Master
Thesis
07/2020

Ozone-Based Regeneration of Granular Zeolites Loaded with Organic Micropollutants

Jiawei Wang

Ozone-Based Regeneration of Granular Zeolites Loaded with Organic Micropollutants

by

Jiawei Wang

17 July 2020

In partial fulfilment of the requirements for the degree of

Master of Science in Civil Engineering (Track of Environmental Engineering)

at the Delft University of Technology

Assessment Committee:

Prof. dr. ir. Jan Peter van der Hoek (Chair)	TU Delft
Dr. ir. Bas Heijman	TU Delft
Dr. ir. Henri Spanjers	TU Delft
Dr. Ir. Monique van der Veen	TU Delft

Preface

I had never given much thought to how I would experience in this magic two years before starting my master study in the Netherlands. Now, I believe that this long journey must be the most valuable, incredible and challenging time of my life.

Nine months ago, I started this research, and I have experienced ups, downs, and extreme downs in this particular lockdown period. Fortunately, I was not alone on this road. First of all, I would like to express my thanks to members of my master thesis committee. Jan Peter van der Hoek, as the chair of the committee, provided me with constructive comments and suggestions. Bas Heijman always answered my questions and gave me much advice and encouragement. Henri Spanjers gave me valuable feedback on my report. Monique van der Veen inspired me a lot in terms of chemical structure of zeolites. I would like to express special thanks to my daily supervisor Mingyan Fu, for his endless help and support on experiments and report, especially on ozonation experiments. Thanks to Nan Jiang, for sharing me knowledge on zeolite and helping me with the LC-MS measurement.

I gratefully thank my fellow students in Environmental Engineering, friends in Delft and roommates in unit 21. The endless help, support, friendship and humor have made it bearable even in the worst time and enjoyable at others.

Last but not least, I would like to express my deepest gratitude and love to my parents. They always give me unconditional support and love, make me a better and braver me.

In the end, thanks to myself. “ What does not kill me, makes me stronger.”

Jiawei Wang

17th July, 2020

Delft

Abstract

The removal of organic micropollutants (OMPs) in the aquatic environment is crucial to avoid health hazards. Zeolites have been confirmed as a selective adsorbent and can effectively remove target OMPs. To achieve sustainable application of adsorbents, regeneration of zeolites is required.

The objective of this study was to investigate the regeneration performance of dried OMP-loaded granular zeolites through gaseous ozonation process, and the regeneration feasibility in long-term adsorption-regeneration processes. Three types of zeolites (MOR, MFI and BEA) were applied for target OMP (benzotriazole, methyl-benzotriazole, carbamazepine, diclofenac hydrochlorothiazide, sulfamethoxazole, metoprolol, sotalol, trimethoprim, propranolol, and clarithromycin) removal. A sequential process coupling zeolite adsorption and oxidation by gaseous ozone was established in batch mode. To assess the ozone effect on OMP degradation and zeolite itself, ozone bubbling tests and adsorption isotherm experiments were executed as pre-experiments. The relative adsorption capacity obtained through regeneration was used to demonstrate regeneration performance. Operating conditions, adsorption duration and regeneration duration were determined and applied. Ultimately the regeneration performance in long-term adsorption-regeneration processes was investigated.

Experimental results showed that all target OMPs were not resistant to ozonation in the water phase. Gaseous ozone was showed no influence on the adsorption capacities of zeolite granules. 120 hours and 500 mgL^{-1} zeolite granules were applied in OMP-loading adsorption experiments. Zeolites always showed high adsorption capacities of metoprolol, trimethoprim and sotalol, which regeneration effect was not evidenced. 60 minutes of ozonation was effective and sufficient for regenerating low and medium adsorption OMPs, except for carbamazepine. The regeneration of carbamazepine probably required a longer regeneration duration. In four cycles of adsorption-regeneration experiments, regeneration of sulfamethoxazole could be achieved after four rounds of ozonation. Regarding carbamazepine, diclofenac, benzotriazole, and methyl-benzotriazole, the regeneration performance were significantly reduced after the first cycle of regeneration. The ozonation duration is supposed to be extended above 60 min in long-term regeneration experiments. Intermediates were potentially responsible for the reduction of regeneration performance in ozonation and adsorption processes. Particularly, the effect of intermediates accumulation might be the main factor that hampered the regeneration performance of low and medium adsorption OMPs in long-term operation.

Contents

List of Figures

List of Tables

List of Attributions

AC	Activated Carbon
AOPs	Advanced Oxidation Processes
CAS	Conventional Activated Sludge
DBPs	Disinfection By-Products
DOC	Dissolved Organic Carbon
EDCs	Endocrine Disrupting Compounds
GAC	Granular Activated Carbon
LC-MS	Liquid Chromatography-Mass Spectrometry
MBR	Membrane Bioreactor
MF	Microfiltration
NF	Nanofiltration
NOM	Natural Organic Matter
OMPs	Organic Micropollutants
PAC	Powdered Activated Carbon
PAHs	Polycyclic Aromatic Hydrocarbons
PCPs	Personal Care Products
RO	Reverse Osmosis
Rq	Relative Adsorption Capacity
TOC	Total Organic Carbon
UF	Ultrafiltration
UV	Ultraviolet
VOCs	Volatile Organic Compounds
WWTPs	Wastewater Treatment Plants

List of Organic Micropollutants

BTA	Benzotriazole
CBZ	Carbamazepine
CLA	Clarithromycin
DIC	Diclofenac
HCTZ	Hydrochlorothiazide
MBTA	Methyl-benzotriazole
MP	Metoprolol
PRO	Propranolol
SOT	Sotalol
SMX	Sulfamethoxazole
TPM	Trimethoprim

Chapter 1 Introduction

1.1 Organic Micropollutants (OMPs)

The earth is facing with climate change and water stress due to the increasing population, rapid urbanization, and industrialization. The contamination of the aquatic environment has contributed to waterborne diseases worldwide. In concern of public health, it is essential to protect the good quality of water resources. Among various pollutants, the elimination of organic micropollutants (OMPs) is recently gaining extensive attention in water treatment processes. OMPs are a range of natural and anthropogenic chemical species, such as pharmaceuticals, antibiotics, pesticides, and personal care products (Loos et al. 2010). They originate from numerous sources, posing adverse risks to health and the environment. A large number of OMPs are observed as resistant substances ranging from ngL^{-1} to µgL^{-1} in surface waters (Westerhoff et al. 2005). In addition, OMPs always occur in the environment as a complex mixture rather than individually, perhaps leading to unwanted synergistic effects (Petrie et al. 2015). The sources of OMPs are elaborated, and the selected OMPs are introduced in this section.

1.1.1 Sources of OMPs

Within the last decades, the extension of the elevated occurrence of natural and synthetic OMPs was widely found in the aquatic environment. As reviewed by Ahmad et al., (2019), the subsistent OMPs are generally categorized as pharmaceuticals, pesticides, polycyclic aromatic hydrocarbons (PAHs), personal care products (PCPs), surfactants and endocrine disrupting compounds (EDCs) (Ahmad et al. 2019). The major potential sources and pathways of OMPs into environment compartments are demonstrated in Figure 1.1 (Ahmad et al. 2019).

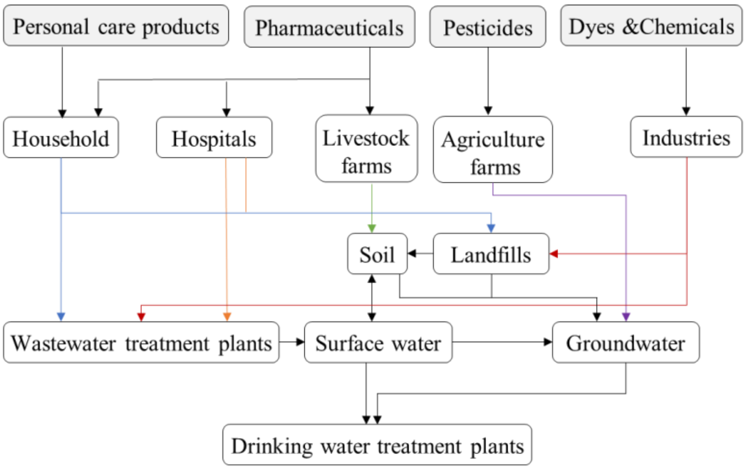


Figure 1.1 The potential sources and pathways of OMPs into the environment (Ahmad et al. 2019)

OMPs enter into the aqueous environment through anthropogenic activities regarding agriculture, farm, household, industrial, water treatment. Additionally, water cycle processes such as runoff and infiltration contribute to the increase and distribution of OMPs in surface waters and ground waters.

Pesticides are reported as one of the most problematic OMPs, since about 4.6 million tons of pesticides are produced and utilized annually in agriculture (Pimentel 2009). Pesticides migrate with irrigation water and contaminate the surface waters and ground waters through precipitation and evaporation. Herbicides such as atrazine and nematicides frequently appear in surface and ground waters, respectively (Cotruvo 1985).

Pharmaceuticals are widely utilized in the household, hospitals, and livestock farms. More than 200 various pharmaceutical substances have been observed in rivers (Hughes and Trafimow 2012). The presence of pharmaceuticals in water bodies is chronically toxic for human beings and animals. Among diverse pharmaceutical products, antibiotics are considered as one of the most commonly used species for bacterial infections. To date, over 250 types and 63,151 tons of antibiotics are reported in use annually (Ashfaq et al. 2016). 70% of antibiotics are not digested or absorbed by human or animals bodies, and they are excreted into nature (Ahmad et al. 2019). In industries, improperly dispose of chemical wastes, and surfactants lead to their accumulation in the environment.

Many of the mentioned OMPs could enter into the wastewater treatment plants through the sewage system. Wastewater discharge is regarded as the primary source of OMPs in the environment (Glassmeyer et al. 2005). Additionally, water treatment processes, such as disinfection are producing treatment by-products. Reemtsma et al. (2006) analyzed 36 substances in eight WWTPs in Western Europe. Over half of the studied OMPs were observed in the wastewater treatment effluent, ranging from 0.1 to 10 μgL^{-1} (Reemtsma et al. 2006). The presence of OMPs increases in the aquatic environment from wastewater discharges. Ultimately, the OMPs in water sources could end up in drinking water, which is supplied to the public.

1.1.2 Target OMPs

The *Dutch ministry of Infrastructure and Water (IenW)* has listed 11 OMPs (carbamazepine, diclofenac, benzotriazole, methyl-benzotriazole, hydrochlorothiazide, sulfamethoxazole, metoprolol, sotalol, trimethoprim, propranolol and clarithromycin) as potential guide substances to monitor the effectiveness of treatment processes for OMP removal from wastewater. They were selected as the target OMPs in this study and their physicochemical characteristics (molecular formula, structure, CAS, molecular weight, water solubility, thermal decomposition temperature and application) are shown in Appendix B.

These target OMPs widely occur in feeding waters such as rivers, groundwater and wastewater effluents. Diclofenac and clarithromycin are on the watch list of substances for EU monitoring (Decision 2015/495/EU). As pointed out in EU Wide Monitoring Survey on Waste Water Treatment Plant Effluents (Loos et al. 2012), carbamazepine, diclofenac, benzotriazole, methyl-benzotriazole, sulfamethoxazole and trimethoprim have an extremely high frequency of occurrence in the effluents of WWTPs, with maximum concentrations over 1 μgL^{-1}.

1.2 Treatments of Organic Micropollutants (OMPs)

As indicated in the preceding section, OMPs originate from diverse sources and widely occur in environment compartments. Regarding this problem, technologies applied in wastewater and drinking water treatment plants are taking an essential role to eliminate OMPs. Treatment processes for OMP removal such as adsorption, oxidation, and membrane technologies have been extensively evaluated and implemented.

1.2.1 Adsorption

Adsorption has broad applicability in water treatment with advantages of low investment, high flexibility of design, and easy operation (Crini and Badot 2011). The existing studies have indicated that adsorption by porous media, such as activated carbon can remove a broad range of organic and inorganic pollutants (Bansal and Goyal 2005). In particular, high-silica zeolites with uniform micropores and high hydrophobicity, which can prevent the entrance of natural organic matter (NOM) (Jiang et al. 2018).

Activated Carbon

Adsorption by activated carbon (AC) is currently recommended and applied as a cost-efficient OMP removal method (Logar et al. 2014). AC has a good porous structure and large surface area from 600 to 2000 m^2g^{-1} (Sillanpää and Bhatnagar 2015), leading to it is affinitive to organic molecules with a broad range of diameter and type (Bansal and Goyal 2005). AC is utilized in water treatment processes in two forms, powdered activated carbon (PAC) and granular activated carbon (GAC). PAC has an excess operating cost if used continuously since it cannot be regenerated. Additionally, PAC may produce sludge and break through filters (Bhatnagar et al. 2013). GAC is also subject to shortcomings. The presence of natural organic matters (NOM) can reduce the OMP removal efficiency of GAC (de Ridder et al. 2011). On the other hand, GAC requires thermal regeneration after saturation, which can consume much energy and emit CO_2 (Sabio et al. 2004). It could also cause mass losses and reduction on adsorption properties of adsorbents, so the effectiveness and life span of GAC are limited (San Miguel et al. 2001).

Zeolites

Zeolites are crystalline aluminosilicates with uniform micropores (Li and Yu 2014). Zeolites consist of SiO_4 and AlO_4 in a tetrahedral structure. Based on silica alumina ratio (Si/Al ratio), zeolites are categorized into low-silica (Si/Al ratio < 2) or high-silica groups (Si/Al ratio up to several thousands). The chemical composition of zeolite determines its surface hydrophobicity, which is defined as the absence of strong sorption of polar compounds like water (Jiang et al. 2018, Olson et al. 2000). Authors proposed that water molecules could interact with Al sites, and highly hydrophobic zeolites were able to prevent water uptake (Bolis et al. 2006, de Ridder et al. 2012). Low-silica zeolites have strong polarity that are utilized as desiccants or softener

(Newsam 1986). High-silica zeolites are commonly synthesised from low-silica zeolites by dealuminating. In contrast to low-silica groups, high-silica zeolites are regarded with high hydrophobicity and can be applied for solute elimination (Anderson 2000, Grieco and Ramarao 2013). Currently, high-silica zeolites have been proved to effectively adsorb multiple OMPs in solutions (Damjanović et al. 2010). Van der Waals force is the driving force for OMP adsorption by high-silica zeolites (Blasioli et al. 2014). Besides, acid-base forces also exist between the functional groups of OMPs and the adsorption sites of zeolites. Zeolites are negatively charged, and cationic species (e.g. H^+, Na^+) are introduced to fulfil overall charge neutrality. Generally, Brønsted acid sites (BAS) and Lewis acid sites (LAS) are two active adsorption sites of protonic zeolites. BAS are formed when protons are compensated between silica and aluminium ($Si\text{-}OH^+\text{-}Al$). The acidic protons inside zeolite micropores can be replaced by other cationic species, giving rise to LAS (Li and Pidko 2019). The number of BAS and LAS can be determined by transmission Fourier-transform infrared spectroscopy (Jiang et al. in preparation). In terms of thermal stability, high-silica zeolites such as MFI is highly stable to heat, and it does not undergo any structural changes at temperatures below 1200 ℃ (Gabelica et al. 1984)

The framework of zeolites describes the connectivity of the atoms in the tetrahedral structure affected by pore opening, cage and channel (McCusker and Baerlocher 2001). The selective adsorption of solutes on high-silica zeolite has been confirmed by many researchers, due to its exclusive and uniform structure (Braschi et al. 2016, de Ridder et al. 2012). de Ridder et al., (2012) proposed a “close-fit ” theory that the high-silica zeolite preferably adsorbs OMPs with similar molecular size to its pore size, while compounds with larger dimensions than the pore size can be excluded (de Ridder et al. 2012). According to Jiang et al., (2018), high-silica zeolites with MFI, MOR and BEA framework are commonly used adsorbents for OMP removal in water treatment, and their characteristics are listed in Table A in Appendix A (Jiang et al. 2018). They also found that the selected OMPs in this study were accessible to the pore of the zeolites (MFI, MOR and BEA) to different extant (Jiang et al. in preparation). Among target OMPs, carbamazepine was hardly adsorbed into the channel of MOR and MFI, due to it could form chains with water molecules that enlarged the size (Martucci et al. 2012).

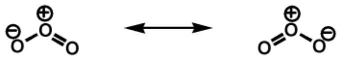
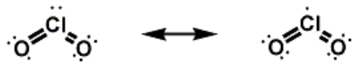
Chemical Oxidation

Chemical oxidation serves as the use of oxidants such as hydrogen peroxide, chlorine dioxide, and ozone to remove non-biodegradable molecules in water treatment (Acero and Von Gunten 2001). Chemical oxidation through ozonation and advanced oxidation processes (AOPs) are introduced in this section.

Ozone

Ozone is a very reactive molecule, considered as one of the strongest oxidants commonly applied in water treatment (Rodríguez et al. 2008). The chemical structure and oxidation potential of ozone compared to other oxidants are illustrated in Table 1.1. It reveals that the oxidation potential of ozone is second to Hydroxyl radicals ($^{\bullet}OH$) and larger than chlorine and chlorine radicals (Benner 2009).

Table 1.1 Chemical structure and oxidation potential of different common oxidants

Oxidant	Chemical structure	Oxidation potential [V]
Hydroxyl radicals	$^{\bullet}OH$	2.8
Ozone		2.1
Chlorine	$Cl_2 + H_2O \longrightarrow HOCl + HCl$	1.36
Chlorine radicals		1.15

Ozone is unstable in water due to its self-decomposition. The decomposition of ozone in water follows a complicated mechanism, shown as reactions (Equation 1.1- 1.2). Ozone is firstly initiated and reacts with a hydroxide ion. The next step is to form several radical oxidizing species like $^{\bullet}OH$. Other reaction chains occurring between various radicals are presented in Appendix C.

$$O_3 + OH^- \longrightarrow HO_2^- + O_2 \quad k = 70\ M^{-1}s^{-1} \tag{1.1}$$

$$O_3 + HO_2^- \longrightarrow {}^{\bullet}OH + O_2 + {}^{\bullet}O_2^- \quad k = 2.8 \cdot 10^{6}\ M^{-1}s^{-1} \tag{1.2}$$

Among all formed radicals, $^{\bullet}OH$ is the only one that can oxidize organic molecules, which makes it a strong oxidant. Therefore, it can be deduced that ozonation in aqueous solution may take place in two ways: 1) ozone directly reacts with organic molecules; 2) by means of hydroxyl radicals yielded from the ozone decomposition of in the water. For direct reactions, ozone reacts rapidly with amines, phenols, and double bonds as a selective electrophile (Brooks and Huggett 2012). In contrast to ozone, the hydroxyl radicals are unspecific on functional groups.

