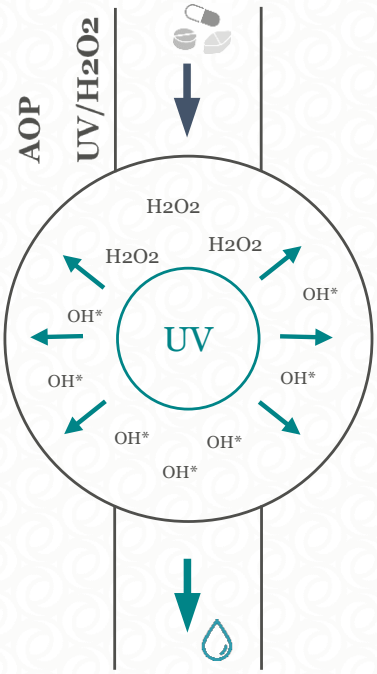

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Removal of pharmaceutical residues from municipal wastewater using UV/H2O2

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In cooperation with Nouryon and Van Remmen UV Technology

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Summary

The advanced treatment of municipal wastewater for the removal of micropollutants and especially pharmaceutical residues has become an important research field. Different studies have indicated limitations of investigated treatment technologies such as ozone oxidation and active carbon for certain particularly persistent substances and when treating difficult water matrices. Therefore, Nouryon and IVL Swedish Environmental Research Institute initiated a study on the use of advanced oxidation treatment using UV light coupled with hydrogen peroxide (UV/H_2O_2) for the oxidation of pharmaceutical residues in municipal wastewater effluents.

The conducted tests, comprising both lab-scale and pilot-scale studies, show good removal efficiencies for all pharmaceuticals observed in the effluent of Stockholm's largest WWTP. A clear dose-response behaviour is observed that can be used for targeting various substances depending on removal target definition. The connected catalytical filter was able to remove all remaining process reagents and potential toxic by-products.

The cost evaluation of the technique reveals that UV/H_2O_2 applications may be more cost intensive compared to other technologies, especially ozonation and activated carbon. However, compared to combinations of several technologies such as ozonation and activated carbon or technologies with ultrafiltration, UV/H_2O_2 applications may be in the same or lower cost range.

Based on the project results it is understood that the gap in costs towards other removal techniques is not that wide and that several advantages of the UV/H_2O_2 technology may favour its application in various cases. For this, further investigations are planned by the project partners.

Sammanfattning

Ett forskningsområde som har blivit viktigt är att behandla kommunalt avloppsvatten i syfte att reducera/eliminera mikroföreningar och särskilt läkemedelsrester. Olika studier har visat på begränsningar för de undersökta behandlingsteknikerna så som ozonoxidation och aktivt kol för vissa särskilt svårnedbrytbara ämnen och vid behandling av svåra vattenmatriser. Därför inledde Nouryon och IVL Svenska Miljöinstitutet en studie om användning av avancerad oxidationsbehandling med UV-ljus i kombination med väteperoxid (UV/H_2O_2) för oxidation av läkemedelsrester i kommunalt avloppsvatten.

De genomförda testerna, som innefattar studier i både laboratorie- och pilotskala, visar god reningseffektivitet för alla läkemedel som observerats i avloppet från Stockholms största reningsverk. Ett tydligt dosresponssamband har observerats som kan användas för en riktad rening av specifika ämnen beroende på definitionen av reningsmål. Det katalytiska filtret som avslutande poleringssteg kunde avlägsna alla återstående processreagens och potentiella toxiska biprodukter.

Kostnadsberäkningarna för en fullskaleimplementering av tekniken visar att UV/H_2O_2-tekniken fortfarande är mer kostnadsintensiv jämfört med andra tekniker, särskilt ozonering. Jämfört med kombinationer av flera tekniker, såsom ozonering och aktivt kol eller tekniker med ultrafiltrering, kan UV/H_2O_2-applikationer emellertid ligga inom samma eller lägre kostnadsområde. Baserat på projektresultaten kan det konstateras att kostandsgapet mot andra reningstekniker inte är så stort och att flera fördelar med UV/H_2O_2-tekniken kan gynna dess tillämpning i olika fall. För detta planeras ytterligare undersökningar av projektpartnerna.

1 Background

Pharmaceutical residues and other emerging substances discharged from our society to the environment can adversely affect aquatic ecosystems. Emissions from wastewater treatment plants (WWTPs) are the most significant source of load on the recipients. WWTPs collect the wastewater flows from many different sectors of our society and represent the final barrier before discharging pollutants into the environment. Specifically pharmaceuticals are designed to be effective at low concentrations in the body and to be stable against e.g. stomach acid and microbial degradation, and many pharmaceuticals are thus persistent to degradation also in the WWTP environment. As they pose a risk of irreversibly disturbing ecosystems in recipients, current wastewater treatment plants (WWTPs) need to supplement their treatment processes with additional systems for reducing these types of emissions.

WWTPs are built to separate suspended solids and to reduce degradable dissolved organic matter, nitrogen and phosphorus, but not for reduction of non-biodegradable dissolved compounds although these may be removed to some extent by e.g. adsorption to sludge. Available measurements of pharmaceutical residues in Swedish wastewater shows that 70 different substances have been observed in the influent wastewater with median concentrations of a few ng/L to ~ 100 µg/L. Several of the detected substances present in high concentrations in the influents, such as ibuprofen, were removed to almost 100%, while others such as diclofenac remained largely unaltered.

In general, the substances considered can be divided into quartiles. Approximately 25% of the substances are removed to a high degree and can certainly be removed by optimized treatment with existing technology. Around 25% of the substances are removed to a modest degree, often with varying degree of removal efficiency. These substances will require additional treatment to ensure sufficient reduction. Around 25% of the substances have no or only limited reduction in traditional Swedish WWTPs and additional treatment is a necessity to remove such substances. Approximately 25% of the substances have a negative reduction in the works, i.e. a higher measurable concentration in the effluent after treatment than in the influent to the WWTPs.

The EU Water framework Directive (WFD), in Sweden implemented in water management (Förordning 2004: 660), requires actions for a number of particularly dangerous substances that are emitted to the aquatic environment. Future definitions of environmental quality standards (EQS) might lead to additional requirements for discharges from WWTPs. In July 2013, the European Parliament decided to include several pharmaceuticals in a "watch list" of emerging pollutants that may be placed on the WFD priority list (Directives 2000/60/EC and 2008/105/EC as regards priority substances in the field of water policy, European Parliament, 2013).

Switzerland has already introduced requirements for additional treatment for the reduction of pharmaceutical residues in larger WWTPs and discussions are ongoing in several other countries. Also in Sweden, having already two full-scale installation for the removal of pharmaceutical residues at WWTPs in Linköping and Simrishamn, both initiated and cofounded by IVL, discussions are ongoing. Studies have shown that antibiotics at concentrations found in the environment may contribute to the appearance of antibiotic-resistant genes in bacteria. The increase in antibiotic resistance is a serious threat to our ability to heal normal infection diseases (WHO 2014).

Various removal methods have been evaluated in several international and national large projects. Especially in Germany and Switzerland, advanced treatment technologies have been tested on a

large scale. In Sweden, the most promising and new technologies have been tested in direct collaboration between WWTPs and research organisations. IVL has been involved in the mentioned two existing full-scale installations at Swedish WWTPs and the evaluation and development of several treatment technologies (Alcala Borao 2015; Baresel et al., 2014, 2015a, b, c, 2016, 2017a-d; 2019a, b; Baresel and Malovanyy, 2019; Ek et al., 2013, 2014; Graae et al., 2017; Lazic et al., 2017; Mparmpagianni 2016; Murad 2018; Sehlén et al., 2015).

2 Introduction

IVL has been working on the advanced treatment of municipal wastewater for the removal of micropollutants and especially pharmaceutical residues for a long time. Different studies have indicated limitations of investigated treatment technologies such as ozone oxidation and active carbon for certain particularly persistent substances and when treating difficult water matrices. Therefore, in 2017, a study on the use of advanced oxidation treatment using UV light coupled with hydrogen peroxide (UV/H_2O_2) for the oxidation of pharmaceutical residues in municipal wastewater effluents was initiated by Nouryon (at that time AkzoNobel Pulp and Performance Chemicals) and IVL.

2.1 Objectives

The general objective of the project was to investigate, through pilot experiments under realistic conditions, the removal efficiency and resource efficiency of the UV/H_2O_2 technique for the removal of persistent organic pollutants from wastewater. Further, integration of the technology into existing WWTPs treatment processes, synergies and further optimization potential and potential limitations were aimed to be investigated. A first assessment of the treatment processes in terms of sustainability and costs compared to competing treatment techniques was aimed for.

