 mg H_2O_2/l 0 mJ/cm²	0.462	< 0.05	< 0.01	< 0.01	0.032	0.571	< 0.05
Effluent + dosed pharmas LP 10 mg H_2O_2/l 300 mJ/cm²	0.375	< 0.05	< 0.01	< 0.01	0.018	0.523	< 0.05
Effluent + dosed pharmas LP 10 mg H_2O_2/l 600 mJ/cm²	0.269	< 0.05	< 0.01	< 0.01	0.008	0.488	< 0.05
Effluent + dosed pharmas +IEX	1.01	< 0.05	< 0.01	0.009	0.923	0.739	< 0.05
Effluent + dosed pharmas +IEX LP 10 mg H_2O_2/l 0 mJ/cm²	0.200	< 0.05	< 0.01	< 0.01	0.016	0.155	< 0.05
Effluent + dosed pharmas +IEX LP 10 mg H_2O_2/l 300 mJ/cm²	0.049	< 0.05	< 0.01	< 0.01	< 0.01	0.079	< 0.05
Effluent + dosed pharmas +IEX LP 10 mg H_2O_2/l 600 mJ/cm²	0.024	< 0.05	< 0.01	< 0.01	< 0.01	0.061	< 0.05
Effluent + pharmas 30 mg AC/L	0.023	< 0.05	< 0.01	< 0.01	0.364	0.116	< 0.05
Effluent + pharmas 60 mg AC/L	0.072	< 0.05	< 0.01	< 0.01	0.218	0.109	< 0.05
Effluent + pharmas 120 mg AC/L	0.013	< 0.05	< 0.01	< 0.01	0.062	0.022	< 0.05
Effluent + pharmas 250 mg AC/L	< 0.01	< 0.05	< 0.01	< 0.01	0.010	< 0.01	< 0.05
Effluent + pharmas 500 mg AC/L	< 0.01	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05
Effluent + pharmas 1000 mg AC/L	0.006	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05
Effluent + pharmas + IEX	0.066	< 0.05	< 0.01	< 0.01	0.109	0.036	< 0.05

30 mg AC/L Effluent + pharmas + IEX	< 0.01	< 0.05	< 0.01	< 0.01	0.008	< 0.01	< 0.05
60 mg AC/L Effluent + pharmas + IEX	0.007	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05
120 mg AC/L Effluent + pharmas + IEX	0.006	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05
250 mg AC/L Effluent + pharmas + IEX	0.010	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05
500 mg AC/L Effluent + pharmas + IEX	0.006	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05
1000 mg AC/L Effluent + pharmas	1.05	< 0.05	< 0.01	0.008	0.930	0.668	< 0.05
0 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas	0.008	< 0.05	< 0.01	< 0.01	< 0.01	0.008	< 0.05
12.5 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas	0.006	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05
31.2 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas	< 0.01	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05
62.4 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas + IEX	0.832	< 0.05	< 0.01	0.007	0.836	0.619	< 0.05
0 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas + IEX	0.007	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05
12.5 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas + IEX	< 0.01	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05
31.2 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas + IEX	< 0.01	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05
62.4 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas	1.26	< 0.05	< 0.01	< 0.01	0.983	0.785	< 0.05
O_3/biofiltration (too short period)							

0 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas O_3/biofiltration (too short period)	< 0.01	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05
12.5 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas O_3/biofiltration (too short period)	< 0.01	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05
31.2 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas O_3/biofiltration (too short period)	0.008	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05
62.4 mg O_3/L, 36 mg H_2O_2/L Effluent + pharmas O_3/biofiltration (too short period)	1.25	< 0.05	< 0.01	< 0.01	0.978	0.799	< 0.05
0 mg O_3/L, UV 120-150 mJ/cm^2 Effluent + pharmas O_3/biofiltration (too short period)	< 0.01	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05
12.5 mg O_3/L, UV 120-150 mJ/cm^2 Effluent + pharmas O_3/biofiltration (too short period)	< 0.01	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05
31.2 mg O_3/L, UV 120-150 mJ/cm^2 Effluent + pharmas O_3/biofiltration (too short	0.928	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05

period)							
62.4 mg O_3/L, UV 120-150 mJ/cm^2							
Effluent + pharmas O_3/biofiltration	0.572	< 0.05	< 0.01	< 0.01	0.726	0.582	< 0.05
0 mg O_3/L, UV 120-150 mJ/cm^2							
Effluent + pharmas O_3/biofiltration	0.010	< 0.05	< 0.01	< 0.01	0.285	0.555	< 0.05
12.5 mg O_3/L, UV 120-150 mJ/cm^2							
Effluent + pharmas O_3/biofiltration	< 0.01	< 0.05	< 0.01	< 0.01	< 0.01	0.005	< 0.05
31.2 mg O_3/L, UV 120-150 mJ/cm^2							
Effluent + pharmas O_3/biofiltration	< 0.01	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05
62.4 mg O_3/L, UV 120-150 mJ/cm^2							
	paracetamol	niacin	naproxen	metronidazole	ifosfamide	Keto-profen	lincomycin
untreated Effluent	< 0.01	0.608	0.182	0.006	< 0.01	0.018	0.011
Effluent + IEX	< 0.01	0.067	< 0.01	0.007	< 0.01	< 0.01	0.009
Effluent + dosed pharmas	< 0.01	0.122	0.173	0.993	< 0.01	1.12	< 0.01
Effluent + dosed pharmas LP 10 mg H_2O_2/l 0 mJ/cm^2	< 0.01	0.185	0.016	0.907	< 0.01	1.02	< 0.01
Effluent + dosed pharmas LP 10 mg H_2O_2/l 300 mJ/cm^2	< 0.01	0.249	0.014	0.836	< 0.01	< 0.01	< 0.01
Effluent + dosed pharmas LP 10 mg H_2O_2/l 600 mJ/cm^2	< 0.01	0.284	0.012	0.722	< 0.01	< 0.01	< 0.01
Effluent + dosed pharmas	< 0.01	0.049	< 0.01	0.874	< 0.01	0.661	0.008

+IEX							
Effluent + dosed pharmas +IEX	< 0.01	0.081	< 0.01	0.563	< 0.01	0.553	< 0.01
LP 10 mg H_2O_2/l 0 mJ/cm^2							
Effluent + dosed pharmas +IEX	< 0.01	0.111	< 0.01	0.349	< 0.01	< 0.01	< 0.01
LP 10 mg H_2O_2/l 300 mJ/cm^2							
Effluent + dosed pharmas +IEX	< 0.01	0.144	< 0.01	0.215	< 0.01	< 0.01	< 0.01
LP 10 mg H_2O_2/l 600 mJ/cm^2							
Effluent + pharmas 30 mg AC/L	< 0.01	0.045	0.044	0.291	< 0.01	0.284	< 0.01
Effluent + pharmas 60 mg AC/L	< 0.01	0.030	0.027	0.191	< 0.01	0.196	< 0.01
Effluent + pharmas 120 mg AC/L	< 0.01	0.023	< 0.01	0.050	< 0.01	0.046	< 0.01
Effluent + pharmas 250 mg AC/L	< 0.01	0.006	< 0.01	0.009	< 0.01	< 0.01	< 0.01
Effluent + pharmas 500 mg AC/L	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Effluent + pharmas 1000 mg AC/L	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Effluent + pharmas + IEX 30 mg AC/L	< 0.01	0.018	< 0.01	0.088	< 0.01	0.021	< 0.01
Effluent + pharmas + IEX 60 mg AC/L	< 0.01	0.502	< 0.01	0.010	< 0.01	< 0.01	< 0.01
Effluent + pharmas + IEX 120 mg AC/L	< 0.01	0.006	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Effluent + pharmas + IEX 250 mg AC/L	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Effluent + pharmas + IEX 500 mg AC/L	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01