In wastewater treatment, DOC-normalized ozone doses are often utilized in ozone treatment as $gO_3/gDOC$. Based on the existing $gO_3/gDOC$ ratio in literature, the O_3 dose can be estimated with known DOC value of wastewater. By adjusting the value of $gO_3/gDOC$, one can compare different source waters with the same DOC concentrations (Buffle et al. 2006). Terns et al., (2003) found that most of the selected compounds in this study have an elimination efficiency of 70% or higher at 0.2 $gO_3/gDOC$ (Ternes et al. 2003).

The effectiveness of ozone and hydroxyl radicals in oxidizing OMPs are generally expressed by the second-order rate coefficients (k_{O_3} and k_{OH}). High rate coefficients can be related to fast kinetics. Many researchers (Benner 2009, Dodd et al. 2006, Huber et al. 2003, Legube et al. 1987) have studied rate coefficients of target OMPs in this study. A subset of these coefficients and the corresponding reaction functional groups are provided in Table 1.2 (Von Gunten 2003).

Table 1.2 Second-order rate constants of target OMPs at pH=7

OMPs	k_{O_3} (M^{-1}s^{-1})	Reference	Expected reactive functional groups
Medium reaction rate with ozone (k_{O_3}= 10^2-10^4 M^{-1}s^{-1})			
Benzotriazole	$1.9 \times 10^2 - 2.3 \times 10^2$	(Legube et al. 1987)	Aromatic ring
Methyl-benzotriazole	$4.0 \times 10^2 - 4.9 \times 10^2$		
Metoprolol	2.0×10^3	(Benner 2009)	Phenyl ring
Rapid reaction rate with ozone (k_{O_3} > 10^4 M^{-1}s^{-1})			
Sotalol	$1.0 \times 10^3 - 1.0 \times 10^4$	(Huber et al. 2003)	Amine (secondary)
Clarithromycin	7.0×10^4	(Sacher et al. 2002)	Amine (tertiary)
Hydrochlorothiazide	8.5×10^4	(Borowska et al. 2016)	Amine (secondary)
Propranolol	1.0×10^5	(Andreozzi et al. 2003)	Phenol
Trimethoprim	2.7×10^5	(Dodd et al. 2006)	2, 4-Diaminopyrimid ring
Carbamazepine	3.0×10^5	(Huber et al. 2003)	Olefin
Sulfamethoxazole	5.5×10^5		Aniline
Diclofenac	6.8×10^5		Amine (tertiary)

The oxidation rate in the aqueous solution depends on the concentration of dissolved ozone (C_{O_3}). Mass transfer plays an essential role in the ozonation process when ozone in the gas phase is dissolved in the aqueous phase. The gaseous ozone dissolves in the water over time, and it will reach an equilibrium concentration. A part of the dissolved ozone is decomposed in water, following first-order kinetics. According to Beltran, a mass balance equation can be established in the organic-free water, written as Equation 1.3 (Beltran 2003).

$$\frac{dC_{O_3}}{dt} = k_La\,(C^*_{O_3} - C_{O_3}) - k_DC_{O_3} \tag{1.3}$$

C_{O_3} is the ozone concentration at time t (M^{-1}), $C^*_{O_3}$ is the equilibrium ozone concentration in the aqueous phase (M^{-1}), k_La is the volumetric aqueous phase mass transfer coefficient of ozone (s^{-1}), and k_D is the first-order self-decomposition rate constant of ozone (s^{-1}).

In the solution with organic compounds, ozone will react with the substances. A combined mass balance is obtained as Equation 2.4, where C_{OMP} represents the concentration of OMPs at time t (M^{-1}), $k_{O_3}$is the reaction rate coefficient of OMPs with ozone (M^{-1}s^{-1}). Equation 1.4 can be solved by the Runge-Kutta fourth-order method (Patel et al. 2019).

$$\frac{dC_{O_3}}{dt} = k_La\,(C^*_{O_3} - C_{O_3}) - k_DC_{O_3} - k_{O_3}C_{OMP}\,C_{O_3} \tag{1.4}$$

AOPs

As stated, ozone molecules are very effective for OMP degradation. However, some recalcitrant compounds are difficult to remove by only ozonation (Snyder et al. 2007). Advanced oxidation processes (AOPs) use highly reactive hydroxyl radicals to oxidize organic pollutants. The most common AOPs include chemical AOPs (e.g. Fenton and O_3/H_2O_2), photochemical AOPs (e.g. UV/H_2O_2 and UV/O_3) and electrochemical AOPs (Oturan et al. 2014). Regarding the use of hydrogen peroxide (H_2O_2), it is added to the water and either reacts with UV or ozone. The H_2O_2 molecule is split into two $^{\bullet}OH$, enhancing oxidation capacity of substances. As illustrated in Table 1.1, the oxidation potential of $^{\bullet}OH$ (2.8 V) is higher than ozone (2.1 V). Compared to ozonation, AOPs have better oxidation ability without selectivity due to $^{\bullet}OH$ that can react on broader types of molecules (Acero and Von Gunten 2001).

1.2.2 Membrane Separation

The efficiency of membrane separation for OMP removal mainly depends on the membrane pore size, membrane properties (i.e. hydrophobicity and charge), and OMPs characteristics (Coday et al. 2014, Peters 2010). Snyder et al., (2017) studied ranges of the pilot and full-scale membrane processes and reported the same removal efficiency of carbamazepine, diclofenac, sulfamethoxazole and trimethoprim (Snyder et al. 2007). After microfiltration (MF) or ultrafiltration (UF), the removal rates of those OMPs were less than 20%. Nanofiltration (NF) can reject 50% - 80% of them, and Reverse Osmosis (RO) had a high removal efficiency over 80%. However, the production of concentrate after membrane filtration contains all retained compounds, which is difficult to be appropriately disposed (Bagastyo et al. 2011). Besides, biofouling of membranes is also an inevitable problem in membrane technologies. Biofouling is formed due to the presence of natural organic matters (NOMs), providing nutrient for biomass (Laîné et al. 2003). Especially in wastewater treatment, the feeding water always contains a large amount of NOM which have low removal efficiency in preceding processes. Therefore, the application of membrane filtration to eliminate OMPs is limited due to the concentrate and biofouling.

1.2.3 Conventional Activated Sludge and Membrane Bioreactor

It was found that the elimination of organic compounds in conventional WWTPs is not always sufficient, resulting in the occurrence of wastewater-derived contaminants in surface waters (Kolpin et al. 2002). Activated sludge processes, either conventional activated sludge (CAS) or membrane biological reactor (MBR) is most commonly applied in the secondary treatment at WWTPs. High removals of hormones (>99%) and analgesics acetaminophen and ibuprofen (>90%) have been surveyed (Radjenović et al. 2009). However, insufficient elimination of target OMPs through biological treatment was reported by researchers. Barbosa et al., (2016) reported that diclofenac was poorly adsorbed to sludge and was non-biodegradable (Barbosa et al. 2016). In several nutrient-removing WWTPs in Switzerland, a low removal rate of carbamazepine (<10%), and no appreciable removal of sulfamethoxazole was found (Joss et al. 2005).

1.3 Regeneration of Adsorbents

Among all introduced treatments, adsorption by zeolites is regarded as a suitable method for OMP removal in water treatment. Nevertheless, adsorbents are facing the problems that limited adsorption capacities after a specific operation period because they need to be regenerated or renewed. Regeneration of the spent adsorbents is generally defined as restoring the adsorption activity, aiming at as little damage as possible to the original pore structure (Salvador et al. 2015a). The following sections review general regeneration methods of adsorbents and the applied one in this study.

1.3.1 General Regeneration Methods

To date, four different regeneration methods have been commonly applied for spent adsorbents such as activated carbon, categorized as: 1) thermal treatment 2) chemical treatment 3) biological treatment 4) vacuum treatment (Salvador et al. 2015a).

Thermal calcination regeneration uses heat to eliminate the retained adsorbate in the saturated adsorbents, in terms of inert hot gas, steam, microwave or ultrasound. Regeneration by inert hot gas and stream employ high temperature ranging from 200 to 900 °C depending on the properties of adsorbents and adsorbates (Sabio et al. 2004). Microwave or ultrasound provide relatively fast and homogeneous heating that can achieve temperatures higher than 1000 °C in a few minutes (Salvador et al. 2015a). Although thermal regeneration is widely utilized as a conventional regeneration method for various adsorbents, eternal destruction and blockage of pores gradually decrease in the adsorption capacity of adsorbents. More importantly, the use of high temperature leads to enormous energy consumption and CO_2 emission. It calls for novel and more efficient processes to conserve energy.

Alternatively, chemical oxidation is a valid regeneration method by oxidizing organic adsorbates. It can on-site restore the adsorption capacity of loaded adsorbents and can also degrade or mineralize organic pollutants (Salvador et al. 2015b). So far, there has been limited discussion about zeolite regeneration based on chemical oxidation. Koryabkina et al., (2007) coated Fe^{2+} on zeolites by a reaction with sodium borohydride. They observed stable adsorption of disinfection byproducts in four cycles of adsorption-regeneration with the addition of H_2O_2 (Koryabkina et al. 2007). However, Fenton reactions require a strong acidic condition and the leaching of immobilized Fe^{2+} can lead to the reduction of oxidation rate (Gonzalez-Olmos et al. 2013). Reungoat et al., (2007) applied ozone in the water phase to generate the nitrobenzene-loaded zeolite and obtained a complete recovery of the adsorption capacity (Reungoat et al. 2007).

Biological regeneration employs microorganisms as regeneration agent. Salvador et al., (2015) reported the low efficiency of bioregeneration and it is a unfeasible method in practice that requires long regeneration times (over two days) (Salvador et al. 2015b). Vacuum regeneration has not been employed as a traditional regeneration methods. The desorption process is occurred by exposing the adsorbents to a vacuum source, which is mainly focus on applied for gaseous stream separation rather than adsorbent regeneration (Salvador et al. 2015b).

1.3.2 Applied Regeneration Method – Gaseous Ozonation

As reviewed in the preceding section (section 1.2.2), ozone is a reactive oxidant to eliminate organic substances. Ozone can either directly reacts with organic molecules or by means of hydroxyl radicals yielded from the ozone decomposition (Brooks and Huggett 2012). The combined use of zeolite adsorption followed by gaseous ozonation was studied by several researchers (Brodu et al. 2013, Monneyron et al. 2003). They proposed the following two mechanisms of gaseous ozone reacted with zeolite, either adsorption or interaction : 1) ozone could diffuse from gas film and be adsorbed on zeolite surface (weak Lewis acid sites) 2) zeolites could catalyze ozone decomposition into radical species on strong LAS (Brodu et al. 2013). Regarding the research on zeolite reactivity toward gaseous ozone (Monneyron et al. 2003), the adsorption capacity of Fau Y was not changed after ozonation. However, the adsorption capacity of Sil Z zeolite was promoted, which was potentially attributed to the generation of highly reactive species on zeolite surface during ozone decomposition.

For the purpose of regeneration, the adsorption of organic compounds on zeolites coupled with gaseous ozonation has been investigated at laboratory scale (Alejandro et al. 2014, Zaitan et al. 2016). However, the use of gaseous ozone to regenerate multiple OMP-loaded zeolites was rarely researched. In addition, the research to date has tended to focus on powdered zeolites, and the regeneration of zeolite granules is novel. The performance in long-term regeneration was only reported in limited studies (He 2019, Zaitan et al. 2016, Zhang et al. 2014). Meanwhile, there was lack of information on the operational conditions that could affect this sequential process (He 2019, Zhang et al. 2016).

The results showed that volatile organic compound removal by sequential adsorption-ozonation was a promising hybrid process since ozone can degrade adsorbed molecules (Alejandro et al. 2014, Zaitan et al. 2016). Four successive cycles of adsorption/ozonation were achieved with stable adsorption efficiency (92%–99%) (Zaitan et al. 2016). Moreover, they confirmed that oxidation by-products of toluene such as acetic acid and acetaldehyde were formed after gaseous ozonation. Zhang et al., (2014) found that FAU zeolite loaded with 2,4,6-trichlorophenol can be effectively regenerated with gaseous ozone (Zhang et al. 2014). The adsorption capacity of zeolites highly depended on the ozone dosage (Zhang et al. 2016). According to the regeneration research on acetaminophen-loaded zeolite granules (BEA) (He 2019), long-term regeneration through the gaseous O_3 process was feasibility accomplished in dried-bed experiments. It was confirmed that the water content of zeolite granules mainly affected regeneration performance. In terms of other operational conditions, the concentration and the flow rate of ozone had less influence on ACE degradation when controlling the same ozone inflow dosage. The regeneration duration was the dominant factor that complete degradation of ACE was observed with long enough ozone contact time.

Chapter 2 Master Thesis Research

2.1 Knowledge Gaps

Based on the state of the art, related research was reviewed in terms of introduction and treatments of OMPs, and regeneration of adsorbents. Granular zeolites have been identified as effective adsorbents to eliminate OMPs and can be regenerated through gaseous ozonation. Sequential adsorption-ozonation processes are supposed to be valid for target OMP removal. However, the following knowledge remains speculative:

- There is a lack of information on ozonation performance of target OMPs in one system. They are always individually observed in various research.
- The research to date has tended to focus on zeolite powders. The regeneration of multiple OMP-loaded zeolite granules is rarely reported with the use of gaseous ozone. In addition, operational conditions such as adsorption duration and ozonation duration in adsorption-regeneration processes are indeterminate.
- The regeneration feasibility and performance of multiple OMP-loaded zeolite granules in long-term adsorption-regeneration processes are unknown.

2.2 Research Objectives

This research aims at the improvement of water quality by eliminating OMPs in wastewater and drinking water treatment. Based on the state of the art and knowledge gaps, the objective of this study is:

To investigate the regeneration performance of dried OMP-loaded zeolites granules through gaseous ozonation, and the regeneration feasibility in long-term adsorption-regeneration processes.

2.3 Research Questions

The following major research questions are formulated to meet the research objectives.

1) How is the ozonation performance of target OMPs in the water phase?

2) What are the optimal operational conditions on granular zeolite adsorption and gaseous ozone-based regeneration experiments in batch mode?

- What is the optimum adsorption duration in OMP-loading adsorption experiments?
- What is the optimal regeneration duration in dried-bed gaseous ozonation experiments with

fixed ozone concentration and flow rate?

3) What is the regeneration performance of OMP-loaded zeolite granules after 3-5 cycles of sequential adsorption-regeneration processes?

2.4 Research Approaches

To answer the research questions, literature review and laboratory research were employed. Related background, theory and present studies were elaborated in Chapter 1. The acquired knowledge established the basis of experiments. Three progressive stages of experiments were designed and conducted to facilitate accomplishing the research objectives. Pre-experiments laid the foundation and confirmed the rationality of applying ozonation for zeolite regeneration in the gas phase. Optimal conditions were determined in the second stage and ultimately applied in long-term experiments.

Preparations

Granulation

According to the previously conducted experiments, high-silica zeolites with framework BEA, MFI, and MOR displayed high adsorption performance on 11 OMPs to some extent. Therefore, they were selected as target zeolites in this research. The granular zeolites were produced by a 3D printer using commercial zeolite powders. Based on the research done by Elshof (2019), the calcination temperature of high-silica zeolite FAU at 750, 850 and 950 °C were tested (Elshof 2019). It was found that the increase of calcination temperature could promote hardness of zeolite pellets at 950 °C. As mentioned in section 1.2.1 that the framework of MFI zeolites collapses above 1200 °C (Gabelica et al. 1984). Therefore, the calcination temperature for synthetic zeolite granules was selected and applied at 950 °C.

Stage I: Pre-experiments

Ozone bubbling tests

Ozone bubbling tests were carried out to verify the feasibility of OMP degradation by ozonation in the water phase. In this experiment, ozonation was conducted in organic-free demineralised water, spiked-demineralised water and spiked-wastewater to determine the transferred ozone dose and consumption.

Fresh and ozonated zeolite adsorption isotherm experiments

Zeolites should undergo regeneration without the change of their adsorption capacities. Consequently, a series of adsorption equilibrium experiments were carried out with various adsorbent dosages in spiked-demineralised water. The effect of ozonation on adsorption properties of zeolites was investigated by comparing the fresh and ozone-treated zeolite adsorption isotherms.

Stage II Operational Condition Determination Experiments

In this study, the regeneration performance was based on the relative adsorption capacity of zeolite granules through sequential adsorption-ozonation processes. Therefore, the second research question regarding operational conditions (i.e. adsorption duration; regeneration duration) were investigated in this stage.

Adsorption capacity indication experiments

Adsorption kinetic experiments were performed in spiked-demineralised water and spiked-wastewater, to determine an optimal adsorption duration and adsorbent dosage before regeneration. The adsorption behavior of zeolite granules was indicated by measuring OMP concentrations at different contact time. An optimal adsorption duration was selected to evidence the regeneration effect.

Regeneration performance indication experiments

Water content, ozone concentration, ozone flow rate and ozonation duration are the main operational conditions in ozonation treatment. As explained in section 1.3.2, He, (2019) proposed that the existence of water molecules in zeolite pores could form water films and have an adverse impact on the ozonation process. Consequently, gaseous ozonation should be carried out in the dried-bed condition in this study. Besides, with the same ozone dosage, ozonation duration was shown as the dominant condition while the concentration and the flow rate of ozone had less influence on regeneration performance (He 2019). Therefore, in regeneration performance indication experiments, an optimal ozonation duration was determined when target OMPs could be degraded to the maximum extent in spiked-demineralised water. The ozone concentration and flow rate were controlled to be constant. The relative adsorption capacities were obtained and evaluated at various ozonation durations.

