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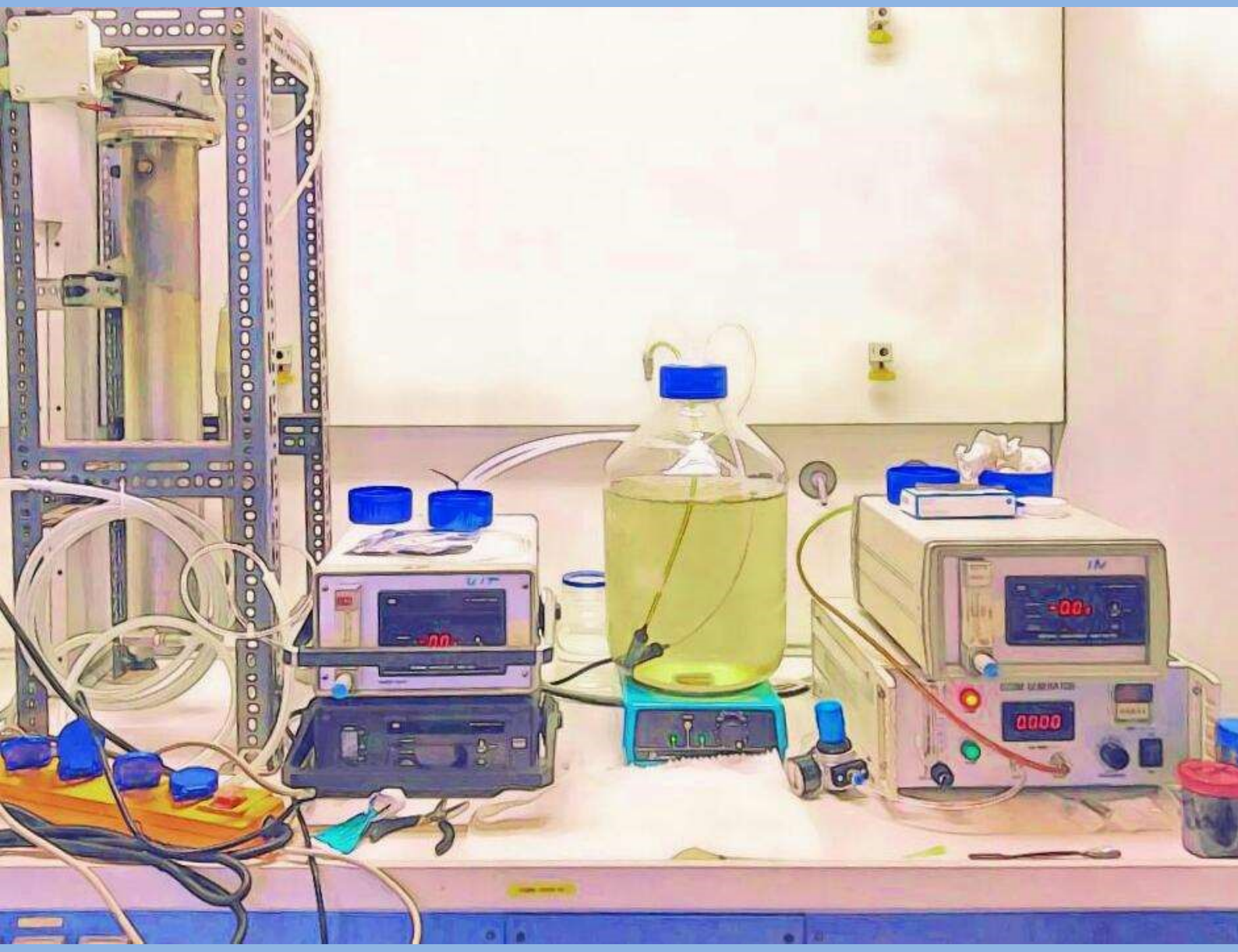
Organic Micropollutant Treatment by Pre-Ozonation and Activated Carbon



TU Delft

Organic Micropollutant Treatment by Pre-Ozonation and Activated Carbon

O3GAC Project Research

By

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In partial fulfilment of the requirements for the degree of

Master of Science
in Civil Engineering (Water Management)

at the Delft University of Technology,
to be defended publicly on Friday 29 September 2017 at 2:00 pm

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Preface

This thesis was written as part of my master's programme. The research is part of an ongoing project between TU Delft, Waternet, Witteveen+Bos, Nijhuis Water Technologies, and CABOT that is exploring the potential of combining ozone and activated carbon treatment (O3GAC) in tackling the problem of organic micropollutants in wastewater. I was introduced to this project while working as an intern at Witteveen+Bos and saw the opportunity to continue researching on micropollutant removal which I have been pursuing since my bachelor studies. Joining this project has been an eye-opening experience, especially setting up experiments from scratch was something new for me. I hope that my efforts in this research can help bring clean water to more people.

I would like to express my gratitude to my supervisors, Jan Peter van der Hoek and Bas Heijman whose guidance, understanding, and patience added considerably to my master's experience in TU Delft. Special thanks go out to the colleagues from Waternet and Witteveen+Bos. Without their valuable input, I would not have been able to complete this thesis. I would also like to thank Nadine Boelee from Nijhuis Water Technology, who kindly came to TU Delft with the ozone generator and for her advice in the ozonation part of the experiments. I am also grateful to the lab technicians for their help in the Waterlab.

Finally, I would also like to thank my father, whose unwavering support and encouragements have allowed me to achieve what I have today. I also dedicate this thesis in memories of my mother, whose love continue to support me to this day.

T.K. Liu

Delft, August 2017

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List of Abbreviations

AC	activated carbon
AOC	assimilable organic carbon
BV	bed volume
DL	detection limit
DOC	dissolved organic carbon
GAC	granular activated carbon
gO3/gDOC	gram of ozone per gram of DOC
O3GAC	Ozone and granular activated carbon
OMP	organic micropollutants
PAC	powdered activated carbon
PACAS	Powdered Activated Carbon in Activated Sludge
PGAC	pulverised granular activated carbon
STOWA	Stichting Toegepast Onderzoek Waterbeheer
WWTP	wastewater treatment plant

Abstract

Inadequate treatment of wastewater effluent is one of the major point sources of pollution of organic micropollutants (OMPs) into aquatic environments. Wastewater treatment plants need to be upgraded to reduce OMP contamination. Recently, the combination of pre-ozonation and granular activated carbon (GAC) filtration has been proposed as a potential OMP treatment method. The aims of this study are to examine the treatment efficiency of selected OMPs, the effects of an ozonated feed water (second clarifier effluent) on GAC adsorption, effects of ozonation on GAC bed life and to identify the dosages of ozone for the design of a pilot plant. Batch adsorption experiments were conducted. The results show that combining the two treatment methods lead to higher elimination/removal rates of the target compounds. The data obtained in the study was used to plot adsorption isotherms and breakthrough curves to investigate the effect of ozonation on GAC bed life. The study found that ozonation reduces the adsorption capacity of the GAC for the selected compounds. Increasing the ozone dosage from 0.2 to 0.4gO3/gDOC further lowers the adsorption capacity. However, at 0.8gO3/gDOC, the adsorption capacity improves. Consequently, according to COMSOL simulations based on the LDF model, ozonation of the feed water at dosages 0.2 and 0.4 gO3/gDOC results in the breakthrough point occurring earlier than without ozonation. However, a later breakthrough point is obtained with a dosage of 0.8gO3/gDOC. This is likely due to the effect of low post-ozonation concentrations outstripping the effects of a poorer adsorption capacity. Therefore, an ozone dose of 0.8g/gDOC is recommended for the pilot plant while a lower dose could be examined to confirm the findings in this study. Further research is recommended to assess the behaviour of the oxidation by-products and their removal efficiency by GAC filtration.

1 Introduction

1.1 Background

In recent decades, the presence of OMPs in aquatic environments has received increasing scientific and public awareness (Hollender et al., 2009). The Dutch government has outlined their attention to this in the Water Policy - Water quality/fresh water and water cycle (Waterkwaliteit/Zoetwater en Waterketen), dated 25 November 2015 by Minister mw. drs. MH Schultz van Haegen to parliament, state secretary Mansveld, water companies, and water boards (Haegen, 2015). Water boards and drinking water companies are urged to perform advanced wastewater treatment and drinking water production to ensure that these substances are removed.

In response, the Foundation for Applied Water Research (STOWA) O3GAC study (2015-2016) was conducted to examine different concepts for extensive removal of organic micropollutants and nutrients from wastewater treatment plant (WWTP) effluent by ozone dosing and GAC filtration (with biological nitrate removal and chemical phosphate removal). Both ozonation and GAC filtration have been separately reported to treat OMPs and there could be added benefits by combining the two methods. Following up from the experience gained from studying the GAC filtration of effluent from the Horstermeer WWTP, Waternet intends to carry out further research, together with the Delft University of Technology, Witteveen+Bos, Nijhuis Water Technology and CABOT focusing on various implementation aspects of the O3GAC concept.

1.2 Objective

The objective of this research is to gain a better understanding of the role and added value of ozonation in the O3GAC concept and the design criteria for implementing this concept with a pilot installation. The research questions this study aims to answer are:

1. What are the removal efficiencies of the target micropollutants?
    - What are the elimination efficiencies by ozonation?
    - What are the removal efficiencies of GAC?
    - What are their removal efficiencies of O3GAC?
2. What is the influence of ozonation?

- On the removal efficiencies of the target compounds?
- On the adsorption isotherms?
- On GAC bed life?

3. What is the range of ozone dosing to improve GAC bed life?
4. What is the estimated bed life by modelling?
5. What are the limitations and restrictions of this study?

1.3 Structure of Thesis

Chapter 1 gives an introduction to the need for advanced wastewater treatment methods and the objectives of this research. The elimination efficiencies of ozonation, removal efficiencies by activated carbon and the potential benefits of combining the two methods are discussed in Chapter 2. The chapter will also explain how the breakthrough behaviour of the filter will be simulated. Next, Chapter 3 describes the target compounds, the experimental setup and the modelling method. The results are shown in Chapter 4 and the effect of ozonation on the removal efficiencies of the target compounds is discussed. The breakthrough behaviour of the target compounds simulated in the 1-STEP® filter will also be discussed in this chapter. Finally, the conclusions and recommendations of this research are made in Chapter 5.

2 Literature Review

2.1 Introduction to OMPs

OMPs are contaminants that occur in low concentrations (ng/L to µg/L). They can be either anthropogenic or naturally derived. OMPs originate from many products that humans consume such as drugs, cosmetics, and pesticides. In the European Union, it is reported that there are more than 100,000 registered chemicals and an estimated 30,000 to 70,000 of these are used daily (Schwarzenbach et al., 2006). However, due to their persistent nature, some of these substances do not biodegrade or adsorp readily and are not removed easily in conventional WWTPs. Ultimately, they end up in surface water or even drinking water and pose various detrimental effects to living organisms and the environment. This study focuses on the following 12 compounds (Table 2-1) which will be further explained in the next chapter.

Table 2-1 Target Pharmaceuticals

Compound	CAS NR	MW	Formula
Atorvastatin	134523-00-5	558.6	$C_{33}H_{35}FN_2O_5$
Benzotriazole	95-14-7	119.1	$C_6H_5N_3$
Bisoprolol	66722-44-9	325.4	$C_{18}H_{31}NO_4$
Carbamazepine	298-46-4	236.3	$C_{15}H_{12}N_2O$
Clarithromycin	81103-11-9	748.0	$C_{38}H_{69}NO_{13}$
Diclofenac	15307-79-6	296.1	$C_{14}H_{11}Cl_2NO_2$
Ibuprofen	15687-27-1	206.3	$C_{13}H_{18}O_2$
Metformin	657-24-9	129.2	$C_4H_{11}N_5$
Metoprolol	37350-58-6	267.4	$C_{15}H_{25}NO_3$
Sotalol	3930-20-9	272.4	$C_{12}H_{20}N_2O_3S$
Sulfamethoxazole	723-46-6	253.3	$C_{10}H_{11}N_3O_3S$
Trimethoprim	738-70-5	290.3	$C_{14}H_{18}N_4O_3$

2.2 Occurrence of OMPs

OMPs enter the sewer systems via various pathways. For example, from toilets due to human excretion and defaecation or improper disposal and leaching from urban areas during rainfall

(Margot et al., 2013). Hospital wastewater also contributes to the OMP load to a certain extent (Ternes, Joss, & Siegrist, 2004). As such, in countries with centralised wastewater treatment systems like the Netherlands, WWTPs can be a major point source for micropollutant discharge into surface waters. Moreover, the amount of OMPs consumed is expected to rise due to decreasing production costs, population expansion, an ageing population and new uses for existing chemicals (Daughton, 2003). Therefore, removing OMPs at WWTPs is essential in mitigating the problem of OMPs entering the water cycle.

In a study of eight WWTPs in Western Europe, 36 pollutants were analysed (Reemtsma et al., 2006). Benzotriazole, diclofenac, and carbamazepine showed averages of 1-10 µg/L in the effluent. Other compounds such as flame retardants and personal care products ranged between 0.1 and 1 µg/L. At least half of the studied compounds were not removed significantly by the WWTPs. The partial degradation and adsorption of pharmaceutical compounds, such as clarithromycin, diclofenac, and trimethoprim, in WWTPs have also been reported in other literature. Diclofenac is shown to poorly adsorb to sludge and is poorly biodegradable, resulting in low removal rates in biological treatment (Barbosa, Moreira, Ribeiro, Pereira, & Silva, 2016). In a study of micropollutant removal efficiencies in several nutrient-removing WWTPs in Switzerland, removal rates of <10% for carbamazepine, >90% for ibuprofen, and no observable removal for sulfamethoxazole are reported (Joss et al., 2005). Moreover, many plants in the EU do not have a solid retention time long enough for sufficient biodegradation of OMPs (Ternes et al., 2004). Even if the OMPs are degraded in the WWTP, there are concerns that the degradation products might be potentially more mobile or persistent (Aga, 2007). The current treatment methods are thus insufficient for the removal of OMPs and part of them remain in the effluent.

The WWTP effluent, from industries and municipalities, then flows or seeps into rivers, lakes, groundwater, or coastal seas (Schwarzenbach et al., 2006). Various organic micropollutants have been detected in surface water. In EU rivers, OMPs such as carbamazepine, ibuprofen, diclofenac, benzotriazole and sulfamethoxazole, have been detected (Loos et al., 2009). The first four compounds are also reported to be within the top 10 most frequently detected in European rivers and streams. The contamination of water bodies with OMPs, even in small amounts, can have detrimental effects on living organisms and human health. Antimicrobial products and antibiotics in surface water have been linked to the emergence of antibiotic-resistant bacteria (Chee-Sanford, Aminov, Krapac, Garrigues-Jeanjean, & Mackie, 2001). The synthetic oestrogen, ethinylestradiol, has been reported to cause reproductive failure in fish (Nash et al., 2004). Moreover, there are concerns that OMPs might have potential to bioaccumulate and affect higher organisms (DeLorenzo et al., 2008; Gomes et al., 2004). This effect has been observed for diclofenac at

concentrations of 1µg/L (Vieno & Sillanpää, 2014). Other OMPs, such as benzotriazole which is commonly found in aircraft deicing and anti-icing fluids, have been reported to increase the toxicity of receiving waters (Cancilla, Baird, Geis, & Corsi, 2003). Besides that, some studies point that under solar irradiation, some OMPs in aquatic environments transform into less biodegradable, more toxic and inhibitory than the parent compound (Fatta-Kassinos, Vasquez, & Kümmerer, 2011).

Ultimately, the OMPs in the aquatic environment could end up in drinking water. Due to the scarcity of water resources, more and more regions are producing drinking water from surface water, which may have originated from WWTPs, or are even reusing treated wastewater in various applications (Levine & Asano, 2004). A study on tap water from City of Boulder, Colorado, USA, found traces of OMPs such as carbamazepine (85 ng/L), diclofenac (252 ng/L), ibuprofen (276 ng/L), sulfamethoxazole (230 ng/L), and trimethoprim (175 ng/L) (Zearley & Summers, 2012). The presence of OMPs in tap water could have adverse effects on human health. Therefore, with proper treatment at WWTPs, the OMPs can be prevented from entering the water cycle and causing various adverse effects.

2.3 Treatment of OMPs

As discussed in the previous section, not all OMPs are easily removed in WWTPs. Even WWTPs in the EU that follow the Urban Wastewater Treatment Directive might not be sufficient to fully reduce the risks of OMPs contamination (Reemtsma et al., 2006). Polar pollutants such as diclofenac, carbamazepine, and benzotriazole are likely to pose a threat in the water cycle as they are highly soluble in water. This has generated multiple discussions on how to upgrade existing treatment plants to improve removal efficiencies of OMPs (Joss, Siegrist, & Ternes, 2008), with one key suggestion focusing on activated carbon and ozonation as a promising solution to reduce micropollutant loads drastically at reasonable costs and energy levels (Margot et al., 2013).

2.3.1 Activated Carbon

Activated carbon is a porous material that can remove OMPs by adsoprtion. OMPs attach to the surface of the carbon. The addition of powdered activated carbon (PAC) has been reported to have high removal efficiencies of OMPs in wastewater (Nowotny, Epp, von Sonntag, & Fahlenkamp, 2007). In a pilot scale study of PAC sorption efficiency, it was found that a dosage of 10-20 mg/L achieved adequate treatment of a broad spectrum of OMPs in secondary effluent with a dissolved organic carbon (DOC) range of 10-20 mg/L (Boehler et al., 2012). Granular activated

carbon (GAC) was also shown to be effective in OMP removal (Snyder et al., 2007). However, polar and negatively charged compounds in neutral pH have been reported to show poor adsorption (Snyder et al., 2007; Ternes et al., 2004). Moreover, in the case of wastewater, due to the higher dissolved organic matter, De Ridder et al. (2011) found that there is more competition for active sites of the carbon and pore blocking, leading to reduced removal efficiencies. They also observed that preloaded GAC became negatively charged which affected the removal of negatively charged compounds significantly. At a GAC dosage of 6.7 mg/L, the removal rate for negatively charged compounds and positively charged compounds ranged from 0-58% and 32-98% respectively. As activated carbon is expensive, used GAC is reactivated thermally, chemically or biologically when possible. However, regeneration can be costly and so it is useful to find ways to extend the GAC running time.

2.3.2 Ozonation

Ozone is a strong oxidising agent and can break down big molecules into smaller parts. Ozonation has been reported to show adequate elimination rates for pharmaceuticals in drinking water (Huber, Canonica, Park, & Von Gunten, 2003). Ternes et al. (2002) reported more than 90% elimination of diclofenac and carbamazepine with 0.5 mg/L ozone in drinking water lab-scale experiments. Similarly, in wastewater, high elimination rates of OMPs with ozone were observed (Table 2-2). As shown in the table, at 0.2gO3/gDOC, most of the target compounds also studied in this research have elimination rates of 75% or higher.

Table 2-2 Elimination Rates (%) of OMPs in Wastewater (Ternes et al., 2003)

	Ozone Concentration (g O3/g DOC)	
Compound	**0.2**	**0.4/0.7**
Carbamazepine	>98	>98
Clarithromycin	>76	>76
Diclofenac	>96	>96
Ibuprofen	48	>62
Metoprolol	>78	>93
Sotalol	>96	>96
Sulfamethoxazole	>92	>92
Trimethoprim	85	>85

However, ozonation typically only results in partial oxidation of OMPs and in the case of pharmaceuticals, the oxidation by-products could still be biologically active (Huber et al., 2005). Effects of the oxidation by-products are still uncertain. Some studies suggest that ozonation generally results in sufficient structural modification of pharmaceutical compounds to eliminate their biological activities (Dodd, Kohler, & Von Gunten, 2009). Even in the case where biological activity was still shown in the oxidation by-products, the mixture of by-products was reported to be less harmful than the mixture of parent compounds (Reungoat et al., 2010). Moreover, a large fraction of the organic by-products formed after oxidation is assimilable organic carbon (AOC) which suggests that they are more biodegradable. Another concern with ozonation is the formation of bromate which is considered a human carcinogen (Von Gunten, 2003).

2.3.3 Combined Ozonation and Activated Carbon

Both ozonation and activated carbon are effective individually in removing a broad range of OMPs. However, each method has its shortcomings. Some substances are removed more efficiently by ozone while some are better removed by activated carbon (Margot et al., 2013). As such, combining the two methods could bring additional benefits.

In a study on pesticide removal by combined ozonation and granular activated carbon filtration to produce drinking water from surface water, it was demonstrated that ozonation significantly improves removal of atrazine by GAC filtration due to the oxidation of background organic matter (Orlandini, 1999). Ozonation reduces the adsorbability and molecular mass of background organic matter which could compete with OMPs. Ozonation could potentially improve OMP removal in GAC filtration of WWTPs as well. Besides that, ozonation increases the AOC content which yields higher bacterial density. This could increase biodegradation of DOC and OMPs and hence increase GAC bed life (Van der Hoek, Hofman, & Graveland, 1999). The GAC could also remove oxidation by-products from ozonation (Reungoat, Escher, Macova, & Keller, 2011). In a study of 54 micropollutants in secondary treated wastewater treated with ozone followed by activated carbon filtration, removal efficiencies were typically higher than 90% and biological effects of the treated wastewater decreased by 62% to 99% compared to the influent (Reungoat et al., 2010). However, there are limited studies on adsorption behaviour of OMPs after the ozonation of wastewater. Hence, the results of this study could serve to reduce the knowledge gaps regarding how ozonation affects activated carbon.

2.4 Modelling of Breakthrough

The breakthrough of a GAC filter refers to the point where the filter is no longer able to remove a target compound and thus shows how long the filter can be used. With the adsorption data collected from batch experiments in this study, the breakthrough curve can be predicted using the linear driving force (LDF) model (Heijman, Siegers, Sterk, & Hopman, 2002). The LDF is a simplified approach that combines the internal and external mass transfer coefficients into an overall kinetic rate constant (Sharma, Petrusevski, Heijman, & Schippers, 2003). The advantage of the LDF model is that all the adsorption parameters can be obtained with batch adsorption experiments.

According to the principle of the conservation of mass, the transfer of matter through the filter can be described by the mass balance equation, written as follows:

$$\frac{\delta C}{\delta t} = D_L \frac{\delta^2 C}{\delta z^2} - v \frac{\delta C}{\delta z} - \left[\frac{1-\varepsilon_b}{\varepsilon_b}\right] \rho_{ads} \frac{\delta q}{\delta t} \quad (1)$$

where,

C = dissolved OMP concentration (g/L)

t = time (s)

D_L = axial dispersion coefficient (m^2/s)

q = loading (mass of adsorbate/mass of adsorbent)

z = longitudinal distance in the filter bed (m)

v = interstitial liquid velocity (m/h)

ε_b = fixed bed porosity (-)

ρ_{ads} = adsorbent density (kg/m^3)

According to the LDF model,

$$\frac{\delta q}{\delta t} = k(q_e - q) \quad (2)$$

where,

k = kinetic rate constant (1/s)

q_e = equilibrium loading (mass of adsorbate/mass of adsorbent)

The axial dispersion coefficient, D_L can be determined experimentally (Heijman et al., 2002) or calculated from correlations (Rastegar & Gu, 2017). The equilibrium loading can be obtained with the Freundlich isotherm equation:

$$q_e = Kc_e^n \quad (3)$$

where K and n are the Freundlich constants. The Freundlich constants can be determined with adsorption equilibrium experiments. c_e is the equilibrium concentration.

By combining equations (2) and (3) and integrating it, the following equation can be obtained:

$$c = (c_0 - c_e)e^{-kt} + c_e \quad (4)$$

In the logarithmic form,

$$\ln\left(\frac{c - c_e}{c_0 - c_e}\right) = -kt \quad (5)$$

k can be determined with the kinetic data from the batch adsorption experiments. c_0 is the initial concentration.