Effluent + pharmas + IEX 1000 mg AC/L	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Effluent + pharmas 0 mg O_3/L, 36 mg H_2O_2/L	< 0.01	0.044	0.139	0.752	< 0.01	0.823	0.009
Effluent + pharmas 12.5 mg O_3/L, 36 mg H_2O_2/L	< 0.01	0.188	< 0.01	0.051	< 0.01	< 0.01	< 0.01
Effluent + pharmas 31.2 mg O_3/L, 36 mg H_2O_2/L	< 0.01	0.082	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Effluent + pharmas 62.4 mg O_3/L, 36 mg H_2O_2/L	< 0.01	0.028	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Effluent + pharmas + IEX 0 mg O_3/L, 36 mg H_2O_2/L	< 0.01	0.053	< 0.01	0.796	< 0.01	0.803	0.006
Effluent + pharmas + IEX 12.5 mg O_3/L, 36 mg H_2O_2/L	< 0.01	0.077	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Effluent + pharmas + IEX 31.2 mg O_3/L, 36 mg H_2O_2/L	< 0.01	0.039	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Effluent + pharmas + IEX 62.4 mg O_3/L, 36 mg H_2O_2/L	< 0.01	0.011	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Effluent + pharmas O_3/biofiltration (too short period) 0 mg O_3/L, 36 mg H_2O_2/L	< 0.01	0.014	< 0.01	0.922	< 0.01	0.956	< 0.01
Effluent + pharmas O_3/biofiltration (too short period) 12.5 mg O_3/L, 36 mg H_2O_2/L	< 0.01	0.035	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Effluent + pharmas O_3/biofiltration (too short period) 31.2 mg O_3/L, 36 mg H_2O_2/L	< 0.01	0.016	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01

Effluent + pharmas O_3/biofiltration (too short period) 62.4 mg O_3/L, 36 mg H_2O_2/L	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Effluent + pharmas O_3/biofiltration (too short period) 0 mg O_3/L, UV 120-150 mJ/cm^2	< 0.01	0.015	< 0.01	0.913	< 0.01	< 0.01	< 0.01
Effluent + pharmas O_3/biofiltration (too short period) 12.5 mg O_3/L, UV 120-150 mJ/cm^2	< 0.01	0.055	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Effluent + pharmas O_3/biofiltration (too short period) 31.2 mg O_3/L, UV 120-150 mJ/cm^2	< 0.01	0.011	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Effluent + pharmas O_3/biofiltration (too short period) 62.4 mg O_3/L, UV 120-150 mJ/cm^2	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Effluent + pharmas O_3/biofiltration 0 mg O_3/L, UV 120-150 mJ/cm^2	< 0.01	0.019	< 0.01	< 0.01	< 0.01	0.728	< 0.01
Effluent + pharmas	< 0.01	0.050	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01

O_3/biofiltration 12.5 mg O_3/L, UV 120-150 mJ/cm^2							
Effluent + pharmas O_3/biofiltration 31.2 mg O_3/L, UV 120-150 mJ/cm^2	< 0.01	0.079	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Effluent + pharmas O_3/biofiltration 62.4 mg O_3/L, UV 120-150 mJ/cm^2	< 0.01	0.037	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
	metformine	metoprolol	venlafaxine	trimethoprim	tramadol	bisoprolol	cafeine
untreated Effluent	5.18	2.11	0.236	0.165	0.398	0.107	0.104
Effluent + IEX	5.19	1.79	0.215	0.129	0.371	0.088	0.102
Effluent + dosed pharmas	9.65	3.06	1.36	1.18	1.35	0.104	0.086
Effluent + dosed pharmas LP 10 mg H_2O_2/l 0 mJ/cm^2	8.01	2.44	1.23	0.379	1.14	0.077	0.058
Effluent + dosed pharmas LP 10 mg H_2O_2/l 300 mJ/cm^2	8.33	2.04	1.00	0.348	0.883	0.066	0.094
Effluent + dosed pharmas LP 10 mg H_2O_2/l 600 mJ/cm^2	8.10	1.80	0.836	0.318	0.701	0.055	0.146
Effluent + dosed pharmas +IEX	9.51	2.52	1.14	0.952	1.13	0.085	0.066
Effluent + dosed pharmas +IEX LP 10 mg H_2O_2/l 0 mJ/cm^2	5.86	1.38	0.846	0.075	0.557	0.060	< 0.05
Effluent + dosed pharmas +IEX LP 10 mg H_2O_2/l 300 mJ/cm^2	5.04	0.652	0.355	0.023	0.223	0.029	< 0.05
Effluent + dosed pharmas +IEX	5.24	0.361	0.176	0.019	0.112	0.016	< 0.05

LP 10 mg H_2O_2/l 600 mJ/cm^2							
Effluent + pharmas	1.51	0.277	0.347	0.059	0.299	0.010	0.055
30 mg AC/L							
Effluent + pharmas	3.43	0.346	0.253	0.102	0.217	0.014	< 0.05
60 mg AC/L							
Effluent + pharmas	2.47	0.062	0.076	0.016	0.052	< 0.01	< 0.05
120 mg AC/L							
Effluent + pharmas	2.30	0.010	0.012	< 0.01	< 0.01	< 0.01	< 0.05
250 mg AC/L							
Effluent + pharmas	2.17	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05
500 mg AC/L							
Effluent + pharmas	2.00	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05
1000 mg AC/L							
Effluent + pharmas + IEX	8.72	0.382	0.362	0.103	0.321	0.014	< 0.05
30 mg AC/L							
Effluent + pharmas + IEX	8.34	0.031	0.074	< 0.01	0.035	< 0.01	< 0.05
60 mg AC/L							
Effluent + pharmas + IEX	8.11	0.006	0.018	< 0.01	0.007	< 0.01	< 0.05
120 mg AC/L							
Effluent + pharmas + IEX	7.73	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05
250 mg AC/L							
Effluent + pharmas + IEX	6.84	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05
500 mg AC/L							
Effluent + pharmas + IEX	5.39	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05
1000 mg AC/L							
Effluent + pharmas	2.18	2.68	1.17	0.987	1.18	0.084	< 0.05
0 mg O_3/L, 36 mg H_2O_2/L							
Effluent + pharmas	1.01	0.041	0.012	< 0.01	< 0.01	< 0.01	< 0.05
12.5 mg O_3/L, 36 mg H_2O_2/L							
Effluent + pharmas	0.084	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05
31.2 mg O_3/L, 36 mg H_2O_2/L							

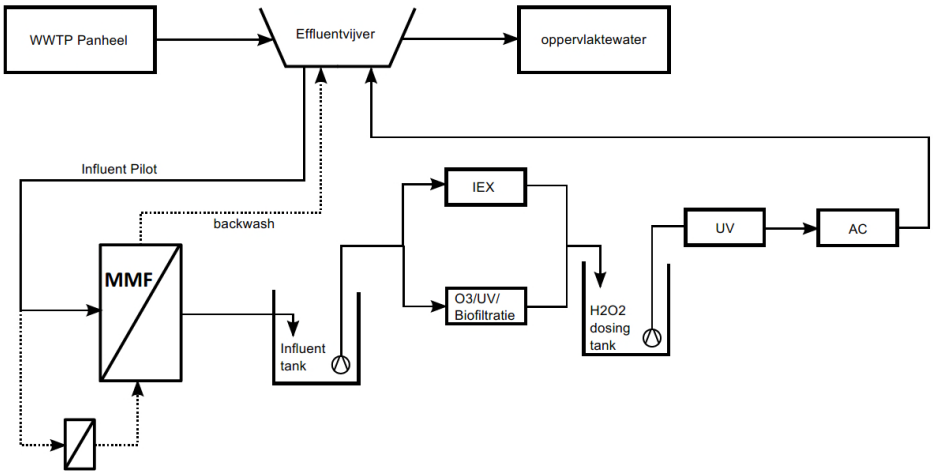
Effluent + pharmas 62.4 mg O_3/L, 36 mg H_2O_2/L	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05
Effluent + pharmas + IEX 0 mg O_3/L, 36 mg H_2O_2/L	7.92	2.17	0.988	0.803	1.00	0.075	< 0.05
Effluent + pharmas + IEX 12.5 mg O_3/L, 36 mg H_2O_2/L	1.14	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05
Effluent + pharmas + IEX 31.2 mg O_3/L, 36 mg H_2O_2/L	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05
Effluent + pharmas + IEX 62.4 mg O_3/L, 36 mg H_2O_2/L	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05
Effluent + pharmas O_3/biofiltration (too short period) 0 mg O_3/L, 36 mg H_2O_2/L	5.66	0.973	0.958	0.858	0.845	< 0.01	< 0.05
Effluent + pharmas O_3/biofiltration (too short period) 12.5 mg O_3/L, 36 mg H_2O_2/L	0.362	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05
Effluent + pharmas O_3/biofiltration (too short period) 31.2 mg O_3/L, 36 mg H_2O_2/L	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05
Effluent + pharmas O_3/biofiltration (too short period) 62.4 mg O_3/L, 36 mg H_2O_2/L	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05
Effluent + pharmas O_3/biofiltration (too short period) 0 mg O_3/L, UV 120-150	5.59	0.998	0.978	0.871	0.868	< 0.01	< 0.05

