Ozonation in Advanced Wastewater Treatment

Practical Aspects and Development of a Prediction Tool for Pharmaceutical Removal

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DEPARTMENT OF CHEMICAL ENGINEERING | LUND UNIVERSITY

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Laboratory-scale ozonation experiments showed comparable results regarding pharmaceutical removal when the ozone dose was normalized to the COD and dissolved organic carbon (DOC). Dissolved matter had a greater effect on the removal efficiency than particles at moderately elevated concentrations of ~25 mg SS/L. However, extremely elevated concentrations of particles, of ~100 mg SS/L, had greater negative effects on slow-reacting pharmaceuticals than fast-reacting ones. A tool was developed for the prediction of the removal of pharmaceuticals, using the parameters typically used in wastewater modelling and monitoring (COD and SS) as input. The predictions agreed with empirical data from pilot-scale ozonation, with deviations of less than 10% for several pharmaceuticals. Such a COD/SS-based tool could contribute to a more practical approach to predicting pharmaceutical removal at WWTPs.

The results of the experiments on the microbial reduction of bromate indicated the potential of reducing the formed bromate in bromide-rich ozonated wastewater using the denitrifying biofilm process after ozonation. A reduction of 80% of the initial bromate to bromide using carriers from a full-scale moving-bed biofilm reactor could be achieved after 60 minutes.

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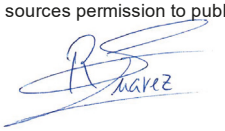
Signature 

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Remember: things can be bad, and getting better

- *Hans Rosling*

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Preface

The studies presented here are the result of an industrial PhD project carried out in collaboration with Sweden Water Research AB and the Water and Environmental Engineering Group at the Department of Chemical Engineering at Lund University. The research was conducted within the framework of the BONUS CLEANWATER project, which has received funding from BONUS (Art. 185), funded jointly by the EU and Innovation Fund Denmark, Sweden's Innovation Agency VINNOVA, and the German Ministry for Education and Science (BMBF). Part of the research was carried out within the project Less is More, which was financed by the Interreg South Baltic Programme 2014-2020 through the European Regional Development Fund, and by the Swedish Agency for Marine and Water Management.

This licentiate thesis is a compilation of studies on wastewater ozonation for the removal of organic micropollutants. The work included pilot- and laboratory-scale ozonation experiments and laboratory-scale denitrifying biofilm experiments.

Abstract

Pharmaceuticals that are not completely metabolized in the human body are excreted in wastewater and may find their way into surface waters, where they can have harmful effects on aquatic fauna and flora. The implementation of ozonation at wastewater treatment plants (WWTPs) can reduce the amount of pharmaceuticals discharged to the environment. Despite the technology readiness level of ozone treatment, some practical aspects remain to be addressed to facilitate the installation of full-scale ozonation units at WWTPs.

In this work, the ozonation process was investigated to optimize the treatment and to facilitate its full-scale implementation. The operating conditions and properties of the wastewater were investigated on pilot and laboratory scale to determine their effects on removal efficiency. In addition, a tool was developed based on chemical oxygen demand (COD) and suspended solids (SS) for the prediction of ozone demand and pharmaceutical removal. Finally, the formation of the undesired by-product bromate during ozonation, and its subsequent reduction using a denitrifying biofilm process was evaluated on laboratory scale.

No significant effects were observed on the efficiency of pharmaceutical removal when varying the hydraulic retention time, ozone dispersion method or wastewater temperature in pilot-scale ozonation experiments. Shorter hydraulic retention times allow more compact ozonation units, reducing both capital expenditure and space requirements. Ozonation performed slightly better after post-precipitation than after the activated sludge process, which led to further studies on the effects of SS.

Laboratory-scale ozonation experiments showed comparable results regarding pharmaceutical removal when the ozone dose was normalized to the COD and dissolved organic carbon (DOC). Dissolved matter had a greater effect on the removal efficiency than particles at moderately elevated concentrations of ~25 mg SS/L. However, extremely elevated concentrations of particles, of ~100 mg SS/L, had greater negative effects on slow-reacting pharmaceuticals than fast-reacting ones. A tool was developed for the prediction of the removal of pharmaceuticals, using the parameters typically used in wastewater modelling and monitoring (COD and SS) as input. The predictions agreed with empirical data from pilot-scale ozonation, with deviations of less than 10% for several pharmaceuticals. Such a COD/SS-based tool could contribute to a more practical approach to predicting pharmaceutical removal at WWTPs.

The results of the experiments on the microbial reduction of bromate indicated the potential of reducing the formed bromate in bromide-rich ozonated wastewater using the denitrifying biofilm process after ozonation. A reduction of 80% of the initial bromate to bromide using carriers from a full-scale moving-bed biofilm reactor could be achieved after 60 minutes.

Populärvetenskaplig sammanfattning

Cirka 4000 aktiva läkemedelsubstanser används världen runt och under de senaste åren har halter av läkemedelsrester detekterats i sjöar och hav och även i fiskar och musslor. Läkemedelsresterna utgörs bland annat av smärtstillande och antiinflammatoriska ämnen, antibiotika, kardiovaskulära och ångestdämpande medel, p-piller och kontrastmedel. De kan vara toxiska och orsaka olika typer av problem för växt- och djurliv. Förekomsten av läkemedelsrester i kommunala avloppsreningsverk kommer huvudsakligen från hushållsavloppsvatten. Eftersom avloppsreningsverk i grund och botten inte är byggda för att bryta ner eller separera läkemedel, kommer vissa av dessa ämnen passera, helt eller delvis, oförändrade och transporteras vidare med renat avloppsvatten till sjöar och vattendrag. Läkemedel är designade för att vara stabila och därför är många persistenta, det vill säga de är svåra att bryta ner och risken är därmed att de ackumuleras i kretsloppet.

För att förebygga att läkemedelsrester ackumuleras och att de förekommer i råvattentäkter till dricksvattenproduktion, där de utgör en potentiell risk, kan man vidta olika åtgärder utifrån olika perspektiv. Uppströmsarbete är åtgärder som berör tillverkning, användning och återlämning av läkemedel för att förhindra förekomst i kommunala avlopp, men uppströmsarbete kommer inte helt kunna förhindra att läkemedelsrester hamnar i avloppet så länge vi människor använder mediciner. Därför behövs avancerad rening för att avskilja läkemedelsrester.

Tekniker för rening från läkemedelsrester kan baseras på två olika principer: avskiljning och nedbrytning. Läkemedelsrester kan avskiljas från avloppsvatten med hjälp av membranfiltrering med liten porstorlek eller med aktivt kol, där läkemedel adsorberas på kolets yta. Nedbrytning kan genomföras biologiskt eller med exempelvis ozon som är ett kraftigt oxidationsmedel. Även om ozonering, som är i fokus i min studie, är en väl utvecklad teknik, finns det fortfarande utmaningar som ska hanteras. Det kan vara förutsägelser av vilken reningsgrad man uppnår med en viss ozondos, hur förändringar i sammansättningen av avloppsvatten påverkar den ozonmängd som krävs eller hantering av oönskade och toxiska biprodukter som bildas när ozon reagerar med avloppsvatten. Ett sådant exempel är bromat som bildas ur bromid.

Ett delmål med den här studien var att studera hur olika driftförhållanden och olika sammansättning av avloppsvatten påverkar vilken ozonmängd som krävs för avskiljning av olika läkemedel. Studien visade att man med enkla laboratorieförsök kan uppskatta reningsgrad och ozonbehov genom att använda ett enkelt beräkningsverktyg som utgår från innehåll av organiskt material och mängden partiklar. Resultaten visade att för ozonbehovet hade variationer i halten organiskt material större påverkan än normalt förekommande halter av partiklar. Om

partikelhalten ökar till följd av olika driftstörningar kan verktyget användas för att uppskatta det ökade ozonbehovet. Ett annat mål var att studera möjligheten att avlägsna bromat som bildas under ozonering. Resultaten visade att bromat kan reduceras i ett rimligt tidsspann med hjälp av en biologisk reningsprocess.

Sammanfattningsvis, har jag med min forskning tagit fram ett verktyg som olika avloppsreningsverk på ett enkelt sätt kan använda för att med befintliga data förutsäga ozonbehov och reningsgrad av läkemedelsrester vid ozonering. Det betyder bland annat att man kan uppskatta energiåtgång och reningsresultat utan att genomföra kostsamma pilotförsök.

Resumen de divulgación científica

Alrededor de 4000 compuestos farmacéuticos diferentes son utilizados en todo el mundo. Durante los últimos años, se han llevado a cabo estudios que han detectado trazas de estos compuestos en el medio ambiente acuático, llegando incluso a peces y moluscos. Estos compuestos farmacéuticos se clasifican en analgésicos, antiinflamatorios, antibióticos, agentes cardiovasculares, ansiolíticos, anticonceptivos y medios de contraste de rayos X entre otros. En el medio natural, la presencia de estos compuestos puede tener efectos tóxicos y generar distintos tipos de problemas a la fauna y flora. También se han detectado en estaciones depuradoras de aguas residuales, llegando a ellas principalmente a través de las aguas residuales domésticas. Dado que las estaciones depuradoras de aguas residuales no fueron inicialmente diseñadas para la separación o degradación de compuestos farmacéuticos, algunos de ellos atraviesan total o parcialmente inalterados las depuradoras y son transportados a través de aguas residuales tratadas al medio acuático. Además, los compuestos farmacéuticos están diseñados para tener una alta estabilidad, por lo que muchos de ellos tienen carácter persistente, es decir, son difíciles de degradar y terminan acumulándose en el medio acuático.

Para prevenir que los compuestos farmacéuticos continúen acumulándose en el medio ambiente acuático y que puedan estar presentes en los recursos para la producción de agua potable, pudiendo suponer un potencial riesgo para la salud humana, pueden establecerse medidas de distinta tipología. Por ejemplo, medidas de control que afectan a la producción, uso y deposición de los compuestos farmacéuticos y evitan que los residuos de estos lleguen a las estaciones depuradoras de aguas residuales municipales. Sin embargo, la implementación de dichas medidas no es capaz de prevenir completamente que los residuos de compuestos farmacéuticos lleguen a las aguas residuales, debido a que el consumo de compuestos farmacéuticos es necesario para prevenir y curar enfermedades. Por esta razón, es necesario la implantación de tratamientos avanzados de aguas residuales para evitar la llegada al medio acuático de estos compuestos a través de las aguas residuales.

Existen diferentes tecnologías de tratamiento para la eliminación de compuestos farmacéuticos presentes en aguas residuales que generalmente están basadas en dos principios: separación y degradación. Estos compuestos se pueden separar de las aguas residuales mediante la filtración a través de membranas con un tamaño de poro menor a los compuestos farmacéuticos o por adsorción en agentes como el carbón activo. Por otro lado, la degradación puede llevarse a cabo por procesos biológicos o mediante agentes oxidantes, como el ozono. Aunque el tratamiento con ozono, sobre el que esta tesis se centra, es una tecnología madura, todavía quedan algunos retos por resolver. Estos retos pueden incluir la predicción del grado de

eliminación de farmacéuticos a distintas dosis de ozono, el efecto en la demanda de ozono debido a cambios en la composición del agua residual o evitar la generación de subproductos tóxicos no deseados que se forman cuando el ozono reacciona con el agua residual, como por ejemplo el bromato, un subproducto que se forma principalmente a partir del bromuro.

Uno de los principales objetivos de esta tesis ha sido el estudio del efecto de distintas condiciones de operación y composiciones del agua residual en la cantidad de ozono necesaria para la eliminación de distintos residuos de compuestos farmacéuticos. Con el presente estudio, se ha demostrado que con ensayos a escala laboratorio se puede predecir el grado de eliminación y la demanda de ozono a través de una herramienta de cálculo basada en el contenido en materia orgánica y partículas. Los resultados revelaron que la variación típicamente observada en el contenido de materia orgánica en las aguas residuales tiene mayores efectos en el consumo de ozono que el contenido habitual de partículas observado en las aguas residuales. En caso de que el contenido de partículas aumente como resultado de distintas alteraciones en el proceso de depuración, el modelo puede ser utilizado para predecir el aumento de las necesidades de ozono en función de la concentración de partículas. El otro objetivo de esta tesis ha sido estudiar la posibilidad de reducir el bromato formado durante el tratamiento con ozono. Los resultados mostraron que el bromato puede ser eliminado en un período de tiempo razonable a través de procesos biológicos de depuración.