The initial and boundary conditions are as follows:

$t = 0 : c = 0, q = 0$ for $0 \leq z \leq L$

$z = 0 : c = c_0$ for $t > 0$

$z = L : \frac{\delta C}{\delta z} = 0$ for $t > 0$, where L is the bed length

Thus, by solving Equations (1) to (2), the breakthrough curve can be plotted. From the curve, the breakthrough point can be identified. In this study, the breakthrough point refers to the time or bed volume when the target compound is no longer completely removed by the activated carbon, i.e. when the outflow concentration is more than zero.

3 Materials and Methods

3.1 Target Compounds

Twelve OMPs were selected as target chemicals (Table 3-1). The selection of these pharmaceuticals is based on a combination of available analytics (Analysis Package 1 from HWL) and the compounds tested in other research projects, such as PACAS and Groote Lucht (Appendix 1). Some of the compounds are also on the EU watch list in Article 8b of Directive 2008/105/EC. The chemicals were obtained from Sigma-Aldrich (Appendix 2). A concentrated stock solution was prepared by dissolving the pure chemical powders in tap water, instead of methanol to prevent the co-solvent effect (Verliefde et al., 2008) and biological growth. A separate stock solution for benzotriazole was made as the compound was added later into the target compounds. The stock solutions were made such that each compound has a concentration 10^6 times the detection limit[1] (Appendix 3). The stock solutions were stored at 4°C and used to spike the feed water with the desired OMP concentrations.

Table 3-1 Target Pharmaceuticals

Compound	Units	Detection Limit Values
Atorvastatin	ng/L	<3
Benzotriazole	ng/L	<50
Bisoprolol	ng/L	<0.2
Carbamazepine	ng/L	<5
Clarithromycin	ng/L	<20
Diclofenac	ng/L	<4
Ibuprofen	Ng/L	<32
Metformin	ng/L	<70
Metoprolol	ng/L	<5
Sotalol	ng/L	<0.1
Sulfamethoxazole	ng/L	<4
Trimethoprim	ng/L	<2

[1] Due to a calculation error, the concentration of metoprolol in the stock solution was roughly $2x10^6$ times the detection limit.

3.2 Sampling Site Information and Treated Wastewater Collection

Treated wastewater from the second clarifier was obtained from WWTP Horstermeer at 12:00 pm on 25 January 2017. This water is also the feed water for the 1-STEP® filter. The water was filled into jerry cans and stored in the refrigerator at a temperature of 5°C. WWTP Horstermeer is operated by Waternet and treats wastewater from Naarden/Bussum, Hilversum West, Gemeente Wijdemeren, 's-Graveland, Loosdrecht and Nederhorst den Berg. The effluent is discharged into the river De Vecht. It is a conventional treatment plant with activated sludge and biological nutrient removal. The plant has a capacity of 160,000 PE (population equivalent) and uses nitrification and denitrification processes in two anoxic tanks and an aerated tank for nitrogen and phosphorus removal.

3.3 Sample Analysis

Water samples were sent to Het Waterlaboratorium for analysis. This detection limit of each target compound is shown in Table 3-1. In addition to the 12 target compounds, DOC was analysed. The feed water DOC was also measured by Waternet and in the TU Delft lab with a TOC analyser (Shimadzu TOC-V CPH) for the calculation of the ozone dosages.

3.4 Sample Preparation

The feed water was filled into a jar. Part of the water was set aside to be analysed for the presence of target compounds. After that, the stock cocktail solutions were spiked (except for the non-spike experiments) into the wastewater at concentrations 10 times or 100 times the detection limit.

3.5 Ozonation of Wastewater

3.5.1 Ozone Installation

The ozone installation includes an ozone generator, two ozone sensors and an ozone destructor. The ozone generator is fed with air of up to 1.4 bar and the ozone produced in the gas phase is bubbled into the wastewater. The equipment was connected with polyvinylidene fluoride (PVDF) and polyurethane (PU) tubing. The ozone in the off gas was then removed thermally with an ozone destructor. The ozone installation was placed in a fume hood. The schematic of the ozone installation is shown in Figure 3-1. Information on the equipment is shown in Table 3-2.

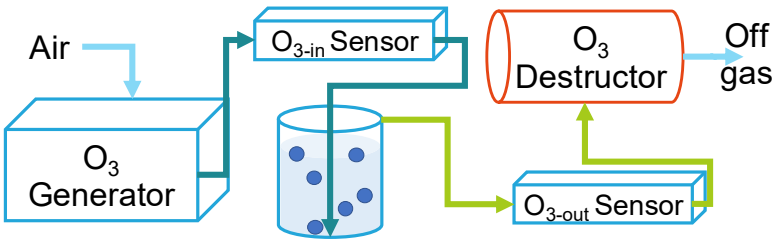


Figure 3-1 Ozone Installation Setup

Table 3-2 Ozone Installation Information

Device	Unit	Range	Model	Manufacturer
Ozone Generator	L/min		NA	NA
Ozone Sensor	g/m3	~5	Ozone Analyser BMT 961	BMT Messtechnik, Berlin
Ozone Sensor	g/m3	~15	Ozone Analyser BMT 961TC	BMT Messtechnik, Berlin

3.5.2 Ozonation Procedures

Sonntag and Von Gunten (2012) reported the elimination of micropollutants in wastewater with a DOC of 5.2 mg/L with ozone dosages ranging from 0.40 to 1.16 gO3/gDOC. With a dosage of 0.40 gO3/gDOC, diclofenac, trimethoprim, carbamazepine, clarithromycin, and sulfamethoxazole were removed by 90% or higher. In agreement with other studies, diclofenac, carbamazepine, and sulfamethoxazole were reported to show more than 90% removal at an ozone dose of 6.7 mg/L (0.47 gO3/gDOC) (Altmann, Ruhl, Zietzschmann, & Jekel, 2014). High elimination rates for some target compounds were also reported at a dose of 0.2 gO3/gDOC (Ternes et al., 2003). As such, in this study, the elimination efficiencies were examined with dosages of 0.2, 0.4, 0.8, and 1.4 gO3/gDOC.

Based on the DOC concentration, the amount of ozone to be applied was calculated. The bubbling time was determined as follows:

$$t = \frac{OD \times c_{DOC} \times V}{c_{O3-in} - c_{O3-out} \times Q} \quad (6)$$

where

t = bubbling time (min)

OD = ozone dosage (g O_3 / g DOC)

c_{DOC} = DOC concentration (mg/L)

V = volume of feed water

c_{O3-in} = ozone concentration measured in $O_{3\text{-in}}$ sensor (g/m^3)

c_{O3-ou} = ozone concentration measured in $O_{3\text{-out}}$ sensor (g/m^3)

Q = gas flow rate measured in $O_{3\text{-in}}$ sensor (L/min)

After the addition of the desired amounts of ozone, the generator was turned off and the water was bubbled with air until no ozone was detected in the $O_{3\text{-out}}$ sensor. Then the residual ozone in the water phase was let to react with the wastewater for 30 minutes. Part of the ozonated water was sent for analysis while the rest was used in the subsequent batch experiment.

3.6 Batch Adsorption Experiments

3.6.1 Activated Carbon

The activated carbon (GAC 612 WB) used in this study was supplied by CABOT. This is the same type of GAC used in the 1-STEP® filter in WWTP Horstermeer. Information on the GAC is shown in Table 3-3. For the batch equilibrium experiments, the GAC was pulverised and passed through a 53 μm sieve to shorten the time needed to achieve equilibrium. For the batch kinetic experiments, the original size of GAC was used.

Table 3-3 GAC Information

Parameter	Unit	Value	Source
Particle diameter	mm	2.5	Cabot[2]
Particle density	kg/m^3	515	Cabot[2]
Bulk density	kg/m^3	400	Cabot[2]
Bed void fraction	-	0.4	Cabot[2]

3.6.2 Batch Equilibrium Experiments

The batch equilibrium experiments were conducted to obtain data to plot the adsorption isotherms. The experiments were conducted with PGAC dosages 0.5, 2, 5, 10, 30, and 50 mg/L. The water and PGAC were stirred with a magnetic stirrer. After 48 hours, the samples were filtered with

[2] Obtained from Cabot by email on 13/6/2017

Whatman® GF/C glass microfiber filters and send to HWL for analysis. The loading of the PGAC was calculated as follows:

$$q_e = \frac{(c_i - c_e) \times V}{m} \quad (7)$$

where

q_e = equilibrium loading (mol/kg)

c_i = concentration before adsorption (mol/m^3)

c_e = equilibrium concentration (mol/m^3)

V = volume of water sample (m^3)

m = mass of PGAC (kg)

With the equilibrium loading and equilibrium concentration, the isotherms were plotted to obtain the Freundlich constants.

3.6.3 Batch Kinetic Experiments

The batch kinetic experiments were conducted to obtain the reaction rate constants. For the kinetic tests, the feed water was spiked with concentrations 100 times the detection limit and separated into 11 jars. 50mg/L of GAC was added to each jar. Samples were taken at 0, 4, 7.5, 24, 48, 72, 144, 192, 384, 576, 720 hours, filtered with Whatman® GF/C glass microfiber filters and send to HWL for analysis.

3.7 Modelling the Breakthrough Curve

3.7.1 Estimating the Axial Dispersion Coefficient

From equation (1), it can be seen that the axial dispersion coefficient, D_L, is required. The dispersion coefficient can be estimated with several methods. Levenspiel (1999) reported correlations for dispersion of fluids in packed beds. The findings are summarised in Figure 3-2. In the figure, D=dispersion coefficient, ε=fixed bed porosity, d_p=particle diameter, and u=interstitial velocity.

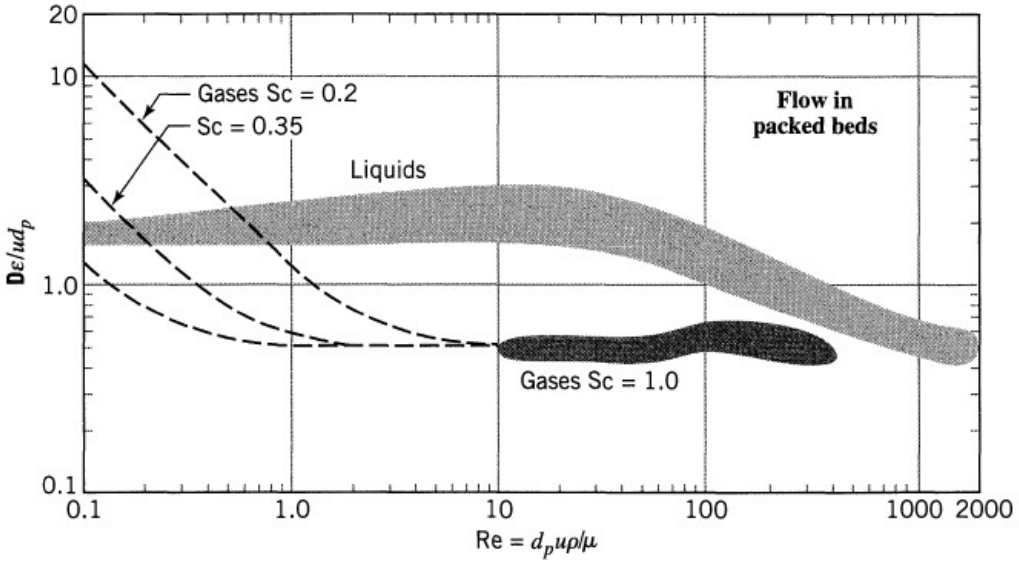


Figure 3-2 Correlations for dispersion of fluids flowing in packed beds (Levenspiel, 1999)

Rastegar and Gu (2017) reported a new correction for the axial dispersion in fixed-bed columns packed with particles. This new correlation takes into account the molecular diffusion term and bed voidage which leads to better accuracy than the commonly used Chung and Wen correlation and the De Ligny correlation. The axial dispersion coefficient can be estimated according to the following equation:

$$D_L = 0.7D_m + \frac{2R_P v\varepsilon_b}{0.18 + 0.008Re^{0.59}} \tag{8}$$

where:

D_m = molecular diffusion coefficient (m^2/s)

R_P = particle radius (m)

ε_b = fixed bed porosity (-)

v = superficial velocity (m/s)

Re = Reynold's number based on superficial velocity (-)

In this study, a D_m of 10^{-9} was assumed which is common for compounds dissolved in water (Cussler, 2009).

3.7.2 Modelling with COMSOL

Equations (1) to (3) were solved using COMSOL Multiphysics® Modelling Software 5.2 with reference to the paper by Aguilera and Ortiz (2016). The model was implemented using the time-dependent, one-dimensional partial differential equations (PDE) module. The software uses the

finite element method to solve the PDE. The input parameters, based on the GAC and operational data of the 1-STEP® filter, are shown in Table 3-4.

Table 3-4 COMSOL Parameters

Parameter	Unit	Value	Source
Particle density	kg/m3	515	Cabot[3]
Bulk density	kg/m3	400	Cabot[3]
Bed void fraction	-	0.4	Cabot[3]
Bed length	m	1.5	Dekker and Zijlstra (2013)
Filtration velocity	m/h	8	Dekker and Zijlstra (2013)

3.8 Experiment Overview

The experiments conducted in this study are summarised in Table 3-5. A total of 8 batches of tests were run and labelled from B1 to B8.

Table 3-5 Experiment Overview

	Ozone Dose (gO3/gDOC)				
Spike Level	0	0.2	0.4	0.8	1.4
No spike				✓(B8)	
10xDL		✓(B6)		✓(B7)	
100xDL	✓(B1)	✓(B2)	✓(B3)	✓(B4)	✓(B5)

DL: detection limit

[3] Obtained from Cabot by email on 13/6/2017

4 Results and Discussion

4.1 Data Processing

The experiments were conducted in batches and analysed in three rounds. The first round consisted of B1, B2, and B3 while the second round consisted of B4 to B8. The third round was for the kinetic tests. Due to technical difficulties at HWL with the compound atorvastatin, this compound was removed from the target list. Despite using the same feed water across the different analysis periods, the analysis results for some compounds showed large disparities in the second round. A trend for the disparities could not be identified. It could be due to the analysis method used for the pharmaceutical compounds as no disparities were seen for benzotriazole which was analysed with a different method.

The first round of results appears to be more consistent so the average was calculated from these batches. Results that were more than 20% different from the average and more than 20% different from the expected concentration after spiking (feed water concentration + spiking concentration) were rejected as shown in Appendix 5. Following these criteria, bisoprolol was also completely removed. Therefore, only 10 of the 12 target compounds could be analysed.

4.2 Feed Water Quality

At the beginning of the study, it was decided to spike the target compounds at 0, 10, and 100 times the detection limit. However, some compounds were found to already have extremely high concentrations in the feed water. Therefore, for some compounds, spiking did not change the concentration significantly. Ibuprofen was the only compound below the detection limit. The feed water quality from this study and the range of concentrations from a previous study are compared in Table 4-1. Besides diclofenac and metformin, the other target compounds had concentrations higher than the range reported in the previous study. Moreover, some of the reported ranges of concentrations showed large differences such as diclofenac which occurred from 0~3100ng/L. Therefore, the concentration of the target compounds can vary substantially. This study focuses on the concentrations from the collected samples. The complete list of feed water and after spiking concentrations is shown in Appendix 6.

Table 4-1 Feed Water Quality

Compound	Unit	Average*	Range in Previous Study**
Benzotriazole	µg/L	6	NA
Carbamazepine	ng/L	473	40~210
Clarithromycin	ng/L	313	NA
Diclofenac	ng/L	467	0~3100
Ibuprofen	ng/L	<32	NA
Metformin	ng/L	757	0~2400
Metoprolol	ng/L	2000	60~340
Sotalol	ng/L	1767	50~330
Sulfamethoxazole	ng/L	163	20~130
Trimethoprim	ng/L	197	0~100

*average of first round of experiments as explained in Section 4.1

**obtained from Bijlage 1 of STOWA 2013 Monitoring 1-STEP® filter Horstermeer

4.3 Ozone Dosage

The DOC concentration of the feed water was 10 mg/L and the bubbling time is presented in Table 4-2. The setup was first tested with tap water to determine the initial operation settings. However, when ozone was applied in B2, the behaviour was slightly different, resulting in a shorter bubbling time than expected. The flow rate was adjusted for the subsequent batches to achieve longer bubbling times. Due to fluctuating ozone production, the variables, c_{O3-in}, c_{O3-out}, and Q, were recorded every 5 minutes and the applied ozone concentration and bubbling time required were calculated as the experiment was running (Appendix 4).

Table 4-2 Ozone Bubbling Time

Batch	Desired Ozone Dose (gO3/gDOC)	Bubbling Time (min)	Applied Ozone Dose (gO3/gDOC)
B2	0.2	5	0.21
B3	0.4	30	0.39
B4	0.8	47.5	0.80
B5	1.4	86.5	1.40
B6	0.2	14	0.20
B7	0.8	39	0.80
B8	0.8	40.5	0.80

4.4 Ozone Elimination Efficiency

4.4.1 Effect of Initial Concentration

The effect of initial concentrations on the elimination efficiencies was studied. B4, B7, and B8 were ozonated at 0.8gO3/gDOC at different initial concentrations (Table 4-3). The elimination efficiencies are compared in Figure 4-1. At 0.8gO3/gDOC, besides metformin, the removal efficiencies were less than 5% apart. This suggests that the elimination rate might not be greatly affected by the initial concentration of the compound for the same bubbling time.

Table 4-3 Initial Concentrations of B4, B7, and B8

Compound	Unit	B4	B7	B8
DOC	mg/L	11	11.1	10.4
Benzotriazole	µg/L	11	6.7	6.4
Clarithromycin	ng/L	NA	540	350
Ibuprofen	ng/L	3200	350	NA
Metformin	ng/L	NA	1200	690
Trimethoprim	ng/L	380	280	NA

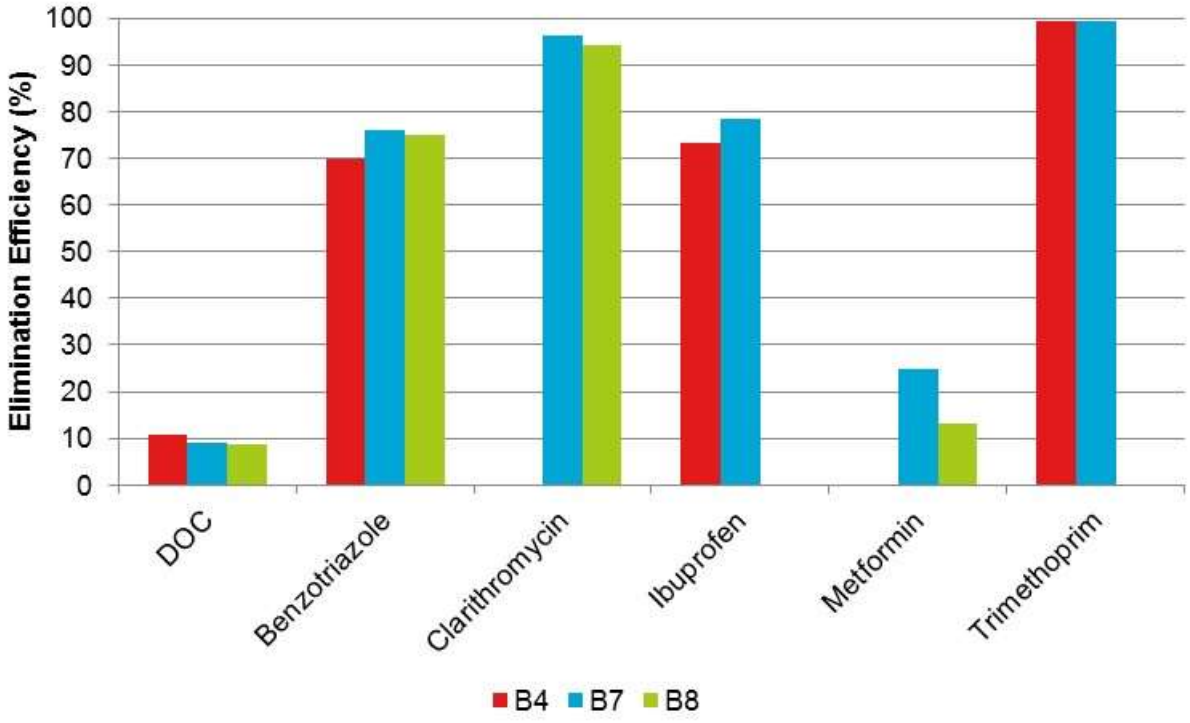


Figure 4-1 Ozone Elimination Efficiency vs Initial Concentrations of the OMPs

4.4.2 Effect of Increasing Ozone Dosage

The elimination efficiencies of the target compounds increase when the dosage rises from 0.2 to 1.4 gO3/gDOC (Figure 4-2). At 0.4 gO3/gDOC, six of the ten compounds are removed at 80% or more. At 0.8 gO3/gDOC, it can be assumed that seven of the ten compounds are removed at 80% or more. At 1.4 gO3/gDOC, it can be assumed that nine of the ten compounds are removed at 80% or more. The results coincide with the elimination efficiencies reported in literature (Altmann et al., 2014; Sonntag & Von Gunten, 2012; Ternes et al., 2002). When compared to Ternes et al. (2003) in Table 2-2, the elimination rates at 0.2gO3/gDOC are lower. This could be due to different conditions in the lab-scale ozone generator used in this study and in the full-scale generators as used in Ternes' study.

Metformin was the most resistant to oxidation. Even at a dosage of 0.8gO3/gDOC, only about 20% elimination was achieved. This is likely due to metformin lacking aromatic rings and unsaturated C-C bonds which result in poor ozone oxidation (Knol et al., 2015). Conversely, high elimination rates for diclofenac, trimethoprim and carbamazepine are due to the presence of oxidisable aromatic rings.