2.2 Advanced oxidation treatment using UV/H_2O_2

Advanced Oxidation Processes (AOP) are chemical treatment methods for the removal of problematic organic matter. The basic principle of AOP involves the production of hydroxyl radicals, which can be generated from hydrogen peroxide (H_2O_2), ozone, oxidants in combination with ultraviolet (UV) radiation or from water in photo-catalysis process. In some cases, two or more radical generators are used in combination. However, it is the hydroxyl radicals that is mainly responsible for the degradation of organic compounds and not the chemical oxidant added itself (e.g. H_2O_2, O_3).

The hydroxyl radical is a non-selective strong chemical oxidant. Once produced, it attacks nearly all organic complexes, which leads to a partial or complete breakdown of the organic compound. The process also leads to that organic chemicals disintegrate and become smaller and easier biodegradable.

In UV/H_2O_2 process the H_2O_2 is added to the water being treated and irradiated by UV-light, which leads to production of hydroxyl radicals. The needed intensity of UV-irradiation depends on the UV light absorbance (UVA) or transmittance (UVT) of the treated water. A higher UVA (lower UVT) implies an increased UV-light absorbance by the water and thus less UV-light reaches H_2O_2, which leads to a need of higher UV-irradiation intensity. In water with a high transmittance (UVT), more UV-light can be absorbed by H_2O_2 and less energy is required to accomplish the same hydroxyl radical production as compared to water with lower transmittance.

The process is non-selective but depends on the UV-absorbance of the treated water, biologically treated and relatively particle-free water is an advantage for the use of UV/H_2O_2 if a resource-efficient and good removal of pharmaceuticals is targeted. Moreover, the content of hydroxyle-scavangers (e.g. nitrite, inorganic ions) preferably needs to be low. Thus, the use of UV/ H_2O_2 is therefore often limited to tertiary treatment steps or specific wastewaters.

As the hydroxyl radicals are the main driver for all AOP-techniques, the effectiveness of the different techniques to produce hydroxyl radicals becomes important for the resource-efficiency of the AOP. Ozonation (O_3), O_3/H_2O_2, Fe/H_2O_2, UV/H_2O_2 are most frequently studied for various applications. Ozone-based AOPs are generally considered to be more energy efficient than the UV/H_2O_2 process at all H_2O_2 levels. However, depending on the level of treatment required, the gap between UV/H_2O_2 and e.g. ozonation becomes small and a further investigation of this technology is therefore motivated.

UV/H_2O_2 systems may be a beneficial method for AOP, as they provide high reaction rates and are flexible in the design. The use of ultraviolet lamps also provides disinfection of the water, which may not be provided by e.g. ozonation at commonly applied ozone dosages in WWTPs. UV/H_2O_2 systems may further have an advantage comparing to other AOP systems using chemicals because of the lower cost and easy availability of hydrogen peroxide. However, there are also some drawbacks. H_2O_2 has poor UV light absorption characteristics, thus most of the UV-input is wasted. At the same time, the UV-light not absorbed by H_2O_2 is also having an effect on pollutants.

Further, in contrast to other technologies, UV/H_2O_2 treatment may yield a higher mineralisation of targeted substances and by-products with less environmental significance (e.g. Lekkerkerker-Teunissen et al., 2012).

Relevant studies in Sweden by Wahlberg et al. (2010) reported lower removal efficiency for UV/H_2O_2 than for e.g. ozone treatment of the same water. Only at very high doses of H_2O_2 could comparable removal efficiencies as for ozone be achieved but at a cost of unwanted high residual concentrations of hydrogen peroxide in the effluent. On more concentrated wastewaters, i.e. hospital or industrial wastewater, UV irradiation with varying dosages of H_2O_2 as tertiary treatment after an MBR-process showed in some scientific lab-scale studies good removal efficiency. In other such studies, however, only high doses of UV could provide sufficient removal efficiencies for the same hospital water type.

Significant differences in sensitivity between compounds for the various treatment methods make a resource-efficient implementation of these already cost-intensive techniques difficult if the target is the removal of as many compounds as possible. Increasing the intensity of the treatment may not be an alternative as long as it is not known which compounds are most important to remove.

2.3 Other relevant technologies

An extensive compilation of different technologies for the removal of micropollutants and specifically pharmaceutical residues is provided by Baresel et al. (2017d).

2.3.1 Ozonation

The most common advanced oxidation process today is the treatment with ozone. Ozone treatment uses the direct chemical reaction of the ozone molecule as well as indirect reactions with hydroxyl radicals, which breaks specific chemical bonds within the targeted substances. There exist several full-scale installations of a complementary treatment step by ozone to oxidize pharmaceutical

residues and other organic compounds. Both existing full-scale installations in Sweden have ozonation as part of its advanced treatment setup.

Commonly applied ozone doses range between 0.3 and 1.2 g O_3/g dissolved organic carbon, DOC, (about 3-12 g O_3/m^3 water) and a significant breakdown of most of the studied compounds is achieved. However, required ozone doses vary for different substances and for some a sufficient removal cannot be accomplished even at very high doses. The formations of toxic by-products and the high energy-demands at WWTPs are main drawbacks of this technology. When using liquid oxygen (LOX) for ozone production, separate and safe installations for LOX handling is required. Working environments aspects due to ozone production onsite are sometimes of concern and have to be handled.

2.3.2 Activated carbon

Powdered and granular activated carbon (PAC and GAC) are other common technologies to remove priority substances from all kinds of polluted waters. The main advantage of using activated carbon is that no by-products are produced and that priority substances are actually removed and not transformed into other compounds such as is the case of biological and oxidation methods. In addition, the regeneration of activated carbon implies a complete oxidation of the removed organic compounds. Especially in treatment of fresh water for drinking water production, technical systems using either PAC or GAC have been applied for many years. Thus, significant knowledge on setup and operation of removal systems is available.

Main aspects regarding the use of activated carbon systems are hydraulic capacity problems caused by reaction volume (PAC), microbial growth in the system, proper backwashing (both for GAC), and handling of big volumes of carbon that needs to be supplied and stored at the WWTP, and then transported out for disposal or regeneration. Drawbacks of using active carbon are the high cost and energy use in the activated carbon production and regeneration.

2.3.3 Membrane filtration

Various membrane filtration technologies can be used as tertiary treatment. The most common technologies are Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF) and Reverse osmosis (RO). MF and UF can remove suspended matter and disinfect the treated water. However, besides particle-bound compounds no efficient removal of pharmaceutical residues or other priority substances is provided. An efficient removal of such substances requires NF or RO. Even though these filtration techniques are commonly used in drinking water treatment, their stand-alone applications in wastewater treatment are rare. Wahlberg et al. (2010) tested both NF and RO in pilot-scale at Hammarby Sjöstadsverk (2010) and results indicate poor removal efficiency of pharmaceuticals for NF but a high (about 95 %) removal rate by RO. An updated study at Sjöstadsverket shows a more efficient removal of pharmaceutical residues in a RO-pilot if compared to ozone and activated carbon treatment (Baresel et al., 2014; Bergström et al., 2014). Considering the energy demand of membrane filtration, especially RO, as well as the need for a further treatment of the residual concentrate, membrane technologies may currently not represent the first alternative as tertiary treatment technology but imply considerable advantages when applied in secondary treatment such as in a Membrane Bioreactor (MBR) process or other new approaches.

2.3.4 Combinations

The combination of several of mentioned technologies is an efficient way to take advantage of single techniques and at the same time trying to compensate their adverse effects. The most obvious combination is ozonation and an activated carbon. Also membrane filtration technologies in combination with activated carbon are gaining more interest. For some wastewaters, the combination of serval techniques can be used as multiple barrier micropollutant treatment and bromate formation control.

2.3.5 Technologies under development

The following methods to remove pharmaceutical residues are either still in the early stage of development or need substantial further improvements to represent competitive treatment solutions.

Chlorine dioxide (ClO_2) is widely used as a disinfectant in public water systems e.g. swimming pools and cooling systems. ClO_2 may also be useful as an oxidant treating wastewater effluents. A recent work shows that ClO_2 can reduce the concentration of pharmaceuticals from different therapeutic classes in WWTP effluents even though the reactivity varied. Drawbacks and risks of using ClO_2 are the inorganic by-products chlorite (ClO_2^-) and chlorate (ClO_3^-), which are toxic to human and the environment. Also, the risk of formation of absorbable organic halogens (AOX) needs to be considered.

Enzymes could be designed to break down the specific organic pollutants in the same way as white-rot fungi use extracellular enzymes to break down many stable compounds. A number of oxidative enzymes from bacteria, fungi and plants may already now play an important role in numerous waste treatment applications even though such processes are not specifically described. There are examples of research on engineered enzymes capable of breaking down some pollutants, but it has yet not been applied for advanced wastewater treatment. The potential, technical applicability, limitations and costs are currently investigated at the R&D-facility Hammarby Sjöstadsverk.