En resumen, con mi investigación he desarrollado una herramienta para predecir los requerimientos de ozonización para la eliminación de residuos de compuestos farmacéuticos, así como el grado de eliminación de estos. Esta herramienta sería aplicable a distintas estaciones de depuración de aguas residuales de una forma sencilla a partir de datos ya existentes. Esto conlleva además que se pueden estimar consumos energéticos y la eficacia de eliminación de los compuestos farmacéuticos sin la necesidad de realizar costosas pruebas a escala piloto.

List of papers

This thesis comprises the following original articles, which will be referred to in the text by their Roman numerals:

Paper I Ekblad, M., **Juárez, R.**, Falås, P., Bester, K., Hagman, M., Cimbritz, M. (2021). Influence of operational conditions and wastewater properties on the removal of organic micropollutants through ozonation. *Journal of Environmental Management*, 286, Article 112205.

Paper II **Juárez, R.**, Karlsson, S., Falås, P., Davidsson, Å., Bester, K., Cimbritz, M. (2021). Integrating dissolved and particulate matter into a prediction tool for ozonation of organic micropollutants in wastewater. Manuscript submitted for publication.

My contribution to the papers

Paper I I participated in the planning of the experiments with the other co-authors, assisted in the pilot plant operation and sampling, performed the laboratory-scale experiments on iron addition, assisted in micropollutant analysis data processing, collaborated in the analysis of the results and contributed to writing the paper.

Paper II I planned the experiments together with my supervisors and co-authors, performed the laboratory-scale experiments, processed the micropollutant data, analyzed the results and wrote the manuscript with input from the other co-authors.

Contents

1 Introduction

Access to drinking water is essential to life, and a basic human right. However, access to clean drinking water is threatened. Surface water catchments for drinking water can be exposed to several microbial, chemical and physical hazards, affecting water quality (WHO, 2007). The presence of organic micropollutants in drinking water sources is attracting increasing attention (Gago-Ferrero et al., 2017; Snyder & Benotti, 2010; Sörengård et al., 2019; Stackelberg et al., 2004; Verliefde et al., 2007).

Organic micropollutants such as pharmaceuticals, endocrine disruptors, contrast media, pesticides and illicit drugs, among others, are discharged into the aquatic environment via treated wastewater (Kasprzyk-Hordern et al., 2009; Loos et al., 2013; Reemtsma et al., 2016). Pharmaceuticals reach wastewater treatment plants (WWTPs) mostly via hospital and domestic wastewater and, to a minor extent, via industrial wastewater and landfill leachate (Luo et al., 2014). Traditionally, WWTPs have been designed to remove organic material and nutrients (N and P) and have only a limited effect on pharmaceuticals (Falås et al., 2016; Miège et al., 2009).

The continuous discharge of pharmaceuticals via wastewater into surface water poses environmental hazards. Pharmaceuticals that are not degraded in the aquatic environment, i.e. persistent pharmaceuticals, may accumulate in living organisms, leading to behavioral changes (Brodin et al., 2013), affecting reproduction (Schultz et al., 2011) and causing toxicity (Kidd et al., 2007; Oaks et al., 2004). Additional concerns include antibiotic-resistant microorganisms (Qiao et al., 2018), and long-term and mixture effects (Kümmerer, 2009; Pomati et al., 2008). These could be mitigated by reducing the amount of pharmaceuticals discharged to the aquatic environment. A number of measures can be taken during the manufacturing process, in the use of pharmaceuticals and in the end-life-phase of pharmaceuticals through wastewater treatment and end-of-pipe measures (OECD, 2019). An example of an end-of-pipe measure is the upgrading of treatment trains in WWTPs.

Several technologies can be applied in the upgrading of WWTPs, which are at different readiness levels, each with their own advantages, limitations and challenges. These technologies may rely on biological treatment (Clara et al., 2005; Falås et al., 2013; Joss et al., 2006), advanced oxidation processes (Miklos et al., 2018), activated carbon-based treatments (Altmann et al., 2016; Altmann et al., 2016), membrane filtration (Al-Rifai et al., 2011; Kimura et al., 2004; Urtiaga et al.,

2013) or hybrid processes. Among these techniques, advanced oxidation processes are established techniques, and ozonation is currently employed in full-scale WWTPs for micropollutant removal (Bourgin et al., 2018; Hollender et al., 2009; Itzel et al., 2020; Nakada et al., 2007) and direct or indirect water reuse (Blackbeard et al., 2016; Reungoat et al., 2010).

However, some practical and process-related aspects must be addressed if we are to achieve more effective facilities in terms of space and energy-related costs. Studies on the effects of hydraulic retention time (HRT), choice of ozone dispersion method, wastewater temperature and type of treatment preceding ozonation on pharmaceutical removal efficiency can help in the design of more compact and less energy-demanding ozonation units. Furthermore, our ability to predict the ozone demand and removal of pharmaceuticals for different wastewater matrixes is still limited due to the simultaneous interaction of ozone with a large number of organic and inorganic wastewater constituents, as well as particulate matter.

Extensive research has been conducted focusing on the normalization of the ozone dose to the dissolved organic carbon (DOC) and corrections for the ozone consumption due to the scavenging effect of the inorganic nitrite anion. However, the influence of particulate matter in ozone oxidation of pharmaceuticals has not been studied to the same extent as dissolved matter, although this may be relevant in the choice of process, including pretreatment or wastewater by-pass when the particle content is too high. By studying both dissolved and particulate matter, the aim in this work was to develop simple tools to assist in the implementation of ozonation for the removal of pharmaceuticals by assessing the ozone demand, and thus the energy consumption.

The oxidation of pharmaceuticals during ozonation leads to the formation of so-called transformation products. Other components present in the wastewater matrix may also be oxidized, resulting in undesirable by-products. The main problems associated with transformation products and by-products are that they may result in undesirable biological effects or toxicity, and some of these compounds may be difficult to remove with biological post-treatment. The formation of the by-product bromate in the ozonation of water and wastewater has attracted particular interest. Levels of bromate in drinking water are regulated (Council Directive 2020/2184, 2020) and an environmental standard has been proposed (Oekotoxzentrum, 2015). Bromate is a potential human carcinogen, and its toxic effect on aquatic organisms has been reported (Richardson et al., 2007; Wu et al., 2019). Numerous efforts have been made to prevent and control the formation of bromate during wastewater ozonation (Chon et al., 2015; Soltermann et al., 2017), as its removal with biological post-treatment is not considered feasible. Relatively high bromide concentrations have been detected in coastal WWTPs in southern Sweden (Edefell et al., 2021; Paper II), leading to particular interest in the possibility of reducing the bromate formed during ozonation using biological post-treatment.

The effective removal of pharmaceuticals from wastewater will improve the quality of the effluent, reducing potential hazardous effects on the aquatic environment and offering the possibility of water reclamation and reuse, after some form of post-treatment. Wastewater has traditionally been considered a waste requiring treatment, but in the current transition to a circular economy, wastewater has become a resource from which clean water, nutrients and energy can be obtained.

1.1 Objective and hypotheses

The main objective of the work presented in this thesis was to investigate the effects of operating conditions and dissolved and particulate matter on the removal of pharmaceuticals from wastewater by ozonation, on both pilot and laboratory scale. The accuracy of a prediction tool based on COD and SS for ozone demand and pharmaceutical removal was also assessed. Finally, the possibility of microbial reduction of the bromate formed during ozonation with a denitrifying biofilm process was investigated. The following hypotheses were posed at the beginning of this work.

- Comparable pharmaceutical removal efficiency can be achieved during ozonation at different seasonal wastewater temperatures and with HRTs shorter than those conventionally applied.
- Particles negatively affect the oxidation of organic pharmaceuticals, and the extent of this effect can be predicted using a simple tool.
- The bromate concentration can be reduced by post-treatment of the ozonated effluent with a denitrifying biofilm process.

The following tasks were performed to test these hypotheses.

- Pilot-scale ozonation experiments were carried out to compare the effects of different operating parameters and treatment steps.
- Laboratory-scale ozonation experiments were performed on activated sludge effluent from six WWTPs. The effects of SS were studied on one of the effluents.
- A prediction tool was developed with constants obtained from the laboratory-scale experiments, including dissolved chemical oxygen demand (COD_{diss}) and SS as input parameters of the prediction tool.

- The predicted pharmaceutical removal efficiency was compared with data obtained from pilot-scale ozonation to assess the reliability of the tool.
- Laboratory-scale ozonation of wastewater effluent was performed to study bromate formation.
- Denitrification using a biofilm process was tested on laboratory scale as a form of ozonation post-treatment to investigate the possibility of bromate reduction.

1.2 Thesis outline

This thesis is based on two papers on ozonation and additional results on the microbial reduction of bromate so far only presented in this thesis. The topics covered in this thesis range from general aspects concerning pharmaceuticals in the aquatic environment, to specific ozonation-related challenges and opportunities. Following the introduction and the objectives presented in this chapter, the next chapter covers the theoretical and practical aspects of wastewater ozonation. Chapter 3 then describes the materials and methods used in this work. The fourth chapter presents the results obtained from ozonation on laboratory and pilot scale, together with the results of the tool developed for the prediction of ozone demand and pharmaceutical removal during ozonation. The results obtained with the prediction tool are then compared with pilot-scale data. Finally, the results obtained from the denitrifying biofilm process for bromate reduction as post-treatment to ozonation are presented. Finally, Chapters 5 and 6 present the conclusions and suggestions for future research.

2 Ozone treatment

Advanced oxidation processes can be used for the degradation of persistent pollutants by producing the highly reactive and non-selective hydroxyl radical •OH. The differences between advanced oxidation processes lie in the method of generating •OH. These methods include photochemical, electrochemical, physical and chemical processes, in which catalysis may be employed. Ozone treatment is a chemical process in which •OH are generated through the decomposition of ozone in the water phase. In this chapter, ozone generation, its properties, applications in water treatment and relevant process parameters are briefly reviewed.

2.1 Ozone and its properties

2.1.1 Ozone generation

Ozone is usually generated on-site, due to its short half-life and high reactivity. Corona discharge is a widely applied method for ozone generation. The generation of ozone using this method is based on the exposure of oxygen gas, pure or in mixture with air, to a high voltage.

In an ozone generator, the oxygen molecules (O_2) are excited to a state with higher energy (O_2^*) according to Equation 1. These then dissociate, forming oxygen radicals (expressed as O as a simplification), according to Equation 2 (von Sonntag & von Gunten, 2015):

$$O_2 + e^- \rightarrow O_2^* + e^- \quad (1)$$

$$O_2^* \rightarrow 2\,O \quad (2)$$

The oxygen radicals, oxygen molecules and a collision partner M (O_2, O_3, O, or N_2 in case of air) react in a three-body reaction, according to Equation 3, to form ozone (O_3):

$$O + O_2 + \mathrm{M} \rightarrow O_3^* + \mathrm{M} \rightarrow O_3 + \mathrm{M} \quad (3)$$

2.1.2 Ozone reactivity in water

After the ozone generator, a gas stream containing a mixture of ozone and oxygen is dissolved into the water by means of different mass transfer equipment, such as bubble diffusers, Venturi injectors or static mixers. Ozone is more soluble at low temperatures and has a solubility approximately 10 times greater than oxygen gas (von Sonntag & von Gunten, 2015). The oxidation potentials of ozone and the hydroxyl radical are considerably higher than other commonly employed oxidizing agents in water treatment (Table 1).

Table 1. Standard oxidation potential of oxidizing agents commonly used in water treatment (Lim et al., 2011; Vanysek, 2000)

Oxidizing agent	Standard oxidation potential (V)
Hydroxyl radical ($^{\bullet}OH$)	2.80
Ozone (O_3)	2.08
Hydrogen peroxide (H_2O_2)	1.78
Permanganate (MnO_4^-)	1.68
Chlorine dioxide (ClO_2)	1.57
Chlorine (Cl_2)	1.36
Oxygen (O_2)	1.23

The action of ozone in an aqueous solution is governed by two mechanisms: direct reaction with ozone, and indirect reaction with hydroxyl radicals formed during ozone decomposition. Ozone decomposition is mainly induced by direct reactions of ozone with dissolved organic matter (DOM). The properties of the DOM and ozone dose strongly affect ozone decomposition (Elovitz et al., 2000a), and hydroxyl radical production (Nöthe et al., 2009).