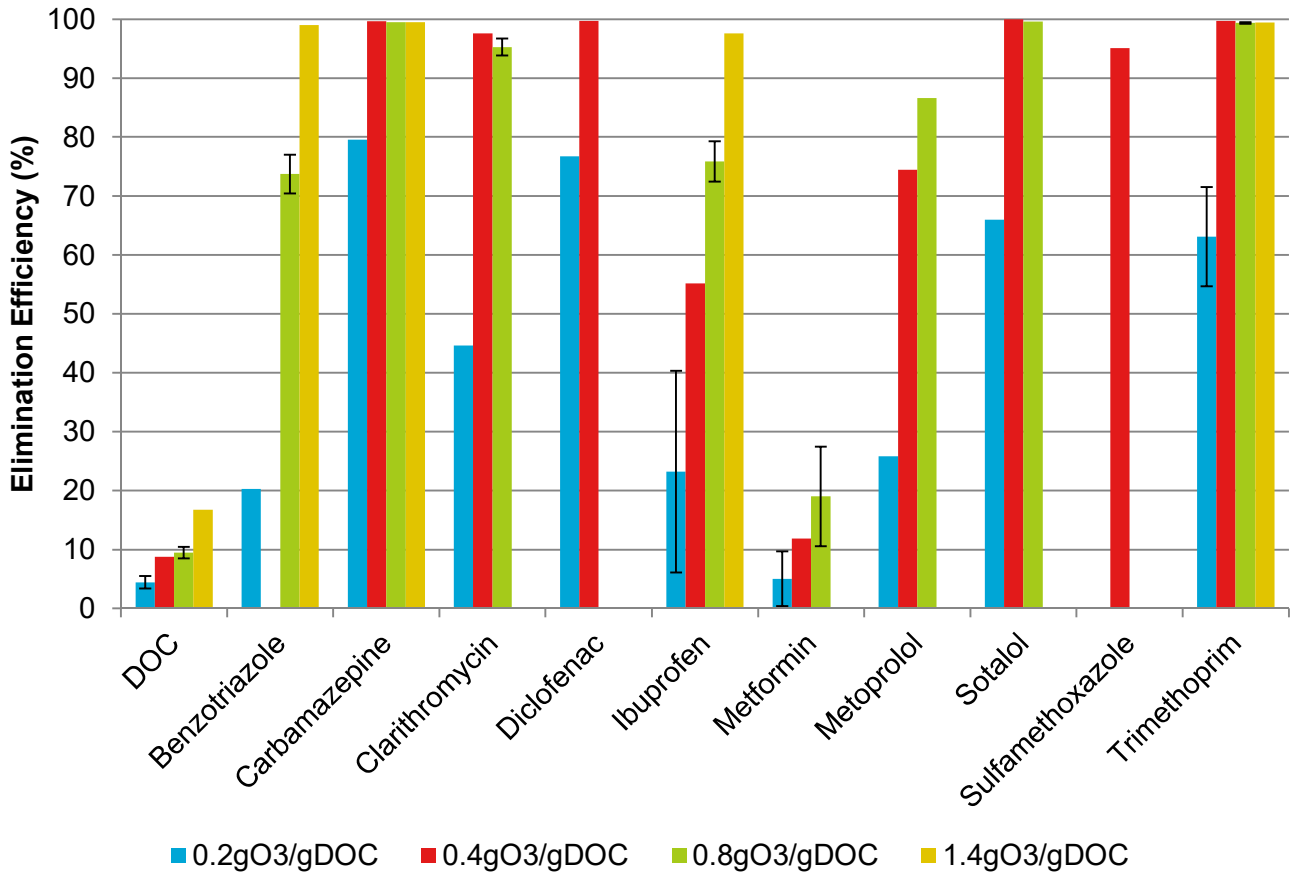


Figure 4-2 Ozone Elimination Efficiency

4.5 PGAC Removal Efficiency

The removal of the target compounds with PGAC is shown in Figure 4-3. No removal is denoted by zeros while rejected data is shown by blanks. The target compounds showed varied affinity to the activated carbon. At 50mg/L of PGAC, seven of the eight compounds were removed at 90% or more. Metformin showed the poorest removal at about 12% even at the highest dosage of PGAC. Similarly, Scheurer, Michel, Brauch, Ruck, and Sacher (2012) reported poor removal of metformin and its metabolite guanylurea with activated carbon filtration. At low dosages (0.5~2 mgAC/L) of PGAC, ibuprofen, sotalol, sulfamethoxazole showed no removal, suggesting that these compounds might have lower affinities for the PGAC compared to benzotriazole, carbamazepine, metoprolol, and trimethoprim.

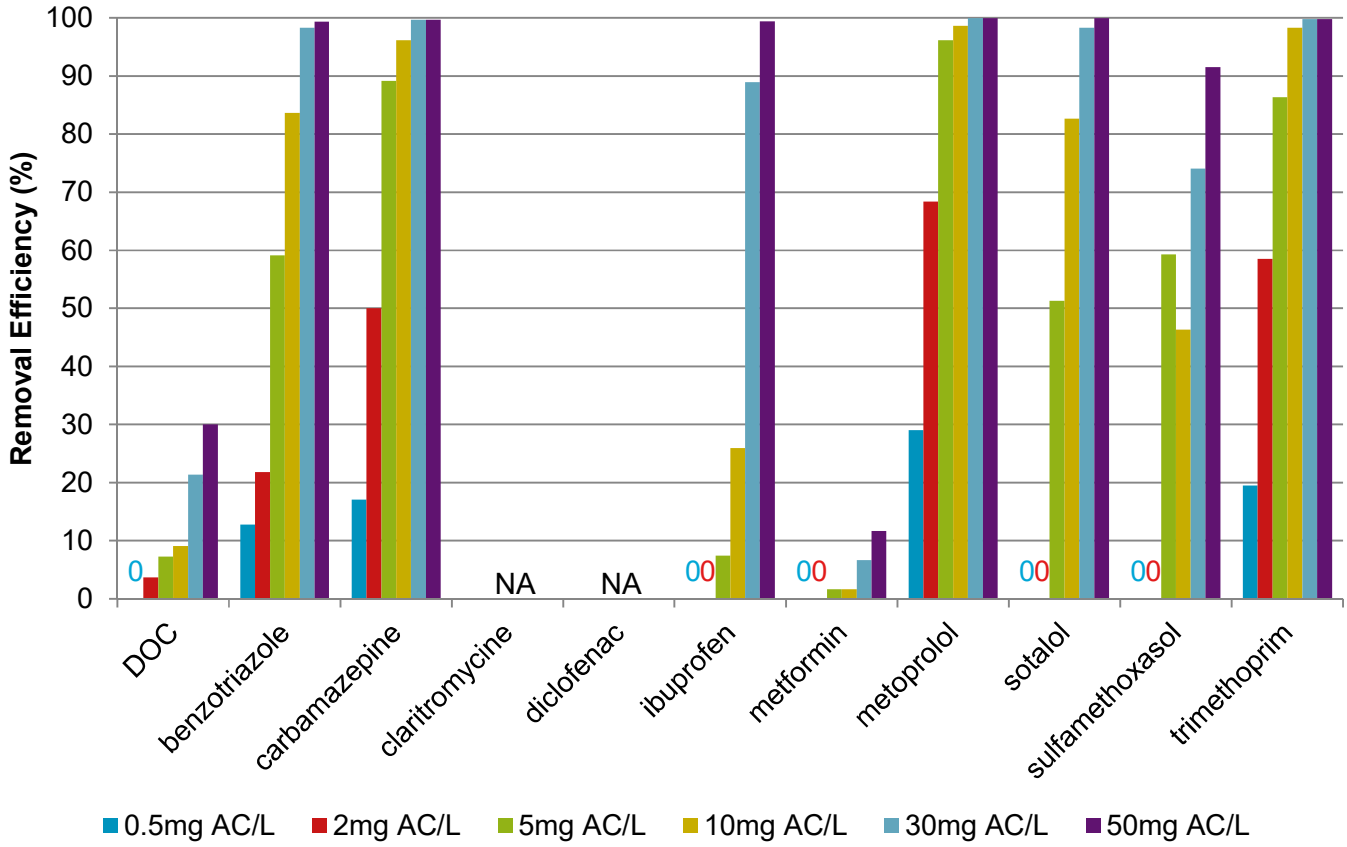


Figure 4-3 PGAC removal of target compounds

4.6 Combined Ozone and PGAC Removal Efficiency

When the two treatment methods are combined, improvements in the overall removal efficiencies can be observed (Appendix 7). Figure 4-4, Figure 4-5 and Figure 4-6 present three cases (low ozone + low AC, low ozone + high AC, high ozone + low AC respectively) to examine the contributions of each method separately and when combined. Both methods complement each other as some compounds are better removed by adsorption (i.e. metoprolol) and some by oxidation (i.e. ibuprofen and sotalol). This shows that with ozonation, for the same amount of activated carbon, higher removal/elimination efficiencies for the target compounds can be expected.

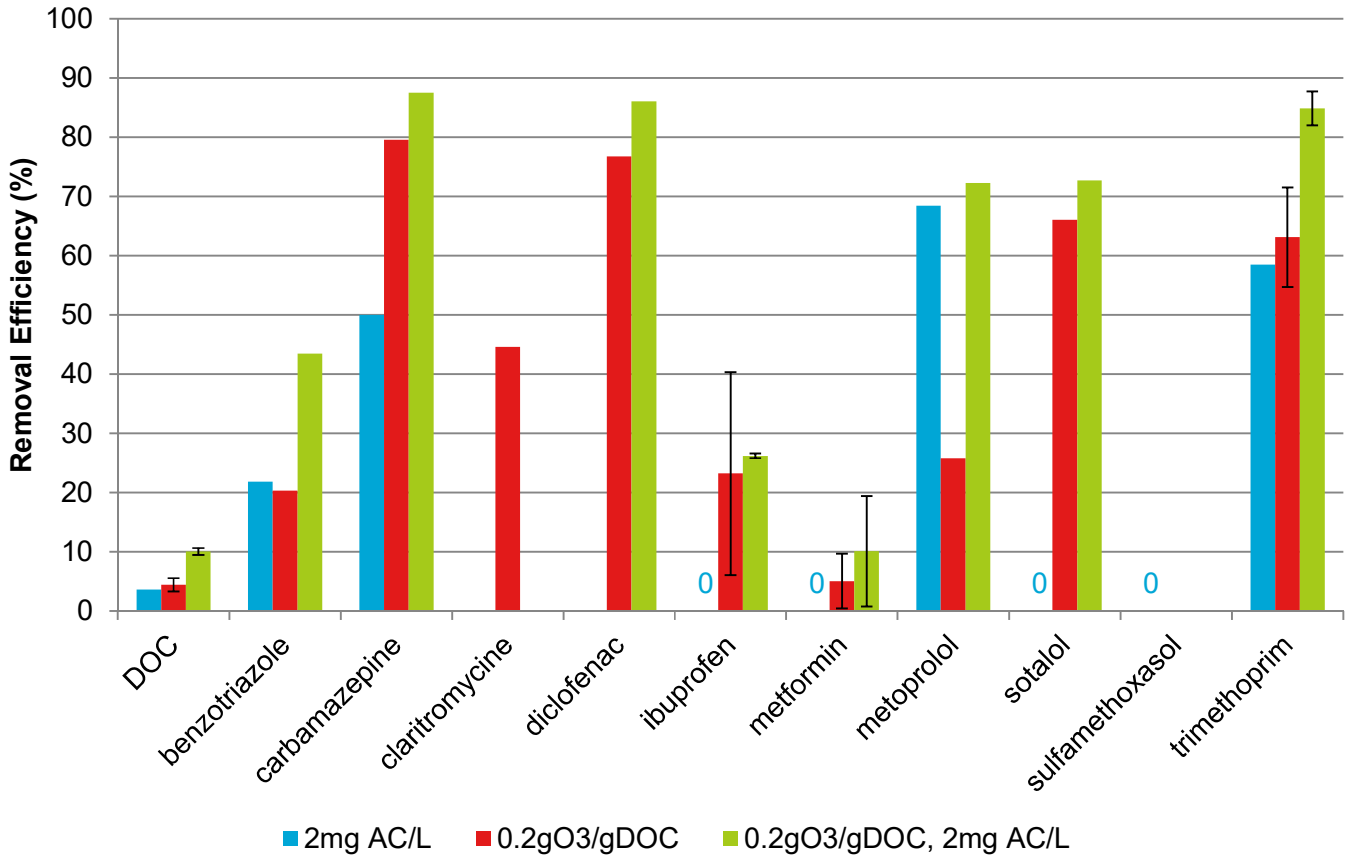


Figure 4-4 Comparison of Removal Efficiencies at 2mg AC/L, 0.2gO3/gDOC, and 0.2gO3/gDOC + 2mg AC/L

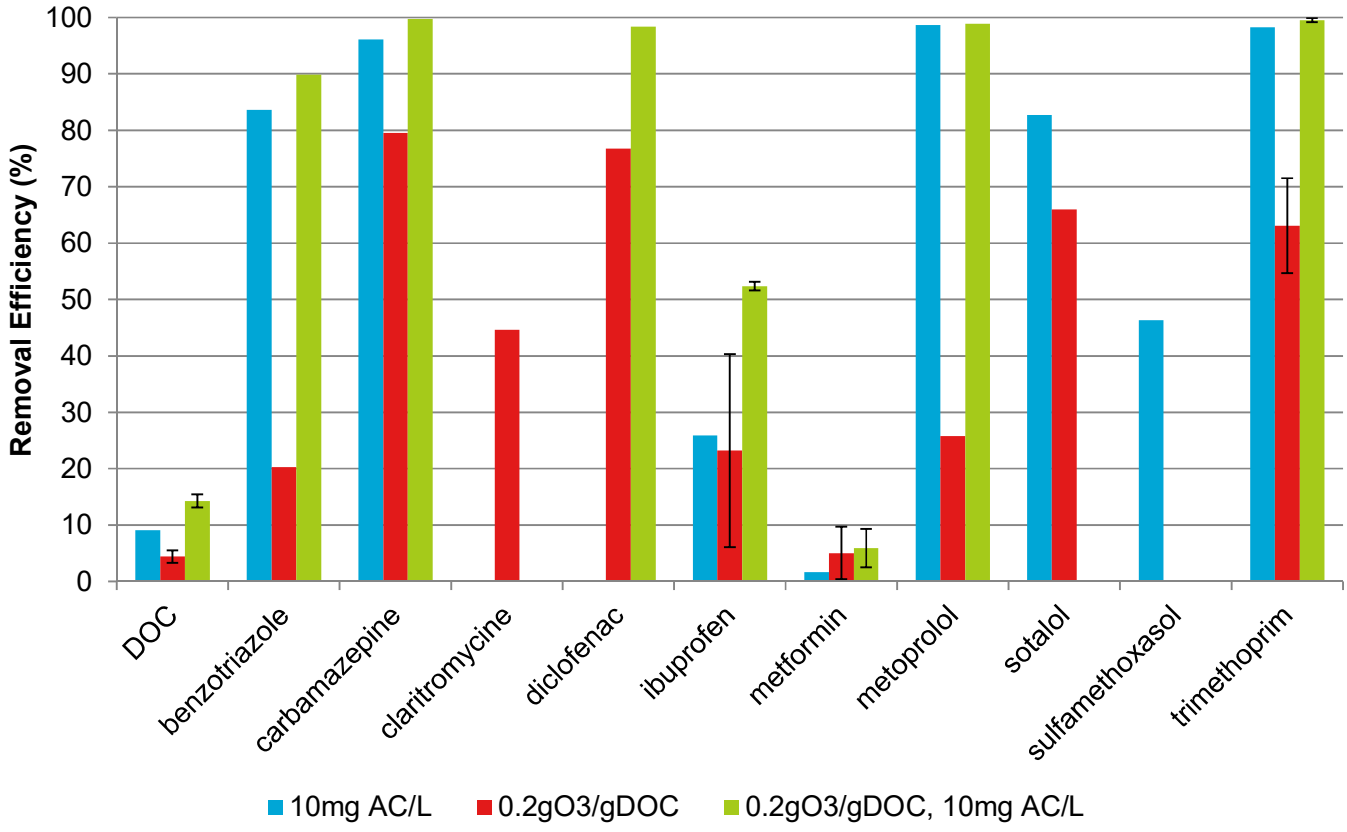


Figure 4-5 Comparison of Removal Efficiencies at 10mg AC/L, 0.2gO3/gDOC, and 0.2gO3/gDOC + 10mg AC/L

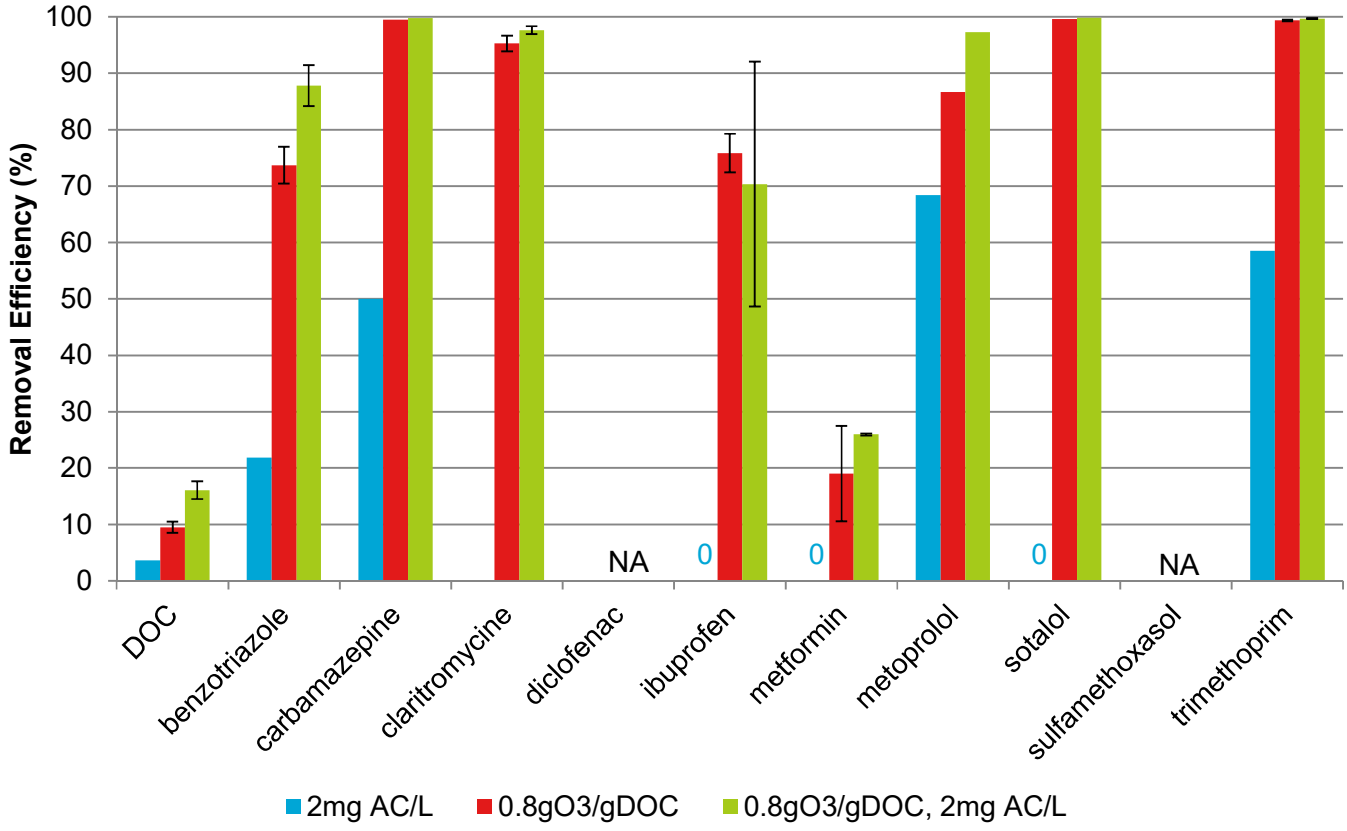


Figure 4-6 Comparison of Removal Efficiencies at 2mg AC/L, 0.8gO3/gDOC, and 0.8gO3/gDOC + 2mg AC/L

4.7 Adsorption Isotherms

The Freundlich constants were obtained by fitting the batch equilibrium data to the Freundlich model, as shown in Equation (3), and presented in Table 4-4. Not all the n and K values could be obtained due to some rejected data (explained in Section 4.1) and values falling below the detection limit. In this study, the GAC was pulverised to reduce the time needed for the batch experiments. The smaller particle size will result in higher adsorption rates (Heijman et al., 2002) and hence overestimations will be expected for the adsorption isotherms and the subsequent breakthrough predictions.

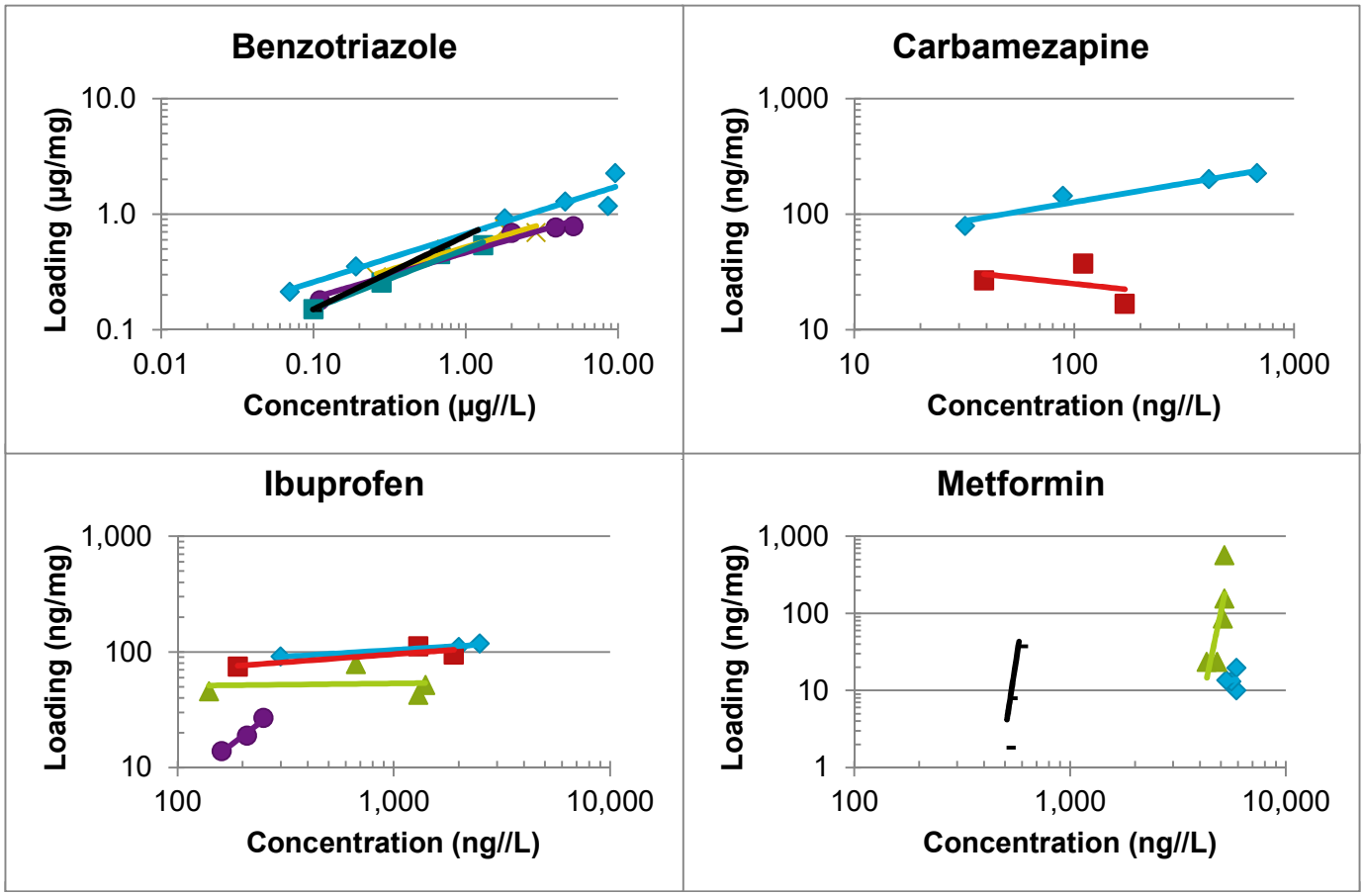
Table 4-4 Freundlich Constants

Compound		B1	B2	B3	B4	B5	B6	B7	B8
Benzotriazole	n	0.42			0.39		0.39	0.52	0.64
	K	0.73			0.44		0.38	1.74	9.19
	R^2	0.94			0.92		0.97	0.99	1.00
Carbamazepine	n	0.33	-0.20						
	K	0.06	5.3e-6						
	R^2	0.94	0.15						
Ibuprofen	n	0.11	0.14	0.02			1.45		
	K	2.0e-3	2.5e-3	3.3e-4			47382		
	R^2	0.97	0.71	0.01			0.97		
Metformin	n	0.40		13.16					18.14
	K	0.01		9.6e54					3.3e93
	R^2	0.00		0.62					0.65
Metoprolol	n	0.37	0.34	0.37	0.28				
	K	0.41	0.18	0.13	0.04				
	R^2	0.97	0.99	1.00	0.99				
Sotalol	n	0.26	0.24	0.71	0.69				
	K	0.02	0.01	0.18	1.38				
	R^2	0.95	0.94	0.95	0.88				
Sulfamethoxazole	n	0.50		1.34					
	K	0.08		16056					
	R^2	0.90		0.84					
Trimethoprim	n	0.32	0.23				0.37		
	K	0.03	4.2e-3				0.04		
	R^2	0.98	0.65				1.00		

n: dimensionless, K: $(m^{3n}mol^{(1-n)})/kg$

The isotherms are shown in Figure 4-7. The blue line indicates the case when ozone was not applied. From the figure, it can be seen that after ozonation, the PGAC shows a reduction in adsorption capacity for all the target compounds, besides metformin. Moreover, when the ozone dosage increases from 0.2gO3/gDOC (,) to 0.4gO3/gDOC ( ), the adsorption capacity decreases further. Interestingly, when the ozone dosage is further increased to 0.8gO3/gDOC (,), the adsorption capacity improves as seen for benzotriazole, metoprolol, and sotalol. Only in the case of metformin, the adsorption capacity improves with increasing ozone dosages. Despite this, metformin is poorly treated by both ozonation and adsorption.