Direct or integrated electrochemical processes may be considered as an alternative due to the significant improvement of the electrode materials and the coupling with low-cost renewable energy sources. *Electrochemical advanced oxidation processes (EAOPs)* can be of two types, electrochemical separation technologies, which only isolate the pollutants from water, and electrochemical degradation technologies. Advantages of electrochemical technologies may be that the main reagent, the electron, is a clean reagent. Further, it may be relatively easy to handle, automated, and safe. Obvious drawbacks are the high amount of energy, the possible formation of by-products as for other oxidation methods and fouling of electrodes due to the deposition of organic material on their surface. Furthermore, the low conductivity of wastewaters may require the addition of electrolytes and pH regulation.

3 Methodology

All tests were carried out on effluent from Stockholm's main WWTP Henriksdal with sand filtration as the final treatment step.

3.1 Initial bench-scale tests

For the purpose of evaluating the use of H_2O_2 in combination with UV and Fenton reagent (Fe^{2+}/H_2O_2) for the removal of pharmaceutical residues from municipal wastewater, initial lab experiments have been carried out at IVL. For this, batch experiments with different doses and dose combinations were carried out. The test water was not temperature- or pH-adjusted except for the Fe^{2+}/H_2O_2 tests. In addition to these tests, a comparative bench-scale ozonation test was carried out.

Samples were analyses for pharmaceuticals. To measure the toxicity of the water after the treatment, Microtox toxicity tests were used. To prevent effects of sample storage, catalase addition was used to stop the reaction in the samples.

The UV/H_2O_2 bench-scale equipment used could treat 650 mL samples with low pressure UV-lamp. To get targets UV-doses, samples could be recirculated over the equipment several times. This equipment is similar to previously used equipment such as by Wahlberg et al. (2010). The effect of a continued recirculation of the sample volume is unknown.

For the Fe^{2+}/H_2O_2 tests, simple batch tests were performed. The H_2O_2 dose was 25 g/m^3 and molar ratio 1:1 to Fe^{2+}.

A representative bench-scale ozonation unit was used. Synthetic air was introduced into an ozone generator (OGK-3G) and an ozone meter (BMT 964 C) connected to the plant. The formed ozone was passed through a glass filter (porosity 4) up into a column containing 1 L of test water. The unit was calibrated so that the amount of ozone formed was 2.5 mg O_3/min. To change the ozone levels to which the wastewater is exposed, the ozonation times were varied. In order to control and calibrate the ozone meter, measurements of the ozone content were also performed using a spectrophotometric indigo method (Bader and Hoigné 1981, http://www.graveslab.org/lab-resources/procedures/ozonequantification).

3.2 Pilot tests at Hammarby Sjöstadsverk

Pilot experiments were based on the results of the initial bench-scale tests and were carried out at the R&D-facility Hammarby Sjöstadsverk using a flexible UV- H_2O_2 pilot plant supplied by Van remmen UV-Technology. The pilot provides precise and reliable UV-C dosing for a wide range of flows and water qualities. The system can be operated in single-pass or recirculating batch process where in both cases the installation can be supplied with water from external and internal sources. Following operating conditions are provided:

- UV-C dose: 2000-15 000 J/m^2
- Transmittance range of water: 20-90 % T10 (@254nm)
- Capacity: 1-2 m^3/h

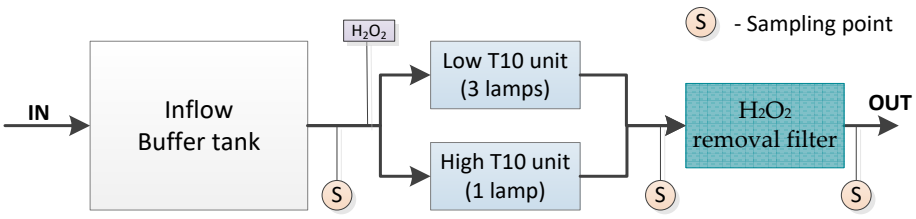

Figure 1. Schematic UV/H_2O_2 pilot setup.

Considering the transmittance of the used WWTP effluent of 61.5 %, only the High T-Cluster (1 lamp) of the UV/H_2O_2 pilot was required for the tests. The internal water volume of the pilot to be considered in the test is then 50 L including UV-lamp, piping and filter.

The pilot is equipped with a catalytic filter for H_2O_2 removal and samples were taken before and after the filter to investigate possible effects of the filter on the overall removal efficiencies.

Two 1 m^3 IBC-tanks were used as buffer and for sampling of influent flows. The pilot tests were performed according to Table 1. Between different operation modes, the water volume in the pilot was exchanged at least 3 times before the next sampling campaign. Correct H_2O_2 dosage was ensured by continuous manual checks of the solution concentration and dosing volumes adjusted accordingly. However, minor deviations were noted. The exact hydrogen peroxide dose can be seen in Figures 2, 3 and 5. The test water was not temperature- or pH-adjusted.

Table 1. Test setup for pilot tests.

	Dosage		Sampling point		Sampling/analyses	
Test Nr	UV J/m^2	H_2O_2 g/m^3	Before filter	After filter	Microtox	Hormones, pharmaceuticals, antibiotics
1	0		x	x	2x	2x
2	5 000			x		x
3	5 000	10	x(K)	x		2x
4	5 000	20	x(K)	x	x	2x
5	5 000	40	x(K)	x		2x
6	10 000			x		x
7	10 000	10		x		x
8	10 000	20		x	x	x
9	10 000	40		x		x
10	3 000			x		x
11	3 000	10		x		x
12	3 000	20		x	x	x
13	3 000	40		x		x

Automatic samplers collected composite samples during the test period. Samples after the treatment were collected directly from manual sampling valves before and after the filter. Samples were collected in 5 L plastic containers but then divided into 1 L bottles for different analysis and storage. Samples were analyses for pharmaceuticals, antibiotics and hormones (see Table A1, Appendix). Catalase addition was used to stop the reaction in the samples taken before the filter.

To measure the toxicity of the water after the treatment, Microtox toxicity tests were used.

3.3 Analytical methods

Pharmaceuticals were analysed using aliquots of 100 to 200 mL thawed composite samples that were spiked with 50 µL internal standard carbamazepine-$^{13}C^{15}N$ (2000 ng/mL) and ibuprofen-D3 (2000 ng/mL). One millilitre of 0.1 wt % ethylenediaminetetraacetate (EDTA-Na_2) dissolved in methanol:water (1:1) was added. Prior to extraction using solid phase extraction (SPE) cartridges (Oasis HLB, 6 mL, Waters), the sample was shaken (30 min, 120 rpm). Cartridges were conditioned with methanol followed by Milli-Q (MQ) water. Thereafter, the samples were applied to the columns at a flow rate of two drops per second. The substances were eluted from the SPE cartridges using 5 mL methanol followed by 5 mL acetone. The supernatants were transferred to vials for final analysis on a high-performance liquid chromatography triple quadrupole mass spectrometer (HPLC-MS/MS). The final determination of the amount of pharmaceuticals in the

samples was performed on a binary liquid chromatography (UFLC) system with auto injection (Shimadzu, Japan). The chromatographic separation was carried out using gradient elution on a C18 reversed phase column (dimensions 50 × 3 mm, 2.5-µm particle size, XBridge, Waters, UK) at a temperature of 35°C and a flow rate of 0.3 mL/ min. The mobile phase consists of 10 mM acetic acid in water.

Microtox analyses were performed according to the ISO 11348-3:2008 (modified) method that utilizes the light emitting ability of the marine bacterium (*Vibrio fisherii*). The light emission is recorded after 5, 15, and 30 min of incubation of the sample. The exposure of the sample provides a dose response relationship, which is used to calculate the 20 % (EC20) or 50 % (EC50) inhibition of the light emission. If the tested sample has low toxicity, a single concentration test (90 % of the tested sample) is performed. The results are expressed as percentage light inhibition of the sample (inhibition at 90 %). Measurements of bacterial bioluminescence is a physiologically relevant method of testing of chemical substances acute toxic effects and often show good agreement with other test organisms as micro-algae, zooplankton and fish. However, results of Microtox cannot readily be extrapolated to other species, and particularly caution should be used in assessments for recipients.

All above analyses were performed by IVL Swedish Environmental Research Institute except for hydrogen peroxide (Chemetrics hydrogen peroxide test kit K-5543) and transmittance (254 nm, 10 mm cuvette length, Real Tech) which were analyzed by Nouryon.

4 Results and discussions

4.1 Bench-scale tests

A summary of the results from the bench-scale test is provided in Table 2 as removal efficiency of a sum of all analyzed substances concentrations. It gives a good generalized picture of average removal efficiencies; however, it is worth mentioning that different substances have different toxicity levels. Complete results are provided in Table A2 in the Appendix. Results from both tables indicate a good removal efficiency in UV/H_2O_2 tests at higher UV-doses. While ozonation has a varying removal efficiency for various substances, treatment with UV/H_2O_2 is more unselective and removes a broader range of substances. Also substances, which are difficult to remove by ozonation, such as Oxazepam, are reduced by UV/H_2O_2.