mJ/cm^2							
Effluent + pharmas O_3/biofiltration (too short period) 12.5 mg O_3/L, UV 120-150 mJ/cm^2	0.689	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05
Effluent + pharmas O_3/biofiltration (too short period) 31.2 mg O_3/L, UV 120-150 mJ/cm^2	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05
Effluent + pharmas O_3/biofiltration (too short period) 62.4 mg O_3/L, UV 120-150 mJ/cm^2	< 0.05	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05
Effluent + pharmas O_3/biofiltration 0 mg O_3/L, UV 120-150 mJ/cm^2	3.87	0.735	0.726	0.627	0.647	< 0.01	< 0.05
Effluent + pharmas O_3/biofiltration 12.5 mg O_3/L, UV 120-150 mJ/cm^2	3.89	0.671	0.668	0.312	0.598	< 0.01	< 0.05
Effluent + pharmas O_3/biofiltration 31.2 mg O_3/L, UV 120-150 mJ/cm^2	3.00	0.017	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05
Effluent + pharmas O_3/biofiltration	0.254	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05

62.4 mg O_3/L, UV 120-150 mJ/cm^2							

Appendix VII

PFD of the pilot



Appendix VIII

Experimental data from pilot plant

Table 12-4: Concentrations of pharmaceuticals and metabolites determined during the pilot tests at 27-11-2015 and 17-12-2015.

Description of sample	carbamazepine	o-desmethyl metoprolol	alfa-hydroxy metoprolol	Dimethyl-aminophenazon	AMPH	hydroxy ibuprofen	norfluoxetine
influent + dosed pharmaceuticals	1.57	< 0.01	0.372	< 0.01	< 0.01	0.746	< 0.50
influent after IEX	1.16	< 0.01	0.311	< 0.01	< 0.01	< 0.50	< 0.50
After IEX, UV 150 mJ/cm^2 and 10 mg H_2O_2	0.088	0.021	0.155	< 0.01	< 0.01	< 0.50	< 0.50
After IEX, UV 300 mJ/cm^2 and 10 mg H_2O_2	0.028	0.010	0.077	< 0.01	< 0.01	< 0.50	< 0.50
influent after IEX, duplo	1.23	< 0.01	0.279	< 0.01	< 0.01	< 0.50	< 0.50
After IEX, UV 150 mJ/cm^2 and 10 mg H_2O_2, duplo	0.049	0.017	0.143	< 0.01	0.016	< 0.50	< 0.50
After IEX, UV 300 mJ/cm2 and 10 mg H_2O_2, duplo	0.027	0.013	0.092	< 0.01	0.015	< 0.50	< 0.50
influent after O_3/biof, 12 mg/L	0.398	0.016	0.267	< 0.01	0.206	0.510	< 0.50
After O_3 (12 mg/L)/biof, UV 150 mJ/cm^2 and 10 mg H_2O_2	0.267	0.024	0.271	< 0.01	0.045	0.524	< 0.50
After O_3 (12 mg/L)/biof, UV 150 mJ/cm^2 and 10 mg H_2O_2	0.225	0.027	0.235	< 0.01	0.042	< 0.50	< 0.50
Influent without dosage	0.433	< 0.01	0.302	< 0.01	< 0.01	2.79	< 0.50

influent + dosed pharmaceuticals	1.19	< 0.01	0.270	< 0.01	< 0.01	1.93	< 0.50
influent after O_3/biof, 18 mg/L	0.112	0.018	0.187	< 0.01	0.258	1.48	< 0.50
After O_3 (18 mg/L)/biof, UV 150 mJ/cm² and 10 mg H_2O_2	0.040	0.012	0.099	< 0.01	0.029	0.807	< 0.50
After O_3 (18 mg/L)/biof, UV 300 mJ/cm² and 10 mg H_2O_2	0.059	0.026	0.152	< 0.01	0.053	1.26	< 0.50
O_3 (18 mg/L)/biof,i ntern UV 150 mJ/cm²	0.518	< 0.01	0.248	< 0.01	0.222	1.81	< 0.50
O_3 (18 mg/L)/biof,i ntern UV 150 mJ/cm², duplo	0.521	< 0.01	0.230	< 0.01	0.215	2.01	< 0.50
After O_3 (18 mg/L)/biof, UV 150 mJ/cm² and 10 mg H_2O_2, duplo	0.079	0.023	0.184	< 0.01	0.045	1.48	< 0.50
After O_3 (18 mg/L)/biof, UV 300 mJ/cm² and 10 mg H_2O_2, duplo	0.051	0.022	0.131	< 0.01	0.041	0.977	< 0.50
influent after O_3/biof, 23 mg/L	0.044	0.019	0.167	< 0.01	0.266	1.44	< 0.50
O_3 (23 mg/L)/biof,i ntern UV 150 mJ/cm²	0.109	0.020	0.226	< 0.01	0.334	1.77	< 0.50
After O_3 (23 mg/L)/biof, UV 150 mJ/cm² and 10 mg H_2O_2	0.030	0.031	0.173	< 0.01	0.064	1.39	< 0.50
After O_3 (23 mg/L)/biof, UV 300 mJ/cm² and 10 mg H_2O_2	0.017	0.026	0.123	< 0.01	0.044	1.02	< 0.50
After O_3 (23 mg/L)/biof, UV 150 mJ/cm² and 10 mg H_2O_2 duplo	0.030	0.031	0.172	< 0.01	0.061	1.53	< 0.50
After O_3 (23 mg/L)/biof, UV 300 mJ/cm² and 10 mg H_2O_2	0.015	0.023	0.109	< 0.01	0.038	0.923	< 0.50
	anhydro erythromycine A	clofibrinezuur	Oxcarbamaze-pine	carbamazepine-10,11-epoxide	10,11-trans-diol-carbamaze-pine (10,11-dihydro-10,11-dihydroxycarbamazepine)	3-hydroxy carbama-zepine	2-hydroxy carbamaze-pine

influent + dosed pharmaceuticals	1.94	< 0.01	< 0.01	0.125	3.30	0.184	0.108
influent after IEX	3.21	< 0.01	0.079	0.111	3.15	0.232	0.114
After IEX, UV 150 mJ/cm^2 and 10 mg H_2O_2	1.85	< 0.01	< 0.01	0.527	0.768	< 0.01	< 0.01
After IEX, UV 300 mJ/cm^2 and 10 mg H_2O_2	1.54	< 0.01	< 0.01	0.348	0.398	< 0.01	< 0.01
influent after IEX, duplo	2.08	< 0.01	0.125	0.124	2.75	0.216	0.118
After IEX, UV 150 mJ/cm^2 and 10 mg H_2O_2, duplo	1.29	< 0.01	< 0.01	0.517	0.649	< 0.01	< 0.01
After IEX, UV 300 mJ/cm2 and 10 mg H_2O_2, duplo	0.989	< 0.01	< 0.01	0.398	0.398	< 0.01	< 0.01
influent after O_3/biof, 12 mg/L	1.04	< 0.01	< 0.01	0.084	2.31	< 0.01	< 0.01
After O_3 (12 mg/L)/biof, UV 150 mJ/cm^2 and 10 mg H_2O_2	1.12	< 0.01	< 0.01	0.197	2.23	< 0.01	< 0.01
After O_3 (12 mg/L)/biof, UV 150 mJ/cm^2 and 10 mg H_2O_2	0.997	< 0.01	< 0.01	0.174	1.81	< 0.01	< 0.01
Influent without dosage	< 0.05	< 0.01	< 0.01	0.065	1.86	0.088	0.060
influent + dosed pharmaceuticals	1.94	< 0.01	< 0.01	0.059	1.47	0.072	0.050
influent after O_3/biof, 18 mg/L	0.964	< 0.01	< 0.01	0.042	1.20	< 0.01	< 0.01
After O_3 (18 mg/L)/biof, UV 150 mJ/cm^2 and 10 mg H_2O_2	0.461	< 0.01	< 0.01	0.041	0.581	< 0.01	< 0.01
After O_3 (18 mg/L)/biof, UV 300 mJ/cm^2 and 10 mg H_2O_2	0.876	< 0.01	< 0.01	0.064	0.845	< 0.01	< 0.01
O_3 (18 mg/L)/biof,i ntern UV 150 mJ/cm^2	1.59	< 0.01	< 0.01	0.044	1.49	< 0.01	< 0.01
O_3 (18 mg/L)/biof,i ntern UV 150 mJ/cm^2, duplo	1.53	< 0.01	< 0.01	0.038	1.46	< 0.01	< 0.01
After O_3 (18 mg/L)/biof, UV 150 mJ/cm^2 and 10 mg H_2O_2, duplo	1.02	< 0.01	< 0.01	0.069	1.10	< 0.01	< 0.01
After O_3 (18 mg/L)/biof, UV 300 mJ/cm^2 and 10 mg H_2O_2, duplo	0.705	< 0.01	< 0.01	0.055	0.781	< 0.01	< 0.01