Stage III Long-term Adsorption-Regeneration Experiments

In this stage, the third research question was explored. The determined operational conditions were applied in four cycles of adsorption-regeneration experiments in spiked-demineralised water. The regeneration performance was revealed by comparing adsorption capacities after and before cycles of regeneration. In parallel, the same rounds of single adsorption experiments were conducted without regeneration to distinguish the regeneration effect.

2.5 Thesis Structure

Chapter 1 elaborates the background knowledge of this research, which is obtained from the literature study. The need and conventional methods for OMP removal and adsorbent regeneration are summarized in Chapter 1. Based on the introduction section, the sequential adsorption-regeneration treatment based on gaseous ozonation is identified as an effective process to eliminate OMPs. Meanwhile, several problems in target adsorption-regeneration treatment are defined as knowledge gaps in Chapter 2. Following, the research objective, research questions and research approaches are proposed. Three stages of experiments were designed and conducted to answer the corresponding three research questions. The specific materials and methods are described in Chapter 3. Chapter 4 displays and discusses the experimental results of three stages. The conclusions, limitations and suggestions of this research are presented in Chapter 5 and Chapter 6.

Chapter 3 Materials and Methods

3.1 Materials

Three commercial high-silica zeolites with framework MOR, MFI and BEA were applied in this study, which were supplied by *Tosoh Corporation, Europe* in a powder form. The chemical compositions of MOR, MFI and BEA are $HO·Al_2O_3·xSiO_2·nH_2O$ ($x = 240, 1500, 500$). Their main properties are listed in Table 3.1. The granular zeolites (diameter: 1 mm; length: 2-4 mm) were generated by MOR, MFI and BEA (28.3wt% each) with bentonite (15 wt%, *Sigma-Aldrich*).

Table 3.1 Main properties of target zeolites

Zeolite	Type	SiO_2/Al_2O_3	Pore size (Å)	Specific surface area (m^2g^{-1})
MOR	HSZ-690	240	6.5	450
MFI	HSZ-890	1500	5.8	310
BEA	980HOA	500	7.0	500

To focus on the OMPs listed by *Dutch ministry of IenW*, eleven OMPs were selected as the target substances in this study. Technical grade (>98% purity) benzotriazole, methyl-benzotriazole, carbamazepine, diclofenac, hydrochlorothiazide, sulfamethoxazole, metoprolol, sotalol, trimethoprim, propranolol and clarithromycin, were purchased from *Sigma-Aldrich*, Germany. Table B in Appendix reports the physicochemical characteristics of target OMPs.

The wastewater was collected from Horstermeer wastewater treatment plant (*Waternet, the Netherlands*). Horstermeer WWTP is a conventional treatment plant with activated sludge, biological N and chemical P removal.

3.2 Methods

In this study, three stages of experiments were conducted based on the research approaches (section 2.4). The experiments were generally defined as adsorption or ozonation processes. The adsorption experiments were carried out at an initial concentration of 4 μgL^{-1}. 1 L of OMP-spiked source solutions were filled in glass flasks and continuously stirred under 20 °C. The ozonation experiments were performed in a fuming hood, under room temperature.

3.2.1 Set-ups of ozonation

The gaseous ozone was produced on-site by liquid oxygen, using a Modular 4HC ozone generator (*WEDECO*, Germany). The maximum ozone production rate is 4 gh^{-1}, the ozone concentration measurement range is from 0 to 90 mgL^{-1}, and the flow rate is from 0.2 to 0.8 $Lmin^{-1}$. Based on the previous research (He 2019), the supply pressure of the ozone was set as 0.5 bar, the ozone concentration and flow rate were varied for different experimental purposes. Two types of set-ups were utilized for ozonation in the gas phase and water phase, respectively. These ozonation set-ups were provided by Mingyan Fun (PhD, TU Delft).

Ozonation in the gas phase

The OMP-loaded zeolite granules were regenerated by gaseous ozone under dried-bed conditions, illustrated as Figure 3.1. Dried and OMP-loaded zeolite granules were packed in a small glass column (inner diameter: 10 mm; length: 25 cm). Gaseous ozone was supplied from the top. Two ozone analyzers were installed at the inlet and outlet points of the column, recording the inflow and outflow concentration of ozone in gas streams. The exhaust gas was destructed to oxygen by a catalytic device before discharging to ambient air.

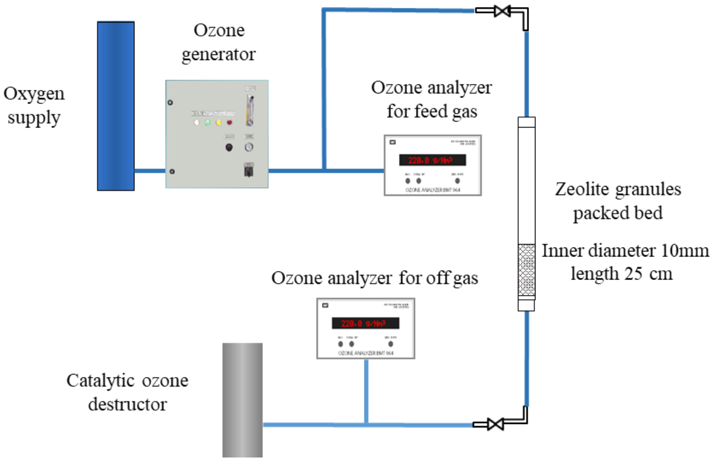


Figure 3.1 The schematic diagram of experimental set-up of ozonation in the gas phase

Ozonation in the water phase

The experimental set-up of ozonation in the water phase (Figure 3.2) was applied for ozone bubbling tests. It was the same as the set-up of ozonation in the gas phase except the use of a big tank (inner diameter: 10 cm; length: 50 cm). The entire volume of the bubbling tank is 3.5 L, and the gaseous ozone was introduced at the bottom of the tank.

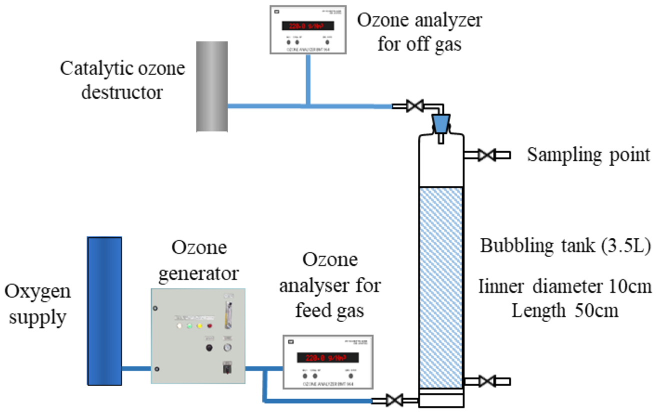


Figure 3.2 The schematic diagram of experimental set-up of ozonation in the water phase

3.2.2 Preparations

The preparatory work before three stages of experiments included granulation, preparing target solutions, and cleaning experimental materials (e.g. glass flasks). The procedure of cleaning was elaborated in Appendix H.

Granulation
The zeolite granules applied in this study were produced by a 3D clay printer (*LUTUM* ®, The Netherlands). The 3D clay printer was pre-programmed to extrude prospective lengths and shapes with manual intervention in the pressure and output speed. Three types of commercial powdered zeolites (MOR, MFI and BEA) were mixed in the same proportion (28.3 wt%) with 15 wt% bentonite and demineralised water. The uniform mixture was printed into cylinder-shaped form (diameter: 1 mm; length: 2-4 mm). After naturally air-drying overnight, the zeolite granules were calcined at 950 °C for 2 hours to enhance the stability of zeolite granules. Adsorbents were kept in a desiccator to prevent ambient humidity from interfering with experiments.

Preparation of solutions
Eleven selected OMPs were spiked into the source water (demineralised water and wastewater effluent) at a target concentration of 4 μgL^{-1}. A stock solution dissolved with these OMPs was firstly prepared at the concentration of 0.2 mgL^{-1}, considering the water solubility of all OMPs (Table B, Appendix B). The target OMP-spiked solutions were then diluted from the stock solution. All the prepared solutions were kept under 5 °C in the fridge before use.

The collected wastewater effluent was treated with a pleated polypropylene cartridge filter (pore size: 1 μm) for solid removal. It was then filled in jerrycans and stored in the fridge under 5 °C. The expiration date for the wastewater was one month.

3.2.3 Stage I: Pre-experiments

Ozone bubbling tests
To explore the ozone degradation efficiency of OMPs in the water phase, ozone bubbling tests were carried out in organic-free demineralised water, OMP-spiked demineralised water, and OMP-spiked wastewater. The set-up is described in section 3.2.1 with the use of the 3.5 L bubbling tank. The gaseous ozone was introduced from the bottom with fixed inflow concentration and flow rate (30 mgL^{-1}; 0.2 $Lmin^{-1}$). Ozonation lasted 30 min, and water samples were collected at certain time intervals. Immediately after sampling, ozone was quenched with a drop of KI solution. The OMP concentrations were measured through LC-MS, which could indicate the residual OMPs after ozone degradation.

As introduced in section 1.2.2, a mass balance of ozone can be written as Equation 1.4, where the second-order rate coefficient (k_{O_3}) is a crucial constant, indicating the ozone reaction rate of OMPs in the water phase. In order to obtain k_{O_3}, Equation 3.1-3.3 were applied. The rate equation can be represented as Equation 3.1. The reaction of OMPs and ozone followed pseudo-first-order kinetics as Equation 3.2, where k_1 expresses the first-order rate coefficient of ozonation, (s^{-1}). k_1 was obtained by fitting the concentration-time profile curve in software. k_{O_3} was then calculated by Equation 3.3, where $C_{O_{3}0}$ was the initial ozone concentration (30 mgL^{-1}).

$$-\frac{dC_{O_3}}{dt} = k_{O_3} C_{OMP}\, C_{O_3} \tag{3.1}$$

$$C_{OMP} = C_{OMP_0}\, e^{-k_1 t} \tag{3.2}$$

$$k_{O_3} = \frac{k_1}{C_{O_{3}0}} \tag{3.3}$$

During the bubbling tests, two detectors consistently measured inflow and outflow concentrations of ozone. The total ozone was either transferred into the water phase or emerged in the outflow. The dose and consumption of ozone could be determined by operating the same conditions of ozone inflow concentration, flow rate and reaction time in various solutions. The mass balance of ozone in gas-liquid phases has been established in section 1.2.2. As mentioned, the accumulation rate of ozone in the water phase depends on the rate of dissolution, self-decomposition, and chemical reaction. The mass balance in the demineralised water without OMPs and OMP-spiked source water were derived as Equation 3.4 and Equation 3.5.

$$D_{O_3\_without\ OMPs} = D_{dissolved\ O_3} + D_{self\text{-}decomposed\ O_3} \tag{3.4}$$

$$D_{O_3\_with\ OMPs} = D_{dissolved\ O_3} + D_{self\text{-}decomposed\ O_3} + D_{reacted\ O_3} \tag{3.5}$$

$D_{dissolved\ O_3}$, $D_{self\text{-}decomposed\ O_3}$ and $D_{reacted\ O_3}$ (mg) represent the fraction of ozone dissolved in water, self-decomposed and reacted with OMPs. The amount of ozone consumed on OMPs can be theoretically calculated by the difference between the above equations, according to the inlet and outlet reactor streams.

The total inflow dosage of ozone was calculated by Equation 3.6, where $D_{O_3\_total}$ is the inflow dosage of ozone (mg), t is the duration of ozonation (min), C_{O_3} is the inflow concentration of ozone (mgL^{-1}), and V_{O_3} is the inflow flow rate of ozone ($Lmin^{-1}$). The total inflow dose of ozone consists of the emergent ozone and ozone transferred in the water. The integration of Equation 3.7 yielded the part of emergent ozone.

$$D_{O_3\_total} = t \cdot C_{O_3} \cdot V_{O_3} \tag{3.6}$$

$$D_{emergent\ O_3} = V_{O_3} \int_0^t C_{O_3\_outflow}\, dt \tag{3.7}$$

$$D_{dissolved\ O_3} = D_{O_3\_total} - V_{O_3} \int_0^t C_{O_3\_outflow\_without\ OMP}\, dt \tag{3.8}$$

$$D_{reacted\ O_3} + D_{self\text{-}decomposed\ O_3} = D_{O_3\_total} - D_{dissolved\ O_3} - D_{emergent\ O_3} = V_{O_3} \int_0^t (C_{O_3\_outflow\_\ without\ OMP} - C_{O_3\_outflow\_\ with\ OMP})\, dt \tag{3.9}$$

The solubility of ozone was calculated by conducting the ozone bubbling test in organic-free demineralised water, through Equation 3.8. The residual was supposed to be the reacted and self-decomposed fractions ($D_{reacted\ O_3} + D_{self\text{-}decomposed\ O_3}$). They were obtained from Equation 3.9, by the difference between the integrated ozone in no-OMP demineralised water and

OMP-spiked demineralised water or OMP-spiked wastewater.

Fresh and ozonated zeolite adsorption isotherm experiments
To investigate the effect of ozonation on zeolite granules, fresh and ozonated zeolite adsorption isotherm experiments were carried out in spiked-demineralised water. Prior to the adsorption experiments, 2 g of fresh zeolite granules were treated with gaseous ozone. The ozonation set-up (Fig 3.1) was introduced in the preceding section (3.2.1). Fresh zeolite granules were packed in the dried-bed column and ozonated for 1 hour under the maximum ozone concentration (90 mgL^{-1}) and flow rate (0.8 Lmin^{-1}). The fresh and ozone-treated zeolite granules were separately ground into powders and applied in adsorption isotherm experiments. Batch equilibrium adsorption experiments were conducted in 1 L glass bottles with adsorbent dosages in the range of 0 to 1000 mgL^{-1}. After 24 or 48 hours, samples were collected and filtered by a syringe filter with 0.2 μm polypropylene membrane.

After equilibrium, the OMP-loading of zeolites (q_e, μgg^{-1}) can be calculated from Equation 3.10, where C_0, C_e is the initial and equilibrium OMP concentration (μgL^{-1}), m is the mass of zeolites (mg), and V is the volume of the OMP-spiked solution (L).

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{3.10}$$

The nonlinear Freundlich isotherm is one of the earliest empirical models to describe equilibrium characteristics, as Equation 3.11 (Freundlich 1906). K_F and n are temperature-dependent Freundlich constants, representing the adsorption capacity and intensity. The nonlinear Freundlich equation can be logarithmically linearized into Equation 3.12, where K_F and n were calculated from the linear regression. Based on many published studies (de Ridder et al. 2012, Jiang et al. 2018), the linear regression of the Freundlich model was commonly applied.

$$q_e = K_F C_e^n \tag{3.11}$$

$$log\ q_e = log\ K_F + nlog\ C_e \tag{3.12}$$

3.2.4 Stage II: Operational Condition Determination Experiments

Determination of adsorption duration & adsorbent dosage

Adsorption capacity indication experiments
The adsorption duration and dosages were determined by conducting adsorption kinetic experiments. Based on the results of adsorption isotherms, adsorbent dosages of 250 and 500 mgL^{-1} were considered as options for regeneration. The adsorption batches were run 12 days in 1L of spiked-demineralised water and spiked-wastewater. Samples were collected at regular time intervals and measured through LC-MS. The average results of triplicate experiments were obtained. The OMP concentration-time profile was plotted to select an optimal adsorption duration.

Determination of regeneration duration

Regeneration performance indication experiments

The regeneration performance of zeolite granules was observed by the comparison of adsorption capacities after and before ozonation. Three phases of experiments were carried out, including OMP-loading on fresh zeolites, ozonation, and OMP-loading on regenerated zeolites. The schematic diagram (Figure 3.3) displays those steps and the corresponding operational conditions, where the Italicized content represents the fixed ones. Due to the influence of COVID-19, the collection of wastewater was inhibited since March of 2020. Therefore, experiments related to regeneration (determination of regeneration duration and long-term regeneration) were only carried out in spiked-demineralised water.

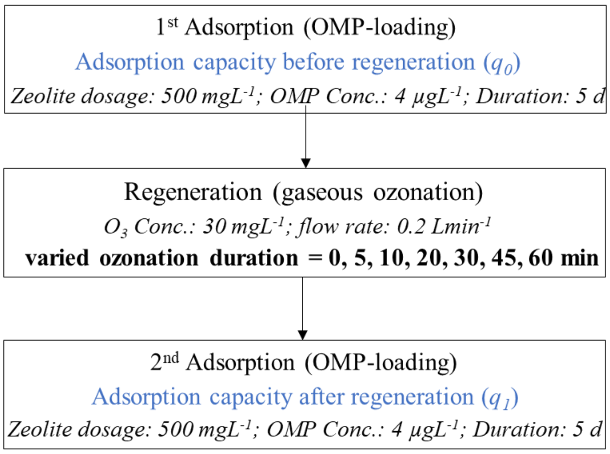


Figure 3.3 The schematic diagram of regeneration performance indication experiments

Prior to gaseous ozonation experiments, fresh zeolite granules were loaded with OMPs. Based on the adsorption kinetic experiments, 500 mg of zeolite granules were applied in batches with 1L of spiked-demineralised water for 120 hours of adsorption. The initial adsorption capacity of fresh zeolites (q_0) was calculated by Equation 3.10. After 120 h, 500 mg of OMP-loaded zeolite granules in each batch were flushed out by demineralised water. Zeolite granules were then dried in an oven overnight at 50 °C, which was far below the thermal decomposition temperature of target OMPs (Table B in Appendix B).

Ozonation experiments were carried out in a dried-bed column, as introduced in section 3.2.1. 500 mg of dried OMP-loaded zeolite granules were charged into the column with the addition of glass beads at the bottom. Gaseous ozone was introduced from the top of the column. As explained in the approaches (section 1.3.2), ozone inflow concentration and flow rate were kept constant (30 mgL^{-1}; 0.2 Lmin^{-1}). The ozonation durations were varied from 0 to 60 min at certain time intervals. After regeneration, zeolite granules were soaked overnight in 100 mL of pure demineralised water, to dissolve the formed by-products.