This process creates a chain reaction, as hydroxyl radicals formed by direct reactions with ozone continue either reacting with the products of these reactions or other oxidizable compounds. Similarly, ozone can continue to react with compounds that in turn can be further attacked by ozone or hydroxyl radicals. Ozone selectively attacks electron-rich moieties (e.g., phenolic, amino and olefinic groups), while hydroxyl radicals react non-selectively. These parallel reaction paths provide are favorable for several applications of ozonation in water treatment.

2.2 The application of ozonation in water and wastewater treatment

Ozone has mainly been used in water treatment for disinfection purposes, due to its capacity to inactivate viruses and bacteria. The disinfection properties of ozone were first investigated at the end of the 19th century, and the first plant using ozone for drinking water treatment was constructed in Oudshoorn, the Netherlands in 1893. After testing of this pilot plant, the first full-scale drinking water treatment plant came into operation in Nice, France in 1906 (Miller et al., 1978). Ozonation was gradually introduced in many countries during the course of the 20th century for the disinfection of drinking water and for taste, odor and color removal (Geering, 1999; Kruithof & Masschelein, 1999; Le Pauloue & Langlais, 1999; Lowndes, 1999; Matsumoto & Watanabe, 1999; Rice, 1999).

Disinfection may be applied to wastewater to comply with water quality requirements for bathing water, irrigation purposes or recreational uses. However, these processes have mainly involved the use of chlorine or UV light (Koivunen & Heinonen-Tanski, 2005). Due to the disinfectant power of ozone and the oxidative property of the combination of ozone and hydroxyl radicals, ozonation appears to be a suitable technology for micropollutant removal from wastewater (Hollender et al., 2009; Huber et al., 2005; Margot et al., 2013; Zimmermann et al., 2010), and in water reuse.

The work presented in this thesis focuses on the oxidative aspect of ozone, and disinfection will therefore not be discussed. Appropriate design and process parameters must be used to ensure adequate oxidation of the micropollutants present in wastewater. Relevant process parameters, some of them addressed in this thesis, are reviewed in the next section.

2.3 Key parameters during ozonation

2.3.1 Ozone depletion kinetics

The combination of process parameters and water quality determines the degree to which pharmaceuticals are oxidized during ozonation. The extent of these oxidation reactions is largely governed by the ozone decay kinetics. Ozone decay kinetics are influenced by factors such as initial ozone dose, DOM content and properties, temperature and pH (Buffle et al., 2006; Elovitz & von Gunten, 1999; Elovitz et al., 2000a; Elovitz et al. 2000b). The decrease in ozone is much faster in wastewater than in drinking water, mainly due to reactions with the DOM components in wastewater. Furthermore, ozone is more stable at acidic pH, while the concentration

deceases more rapidly at neutral and basic pH values, which is the common range in wastewater. The ozone depletion time is also shorter at higher temperatures. Thus, changes in wastewater properties can affect the ozone oxidation of pharmaceuticals. The HRT must therefore be long enough to ensure that as much of the pharmaceuticals is oxidized as possible, but not too long to avoid any residual ozone leaving in the effluent of the ozonation unit. The HRT in full-scale ozonation units installed at WWTPs ranges from 15 to 60 min (Bourgin et al., 2018; Margot et al., 2013). Further studies on HRT could lead to the design of ozonation units with shorter HRTs, leading to smaller reaction volumes and more compact units.

2.3.2 Reactivity and ozone demand

The reactivity between pharmaceuticals and ozone varies (Benner et al., 2008; Dodd et al., 2006; Lee & von Gunten, 2010), and pharmaceuticals make up only a small fraction of the DOM. Pharmaceuticals react with ozone and hydroxyl radicals in competition with many other components present in the wastewater matrix arising from dissolved and particulate matter. The ozone dose is therefore usually normalized to the DOC to allow comparison between different wastewater effluents. Readily oxidizable inorganic compounds present at relatively high concentrations can increase the ozone demand, and must therefore be considered in dose prediction calculations. However, particulate matter is usually not included in ozone demand calculations, despite the fact that this has a negative effect on ozone oxidation of some pharmaceuticals (Zucker et al., 2015). Predictions of micropollutant removal, ozone demand and by-product formation have largely relied on kinetic second-order rate constants (Lee et al., 2013; Zimmermann et al., 2010) and data on ozone decay kinetics based on ozone dose normalized to DOC.

2.3.3 By-product formation

The formation of by-products is of concern due to the potential harmful effects on the aquatic ecosystem resulting from the discharge of wastewater into water bodies. When ozone treatment is applied to wastewater, not only does it oxidize organic matter and pharmaceuticals, but bromide is also oxidized, leading to the formation of bromate. Considerable attention has been directed to the formation of bromate during ozonation, due to the toxicological significance of this by-product. The formation of bromate involves a complex set of reaction pathways including the direct reaction of bromide, the main precursor of bromate, and intermediate species, with ozone and hydroxyl radicals (von Gunten & Hoigné, 1994; von Gunten & Oliveras, 1998). Ozonation of bromide-rich wastewater is therefore not recommended (Schindler Wildhaber et al., 2015). Bromate control strategies during ozonation are typically aimed at lowering bromide concentrations through source control and the inhibition of reaction pathways leading to the formation of bromate

(Soltermann et al., 2017), and even multi-point dosing strategies have been proposed. Post-treatment options under aerobic conditions have not been regarded as feasible for bromate removal. However, the possibility of biologically reducing bromate in wastewater under anoxic conditions has not been widely studied.

WWTPs can be upgraded with a post-denitrification step to comply with effluent requirements for nitrogen, where the nitrate formed during the activated sludge treatment step is reduced to nitrogen gas. To achieve a more compact and robust process, denitrification can be carried out using a carrier-borne biofilm instead of suspended growth systems, by means of a moving-bed biofilm reactor (MBBR) (Ødegaard et al., 1994). Treatment plants in southern Sweden such as the Sjölunda and Klagshamn WWTPs have such a treatment step. Installing an ozonation unit for pharmaceutical removal before post-denitrification could be beneficial if bromate is successfully reduced during the post-denitrification step.

3 Materials and methods

Pilot-scale ozonation experiments were performed to compare the effects of several operating conditions and treatment steps. Laboratory-scale ozonation experiments were then carried out to investigate the ozone oxidation of activated sludge effluents from six WWTPs, and the influence of particles and iron on the removal of pharmaceuticals. Finally, the microbial reduction of bromate was investigated on laboratory scale.

The pilot-scale experiments were performed to investigate practical aspects of ozonation, such as the HRT, ozone dispersion method and which treatment step effluent should be treated, once the technique is in place. Some process conditions, such as temperature, and the particulate and dissolved matter content varied during the experiments, which could have led to uncertainties. Therefore, studies were carried out more systematically and in a more controlled environment on laboratory scale, to investigate ozone oxidation of different activated sludge effluents and different particulate matter contents. The effect of the presence of iron during ozone oxidation of pharmaceuticals was also investigated.

A tool for the prediction of the removal of pharmaceuticals was developed and assessed by comparing the predicted removal with data from pilot-scale ozonation. The aim of this was to provide an easy-to-implement tool for the prediction of ozone demand and pharmaceutical removal to facilitate the assessment of preliminary investment and operating costs, and treatment strategies.

Bromate reduction experiments were performed on laboratory scale as a first step in the assessment of the feasibility of the process as a form of ozonation post-treatment.

3.1 Ozonation

3.1.1 Pilot-scale experiments

An ozone pilot plant was operated at a flow of 3 m^3/h downstream of the Lundåkra WWTP (Landskrona, Sweden). The flow and reaction volume could be modified to obtain the desired HRT, a static mixer or Venturi injection could be used for ozone dispersion, and the configuration of the pilot plant allowed the treatment of activated

sludge or post-precipitation effluent. The setup is illustrated in Figure 1, and is described in more detail in Paper I. In short, oxygen was separated from air, using a pressure swing adsorption module, and then concentrated. Ozone was generated from this oxygen and dispersed in the wastewater using one of the methods mentioned above. Finally, the ozonated wastewater was led to the reaction tanks.

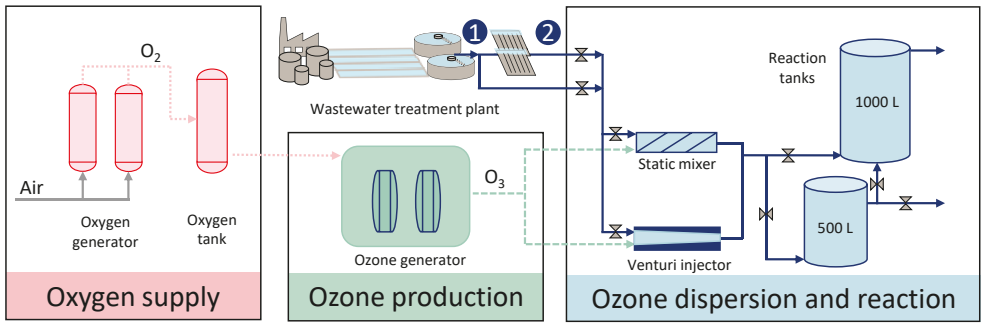

Figure 1. Schematic of the ozonation pilot plant. The ozone pilot plant configuration allowed feeding with either activated sludge effluent (1) or post-precipitation effluent (2).

A photograph of the container housing the ozone pilot plant is shown in Figure 2. The pilot plant was located next to the facility where coagulant is added, thus allowing access to both activated sludge and post-precipitation effluent.

Figure 2. Photograph of the ozone pilot plant housed in a container located at the Lundåkra WWTP.

The equipment inside the container, including the components described above, is shown in Figure 3. The operating parameters of the ozone pilot plant were adjusted with a fully automated programmable logic control system.

Figure 3. Three photographs of the machine room of the ozone pilot plant. A) pressure swing adsorption module and oxygen tank, B) ozone generator, C) reaction tanks and D) Venturi injector (left) and static mixer (right).

3.1.2 Laboratory-scale experiments

An ozone stock solution (>65 mg O_3/L) was prepared as described in Paper II. In brief, ozone gas produced from pressurized oxygen was sparged into a refrigerated vessel containing deionized water or ultrapure water, as illustrated in Figure 4. For safety reasons, the vessel containing the ozone stock solution was placed in a fume cupboard (Figure 5). The addition of ozone to wastewater, with a glass pipette, and the reaction of ozone with wastewater in continuously stirred glass bottles, were also performed in the fume cupboard. The ozonated wastewater samples were incubated for at least 60 minutes and then sampled by transferring the ozonated wastewater to amber glass vials for pharmaceutical analysis. The laboratory-scale ozonation experiments were performed with various types of effluents, as described Paper II.

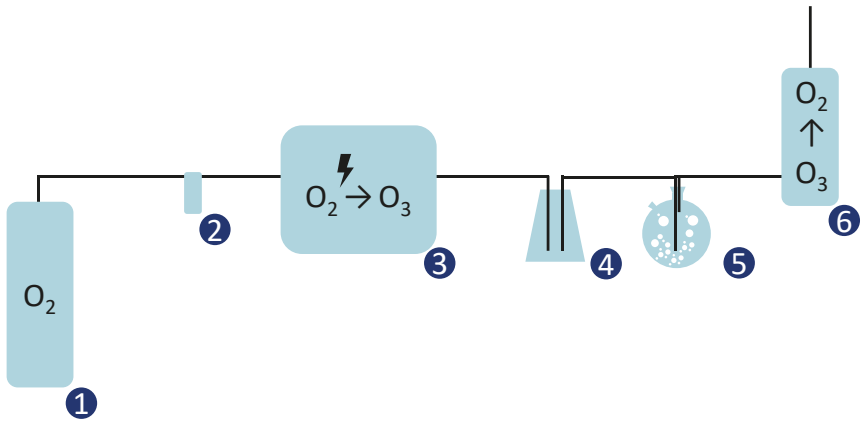

Figure 4. Schematic of the laboratory-scale ozonation experiments. 1) Oxygen supply, 2) air filter, 3) ozone generator, 4) water trap, 5) contact vessel and 6) ozone destructor.