influent after O_3/biof, 23 mg/L	0.666	< 0.01	< 0.01	0.033	0.987	< 0.01	< 0.01
O_3 (23 mg/L)/biof,i ntern UV 150 mJ/cm^2	1.03	< 0.01	< 0.01	0.041	1.44	< 0.01	< 0.01
After O_3 (23 mg/L)/biof, UV 150 mJ/cm^2 and 10 mg H_2O_2	0.798	< 0.01	< 0.01	0.047	1.05	< 0.01	< 0.01
After O_3 (23 mg/L)/biof, UV 300 mJ/cm^2 and 10 mg H_2O_2	0.457	< 0.01	< 0.01	0.035	0.721	< 0.01	< 0.01
After O_3 (23 mg/L)/biof, UV 150 mJ/cm^2 and 10 mg H_2O_2 duplo	0.793	< 0.01	< 0.01	0.047	1.05	< 0.01	< 0.01
After O_3 (23 mg/L)/biof, UV 300 mJ/cm^2 and 10 mg H_2O_2	0.451	< 0.01	< 0.01	0.031	0.616	< 0.01	< 0.01
	salicylzuur	o-desmethyltramadol	N4-acetyl sulfamethoxazole (acetyl-sulfame-thoxazole	acetyl sulfadiazine	4-formylamino-antipyrine (N-formyl-4-aminoanti-pyrine)	4-acetami-nophen sulfaat	o-desmethyl naproxen
influent + dosed pharmaceuticals	< 5.0	0.307	0.034	< 0.01	0.061	< 0.03	< 0.05
influent after IEX	< 5.0	0.295	0.019	< 0.01	0.056	< 0.03	< 0.05
After IEX, UV 150 mJ/cm^2 and 10 mg H_2O_2	< 5.0	0.046	< 0.01	< 0.01	< 0.01	< 0.03	< 0.05
After IEX, UV 300 mJ/cm^2 and 10 mg H_2O_2	< 5.0	0.014	< 0.01	< 0.01	< 0.01	< 0.03	< 0.05
influent after IEX, duplo	< 5.0	0.268	0.016	< 0.01	0.039	< 0.03	< 0.05
After IEX, UV 150 mJ/cm^2 and 10 mg H_2O_2, duplo	< 5.0	0.035	< 0.01	< 0.01	< 0.01	< 0.03	< 0.05
After IEX, UV 300 mJ/cm2 and 10 mg H_2O_2, duplo	< 5.0	0.020	< 0.01	< 0.01	< 0.01	< 0.03	< 0.05
influent after O_3/biof, 12 mg/L	< 5.0	0.028	0.026	< 0.01	0.028	< 0.03	< 0.05
After O_3 (12 mg/L)/biof, UV 150 mJ/cm^2 and 10 mg H_2O_2	< 5.0	0.020	0.022	< 0.01	< 0.01	< 0.03	< 0.05
After O_3 (12 mg/L)/biof, UV 150 mJ/cm^2 and 10 mg H_2O_2	< 5.0	0.020	0.017	< 0.01	< 0.01	< 0.03	< 0.05

Influent without dosage	< 5.0	0.185	0.039	< 0.01	< 0.01	0.035	< 0.05
influent + dosed pharmaceuticals	< 5.0	0.154	0.032	< 0.01	< 0.01	< 0.03	< 0.05
influent after O_3/biof, 18 mg/L	< 5.0	0.016	0.026	< 0.01	< 0.01	< 0.03	< 0.05
After O_3 (18 mg/L)/biof, UV 150 mJ/cm^2 and 10 mg H_2O_2	< 5.0	< 0.01	0.013	< 0.01	< 0.01	< 0.03	< 0.05
After O_3 (18 mg/L)/biof, UV 300 mJ/cm^2 and 10 mg H_2O_2	< 5.0	0.014	0.024	< 0.01	< 0.01	< 0.03	< 0.05
O_3 (18 mg/L)/biof,i ntern UV 150 mJ/cm^2	< 5.0	0.054	0.034	< 0.01	< 0.01	0.035	< 0.05
O_3 (18 mg/L)/biof,i ntern UV 150 mJ/cm^2, duplo	< 5.0	0.051	0.028	< 0.01	< 0.01	< 0.03	< 0.05
After O_3 (18 mg/L)/biof, UV 150 mJ/cm^2 and 10 mg H_2O_2, duplo	< 5.0	0.015	0.029	< 0.01	< 0.01	< 0.03	< 0.05
After O_3 (18 mg/L)/biof, UV 300 mJ/cm^2 and 10 mg H_2O_2, duplo	< 5.0	0.013	0.016	< 0.01	< 0.01	< 0.03	< 0.05
influent after O_3/biof, 23 mg/L	< 5.0	< 0.01	0.031	< 0.01	< 0.01	< 0.03	< 0.05
O_3 (23 mg/L)/biof,i ntern UV 150 mJ/cm^2	< 5.0	< 0.01	0.030	< 0.01	< 0.01	< 0.03	< 0.05
After O_3 (23 mg/L)/biof, UV 150 mJ/cm^2 and 10 mg H_2O_2	< 5.0	0.013	0.029	< 0.01	< 0.01	< 0.03	< 0.05
After O_3 (23 mg/L)/biof, UV 300 mJ/cm^2 and 10 mg H_2O_2	< 5.0	< 0.01	0.019	< 0.01	< 0.01	< 0.03	< 0.05
After O_3 (23 mg/L)/biof, UV 150 mJ/cm^2 and 10 mg H_2O_2 duplo	< 5.0	0.014	0.024	< 0.01	< 0.01	< 0.03	< 0.05
After O_3 (23 mg/L)/biof, UV 300 mJ/cm^2 and 10 mg H_2O_2	< 5.0	0.011	0.014	< 0.01	< 0.01	< 0.03	< 0.05

	cortisone	cortisol	clindamycin	clenbuterol	bezafibrate	atenolol	guanylureum
influent + dosed pharmaceuticals	2.61	2.98	1.55	0.648	1.50	0.997	64.3
influent after IEX	2.68	2.33	1.16	0.850	0.125	1.13	76.0
After IEX, UV 150 mJ/cm^2 and 10 mg H_2O_2	1.43	0.335	< 0.01	0.190	0.044	0.394	73.9
After IEX, UV 300 mJ/cm^2 and 10 mg H_2O_2	0.776	0.094	< 0.01	0.093	0.022	0.190	68.6