Table 2. Bench-scale test results.

Sample, treatment	Sum of substance concentration	Total removal efficiency
Influent, WWTP effluent	7 600 ng/L	-
UV/H_2O_2 (low UV-dose & 10 g /m^3)	4 800 ng/L	37 %
UV/H_2O_2 (high UV-dose & 25 g /m^3)	230 ng/L	97 %
UV/H_2O_2 (low UV-dose & 40 g /m^3)	2 700 ng/L	64 %
UV/H_2O_2 (high UV-dose & 40 g /m^3)	30 ng/L	100 %
Fe^{2+}/H_2O_2 (40 g/m^3 & 25 g /m^3 HRT 10 min)	-6 ng/L	100 %
Fe^{2+}/H_2O_2 (40 g/m^3 & 25 g /m^3 HRT 20 min)	0 ng/L	100 %
O_3 (6 g/m^3)	2400 ng/L	69 %

Microtox analyses indicated a toxicity only for samples where catalase addition was used to stop the reaction after the targeted reaction time. That catalase was causing this effect, which was confirmed by Microtox analyses of catalase only. Probably also remaining hydrogen peroxide gave some effect in the test, but this was difficult to examine.

These bench-scale tests showed promising results using UV/H_2O_2 and Fe^{2+}/H_2O_2. A rough cost estimation based on the energy and chemical use during the bench-scale tests indicated significantly higher cost of the use of Fenton compared to UV even if Fenton doses could be reduced significantly. This is mainly explained by the required pH-justification. For the UV/H_2O_2, concerns about the reliability of the results came up as the used bench-scale pilot did not represent real conditions at WWTPs and actual provided UV-doses were difficult to quantify. As in other similar test in the literature, test water is circulated several times over the UV-lamp while UV-treatment at a WWTPs would normally consists of a one pass treatment even so several UV-reactors in series could be applied.

4.2 Pilot tests

The pilot tests were performed using the effluent from Henriksdal WWTP, Stockholm. The water temperature varied between 13.5 – 14.5 °C, pH between 6.8 – 7.0 and transmittance (UVT) between 60 and 64 % during the tests. Figure 2 shows the transmittance of the treated water after the UV/H_2O_2 treatment for the various dose combinations applied. A clear increase of the UVT is indicated with both increasing UV- and H_2O_2-dose. Even without any dosage, the effluent UVT is higher (70%) than in the effluent from Henriksdal WWTP, which may be explained by the effect of the catalytical filter in the pilot.

Analyses results of metal concentrations in the test water are provided in Table A3 in the Appendix.

Substance concentrations below level of detection (LOD) or quantification (LOQ) are considered as the defined LOD and LOQ, respectively. This implies that actual concentrations may be lower than LOQ respective LOD and associated removal efficiencies higher than reported.

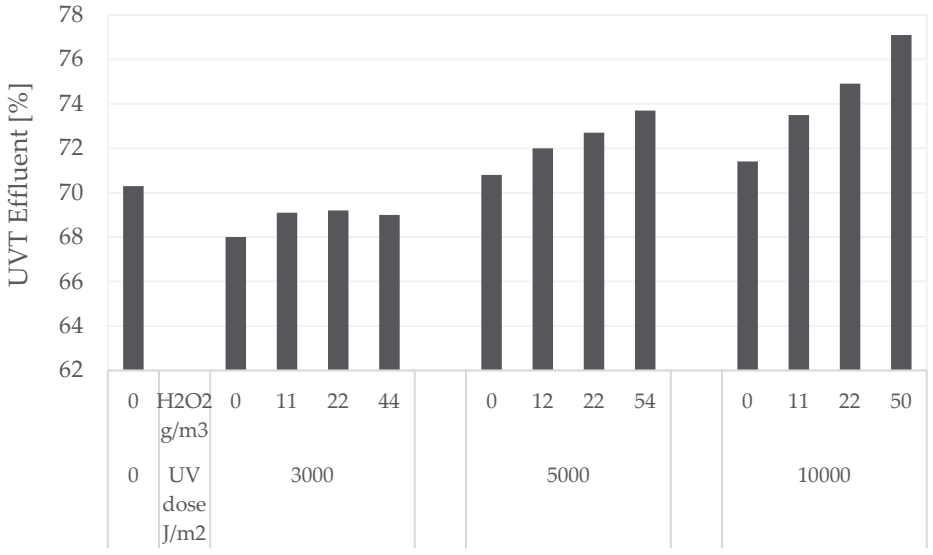

Figure 2. Transmittance of the treated water after the UV/H_2O_2 treatment for the various dose combinations.

4.2.1 Treatment efficiency

Figure 3 shows results for pharmaceuticals analyses of various samples. The figure presents the total sum of all considered pharmaceutical substances except antibiotics and hormones according to Table A1. A potential reduction target of 80% is inserted to compare removal efficiencies of the various treatment configurations. The influent is a one-day composite sample of Henriksdal WWTP effluent, while the treated values are grab samples.

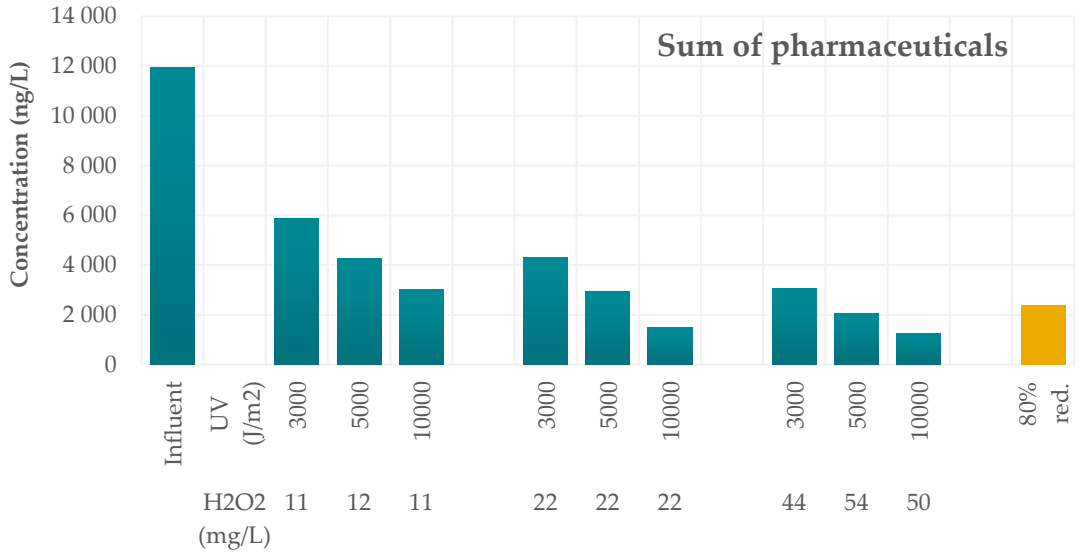

Figure 3. Sum of pharmaceutical concentrations analyses in the pilot tests.

A reduction of the summed concentration of all pharmaceuticals with at least 80 % is achieved by applying a UV-dose of at least 5000 J/m² and 50 mg H_2O_2/L or a UV-dose of 10 000 J/m² and 22 mg H_2O_2/L (Figure 3). Already the lowest dose combination of 3000 J/m² and 11 mg H_2O_2/L provides a reduction of the sum of concentrations of all pharmaceuticals by >50 %.

Figure 3 further indicates a clear dose-response characteristic both for UV-intensity and the H_2O_2-dose. From Figure 4 it may be concluded that the an increased H_2O_2 addition has less effect with increasing UV-intensity. An UV-dose of 10 000 J/m² and ~20 mg H_2O_2/L gives almost the same removal of pharmaceuticals as the same UV-dose but a higher H_2O_2-dose of 50 mg H_2O_2/L This is explained by the fact that an effective degradation of the targeted pharmaceuticals requires an optimum concentration of H_2O_2 which favors photosplitting of H_2O_2 molecules but at the same time limits recombination of OH radicals to form H_2O_2. Increase in concentration of H_2O_2 above the optimum may then not provide any increase in reaction rates as for example reported by Somathilake et al. (2018).

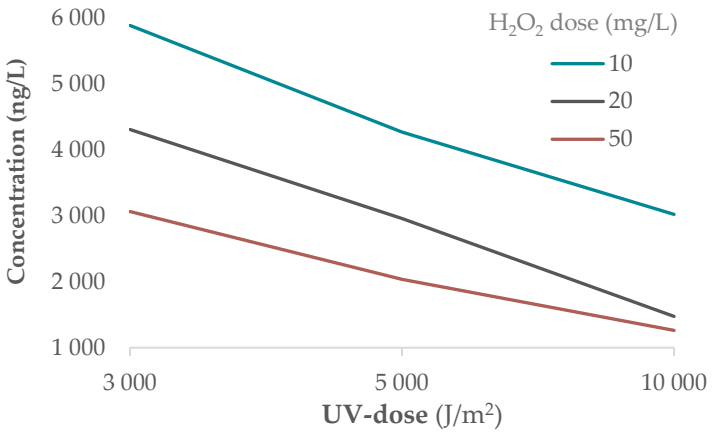

Figure 4. Dose response characteristics for the pilot test.