Subsequently, the regenerated zeolite granules were applied into a second-round of adsorption experiment with the same operational conditions as the previous adsorption experiment. In parallel, a group of continuous adsorption experiments without regeneration experiment was carried out, which can be considered as evidence of regeneration effectiveness. The adsorption capacity before (q_0) and after (q_1) regeneration were calculated by Equation 3.10. The relative adsorption capacity (*Rq*) was obtained (Equation 3.13), representing the regeneration performance in terms of the comparison of adsorption capacities after and before regeneration.

$$Rq = \frac{q_1}{q_0} \tag{3.13}$$

For each regeneration duration, triplicate experiments were executed to reduce experimental errors. The average values, standard deviations (*SD*) and relative standard deviation (*RSD*) were calculated in the data processing, as Equation 3.14 - 3.15. Zeolite granules were weighed after each step to ensure the accuracy of experiments. The mass of zeolite granules in a group of experiments should always be in a credible interval close to 500 mg.

$$SD = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}} \tag{3.14}$$

$$RSD = \frac{SD}{x_i} \times 100\% \tag{3.15}$$

3.2.5 Stage III: Long-Term Adsorption-Regeneration Experiments

To answer the third research question, four cycles of adsorption-regeneration experiments were carried out in this stage. As mentioned, long-term regeneration experiments were only conducted in spiked-demineralised water. Figure 3.4 displays the general steps of a cycle of long-term adsorption-regeneration experiments. Long-term experiments were the extension of the regeneration performance indication experiment by applying the determined operational conditions. The specific experimental procedure of long-term experiments was consistent with that described in the preceding section. In parallel, the same cycles of adsorption experiments were performed by applying OMP-loaded zeolite granules directly in adsorption instead of ozonation. The relative adsorption capacities (*Rq*) of various OMPs with and without regeneration can be obtained and compared.

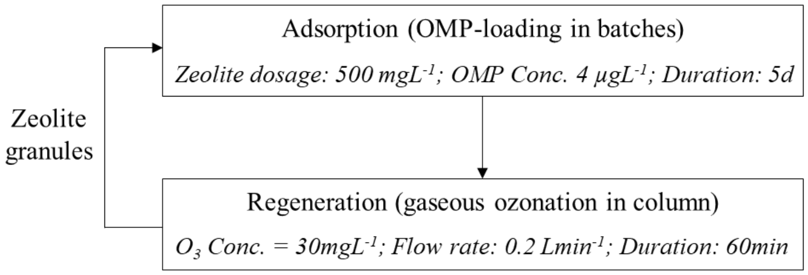


Figure 3.4 Schematic diagram of the long-term adsorption-regeneration experiments

In adsorption phase, 500 mg of zeolite granules and 5 days of adsorption duration were applied in batch experiments. For regeneration, those 500 mg OMP-loaded zeolite granules were dried and then ozonated at ozone concentration of 30 mgL^{-1}, flow rate of 0.2 $Lmin^{-1}$ and duration of 60 min. Subsequently, the regenerated zeolites were applied in the next cycle of adsorption-regeneration experiments. To calculate adsorption capacities, samples were taken at the initial and ending time in every adsorption experiments. The regeneration performance of every cycle was based on the adsorption capacity in the next cycle. The n^th^ relative adsorption capacity was obtained by Equation 3.16, where q_n is the adsorption capacity of granules after the n^th^ regeneration (μgg^{-1}); q_0 is the initial adsorption capacity of fresh zeolite granules (μgg^{-1}).

$$Rq_n = \frac{q_n}{q_0} \tag{3.16}$$

3.2.6 Analytical methods

The quantification of OMPs was accomplished by liquid chromatography-tandem mass spectrometry (LC-MS, *Waters^{TM}, USA*). LC-MS is a hyphenated technique, which combines physical separation capacities and mass analysis capacities. LC uses high performance to separate the sample components and then introduce them to MS for mass analysis. The installed type of LC in this study was ACQUITY UPLC I-Class Plus (*Waters^{TM}, USA*). An ACQUITY UPLC® BEH C18 pump (particle size: 1.7μm, column size: 2.1x50 mm, *Waters^{TM}, Ireland*) was equipped in LC at an elution flow rate of 0.35 ml/min. MS (Xevo TQ-S micro, *Waters^{TM}, USA*) was applied to sort ions according to their mass/charge ratio. Analytes were tracked by corresponding deuterated internal standards. Data were processed through MassLynx software. The detection limits of eleven OMPs are listed in Appendix F.

All samples were filtrated through a syringe filter in case of the blockage of the machine. Calibration standard solutions at levels from 0.0025 μg/L to 10 μg/L were prepared to determine the calibration lines. The internal standard solution was manually added into every water samples at a volume ratio of 1: 99 (internal standard: sample).

Prior to applying the filtered wastewater effluent in target experiments, indicators of wastewater characteristics, including pH, EC, UV_{265}, TN, TP, S, COD and DOC were quantified based on standard methods.

Chapter 4 Results and Discussion

4.1 Results of Stage I

In the first stage, pre-experiments were carried out to investigate the ozone effects on OMPs and zeolite granules. Ozone bubbling tests were carried out in spiked-demineralised water and wastewater, to examine the non-degradable OMPs through ozonation process in the water phase. Fresh and ozonated zeolite adsorption isotherms were performed in spiked-demineralised water to determine the gaseous ozone effect on zeolite itself. Prior to the pre-experiments, characteristics of the treated wastewater effluent were detected, as table 4.1. Propranolol and clarithromycin were unable to be measured in LC-MS in all spiked-demineralised water experiments. The available results of 9 OMPs are discussed in the following sections.

Table 4.1 Wastewater characteristics

UV_{254} ($AUcm^{-1}$)	pH	EC (μscm^{-1})	DO (mg/L)	COD (mgL^{-1})	DOC (mgL^{-1})	PO_4^{3-} (mgL^{-1})	TN (mgL^{-1})	SO_4^{2-} (mgL^{-1})
0.181	7.074	426.333	9.054	20.500	6.750	0.204	4.833	30.333

4.1.1 OMP degradation by ozonation in the water phase

Ozone bubbling tests were conducted to investigate whether ozone can degrade target OMPs in the water phase. Figure 4.1 and Figure 4.2 are plotted as OMP concentration over time in spiked-demineralised water and spiked-wastewater, respectively. It can be observed that all 9 OMPs can be completely degraded in the water phase, and no one was resistant to ozonation. Figure 4.1 shows that the ozonation of benzotriazole (BTA) lasted 10 minutes, which was the slowest reaction in spiked-demineralised water. Methyl-benzotriazole (MBTA) and metoprolol (MP) required 5minutes. Regarding the other 6 OMPs, 2 minutes of ozonation were sufficient to oxidize them.

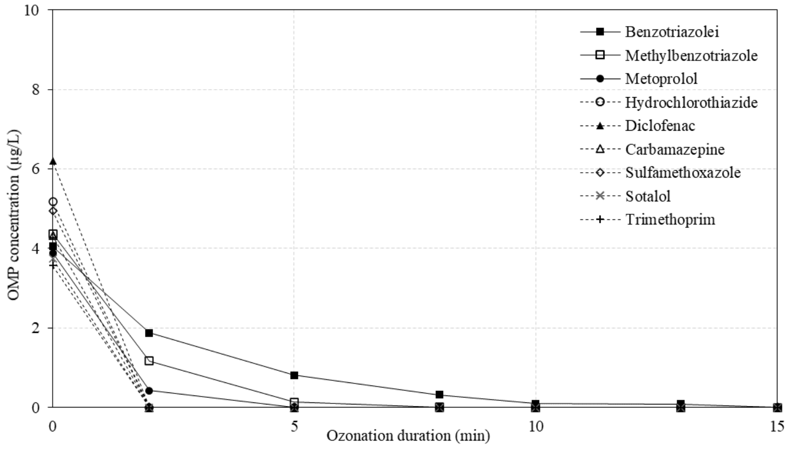


Figure 4.1 OMP degradation over time in spiked-demineralised water
(Ozone conditions: concentration = 30 mgL^{-1}; flow rate = 0.2 $Lmin^{-1}$; duration = 30min)

In spiked-wastewater, some OMPs could be found in the wastewater effluent as background substances (Figure 4.2). Consequently, the initial concentrations of target OMPs such as BTA, and MBTA were increased in wastewater solution. It can be noticed that in the first 2 min, the reaction rate was slower, which can be deduced that ozone reacted with natural organic matters (NOM) in advance of target compounds in spiked-wastewater. Compared to the demineralised solution, all OMPs were degraded with a longer reaction time due to the existence of NOM. Such results confirmed that more ozone was consumed in the wastewater.

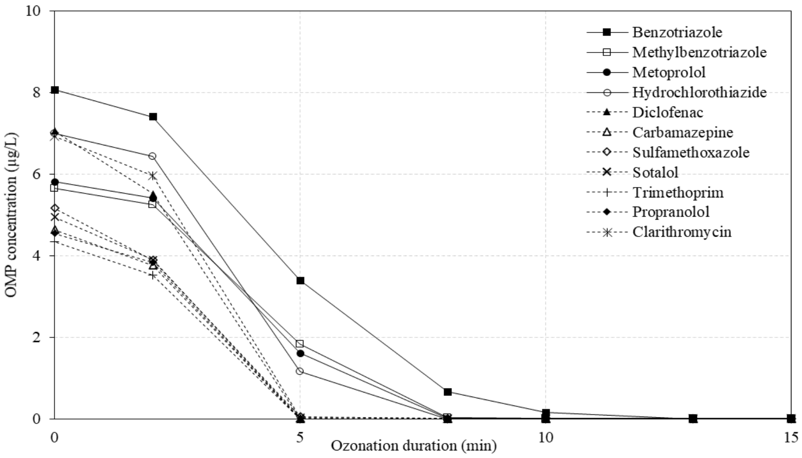


Figure 4.2 OMP degradation over time in spiked-wastewater

(Ozone conditions: concentration = 30 mgL^{-1}; flow rate = 0.2 Lmin^{-1}; duration = 30min)

As introduced in section 1.2.2, $gO_3/gDOC$ at a specific time can be calculated. The results were listed in Table G.1 in Appendix, and it shows that after 10 minutes of ozonation in wastewater, 9 compounds were entirely removed at 1.79 $gO_3/gDOC$. To be noticed, $gO_3/gDOC$ ratio is commonly used in a continuous reactor, where the ozone dose is the ozone concentration in water. Here the amount of ozone expresses the consumed ozone in batch experiments, which was different from the practice.

Table 4.2 lists the second-order rate coefficients obtained from literature and calculated by experimental results. The results displayed in Figure 4.1 coincide with the second-order rate coefficients from the literature. Among all 9 OMPs, BTA, MBTA and MP exhibited relatively slower reaction rate in spiked-demineralised water, and they had low rate coefficients. In terms of other OMPs, they could react rapidly with ozone due to their k_{O_3} are larger than 10^4 $M^{-1}s^{-1}$, as indicated by rate coefficients from literature. However, there was a magnitude difference between k_{O_3} from literature and spiked-demineralised water experiments. It might be influenced by various pH conditions, since k_{O_3} is a pH-dependent constant. It is reported that phenol can react about 10 times faster with ozone at pH of 7 than at pH of 6 (Huber et al. 2003). Nevertheless, k_{O_3} of BTA, MBTA and MP obtained from experimental results were still 100 times smaller than other OMPs. As introduced in section 1.2.2, oxidation with ozone is a highly selective reaction. Ozone can react quickly with electron-rich moieties, e.g., olefins, tertiary amines, thioethers and activated aromatics (Von Gunten 2003). Therefore, the lower rate constants of BTA, MBTA and MP might be explained by the absence of more reactive functional groups, and an aromatic or phenyl ring that is only slightly activated (Huber et al. 2003). Moreover, k_{O_3} in spiked-wastewater were always smaller than it in spiked-demineralised water, showing the effect of NOM.

Table 4.2 k_{O_3} from literature and experimental results

OMPs	k_{O_3} ($M^{-1}s^{-1}$)			Expected reactive functional groups
	Literature (pH = 7)	Experiment (demineralised water)	Experiment (wastewater)	
Benzotriazole	$1.9 \times 10^2 - 2.3 \times 10^2$	3.3×10^4	2.1×10^4	Aromatic ring
Methyl-benzotriazole	$4.0 \times 10^2 - 4.9 \times 10^2$	6.4×10^4	2.3×10^4	Aromatic ring
Metoprolol	2.0×10^3	1.1×10^5	2.4×10^4	Phenyl ring
Sotalol	$1.0 \times 10^3 - 1.0 \times 10^4$	1.1×10^6	3.2×10^4	Amine (secondary)
Clarithromycin	7.0×10^4	n/a	3.1×10^4	Amine (tertiary)
Hydrochlorothiazide	8.5×10^4	1.1×10^6	2.6×10^4	Amine (secondary)
Propranolol	1.0×10^5	n/a	3.1×10^4	Phenol
Trimethoprim	2.7×10^5	1.1×10^6	3.2×10^4	2, 4-Diaminopyrimid ring
Carbamazepine	3.0×10^5	4.0×10^5	3.2×10^4	Olefin
Sulfamethoxazole	5.5×10^5	3.0×10^5	3.3×10^4	Aniline
Diclofenac	6.8×10^5	8.9×10^5	3.2×10^4	Amine (tertiary)

Figure 4.3 shows the inflow and outflow concentration against time in ozone bubbling tests with various solutions. As introduced in the methods (section 3.2.2), the total dose of ozone consists of the emergent ozone and fraction dissolved in water, self-decomposed and reacted with OMPs. The consumption of ozone could be calculated by integration and difference of outflow concentration-time profiles. The specific results are displayed in Table G.2 in Appendix G. It can be found that the consumption of ozone in spiked-wastewater (50.7 mg) was 10 times larger than in spiked demineralised water (5.57 mg). The persistence of NOM was evidenced in wastewater that consuming a large amount of ozone in the water phase.

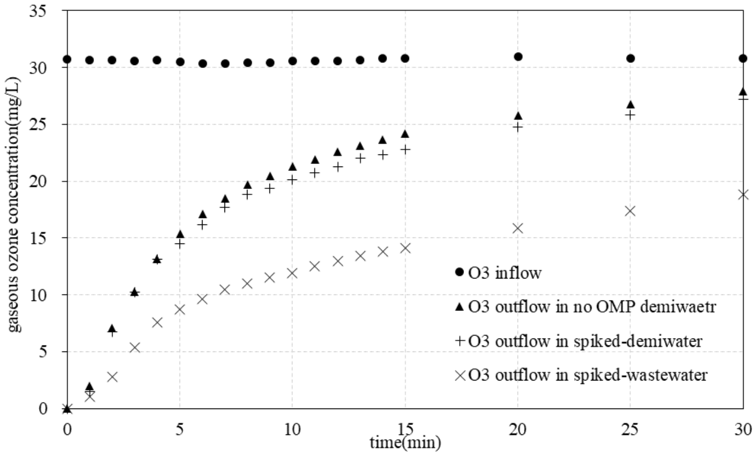


Figure 4.3 Inflow and outflow concentration of gaseous ozone in no-OMP demineralised water, spiked-demineralised water and spiked-wastewater. (Ozonation conditions: concentration = 30 mgL^{-1}; flow rate = 0.2 Lmin^{-1}; duration = 30min)

4.1.2 Ozone effect on zeolite granules

Whether ozonation destroyed the zeolite adsorption properties were investigated through equilibrium batch experiments in spiked-demineralised water. Two adsorbents, fresh and ozone-treated zeolite granules were ground into powders and applied in the comparative adsorption isotherm experiments. The adsorption isotherms were obtained, displaying the equilibrium adsorption capacity via the concentration. The entire results with 24 and 48 hours of adsorption are shown in Figure G.3 in Appendix G, which illustrates that 24 hours of adsorption has reached equilibrium.

Fresh and ozonated zeolite adsorption results of benzotriazole (BTA), methyl-benzotriazole (MBTA), and sulfamethoxazole (SMX) are plotted in Figure 4.4 as solid and hollow spots, respectively. It can be observed that adsorption isotherms have significant similarity between fresh and ozonated zeolites, showing that gaseous ozone did not affect adsorption capacities. It confirms the statement by Reungoat that the mineral composition of zeolites makes them highly resistant to ozone (Reungoat et al. 2007). Therefore, the changes in adsorption capacities through regeneration could be attributed to the degradation of OMPs. Nevertheless, the influence of ozone on zeolite itself still could be a potential factor in the long-term application, which needs further research.