influent after IEX, duplo	2.57	2.26	1.07	0.798	0.117	1.09	68.8
After IEX, UV 150 mJ/cm^2 and 10 mg H_2O_2, duplo	1.46	0.257	< 0.01	0.093	0.034	0.342	64.7
After IEX, UV 300 mJ/cm2 and 10 mg H_2O_2, duplo	0.924	0.107	< 0.01	0.059	0.021	0.198	70.6
influent after O_3/biof, 12 mg/L	2.24	2.49	0.344	0.447	1.14	0.767	55.7
After O_3 (12 mg/L)/biof, UV 150 mJ/cm^2 and 10 mg H_2O_2	2.14	1.59	< 0.01	0.338	1.03	0.698	54.4
After O_3 (12 mg/L)/biof, UV 150 mJ/cm^2 and 10 mg H_2O_2	1.61	1.06	< 0.01	0.248	0.880	0.585	51.4
Influent without dosage	< 0.03	< 0.03	0.056	< 0.01	0.133	0.221	37.8
influent + dosed pharmaceuticals	2.15	2.58	1.32	0.488	1.17	0.878	40.1
influent after O_3/biof, 18 mg/L	1.81	1.89	0.153	0.405	0.793	0.542	39.0
After O_3 (18 mg/L)/biof, UV 150 mJ/cm^2 and 10 mg H_2O_2	0.906	0.634	< 0.01	0.151	0.336	0.304	24.6
After O_3 (18 mg/L)/biof, UV 300 mJ/cm^2 and 10 mg H_2O_2	1.33	0.745	< 0.01	0.226	0.626	0.462	38.6
O_3 (18 mg/L)/biof,i ntern UV 150 mJ/cm^2	2.12	1.95	0.565	0.510	1.09	0.724	38.9
O_3 (18 mg/L)/biof,i ntern UV 150 mJ/cm^2, duplo	2.07	1.95	0.577	0.526	1.10	0.721	38.9
After O_3 (18 mg/L)/biof, UV 150 mJ/cm^2 and 10 mg H_2O_2, duplo	1.75	1.23	< 0.01	0.312	0.753	0.506	44.4
After O_3 (18 mg/L)/biof, UV 300 mJ/cm^2 and 10 mg H_2O_2, duplo	1.10	0.670	< 0.01	0.171	0.524	0.393	40.6
influent after O_3/biof, 23 mg/L	1.59	1.62	0.046	0.316	0.705	0.554	33.1
O_3 (23 mg/L)/biof,i ntern UV 150 mJ/cm^2	2.08	2.04	0.102	0.515	1.01	0.683	39.6
After O_3 (23 mg/L)/biof, UV 150 mJ/cm^2 and 10 mg H_2O_2	1.64	1.13	< 0.01	0.234	0.692	0.511	42.7
After O_3 (23 mg/L)/biof, UV 300 mJ/cm^2 and 10 mg H_2O_2	1.06	0.572	< 0.01	0.122	0.464	0.392	35.3

After O_3 (23 mg/L)/biof, UV 150 mJ/cm^2 and 10 mg H_2O_2 duplo	1.81	1.17	< 0.01	0.230	0.739	0.517	39.3
After O_3 (23 mg/L)/biof, UV 300 mJ/cm^2 and 10 mg H_2O_2	0.984	0.504	< 0.01	0.110	0.422	0.339	31.0
	gemfibrozil	furosemide	fluoxetine	erythromycin A	diclofenac	diatrizoic acid	Cyclophos-phamide
influent + dosed pharmaceuticals	1.71	0.478	1.08	2.80	1.24	0.964	1.19
influent after IEX	0.411	0.047	1.03	1.82	0.042	0.168	1.09
After IEX, UV 150 mJ/cm^2 and 10 mg H_2O_2	0.187	< 0.01	0.454	1.25	< 0.01	0.109	0.303
After IEX, UV 300 mJ/cm^2 and 10 mg H_2O_2	0.112	< 0.01	0.260	0.923	< 0.01	0.062	0.153
influent after IEX, duplo	0.365	0.054	1.04	2.27	0.037	0.237	0.956
After IEX, UV 150 mJ/cm^2 and 10 mg H_2O_2, duplo	0.129	< 0.01	0.431	1.46	< 0.01	0.140	0.231
After IEX, UV 300 mJ/cm2 and 10 mg H_2O_2, duplo	0.087	< 0.01	0.247	1.27	< 0.01	0.090	0.164
influent after O_3/biof, 12 mg/L	1.04	< 0.01	0.553	1.83	0.329	0.956	1.08
After O_3 (12 mg/L)/biof, UV 150 mJ/cm^2 and 10 mg H_2O_2	0.815	< 0.01	0.404	1.68	< 0.01	0.603	0.988
After O_3 (12 mg/L)/biof, UV 150 mJ/cm^2 and 10 mg H_2O_2	0.651	< 0.01	0.282	1.34	< 0.01	0.384	0.916
Influent without dosage	0.690	0.201	< 0.01	0.038	0.128	< 0.01	< 0.01
influent + dosed pharmaceuticals	1.54	0.284	1.09	2.11	0.639	1.07	1.02
influent after O_3/biof, 18 mg/L	0.620	< 0.01	0.446	1.10	0.115	1.16	0.988
After O_3 (18 mg/L)/biof, UV 150 mJ/cm^2 and 10 mg H_2O_2	0.239	< 0.01	0.237	0.571	< 0.01	0.427	0.442
After O_3 (18 mg/L)/biof, UV 300 mJ/cm^2 and 10 mg H_2O_2	0.371	< 0.01	0.200	0.945	< 0.01	0.460	0.814
O_3 (18 mg/L)/biof,i ntern UV 150 mJ/cm^2	1.16	< 0.01	0.522	1.83	0.225	0.791	1.08
O_3 (18 mg/L)/biof,i ntern UV 150 mJ/cm^2,	1.18	< 0.01	0.484	1.70	0.239	0.761	1.05

duplo							
After O_3 (18 mg/L)/biof, UV 150 mJ/cm^2 and 10 mg H_2O_2, duplo	0.490	< 0.01	0.288	1.07	< 0.01	0.744	0.931
After O_3 (18 mg/L)/biof, UV 300 mJ/cm^2 and 10 mg H_2O_2, duplo	0.320	< 0.01	0.205	0.770	< 0.01	0.420	0.694
influent after O_3/biof, 23 mg/L	0.445	< 0.01	0.352	0.769	0.036	0.965	0.865
O_3 (23 mg/L)/biof,i ntern UV 150 mJ/cm^2	0.788	< 0.01	0.305	1.12	0.064	0.886	1.08
After O_3 (23 mg/L)/biof, UV 150 mJ/cm^2 and 10 mg H_2O_2	0.344	< 0.01	0.217	0.812	< 0.01	0.589	0.905
After O_3 (23 mg/L)/biof, UV 300 mJ/cm^2 and 10 mg H_2O_2	0.206	< 0.01	0.148	0.577	< 0.01	0.388	0.687
After O_3 (23 mg/L)/biof, UV 150 mJ/cm^2 and 10 mg H_2O_2 duplo	0.376	< 0.01	0.236	0.812	< 0.01	0.658	0.927
After O_3 (23 mg/L)/biof, UV 300 mJ/cm^2 and 10 mg H_2O_2	0.200	< 0.01	0.146	0.528	< 0.01	0.332	0.593
	terbutaline	sulfaquinoxalin	Sulfame-thoxazole	sulfadiazine	Sulfachloro-pyridazine	sotalol	salbutamol
influent + dosed pharmaceuticals	0.015	0.165	0.105	0.074	0.079	1.90	1.27
influent after IEX	0.961	< 0.01	0.021	0.030	< 0.01	1.69	1.19
After IEX, UV 150 mJ/cm^2 and 10 mg H_2O_2	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.625	0.169
After IEX, UV 300 mJ/cm^2 and 10 mg H_2O_2	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.339	0.054
influent after IEX, duplo	0.880	< 0.01	0.018	0.030	< 0.01	1.49	1.07
After IEX, UV 150 mJ/cm^2 and 10 mg H_2O_2, duplo	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.552	0.086
After IEX, UV 300 mJ/cm2 and 10 mg H_2O_2, duplo	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.344	0.044
influent after O_3/biof, 12 mg/L	< 0.01	0.020	0.023	0.014	0.012	0.765	0.033
After O_3 (12 mg/L)/biof, UV 150 mJ/cm^2 and 10 mg H_2O_2	< 0.01	0.017	0.019	0.013	0.010	0.628	0.010