With the K and n values obtained in this section, the breakthrough curves were simulated in COMSOL. However, compounds which have n values (red) of more than 1 or less than 0 were excluded as these cases are highly unlikely and possibly a result of data errors. n values are typically between 0 and 1.



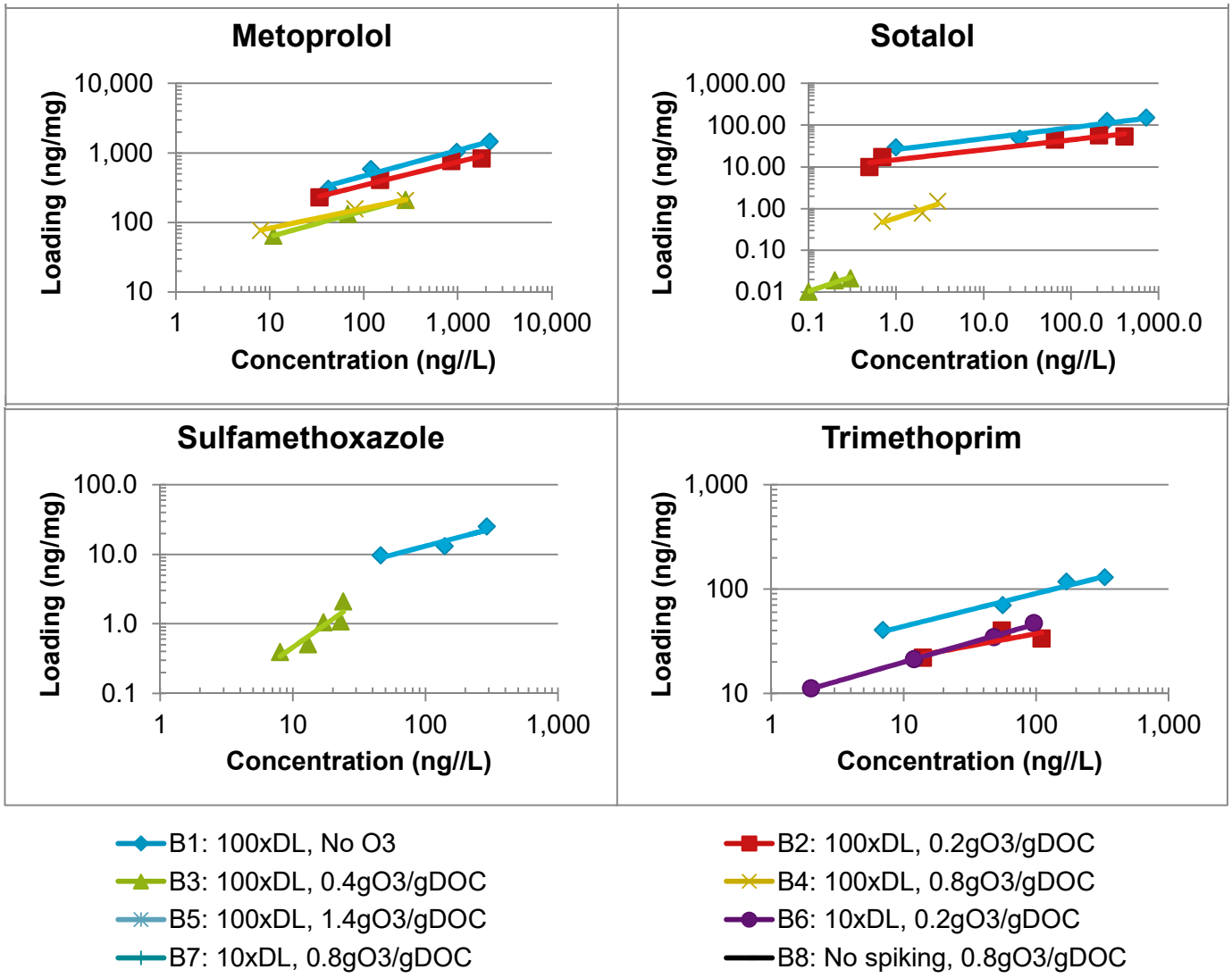


Figure 4-7 Adsorption Isotherms

4.8 Reaction Rate Constant

According to Equation (4), the reaction rate constant (k) was determined from the kinetic equilibrium experiments. Due to different analysis methods, the data for benzotriazole was obtained first. Figure 4-8 shows the concentration curve of benzotriazole with the calculated k (3.78×10^{-6} 1/s) and the points from the batch experiment. Simulations in the next section (Figure 4-16) show that this variable plays an insignificant role and so the value based on benzotriazole was used for the simulations of the other target compounds. The data for the other compounds was received at a later date. The k values were calculated and shown in Table 4-5 but not used for the simulations.

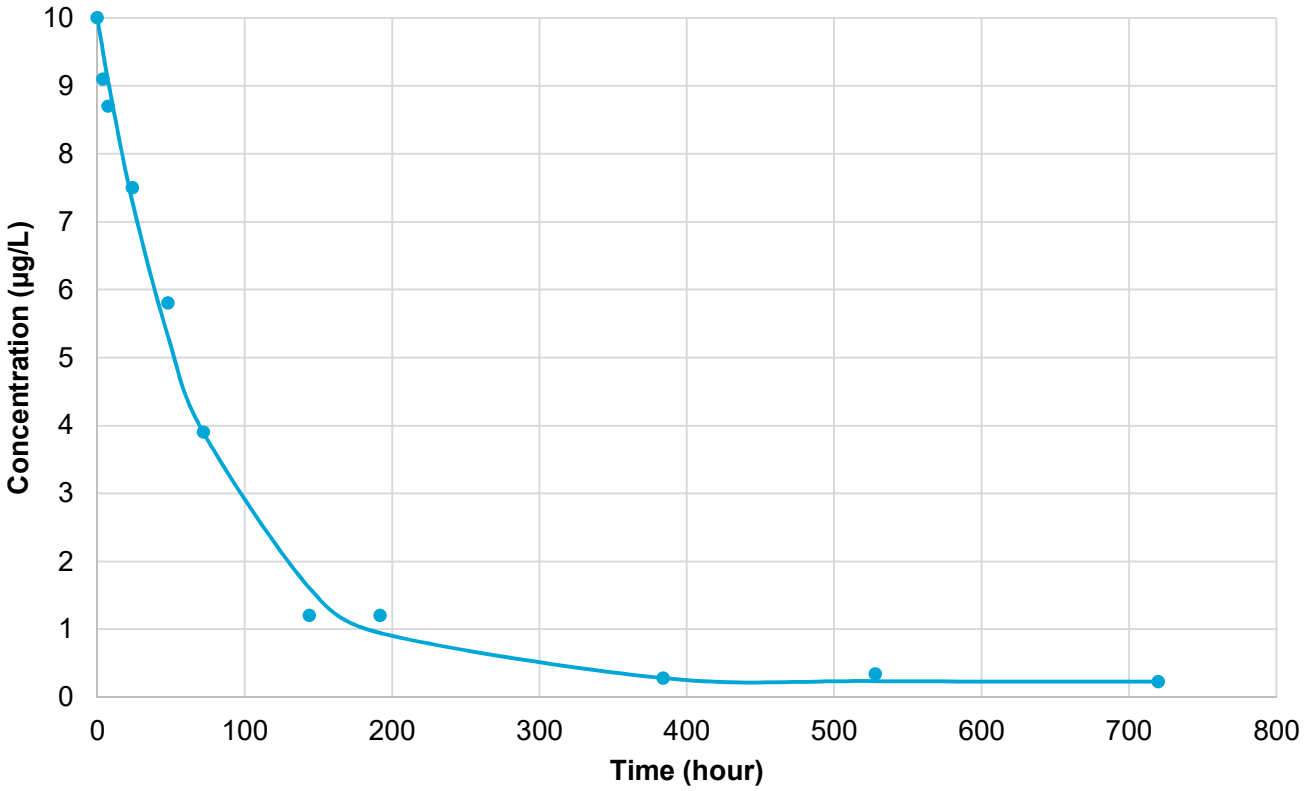


Figure 4-8 Batch experiment measuring reaction rate of benzotriazole

Table 4-5 Reaction rate constant values

Compound	Unit	k
Benzotriazole	1/s	3.78e-6
Carbamazepine	1/s	1.69e-6
Clarithromycin	1/s	NA
Diclofenac	1/s	2.14e-6
Ibuprofen	1/s	NA
Metformin	1/s	2.11e-6
Metoprolol	1/s	NA
Sotalol	1/s	1.64e-6
Sulfamethoxazole	1/s	NA
Trimethoprim	1/s	2.06e-6

The relationship between the reaction rate constant and molecular weight was studied in Figure 11. The reaction rate constant has a somewhat inverse relationship with molecular weight and the value decreases with increasing weight.

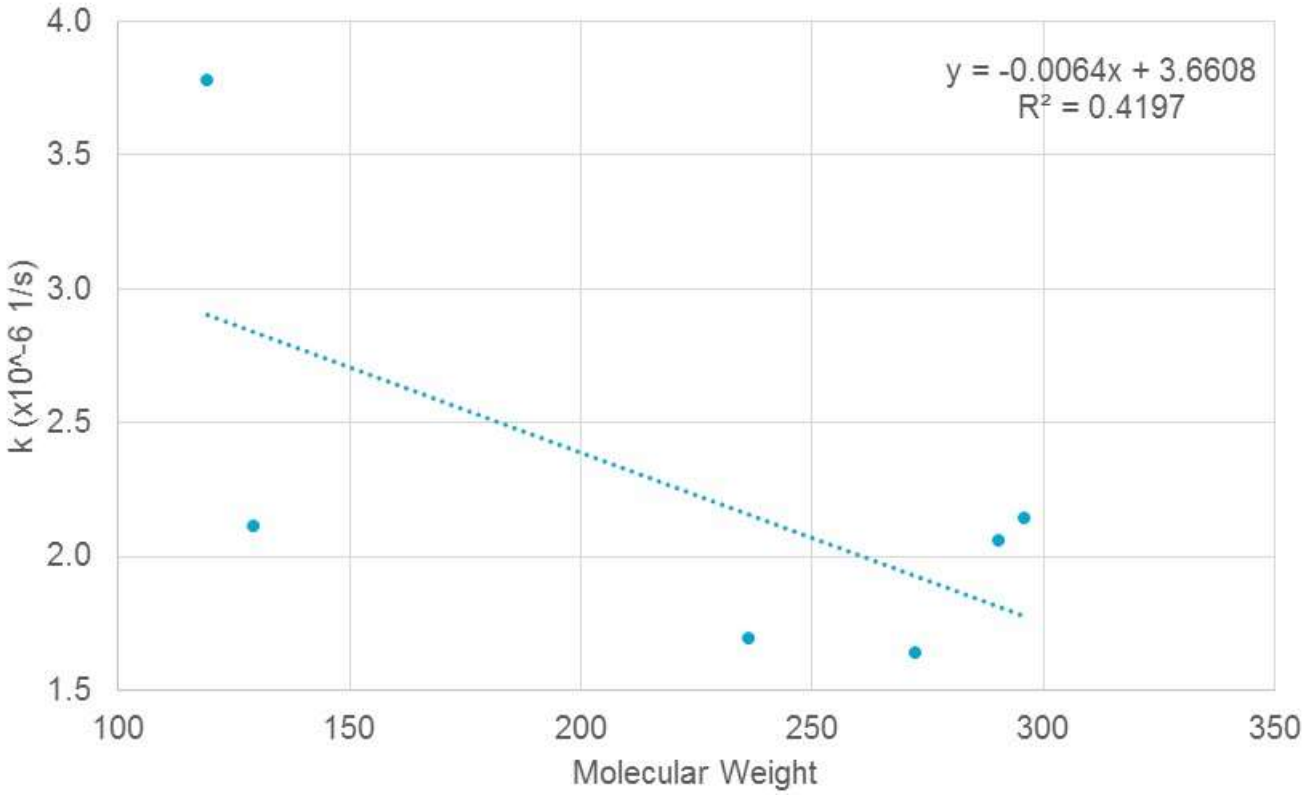


Figure 11 Reaction rate constant and molecular weight

4.9 Prediction of Breakthrough

Table 4-6 shows the breakthrough curves simulated in this study. Ibuprofen could not be modelled due to unknown errors that occurred during simulation.

Table 4-6 Simulated Breakthrough Curves

Compound	B1	B2	B3	B4	B5	B6	B7	B8
Benzotriazole	✓			✓		✓	✓	✓
Carbamazepine	✓							
Metformin	✓							
Metoprolol	✓	✓	✓	✓				
Sotalol	✓	✓	✓	✓				
Sulfamethoxazole	✓							
Trimethoprim	✓	✓				✓		

4.9.1 Determination of the Axial Dispersion Coefficient

The axial dispersion coefficient was calculated based on Figure 3-2 and Equation (7). The values obtained were 3.8-7.3x10^{-5} m^2/s and 2.8x10^{-5} m^2/s respectively. However, this was found to be much smaller than the experimentally obtained value of 3x10^{-3} m^2/s (Sterk, 1998). Other reported values were 1.6-2.0x10^{-4} m^2/s (Sharma et al., 2003), 5.4x10^{-4} m^2/s (Aguilera & Ortiz, 2016). Figure 4-12 shows the breakthrough of benzotriazole at three different values ofD_L. As seen in the figure, the coefficient plays at large role in plotting the curve. Comparison with the curves reported in literature (Aguilera & Ortiz, 2016; Sharma et al., 2003; Sterk, 1998), a value of 3x10^{-3} m^2/s appears to be most similar to actual breakthrough behaviour. As such, this will be used in subsequent modelling. Ideally, the actual axial dispersion coefficient should be experimentally obtained by spiking the pilot setup with a NaCl solution (Heijman et al., 2002).

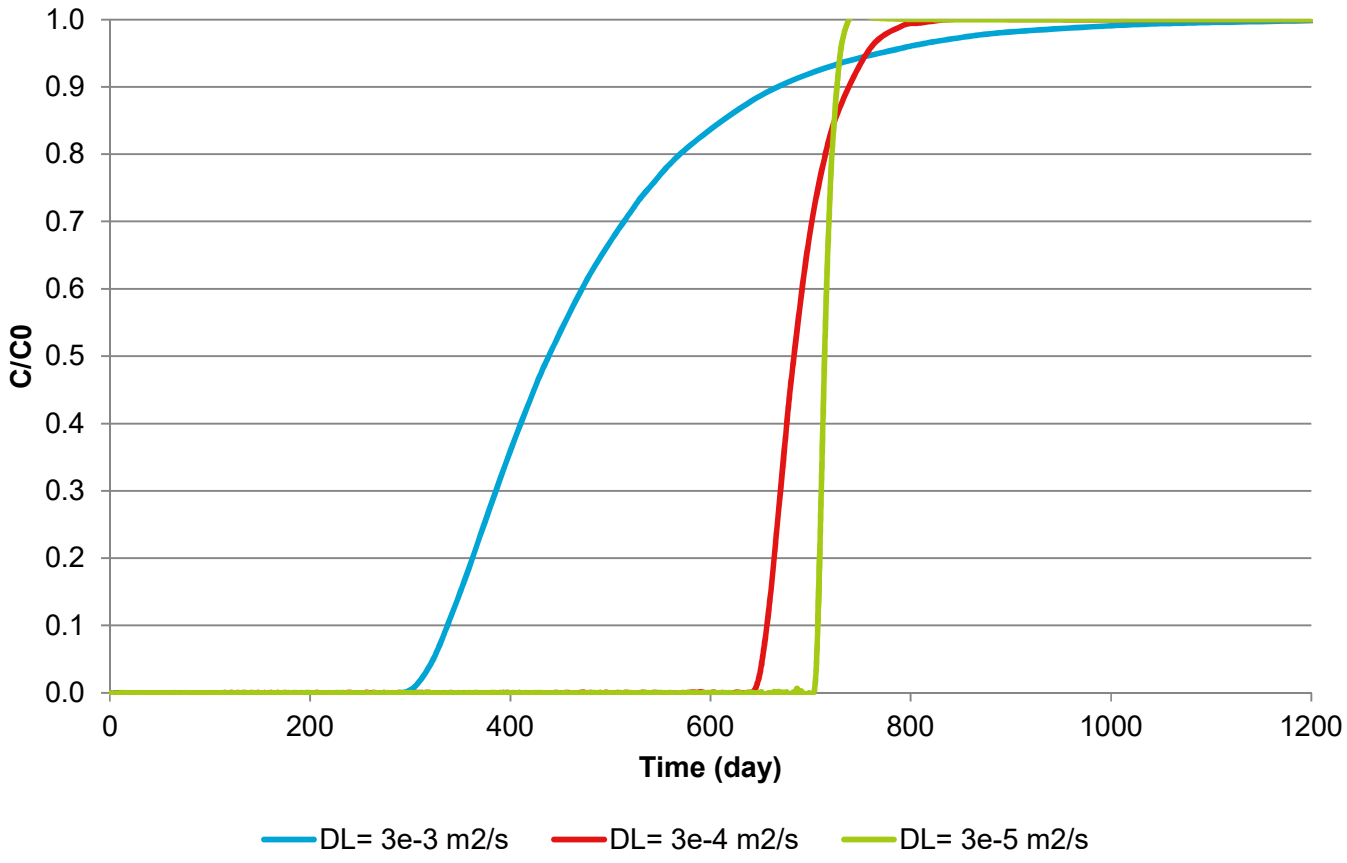


Figure 4-12 Benzotriazole Breakthrough at different dispersion coefficient values

4.9.2 Breakthrough without ozonation

The breakthrough behaviour at 1µg/L of each target compound when no ozone is applied was modelled (Figure 4-13). Metformin shows the earliest breakthrough, followed by sulfamethoxazole and sotalol. Metoprolol shows the latest breakthrough.

The breakthrough behaviour based on the initial concentrations of the feed water when no ozone is applied was modelled (Figure 4-14). From the two figures, it can be seen that the initial concentrations of the target compounds greatly influence the breakthrough behaviour. The feed water concentrations in this study were analysed from a grab sample and thus further study on the initial concentrations in the feed water is needed to identify which compounds reach breakthrough earliest.

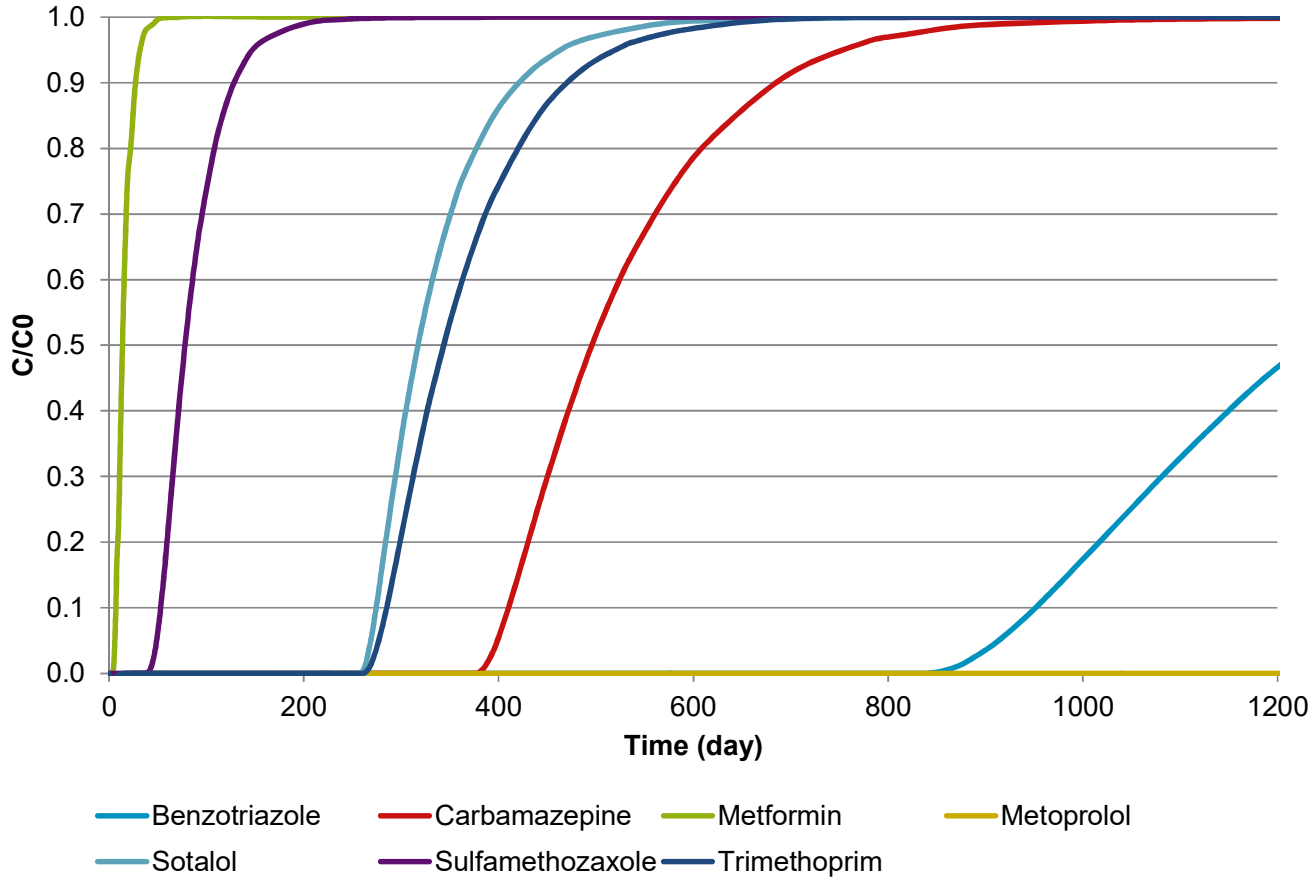


Figure 4-13 Breakthrough Curve of Target Compounds at 1µg/L (no ozone)

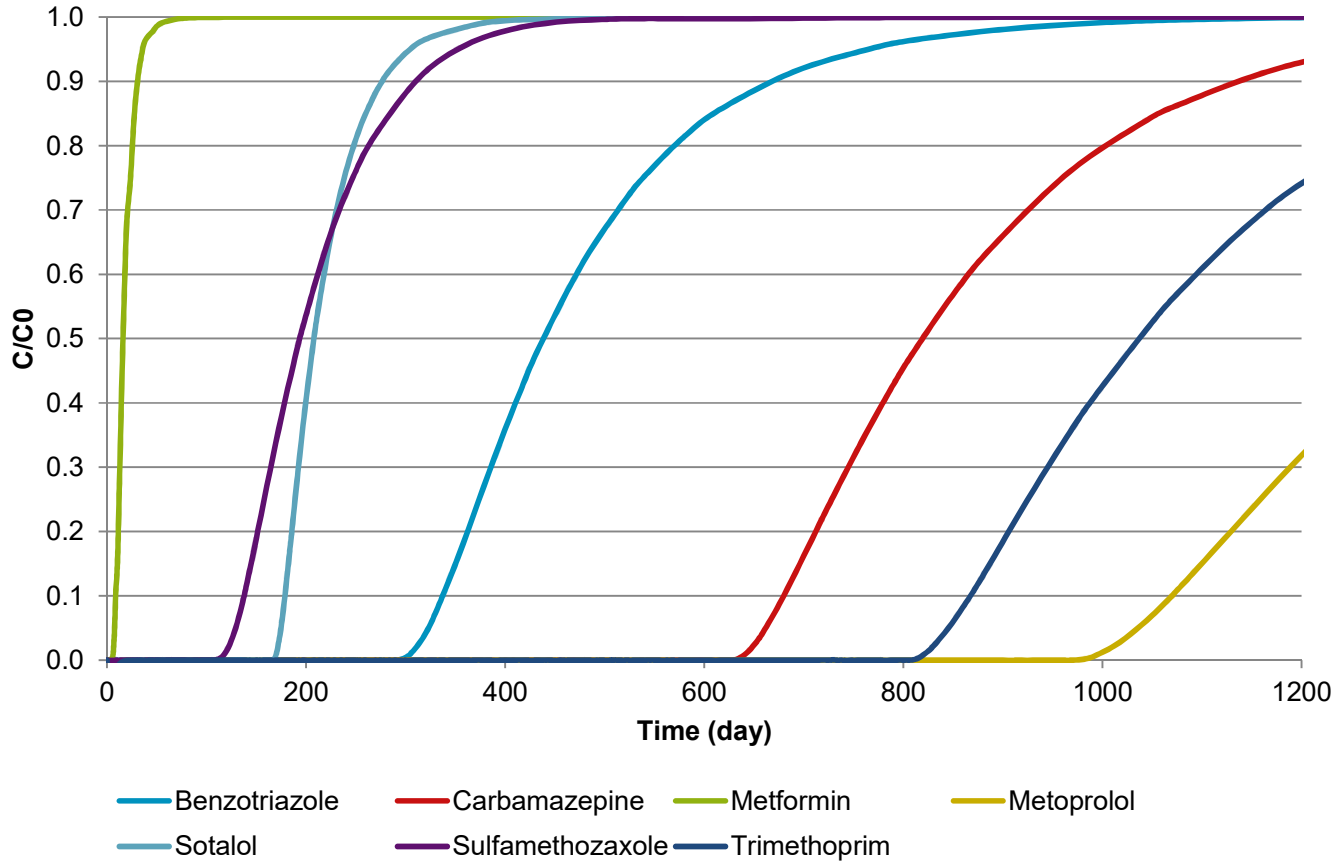


Figure 4-14 Breakthrough Curve of Target Compounds at feed water concentrations (no ozone)

Table 4-7 shows the removal efficiencies of the target compounds reported in the STOWA report for the 1-STEP® filter after 1,054 and 43,500 bed volumes (Dekker & Zijlstra, 2013). For comparison with the simulation results, Figure 4-14 was expressed in terms of bed volumes (BV) in Figure 4-15. The calculation for bed volume is shown in Appendix 7. In Figure 4-15, it can be seen that at 1,054 BV, only metformin is detected in the effluent. However, according to the study, sulfamethoxazole and small quantities of the other compounds in Table 4-7 were detected. Similarly, at 43,500 BV in Figure 4-15, metformin, sotalol, and sulfamethoxazole were detected while in STOWA report all the compounds in Table 4-7 were found in the effluent. This is not unexpected due to the simplification of the parameters in the model, the simulation results have predicted later breakthrough points of the target compounds. The conditions for the 1-STEP® filter were also more dynamic and varied (i.e. differences in inflow and concentrations) compared to the simulation conditions.