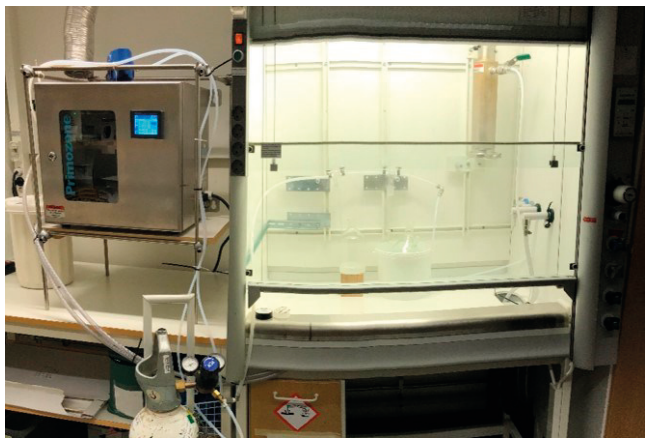

Figure 5. Photograph of the laboratory-scale ozonation setup.

The concentration of the ozone stock solution was determined spectrophotometrically at 600 nm, according to Equation 4 (Bader, 1982), where a volume of the ozone stock solution was added to a $2 \cdot 10^{-4}$M potassium indigotrisulfonate solution.

$$O_{3,stock} = \frac{(A - A_0) \cdot V_T}{f \cdot b \cdot V_{O3}} \qquad (4)$$

where:

$O_{3,\,stock}$: Ozone concentration in the stock solution [mg O_3/L]

A: Absorbance of the indigotrisfulfonate solution before ozone addition

A_0: Absorbance of the indigo trisulfonate solution after ozone addition

V_T: Total volume in the cuvette [mL]

f: Proportionality constant = 0.42 [L/(mg O_3·cm)]

b: Cuvette pathlength [cm]

V_{O3}: Volume of stock solution added to the indigotrisulfonate solution [mL]

The applied ozone dose was calculated according to Equation 5:

$$O_{3,applied} = \frac{O_{3,stock} \cdot V_{O3}}{V_{WW}} \quad (5)$$

where:

$O_{3,\,applied}$: Ozone concentration applied to the wastewater [mg O_3/L]

$O_{3,\,stock}$: Ozone concentration in the stock solution [mg O_3/L]

V_{O3}: Volume of the stock solution added to the wastewater [mL]

V_{WW}: Volume of the stock solution added to the wastewater [mL]

3.2 Microbial reduction of bromate

The reduction of bromate by microbial denitrification was studied in batch experiments on laboratory scale with carrier-attached biofilms. The effluent wastewater from the Sjölunda WWTP was used as this plant has a separate MBBR unit for post-denitrification, using methanol as an external carbon source (Aspegren et al., 1998; Hanner et al., 2003). The MBBR unit at Sjölunda WWTP employs K1 carriers (Veolia Water Technologies, AnoxKaldnes, Sweden) at a 50% filling ratio. The experiments were carried out in three parallel reactors (1.3 L) containing

ozonated water (1 mg O_3/ mg DOC) and 800 K1 carriers, providing an initial biomass in the reactors of 3.03 ± 0.01 g/L (Figure 6).

The wastewater in all reactors was buffered to pH ~7.1 (10^{-3} M KH_2PO_4 and NaOH) and sparged with nitrogen gas to create anoxic conditions (dissolved oxygen <0.1 mg O_2/L). The first experiment was run without any carbon source or nitrate (Figure 6a). Two of the experiments were run with excess methanol (MeOH) as an additional carbon source (300 mg COD/L), (Figure 6b and c), and the last one was also supplemented with nitrate as KNO_3 (50 mg NO_3^--N/L) (Figure 6c). Sampling was performed after 1, 15, 30, 45, 60, 90, 120, and 180 minutes, at which time carriers were removed from the Erlenmeyer flasks to maintain a constant ratio between carriers and wastewater volume.

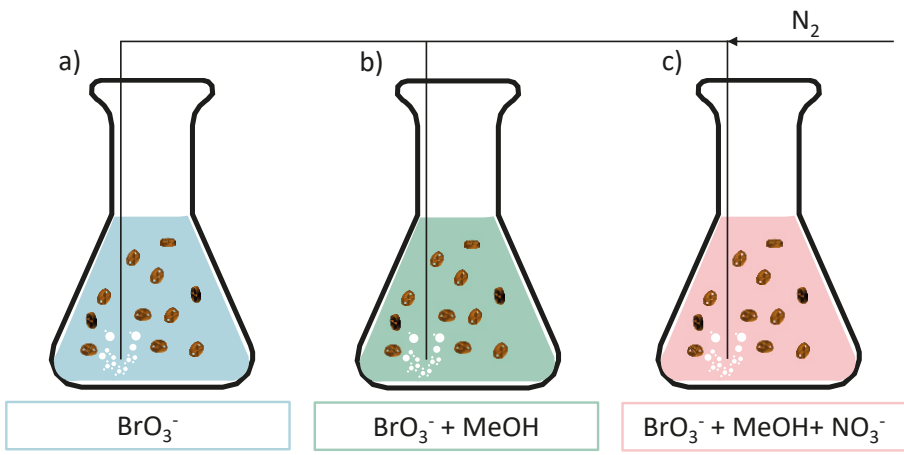

Figure 6. Schematic of the batch experiments for microbial bromate reduction. Each flask contains ozonated wastewater (~0.1 mg BrO_3^-/L) and carriers (brown plastic pieces). Flask b and c were supplemented with excess MeOH and Flask c was also supplemented with excess nitrate (NO_3^-).

3.3 Analytical methods

High-performance liquid chromatography with tandem mass spectrometry (HPLC/MS-MS) was used to evaluate the results of the ozonation experiments. In short, wastewater samples of 100 µL were injected into an Ultimate 3000 dual-gradient low-pressure mixing HPLC system with an Ultimate 3000 autosampler (Dionex, Sunnyvale, CA, USA) connected to an API 4000 triple-quadrupole mass spectrometer (AB Sciex, Framingham, MA, USA). Chromatographic separation was accomplished using a Synergi Polar-RP column (150x2 mm I.D., particle size

4 µm, Phenomenex, Torrance, CA, USA) with acidic elution using formic acid (0.2%) in both mobile phase A (water) and phase B (methanol), and multiple reaction monitoring was used to quantify the analytes. The data were processed using the software Analyst 1.6.3 (AB Sciex, Farmingham, MA, USA). More detailed information on pharmaceutical analyses is provided in the papers. Nitrogen species, total organic carbon (TOC) and COD fractions were analyzed spectrophotometrically (Hach-Lange DR 2800, Hach, Düsseldorf, Germany), the dissolved fractions being analyzed after filtration (Whatman™ 0.45 µm cellulose nitrate filter). The concentration of SS was determined according to the Swedish standard SS-EN 872:2005.

In the bromate experiments, bromide and bromate contents were measured in filtered samples (0.45 µm, Minisart™ RC Syringe filters, Sartorius, Germany). Bromate was analyzed at an external laboratory (Eurofins, Linköping, Sweden) according to SS-EN ISO 17294-2:2016. Bromide and nitrogen species were analyzed using ion chromatography (Metrohm ECO IC, Switzerland) and conductivity detection, where separation was achieved with either an anion column (Metrosep A Supp 5 - 254/4.0) or a cation column (Metrosep C 6 - 150/4.0). Hach cuvettes were used for the measurement of COD (LCK 1414) and DOC (LCK 385).

3.4 Modelling the ozonation of pharmaceuticals

As a result of the observed linearity of the dose–response curves, the following linear expression, based on COD_{diss} and SS, as described in Equations 6-8, was proposed:

$$R_s = o_s \cdot (O_3/\mathrm{sCOD}) \cdot 100 \qquad (6)$$

where:

R_s is the predicted removal in the absence of particles [%]

o_s the removal constant in the absence of particles [mg COD/mg O_3]

O_3 is the ozone concentration in wastewater [mg O_3/L] and

sCOD is the dissolved COD [mg COD/L]

$$o_{sp} = o_s - k_p \cdot X \qquad (7)$$

where:

o_{sp} is the removal constant in the presence of particles [mg COD/mg O_3]

k_p is the particle constant [(mg COD·L)/(mg O_3·g SS)] and

X is the SS concentration [g SS/L]

$$R = o_{sp} \cdot (O_3/sCOD) \cdot 100 \quad (8)$$

where:

R is the predicted removal in the presence of particles [%].

This tool based on linear expressions was used for predicting the removal of pharmaceuticals during ozonation by using the new set of removal constants (o_s, o_{sp}, k_p) obtained from laboratory-scale experiments. The predictions were then compared with measured data from pilot-scale ozonation.

4 Results and discussion

This section presents the principal findings of this work. The results concerning the effects of operating conditions and wastewater properties on pharmaceutical removal on pilot and laboratory scale are given in Section 4.1. The results of modelling to predict pharmaceutical removal and comparison with pilot-scale measurements are given in Section 4.2. Finally, the results on bromate formation and microbial bromate reduction using a denitrifying MBBR process are presented in Section 4.3.

4.1 Influence of operating conditions and wastewater properties

4.1.1 Operating conditions

Paper I describes the study of the influence of various process parameters and other operating conditions on pharmaceutical removal during ozonation. The two effluents investigated had similar wastewater properties in DOC, COD_{diss}, UV absorption at 254 nm (UVA_{254}), nitrite and pH, while they differed in SS concentrations (Table 2).

Table 2. Wastewater properties of the activated sludge samples (n=35-46) and post-precipitation effluent samples (n=22-25) presented as averages ± one standard deviation

	DOC (mg/L)	COD_{diss} (mg/L)	UVA_{254} (1/m)	NO_2^-–N (mg /L)	SS (mg/L)	pH (-)
Activated sludge effluent	10.6 ± 1.0	35.1 ± 9.8	20.4 ± 3.3	0.15 ± 0.05	7.5 ± 6.9	7.6 ± 0.3
Post-precipitation effluent	10.0 ± 0.8	27.5 ± 1.8	20.4 ± 2.1	0.17 ± 0.05	1.8 ± 0.9	7.6 ± 0.1

Operating conditions such as HRT and ozone dispersion method were varied, and ozonation was performed on different effluents. Variation in wastewater temperature was captured by sampling during different seasons. The results of the

pilot-scale experiments are presented for four representative pharmaceuticals, two representing intermediate-reactive pharmaceuticals (venlafaxine and metoprolol) and two representing slow-reactive pharmaceuticals (oxazepam and iohexol), using a nitrite-corrected specific ozone dose (mg O_3/mg DOC).

Hydraulic retention time

The influence of HRT on the removal of pharmaceuticals from activated sludge effluent during ozone oxidation was studied. The HRT was modified by adjusting the wastewater flow at a fixed reaction volume (500 L) using the static mixer as the ozone dispersion method. No residual ozone was detected in the ozonated effluents (<0.01 mg O_3/L). A HRT of 7 minutes was sufficient to achieve adequate pharmaceutical removal, compared to the longest investigated HRT of 20 minutes under the conditions used (Figure 7). The studied HRT interval (7-20 min) allowed sufficient time for ozone decay, as reported previously (Cséfalvay et al., 2007, Hansen et al., 2016; Nöthe et al., 2009). Previous studies have also shown high removal percentages at HRTs of 5 min (Nilsson et al., 2017) and 10 min (El-taliawy et al., 2017).