After O_3 (12 mg/L)/biof, UV 150 mJ/cm^2 and 10 mg H_2O_2	< 0.01	0.011	0.011	< 0.01	< 0.01	0.498	< 0.01
Influent without dosage	< 0.01	< 0.01	0.010	< 0.01	< 0.01	0.570	< 0.01
influent + dosed pharmaceuticals	0.015	0.123	0.078	0.059	0.066	1.27	1.08
influent after O_3/biof, 18 mg/L	< 0.01	< 0.01	0.017	0.015	< 0.01	0.374	0.016
After O_3 (18 mg/L)/biof, UV 150 mJ/cm^2 and 10 mg H_2O_2	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.176	< 0.01
After O_3 (18 mg/L)/biof, UV 300 mJ/cm^2 and 10 mg H_2O_2	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.246	< 0.01
O_3 (18 mg/L)/biof,i ntern UV 150 mJ/cm^2	< 0.01	0.039	0.026	0.027	0.027	0.764	0.180
O_3 (18 mg/L)/biof,i ntern UV 150 mJ/cm^2, duplo	< 0.01	0.040	0.030	0.026	0.025	0.750	0.169
After O_3 (18 mg/L)/biof, UV 150 mJ/cm^2 and 10 mg H_2O_2, duplo	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.324	0.011
After O_3 (18 mg/L)/biof, UV 300 mJ/cm^2 and 10 mg H_2O_2, duplo	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.231	< 0.01
influent after O_3/biof, 23 mg/L	< 0.01	< 0.01	0.010	< 0.01	< 0.01	0.186	< 0.01
O_3 (23 mg/L)/biof,i ntern UV 150 mJ/cm^2	< 0.01	< 0.01	0.014	< 0.01	< 0.01	0.216	< 0.01
After O_3 (23 mg/L)/biof, UV 150 mJ/cm^2 and 10 mg H_2O_2	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.166	< 0.01
After O_3 (23 mg/L)/biof, UV 300 mJ/cm^2 and 10 mg H_2O_2	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.107	< 0.01
After O_3 (23 mg/L)/biof, UV 150 mJ/cm^2 and 10 mg H_2O_2 duplo	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.170	< 0.01
After O_3 (23 mg/L)/biof, UV 300 mJ/cm^2 and 10 mg H_2O_2	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.099	< 0.01

	propranolol	prednisolone	pindolol	propyfenazon	fenazon	Pentoxi-fylline	paroxetine
influent + dosed pharmaceuticals	1.08	5.69	0.012	1.57	0.798	0.979	3.43

influent after IEX	1.01	3.81	0.211	1.35	0.869	0.874	4.02
After IEX, UV 150 mJ/cm^2 and 10 mg H_2O_2	0.052	< 0.05	< 0.01	0.031	< 0.01	0.124	0.757
After IEX, UV 300 mJ/cm^2 and 10 mg H_2O_2	0.013	< 0.05	< 0.01	0.011	< 0.01	0.031	0.307
influent after IEX, duplo	0.938	3.81	0.252	1.35	0.842	0.798	3.95
After IEX, UV 150 mJ/cm^2 and 10 mg H_2O_2, duplo	0.032	< 0.05	0.010	0.020	< 0.01	0.066	0.687
After IEX, UV 300 mJ/cm2 and 10 mg H_2O_2, duplo	0.015	< 0.05	< 0.01	< 0.01	< 0.01	0.036	0.319
influent after O_3/biof, 12 mg/L	0.435	4.48	< 0.01	0.015	0.513	0.696	0.050
After O_3 (12 mg/L)/biof, UV 150 mJ/cm^2 and 10 mg H_2O_2	0.096	< 0.05	< 0.01	< 0.01	0.041	0.618	< 0.05
After O_3 (12 mg/L)/biof, UV 150 mJ/cm^2 and 10 mg H_2O_2	0.076	< 0.05	< 0.01	< 0.01	0.024	0.535	< 0.05
Influent without dosage	0.078	< 0.05	< 0.01	< 0.01	< 0.01	0.016	< 0.05
influent + dosed pharmaceuticals	0.886	4.85	0.019	1.35	0.692	0.874	2.70
influent after O_3/biof, 18 mg/L	0.183	3.49	< 0.01	< 0.01	0.260	0.578	< 0.05
After O_3 (18 mg/L)/biof, UV 150 mJ/cm^2 and 10 mg H_2O_2	0.013	< 0.05	< 0.01	< 0.01	0.018	0.283	< 0.05
After O_3 (18 mg/L)/biof, UV 300 mJ/cm^2 and 10 mg H_2O_2	0.020	< 0.05	< 0.01	< 0.01	0.012	0.423	< 0.05
O_3 (18 mg/L)/biof,i ntern UV 150 mJ/cm^2	0.423	0.154	< 0.01	0.027	0.415	0.768	< 0.05
O_3 (18 mg/L)/biof,i ntern UV 150 mJ/cm^2, duplo	0.439	0.141	< 0.01	0.033	0.410	0.760	< 0.05
After O_3 (18 mg/L)/biof, UV 150 mJ/cm^2 and 10 mg H_2O_2, duplo	0.031	< 0.05	< 0.01	< 0.01	0.039	0.490	< 0.05
After O_3 (18 mg/L)/biof, UV 300 mJ/cm^2 and 10 mg H_2O_2, duplo	0.013	< 0.05	< 0.01	< 0.01	0.013	0.373	< 0.05
influent after O_3/biof, 23 mg/L	0.105	2.59	< 0.01	< 0.01	0.199	0.545	< 0.05
O_3 (23 mg/L)/biof,i ntern UV 150 mJ/cm^2	0.201	0.200	< 0.01	< 0.01	0.288	0.704	< 0.05
After O_3 (23 mg/L)/biof, UV 150 mJ/cm^2	0.014	< 0.05	< 0.01	< 0.01	0.023	0.490	< 0.05

and 10 mg H_2O_2							
After O_3 (23 mg/L)/biof, UV 300 mJ/cm² and 10 mg H_2O_2	< 0.01	< 0.05	< 0.01	< 0.01	< 0.01	0.341	< 0.05
After O_3 (23 mg/L)/biof, UV 150 mJ/cm² and 10 mg H_2O_2 duplo	0.020	< 0.05	< 0.01	< 0.01	0.026	0.505	< 0.05
After O_3 (23 mg/L)/biof, UV 300 mJ/cm² and 10 mg H_2O_2	< 0.01	< 0.05	< 0.01	< 0.01	< 0.01	0.309	< 0.05
	paracetamol	niacin	naproxen	metronidazole	ifosfamide	Keto-profen	lincomycin
influent + dosed pharmaceuticals	0.096	0.192	1.15	1.00	1.27	1.13	2.49
influent after IEX	0.480	0.065	0.127	0.891	1.14	0.020	2.05
After IEX, UV 150 mJ/cm² and 10 mg H_2O_2	< 0.01	0.139	< 0.01	0.448	0.156	< 0.01	< 0.01
After IEX, UV 300 mJ/cm² and 10 mg H_2O_2	< 0.01	0.143	< 0.01	0.274	0.062	< 0.01	< 0.01
influent after IEX, duplo	0.547	0.060	0.124	0.820	1.03	0.020	1.78
After IEX, UV 150 mJ/cm² and 10 mg H_2O_2, duplo	< 0.01	0.089	< 0.01	0.411	0.106	< 0.01	< 0.01
After IEX, UV 300 mJ/cm2 and 10 mg H_2O_2, duplo	< 0.01	0.113	< 0.01	0.297	0.069	< 0.01	< 0.01
influent after O_3/biof, 12 mg/L	0.053	0.311	0.291	0.769	1.05	0.898	0.709
After O_3 (12 mg/L)/biof, UV 150 mJ/cm² and 10 mg H_2O_2	< 0.01	0.412	0.057	0.744	0.930	< 0.01	< 0.01
After O_3 (12 mg/L)/biof, UV 150 mJ/cm² and 10 mg H_2O_2	< 0.01	0.393	0.050	0.656	0.820	< 0.01	< 0.01
Influent without dosage	< 0.01 X	0.209	0.645	< 0.01 X	< 0.01	0.114	0.033
influent + dosed pharmaceuticals	0.035	0.238	1.16	0.824	1.01	0.689	2.05
influent after O_3/biof, 18 mg/L	0.063	0.700	0.136	0.631	0.977	0.530	0.298
After O_3 (18 mg/L)/biof, UV 150 mJ/cm² and 10 mg H_2O_2	< 0.01	0.415	0.011	0.323	0.413	< 0.01	< 0.01
After O_3 (18 mg/L)/biof, UV 300 mJ/cm² and 10 mg H_2O_2	< 0.01	0.636	0.015	0.512	0.683	< 0.01	< 0.01