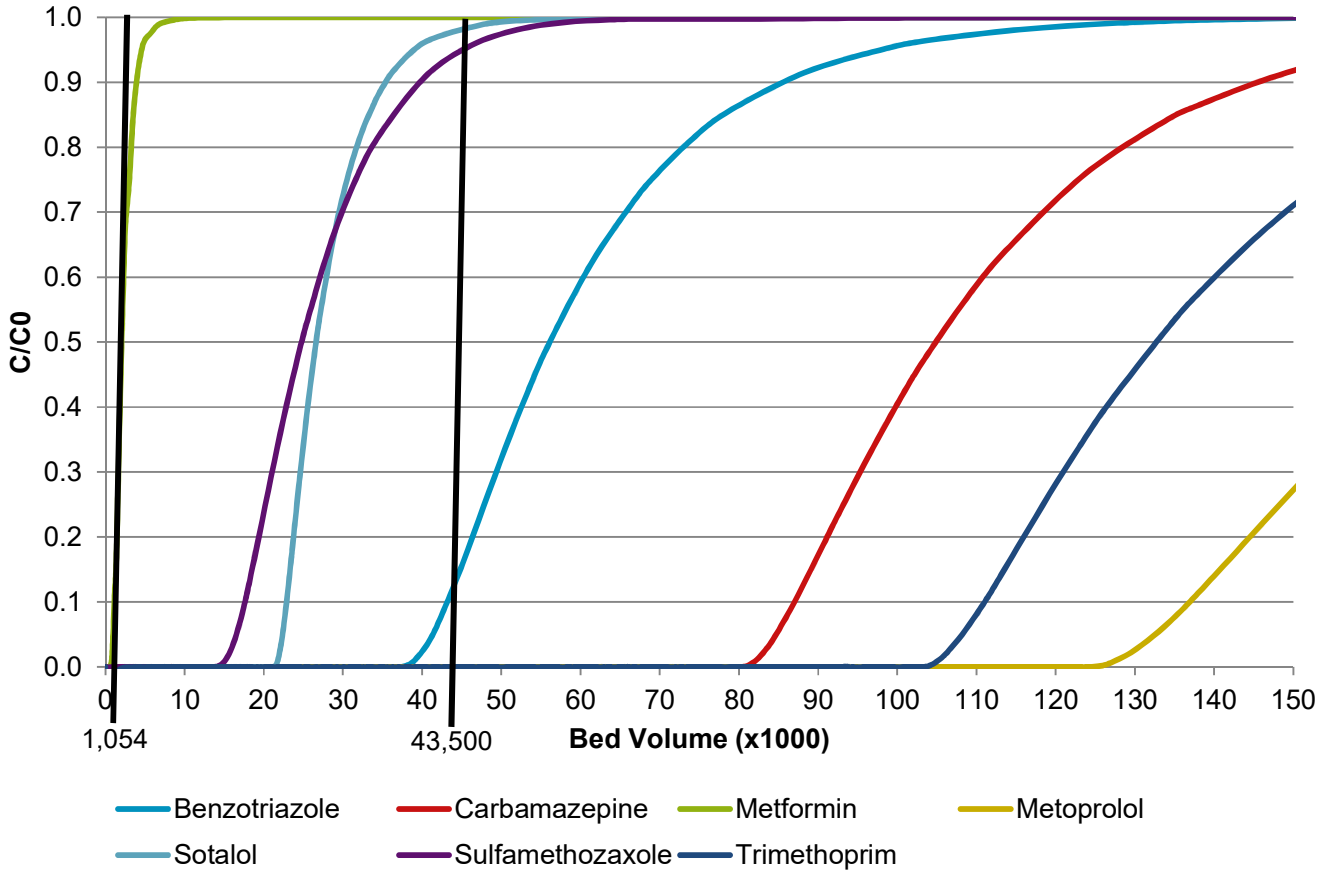


Figure 4-15 Breakthrough Curve of Target Compounds at feed water concentrations vs bed volumes (no ozone)

Table 4-7 Removal Efficiency of Target Compounds in 1-STEP filter

Compound	**Unit**	**1,054 BV**		**43,500 BV**	
		Removed	In Effluent	Removed	In Effluent
Carbamazepine	%	65	35	12	88
Metoprolol	%	80	20	18	82
Sotalol	%	75	25	28	72
Sulfamethoxazole	%	18	82	10	90
Trimethoprim	%	84	16	34	66

4.9.3 Breakthrough with ozonation

The breakthrough curve based on feed water concentrations was simulated (Figure 4-16). In the legends of the chart, the ozone dosage and the concentration of the target compound entering the filter based on the corresponding ozone elimination efficiency are shown. Carbamazepine, metformin and sulfamethoxazole were excluded as only the non-ozonated parameters were available. The estimated bed life of GAC for the target compounds are presented in Table 4-8.

When more than one breakthrough point for one ozone dosage was modelled, the average was calculated.

Table 4-8 Estimated GAC bed life

Compound	Unit	No O3	0.2gO3/gDOC	0.4gO3/gDOC	0.8gO3/gDOC
Benzotriazole	Day	300	250	NA	530
Metoprolol	Day	980	800	790	1240
Sotalol	Day	180	190	50	250
Trimethoprim	Day	820	600	NA	NA

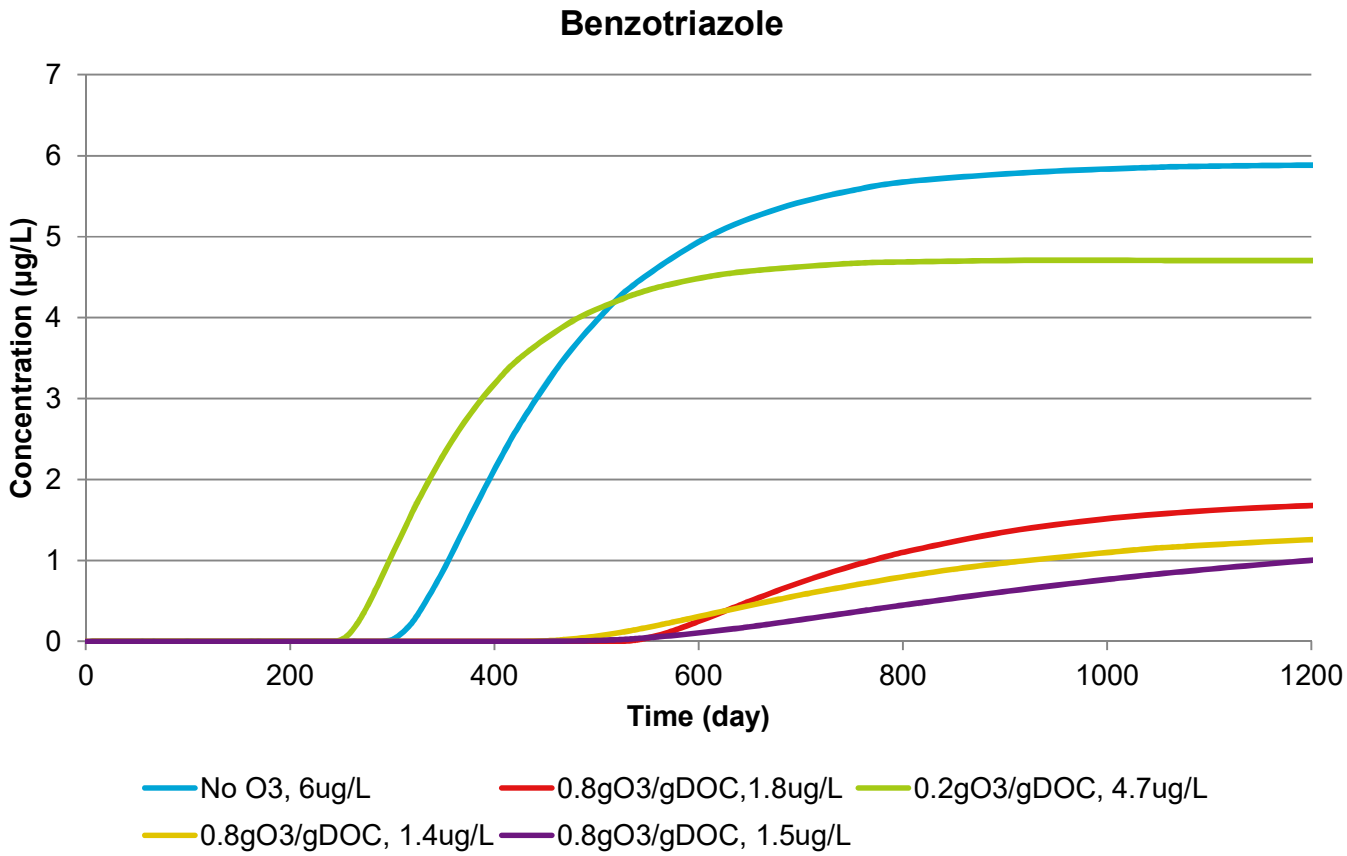
Compound	Unit	No O3	0.2gO3/gDOC	0.4gO3/gDOC	0.8gO3/gDOC
Benzotriazole	BV	38400	32000	NA	67840
Metoprolol	BV	125440	102400	101120	158720
Sotalol	BV	23040	24320	6400	32000
Trimethoprim	BV	104960	76800	NA	NA

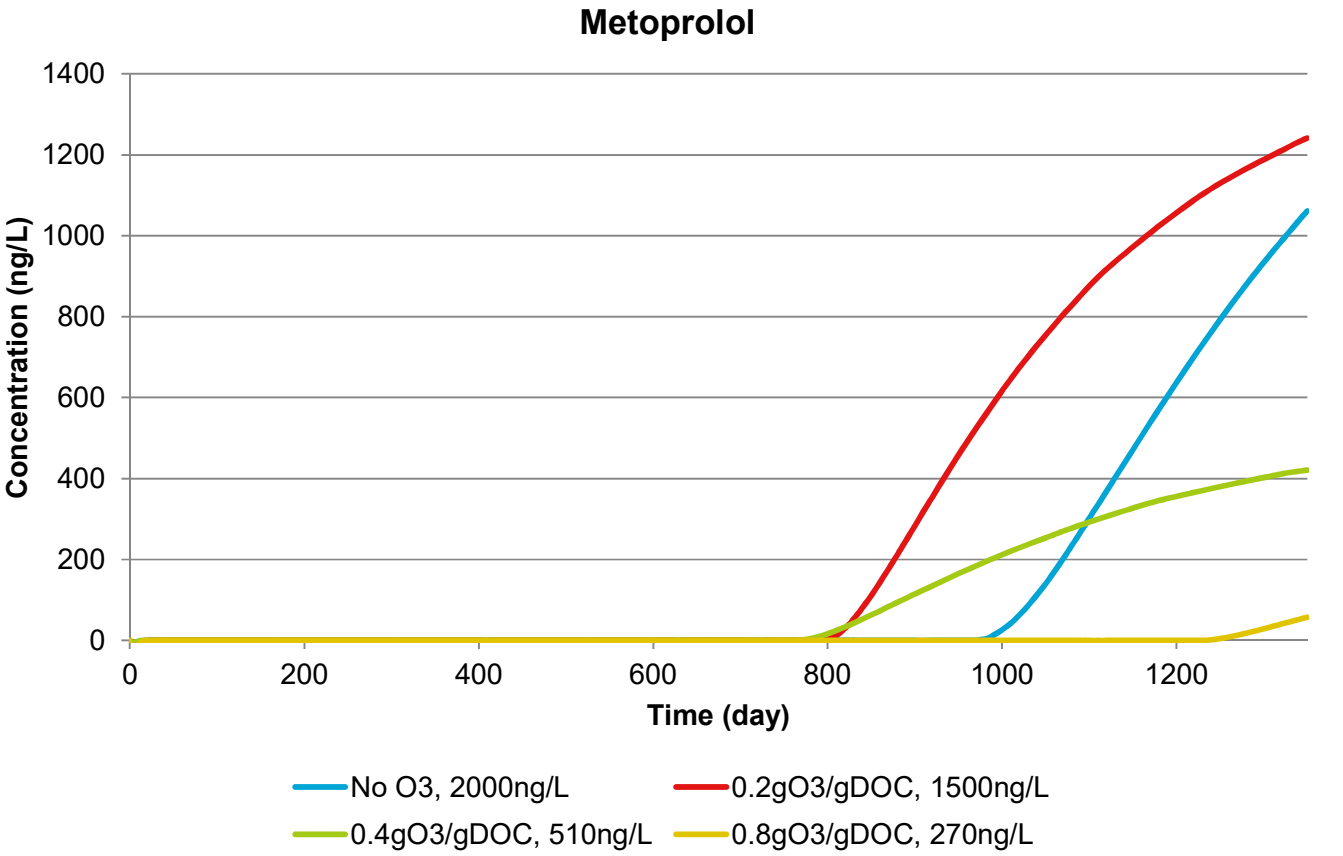
According to the figures, when ozone was applied to the feed water, the breakthrough points of the target compounds, except sotalol, occur earlier than the case without ozone, despite lower initial concentrations. For example, in the case of benzotriazole, the breakthrough point falls from 300 days (38,400 BV) to 250 days (32,000 BV) when the feed water is ozonated at 0.2gO3/gDOC. This is due to the lower adsorption isotherms which were obtained in the previous section. The breakthrough point continues to fall when the ozone dosage is further increased to 0.4gO3/gDOC. However, at 0.8gO3/gDOC, a significant improvement in the bed life of the activated carbon was predicted. In the previous section, after a dosage of 0.8gO3/gDOC, the adsorption capacity of the activated carbon, while still poorer than without ozone, is better than at dosages of 0.2~0.4gO3/gDOC. In the case for benzotriazole, the breakthrough point increased to 530 days (67,840 BV). This suggests that if the fall in concentration, in this case, is enough to overcome the reduced adsorption of the target compounds, the breakthrough point could occur later.

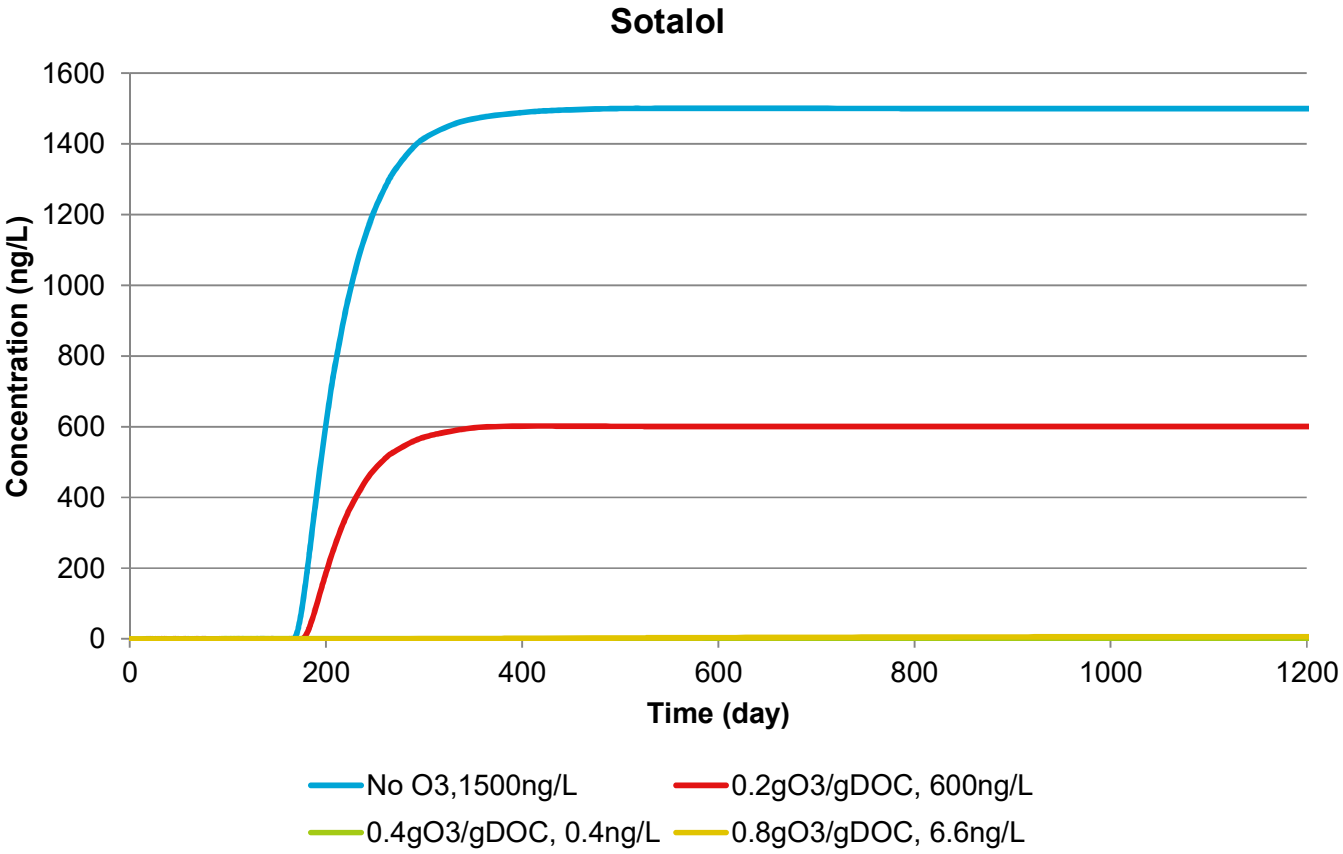
The results of the adsorption isotherms and simulation appear to be opposite of what is reported for similar experiments conducted on surface water for drinking water treatment. Orlandini (1999) reported improved adsorption of atrazine in filters receiving ozonated influent. The differences could be due to the different qualities of surface water and WWTP effluent. Wastewater has a higher DOC concentration than surface water and hence more competition for the active sites of the carbon. Moreover, atrazine was spiked into the feed water after ozonation which avoided the effects of the oxidation by-products. Besides that, in drinking water treatment, the influent is

subjected to coagulation and flocculation prior to ozonation but not in wastewater treatment. This treatment step could have changed the characteristics of the DOC and affected the ozonation.

Several theories could explain the change in adsorption behaviour. The ozonation of the feed water could have broken down the original dissolved matter into smaller molecules, leading to increased competition with the target compounds. However, if the ozone dose is further increased to 0.8gO3/gDOC, the oxidised compounds become more polar and become less absorbable by the activated carbon.