Considering specific substances, Figure 5 shows four substances frequently observed in the effluent of Swedish WWTPs at levels that require an additional treatment to reduce concentrations to below Predicted No-Effect Concentrations (PNECs). Oxazepam is often the substance defining treatment requirements if defined on PNECs (Baresel and Malovanyy, 2019; Sehlén et al., 2015). Oxazepam is also one of the substances where an enhance biological removal in existing WWTPs cannot provide any enhanced treatment effect as negative reductions are normally observed. Also, advanced technologies such as ozonation or activated carbon require significant higher dosages to remove Oxazepam compared to the removal of most other substances (Baresel et al., 2015c; 2017b). Figure 5a indicates that a UV-effect of 10 000 J/m² and > 20 mg H_2O_2/L or 5 000 J/m² and > 50 mg H_2O_2/L are required to achieve a substantial reduction of Oxazepam.

For Citalopram, a substance that also may be target for additional treatment due to reported concentration in WWTPs effluents and its low PNEC, a significant reduction can be achieved already at the lowest UV-intensity and H_2O_2 doses (Figure 5b). The same effect is achieved for Diclofenac, one of the substances of concern in municipal wastewaters (Figure 5c). Against that, Metoprolol seems to require an even more intense treatment than applied in the current tests as a reduction of 80% could not be achieved (Figure 5d).

However, when defining proper treatment methods for pharmaceuticals it may not be the specific reduction of a substance over the WWTP or the additional treatment step that may define the treatment goal. Firstly, even very low concentrations of some substances may cause effects in the environment and a defined reduction over a treatment by e.g. 80 % may not achieve levels below PNECs in the recipient. On the other hand, a defined reduction by 80 % may imply treatment actions although no negative effect is expected at observed concentrations. This may instead then lead to a negative environmental impact due to the addition resource and energy use for the "unnecessary" treatment. It may further not favor upstream measures to reduce concentrations in the sewage as this would virtually decrease the treatment efficiency at the WWTP.

Complete results are provided in Table A4 in the Appendix.

Figure 5. Pharmaceutical concentrations for 4 selected analytes, a) Oxazepam; b) Citalopram, c) Diclofenac; and d) Metoprolol.

Hormone analyses showed that levels of Estrone (E1), Estradiol (E2) and Etinylestradiol (EE2) were below level of detection (LOD) for all samples including the WWTP effluent used as test water.

Analyses of antibiotics indicated concentrations below level of detection (LOD) or quantification (LOQ) for 10 out of 17 analysed substances. Amoxicillin could not be evaluated because of its poor recovery in the sample preparation. This implies it is not possible to detect or exclude the presence of the analyte. Remaining antibiotics were completely or partly removed by UV/H_2O_2. Complete results are provided in Table A5 in the Appendix.

4.2.2 Filter bed/Removal of by-products

Not all the H_2O_2 added during the treatment is consumed as the production of hydroxyl radicals from hydrogen peroxide requires a surplus of H_2O_2. H_2O_2 has then to be removed from the treated water. In the pilot, a catalytic bed was used consisting of an optimised composition for removal of residual H_2O_2. Analyses of the water after the filter bed did only show low remaining concentrations (< 1 mg/L) of H_2O_2 indicating an efficient removal in the filter bed. It must be noted that the filter bed was filled with fresh filter material before the tests were initiated.

Microtox analyses shown in Table 3 indicate that only the reference sample with deionized water with 2.4 mg/L H_2O_2 added showed a slight inhibition of light formation at the highest mixing rate. This is most likely due to the content of H_2O_2 contained in the sample. All other samples, including the WWTP effluent used for treatment, did not show any toxicity effect independent of UV and H_2O_2 doses. This indicates the importance of the H_2O_2 removal by the catalytical bed. Samples before the filter were not analysed for toxicity because of the difficulties performing the test on samples with catalase addition.

Table 3. Microtox results.

Sample, treatment	Residual H_2O_2 (mg/L)	% Inhibition at 90% admixture of the test water
UV/H_2O_2 (0 J/m² & 0 g/m³) before filter bed*	-	0
UV/H_2O_2 (0 J/m² & 0 g/m³) after filter bed*	-	0
UV/H_2O_2 (5 000 J/m² & 20 g/m³) after filter bed	<1	0
UV/H_2O_2 (3 000 J/m² & 20 g/m³) after filter bed	<1	0
UV/H_2O_2 (10 000 J/m² & 20 g/m³) after filter bed	<1	0
Deionized water with 2.4 H_2O_2 g/m³	2.4	8

* test without any use of UV/H2O2 but water flow through the pilot

Figure 6 shows analyses results for some tests where samples were collected before and after the filter bed. The first two columns show results from test without any use of UV/H_2O_2 but simply pumping the test water through the pilot including the filter bed. The observed removal effect of about 20% for the sum of all pharmaceuticals may thus be accounted for by the catalytical bed. However, this needs more attention in future work as this conclusion is based only on one sample. Nevertheless, also the measured increase in transmittance of the test water over the filter (Figure 2) indicated this treatment effect. An explanation for this removal may be the adsorption of substances on the surface area of the filter material or by oxidative environment, induced by the filter material. The complete results in Table A6 in the Appendix show varying effect for the various substances.

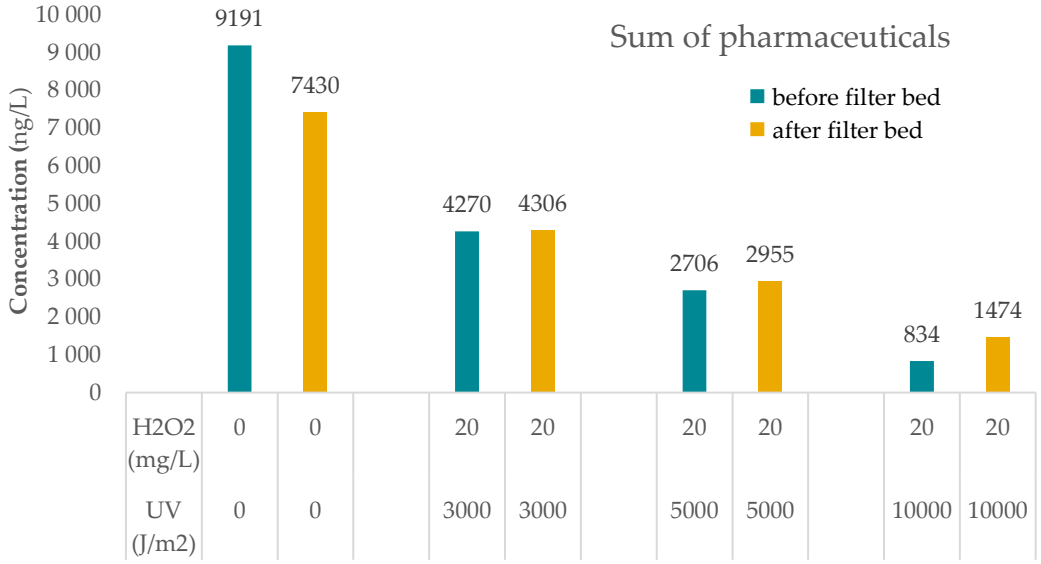

Figure 6. Effect of filter bed on pharmaceutical concentrations.

Results from Figure 6 further indicate lower concentrations of pharmaceuticals before the filter when applying actual UV and H_2O_2 doses. However, several aspects have to be considering in the interpretation of test results:

- Some analysed concentrations before and after the filter bed are very low, for several substances below or around LOQ or LOD.
- Samples collected before the filter bed may contain hydrogen peroxide, even though catalase was added. This may not be accounted for in the used lab methods for determining pharmaceuticals or have caused further reaction. Samples collected after the filter bed contain no or only very low hydrogen peroxide as the filter bed removed the H_2O_2.
- Samples collected before the filter bed contain catalase added to stop the reaction of H_2O_2. How much catalase may influence the sample preparation, recovery rates and analytical method is not clear. This may not be accounted for in the used lab methods. Samples collected after the filter bed contain no catalase.

Considering these aspects, a more detailed investigation on the effect of filter bed after UV/H_2O_2 is recommended. As the treatment performance would be evaluated using samples after the filter bed, this does however not impact the overall performance of the UV/H_2O_2 technique as eventual negative reductions in the filter bed would be incorporated in the overall treatment assessment of the UV/H_2O_2-system.