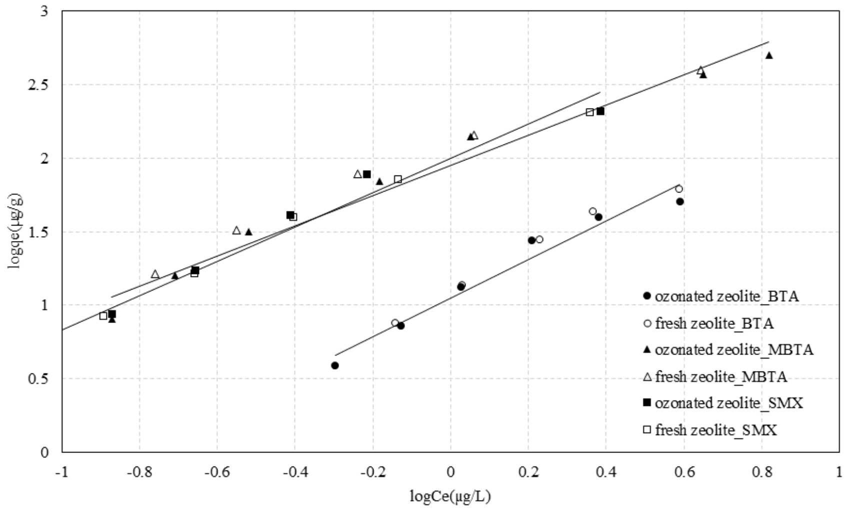


Figure 4.4 Adsorption isotherms of Benzotriazole (BTA), Methyl-benzotriazole (MBTA), Sulfamethoxazole (SMX) over mixed zeolite powders in spiked demineralised water (OMP initial concentration was spiked at 4 µgL^{-1}; zeolite dosage was from 0 to 1000 mgL^{-1})

As plotted in Figure 4.4, three compounds were well fitted in Linear Freundlich model. The Freundlich parameters K_F and n_F of them were derived in Table 4.3. Other 6 OMPs were regarded as outliers and their results are displayed in Appendix G. Among them, carbamazepine (CBZ), diclofenac (DIC) and hydrochlorothiazide (HCTZ) showed no appreciable removal and metoprolol (MP), trimethoprim (TMP), and sotalol (SOT) were completely adsorbed. According to other researches (de Ridder et al. 2012, Martucci et al. 2012), zeolite with MOR and ZSM-5 frameworks also show low removal on CBZ, and high removal on MP. They found that CBZ may form molecular chains through molecular interactions, resulting in the enlarged size and the incapacity to enter MOR and MFI zeolites. In this study, the applied adsorbents were synthesized by three types of high-silica zeolites. The assumption was made that with the combination of three selective zeolites, the adsorption capacity of target OMPs would be enhanced. But due to the information on adsorption performance of signal zeolites is incomplete, the comparison is limited and needs further research.

Table 4.3 pKa, charge, K_F and n_F of target OMPs

OMPs	p*Ka* (at 20 °C)	Charge (at pH=7)	K_F and n_F (Freundlich parameters)
Benzotriazole	8.37	+	K_F: 21.56 n_F: 1.04 ($R^2 = 0.9628$)
Methyl-benzotriazole	8.85	+	K_F: 11.56 n_F: 1.94 ($R^2 = 0.9754$)
Sulfamethoxazole	5.70	-	K_F: 14.08 n_F: 1.92 ($R^2 = 0.9723$)
Carbamazepine	n/a	0	No appreciable removal
Diclofenac	4.15	-	
Hydrochlorothiazide	7.9	+/0	
Metoprolol	9.49	+	Complete removal
Trimethoprim	7.3	0	
Sotalol	8.3	+	

4.2 Results of Stage II

The regeneration performance of zeolite granules was examined by comparing the adsorption capacity after and before ozonation. Hence, the objective of this stage was to determine related operational conditions (i.e. adsorption duration, dosage and regeneration duration) in adsorption and ozonation experiments.

4.2.1 Adsorption duration and dosage

Adsorption kinetic experiments were conducted in spiked-demineralised water and wastewater, both with 500 mgL^{-1} and 250 mgL^{-1} zeolite granules. The results of 500 mgL^{-1} adsorbents were plotted in Figure 4.5 and 4.6, showing the OMP concentration changes over time. The results of the zeolite dosage of 250 mgL^{-1} are shown in Figure G.3 in Appendix G.

The adsorption kinetics with 500 mgL^{-1} zeolite granules in spiked-demineralised water is illustrated in Figure 4.5. It can be observed that after 150 hours, all 9 OMPs approximately reached equilibrium. Notably, OMPs were divided into three categories concerning zeolite adsorption capacities. CBZ and DIC represented with solid points were hardly removed and the adsorption mostly happened at the beginning ten hours. TPM, SOT and MP drawn in single lines were completely adsorbed on zeolite granules. Regarding other OMPs (BTA, MBTA, SMX, HCTZ), zeolite granules exhibited average adsorption capacities.

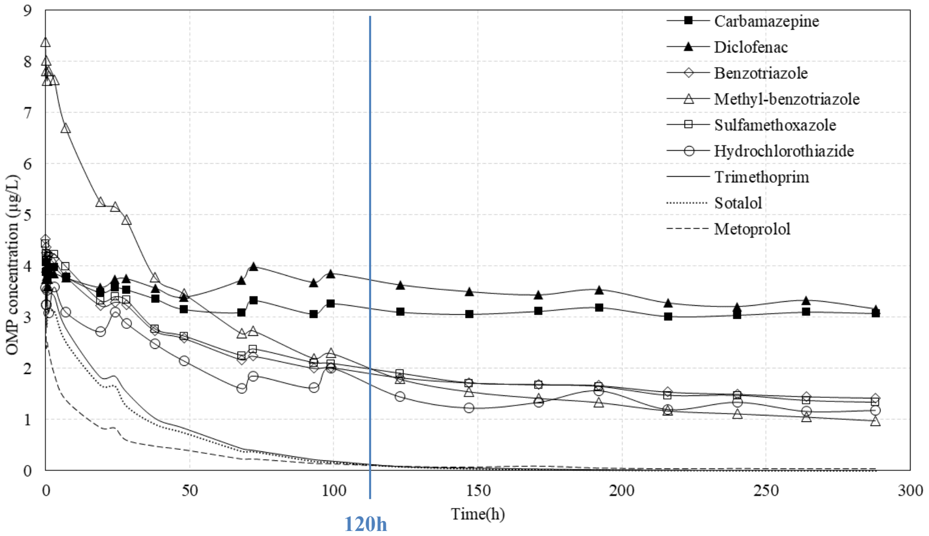


Figure 4.5 The adsorption kinetics of 9 OMPs over zeolite granules in spiked-demineralised water (OMP initial concentration was spiked at 4 µgL^{-1}; zeolite dosage was 500 mgL^{-1})

It can be noticed in Figure 4.5 that the initial concentration of MBTA was around two times more than others, at 8 µgL^{-1}. It is attributed to both 4-MBTA and 5-MBTA were dosed into the stock solution, while LC-MS failed to recognize them. Subsequently, a new stock solution with correct MBTA dosage was prepared and applied in the following experiments.

The objective of this experiment is to determine an adsorption duration. By comparing the adsorption capacity before and after regeneration, the regeneration performance of dried loaded zeolite granules by gaseous ozone was investigated. Consequently, OMP-loading adsorption experiments should be carried out and stopped at a specific time interval before equilibrium. An adsorption duration that at least adsorption on most OMPs can exhibit distinction through ozonation were accepted. If the adsorption stops earlier before 150 h such as 50 h, it is probably still in a rapid adsorption phase. The recovery of adsorption capacity may be not only caused by OMP degradation but also due to the remaining adsorption sites in zeolites which can adsorb more molecules. Likewise, longer adsorption after equilibrium is also unreasonable since next time it may reach the same value with a slower adsorption rate. The comparison was based on single points, rather than curves with an observable slope. Only one sample at the ending time was measured in adsorption-regeneration experiments, instead of a series. Therefore, an adsorption duration between 100 to 150 hours is considered as an appropriate operational condition in spiked-demineralised water adsorption experiment for OMP-loading. Ultimately, 120 hours (5 days) was applied in the further regeneration experiments, as marked in Figure 4.5.

Figure 4.6 illustrates the adsorption kinetics in spiked-wastewater experiment, with 500 mgL^{-1} zeolite granules. As explained in ozone bubbling tests, the initial concertation of most OMPs such as BTA, MBTA, DIC and HCTZ were increased in wastewater solution due to the existence of background matrices, which could also result in longer equilibrium time. HCTZ showed an extremely flatulating trend due to it was sensitive in LC-MS measurement.

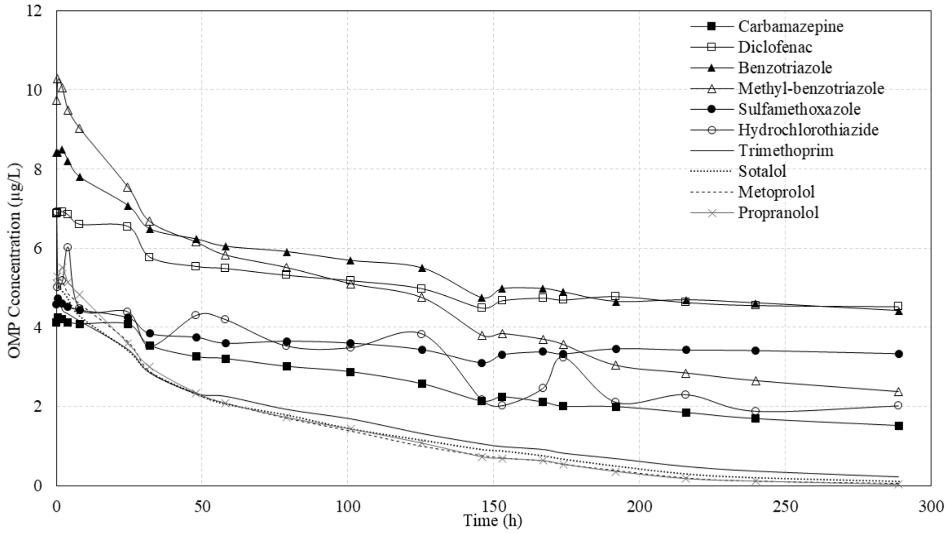


Figure 4.6 The adsorption kinetics of 9 OMPs over mixed zeolite granules in spiked-wastewater (OMP initial concentration was spiked at 4 μgL-1; zeolite dosage was 500 mgL-1)

It was found in Figure 4.6 that SMX and CBZ had relative worse and better adsorption compared to the results in demineralised solution. NOM was a contributing factor to these phenomena. NOM is possible to either negatively or positively influence on the adsorption of various OMPs (Jiang et al. 2018). Braschi et al. (2016) studied that SMX was also lower adsorbed on FAU zeolites with the addition of humic monomers, confirming the competition caused by NOM. Nevertheless, most OMPs in wastewater kinetic experiments had similar adsorption performance as in demineralised solution. Unfortunately, the collection of wastewater was prohibited since March, 2020. In this situation, remaining regeneration experiments were only conducted in demineralised solutions. The adsorption kinetics and ozone bubbling tests could imply that results of demineralised solution are relatively instructive and representative to wastewater experiments.

The results of 250 mgL^{-1} zeolite granules in spiked-demineralised water and wastewater are displayed in Appendix G. Adsorption equilibrium was not achieved after 12 days in spiked-demineralised water. Meanwhile, when packing 250 mg of zeolite granules into the small column for regeneration, the height of total granules was less than 1 cm. Therefore, 500 mgL^{-1} of the adsorption dosage was more suitable in regeneration experiments.

4.2.2 Regeneration duration

The ozonation duration was regarded as a dominant operational condition in the regeneration process, based on the finding that a complete degradation was achieved with a long enough ozonation duration (He 2019). The results of ozone bubbling tests (section 4.1.1) confirm that all target OMPs can be decomposed by ozone in the water phase. Therefore, the degradation of the selected OMPs through gaseous ozonation was supposed to be valid. In this case, a series of time-dependent regeneration experiments were executed with fixed ozone concentration (30 mgL^{-1}) and flow rate (0.2 $Lmin^{-1}$). 0.5 g of dried OMP-loaded zeolite granules were ozonated at different durations from 0 to 60 min. The relative adsorption capacity (*Rq*) of fresh and ozonated zeolite granules were obtained by 120 hours of adsorption experiments. q_1 and q_0 express the adsorption capacities per unit of mass of the regenerated and the original zeolite granules. The value "*1*" of *Rq* indicates that zeolite granules could reach the same adsorption capacities before and after regeneration.

According to the adsorption kinetic results in the preceding section, 9 OMPs could be categorized into three groups on behalf of their adsorption performance (high, medium, and low adsorption). Likewise, this classification was applied in the determination of regeneration durations. Figure 4.7 - 4.9 depict the experimental results of three groups in spiked-demineralised water, where the relative adsorption capacity (*Rq*) was plotted against ozonation durations. Every series represents a specific OMP. Standard deviations (*SD*) obtained from triplicate experiments are displayed as error bars. Results of the relative standard deviations (*RSD*) are shown in Table G.4 in Appendix G. Normally, data with *RSD* of 25% or greater are subject to high errors and should be used with caution.

(1) High adsorption OMPs (SOT, MP, TMP)

Figure 4.7 displays *Rq* of high adsorption OMPs (SOT, MP, TMP) versus ozonation durations. It can be found that *Rq* of SOT, MP, and TMP were consistently and stably close to 1 regardless of with or without regeneration. Related to their adsorption kinetics, SOT, MP, and TMP were completely adsorbed by zeolite granules after 120 hours of adsorption. The *Rq* value of without regeneration series reached 1, which reveals that zeolite granules still had vacant adsorption sites for high adsorption OMPs after 1st adsorption experiments. As a consequence, the recovered adsorption capacities of these OMPs after ozonation were probably attributed to both adsorption properties and OMP degradation. Nevertheless, the behavior of SOT, MP, and TMP is worthwhile of investigation in long-term adsorption-regeneration experiments. Considering the errors, only the first and last data of MP showed relatively large *SD*, others were less apparent.

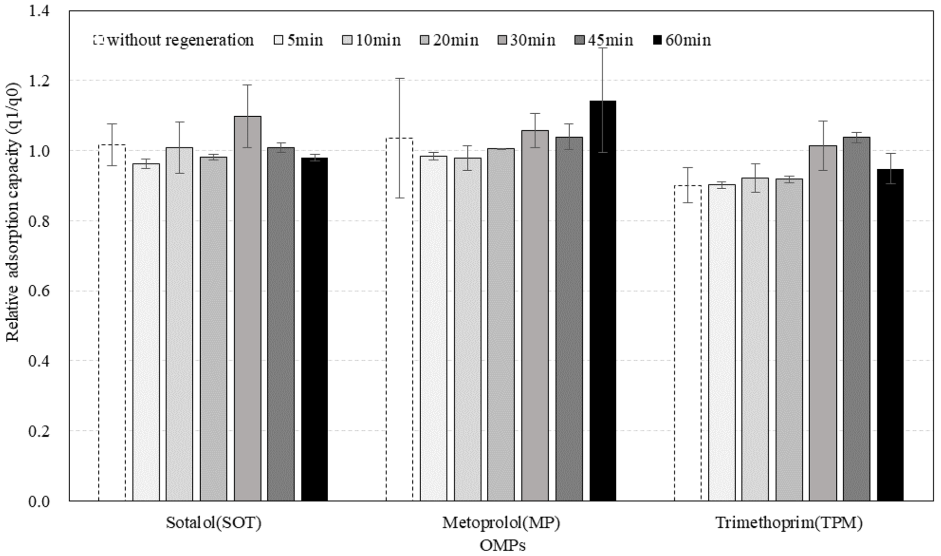


Figure 4.7 The relative adsorption capacity (*Rq*) of high adsorption OMPs: sotalol (SOT), metoprolol (MP), and trimethoprim (TMP) at various ozonation durations in spiked-demineralised water. (Adsorption conditions: OMP initial concentration = 4 μgL^{-1}; zeolite dosage = 500 mgL^{-1}; adsorption duration = 120 h; Ozonation conditions: O_3 concentration = 30 mgL^{-1}; flow rate = 0.2 Lmin^{-1}, 0.04 ms^{-1})

(2) Medium adsorption OMPs (BTA, MBTA, SMX)

Figure 4.8 illustrates *Rq* of BTA, MBTA, and SMX against various regeneration durations. The *Rq* values of without regeneration series were all less than 1, showing the effectiveness of ozonation on OMP degradation. After 45 or 60 minutes of ozonation, *Rq* of medium adsorption OMPs were close to 1. It demonstrates that 45 or 60 minutes of ozonation worked on regenerating them. For error analysis, except the first point of MBTA, *RSD* of all the other results were less than 20%.

As can be noticed in Figure 4.8, with the increase of the ozonation duration, *Rq* of medium adsorption OMPs were larger. Results of SMX were slightly fluctuated at the first 20 min and then rose to 1. The peak value of *Rq* (1.25) at 30 min was unreasonable and possibly due to the experimental error. BTA and MBTA followed the tendency that *Rq* were gradually promoted with longer ozonation durations. Such results are in agreement with the hypothesis that a longer ozone duration was supposed to result in a larger *Rq* with the fixed ozone concentration and flow rate. It was proposed on the basis of the regeneration research on acetaminophen-loaded zeolites (He 2019) and gas transfer mechanisms (Benjamin and Lawler 2013). He, (2019) found that when controlling the same ozone dosage, a longer ozonation time could cause an increase of ACE degradation efficiency. It was probably explained as the gas could stay at the interface for a longer time, leading to a longer diffusion distance to the inner pores of zeolite granules. In this research, the ozone concentration and flow rate were kept constant. Higher ozone dosage and longer ozone diffusion distance were achieved by the longer time of ozonation. Consequently, the results of medium adsorption OMPs could evidence the assumption that the longer ozonation duration would lead to the enhancement of *Rq*.