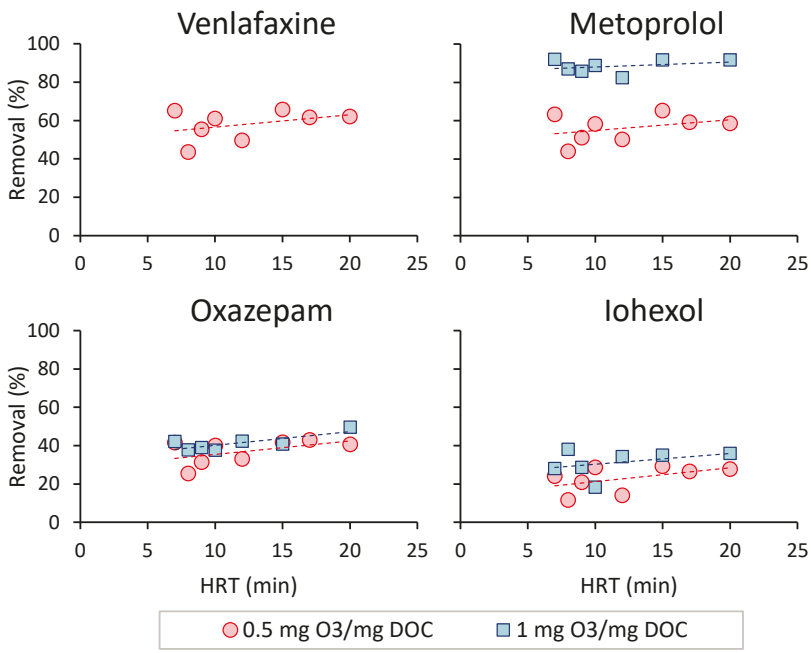

Figure 7. Removal (%) of four pharmaceuticals (two intermediate-reactive pharmaceuticals, above) and two slow-reactive pharmaceuticals, below) at an ozone dose of 0.5 mg O_3/mg DOC (circles) and 1 mg O_3/mg DOC (squares) as a function of HRT (7-20 minutes). Activated sludge effluent was ozonated in this experiment. The dashed lines show the results of linear regression.

Ozone dispersion method

Possible differences in pharmaceutical removal when using different ozone dispersion methods were also studied. The Venturi injector and the static mixer were used to disperse ozone in the wastewater at increasing ozone doses on different occasions. Comparison of the dose-response curves using the two dispersion methods revealed no significant differences between them, however, a somehow higher removal of the slow-reacting pharmaceutical oxazepam was observed with the Venturi injector (Figure 8). Similar observations were also made for some other slow-reacting pharmaceuticals (see Paper I). The removal of some pharmaceuticals was slightly higher with the Venturi injectors, and in other cases with the static mixer. There was thus no conclusive evidence that one or the other dispersion method was better.

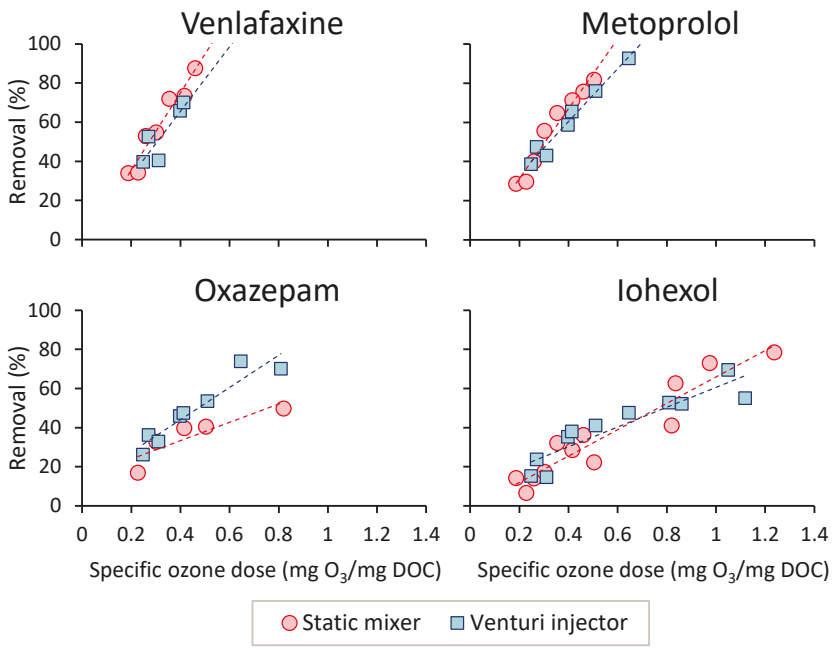

Figure 8. Dose–response curves for the four selected pharmaceuticals comparing the static mixer (circles) and the Venturi injector (squares). Post-precipitation effluent was ozonated with a HRT of 10 minutes. The dashed lines show the results of linear regression.

Wastewater temperature

The effect of wastewater temperature due to seasonal variations between summer and winter was studied over a 7-month period. The average temperature during the winter months was 13.0 ± 0.4°C, while during the summer months it was 20.2 ±

1.7°C. Temperature was found to affect both the ozone solubility and the ozone decay rate. Lower temperatures resulted in higher ozone solubility and slower ozone decay rate; higher temperatures leading to the opposite effects. Despite the influence of temperature on ozone solubility and decay rate, no significant differences were observed in the efficiency of pharmaceutical removal between the winter and the summer months (Figure 9). Thus, from a practical point of view, temperature did not seem to affect the removal of pharmaceuticals.

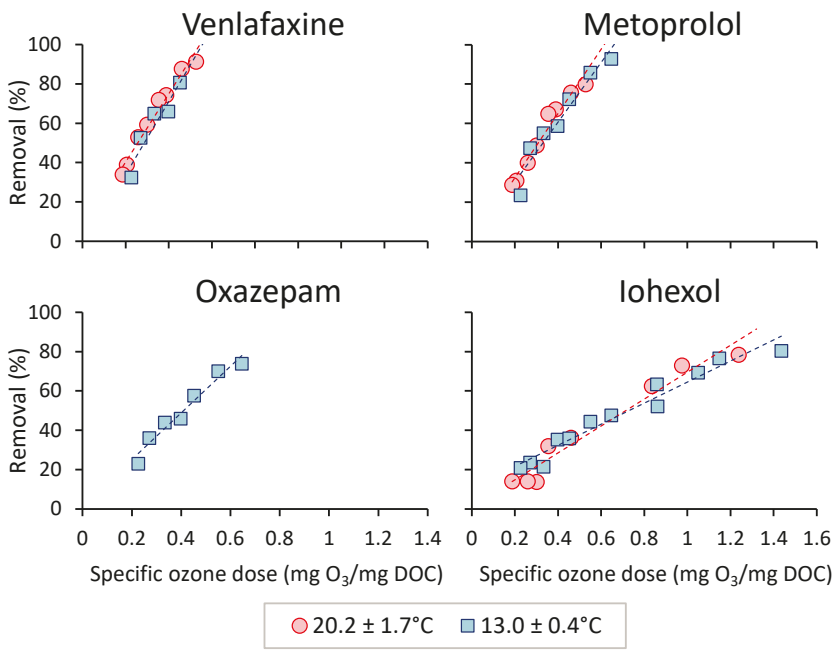

Figure 9. Dose–response curves for the four selected pharmaceuticals comparing summer temperature (circles) and winter temperature (squares). No results were available for oxazepam for summer temperature. Activated sludge effluent was ozonated using the static mixer with a HRT of 10 minutes. The dashed lines show the results of linear regression.

Post-precipitation

In most cases, ozonation units are installed after the activated sludge treatment stage. If further treatment steps are employed at the WWTP, the ozonation unit may be installed at the end of the treatment train. In WWTPs including a biological polishing step after activated sludge treatment, it may be appropriate to apply ozonation after the activated sludge treatment, and to use the existing biological step as post-treatment following ozonation. In this study, post-precipitation followed the activated sludge treatment, consisting of aluminum chloride addition (2.2–4.8 mg

Al^{3+}/L) with subsequent lamella sedimentation. To assess the possible influence of coagulant dosing on the ozonation of pharmaceuticals, dose–response curves were obtained for both activated sludge and post-precipitation effluents (Figure 10). It can be seen from the figure that the removal of pharmaceuticals appeared to be slightly higher in post-precipitation effluent than in activated sludge effluent.

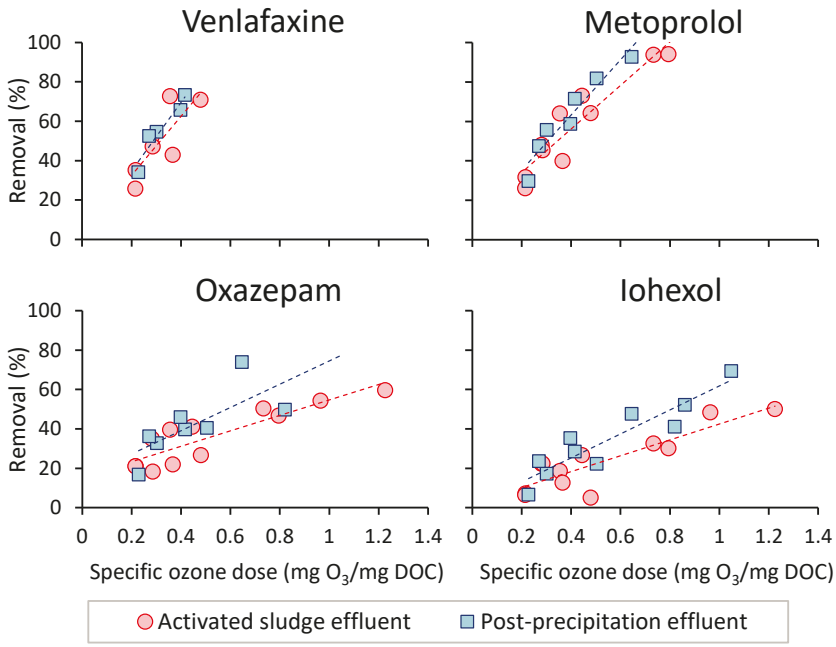

Figure 10. Dose–response curves for the four selected pharmaceuticals comparing activated sludge effluent (circles) and post-precipitation effluent (squares). Both effluents were ozonated using the static mixer with a HRT of 10 minutes. The dashed lines indicate the results of linear regression.

The wastewater properties, in terms of DOC, COD_{diss}, nitrogen species or pH, did not differ significantly between the effluents. However, the SS concentrations differed, being 7.5 ± 6.9 mg SS/L in the activated sludge effluent and 1.8 ± 0.9 mg SS/L in the post-precipitation effluent. The presence of particles in wastewater has been reported to increase the ozone demand for the oxidation of pharmaceuticals (Zucker et al., 2015), and this could be included in the predictions of the ozone demand and removal of pharmaceuticals through ozone oxidation.

To further investigate the influence of coagulant addition, dissolved matter in wastewater and the SS concentration on the ozone oxidation of pharmaceuticals,

laboratory experiments were performed, and the findings are presented in the next section.

4.1.2 Coagulant addition

Iron is a commonly used coagulant in wastewater treatment. To study the effects of iron dosing during ozonation for pharmaceutical removal in a more controlled environment than in pilot-scale plant tests, experiments were performed on laboratory scale. To investigate the effect of iron dosing on pharmaceutical removal, effluent wastewater from the Lundåkra WWTP was ozonated after adding 10 mg Fe/L in two oxidation states (Fe(II) and Fe(III)) before undergoing ozonation. The results obtained showed that the addition of Fe(II) had a negative effect on the ozone oxidation of all the pharmaceuticals analyzed, while the addition of Fe(III) had no clear effect compared with samples ozonated without iron addition. The results of these experiments are available in the supplementary information of Paper I.

To study the effect of Fe(II) dosing on the ozone oxidation of pharmaceuticals in more detail, the iron dose was gradually increased from 2 to 20 mg Fe/L at a fixed ozone dose of 0.7 mg O_3/mg DOC. According to the stoichiometric relationship between ozone and iron, 0.48 mg O_3 are needed to oxidize 1 mg of Fe(II) (Langlais et al., 1991). The gradual increase in Fe(II) in wastewater before ozonation resulted in a decrease in the removal of the analyzed pharmaceuticals (Figure 11). These results were compared to the theoretical values of the removal of pharmaceuticals by subtracting the ozone equivalent dose at each Fe(II) concentration. This resulted in contradictory results. For some of the pharmaceuticals, the observed removal was higher than the theoretical removal, while for others the observed removal was lower than the predicted value. This could perhaps be explained by pH and hydroxyl radical formation. On the one hand, the addition of an iron dose corresponding to 20 mg Fe(II)/L results in a decrease in the pH, from 7.9 to 7.2. At lower pH, the kinetic second-order rate constant of the direct reaction of ozone with pharmaceuticals (k_{O3}) is reduced for pharmaceuticals with intermediate k_{O3} values, such as venlafaxine and metoprolol (Lee et al., 2014), thus resulting in lower removal than the expected removal after withdrawing the theoretical quantity of ozone consumed by Fe(II) from the applied ozone dose. On the other hand, the removal of pharmaceuticals that mainly react with hydroxyl radicals, such as oxazepam and iohexol, may be enhanced due to an Fe(II)-induced increase in hydroxyl radical formation (Zhang et al., 2013).