4.3 Estimated cost of full-scale implementation

As for ozonation, the main cost aspect for operation of UV/H_2O_2 systems is the use of electricity. In addition, the H_2O_2 consumption has to be considered. Based on the pilot tests, a first energy calculation can be made considering the UV-lamp power usage. As only the high transmittance lamp with a single 360 W unit was utilized, this effect can be divided by measured water flows to obtain an effective energy use per cubic meter treated wastewater. Considering that a full-scale implementation would be more energy-efficient, corresponding full-scale application would

probably use at least 20 % less energy if other conditions are considered normal. Dosing H_2O_2 and pumping of water to be treated would add some extra energy requirements.

For the pilot test this would imply energy demands of 0.15 kWh/m³ for 3 000 J/m², 0.3 kWh/m³ for 5 000 J/m² and 0.56 kWh/m³ for 10 000 J/m², respectively. This can be compared to an energy demand of about 10 kWh/kg ozone produced if using ozonation. Considering the example from the bench-scale test with an ozone dose of 6 g O_3/m³, this would imply an energy demand of 0.06 kWh/m³. From Table 2 it becomes clear that 6 g O_3/m³ would not be enough to remove pharmaceuticals enough for this water. Oxazepam is actually only removed by 30% (Table A2, Appendix) and an ozone dose of at least 10-12 g O_3/m³ would be required for a similar reduction as for the UV/H_2O_2 combination 5 000 J/m² and 50 mg H_2O_2/L. The energy needed to produce this amount of ozone would then be 0.12 kWh/m³, which is still significantly lower than the energy required to provide a UV-effect of 5 000 J/m².

Scheideler et al. (2011) estimated the total treatment costs (CAPEX plus OPEX) for AOP treatment with UV/H_2O_2 at a larger WWTP, i.e. 10 000 m³/h, to below 0.04 €/m³, without providing specific UV and H_2O_2 dosages used for the calculations. This is based on energy cost of 0.08 €/kWh and costs for H_2O_2 of 0.4 €/kg. Cost for CAPEX, maintenance and spares is according to the authors based on data from existing plants but without referring to those. Karl and Dolling (2018) are suggesting specific cost for a UV/H_2O_2 treatment of the effluent from a medium size WWTP (here 1250 m³/h) between 0.08-0.13 €/m³. Both cost calculations would place the UV/H_2O_2 in a position similar to other advanced technologies mostly considered e.g. in Sweden, Germany and Switzerland. A recent study focusing on Swedish WWTPs suggest cost for removal of 80% of pharmaceuticals with ozonation, activated carbon and both technologies in combination for medium and large WWTPs to be between 0.015 – 0.055 €/m³ (Baresel et al., 2017a). The assumed energy cost was then of 0.8 SEK/kWh, which with current exchanges rates corresponds to about 0.075 €/kWh and thus comparable to Scheideler et al. (2011). However, as for other technologies, the actual required dosages of ozone, activated carbon, UV and H_2O_2 will influence costs. The higher the required dosages are, the higher the operational costs. In addition, cost can vary significantly and depend on assumptions and simplifications made.

van Remmen UV Technology performed an updated cost calculation for a full-scale implementation based on current project results and similar conditions as used by Baresel et al. (2017a) and currently related large-scale (~100 m³/h) during one month at Sundet WWTP, Växjö Sweden. In specific this implies a constant design flow of 1 400 m³/h with a transmittance of 60 %, a UV-dose of 5 000 J/m² and a H_2O_2-dose of 20 mg/L. H_2O_2 costs of 700 € per dry metric ton and a price of electricity of 0.075 €/kWh were used. Results of this calculation indicate an initial investment cost (CAPEX) of about 2 M€ for the UV/H_2O_2 installation plus about 80 000 € for buildings and pumps. Operating costs (OPEX) are estimated to about 790 000 € per year including replacement of lamps every 1.5 years and replacement of other equipment according to industrial standards. This corresponds to about 0.064 €/m³ of which the energy consumption accounts for about 35 %. Increasing or decreasing energy prices can thus have a significant impact on operational costs. Further, a different transmittance of the water to be treated and required UV-doses affect operational costs related to energy use. Specific treatment costs per m³ considering both OPEX and CAPEX of a 10-year period assuming full depreciation of the installation and peripherals are calculated to < 0.08 €/m³. Considering that this costs calculation is based on a constant design flow and including some simplifications, the calculated cost may be considered comparable to Karl and Dolling (2018).

Note that a required polishing of the treated water either by UV/H_2O_2 or ozonation are commonly not included in these cost estimations. The lifetime of the catalytical bed as used in the pilot tests at

Hammarby Sjöstadsverk or other polishing techniques such as activated carbon may be an important operational cost aspect not included in these calculations.

5 Conclusions and recommendations

The conducted test with the advanced oxidation process consisting of UV and hydrogen peroxide (UV/H_2O_2) showed good removal efficiencies for all pharmaceuticals observed in the effluent of Stockholm's largest WWTP. A clear dose-response behaviour could be observed that can be used targeting various substances depending on removal targeted definition. The connected catalytical filter was able to remove all remaining process reagents and potential toxic by-products.

The cost evaluation of the technique reveals that UV/H_2O_2 applications may still not be competitive with other technologies such as ozonation or activated carbon as updated cost calculations indicate higher specific cost per treated m^3. This is true even at high required ozone dosage or combination of ozonation and activated carbon in order to remove specific substances.

However, based on the project results it is understood that the gap towards other removal techniques is not that wide and that several advantages of the UV/H_2O_2 technology may favour its application in various cases. For this, further investigations should be conduction including following but not exclusive application of UV/H_2O_2:

- if high removal efficiencies for specific substances are required that would increase both cost of competing technologies and risk to produce harmful by-products by e.g. very high ozone dosages.
- if high removal efficiencies for specific substances are required and conditions such as bromide/bromate concentrations in the wastewater exclude the use of e.g. ozonation. However, the bromate production using UV/H_2O_2 needs further studies.
- to achieve a better combined effect of micropollutant removal and disinfection. This as the disinfection abilities of active carbon and ozonation may be limited especially at commonly applied doses.
- to achieve a removal of antibiotic resistance bacteria (ARB) and antibiotic resistance genes (ARG) that may be difficult to remove by other technologies.

To increase the resource-efficiency of UV/H_2O_2 following aspects require further investigation:

- Lifetime and environmental performance of the filter bed material. This has an impact on both lifecycle costs and environmental impacts depending on the materials origin, production and handling.
- Intermediate process application as applied for e.g. ozonation to provide process integration synergies and an overall improved resource efficiency.
- Quality of treated water and how this affects the resource efficiency of UV/H_2O_2.
- Treatment of various specific wastewaters such as sewage from hospitals containing specific substances at high concentrations and resistant bacteria.
- Applications where an efficient removal of a broad range of pharmaceuticals is required.

6 References

Alcala Borao, R. 2015. Oxidation of pharmaceuticals by chlorine dioxide in wastewater effluent. Examensarbete LWR - EX - 2015:16, Kungl tekniska Högskolan KTH & IVL Svenska Miljöinstitutet, Stockholm.

Bader, H. och Hoigné, J. 1981. Determination of ozone in water by the indigo method. Water Research 15(4), 449-456.

Baresel, C., Ek, M., Ejhed, H., Allard, A.S., Magnér, J., Dahlgren, L., Westling, K., Wahlberg, C., Fortkamp, U., Söhr, S., Harding, M., Fång, J., Karlsson, J. 2019a. Sustainable Treatment Systems for Removal of Pharmaceutical Residues and Other Priority Persistent Substances. Water Science and Technology, 79(3), 537-543.

Baresel, C.; Harding, M.; Fång, J. 2019b. Ultrafiltration/Granulated Active Carbon-Biofilter: Efficient Removal of a Broad Range of Micropollutants. Appl. Sci. 2019, 9, 710.

Baresel, C., Malovanyy, A. 2019. Införande av läkemedelsrening vid Himmerfjärdsverket - Sammanställning av tidigare undersökningar vid Himmerfjärdsverket. IVL Svenska Miljöinstitutet, Rapport B2239.

Baresel, C., Ek, M., Ejhed, H., Allard, A.-S., Magnér, J., Dahlgren, L., Westling, K., Wahlberg, C., Fortkamp, U., Söhr, S. 2017a. Handbok för rening av mikroföroreningar vid avloppsreningsverk - Planering och installation av reningstekniker för läkemedelsrester och andra mikroföroreningar. Slutrapport SystemLäk projekt. IVL Svenska Miljöinstitutet, Rapport B2288.

Baresel, C., Ek, M., Harding, M., Magnér, J., Allard, A.-S., Karlsson, J. 2017b. Kompletterande tester för en resurseffektiv avancerad rening av avloppsvatten. Delrapport SystemLäk projekt. IVL Svenska Miljöinstitutet, Rapport B2287.