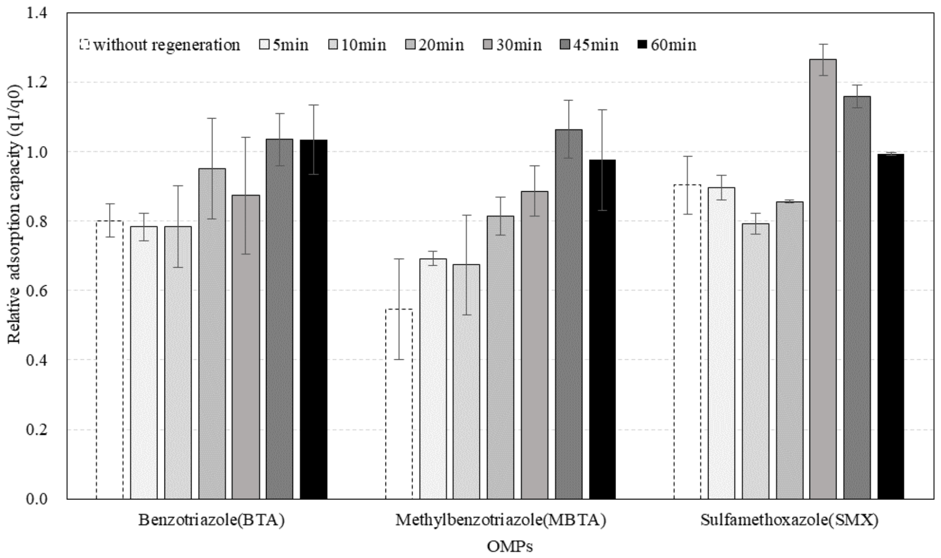


Figure 4.8 The relative adsorption capacity (*Rq*) of medium adsorption OMPs: benzotriazole (BTA), methyl-benzotriazole (MBTA), and sulfamethoxazole (SMX) at various ozonation durations in spiked-demineralised water. (Adsorption conditions: OMP initial concentration = 4 μgL^{-1}; zeolite dosage = 500 mgL^{-1}; adsorption duration = 120 h; Ozonation conditions: O_3 concentration = 30 mgL^{-1}; flow rate = 0.2 Lmin^{-1}, 0.04 ms^{-1})

(3) Low adsorption OMPs (CBZ, DIC, HCTZ)

Rq of low adsorption OMPs (CBZ, DIC and HCTZ) at various ozonation durations are illustrated in Figure 4.9. It can be observed that *Rq* of those OMPs were less than 0.5 when without regeneration, due to low adsorption capacities of zeolites. After 60 min of ozonation, *Rq* of DIC and HCTZ were close to or larger than 1. It reflects that regeneration duration of 60 minutes was valid and sufficient for them. However, q_1 of CBZ was only 0.6 times of its q_0 with 60 min of ozonation.

Such results of CBZ indicate that 60 min of ozonation was not long enough for CBZ regeneration in this multi-solute system. As mentioned, the degradation of the selected OMPs through gaseous ozonation was supposed to be valid, according to the results of ozone bubbling tests. CBZ was observed to be rapidly degradable in spiked-demineralised water and spiked-wastewater. A research on ozonation of several pharmaceuticals in spiked-drinking water also reported that CBZ which had tertiary amine groups was among the fastest reacting pharmaceuticals with ozone (Mcdowell et al. 2005). The transformation pathway of CBZ in ozonation process is illustrated in Figure D.3 in Appendix D (Hübner et al. 2013). It can be implied that gaseous ozone should be able to react with CBZ in zeolite granules. Therefore, a long enough ozonation duration (e.g. 6 hours) is suggested to be applied in this multi-solute system, to investigate whether *Rq* of CBZ can be returned to 1. Meanwhile, regeneration experiments of single CBZ-loaded zeolite granules are recommended to conduct in the next step, to confirm the hypothesis that CBZ can be degraded through gaseous ozone.

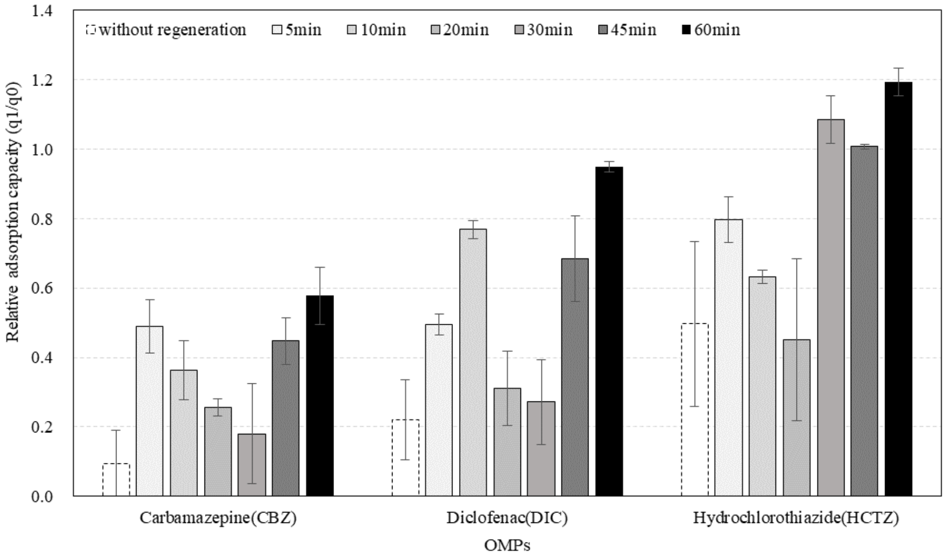


Figure 4.9 The relative adsorption capacity (*Rq*) of low adsorption OMPs: carbamazepine (CBZ), diclofenac (DIC), and hydrochlorothiazide (HCTZ) at various ozonation durations in spiked-demineralised water. (Adsorption conditions: OMP initial concentration = 4 μgL^{-1}; zeolite dosage = 500 mgL^{-1}; adsorption duration = 120 h; Ozonation conditions: O_3 concentration = 30 mgL^{-1}; flow rate = 0.2 $Lmin^{-1}$, 0.04 ms^{-1})

CBZ, DIC and HCTZ showed similar trends when associating various ozonation durations with *Rq* (Figure 4.9). The evident decline of *Rq* between 5-30 min could be observed and then *Rq* rise to a peak at 60 min. These fluctuations might be explained by the production and transformation of intermediates through ozonation. It is well known that disinfection by-products are commonly generated through ozonation process. Alejandro et al., (2014) found that the presence of adsorbed toluene oxidation intermediates on the zeolite surface adversely affected the regeneration process and caused site competition in adsorption (Alejandro et al. 2014). In this study, the oxidation of multiple organic compounds could contribute to an extensive range of intermediates. The existence of intermediates may block the pore to hinder the ozone molecules contact target OMPs, or to affect the adsorption capacities of zeolite granules by site competition. Ozone might react with target OMPs yielding the increased polarity and functional groups (Ternes et al. 2003). Polar intermediates were less adsorbable and could be removed by soaking in the demineralised water after ozonation. On the other hand, the nonpolar molecules could be formed, which likely remain in the zeolites and influence on adsorption processes. For instance, Mcdowell et al., (2015) reported 1-(2-benzaldehyde)-(1H,3H)-quinazoline-2,4-dione (BQD) was sufficiently nonpolar and identified as a major ozonation product of CBZ (Mcdowell et al. 2005). The chemical structure of BQD is exhibited in Figure D.3 in Appendix D.

It can be seen in Figure 4.9 that, *Rq* dropped down at 5-30 min for CBZ, 10-30 min for DIC and 5-20 min for HCTZ. During these periods, more intermediates were probably formed and negatively affected the adsorption capacity of CBZ, DIC and HCTZ. A minimum *Rq* then reflected the most considerable intermediate influence. After that, those intermediates were probably decomposed into smaller forms, leading to the availability of degradation or adsorption of CBZ, DIC and HCTZ. Subsequently, the gradual enhancement of *Rq* was observed at 45-60 min of regeneration. Hence, it might be derived that for low adsorption OMPs, the formation and transformation of intermediates potentially dominated the optimal ozonation duration. The increase of ozone duration is suggested to promote regeneration performance by eliminating the adverse influence of intermediates.

In terms of error analysis, *RSD* of blank experiment results (without regeneration) were approximately 50% for DIC and HCTZ and up to 100% for CBZ. Nevertheless, the conclusion that their *Rq* was less than 1 when without regeneration remains the same with an addition of *SD*. Other points such as 30 min of CBZ and DIC also showed large *SD* and *RSD*. Low zeolite adsorption capacities of these OMPs were potentially responsible for the significant errors. Especially for CBZ and DIC, zeolite adsorption capacities of them were merely at around 0.2 $\mu g g^{-1}$ in spiked-demineralised water. In this case, the imperceptible adsorbed fractions resulted in less accurate calculation of q_1.

(4) Overall discussion on regeneration duration determination results

Table 4.3 summarizes the related factors in regeneration performance with respect to three categories of OMPs. Among them, *Rq* of low adsorption (CBZ, DIC, HCTZ) and medium adsorption (BTA, MBTA, SMX) OMPs can evidence regeneration effectiveness due to their *Rq* were less than 1 when without regeneration. After 60 min of ozonation, adsorption capacities of DIC, BTA, MBTA, and HCTZ have achieved the same level as fresh zeolites. CBZ was the only one that showed 60% of the initial adsorption capacity after 60 min. It illustrates that 60 min was sufficient for regeneration of zeolites, regarding degradation of low and medium adsorption OMPs except for CBZ. Therefore, 60 minutes of ozonation was selected as an optimal operational condition and applied in the following long-term experiments.

Moreover, low adsorption OMPs (CBZ, DIC, HCTZ) showed a down-up fluctuation with the increase of ozonation duration, which was probably caused by the formation and transformation of intermediates. In contrast, medium adsorption OMPs might be less affected by intermediates, since BTA and MBTA showed a positive correlation between *Rq* and ozonation duration. It proves the hypothesis that longer ozonation duration was responsible for the enhancement of *Rq*. For well adsorbed substances (SOT, MP, TMP), there might be enough adsorption sites when without regeneration, and intermediates did not pose a threat to those OMPs.

Table 4.4 Summaries of regeneration performance of different categories of OMPs

Categories of OMPs	*Rq*		Relation of *Rq* - regeneration duration	Errors
	without ozonation	after 60min ozonation		
Low adsorption (CBZ, DIC, and HCTZ)	< 0.5	CBZ < 0.6 Others ~ 1	*Rq*: rise-descend-rise	Significant
Medium adsorption (BTA, MBTA, and SMX)	0.5 - 1	~ 1	positive correlation	Less significant
High adsorption (SOT, MP, and TMP)	~ 1	~ 1	*Rq*: consistently near 1	Not significant

It can be noticed that the errors of high adsorption OMPs were less than the medium adsorption ones. Low adsorption OMPs had the most appreciable *SD*. The complete removal of MP, TMP and SOT could contribute to relative constant adsorption capacities. It illustrates that the adsorption process was more sensitive in the related experiments regarding error analysis. Meanwhile, most *RSD* of 9 OMPs were in an acceptable range (< 25%), on behalf of the accuracy and repeatability of this study.

4.3 Results of Stage III

This stage aimed to investigate the long-term regeneration behavior of OMP-loaded zeolites based on gaseous ozonation. Four cycles of adsorption-regeneration experiments were performed in spiked-demineralised water by applying the determined operational conditions, 0.5 g of zeolite granules, 120 hours of adsorption duration and 60 min of ozonation duration. Other fixed operational conditions remained the same as the previous experiments (i.e. O_3 concentration: 30 mgL^{-1}; O_3 flow rate: 0.2 Lmin^{-1}). For comparison purpose, four cycles of single adsorption experiments were conducted to exhibit the relative adsorption capacity (*Rq*) without regeneration. q_n expresses the adsorption capacity after the n rounds of ozonation. The regeneration duration determination experiments were regarded as the first cycle of adsorption-regeneration processes, where q_0 represents the initial adsorption capacity of fresh zeolites. Triplicate experiments were carried out, and *RSD* of the data were calculated as Table G.5-6 in Appendix G. The results of HCTZ in this stage was missing due to LC-MS happened to be unable to measure it since May of 2020. As the preceding section, results of long-term experiments are also discussed in three categories of OMPs.

(1) High adsorption OMPs (SOT, MP, TMP)

Figure 4.10 (a) and (b) illustrate *Rq* of high adsorption OMPs after different cycles of adsorption-regeneration and single adsorption experiments, respectively. During four cycles of single adsorption processes (Figure 4.10.b), *Rq* of SOT, MP, and TMP constantly remained around 1. This phenomenon indicates that zeolite granules were still able to adsorb much of SOT, MP, and TMP after four rounds of 120-hour adsorption in spiked-demineralised water (4μgL^{-1}). In this case, the regeneration effect on high adsorption OMPs could not be observed by four cycles of regeneration experiments. Whether the gaseous ozone can effectively degrade these OMPs in zeolites should be investigated by conducting more cycles of single adsorption and adsorption-regeneration experiments. Nevertheless, such results were evidence that the applied zeolite granules which were mixed with MOR, MFI and BEA had relatively high adsorption capacities of SOT, MP, and TMP. As can be noticed that only *Rq* of TMP in the fourth single adsorption experiment was less than 1. It was probably caused by the experimental error, which *RSD* was 19%.

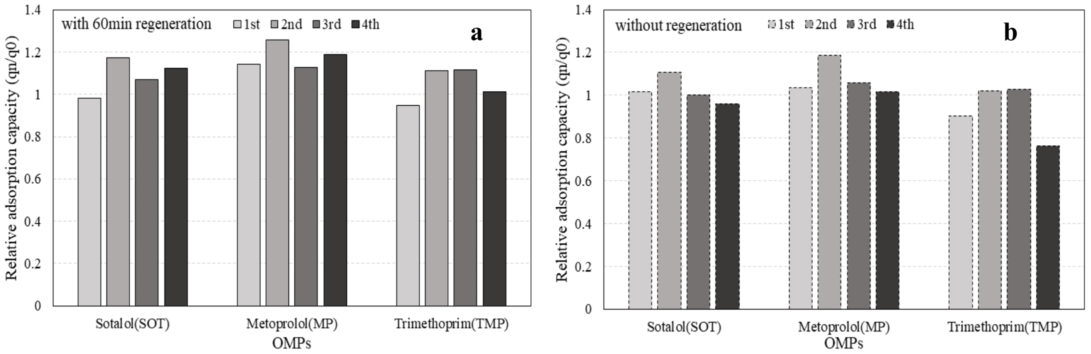


Figure 4.10 The relative adsorption capacity (*Rq*) of high adsorption OMPs: sotalol (SOT), metoprolol (MP), and trimethoprim (TMP) after different cycles of (a) 60 min ozone regeneration; (b) adsorption without regeneration in spiked-demineralised water. (Adsorption conditions: OMP initial concentration = 4 μgL^{-1}; zeolite dosage = 500 mgL^{-1}; adsorption duration = 120 h; Ozonation conditions: O_3 concentration = 30 mgL^{-1}; O_3 flow rate = 0.2 Lmin^{-1}, 0.04 ms^{-1}; regeneration duration = 60 min (a) or 0 min (b))

(2) Medium adsorption OMPs (BTA, MBTA, SMX)

Rq of BTA, MBTA and SMX were plotted versus different cycles of adsorption-regeneration and single adsorption experiments in Figure 4.11.a and Figure 4.11.b. As can be noticed in Figure 4.11.b, their *Rq* were always smaller than 1 in single adsorption experiments. These results illustrate that the effectiveness of ozonation could be exhibited in long-term regeneration experiments. Moreover, Figure 4.11.b displays that *Rq* of SMX and BTA declined during the four cycles of experiments, showing adsorption sites were occupied after cycles of adsorption.

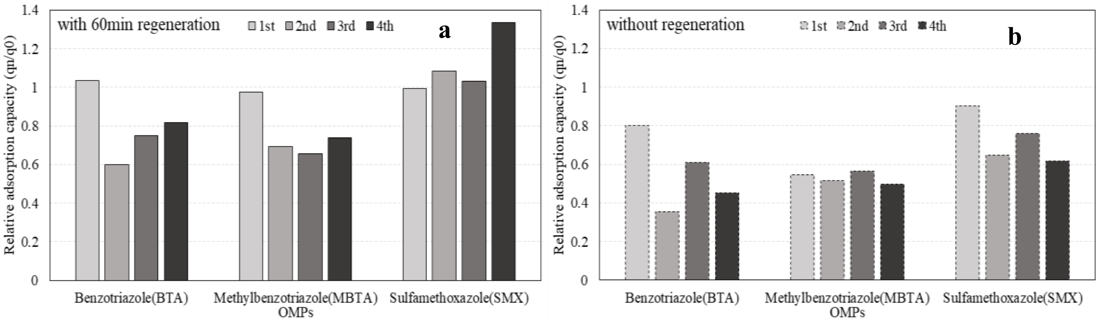


Figure 4.11 The relative adsorption capacity (*Rq*) of medium adsorption OMPs: benzotriazole (BTA), methyl-benzotriazole (MBTA), and sulfamethoxazole (SMX) after different cycles of (a) 60 min ozone regeneration; (b) adsorption without regeneration in spiked-demineralised water. (Adsorption conditions: OMP initial concentration = 4 μgL^{-1}; zeolite dosage = 500 mgL^{-1}; adsorption duration = 120 h; Ozonation conditions: O_3 concentration = 30 mgL^{-1}; O_3 flow rate = 0.2 Lmin^{-1}, 0.04 ms^{-1}; regeneration duration = 60 min (a) or 0 min (b))

Results of *Rq* in four cycles of adsorption-regeneration experiments are depicted in Figure 4.11.a. As mentioned, the regeneration duration determination experiment was applied as the first cycle of regeneration in long-term operation. It has been confirmed in the preceding section that BTA, MBTA and SMX loaded zeolites can be regenerated after the first cycle of 60 min ozonation. However, *Rq* of BTA and MBTA decreased to 0.7 after two - four cycles of regeneration. It is hypothesized to be explained by the effect of intermediates accumulation in the zeolite pores. As discussed in the preceding section, ranges of intermediates were probably formed and affected the adsorption capacities of OMPs after regeneration. In this multi-solute system, the generated intermediates might not be completely degraded and remained adsorbed in the zeolite granules after the first cycle of 60 min ozonation. During the next time of regeneration, part of ozone molecules probably decomposed intermediates instead of target substances. Meanwhile, numerous intermediates were formed again through ozonation, which could hinder OMP oxidation or cause site competition in the next round of adsorption. By means of this, intermediates were potentially accumulated cycle by cycle, causing a decrease of *Rq*. Therefore, it is suggested that longer ozonation duration should be applied in long-term regeneration experiments to abase the intermediates accumulation effect. As proposed in the research of three cycles of ACE-loaded zeolite regeneration experiments (He 2019), the intermediates accumulation was also regarded as a dominant factor to influence on the regeneration performance of zeolite granules.

For SMX, it is evident that *Rq* were increased when comparing the results of with 60 min regeneration to without regeneration. Notably, *Rq* of SMX remained at 1 in four cycles of adsorption-regeneration experiments. It indicates that 60 min of gaseous ozonation effectively worked on four rounds of regeneration of SMX-loaded zeolite granules in this system. It could be inferred that SMX was less affected by intermediates, which was in line with the deduction of SMX in regeneration duration determination experiments. Hence, more cycles of regeneration experiments are suggested to be carried out to pay more attention to SMX.