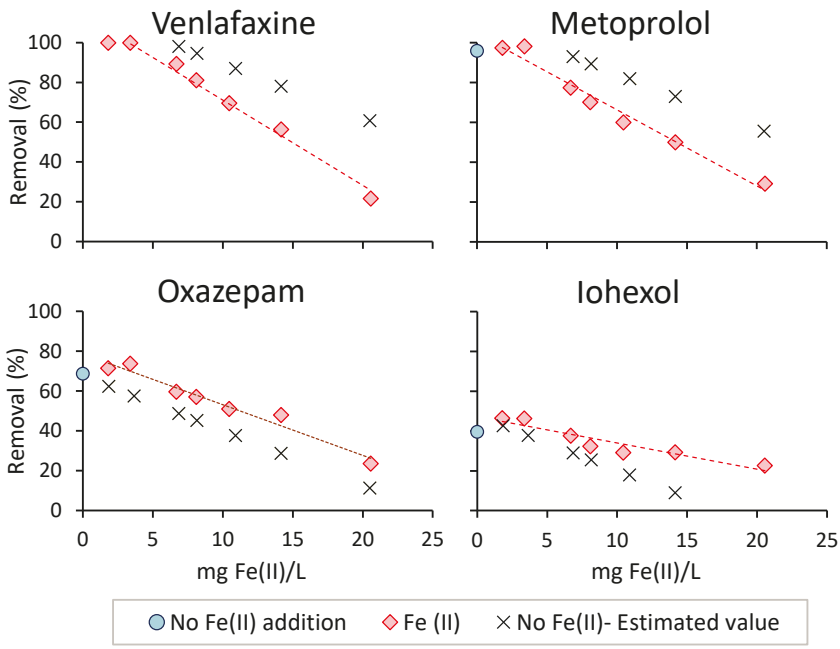

Figure 11. Dose–response curves for the four selected pharmaceuticals comparing increasing Fe(II) concentrations (2-20 mg Fe/L) at a fixed ozone dose (0.7 mg O_3/mg DOC), together with the estimated value of the removal of pharmaceuticals without iron addition.

The negative effects of Fe(II) on pharmaceutical removal during ozonation were observed in all the pharmaceuticals analyzed. Despite this, Fe(II) is often added in precipitation treatment steps in full-scale WWTPS, before or during aeration where Fe(II) is oxidized to Fe(III) via dissolved oxygen in less than 5 minutes at pH>7.6 (Morgan & Lahav, 2007). This suggests that the reduction in the removal of pharmaceuticals during ozonation as a result of the addition of iron as Fe(II) can be considered rather limited.

4.1.3 Dissolved and particulate matter

The effect of dissolved and particulate matter on ozonation was investigated on laboratory scale. The effect of dissolved matter in ozone oxidation of pharmaceuticals was studied in activated sludge effluents from 6 WWTPs, whereas the effect of particulate matter was studied in the treated effluent from only one of the WWTPs. The wastewater properties for the investigated effluents are presented in Table 3. Further wastewater quality data can be found in Paper II. The ratios between COD_{diss} and DOC (2.6 ± 0.1), and the UVA_{254} per unit DOC (2.1 ± 0.2),

also known as SUVA, were similar in the six activated sludge effluents. This suggests that the investigated effluents have comparable fractions of oxidizable compounds and UVA_{254}-absorbing moieties per unit DOC.

Table 3. Properties of activated sludge effluent from six WWTPs (average ± one standard deviation, n=3; pH is presented as a single measurement)

WWTP	DOC (mg/L)	COD_{diss} (mg/L)	UVA_{254} (1/m)	NO_2^-–N (mg /L)	pH (-)
Lundåkra WWTP	9.5 ± 0.2	24.6 ± 0.5	22.7 ± 0.0	0.2 ± 0.0	8.0
Källby WWTP	11.7 ± 0.4	29.9 ± 0.6	27.0 ± 0.1	0.1 ± 0.0	8.0
Svedala WWTP	17.0 ± 0.1	42.6 ± 0.3	32.5 ± 0.0	0.7 ± 0.0	8.0
Öresund WWTP	8.0 ± 0.2	20.2 ± 0.4	17.7 ± 0.0	0.2 ± 0.0	7.6
Klagshamn WWTP	13.2 ± 0.2	35.1 ± 0	25.4 ± 0.2	1.6 ± 0.0	7.9
Sjölunda WWTP	17.4 ± 0.3	43.1 ± 0	30.9 ± 0.1	<0.1	8.3

Experiments to investigate the effect of different SS concentrations were performed with effluent wastewater from the Lundåkra WWTP (SS = 0.1, 0.4 and 4.9 mg NO_2^-–N/L). SS were added as a suspension of thickened activated sludge (7.6 ± 0.4 g SS/L). The results are given in Table 4. The correlations between TOC and COD and SS concentration were linear, and consistent ratios were observed (0.31 ± 0.02 mg TOC/mg SS; 1.1 ± 0.1 mg COD/mg SS).

Table 4. Properties of the Lundåkra WWTP effluent at increasing suspended solids (SS) concentrations (average ± one standard deviation, n=3; SS and pH are presented as single measurements)

SS concentration	TOC (mg/L)	COD (mg/L)	SS (mg/L)	pH (-)
0 mg SS/L	7.5 ± 0.2	17.2 ± 0.4	n.a.	8
50 mg SS/L	23.9 ± 0.9	77 ± 6.1	48	7.8
75 mg SS/L	32.5 ± 0.7	99 ± 6.6	80	7.8
200 mg SS/L	69.8 ± 0.5	214.6 ± 9.0	196	7.8

The results of the dose–response curves are presented for four representative pharmaceuticals: venlafaxine and metoprolol, representing intermediate-reactive pharmaceuticals, and iohexol and gabapentin, representing slow-reactive pharmaceuticals, in Figure 12. The ozonation dose–response curves in which the ozone dose was normalized to DOC and COD_{diss} show comparable linear trajectories, in line with the results of previous investigations (Altmann et al., 2014; Ekblad et al., 2019; El-taliawy et al., 2017; Yang et al., 2017). Typical R^2 values were >0.88 for DOC normalization and >0.90 for COD normalization for the

individual WWTP effluents (Paper II). In contrast to the results from the pilot-scale ozonation experiments, the ozone dose normalized to the DOC was not nitrite-corrected, partly because it did not provide a more convergent set of dose–response curves (Paper II), and partly because normalization to COD_{diss} should account for nitrite-scavenging effects.

While DOC is often used to normalize the ozone dose, COD is frequently used in the monitoring and modelling of wastewater treatment. To provide a practical solution, COD_{diss} was used as the normalization parameter for the following experiments on the effect of particulate matter on ozone oxidation of pharmaceuticals. Although the concentration of particulate matter in the form of SS is frequently used as a parameter in wastewater treatment, (as is COD), it is not usually included in ozone requirement calculations. Ozonation of wastewater with increasing SS concentration led to a reduction in the removal of pharmaceuticals, as shown in Figure 13. However, the linearity of the dose–response curves was retained.

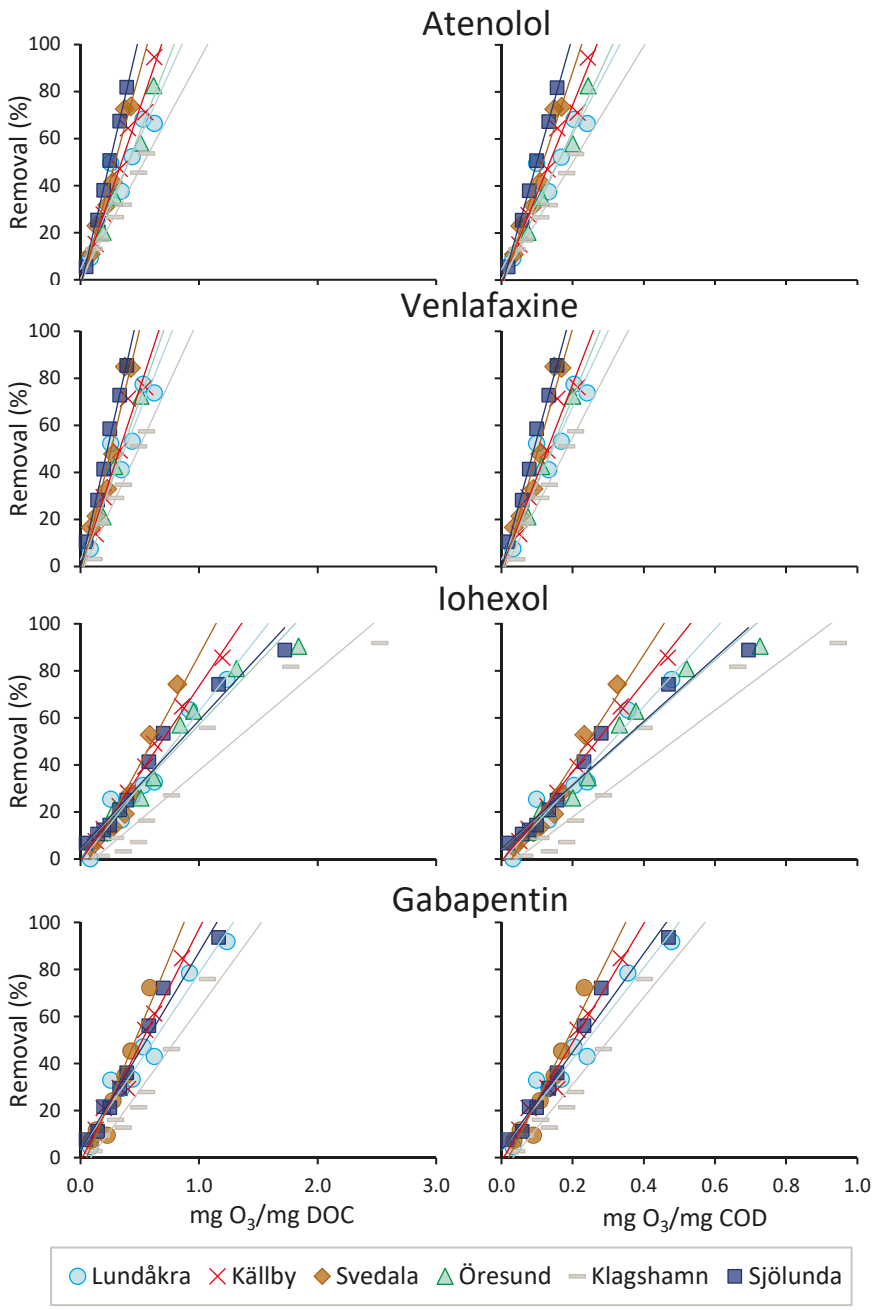

Figure 12. Ozonation dose–response curves for atenolol, venlafaxine, iohexol and gabapentin in activated sludge effluents from six WWTPs after normalization to DOC (left column) and COD_{diss} (right column). The lines show the results of linear regression.