O_3 (18 mg/L)/biof,i ntern UV 150 mJ/cm²	0.095	0.508	0.491	0.742	1.02	0.018	1.04
O_3 (18 mg/L)/biof,i ntern UV 150 mJ/cm², duplo	0.080	0.510	0.517	0.724	1.03	0.017	1.08
After O_3 (18 mg/L)/biof, UV 150 mJ/cm² and 10 mg H_2O_2, duplo	0.015	0.639	0.030	0.616	0.893	< 0.01	< 0.01
After O_3 (18 mg/L)/biof, UV 300 mJ/cm² and 10 mg H_2O_2, duplo	< 0.01	0.564	0.011	0.461	0.569	< 0.01	< 0.01
influent after O_3/biof, 23 mg/L	0.041	0.567	0.055	0.577	0.876	0.388	0.117
O_3 (23 mg/L)/biof,i ntern UV 150 mJ/cm²	0.047	0.304	0.118	0.716	1.13	0.021	0.227
After O_3 (23 mg/L)/biof, UV 150 mJ/cm² and 10 mg H_2O_2	< 0.01	0.644	0.010	0.582	0.828	< 0.01	< 0.01
After O_3 (23 mg/L)/biof, UV 300 mJ/cm² and 10 mg H_2O_2	< 0.01	0.567	< 0.01	0.448	0.556	< 0.01	< 0.01
After O_3 (23 mg/L)/biof, UV 150 mJ/cm² and 10 mg H_2O_2 duplo	< 0.01	0.631	< 0.01	0.622	0.884	< 0.01	< 0.01
After O_3 (23 mg/L)/biof, UV 300 mJ/cm² and 10 mg H_2O_2	< 0.01	0.464	< 0.01	0.390	0.479	< 0.01	< 0.01
	metformine	metoprolol	venlafaxine	trimethoprim	tramadol		
influent + dosed pharmaceuticals	35.8	2.41	1.40	1.35	1.42		
influent after IEX	36.0	2.09	1.27	1.17	1.28		
After IEX, UV 150 mJ/cm² and 10 mg H_2O_2	23.6	0.642	0.499	0.030	0.320		
After IEX, UV 300 mJ/cm² and 10 mg H_2O_2	20.3	0.284	0.250	< 0.01	0.118		
influent after IEX, duplo	32.4	1.92	1.18	1.06	1.16		
After IEX, UV 150 mJ/cm² and 10 mg H_2O_2, duplo	20.6	0.493	0.453	0.017	0.251		
After IEX, UV 300 mJ/cm2 and 10 mg H_2O_2, duplo	20.6	0.263	0.264	< 0.01	0.128		
influent after O_3/biof, 12 mg/L	31.1	1.70	1.07	0.412	1.04		
After O_3 (12 mg/L)/biof, UV 150 mJ/cm²	28.3	1.55	0.982	0.238	0.922		

and 10 mg H_2O_2							
After O_3 (12 mg/L)/biof, UV 150 mJ/cm² and 10 mg H_2O_2	26.1	1.36	0.842	0.197	0.801		
Influent without dosage	34.3	1.13	0.150	0.133	0.174		
influent + dosed pharmaceuticals	40.4	1.72	1.05	1.15	1.09		
influent after O_3/biof, 18 mg/L	38.8	1.08	0.678	0.201	0.693		
After O_3 (18 mg/L)/biof, UV 150 mJ/cm² and 10 mg H_2O_2	20.1	0.560	0.346	0.060	0.318		
After O_3 (18 mg/L)/biof, UV 300 mJ/cm² and 10 mg H_2O_2	35.1	0.825	0.525	0.074	0.501		
O_3 (18 mg/L)/biof,i ntern UV 150 mJ/cm²	41.5	1.45	0.924	0.574	0.956		
O_3 (18 mg/L)/biof,i ntern UV 150 mJ/cm², duplo	40.6	1.43	0.916	0.576	0.918		
After O_3 (18 mg/L)/biof, UV 150 mJ/cm² and 10 mg H_2O_2, duplo	39.7	0.990	0.617	0.112	0.597		
After O_3 (18 mg/L)/biof, UV 300 mJ/cm² and 10 mg H_2O_2, duplo	32.0	0.747	0.464	0.073	0.437		
influent after O_3/biof, 23 mg/L	34.5	1.00	0.601	0.082	0.623		
O_3 (23 mg/L)/biof,i ntern UV 150 mJ/cm²	42.0	1.31	0.804	0.118	0.846		
After O_3 (23 mg/L)/biof, UV 150 mJ/cm² and 10 mg H_2O_2	37.4	0.930	0.584	0.039	0.584		
After O_3 (23 mg/L)/biof, UV 300 mJ/cm² and 10 mg H_2O_2	30.5	0.646	0.409	0.021	0.387		
After O_3 (23 mg/L)/biof, UV 150 mJ/cm² and 10 mg H_2O_2 duplo	38.9	0.967	0.595	0.046	0.613		
After O_3 (23 mg/L)/biof, UV 300 mJ/cm² and 10 mg H_2O_2	25.8	0.595	0.373	0.018	0.352		

Appendix IX

Cost estimations

Effluent + ACF (Hofman et al., 2013)

								BK	Inv	Totaal	Afschrijving		M€ / j			Variable kosten		M€ / j			Totale kosten								
Proces		Spoel	Jaarcap	Uurcap	Procesparameters			M€	M€	M€	Civ	Wtb	Elec	Overig	Totaal	Energie		Overige			M€ / j	€ / m3		Civiel	Wtb	Elek	Leiding	Totaal
			1,881																												
Pompkelder			1,881	214,7	Verblijftijd	15	minuten	0,02	0,03	0,03	0,001	0,001	0,001			Wh/m3				Onderhoud				40%	40%	20%		100%
																20				4,00%								
															0,003		0,005				0,001	0,009	0,005					
LD pomp zuivering			1,881	214,7	opvoerhoogte	150	kPa	0,18	0,28	0,28	0,004	0,015	0,009			Wh/m3				Onderhoud				20%	50%	30%		100%
					efficiency	70%										60				4,00%								
															0,027		0,015				0,007	0,049	0,027					
Snelfiltratie		2,5%	1,881	214,7	snelheid	10	m/h	0,67	1,06	1,07	0,041	0,036	0,016	0,001		Wh/m3				Onderhoud				52,5%	32,5%	15%		100%
					Zand	2	meter	Vullingen						Vullingen		0				4,00%								
								0,006							0,093		0,000				0,027	0,120	0,066					
Actieve-koolfiltratie		0,5%	1,834	209,4	Contacttijd	40	minuten	1,67	2,66	2,78	0,087	0,103	0,048	0,030		Wh/m3		Reactivatie		Onderhoud				45%	37,5%	17,5%		100%
					Reactivaties	6	maanden	Kool						Kool		0				4,00%								
					nieuw na	10	react.	0,126							0,267		0		0,0977		0,067	0,431	0,236					
			1,825																										
							Totaal Investeringen			4,17							Subtotaal processen					0,609						
Bediening				0,10	mensjaar à €	50000											Bediening					0,005						
Adm. Beheerskosten				20%	van bediening												Adm. Beheerskosten					0,001						
Kwal. Bewaking																	Kwal. Bewaking					pm						
																	Totaal				M€/j	0,615						
Zuiveringsrendement			97,01%														Exploitatiekosten				€/m3	0,337						
																					€/IE	24,6						

Effluent + FIX + ACF (Hofman et al., 2013)