Baresel, C., Westling, K., Samuelsson, O., Andersson, S., Royen, H., Andersson, S., Dahlén, N. 2017c. Membrane Bioreactor Processes to Meet Todays and Future Municipal Sewage Treatment Requirements? Int. J. Water Wastewater Treat. 3(2).

Baresel, C., Magnér, J., Magnusson, K., Olshammar, M. 2017d. Tekniska lösningar för avancerad rening av avloppsvatten. IVL Svenska Miljöinstitutet, Rapport C235.

Baresel, C., Malmborg, J., Ek, M., Sehlén, R. 2016. Removal of pharmaceutical residues using ozonation as intermediate process step at Linköping WWTP, Sweden. Water Science and Technology, 73(8), 2017-2024.

Baresel, C., Dahlgren, L., Nikolic, A., de Kerchove, A., Almemark, M., Ek, M., Harding, M., Ottosson, E., Karlsson, J., Yang, J. 2015a. Reuse of treated wastewater for nonpotable use (ReUse) - Final Report. IVL Swedish Environmental Research Institute, report B2219.

Baresel, C., Dahlgren, L., Almemark, M., Lazic, A. 2015b. Municipal wastewater reclamation for non-potable reuse – Environmental assessments based on pilot-plant studies and system modelling. Water Science & Technology, 72(9), 1635-1643.

Baresel, C., Cousins, A.P., Hörsing, M., Ek, M., Ejhed, H., Allard, A.S., Magnér, J., Westling, K., Wahlberg, C., Fortkamp, U., Söhr, S. 2015c. Pharmaceutical residues and other emerging

substances in the effluent of sewage treatment plants - Review on concentrations, quantification, behaviour, and removal options. IVL Swedish Environmental Research Institute, Report 2226, Stockholm.

Baresel, C., Ek, M., Harding, M. och Bergström, R. 2014. Behandling av biologiskt renat avloppsvatten med ozon eller aktivt kol. IVL rapport B2203.

Bergström, R., Bengtsson, L., Fortkamp, U., Berg, S. 2014. Membranfiltrering och fällning för behandling av kommunalt avloppsvatten - En innovativ metod för högre resurseffektivitet. IVL Rapport C48.

Ek, M., Baresel, C., Magnér, J., Bergström, R., Harding, M. 2014. Activated carbon for the removal of pharmaceutical residues from treated wastewater. Water Science and Technology, 69(11), 2372-2380.

Ek, M., Bergström, R., Magnér, J., Harding, H. Baresel, C. 2013. Activated carbon to remove residues from the treated wastewater. Report nr.: B2089, IVL Swedish Environmental research Institute, Stockholm, (in Swedish).

Graae, L., Magnér, J., Ryding, S.O., Westergren, R. 2017. Miljönyttan av uppströmsåtgärder för minskad spridning av läkemedel till miljön. IVL Svenska Miljöinstitutet, Rapport B2280.

Karl, P., Dolling, E. 2018. Weitergehende Abwasserreinigungv mit der Aktivkoks-Festbett-Biologie und nachfolgender UV-Behandlung mit H2O2-Oxidation. KA - Korrespondenz Abwasser, 5, 398-412. Doi:10.3242/kae2018.05.002

Lazic, A., de Kerchove, A., Windsor, R., Baresel, C., Dahlgren, L. 2017. Novel approach defines sustainability of non-potable water reuse treatment. Water reuse & desalination, 8(2), 17-19.

Lekkerkerker-Teunissen, K., Benotti, M.J., Snyder, S.A., van Dijk, H.C. 2012. Transformation of atrazine, carbamazepine, diclofenac and sulfamethoxazole by low and medium pressure UV and UV/H2O2 treatment. Separation and Purification Technology 96, 33–43. https://doi.org/10.1016/j.seppur.2012.04.018

Mparmpagianni, S. 2016. Powdered activated carbon (PAC) addition in membrane bioreactor (MBR) for increased removal of organic pollutants in municipal wastewater. Dept. of Environmental Science and Analytical Chemistry, Division of Analytical and Toxicological Chemistry, Stockholm University IVL Swedish Environmental Research Institute.

Murad, H. 2018. Membranbioreaktorer och deras förmåga att avlägsna prioriterade mikroföroreningar. Examensarbete UPTEC W18 048, Sveriges Lantbruksuniversitet SLU, Uppsala.

Scheideler, J., 2011. Combination of O3/H2O2 and UV for multiple barrier micropollutant treatment and bromate formation control – an economic attractive option. Water Practice & Technology 6, 1–2. https://doi.org/10.2166/wpt.2011.0063

Sehlén, R., Malmborg, J., Baresel, C., Ek, M., Magnér, J., Allard, A.-S., Yang, J. 2015. Pilotanläggning för ozonoxidation av läkemedelsrester i avloppsvatten vid tekniska verken i Linköping AB. IVL Rapport B 2218.

Somathilake, P., Dominic, J.A., Achari, G., Langford, C.H., Tay, J.-H. 2018. Influence of UV dose on the UV/H 2 O 2 process for the degradation of carbamazepine in wastewater. Environmental Technology 1–9. https://doi.org/10.1080/09593330.2018.1464065

Wahlberg, C., Björlenius, B., Paxéus, N. 2010. Läkemedelsrester i Stockholms vattenmiljö - Förekomst, förebyggande åtgärder och rening av avloppsvatten (No. ISBN 978-91-633-6642-0). Stockholm Vatten AB.

WHO 2014. Antimicrobial resistance: global report on surveillance. World Health Organization, Geneva, Switzerland. ISBN 978 92 4 156474 8

7 Appendix

Table A1. Analysed substances.

Substance	Mode of action	Substance
Pharmaceuticals		*Antibiotics*
Amlodipine	*Antihypertensive*	Amoxicillin
Atenolol	*Antihypertensive*	Ampicillin
Bisoprolol	*Antihypertensive*	Benzylpenicillin
Caffeine	*Stimulant*	Ciprofloxacin
Carbamazepine	*Sedative*	Clarithromycin
Citalopram	*Antidepressant*	Clindamycin
Diclofenac	*Anti-inflammatory*	Doxycycline
Fluoxetine	*Antidepressant*	Erythromycin
Furosemide	*Diuretic*	Fusidic acid
Hydrochlorothiazide	*Antihypertensive*	Linezolid
Ibuprofen	*Anti-inflammatory*	Metronidazole
Ketoprofen	*Anti-inflammatory*	Moxifloxacin
Metoprolol	*Antihypertensive*	Norfloxacin
Naproxen	*Anti-inflammatory*	Rifampicin
Oxazepam	*Sedative*	Sulfamethoxazole
Paracetamol	*Analgesic*	Tetracycline
Propranolol	*Antihypertensive*	Trimethoprim
Ramipril	*Antihypertensive*	
Ranitidine	*Antiulcer*	*Hormones*
Risperidone	*Antipsychotic*	Estrone E1
Sertralin	*Antidepressant*	Estradiol E2
Simvastatin	*Lipid-regulating*	Etinylestradiol EE2
Terbutaline	*Asthma medication*	
Warfarin	*Anticoagulant*	

Table A2. Pharmaceutical concentrations during bench-scale tests (ng/L).