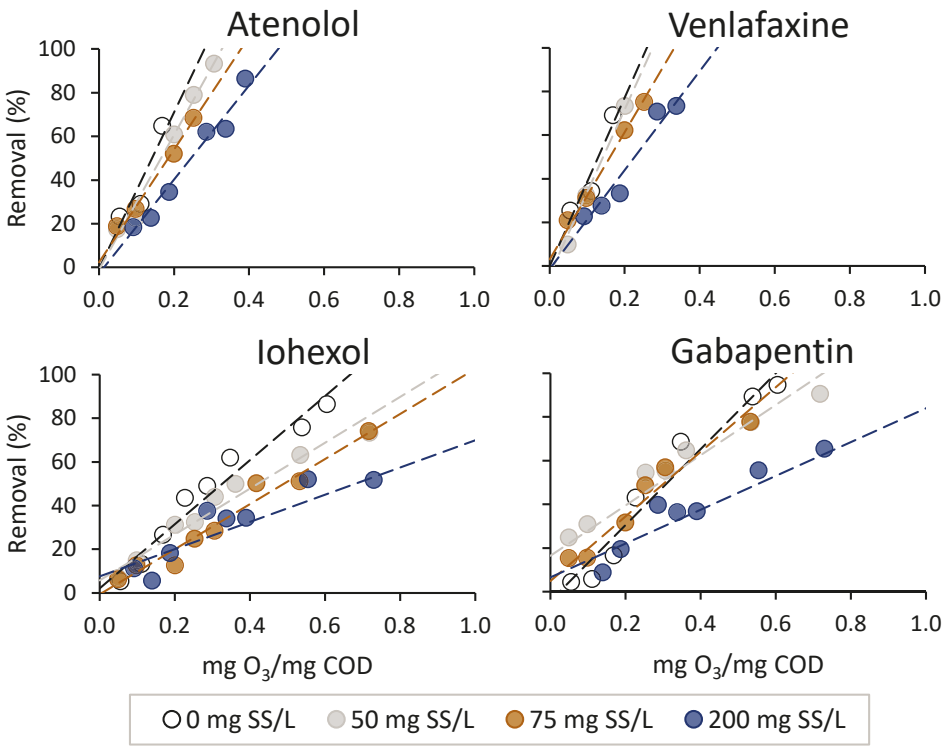

Figure 13. Ozonation dose–response curves for atenolol, venlafaxine, iohexol and gabapentin at increasing suspended solids (SS) concentrations. Dashed lines show the results of linear regression.

4.2 A prediction tool for the removal of pharmaceuticals

The findings discussed above suggest that the inclusion of COD_{diss} and SS in a tool for the prediction of ozone demand and removal of pharmaceuticals indeed possible and that the implementation of such a prediction tool would facilitate the design and assessment of ozonation units by reducing the uncertainties related to the concentrations of particles and inorganic compounds.

4.2.1 New removal constants

Two new removal constants (o_s and o_{sp}) were calculated by linear regression with the least-squares method for each of the pharmaceuticals analyzed in the ozonation experiments described in Section 4.1.3, according to the equations presented in Section 3.4. Up to 95% removal was considered, at which a linear response was observed, and it was assumed that the removal was 0% at an ozone dose of 0 mg/L. The average values of the removal constant o_s across the activated sludge effluents from the six WWTPs for all the pharmaceuticals studied were classified into two groups, A and B, as shown in Figure 14. Group A includes slow-reactive compounds, while Group B includes fast-reactive compounds with ozone.

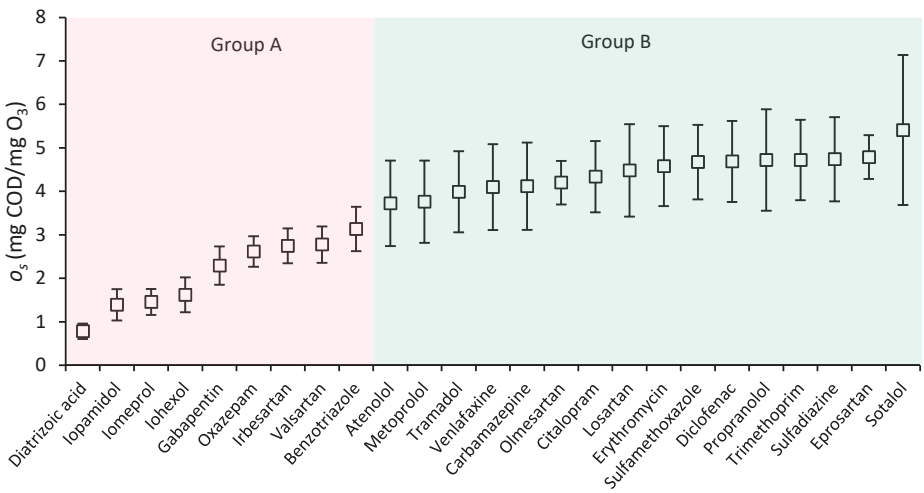

Figure 14. Average value of the removal constant, o_s, for the pharmaceuticals studied across activated sludge effluents from six WWTPs. Bars represent the standard deviation.

A decrease was observed in the removal constant in the presence of particles, o_{sp}, for all the pharmaceuticals investigated, and this effect was greater at higher SS concentrations (Figure 15). This observation indicates an ozone scavenging effect by the SS.

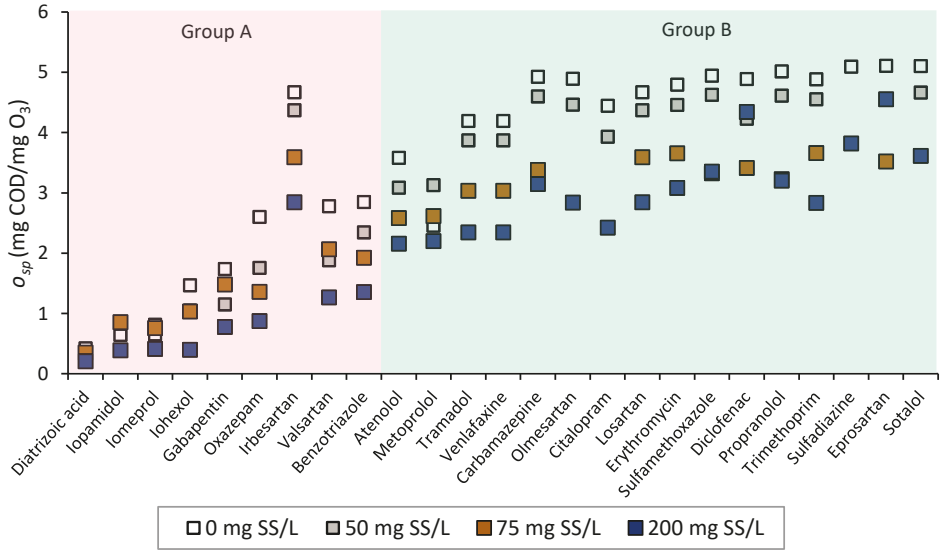

Figure 15. Average value of the removal constant, o_{sp}, for the pharmaceuticals investigated at various suspended solids (SS) concentrations.

The linearity of the decrease in the removal constant, o_{sp}, with increasing SS concentration, in accordance with Equation 7, was verified (Paper II). The particle constant, k_p, was obtained by calculating the slope of the line when plotting o_{sp} against SS for each of the pharmaceuticals investigated. The ozone scavenging effect of the particles, estimated with the particle constant k_p, seemed comparable for most compounds within each group, despite some inconsistencies in the results for metoprolol, sulfamethoxazole and sulfadiazine. The average particle constant, k_p, was calculated for each group and found to be 4.6 ± 2.0 [(mg COD·L)/(mg O_3·g SS)] for Group A, and 5.8 ± 2.5 [(mg COD·L)/(mg O_3·g SS)] for Group B. However, there was no statistical difference between the values of k_p for the two groups ($p > 0.05$), and an average value of k_p of 5.4 ± 2.4 [(mg COD·L)/(mg O_3·g SS)] was therefore assumed for all pharmaceuticals.

The effect of SS concentration on the removal of pharmaceuticals during ozonation was evaluated using the predicted removal values. First, typical removal constants in the absence of particles (Group A: o_s=2; Group B: o_s=4) were combined with the average particle constant (Group A and B: k_p= 5.4 ± 2.4) in accordance with

Equation 7, to obtaining the removal constant in the presence of particles, o_{sp}, at various SS concentrations (0 to 100 mg SS/L). The predicted values of pharmaceutical removal were then obtained using Equation 8 at a fixed COD_{diss} of 30 mg/L (Figure 16).

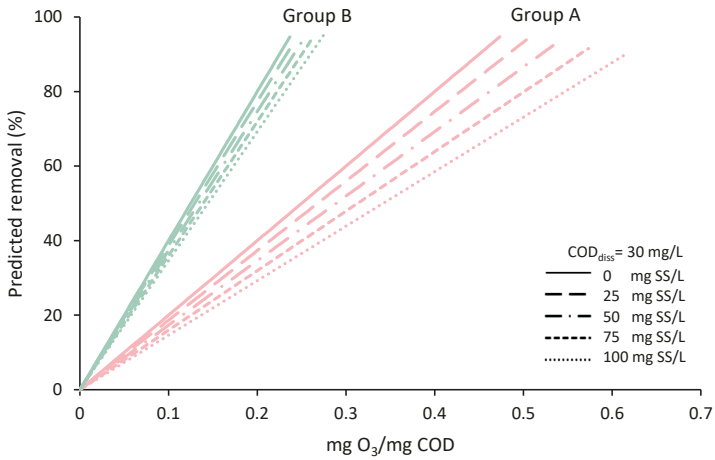

Figure 16. Predicted removal of model pharmaceuticals in Groups A and B by ozone oxidation of wastewater with 30 mg COD/L and various suspended solids (SS) concentrations.

The results indicated that the ozone required for 80% removal increased by less than 10% at an elevated concentration of SS (~25 mg SS/L) in comparison to the typical values in the secondary clarifier effluent (5-15 mg SS/L). This suggests that frequently observed variations in SS contents in wastewater effluents have a minor effect on the removal efficiency of pharmaceuticals compared with the effects of variations in the dissolved matter across the wastewater effluents (± 20%). However, in the case of very high SS concentrations, corresponding to the extreme situation of sludge escaping the secondary clarifiers (~100 mg SS/L), the ozone dose had to be increased by 16% for fast-reacting, and by 37% for slow-reacting, pharmaceuticals to achieve a removal of 80%. These findings suggest that the model presented here could be useful during the design of ozonation units, and in the evaluation of scenarios in which by-pass or pre-filtration could be necessary due to high levels of SS in wastewater to be treated with ozone for the removal of pharmaceuticals.

4.2.2 Verification of the prediction tool

The prediction tool was verified by comparing the predicted removal with the removal measured at the ozonation pilot plant (Figure 17). The predictions of pharmaceutical removal were based on the values of o_{sp} and o_s for the different pharmaceuticals, together with the particle constants, k_p, together with COD_{diss} concentrations (24.2–36.3 mg/L) and SS concentrations (2.4–27.4 mg SS/L) measured at the inlet of the ozonation pilot plant, which was fed with activated sludge effluent.

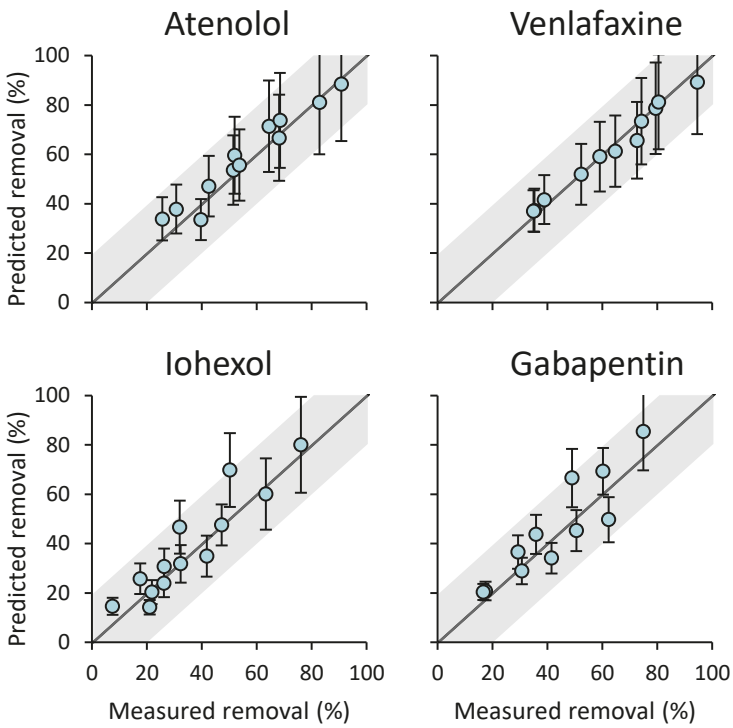

Figure 17. Predicted versus measured removal (%) of atenolol, venlafaxine, iohexol and gabapentin. The gray-shaded area indicates 20% deviation, and the error bars indicate the standard deviation.