							BK	Inv	Totaal	Afschrijving		M€ / j			Variable kosten		M€ / j			Totale kosten							
Proces	Spoel	Jaarcap	Uurcap	Procesparameters			M€	M€	M€	Civ	Wtb	Elec	Overig	Totaal	Energie	Overige				M€ / j	€ / m3		Civiel	Wtb	Elek	Leidin	Totaal
		1,891																									
Pompkelder		1,891	215,8	Verblijftijd	15	minuten	0,02	0,03	0,03	0,001	0,001	0,001			Wh/m3				Onderhoud				40%	40%	20%		100%
															20				4,00%								
														0,003		0,005				0,001	0,009	0,005					
LD pomp zuivering		1,891	215,8	opvoerhoogte	150	kPa	0,18	0,28	0,28	0,004	0,015	0,009			Wh/m3				Onderhoud				20%	50%	30%		100%
				efficiency	70%										60				4,00%								
														0,028		0,015				0,007	0,049	0,027					
Snelfiltratie	2,5%	1,891	215,8	snelheid	10	m/h	0,67	1,07	1,07	0,041	0,036	0,016	0,001		Wh/m3				Onderhoud				#####	32,5%	15%		100%
				Zand	2	meter	Vullingen						Vullingen		0				4,00%								
							0,006							0,094		0,000				0,027	0,120	0,066					
IEX	0,5%	1,843	210,4	snelheid	40	m/h	1,10	1,76	1,80	0,067	0,059	0,027	0,005		Wh/m3				Onderhoud				#####	32,5%	15%		100%
				Hars	1,5	meter	Vullingen						Vullingen		0				4,00%								
							0,04							0,158		0,000				0,044	0,203	0,111					
Actieve-koolfiltratie	0,5%	1,834	209,4	Contacttijd	40	minuten	1,67	2,66	2,78	0,087	0,103	0,048	0,017		Wh/m3		Reactivatie		Onderhoud				45%	37,5%	#####		100%
				Reactivaties	12	maanden	Kool						Kool		0				4,00%								
				nieuw na	10	react.	0,126							0,254		0		0,0489		0,067	0,370	0,203					
		1,825																									
						Totaal Investeringen			5,97							Subtotaal processen					0,751						
Bediening			0,20	mensjaar à €	50000											Bediening					0,01						
Adm. Beheerskosten			20%	van bediening												Adm. Beheerskosten					0,002						
Kwal. Bewaking																Kwal. Bewaking					pm						
																Totaal				M€/j	0,763						
Zuiveringsrendement		96,53%														Exploitatiekosten				€/m3	0,418						
																				€/IE	30,5						

Effluent + FIX + UV/H_2O_2 (Hofman et al., 2013)

								BK	Inv	Totaal	Afschrijving		M€ / j			Variable kosten		M€ / j			Totale kosten								
Proces		Spoel	Jaarcap	Uurcap	Procesparameters			M€	M€	M€	Civ	Wtb	Elec	Overig	Totaal	Energie		Overige				M€ / j	€ / m3		Civiel	Wtb	Elek	Leiding	Totaal
			1,881																										
Pompkelder			1,881	214,7	Verblijftijd	15	minuten	0,02	0,03	0,03	0,001	0,001	0,001			Wh/m3				Onderhoud					40%	40%	20%		100%
																20				4,00%									
															0,003		0,005				0,001	0,009	0,005						
LD pomp zuivering			1,881	214,7	opvoerhoogte	150	kPa	0,18	0,28	0,28	0,004	0,015	0,009			Wh/m3				Onderhoud					20%	50%	30%		100%
					efficiency	70%										60				4,00%									
															0,027		0,015				0,007	0,049	0,027						
Snelfiltratie		2,5%	1,881	214,7	snelheid	10	m/h	0,67	1,06	1,07	0,041	0,036	0,016	0,001		Wh/m3				Onderhoud					#####	32,5%	15%		100%
					Zand	2	meter	Vullingen						Vullingen		0				4,00%									
								0,006							0,093		0,000				0,027	0,120	0,066						
IEX		0,5%	1,834	209,4	snelheid	40	m/h	1,10	1,75	1,79	0,067	0,059	0,027	0,005		Wh/m3				Onderhoud					#####	32,5%	15%		100%
(BK als SF)					Hars	1,5	meter	Vullingen						Vullingen		0				4,00%									
								0,04							0,158		0,000				0,044	0,202	0,111						
Dosering	H2O2		1,825	208,3	dosering	10	mg/l	0,025	0,04	0,04	0,000	0,003	0,001					Chemicaliën		Onderhoud					10%	75%	15%		100%
																				4,00%									
															0,004				0,0183		0,001	0,023	0,013						
UV-desinfectie			1,825	208,3				0,32	0,50	0,50	0,003	0,038	0,010			Wh/m3		Lampen		Onderhoud					7,5%	72,5%	20%		100%
																260				4,00%									
															0,051		0,062		0,0018		0,013	0,127	0,069						
			1,825																										
							Totaal Investeringen			3,72							Subtotaal processen					0,530							
Bediening				0,20	mensjaar à €	50000											Bediening					0,01							
Adm. Beheerskosten				20%	van bediening												Adm. Beheerskosten					0,002							
Kwal. Bewaking																	Kwal. Bewaking					pm							
																	Totaal				M€/j	0,542							
Zuiveringsrendement			97,01%														Exploitatiekosten				€/m3	0,297							
																					€/IE	21,7							

Effluent + FIX + UV/H_2O_2 + ACF (Hofman et al., 2013)

									BK	Inv	Totaal	Afschrijving		M€ / j			Variable kosten			M€ / j			Totale kosten								
Proces		Spoel	Jaarcap	Uurcap	Procesparameters				M€	M€	M€	Civ	Wtb	Elec	Overig	Totaal	Energie		Overige				M€ / j	€ / m3		Civiel	Wtb	Elek	Leiding	Totaal
			1,881																											
Pompkelder			1,881	214,7	Verblijftijd	15	minuten		0,02	0,03	0,03	0,001	0,001	0,001			Wh/m3				Onderhoud					40%	40%	20%		100%
																	20				4,00%									
																0,003		0,005				0,001	0,009	0,005						
LD pomp zuivering			1,881	214,7	opvoerhoogte	150	kPa		0,18	0,28	0,28	0,004	0,015	0,009			Wh/m3				Onderhoud					20%	50%	30%		100%
					efficiency	70%											60				4,00%									
																0,027		0,015				0,007	0,049	0,027						
Snelfiltratie		2,5%	1,881	214,7	snelheid	10	m/h		0,67	1,06	1,07	0,041	0,036	0,016	0,001		Wh/m3				Onderhoud					#####	32,5%	15%		100%
					Zand	2	meter		Vullingen						Vullingen		0				4,00%									
									0,006							0,093		0,000				0,027	0,120	0,066						
IEX		0,5%	1,834	209,4	snelheid	40	m/h		1,10	1,75	1,79	0,067	0,059	0,027	0,005		Wh/m3				Onderhoud					#####	32,5%	15%		100%
(BK als SF)					Hars	1,5	meter		Vullingen						Vullingen		0				4,00%									
									0,04							0,158		0,000				0,044	0,202	0,111						
Dosering	H2O2		1,825	208,3	dosering	10	mg/l		0,025	0,04	0,04	0,000	0,003	0,001					Chemicaliën		Onderhoud					10%	75%	15%		100%
																					4,00%									
																0,004				0,0183		0,001	0,023	0,013						
UV-desinfectie			1,825	208,3					0,32	0,50	0,50	0,003	0,038	0,010			Wh/m3		Lampen		Onderhoud					7,5%	72,5%	20%		100%
																	90				4,00%									
																0,051		0,021		0,0018		0,013	0,086	0,047						
Actieve-koolfiltratie		0,5%	1,834	209,4	Contacttijd	10	minuten		0,63	1,01	1,04	0,033	0,039	0,018	0,003		Wh/m3		Reactivatie		Onderhoud					45%	37,5%	#####		100%
					Reactivaties	24	maanden		Kool						Kool		0				4,00%									
					nieuw na	10	react.		0,031							0,093		0		0,0061		0,025	0,124	0,068						
			1,825																											
							Totaal Investeringen				4,76							Subtotaal processen					0,613							
Bediening				0,20	mensjaar à €	50000												Bediening					0,01							
Adm. Beheerskosten				20%	van bediening													Adm. Beheerskosten					0,002							
Kwal. Bewaking																		Kwal. Bewaking					pm							
																		Totaal				M€/j	0,625							
Zuiveringsrendement			97,01%															Exploitatiekosten				€/m3	0,343							
																						€/IE	25,0							