(3) Low adsorption OMPs (CBZ, DIC)

Figure 4.12 shows *Rq* in four cycles of long-term experiments regarding CBZ and DIC. *Rq* of these OMPs were relatively low that in the range of 0 to 0.2 in single adsorption experiments (Figure 4.12.b). Four cycles of enhanced *Rq* of CBZ could be observed, when comparing the results of with and without regeneration experiments. Figure 4.12.a illustrates that *Rq* of CBZ with 60 min regeneration were near 0.6 after the first and second cycles of regeneration. It decreased after three cycles of regeneration, which was possibly affected by intermediates accumulation. However, the recovered *Rq* of CBZ after four cycles of regeneration was difficult to explain.

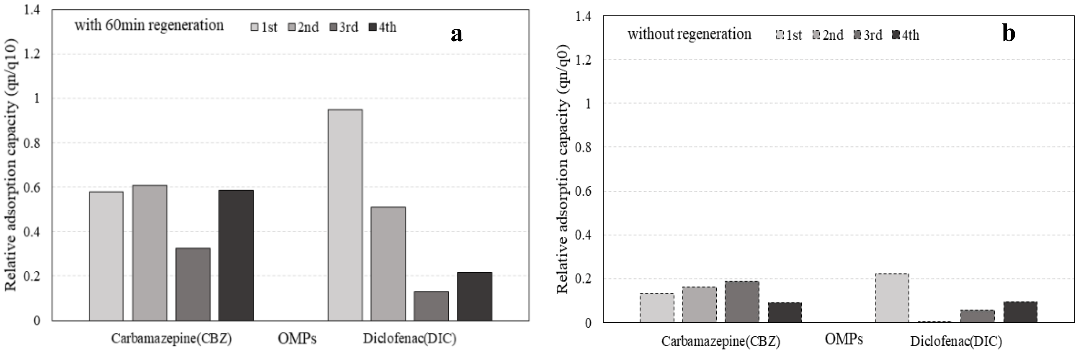


Figure 4.12 The relative adsorption capacity (*Rq*) of low adsorption OMPs: carbamazepine (CBZ), and diclofenac (DIC) after different cycles of (a) 60 min ozone regeneration; (b) adsorption without regeneration in spiked-demineralised water. (Adsorption conditions: OMP initial concentration = 4

μgL^{-1}; zeolite dosage = 500 mgL^{-1}; adsorption duration = 120 h; Ozonation conditions: O_3 concentration = 30 mgL^{-1}; O_3 flow rate = 0.2 Lmin^{-1}, 0.04 ms^{-1}; regeneration duration = 60 min (a) or 0 min (b))

For DIC, Figure 4.12.a displays an apparent decline of *Rq* over four cycles of regeneration. In comparison with the first and the second cycle of regeneration, *Rq* of DIC decreased by half, that from 1 to 0.5. It was lower at around 0.2 after three or four cycles of regeneration, that the adsorption capacity was not promoted by ozonation. Such results might reveal that intermediates had a significant impact on DIC.

Due to CBZ and DIC were hardly adsorbed by zeolite granules, the accumulation of intermediates could be responsible for more difficult adsorption of them on zeolites. As discussed in the previous section, 60 min of ozonation did not work on the first cycle of regeneration of CBZ. Therefore, the ozonation duration is suggested to be enhanced in long-term regeneration experiments to improve regeneration performance of low adsorption OMPs.

(4) Overall discussion on long-term adsorption-regeneration results

The regeneration effect on high adsorption OMPs (SOT, MP, TMP) could not be observed through four cycles of regeneration experiments. Among target OMPs, SMX is the only one that could be adequately regenerated after four cycles of 60 min regeneration experiments. More cycles of regeneration are suggested to focus on SOT, MP, TMP and SMX. In contrast, *Rq* of other OMPs (BTA, MBTA, CBZ and DIC) reduced after the second cycle of regeneration, which probably attributed to the intermediate accumulation. Hence, longer ozonation duration is supposed to be applied in long-term adsorption-regeneration experiments to accomplish better regeneration performance of medium and low adsorption OMPs.

Chapter 5 Conclusions

5.1 Recap of research objective and questions

The main objective of this study was to evaluate the granular zeolite regeneration performance by gaseous ozonation. Based on the three stages of experiments, the proposed research questions can be answered:

1) *How is the ozonation performance of target OMPs in the water phase?*

   The results of ozone bubbling tests indicate that all target OMPs can be degraded entirely through ozonation in the water phase. There are no resistant molecules to ozonation.

2) *What are the optimal operational conditions on granular zeolite adsorption and gaseous ozone-based regeneration experiments in batch mode?*

- *What is the optimum adsorption duration in OMP-loading adsorption experiments?*

  An optimum adsorption duration was selected when adsorption capacities of medium and low adsorption OMPs (benzotriazole, methyl-benzotriazole, sulfamethoxazole, carbamazepine, diclofenac, and hydrochlorothiazide) can exhibit distinctions after and before ozonation. 120 hours of adsorption duration was determined as an optimum condition in spiked-demineralised water experiments for OMP-loading.

- *What is the optimal regeneration duration in dried-bed gaseous ozonation experiments with fixed ozone concentration and flow rate?*

  According to the results of 0-60 min of regeneration duration experiments, 60 min of ozonation was selected as the optimal regeneration duration in this multi-solute system. It was sufficient for the regeneration of benzotriazole, methyl-benzotriazole, sulfamethoxazole, diclofenac, and hydrochlorothiazide. Aside from them, the zeolite adsorption capacity of carbamazepine was failed to achieve the same level as the fresh ones through 60 min of regeneration. A longer ozonation duration was probably needed for degrading carbamazepine.

3) *What is the regeneration performance of OMP-loaded zeolite granules after 3-5 cycles of sequential adsorption-regeneration processes?*

   In four cycles of adsorption-regeneration experiments, zeolites still had high adsorption capacities of metoprolol, trimethoprim and sotalol, which regeneration effect were not evidenced. Besides, 60 min of gaseous ozonation was adequate for four rounds of regenerating sulfamethoxazole. Regarding carbamazepine, diclofenac, benzotriazole, and methyl-benzotriazole, the regeneration performance was significantly reduced after the first cycle of regeneration, and these compounds might require a longer regeneration time.

5.2 Overall conclusions

The overall conclusions of this study are summarized below:

1) In the water phase, all target OMPs were not resistant to ozonation. The existence of natural organic matters in wastewater consumed more ozone.
2) It was confirmed that zeolites could undergo regeneration through gaseous ozonation without influence on their adsorption capacities by adsorption isotherms.
3) The elimination of target OMPs through sequential adsorption-regeneration processes was complicated and case-specific in this multi-solute system. The regeneration performance of granular zeolites could be illustrated by the relative adsorption capacity, applying 120 hours of adsorption in spiked-demineralised water. The regeneration duration should be regarded as a crucial and dominant operational condition.
4) 60 minutes of ozonation was effective and sufficient to regenerate low and medium adsorption OMPs (diclofenac, hydrochlorothiazide, benzotriazole, methyl-benzotriazole, and sulfamethoxazole). Only the regeneration of carbamazepine was inadequate after 60 minutes of ozonation, which potentially required a longer regeneration duration.
5) The regeneration effectiveness of high adsorption substances (metoprolol, trimethoprim and sotalol) could not be concluded with 60 minutes of ozonation or in four cycles of adsorption-regeneration experiments. The applied zeolite granules had relatively high adsorption capacities of these OMPs.
6) In four cycles of adsorption-regeneration experiments, 60 min of gaseous ozonation was valid for regenerating sulfamethoxazole. Regarding carbamazepine, diclofenac, benzotriazole, and methyl-benzotriazole, the regeneration performance was significantly reduced after the first cycle of regeneration. The ozonation duration should probably be extended above 60 min in long-term regeneration experiments to improve regeneration performance.
7) Intermediates might have significantly affected regeneration performance in ozonation and adsorption processes. In particular, the effect of intermediates accumulation was hypothesized to be the main factor that abased the regeneration performance of carbamazepine, diclofenac, benzotriazole and methyl-benzotriazole in long-term regeneration. Regeneration of sulfamethoxazole might be less influenced by intermediates.

Chapter 6 Limitations and Suggestions

6.1 Limitations

The methods employed in this study had several limitations that should be clarified:

- Initially, 11 OMPs were targeted in this study. However, LC-MS were unable to measure propranolol and clarithromycin in all spiked-demineralised water experiments. They were possibly adsorbed on filters while taking samples in adsorption batch experiments. Besides, hydrochlorothiazide also could not be measured since May of 2020. These problems regarding OMP measurement should be addressed in future research.
- The current study did not include the matrix effects of wastewater due to COVID-19, and it was replaced by demineralised water. Prior to applying regeneration in real wastewater, experiments carried out in demineralised water could be considered as a predictive reference and guidance. However, it hardly contains any natural organic matters which may influence on the adsorption process. Regeneration experiments in real wastewater should be carried out soon when it is available.
- As mentioned in the introduction section, the complex matrices of OMPs in the aquatic environment result in more difficulties for water treatment plants to remove them. In this study, 11 substances were aimed to be adsorbed on zeolites and degraded by gaseous ozone. Even though the ozonation mechanisms of single compounds in the water phase are proposed in the literature, there has been little discussion about gaseous ozonation on multiple OMP-loaded zeolite granules.
- The conducted experiments were a primary step in batch mode, and column tests are needed in future research. It is still a long way to upscale for practical application.

6.2 Suggestions

The following suggestions are proposed through this study:

- Regarding regeneration duration, carbamazepine was not adequately regenerated after 60 minutes of ozonation. A longer ozonation duration should be examined to achieve better regeneration performance.
- Further experiments and analysis of single carbamazepine-loaded zeolite regeneration by gaseous ozone are suggested to be conducted to confirm the hypothesis that carbamazepine can be regenerated with the use of gaseous ozone.
- In long-term adsorption-regeneration experiments, the enhancement of ozonation duration and numbers of cycles may be valuable for the next step research.
- The influence of ozone on zeolite itself could be a potential factor in the long-term application. The characteristics of zeolite can be investigated in further research.

Chapter 7 Bibliography

Abellán, M., Gebhardt, W., Schröder, H.F.J.W.S. and Technology (2008) Detection and identification of degradation products of sulfamethoxazole by means of LC/MS and− MSn after ozone treatment. 58(9), 1803-1812.

Acero, J.L. and Von Gunten, U. (2001) Characterization of Oxidation processes: ozonation and the AOP O3/H2O2. Journal - AWWA 93(10), 90-100.

Ahmad, J., Naeem, S., Ahmad, M., Usman, A.R.A. and Al-Wabel, M.I. (2019) A critical review on organic micropollutants contamination in wastewater and removal through carbon nanotubes. Journal of Environmental Management 246, 214-228.

Alejandro, S., Valdés, H., Manéro, M.-H. and Zaror, C.A. (2014) Oxidative regeneration of toluene-saturated natural zeolite by gaseous ozone: The influence of zeolite chemical surface characteristics. Journal of Hazardous Materials 274, 212-220.

Anderson, M.A. (2000) Removal of MTBE and other organic contaminants from water by sorption to high silica zeolites. Environmental Science and Technology 34(4), 725-727.

Andreozzi, R., Raffaele, M. and Nicklas, P.J.C. (2003) Pharmaceuticals in STP effluents and their solar photodegradation in aquatic environment. 50(10), 1319-1330.

Ashfaq, M., Khan, K.N., Rasool, S., Mustafa, G., Saif-Ur-Rehman, M., Nazar, M.F., Sun, Q. and Yu, C.-P. (2016) Occurrence and ecological risk assessment of fluoroquinolone antibiotics in hospital waste of Lahore, Pakistan. Environmental Toxicology and Pharmacology 42, 16-22.

Baerlocher, C., McCusker, L.B. and Olson, D.H. (2007) Atlas of zeolite framework types, Elsevier.

Bagastyo, A.Y., Keller, J., Poussade, Y. and Batstone, D.J. (2011) Characterisation and removal of recalcitrants in reverse osmosis concentrates from water reclamation plants. Water Research 45(7), 2415-2427.

Bansal, R.C. and Goyal, M. (2005) Activated carbon adsorption, CRC press.

Barbosa, M.O., Moreira, N.F.F., Ribeiro, A.R., Pereira, M.F.R. and Silva, A.M.T. (2016) Occurrence and removal of organic micropollutants: An overview of the watch list of EU Decision 2015/495. Water Research 94, 257-279.

Beltran, F.J. (2003) Ozone reaction kinetics for water and wastewater systems, crc Press.

Benjamin, M.M. and Lawler, D.F. (2013) Water quality engineering: Physical/chemical treatment processes, John Wiley & Sons.

Benner, J. (2009) Ozone reactivity in wastewater treatment plant effluent and reverse osmosis concentrate Ozonation of beta blockers: kinetic studies, identification of oxidation products and pathways.

Benner, J., Ternes, T.A.J.E.S. and Technology (2009) Ozonation of metoprolol: elucidation of oxidation pathways and major oxidation products. 43(14), 5472-5480.

Bhatnagar, A., Hogland, W., Marques, M. and Sillanpää, M. (2013) An overview of the modification methods of activated carbon for its water treatment applications. Chemical Engineering Journal 219, 499-511.

Blasioli, S., Martucci, A., Paul, G., Gigli, L., Cossi, M., Johnston, C.T., Marchese, L. and Braschi, I. (2014) Removal of sulfamethoxazole sulfonamide antibiotic from water by high silica zeolites: a study of the involved host-guest interactions by a combined structural, spectroscopic, and computational approach. J Colloid Interface Sci 419, 148-159.

Bolis, V., Busco, C. and Ugliengo, P. (2006) Thermodynamic Study of Water Adsorption in High-Silica Zeolites. The Journal of Physical Chemistry B 110(30), 14849-14859.

Borowska, E., Bourgin, M., Hollender, J., Kienle, C., McArdell, C. and Gunten, U. (2016) Oxidation of cetirizine, fexofenadine and hydrochlorothiazide during ozonation: Kinetics and formation of transformation products. Water Research 94, 350-362.

Braschi, I., Martucci, A., Blasioli, S., Mzini, L.L., Ciavatta, C. and Cossi, M. (2016) Effect of humic monomers on the adsorption of sulfamethoxazole sulfonamide antibiotic into a high silica zeolite Y: An interdisciplinary study. Chemosphere 155, 444-452.

Brodu, N., Manero, M.-H., Andriantsiferana, C., Pic, J.-S. and Valdés, H. (2013) Role of Lewis acid sites of ZSM-5 zeolite on gaseous ozone abatement. Chemical Engineering Journal 231, 281-286.

Brooks, B. and Huggett, D. (2012) Human Pharmaceuticals in the Environment: Current and Future Perspectives.

Buffle, M.-O., Schumacher, J., Meylan, S., Jekel, M., von Gunten, U.J.O.S. and Engineering (2006) Ozonation and advanced oxidation of wastewater: Effect of O3 dose, pH, DOM and HO•-scavengers on ozone decomposition and HO• generation. 28(4), 247-259.

Coday, B.D., Yaffe, B.G.M., Xu, P. and Cath, T.Y. (2014) Rejection of Trace Organic Compounds by Forward Osmosis Membranes: A Literature Review. Environmental Science & Technology 48(7), 3612-3624.

Cotruvo, J.A. (1985) Organic micropollutants in drinking water: An overview. Science of The Total Environment 47, 7-26.

Crini, G. and Badot, P.-M. (2011) Sorption processes and pollution: Conventional and non-conventional sorbents for pollutant removal from wastemasters, Presses Univ. Franche-Comté.

Damjanović, L., Rakić, V., Rac, V., Stošić, D. and Auroux, A. (2010) The investigation of phenol removal from aqueous solutions by zeolites as solid adsorbents. Journal of Hazardous Materials 184(1), 477-484.

de Ridder, D.J., Verberk, J.Q.J.C., Heijman, S.G.J., Amy, G.L. and van Dijk, J.C. (2012) Zeolites for nitrosamine and pharmaceutical removal from demineralised and surface water:

Mechanisms and efficacy. Separation and Purification Technology 89, 71-77.

de Ridder, D.J., Verliefde, A.R.D., Heijman, S.G.J., Verberk, J.Q.J.C., Rietveld, L.C., van der Aa, L.T.J., Amy, G.L. and van Dijk, J.C. (2011) Influence of natural organic matter on equilibrium adsorption of neutral and charged pharmaceuticals onto activated carbon. Water Science and Technology 63(3), 416-423.

Dodd, M.C., Buffle, M.-O., Von Gunten, U.J.E.s. and technology (2006) Oxidation of antibacterial molecules by aqueous ozone: moiety-specific reaction kinetics and application to ozone-based wastewater treatment. 40(6), 1969-1977.

Elshof, A. (2019) Engineering zeolite pellets for the adsorption of organic micropollutants.

Foster, M.D., Rivin, I., Treacy, M.M.J. and Delgado Friedrichs, O. (2006) A geometric solution to the largest-free-sphere problem in zeolite frameworks. Microporous and Mesoporous Materials 90(1), 32-38.

Freundlich, H.J.J.P.C. (1906) Over the adsorption in solution. 57(385471), 1100-1107.

Gabelica, Z., Nagy J, B., Derouane, E.G. and Gilson, J.P. (1984) The use of combined thermal analysis to study crystallization, pore structure, catalytic activity and deactivation of synthetic zeolites. Clay Minerals 19(5), 803-824.

Glassmeyer, S.T., Furlong, E.T., Kolpin, D.W., Cahill, J.D., Zaugg, S.D., Werner, S.L., Meyer, M.T. and Kryak, D.D. (2005) Transport of Chemical and Microbial Compounds from Known Wastewater Discharges: Potential for Use as Indicators of Human Fecal Contamination. Environmental Science & Technology 39(14), 5157-5169.

Gonzalez-Olmos, R., Kopinke, F.-D., Mackenzie, K. and Georgi, A. (2013) Hydrophobic Fe-Zeolites for Removal of MTBE from Water by Combination of Adsorption and Oxidation. Environmental Science & Technology 47(5), 2353-2360.