Metoprolol
1400
1200
1000
800
600
400
200
0
Concentration (ng/L)
0
200
400
600
800
1000
1200
Time (day)
No O3, 2000ng/L
0.2gO3/gDOC, 1500ng/L
0.4gO3/gDOC, 510ng/L
0.8gO3/gDOC, 270ng/L


Sotalol
1600
1400
1200
1000
800
600
400
200
0
Concentration (ng/L)
0
200
400
600
800
1000
1200
Time (day)
No O3,1500ng/L
0.2gO3/gDOC, 600ng/L
0.4gO3/gDOC, 0.4ng/L
0.8gO3/gDOC, 6.6ng/L

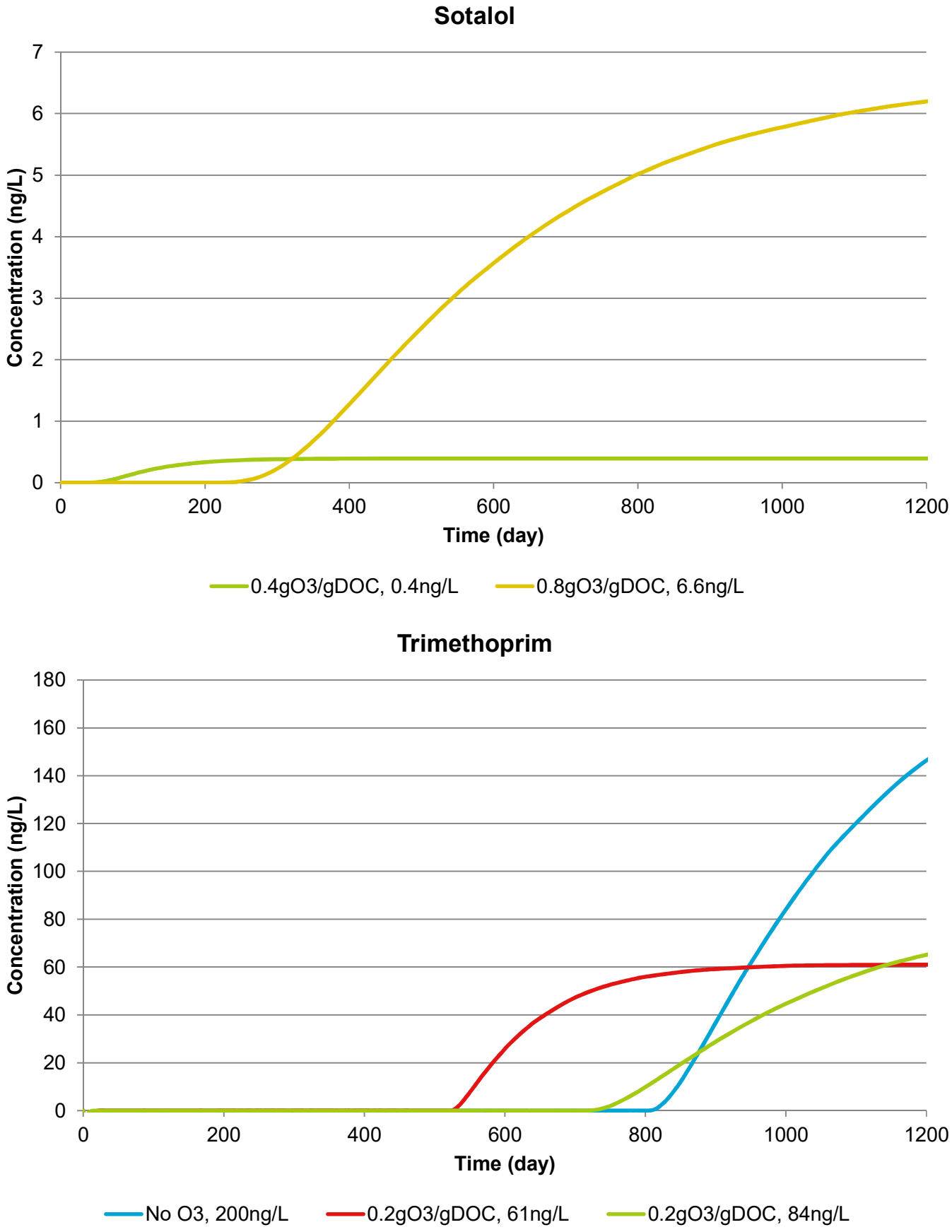


Figure 4-16 Simulated Breakthrough Curves with and without ozonation

At the time of this study, there did not seem to be other research on the adsorption behaviour of activated carbon after the feed water was dosed with ozone. As such, explanations for the change in adsorption capacity when the ozone dose was increased could not be found. It has been reported that when combining ozone and activated carbon into one single treatment, the prolonged exposure of activated carbon to ozone causes basic sites on the carbon surface to become acid sites (Valdés, Sánchez-Polo, Rivera-Utrilla, & Zaror, 2002). Besides that, the ozone changes the textural characterises of the activated carbon which decreases surface area and causes pore blockage. Therefore, exposure of activated carbon to ozone could reduce adsorption capacity. However, this is unlikely to be the case in this study as the water is ozonated separately from the PGAC and due to the short half-life of ozone, contact with the carbon would be minimal.

4.9.4 Limitations

As seen in Figure 4-15, the simulation results tend to predict later breakthrough points than what was observed with the 1-STEP® filter. This is inevitable due to various assumptions used in simplifying the model for simulation. In the experiments, PGAC was used to shorten the experiment time of each batch to 48 hours which otherwise would have taken up to 5 weeks to achieve equilibrium. The GAC particle size affects the value of the Freundlich constants (Heijman & Hopman, 1999). The model does not consider the preloading effect on the GAC and assumes constant inflow concentrations. Moreover, in the actual filter, there is likely to be pore blocking effects and even biological activity which could affect the performance of the GAC. However, the results showed the relative breakthrough points of the target compounds which helps with identifying compounds that are difficult to treat. Moreover, the results are able to show that low levels of ozone dosages might have an adverse effect on GAC bed life.

4.10 Sensitivity Analysis

The influences of the initial concentration, reaction rate constant (k), filtration velocity (v), and bed length (L) were investigated for the case of benzotriazole without ozonation. At higher initial concentrations, the breakthrough point occurs earlier. The reaction rate constant was varied from 3.87×10^{-7} to 3.87×10^{-4} 1/s (Figure 4-16). It appears that the rate constant has a minimal effect in determining the breakthrough curve. However, when the filtration velocity is increased, the curves have a steeper slope and the breakthrough point decreases (Figure 4-19). This is likely due to the reduced residence time of the target compound. Lastly, when the bed length increases, the breakthrough point increases as there is more activated carbon and thus a longer contact time (Figure 4-20).

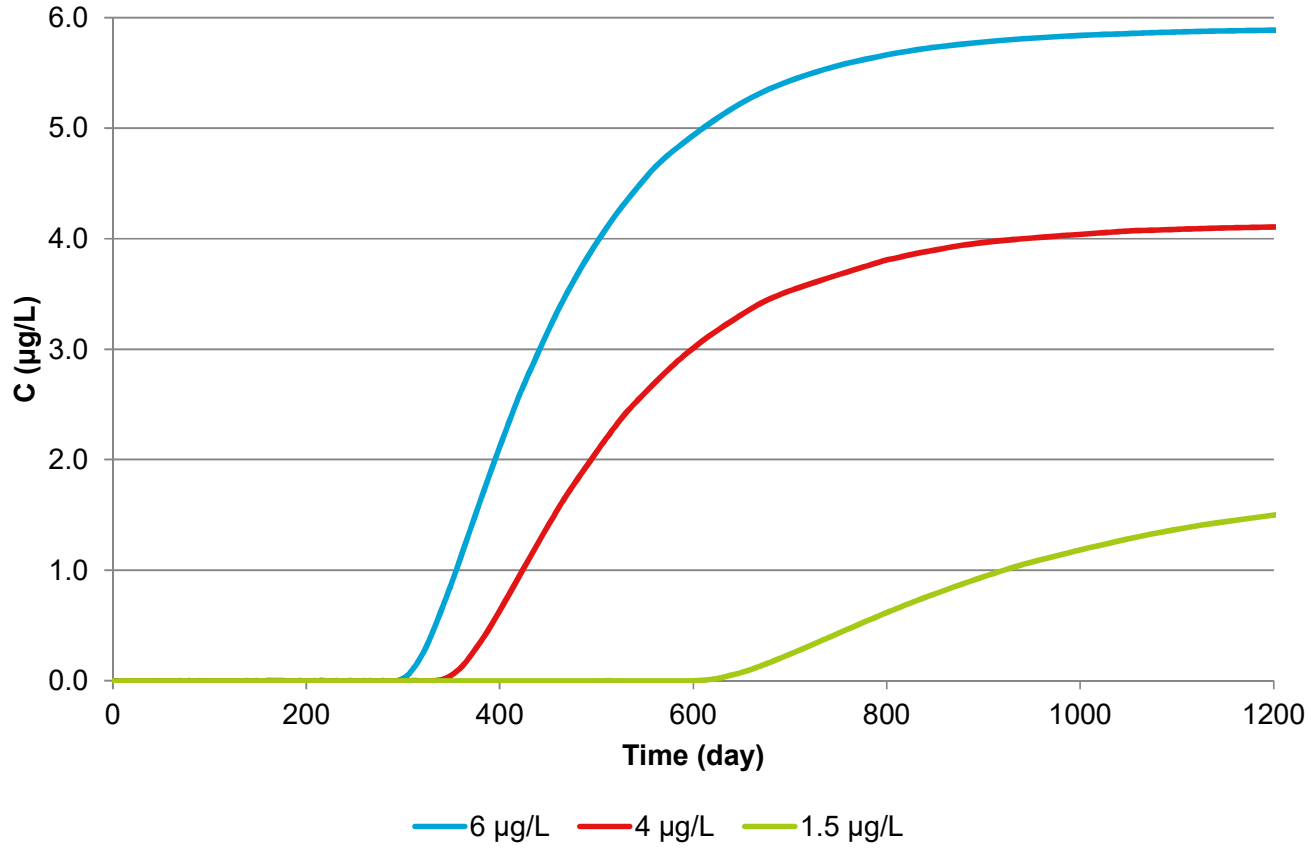


Figure 4-15 Breakthrough curves at varying initial concentrations

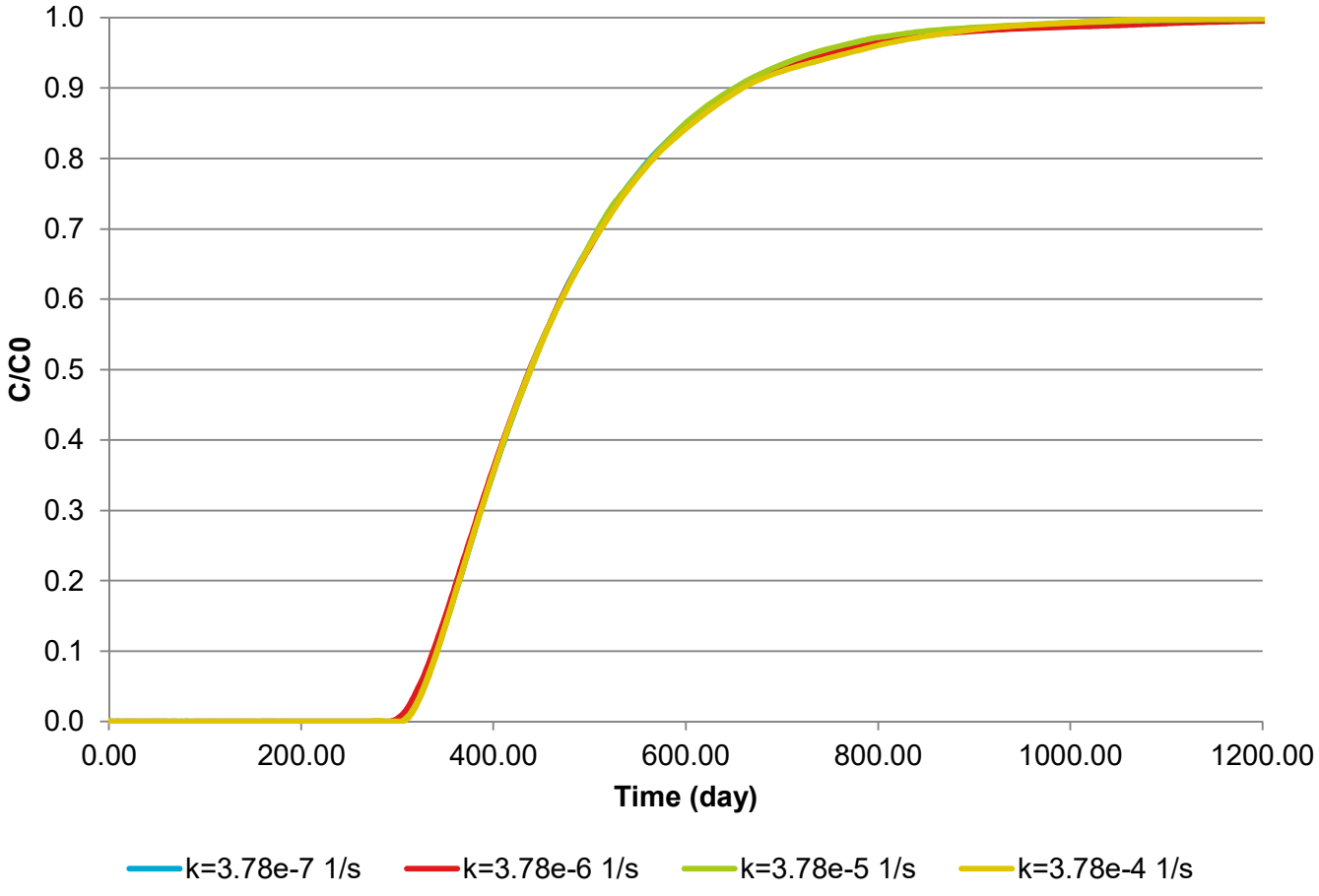


Figure 4-16 Breakthrough curves at varying reaction rate constants

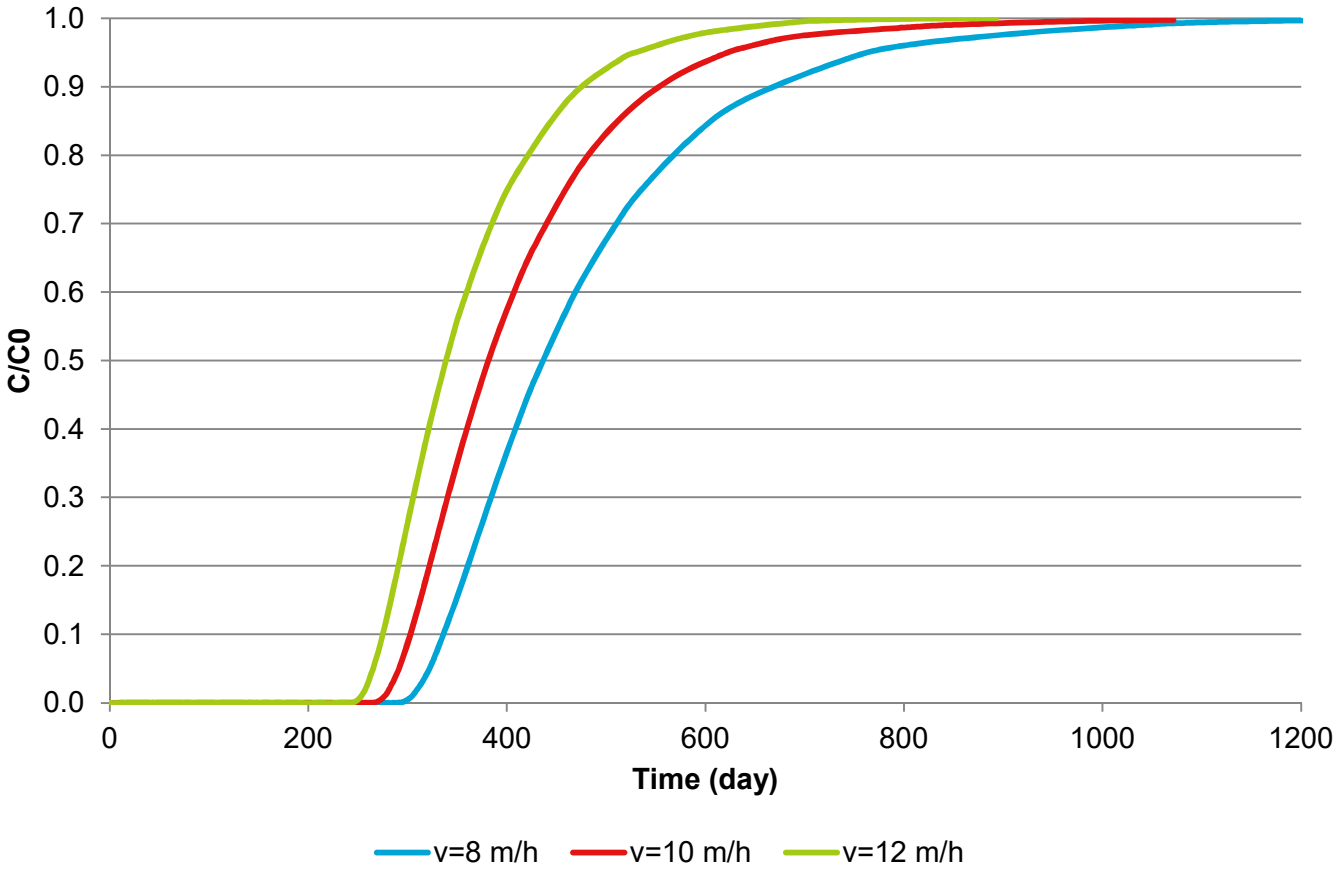


Figure 4-19 Breakthrough curves at varying filtration velocities

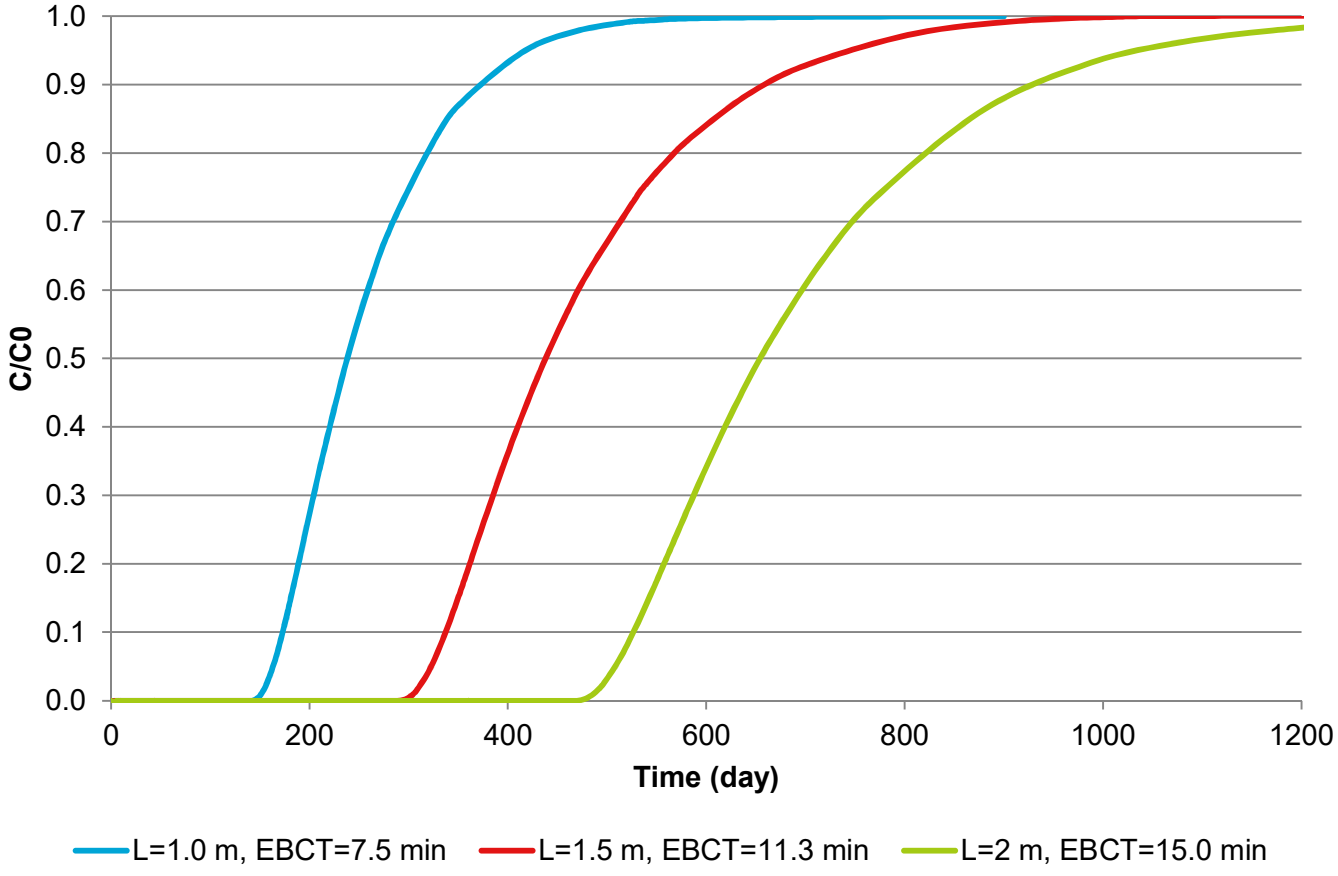


Figure 4-20 Breakthrough curves at varying bed length

4.11 Bromate Formation

Due to the potentially harmful effects of the ozonation by-product, bromate, its concentrations were analysed. In all ozone dosages up to 1.4gO3/gDOC, the concentrations of bromate were below the detection limit of 2.5 µg/L (Appendix 7). As such, changes in bromate concentration could not be measured. It should be noted that in the pilot or full scale, higher initial concentrations of ozone than in the lab scale can be expected which might increase bromate formation.

4.12 Further Research

The study has identified several areas that could be further explored. One of the interesting results is the fall in adsorption capacity with ozonation which is contrary to what was observed in research on drinking water treatment. This could be due to the differences in water quality or the treatment the water went through prior to ozonation. Wastewater not only has a higher DOC content but has also less variability compared to surface water (Westerhoff & Anning, 2000). This suggests that perhaps wastewater has higher concentrations of similar molecules which could result in more competition with the target compounds. Identifying the factors that lead to the contradictory results could help in improving the treatment of wastewater with O3GAC. Besides that, the fate of the oxidation by-products and their behaviour in the GAC filter should be further studied.

Also, the effects of biological activity in the column were not investigated in this study. Research suggests that biodegradation could lead to higher removal efficiencies (Onesios, Jim, & Bouwer, 2009). This has been observed in drinking water treatment using biological activated carbon and has been proven to remove OMPs, oxidation by-products effectively and decrease toxicity in treated wastewater (Reungoat et al., 2011). Moreover, due to ozonation, the amount of AOC increases, which could increase biological activity. The effect of increased biological activity could have adverse effects such as decreased diffusion of target compounds to the activated carbon by a thicker biofilm. Therefore, researching the effects of biological activity is needed to optimise the O3GAC process.

The effects of ozonation on phosphorus and nitrogen removal and carbon dose in the 1-STEP® filter were also not studied in this research. Ozonation not only changes the DOC characteristics of the wastewater but could also increase the oxygen content in the water. How these conditions alter the behaviour of the 1-STEP® filter is still unknown.

Finally, economic evaluations and life cycle assessments could be conducted to fully understand the economic and environmental effects of the O3GAC concept. Can the increase in cost due to ozonation cover the savings from a longer GAC bed life? Is O3GAC more environmentally friendly than ozone treatment or GAC filtration individually? Such questions have to be answered.

5 Conclusions

This study examined the O3GAC concept in three major parts: elimination/removal efficiency, PGAC adsorption capacity, and GAC bed life.

The results point that pre-ozonation of the wastewater prior to GAC filtration will lead to higher removal rates of OMPs. Moreover, the two methods complement each other by tackling compounds that are not efficiently removed when the methods are used individually.

However, the adsorption isotherms showed that after ozonation, the adsorption capacity of the PGAC for the target compounds decreases. The capacity continues to fall as the ozone dosage is increased from 0.2 to 0.4gO3/gDOC but at 0.8gO3/gDOC, the capacity increases again. The cause of this phenomena is not clear and is contrary to similar studies on drinking water treatment. It could be due to the effect of the oxidation by-products, differences in water quality or treatment used prior to ozonation.

With the data obtained in this study, the breakthrough curves of the target compounds were simulated with the software COMSOL. Due to assumptions and simplifications used in the LDF model, the simulation results have a tendency to predict later breakthrough points than what was observed in reality. Several steps have been highlighted in the previous chapter to improve the simulation results in the future. However, the results are still useful in pinpointing the relative breakthroughs of the target compounds and the effect of ozonation on GAC bed life. For most compounds, the breakthrough point at 0.2 and 0.4gO3/gDOC is worse than no ozonation while, at 0.8gO3/gDOC, it occurs later. This is likely due to the fall in concentration outstripping the effect of the lowered adsorption capacity and the changes in DOC characteristics. Therefore, applying 0.8gO3/gDOC does have the effect of improving bed life but whether it is economic to do so depends on the cost of ozonation and the savings from an improved bed life.

Finally, the study recommends further research in several areas. More knowledge on the oxidation by-products is required to determine whether they are removed by the GAC and their toxicity. The ozonation of wastewater also changes the composition of the water which affects biological activity which could affect the performance of the GAC filter. The economic and environmental costs and benefits of the O3GAC concept need to be studied as well.