For most of the pharmaceuticals investigated, the difference between the predicted and the measured removal was less than 10%. Although some deviations were observed for iomeprol and citalopram, the overall agreement between the predicted and the measured values indicates that this COD/SS-based prediction tool is useful for the prediction of pharmaceutical removal by ozone oxidation of wastewater.

(Complete results are given in Paper II). The new removal constants could be adjusted to suit the site-specific properties of other WWTP effluents, based on laboratory ozonation experiments.

4.3 Bromate formation and mitigation

4.3.1 Bromide content and bromate yield

Bromate formation during ozonation was investigated in laboratory-scale experiments using effluent wastewater from the Sjölunda WWTP. Ozonation was performed as described in Section 3.1.1, at seven ozone doses (from 0 to 2.5 mg O_3/mg DOC). The properties of the wastewater are given in Table 5. The low levels of nitrite were not expected to result in a noticeable ozone scavenging effect competing with bromide. The bromide concentration in the effluent of Sjölunda WWTP is higher than concentrations from guidelines in Germany (>0.15 mg Br^-/L) and Switzerland (>0.4 mg Br^-/L), for which ozonation is not recommended or has to be assessed from case to case (Antakyali et al., 2016; Wunderlin et al., 2017). The measured high bromide concentration is expected to lead to the formation of a non-negligible amount of bromate.

Table 5. Properties of the wastewater effluent from the Sjölunda WWTP before ozonation. The values are expressed as the average ± one standard deviation (n=3).

DOC (mg/L)	COD_{diss} (mg/L)	UVA_{254} (1/m)	NH_4^+–N (mg /L)	NO_3^-–N (mg /L)	NO_2^-–N (mg /L)	Br^- (mg/L)	SS (mg/L)	pH (-)
15.4 ± 0.3	40.7 ± 0.1	24.4 ± 0	13.2 ± 0	<0.05	<0.02	0.559 ± 0.002	4.7 ± 0.5	7.6 ± 0

The increase in bromate concentration at increasing ozone doses was accompanied by a decrease in the bromide concentration (Figure 18). To further study bromate formation during ozonation and to improve the comparability of the data, bromate yields (mg BrO_3^-/mg Br^-) were calculated for each ozone dose (Figure 19). The bromate yield increased linearly and was comparable with previously reported results, despite differences in the initial bromide concentration in the wastewater (Edefell et al., 2021; Soltermann et al., 2016).

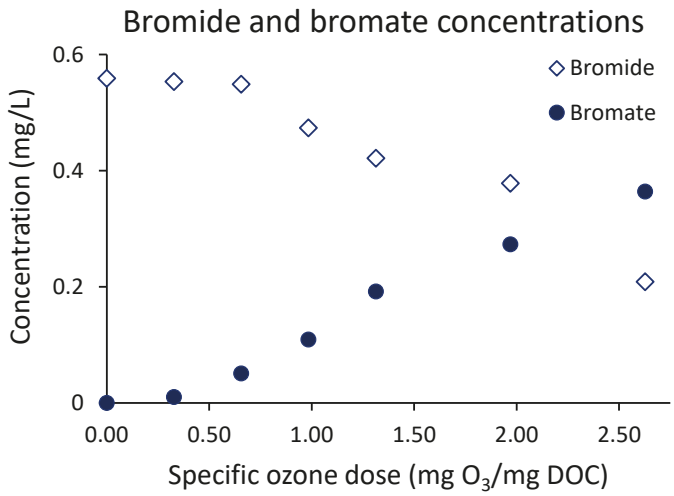

Figure 18. Bromide and bromate concentrations at various ozone doses for the Sjölunda WWTP effluent.

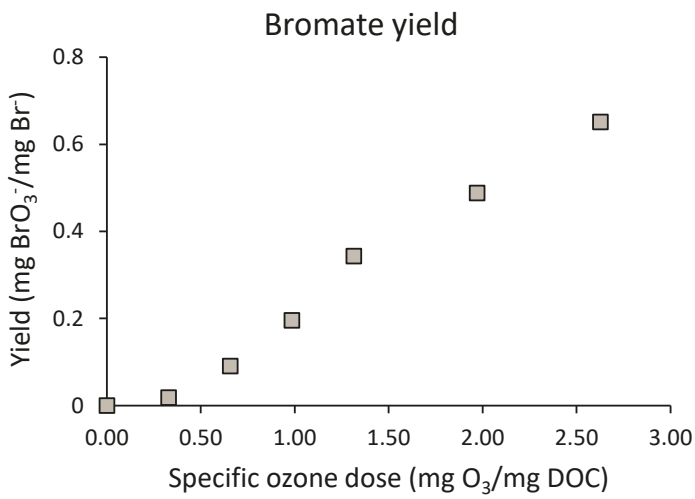

Figure 19. Bromate yield at various ozone doses for the Sjölunda WWTP effluent.

These findings suggest that the ozonation of bromide-rich wastewater, such as that from the Sjölunda WWTP, may produce bromate concentrations close to, or exceeding, the proposed environmental standard of 50 µg/L (Oekotoxzentrum, 2015), even at relatively low ozone doses of 0.5 mg O_3/mg DOC. Several strategies could be applied to limit bromate formation, such as source control to decrease the bromide concentration in the wastewater, or the addition of process solutions such as hydrogen peroxide (H_2O_2) and ammonia, (NH_3), or pH-lowering measures to suppress the oxidation pathways involved in bromate formation (Pinkernell & von Gunten, 2001; Soltermann et al., 2017). In contrast to the investigated strategies for limiting bromate formation, the reduction of bromate by a biological treatment after wastewater ozonation has not been considered as an option. However, a biological treatment in anoxic conditions, such a denitrification step, could reduce the bromate to bromide.

4.3.2 Post-treatment for bromate reduction

Laboratory-scale experiments were performed to evaluate microbial bromate reduction by denitrifying biofilms after ozonation, as described in Section 3.2. The properties of the ozonated Sjölunda WWTP effluent before the denitrifying biofilm experiments are presented in Table 6. At high ozone doses, DOC, COD_{diss} and UVA_{254} showed similar decreases, when comparing data from Table 5 and 6, to those reported previously (Altmann et al., 2014; Cruz-Alcalde et al., 2020; Nöthe et al., 2009), together with an increase in nitrate concentration due to the ozone oxidation of nitrite and ammonium.

Table 6. Characteristics of the ozonated wastewater effluent from the Sjölunda WWTP before bromate reduction experiments with denitrifying carriers. The values are expressed as the average ± one standard deviation (n=3).

DOC (mg/L)	COD_{diss} (mg/L)	UVA_{254} (1/m)	NH_4^+–N (mg/L)	NO_3^-–N (mg/L)	NO_2^-–N (mg/L)	Br^- (mg/L)	BrO_3^- (mg/L)
12.3	28.6	6.92	11.9	0.2	<0.02	0.434	0.106
± 0.2	± 0.3	± 0	± 0	± 0		± 0.006	± 0.002

The decrease in bromate in the ozonated wastewater (1 mg O_3/mg DOC) from the Sjölunda WWTP over time, with and without an external carbon source and nitrate, is shown in Figure 20. A higher bromate reduction rate was seen without nitrate than in the presence of excess nitrate. Despite the preference of nitrate over bromate as an electron acceptor under anoxic conditions (Butler et al., 2005), the amount of bromate was slightly reduced, even in the presence of excess nitrate.

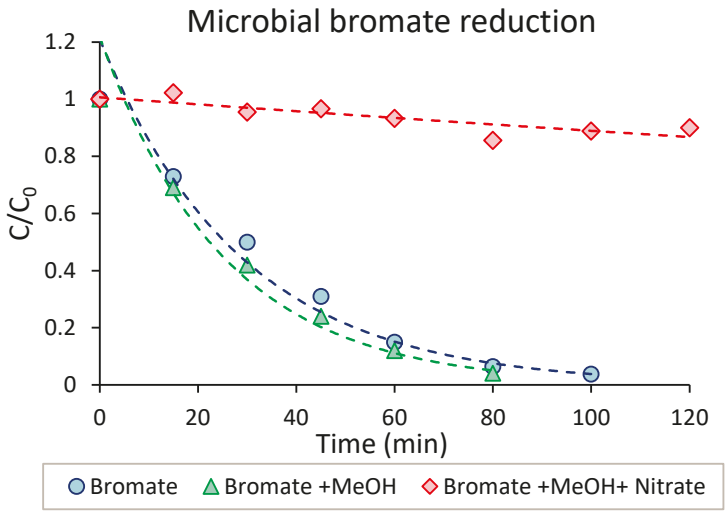

Figure 20. Reduction of bromate (C_0 ~0.1 mg/L) with denitrifying carriers, with and without an external carbon source (MeOH) and nitrate.

The addition of methanol as an external carbon source did not improve the bromate reduction rates, compared to the experiments without the additional carbon source or nitrate, suggesting that the readily degradable organic matter produced during ozonation was sufficient for bromate reduction in the denitrifying biofilm process. The consumption of the external carbon source, measured as COD_{diss}, was higher in the experiments with excess nitrate (~60 mg COD/L) than in those without additional nitrate (~15 mg COD/L). This was due to the higher bacterial activity in the reactors containing excess nitrate. The findings of these experiments indicate that microbial denitrification using MBBRs after ozonation can reduce the concentration of bromate in the effluent by 80% after 60 minutes (Figure 20), which is a typical HRT in full-scale MBBR units.

5 Conclusions

This thesis describes studies on the effect of operating conditions and wastewater properties on the removal of pharmaceuticals during ozonation of wastewater, and the possibility of reducing the amount of bromate using a microbial denitrifying process. The studies carried out have contributed to our knowledge on the effects of operating conditions and the effects of particulate matter on the removal of pharmaceuticals. The findings were combined with COD to develop a simple tool for the prediction of the ozone demand and pharmaceutical removal. Laboratory-scale experiments, together with modelling, provided useful information for the initial assessment of ozone oxidation for pharmaceutical removal without the need for pilot-scale studies. Additionally, the possibility of reducing the bromate formed during ozonation to bromide by means of a denitrifying biofilm process was investigated.

Seasonal variations in wastewater temperature do not appear to affect the removal efficiency of pharmaceuticals during ozone oxidation, and shorter HRTs than those typically employed for the design of ozonation units, can possibly be applied. Typical (5-15 mg SS/L) or moderately elevated (~25 mg SS/L) particle concentrations in wastewater effluent do not notably compromise ozonation efficiency. However, the presence of highly elevated concentrations of SS (~100 mg SS/L) negatively affects the removal efficiency during ozone oxidation and increases ozone demand, which can be predicted by means of a tool based on COD and SS. The bromate formed during ozonation of bromide-rich wastewater could potentially be reduced by using a denitrifying MBBR, an already existing process step in a number of WWTPs that might be considering installing ozonation for pharmaceutical removal or reuse purposes.

6 Future research

The findings presented in this thesis suggest that the ozone demand and the removal efficiency of pharmaceuticals during ozone oxidation of wastewater can be predicted using a simple tool based on COD and SS, together with relatively simple laboratory-scale ozonation experiments. This would remove the need for pilot-scale testing at a first stage of the evaluation of ozone as a technique for pharmaceutical removal, and the related construction and operating costs of the pilot plant. However, the prediction tool should be verified using effluents from other WWTPs. A more thorough analysis of the interaction between particles and ozone and the hydroxyl radicals, taking particle size distribution into consideration would help in assessing the need for pretreatment to remove particles before ozonation.

Bromate is the main cause for concern in the ozonation of water containing bromide. The amount of bromate was reduced using a denitrifying MBBR process on laboratory scale, however, experiments must be performed in continuous mode and on a larger scale before full-scale implementation will be possible. Apart from the mitigation of bromate demonstrated in this thesis, strategies for controlling bromate formation during ozonation should be further explored.

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