	Influent, WWTP effluent	UV/H2O2 (200 Wh/m³ & 10 g/m³)	*Reduction (%)*	UV/H2O2 (300 Wh/m³ & 25 g/m³)	*Reduction (%)*	UV/H2O2 (200 Wh/m³ & 40 g/m³)	*Reduction (%)*	UV/H2O2 (300 Wh/m³ & 40 g/m³)	*Reduction (%)*	Fe/H2O2, HRT 10 min (40 mg/m³ & 25 g/m³)	*Reduction (%)*	Fe/H2O2, HRT 20 min (40 mg/m³ & 25 g/m³)	*Reduction (%)*	O_3 (6 g/m³)	*Reduction (%)*
Amlodipine	89	62	*30*	1	*99*	44	*50*	5	*95*	1	*99*	1	*99*	6	*93*
Atenolol	246	210	*15*	19	*92*	130	*47*	2	*99*	0	*100*	0	*100*	154	*37*
Bisoprolol	105	79	*25*	1	*99*	42	*60*	0	*100*	0	*100*	0	*100*	57	*46*
Caffeine	52	75	*-44*	32	*39*	44	*16*	1	*99*	-6	*112*	-5	*110*	19	*63*
Carbamazepine	312	200	*36*	-3	*101*	110	*65*	-6	*102*	-6	*102*	-6	*102*	11	*97*
Citalopram	270	190	*30*	3	*99*	100	*63*	1	*100*	0	*100*	0	*100*	96	*64*
Diclofenac	654	110	*83*	0	*100*	58	*91*	0	*100*	2	*100*	1	*100*	10	*98*
Fluoxetine	12	4	*65*	0	*97*	3	*75*	0	*97*	0	*100*	0	*100*	5	*57*
Furosemide	1497	990	*34*	13	*99*	470	*69*	0	*100*	-8	*101*	-6	*100*	1	*100*
Hydrochlorothiazide	1022	670	*34*	14	*99*	500	*51*	1	*100*	1	*100*	1	*100*	600	*41*
Ibuprofen	175	130	*26*	7	*96*	77	*56*	3	*98*	1	*100*	2	*99*	127	*27*
Ketoprofen	204			2	*99*			2	*99*	0	*100*	0	*100*	155	*24*
Metoprolol	1595	1200	*25*	65	*96*	670	*58*	3	*100*	-1	*100*	-1	*100*	868	*46*
Naproxen	522	310	*41*	0	*100*	180	*65*	0	*100*	0	*100*	1	*100*	23	*95*
Oxazepam	297	240	*19*	11	*96*	160	*46*	0	*100*	-1	*100*	0	*100*	212	*29*
Paracetamol	55	29	*47*	8	*85*	22	*60*	4	*93*	13	*76*	16	*71*	15	*73*
Propranolol	107	58	*46*	0	*100*	29	*73*	0	*100*	0	*100*	0	*100*	6	*94*
Ramipril	4			1	*85*			1	*86*	0	*100*	0	*101*	2	*53*
Ranitidine	364	210	*42*	1	*100*	62	*83*	0	*100*	-1	*100*	-1	*100*	0	*100*
Risperidone	0.39			0.05	*86*			-0.05	*114*	-0.16	*142*	-0.18	*146*	-0.11	*127*
Sertralin	19	11	*41*	0	*99*	10	*46*	0	*98*	1	*96*	1	*92*	8	*56*
Simvastatin	1			58	*-5087*			13	*-1102*	-3	*335*	-5	*547*	-4	*470*
Terbutaline	39	8	*79*	0	*99*			1	*98*	1	*97*	1	*98*	0	*99*
Warfarin	8	11	*-46*	0	*99*	6	*20*	0	*100*	0	*100*	0	*100*	0	*100*
Sum	**7647**	**4798**	***37***	**234**	***97***	**2717**	***64***	**31**	***100***	**-6**	***100***	**0**	***100***	**2371**	***69***

Table A3. Concentrations of metals in the test water.

Metal	**Al**	**As**	**B**	**Ba**	**Ca**	**Cd**	**Co**	**Cr**	**Cu**	**Fe**	**K**	**Mg**	**Mn**	**Mo**	**Na**
Concentration (mg/L)	0.009	<0.01	0.04	0.005	43	<0.001	0.002	<0.003	<0.006	0.12	17	7.1	0.04	<0.003	68

Metal	**Ni**	**P**	**Pb**	**Pd**	**Pt**	**Sn**	**S**	**Sb**	**Si**	**Sr**	**Ti**	**V**	**Zn**	**Zr**
Concentration (mg/L)	0.006	0.1	<0.003	<0.03	<0.1	<0.003	29	<0.02	3.2	0.1	<0.003	<0.003	<0.03	<0.004

Table A4. Pharmaceutical concentrations during pilot tests (ng/L).

	Influent	UV 0 J/m² H_2O_2 [g/m³]	UV 3000 J/m² H_2O_2 [g/m³]			UV 5 000 J/m² H_2O_2 [g/m³]			UV 10 000 J/m² H_2O_2 [g/m³]		
		0	11	22	44	12	22	54	11	22	50
Amlodipine	95	120	78	46	34	38	34	34	10	10	10
Atenolol	160	140	110	80	60	100	78	56	84	57	46
Bisoprolol	96	84	56	39	30	48	36	28	68	26	26
Caffeine	960	280	710	590	510	580	550	550	550	410	390
Carbamazepine	280	280	200	130	82	140	82	82	82	25	25
Citalopram	340	340	17	17	18	9	3	3	14	9	3
Diclofenac	760	650	61	52	40	30	30	9	9	9	9
Fluoxetine	44	38	1	1	1	3	1	3	1	1	3
Furosemide	1900	1800	840	610	300	480	250	120	150	40	40
Hydrochlorothiazide	1300	960	770	600	440	510	380	220	260	110	35
Ibuprofen	560	400	330	270	180	300	160	69	79	27	16
Ketoprofen	340	190	5	5	5	5	5	5	5	5	5
Metoprolol	1300	1100	790	570	460	750	560	420	640	430	370
Naproxen	1500	890	540	350	200	280	130	50	52	7	7
Oxazepam	1800	1400	1200	800	570	840	520	270	850	190	170
Paracetamol	5	3	1	3	3	1	3	1	5	1	1
Propranolol	100	110	66	52	41	72	58	41	40	38	35
Ramipril	30	30	30	30	30	30	30	30	30	30	30
Ranitidine	250	260	17	10	7	4	3	4	15	3	3
Risperidone	15	15	15	15	15	15	15	15	15	15	15
Sertralin	89	84	22	20	20	18	18	17	47	16	16
Simvastatin	4	4	12	12	12	4	4	4	4	12	4
Terbutaline	5	6	5	3	3	3	3	3	3	1	1
Warfarin	7	7	7	2	2	7	2	2	7	2	2
Sum	**11940**	**9191**	**5883**	**4306**	**3063**	**4267**	**2955**	**2036**	**3020**	**1474**	**1262**

XXX – LOQ; XXX - LOD

Table A5. Results for antibiotics from pilot tests.

	Influent	UV 0 J/m² H_2O_2 [g/m³]	UV 3000 J/m² H_2O_2 [g/m³]			UV 5 000 J/m² H_2O_2 [g/m³]			UV 10 000 J/m² H_2O_2 [g/m³]		
		0	11	22	44	12	22	54	11	22	50
Ampicillin	*	*	*	*	*	*	*	*	*	*	*
Benzylpenicillin	*	*	*	*	*	*	*	*	*	*	*
Ciprofloxacin	*	**	*	*	*	*	*	*	*	*	*
Clarithromycin	17	14	**	**	**	**	**	**	**	**	**
Clindamycin	14	14	10	8	6	9	8	6	4	4	3
Doxycycline	*	*	*	*	*	*	*	*	*	*	*
Erythromycin	11	10	7	5	5	4	4	4	5	4	5
Fusidic acid	*	*	*	*	*	*	*	*	*	*	*
Linezolid	*	*	*	*	*	*	*	*	*	*	*
Metronidazole	7	7	6	4	4	5	3	**	*	**	*
Moxifloxacin	*	*	*	*	*	*	*	*	*	*	*
Norfloxacin	*	**	*	*	*	*	*	*	*	*	*
Rifampicin	*	*	*	*	*	*	*	*	*	*	*
Sulfamethoxazole	33	16	**	**	**	*	**	*	**	*	*
Tetracycline	*	*	*	*	*	*	*	*	*	*	*
Trimethoprim	13	14	10	**	**	**	**	**	**	**	**

* substance cannot be detected, content is below the detection limit (LOD S / N = 3)

** substance can be detected but not quantified, the content is between the detection limit (LOD) and the quantification limit (LOQ S / N = 10)

Table A6. Effect of filter bed on pharmaceutical concentrations.

	UV 0 J/m²		UV 3000 J/m²		UV 5000 J/m²		UV 10 000 J/m²	
	H_2O_2 0 g/m³		H_2O_2 20 g/m³		H_2O_2 20 g/m³		H_2O_2 20 g/m³	
	before filter	after filter	before filter	after filter	before filter	after filter	before filter	after filter
Amlodipine	120	**	*	46	**	**	*	*
Atenolol	140	110	73	80	41	78	**	57
Bisoprolol	84	47	32	39	15	36	*	26
Caffeine	280	**	650	590	710	550	320	410
Carbamazepine	280	250	129	130	**	**	*	*
Citalopram	340	*	125	17	62	*	10	9
Diclofenac	650	620	43	52	**	**	*	*
Fluoxetine	38	**	14	*	7	*	**	*
Furosemide	1800	1800	580	610	240	250	*	*
Hydrochlorothiazide	960	970	580	600	330	380	92	110
Ibuprofen	400	380	290	270	160	160	18	27
Ketoprofen	190	190	*	*	*	*	*	*
Metoprolol	1100	710	500	570	250	560	44	430
Naproxen	890	850	330	350	110	130	*	*
Oxazepam	1400	1300	730	800	520	520	**	190
Paracetamol	3	4	*	**	**	**	*	*
Propranolol	110	60	42	52	20	58	4	38
Ramipril	*	*	*	*	*	*	*	*
Ranitidine	260	3	30	10	10	3	*	3
Risperidone	*	*	*	*	*	*	*	*
Sertralin	84	**	38	20	23	18	**	16
Simvastatin	*	*	**	**	*	*	*	**
Terbutaline	6	7	3	**	**	**	*	*
Warfarin	**	**	**	*	*	*	*	*

* substance cannot be detected, content is below the detection limit (LOD S / N = 3)
** substance can be detected but not quantified, the content is between the detection limit (LOD) and the quantification limit (LOQ S / N = 10)

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