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Appendices

Appendix 1. Target OMP Selection

Compound Name	Type	Desirable for O3GAC	PACAS	De Groote Lucht	TAPES	P-CDP
Atorvastatin	Medicine					
Benzotriazole	Corrosion inhibitor	**X**	X	X		
Bisoprolol	Medicine					
Carbamazepine	Medicine	**X**	X		X	x
Clarithromycin	antibiotic		X			
Diclofenac	Medicine	**X**	X	X	X	x
Ibuprofen	Medicine		X			x
Metformin	Medicine	**X**	X	x		
Metoprolol	Medicine	**X**	X		X	x
Sotalol	Medicine	**X**	X	x		
Sulfamethoxazole	Medicine	**X**	X		X	x
Trimethoprim	Medicine		X			x

Appendix 2. Product Information of OMPs

Compound	Product Number	Product Chemical Formula	Product MW
Atorvastatin	PZ0001	$C_{33}H_{34}FN_2O_5 \cdot 0.5\ Ca \cdot 1.5\ H_2O$	604.7
Benzotriazole	76457-50MG	$C_6H_5N_3$	119.1
Bisoprolol	50787-25MG	$C_{18}H_{31}NO_4$	325.4
Carbamazepine	C4024-1G	$C_{15}H_{12}N_2O$	236.3
Clarithromycin	C9742-100MG	$C_{38}H_{69}NO_{13}$	748.0
Diclofenac	D6899-10G	$C_{14}H_{10}Cl_2NNaO_2$	318.1
Ibuprofen	I4883-1G	$C_{13}H_{18}O_2$	206.3
Metformin	53183-5MG	$C_4D_6H_5N_5 \cdot HCl$	171.7
Metoprolol	M5391-1G	$(C_{15}H_{25}NO_3)_2 \cdot C_4H_6O_6$	684.8
Sotalol	39863-10MG	$C_{12}H_{20}N_2O_3S \cdot HCl$	308.8

Sulfamethoxazole	S7507-10G	$C_{10}H_{11}N_3O_3S$	253.3
Trimethoprim	46984-250MG	$C_{14}H_{18}N_4O_3$	290.3

Appendix 3. Concentration of Target Compounds in Stock Solution

Compound	Volume of Stock (L)	Concentration (mg/L)
Atorvastatin	1	3.10
Benzotriazole	0.5	50.86
Bisoprolol	1	0.20
Carbamazepine	1	4.80
Clarithromycin	1	20.30
Diclofenac	1	4.19
Ibuprofen	1	32.50
Metformin	1	70.74
Metoprolol	1	10.23
Sotalol	1	0.11
Sulfamethoxazole	1	3.80
Trimethoprim	1	2.50

Appendix 4. Ozone Bubbling Time Calculations

Batch	Ozone Dose	DOC	Ozone Concentration	Volume	Ozone	Flow Rate	Ozone In	Ozone Out	Bubbling Time	Actual Dose	Ozone Concentration	Ozone Dose
	gO3/gDOC	mg/L	mg/L	L	mg	L/min	g/m3	g/m3	min	mg	mg/L	gO3/gDOC
B2	0.2	10	2	8.6	17.2	1.5	5.50	3.10	**5**	18.0	2.1	**0.2**
								Total:	**5**		**Total:**	**0.2**
B3	0.4	10	4	8.6	34.4	1.2	2.24	1.22	5	6.1	0.7	0.07
	0.4	10	4	8.6	34.4	1.1	2.80	1.48	5	7.3	0.8	0.08
	0.4	10	4	8.6	34.4	1.1	2.47	1.49	5	5.4	0.6	0.06
	0.4	10	4	8.6	34.4	1.1	2.60	1.73	5	4.8	0.6	0.06
	0.4	10	4	8.6	34.4	1.1	2.65	1.74	5	5.0	0.6	0.06
	0.4	10	4	8.6	34.4	1.1	2.71	1.73	5	5.4	0.6	0.06
								Total:	**30**		**Total:**	**0.39**
B4	0.8	10	8	8.6	68.8	1.1	2.70	1.60	5	6.1	0.7	0.07
	0.8	10	8	8.6	68.8	1.1	3.31	1.55	5	9.7	1.1	0.11
	0.8	10	8	8.6	68.8	1.1	2.75	1.51	5	6.8	0.8	0.08
	0.8	10	8	8.6	68.8	1.1	3.16	1.70	5	8.0	0.9	0.09
	0.8	10	8	8.6	68.8	1.1	3.31	1.89	5	7.8	0.9	0.09
	0.8	10	8	8.6	68.8	1.1	2.76	1.60	5	6.4	0.7	0.07
	0.8	10	8	8.6	68.8	1.1	2.96	1.66	5	7.2	0.8	0.08
	0.8	10	8	8.6	68.8	1.1	2.91	1.70	5	6.7	0.8	0.08
	0.8	10	8	8.6	68.8	1.1	2.94	1.72	5	6.7	0.8	0.08
	0.8	10	8	8.6	68.8	1.1	2.94	1.73	2.5	3.3	0.4	0.04

								Total:	**47.5**			**Total:**	**0.80**
B5	1.4	10	14	8.6	120.4	1.1	2.96	1.20	5	9.7	1.1	0.11
	1.4	10	14	8.6	120.4	1.1	2.71	1.47	5	6.8	0.8	0.08
	1.4	10	14	8.6	120.4	1.1	3.33	1.79	5	8.5	1.0	0.10
	1.4	10	14	8.6	120.4	1.1	3.05	1.83	5	6.7	0.8	0.08
	1.4	10	14	8.6	120.4	1.1	3.12	1.93	5	6.5	0.8	0.08
	1.4	10	14	8.6	120.4	1.1	3.15	1.93	5	6.7	0.8	0.08
	1.4	10	14	8.6	120.4	1.1	3.21	1.99	5	6.7	0.8	0.08
	1.4	10	14	8.6	120.4	1.1	3.21	1.99	5	6.7	0.8	0.08
	1.4	10	14	8.6	120.4	1.1	3.34	2.08	5	6.9	0.8	0.08
	1.4	10	14	8.6	120.4	1.1	3.34	2.08	5	6.9	0.8	0.08
	1.4	10	14	8.6	120.4	1.1	3.01	1.89	5	6.2	0.7	0.07
	1.4	10	14	8.6	120.4	1.1	3.01	1.89	5	6.2	0.7	0.07
	1.4	10	14	8.6	120.4	1.1	3.30	2.02	5	7.0	0.8	0.08
	1.4	10	14	8.6	120.4	1.1	3.30	2.02	5	7.0	0.8	0.08
	1.4	10	14	8.6	120.4	1.1	3.05	1.91	5	6.3	0.7	0.07
	1.4	10	14	8.6	120.4	1.1	3.05	1.91	5	6.3	0.7	0.07
	1.4	10	14	8.6	120.4	1.1	3.33	1.99	5	7.4	0.9	0.09
	1.4	10	14	8.6	120.4	1.1	3.33	1.99	1.5	2.2	0.3	0.03
								Total:	**86.5**			**Total:**	**1.40**
B6	0.2	10	2	8.6	17.2	1.1	2.08	0.94	5	6.3	0.7	0.07
	0.2	10	2	8.6	17.2	1.1	2.41	1.26	5	6.3	0.7	0.07
	0.2	10	2	8.6	17.2	1.1	2.50	1.44	4	4.7	0.5	0.05
								Total:	**14**			**Total:**	**0.20**
B7	0.8	10	8	8.6	68.8	1.1	2.88	1.24	5	9.0	1.0	0.10
	0.8	10	8	8.6	68.8	1.1	3.31	1.69	5	8.9	1.0	0.10

	0.8	10	8	8.6	68.8	1.1	3.80	2.10	5	9.4	1.1	0.11
	0.8	10	8	8.6	68.8	1.1	3.82	2.19	5	9.0	1.0	0.10
	0.8	10	8	8.6	68.8	1.1	3.89	2.30	5	8.7	1.0	0.10
	0.8	10	8	8.6	68.8	1.1	3.95	2.39	5	8.6	1.0	0.10
	0.8	10	8	8.6	68.8	1.1	3.95	2.39	5	8.6	1.0	0.10
	0.8	10	8	8.6	68.8	1.1	3.93	2.38	4	6.8	0.8	0.08
								Total:	**39**		**Total:**	**0.80**
B8	0.8	10	8	8.6	68.8	1.1	2.80	1.15	5	9.1	1.1	0.11
	0.8	10	8	8.6	68.8	1.1	3.45	1.64	5	10.0	1.2	0.12
	0.8	10	8	8.6	68.8	1.1	3.83	2.04	5	9.8	1.1	0.11
	0.8	10	8	8.6	68.8	1.1	3.97	2.26	5	9.4	1.1	0.11
	0.8	10	8	8.6	68.8	1.1	3.20	1.91	5	7.1	0.8	0.08
	0.8	10	8	8.6	68.8	1.1	3.15	1.86	5	7.1	0.8	0.08
	0.8	10	8	8.6	68.8	1.1	3.33	1.89	5	7.9	0.9	0.09
	0.8	10	8	8.6	68.8	1.1	3.30	1.93	5.5	8.3	1.0	0.10
								Total:	**40.5**		**Total:**	**0.80**

Appendix 5. Data Processing

Blue: First round

Green: Second round

Red: Rejected

Batch	Compound	Unit	Diluted Stock Concentration	Spike Level	Feed	After Spike	Expected	Feed average	Feed/Feed average	Spike/Expected	Usable Value?
B1	benzotriazole	µg/L	5.7	100	5.9	11	11.6	6	1.0	0.9	yes
B4	benzotriazole	µg/L	5.7	100	6	11	11.7	6	1.0	0.9	yes
B5	benzotriazole	µg/L	5.7	100	6	12	11.7	6	1.0	1.0	yes
B6	benzotriazole	µg/L	5.7	10	6.2	6.9	6.77	6	1.1	1.0	yes
B7	benzotriazole	µg/L	5.7	10	6	6.7	6.57	6	1.0	1.0	yes
B8	benzotriazole	µg/L	5.7	0	6.4	6.4	6.4	6	1.1	1.0	yes
B1	bisoprolol	ng/L	15	100	49	81	64	52	0.9	1.3	
B2	bisoprolol	ng/L	15	100	58	92	73	52	1.1	1.3	
B3	bisoprolol	ng/L	15	100	48	-	63	52	0.9		
B4	bisoprolol	ng/L	15	100	NA	12	NA	52			
B5	bisoprolol	ng/L	15	100	9	10	24	52	0.2	0.4	
B6	bisoprolol	ng/L	15	10	10	10	11.5	52	0.2	0.9	
B7	bisoprolol	ng/L	15	10	10	11	11.5	52	0.2	1.0	
B8	bisoprolol	ng/L	15	0	9	9	9	52	0.2	1.0	
B1	carbamazepine	ng/L	410	100	450	820	860	473	1.0	1.0	yes
B2	carbamazepine	ng/L	410	100	550	880	960	473	1.2	0.9	yes
B3	carbamazepine	ng/L	410	100	420	750	830	473	0.9	0.9	yes

B4	carbamazepine	ng/L	410	100	530	990	940	473	1.1	1.1	yes
B5	carbamazepine	ng/L	410	100	570	990	980	473	1.2	1.0	yes
B6	carbamazepine	ng/L	410	10	38	40	79	473	0.1	0.5	
B7	carbamazepine	ng/L	410	10	38	41	79	473	0.1	0.5	
B8	carbamazepine	ng/L	410	0	36	36	36	473	0.1	1.0	
B1	clarithromycin	ng/L	900	100	270	3300	1170	313	0.9	2.8	
B2	clarithromycin	ng/L	900	100	390	3900	1290	313	1.2	3.0	
B3	clarithromycin	ng/L	900	100	280	1200	1180	313	0.9	1.0	yes
B4	clarithromycin	ng/L	900	100	920	5300	1820	313	2.9	2.9	
B5	clarithromycin	ng/L	900	100	810	5300	1710	313	2.6	3.1	
B6	clarithromycin	ng/L	900	10	370	650	460	313	1.2	1.4	
B7	clarithromycin	ng/L	900	10	390	540	480	313	1.2	1.1	yes
B8	clarithromycin	ng/L	900	0	350	350	350	313	1.1	1.0	yes
B1	diclofenac	ng/L	460	100	430	590	890	467	0.9	0.7	
B2	diclofenac	ng/L	460	100	540	860	1000	467	1.2	0.9	yes
B3	diclofenac	ng/L	460	100	430	700	890	467	0.9	0.8	yes
B4	diclofenac	ng/L	460	100	1100	1900	1560	467	2.4	1.2	
B5	diclofenac	ng/L	460	100	990	880	1450	467	2.1	0.6	
B6	diclofenac	ng/L	460	10	110	120	156	467	0.2	0.8	
B7	diclofenac	ng/L	460	10	110	120	156	467	0.2	0.8	
B8	diclofenac	ng/L	460	0	120	120	120	467	0.3	1.0	
B1	ibuprofen	ng/L	3100	100	0	2700	3100	0	1.0	0.9	yes
B2	ibuprofen	ng/L	3100	100	0	2700	3100	0	1.0	0.9	yes
B3	ibuprofen	ng/L	3100	100	0	2900	3100	0	1.0	0.9	yes
B4	ibuprofen	ng/L	3100	100	0	<3200	3100	0	1.0		
B5	ibuprofen	ng/L	3100	100	0	<3200	3100	0	1.0		

B6	ibuprofen	ng/L	3100	10	0	340	310	0	1.0	1.1	yes
B7	ibuprofen	ng/L	3100	10	0	350	310	0	1.0	1.1	yes
B8	ibuprofen	ng/L	3100	0	0	0	0	0	1.0	1.0	yes
B1	metformin	ng/L	5700	100	650	6000	6350	757	0.9	0.9	yes
B2	metformin	ng/L	5700	100	810	5700	6510	757	1.1	0.9	yes
B3	metformin	ng/L	5700	100	810	5900	6510	757	1.1	0.9	yes
B4	metformin	ng/L	5700	100	710	2100	6410	757	0.9	0.3	
B5	metformin	ng/L	5700	100	700	2100	6400	757	0.9	0.3	
B6	metformin	ng/L	5700	10	720	1200	1290	757	1.0	0.9	yes
B7	metformin	ng/L	5700	10	730	1200	1300	757	1.0	0.9	yes
B8	metformin	ng/L	5700	0	690	690	690	757	0.9	1.0	yes
B1	metoprolol	ng/L	920	100	1900	3100	2820	2000	1.0	1.1	yes
B2	metoprolol	ng/L	920	100	2400	3100	3320	2000	1.2	0.9	yes
B3	metoprolol	ng/L	920	100	1700	2700	2620	2000	0.9	1.0	yes
B4	metoprolol	ng/L	920	100	1900	3000	2820	2000	1.0	1.1	yes
B5	metoprolol	ng/L	920	100	2600	2700	3520	2000	1.3	0.8	
B6	metoprolol	ng/L	920	10	270	280	362	2000	0.1	0.8	
B7	metoprolol	ng/L	920	10	280	290	372	2000	0.1	0.8	
B8	metoprolol	ng/L	920	0	250	250	250	2000	0.1	1.0	
B1	sotalol	ng/L	11	100	1500	1500	1511	1767	0.8	1.0	yes
B2	sotalol	ng/L	11	100	1700	1500	1711	1767	1.0	0.9	yes
B3	sotalol	ng/L	11	100	2100	1800	2111	1767	1.2	0.9	yes
B4	sotalol	ng/L	11	100	1500	1600	1511	1767	0.8	1.1	yes
B5	sotalol	ng/L	11	100	760	1600	771	1767	0.4	2.1	
B6	sotalol	ng/L	11	10	1000	2100	1001.1	1767	0.6	2.1	
B7	sotalol	ng/L	11	10	980	1000	981.1	1767	0.6	1.0	

B8	sotalol	ng/L	11	0	1100	1100	1100	1767	0.6	1.0	
B1	sulfamethoxazole	ng/L	420	100	150	540	570	163	0.9	0.9	yes
B2	sulfamethoxazole	ng/L	420	100	180	820	600	163	1.1	1.4	
B3	sulfamethoxazole	ng/L	420	100	160	570	580	163	1.0	1.0	yes
B4	sulfamethoxazole	ng/L	420	100	NA	800	NA	163			
B5	sulfamethoxazole	ng/L	420	100	430	560	850	163	2.6	0.7	
B6	sulfamethoxazole	ng/L	420	10	47	52	89	163	0.3	0.6	
B7	sulfamethoxazole	ng/L	420	10	48	52	90	163	0.3	0.6	
B8	sulfamethoxazole	ng/L	420	0	46	46	46	163	0.3	1.0	
B1	trimethoprim	ng/L	230	100	190	410	420	197	1.0	1.0	yes
B2	trimethoprim	ng/L	230	100	210	420	440	197	1.1	1.0	yes
B3	trimethoprim	ng/L	230	100	190	390	420	197	1.0	0.9	yes
B4	trimethoprim	ng/L	230	100	220	380	450	197	1.1	0.8	yes
B5	trimethoprim	ng/L	230	100	200	360	430	197	1.0	0.8	yes
B6	trimethoprim	ng/L	230	10	230	280	253	197	1.2	1.1	yes
B7	trimethoprim	ng/L	230	10	220	280	243	197	1.1	1.2	yes
B8	trimethoprim	ng/L	230	0	250	250	250	197	1.3	1.0	

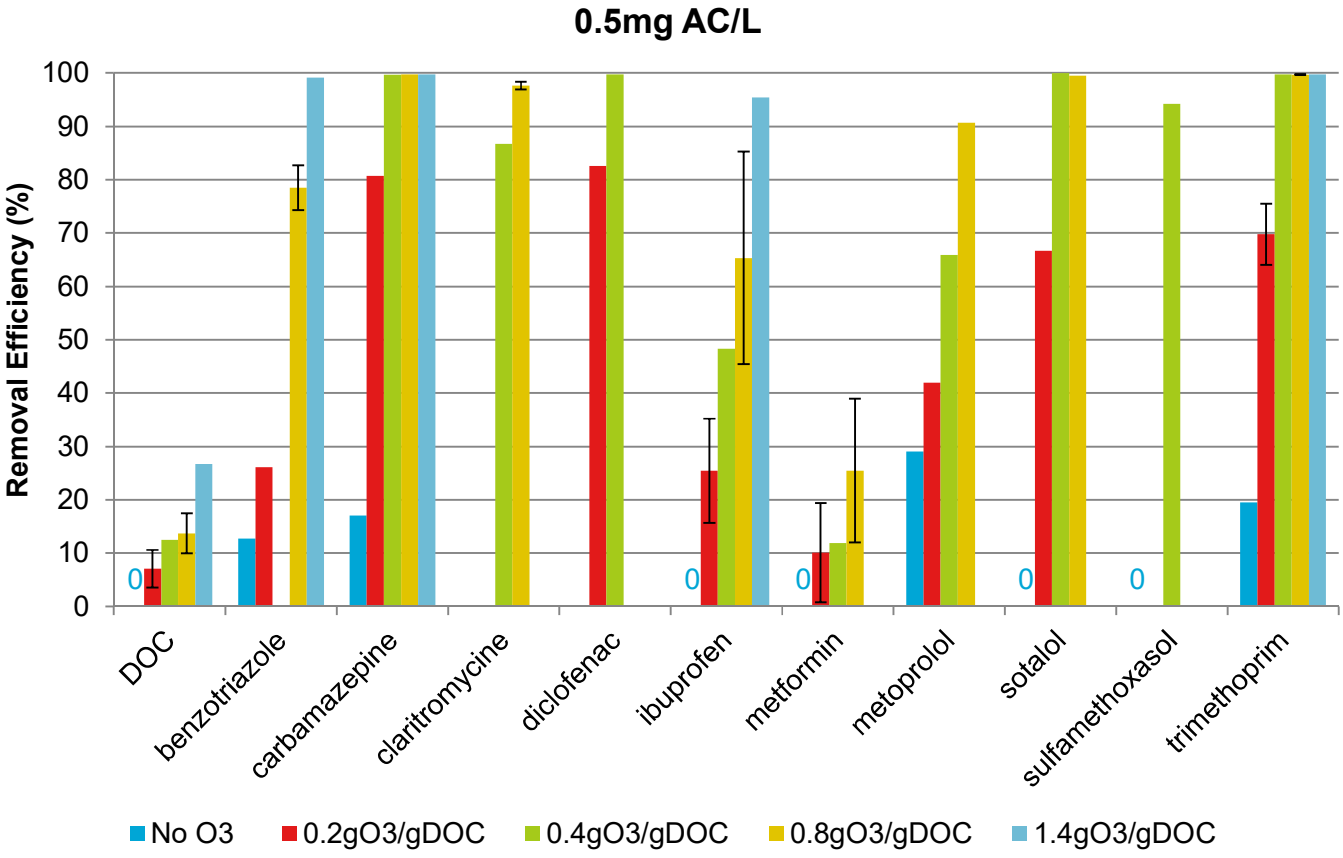
Appendix 6. Feed Water Quality

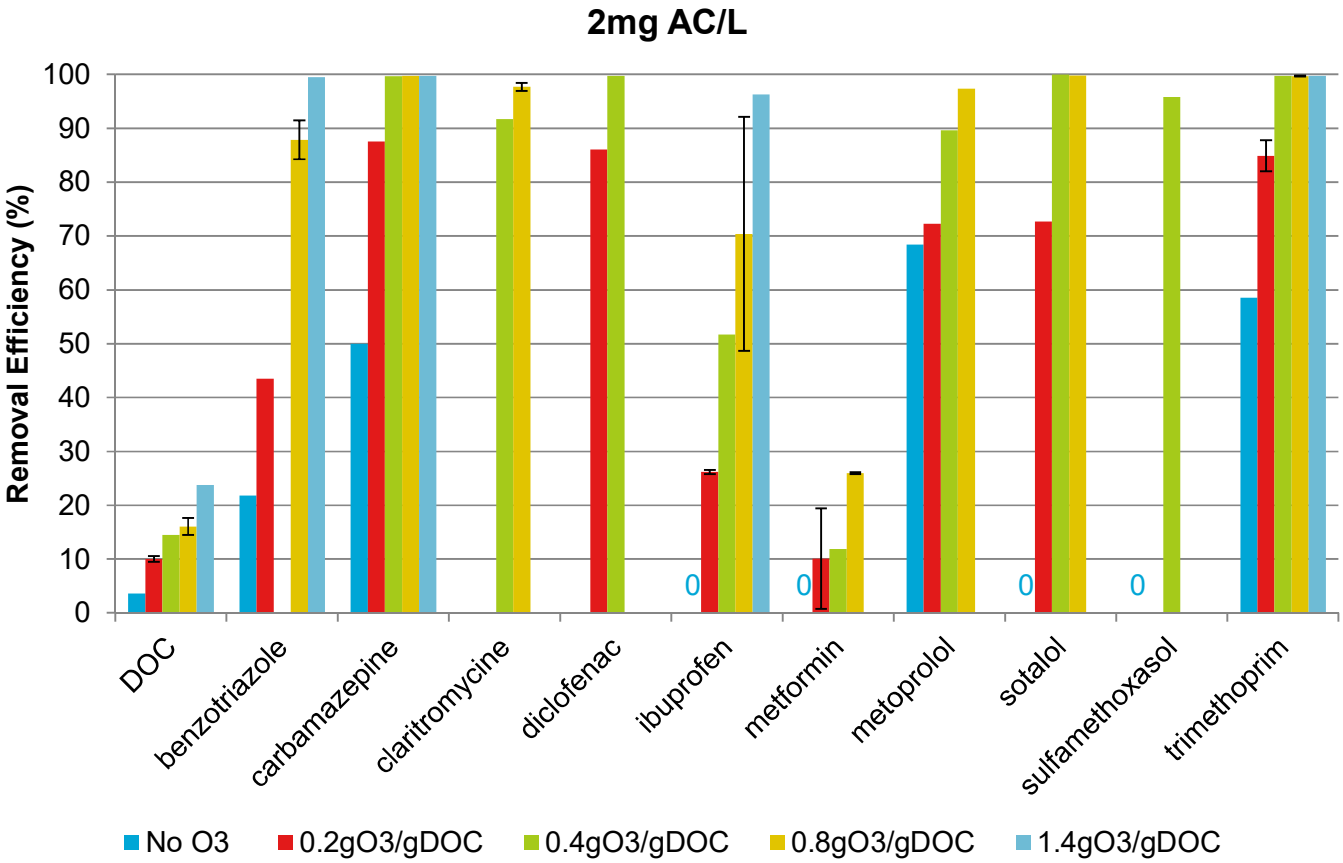
Batch	Compound	Unit	Feed	After Spike	After Spike/Feed
B1	DOC	mg/L	11	11	1.0
B2	DOC	mg/L	11.6	11.5	1.0
B3	DOC	mg/L	11.6	11.4	1.0
B4	DOC	mg/L	10.9	11	1.0
B5	DOC	mg/L	10.9	11.7	1.1
B6	DOC	mg/L	10.9	10.9	1.0
B7	DOC	mg/L	10.9	11.1	1.0
B8	DOC	mg/L	10.7	10.7	1.0
B1	atorvastatin	ng/L	25	260	10.4
B2	atorvastatin	ng/L	70	380	5.4
B3	atorvastatin	ng/L	87	200	2.3
B4	atorvastatin	ng/L			
B5	atorvastatin	ng/L			
B6	atorvastatin	ng/L			
B7	atorvastatin	ng/L			
B8	atorvastatin	ng/L			
B1	benzotriazole	µg/L	5.9	11	1.9
B2	benzotriazole	µg/L			
B3	benzotriazole	µg/L			
B4	benzotriazole	µg/L	6	11	1.8
B5	benzotriazole	µg/L	6	12	2.0
B6	benzotriazole	µg/L	6.2	6.9	1.1
B7	benzotriazole	µg/L	6	6.7	1.1
B8	benzotriazole	µg/L	6.4	6.4	1.0
B1	bisoprolol	ng/L	49	81	1.7
B2	bisoprolol	ng/L	58	92	1.6
B3	bisoprolol	ng/L	48	NA	NA
B4	bisoprolol	ng/L	10	12	1.2
B5	bisoprolol	ng/L	9	10	1.1
B6	bisoprolol	ng/L	10	10	1.0
B7	bisoprolol	ng/L	10	11	1.1
B8	bisoprolol	ng/L	9	9	1.0
B1	carbamazepine	ng/L	450	820	1.8
B2	carbamazepine	ng/L	550	880	1.6

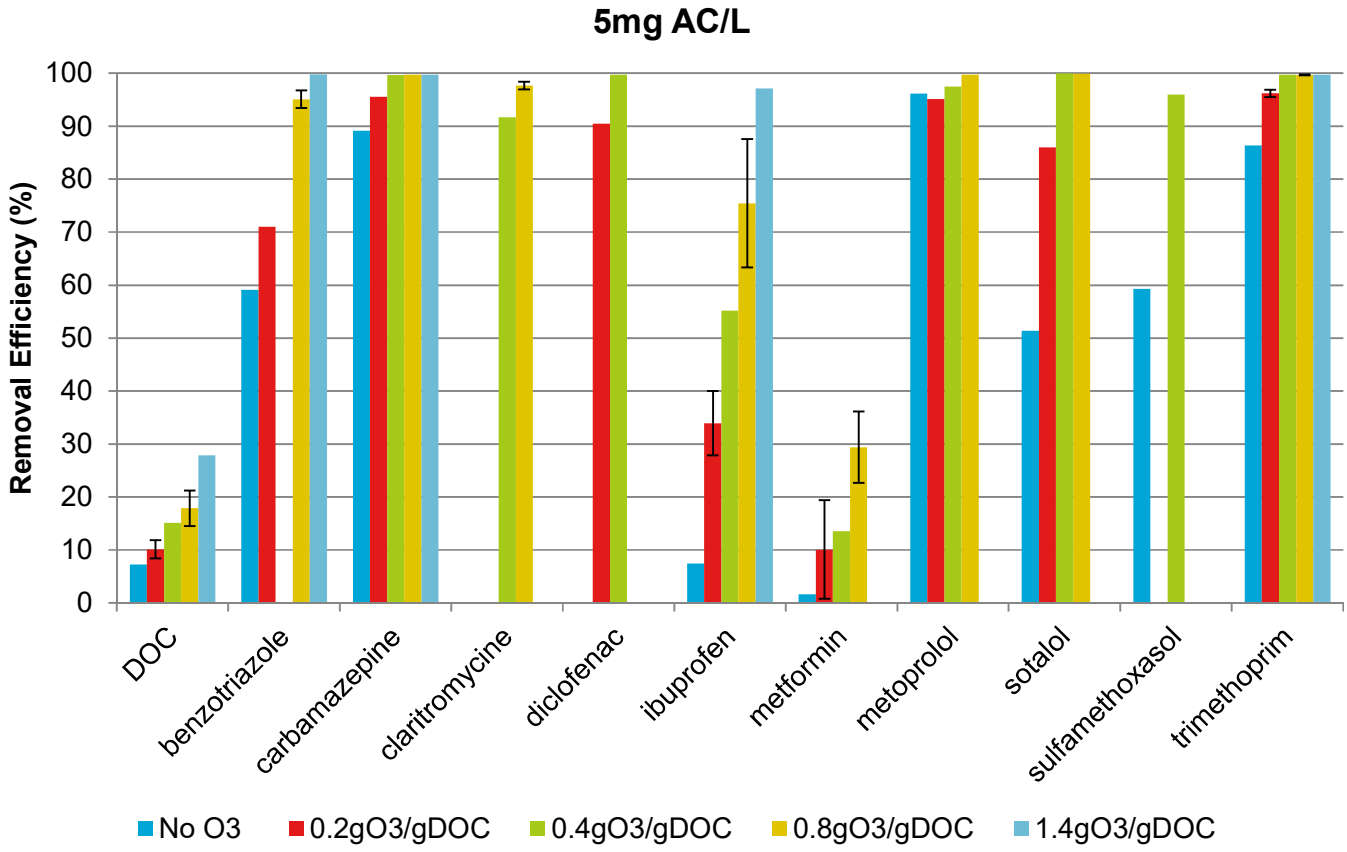
B3	carbamazepine	ng/L	420	750	1.8
B4	carbamazepine	ng/L	530	990	1.9
B5	carbamazepine	ng/L	570	990	1.7
B6	carbamazepine	ng/L	38	40	1.1
B7	carbamazepine	ng/L	38	41	1.1
B8	carbamazepine	ng/L	36	36	1.0
B1	clarithromycin	ng/L	270	3300	12.2
B2	clarithromycin	ng/L	390	3900	10.0
B3	clarithromycin	ng/L	280	1200	4.3
B4	clarithromycin	ng/L	920	5300	5.8
B5	clarithromycin	ng/L	810	5300	6.5
B6	clarithromycin	ng/L	370	650	1.8
B7	clarithromycin	ng/L	390	540	1.4
B8	clarithromycin	ng/L	350	350	1.0
B1	diclofenac	ng/L	430	590	1.4
B2	diclofenac	ng/L	540	860	1.6
B3	diclofenac	ng/L	430	700	1.6
B4	diclofenac	ng/L	1100	1900	1.7
B5	diclofenac	ng/L	990	880	0.9
B6	diclofenac	ng/L	110	120	1.1
B7	diclofenac	ng/L	110	120	1.1
B8	diclofenac	ng/L	120	120	1.0
B1	ibuprofen	ng/L	<32	2700	~100
B2	ibuprofen	ng/L	<32	2700	~100
B3	ibuprofen	ng/L	<32	2900	~100
B4	ibuprofen	ng/L	<32	<3200	~100
B5	ibuprofen	ng/L	<32	<3200	~100
B6	ibuprofen	ng/L	<32	340	>10
B7	ibuprofen	ng/L	<32	350	>10
B8	ibuprofen	ng/L	<32	<32	1.0
B1	metformin	ng/L	650	6000	9.2
B2	metformin	ng/L	810	5700	7.0
B3	metformin	ng/L	810	5900	7.3
B4	metformin	ng/L	710	2100	3.0
B5	metformin	ng/L	700	2100	3.0
B6	metformin	ng/L	720	1200	1.7
B7	metformin	ng/L	730	1200	1.6
B8	metformin	ng/L	690	690	1.0
B1	metoprolol	ng/L	1900	3100	1.6

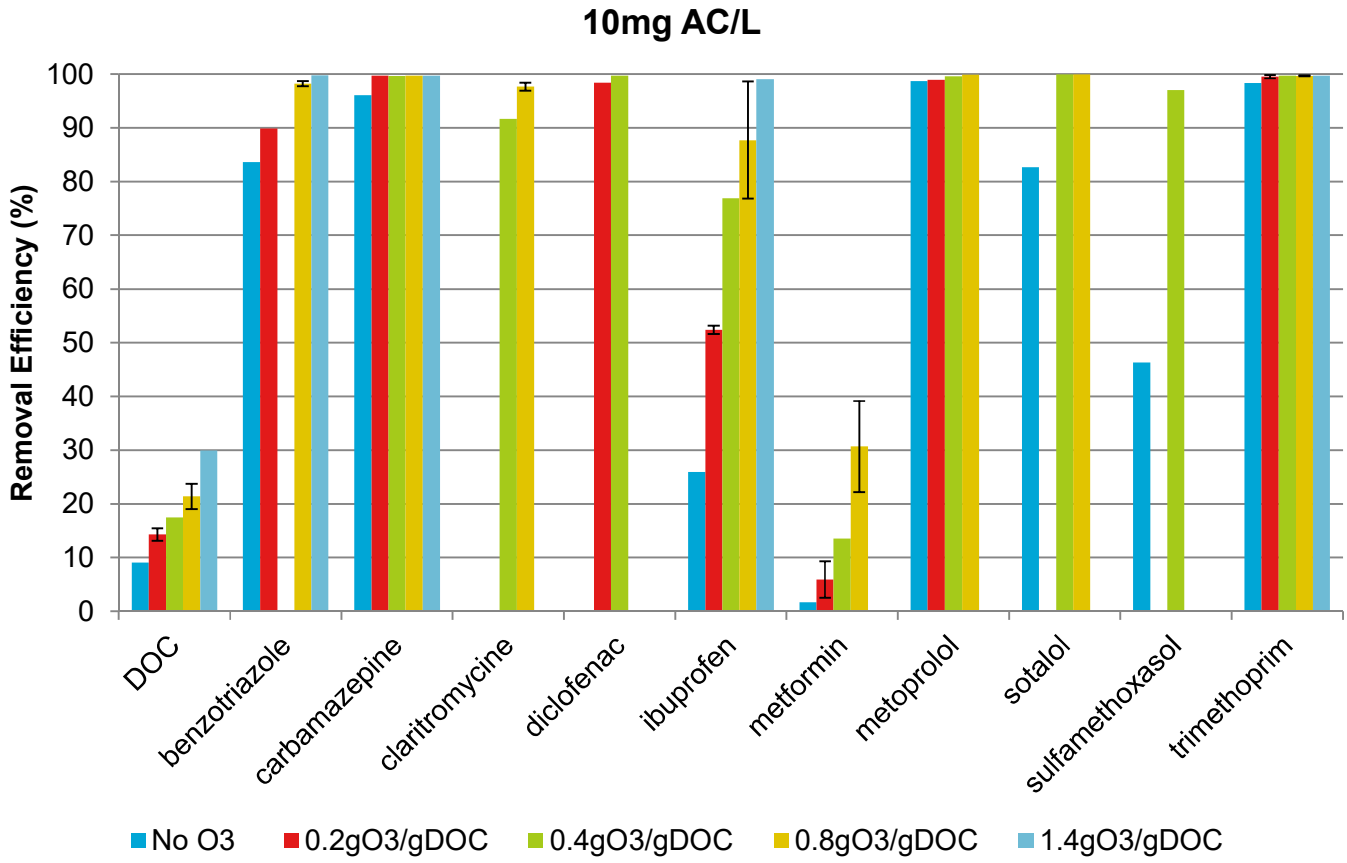
B2	metoprolol	ng/L	2400	3100	1.3
B3	metoprolol	ng/L	1700	2700	1.6
B4	metoprolol	ng/L	1900	3000	1.6
B5	metoprolol	ng/L	2600	2700	1.0
B6	metoprolol	ng/L	270	280	1.0
B7	metoprolol	ng/L	280	290	1.0
B8	metoprolol	ng/L	250	250	1.0
B1	sotalol	ng/L	1500	1500	1.0
B2	sotalol	ng/L	1700	1500	0.9
B3	sotalol	ng/L	2100	1800	0.9
B4	sotalol	ng/L	1500	1600	1.1
B5	sotalol	ng/L	760	1600	2.1
B6	sotalol	ng/L	1000	2100	2.1
B7	sotalol	ng/L	980	1000	1.0
B8	sotalol	ng/L	1100	1100	1.0
B1	sulfamethoxazole	ng/L	150	540	3.6
B2	sulfamethoxazole	ng/L	180	820	4.6
B3	sulfamethoxazole	ng/L	160	570	3.6
B4	sulfamethoxazole	ng/L	<400	800	>2
B5	sulfamethoxazole	ng/L	430	560	1.3
B6	sulfamethoxazole	ng/L	47	52	1.1
B7	sulfamethoxazole	ng/L	48	52	1.1
B8	sulfamethoxazole	ng/L	46	46	1.0
B1	trimethoprim	ng/L	190	410	2.2
B2	trimethoprim	ng/L	210	420	2.0
B3	trimethoprim	ng/L	190	390	2.1
B4	trimethoprim	ng/L	220	380	1.7
B5	trimethoprim	ng/L	200	360	1.8
B6	trimethoprim	ng/L	230	280	1.2
B7	trimethoprim	ng/L	220	280	1.3
B8	trimethoprim	ng/L	250	250	1.0

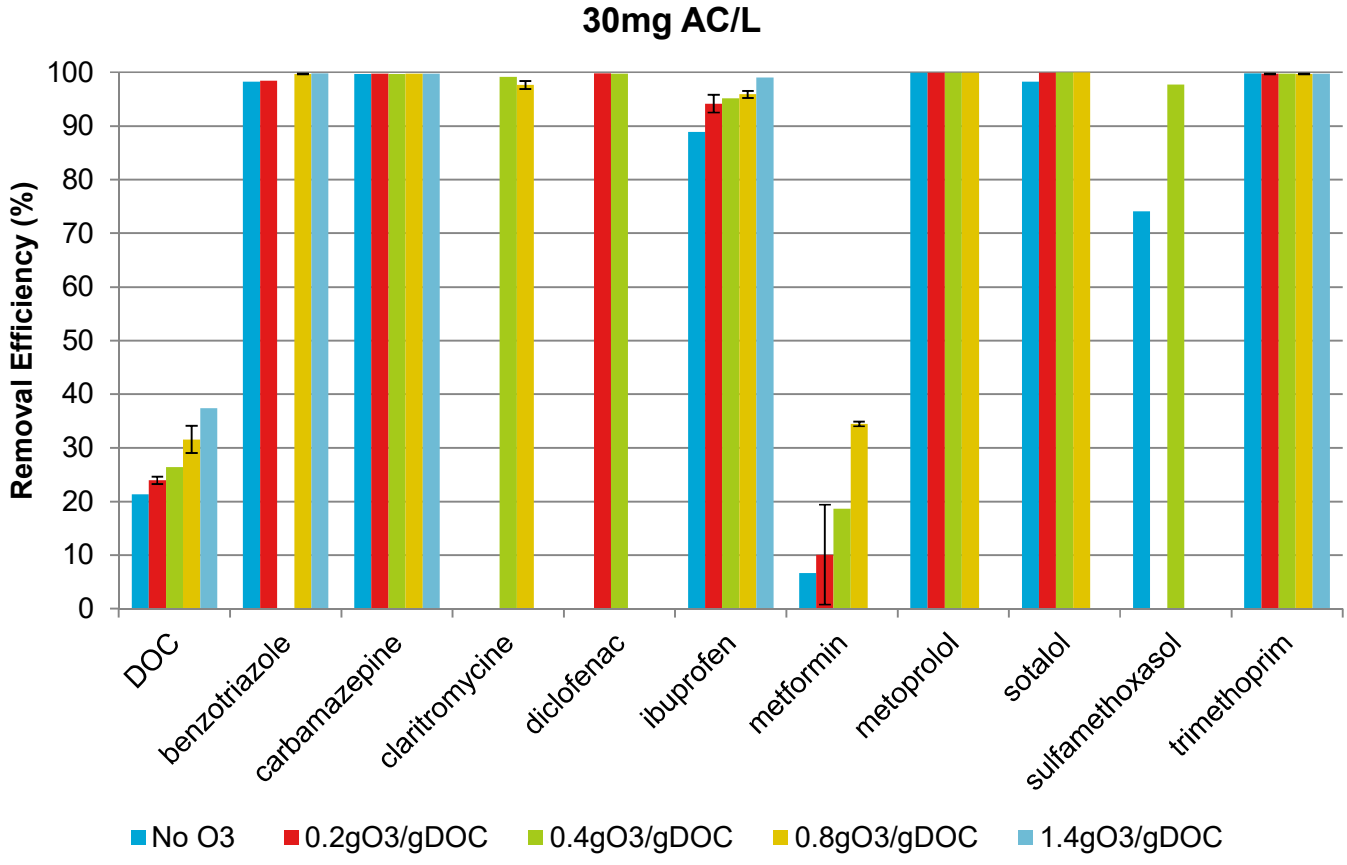
Appendix 7. Combined O3GAC Removal Efficiency

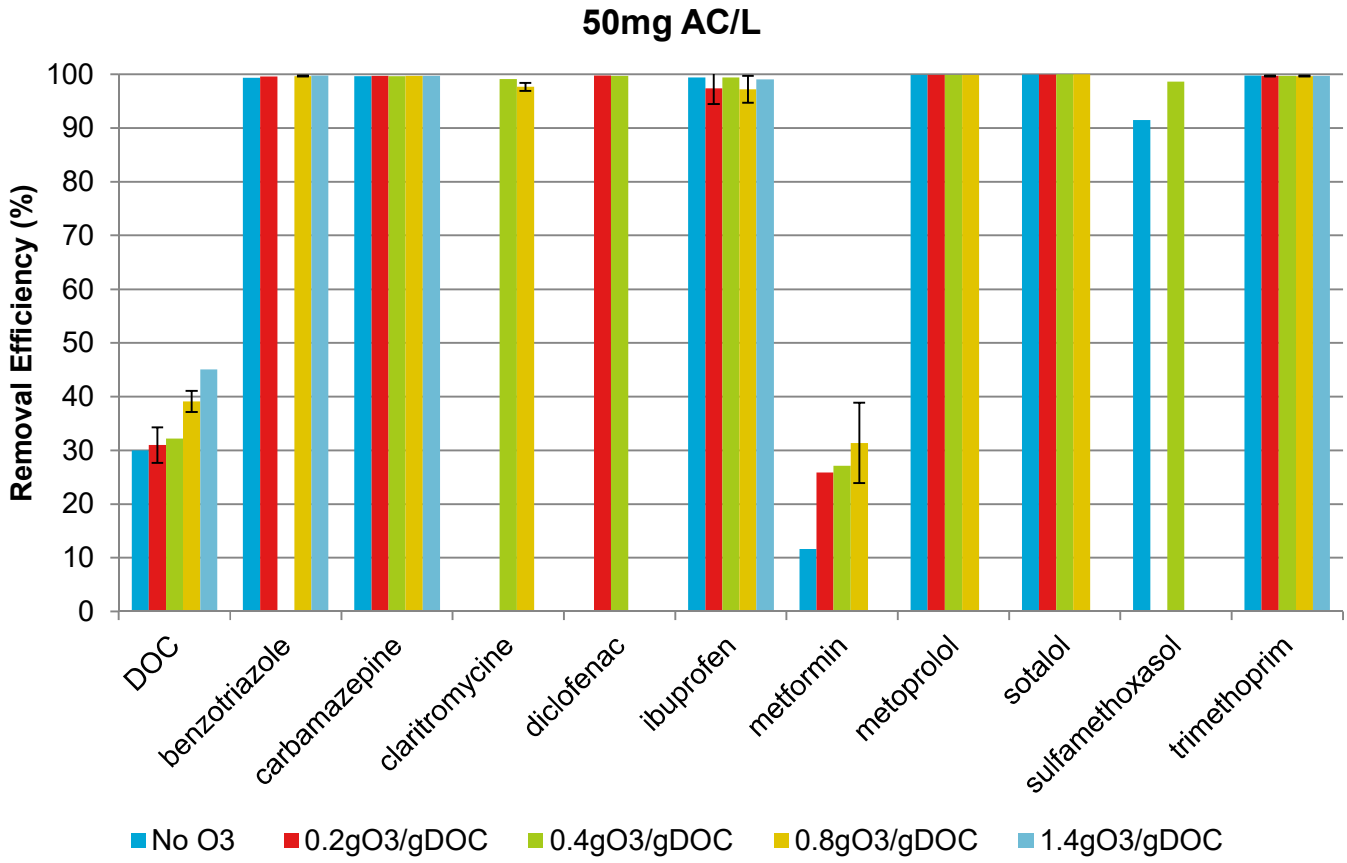





5mg AC/L
Removal Efficiency (%)
100
90
80
70
60
50
40
30
20
10
0
DOC
benzotriazole
carbamazepine
claritromycine
diclofenac
ibuprofen
metformin
metoprolol
sotalol
sulfamethoxasol
trimethoprim
No O3
0.2gO3/gDOC
0.4gO3/gDOC
0.8gO3/gDOC
1.4gO3/gDOC


10mg AC/L
Removal Efficiency (%)
100
90
80
70
60
50
40
30
20
10
0
DOC
benzotriazole
carbamazepine
claritromycine
diclofenac
ibuprofen
metformin
metoprolol
sotalol
sulfamethoxasol
trimethoprim
No O3
0.2gO3/gDOC
0.4gO3/gDOC
0.8gO3/gDOC
1.4gO3/gDOC


30mg AC/L
Removal Efficiency (%)
100
90
80
70
60
50
40
30
20
10
0
DOC
benzotriazole
carbamazepine
claritromycine
diclofenac
ibuprofen
metformin
metoprolol
sotalol
sulfamethoxasol
trimethoprim
No O3
0.2gO3/gDOC
0.4gO3/gDOC
0.8gO3/gDOC
1.4gO3/gDOC


50mg AC/L
Removal Efficiency (%)
100
90
80
70
60
50
40
30
20
10
0
DOC
benzotriazole
carbamazepine
claritromycine
diclofenac
ibuprofen
metformin
metoprolol
sotalol
sulfamethoxasol
trimethoprim
No O3
0.2gO3/gDOC
0.4gO3/gDOC
0.8gO3/gDOC
1.4gO3/gDOC

Appendix 8. Bed Volume Calculations

Length of activated carbon in filter = 1.5 m

Surface area of filter = 28 m^2

Volume of activated carbon = 1.5*28 = 42 m^3

Filtration velocity = 8 m/h = 192 m/day

Hydraulic load = 192*28 = 5376 m^3/day

Therefore, the bed volume in 1 day of operation: 5376/42 = 128

Appendix 9. Bromate Concentrations

Batch	Ozone Dosage	Unit	Value
B2	0.2gO3/gDOC	µg/L	<0.5
B3	0.4gO3/gDOC	µg/L	<0.5
B4	0.8gO3/gDOC	µg/L	<2.5
B5	1.4gO3/gDOC	µg/L	<2.5
B6	0.2gO3/gDOC	µg/L	<2.5
B7	0.8gO3/gDOC	µg/L	<2.5
B8	0.8gO3/gDOC	µg/L	<2.5