Grieco, S.A. and Ramarao, B.V. (2013) Removal of TCEP from aqueous solutions by adsorption with zeolites. Colloids and Surfaces A: Physicochemical and Engineering Aspects 434, 329-338.

He, M. (2019) On-site Regeneration of Acetaminophen Loaded Zeolite Granules by Applying Gaseous Ozone Based Oxidation Process.

Huber, M.M., Canonica, S., Park, G.-Y., Von Gunten, U.J.E.s. and technology (2003) Oxidation of pharmaceuticals during ozonation and advanced oxidation processes. 37(5), 1016-1024.

Hübner, U., Seiwert, B., Reemtsma, T. and Jekel, M. (2013) Ozonation products of carbamazepine and their removal from secondary effluents by soil aquifer treatment - Indications from column experiments. Water Research 49C, 34-43.

Hughes, J.S. and Trafimow, D. (2012) Inferences about character and motive influence intentionality attributions about side effects. British Journal of Social Psychology 51(4), 661-673.

Jiang, N., Shang, R., Heijman, S.G.J. and Rietveld, L.C. (2018) High-silica zeolites for adsorption of organic micro-pollutants in water treatment: A review. Water Res 144, 145-161.

Joss, A., Keller, E., Alder, A.C., Göbel, A., McArdell, C.S., Ternes, T. and Siegrist, H. (2005) Removal of pharmaceuticals and fragrances in biological wastewater treatment. Water Research 39(14), 3139-3152.

Kolpin, D.W., Furlong, E.T., Meyer, M.T., Thurman, E.M., Zaugg, S.D., Barber, L.B. and Buxton, H.T. (2002) Pharmaceuticals, Hormones, and Other Organic Wastewater Contaminants in U.S. Streams, 1999−2000: A National Reconnaissance. Environmental Science & Technology 36(6), 1202-1211.

Koryabkina, N., Bergendahl, J.A., Thompson, R.W. and Giaya, A. (2007) Adsorption of disinfection byproducts on hydrophobic zeolites with regeneration by advanced oxidation. Microporous and Mesoporous Materials 104(1), 77-82.

Laîné, J.-M., Campos, C., Baudin, I. and Janex, M.-L. (2003) Understanding membrane fouling: a review of over a decade of research. Water Supply 3(5-6), 155-164.

Legube, B., Guyon, S. and Doré, M. (1987) Ozonation of Aqueous Solutions of Nitrogen Heterocyclic Compounds : Benzotriazoles, Atrazine and Amitrole. Ozone: Science & Engineering 9(3), 233-246.

Li, G. and Pidko, E.A. (2019) The Nature and Catalytic Function of Cation Sites in Zeolites: a Computational Perspective. 11(1), 134-156.

Li, Y. and Yu, J. (2014) New Stories of Zeolite Structures: Their Descriptions, Determinations, Predictions, and Evaluations. Chemical Reviews 114(14), 7268-7316.

Logar, I., Brouwer, R., Maurer, M. and Ort, C. (2014) Cost-Benefit Analysis of the Swiss National Policy on Reducing Micropollutants in Treated Wastewater. Environmental Science & Technology 48(21), 12500-12508.

Loos, R., Carvalho, R., Comero, S., António, D.C., Ghiani, M., Lettieri, T., Locoro, G., Paracchini, B., Tavazzi, S. and Gawlik, B.M.J.P.O.o.t.E.U., Luxembourg (2012) EU wide monitoring survey on waste water treatment plant effluents.

Loos, R., Locoro, G., Comero, S., Contini, S., Schwesig, D., Werres, F., Balsaa, P., Gans, O., Weiss, S., Blaha, L., Bolchi, M. and Gawlik, B.M. (2010) Pan-European survey on the occurrence of selected polar organic persistent pollutants in ground water. Water Research 44(14), 4115-4126.

Martucci, A., Pasti, L., Marchetti, N., Cavazzini, A., Dondi, F. and Alberti, A. (2012) Adsorption of pharmaceuticals from aqueous solutions on synthetic zeolites. Microporous and Mesoporous Materials 148(1), 174-183.

Mawhinney, D.B., Vanderford, B.J., Snyder, S.A.J.E.s. and technology (2012) Transformation of 1 H-benzotriazole by ozone in aqueous solution. 46(13), 7102-7111.

McCusker, L.B. and Baerlocher, C. (2001) Studies in Surface Science and Catalysis. van Bekkum, H., Flanigen, E.M., Jacobs, P.A. and Jansen, J.C. (eds), pp. 37-67, Elsevier.

Mcdowell, D.C., Huber, M.M., Wagner, M., von Gunten, U., Ternes, T.A.J.E.s. and technology (2005) Ozonation of carbamazepine in drinking water: identification and kinetic study of major oxidation products. 39(20), 8014-8022.

Monneyron, P., Mathé, S., Manero, M.H. and Foussard, J.N. (2003) Regeneration of High Silica Zeolites via Advanced Oxidation Processes—A Preliminary Study About Adsorbent Reactivity Toward Ozone. Chemical Engineering Research and Design 81(9), 1193-1198.

Newsam, J.M. (1986) The Zeolite Cage Structure. Science 231(4742), 1093.

Olson, D.H., Haag, W.O. and Borghard, W.S. (2000) Use of water as a probe of zeolitic properties: interaction of water with HZSM-5. Microporous and Mesoporous Materials 35-36, 435-446.

Oturan, M.A., Aaron, J.-J.J.C.R.i.E.S. and Technology (2014) Advanced oxidation processes in water/wastewater treatment: principles and applications. A review. 44(23), 2577-2641.

Patel, S., Agarwal, R., Majumder, S.K., Das, P. and Ghosh, P. (2019) Kinetics of ozonation and mass transfer of pharmaceuticals degraded by ozone fine bubbles in a plant prototype. Heat and Mass Transfer.

Peters, T. (2010) Membrane Technology for Water Treatment. Chemical Engineering & Technology 33(8), 1233-1240.

Petrie, B., Barden, R. and Kasprzyk-Hordern, B.J.W.r. (2015) A review on emerging contaminants in wastewaters and the environment: current knowledge, understudied areas and recommendations for future monitoring. 72, 3-27.

Pimentel, D. (2009) Integrated pest management: innovation-development process, pp. 83-87, Springer.

Radjenovic, J., Godehardt, M., Hein, A., Farré, M., Jekel, M., Barceló, D.J.E.S. and Technology (2009) Evidencing generation of persistent ozonation products of antibiotics roxithromycin and trimethoprim. 43(17), 6808-6815.

Radjenović, J., Petrović, M. and Barceló, D. (2009) Fate and distribution of pharmaceuticals in wastewater and sewage sludge of the conventional activated sludge (CAS) and advanced membrane bioreactor (MBR) treatment. Water Research 43(3), 831-841.

Reemtsma, T., Weiss, S., Mueller, J., Petrovic, M., González, S., Barcelo, D., Ventura, F. and Knepper, T.P. (2006) Polar Pollutants Entry into the Water Cycle by Municipal Wastewater: A European Perspective. Environmental Science & Technology 40(17), 5451-5458.

Reungoat, J., Pic, J.S., Manéro, M.H. and Debellefontaine, H. (2007) Adsorption of Nitrobenzene from Water onto High Silica Zeolites and Regeneration by Ozone. Separation Science and Technology 42(7), 1447-1463.

Rodríguez, A., Rosal, R., Perdigón-Melón, J., Mezcua, M., Agüera, A., Hernando, M., Letón, P., Fernández-Alba, A. and García-Calvo, E. (2008) Emerging Contaminants from Industrial and Municipal Waste, pp. 127-175, Springer.

Sabio, E., González, E., González, J., González-García, C., Ramiro, A. and Ganan, J.J.C. (2004) Thermal regeneration of activated carbon saturated with p-nitrophenol. 42(11), 2285-2293.

Sacher, F., Lange, F.T., Brauch, H.J. and Vetter, I. (2002) Pharmaceuticals in groundwaters:: Analytical methods and results of a monitoring program in Baden-Württemberg, Germany. Journal of chromatography. A 938, 199-210.

Salvador, F., Martin-Sanchez, N., Sanchez-Hernandez, R., Sanchez-Montero, M.J. and Izquierdo, C. (2015a) Regeneration of carbonaceous adsorbents. Part I: Thermal Regeneration. Microporous and Mesoporous Materials 202, 259-276.

Salvador, F., Martin-Sanchez, N., Sanchez-Hernandez, R., Sanchez-Montero, M.J. and Izquierdo, C. (2015b) Regeneration of carbonaceous adsorbents. Part II: Chemical, Microbiological and Vacuum Regeneration. Microporous and Mesoporous Materials 202, 277-296.

San Miguel, G., Lambert, S. and Graham, N.J.D. (2001) The Regeneration of Field-Spent Granular Activated Carbons. Water Research 35, 2740-2748.

Sein, M.M., Zedda, M., Tuerk, J., Schmidt, T.C., Golloch, A. and von Sonntag, C. (2008) Oxidation of Diclofenac with Ozone in Aqueous Solution. Environmental Science & Technology 42(17), 6656-6662.

Sillanpää, M. and Bhatnagar, A. (2015) Natural Organic Matter in Water. Sillanpää, M. (ed), pp. 213-238, Butterworth-Heinemann.

Snyder, S.A., Lei, H. and Wert, E.C. (2007) Fate of pharmaceuticals in the environment and in water treatment systems, pp. 229-260, CRC Press.

Ternes, T.A., Stüber, J., Herrmann, N., McDowell, D., Ried, A., Kampmann, M. and Teiser, B. (2003) Ozonation: a tool for removal of pharmaceuticals, contrast media and musk fragrances from wastewater? Water Research 37(8), 1976-1982.

Von Gunten, U.J.W.r. (2003) Ozonation of drinking water: Part I. Oxidation kinetics and product formation. 37(7), 1443-1467.

Westerhoff, P., Yoon, Y., Snyder, S. and Wert, E. (2005) Fate of Endocrine-Disruptor, Pharmaceutical, and Personal Care Product Chemicals during Simulated Drinking Water Treatment Processes. Environmental Science & Technology 39(17), 6649-6663.

Zaitan, H., Manero, M.H. and Valdés, H.J.J.o.E.S. (2016) Application of high silica zeolite ZSM-5 in a hybrid treatment process based on sequential adsorption and ozonation for VOCs elimination. 41, 59-68.

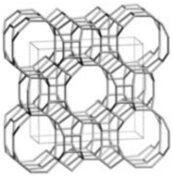
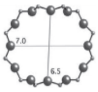
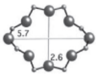
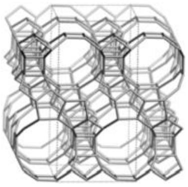
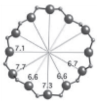
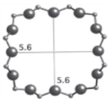
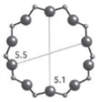
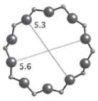
Zhang, Y., Mancke, R.G., Sabelfeld, M. and Geißen, S.-U. (2014) Adsorption of trichlorophenol on zeolite and adsorbent regeneration with ozone. Journal of Hazardous Materials 271, 178-184.

Zhang, Y., Prigent, B. and Geißen, S.-U. (2016) Adsorption and regenerative oxidation of trichlorophenol with synthetic zeolite: Ozone dosage and its influence on adsorption performance. Chemosphere 154, 132-137.

Chapter 8 Appendices

Appendix A: Properties of zeolites

Table A Common properties of MFI, MOR and BEA

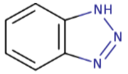
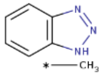
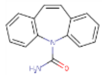
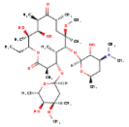
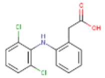
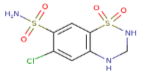
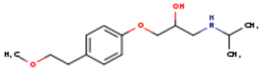
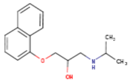
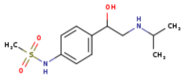
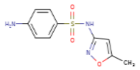
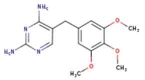
Framework type & Chemical formula	Framework structure [a]	Pore opening [a]	Ring number and pore opening size [a] (Å × Å)	Maximum diameter of a sphere can be included (Å) [b]	Framework density (T atoms $(/\text{Å}^3)$) [a]	Accessible area(m^2/g) [b]
MOR		 	12 rings 6.5×7.4 8 rings 2.6×5.7	6.70	17.2	1010.22
BEA		 	12 rings 6.6×6.7 12 rings 5.6×5.6	6.68	15.1	1220.45
MFI		 	10 rings 5.1×5.5 10 rings 5.3×5.6	6.36	17.9	834.41

[a] (Baerlocher et al. 2007)

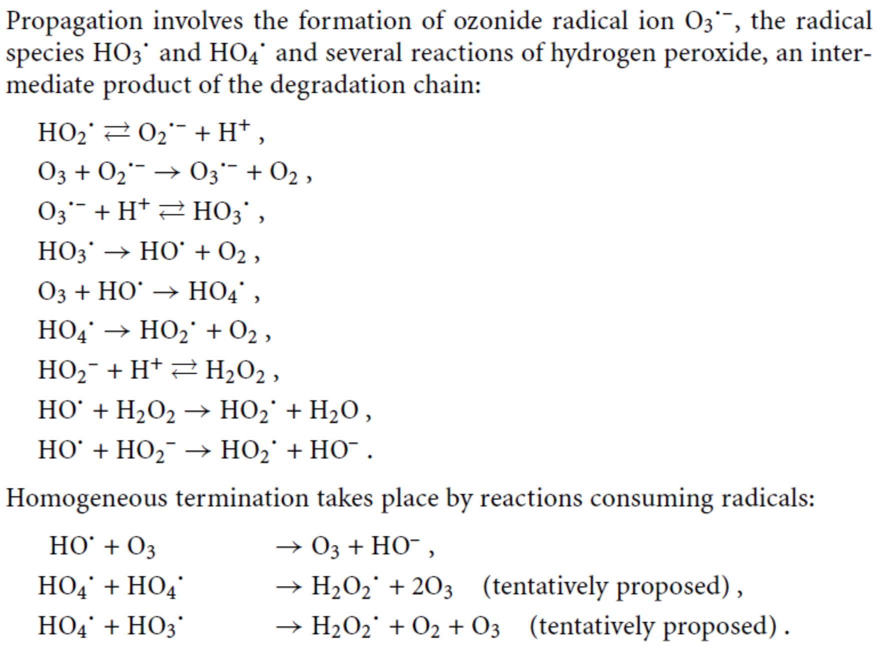
[b] (Foster et al. 2006)

Appendix B: Physicochemical characteristics of Target Organic Micropollutants

Table B Physicochemical characteristics of 11 target OMPs

Chemical name	Molecular formula	Structure	CAS	pKa (at 20 °C)	Charge (at pH=7)	Molecular weight (g/mol)	Water solubility (mg/L)	Thermal decomposition temperature (°C)	Application
Benzotriazole (BTA)	C6H4N3		95-14-7	8.37	+	119	1000-5000	>150°C	Corrosion inhibitors
Methyl-benzotriazole (MBTA)	C7H7N3		3048-48-4	8.85	+	134	1000-5000	N/A	Corrosion inhibitors
Carbamazepine (CBZ)	C15H12N2O		298-46-4	n/a	0	236	17.7	>260°C	Anti-epileptic
Clarithromycin (CLA)	C38H69NO13		81103-11-9	8.90	+	797	0.33	>296°C	Antibiotic (macrolide)
Diclofenac (DIC)	C14H10Cl2NNaO2		15307-86-5	4.15	-	296	2.37	>260°C	Analgesics/Anti-inflammatories
Hydrochlorothiazide (HCTZ)	C7H8ClN3O4S2		58-93-5	7.9	+/0	297	722	>260°C	Diuretics
Metoprolol (MP)	C15H25NO3		51384-51-1	9.49	+	267	4777	>150°C	Betablocker
Propranolol (PRO)	C16H21NO2		318-98-9	9.42	+	259	79.4	>250°C	Betablocker
Sotalol (SOT)	C12H20N2O3S		959-24-0	8.3	+	308	782	>135°C	Betablocker
Sulfamethoxazole (SMX)	C10H11N3O3S		723-46-6	5.70	-	253	500	>205°C	Antibiotic (Sulfonamide)
Trimethoprim (TMP)	C14H18N4O3		738-70-5	7.3	0	290	400	>240°C	Antibiotic (Sulfonamide)

Appendix C: Decomposition reactions of ozone in water



Propagation involves the formation of ozonide radical ion $O_3^{\bullet-}$, the radical species $HO_3^{\bullet}$ and $HO_4^{\bullet}$ and several reactions of hydrogen peroxide, an intermediate product of the degradation chain:

$HO_2^{\bullet} \rightleftarrows O_2^{\bullet-} + H^+$,
$O_3 + O_2^{\bullet-} \rightarrow O_3^{\bullet-} + O_2$,
$O_3^{\bullet-} + H^+ \rightleftarrows HO_3^{\bullet}$,
$HO_3^{\bullet} \rightarrow HO^{\bullet} + O_2$,
$O_3 + HO^{\bullet} \rightarrow HO_4^{\bullet}$,
$HO_4^{\bullet} \rightarrow HO_2^{\bullet} + O_2$,
$HO_2^- + H^+ \rightleftarrows H_2O_2$,
$HO^{\bullet} + H_2O_2 \rightarrow HO_2^{\bullet} + H_2O$,
$HO^{\bullet} + HO_2^- \rightarrow HO_2^{\bullet} + HO^-$.

Homogeneous termination takes place by reactions consuming radicals:

$HO^{\bullet} + O_3 \rightarrow O_3 + HO^-$,
$HO_4^{\bullet} + HO_4^{\bullet} \rightarrow H_2O_2^{\bullet} + 2O_3$ (tentatively proposed) ,
$HO_4^{\bullet} + HO_3^{\bullet} \rightarrow H_2O_2^{\bullet} + O_2 + O_3$ (tentatively proposed) .

Appendix D: Transformation pathway of target OMPs through ozonation

Benzotriazole

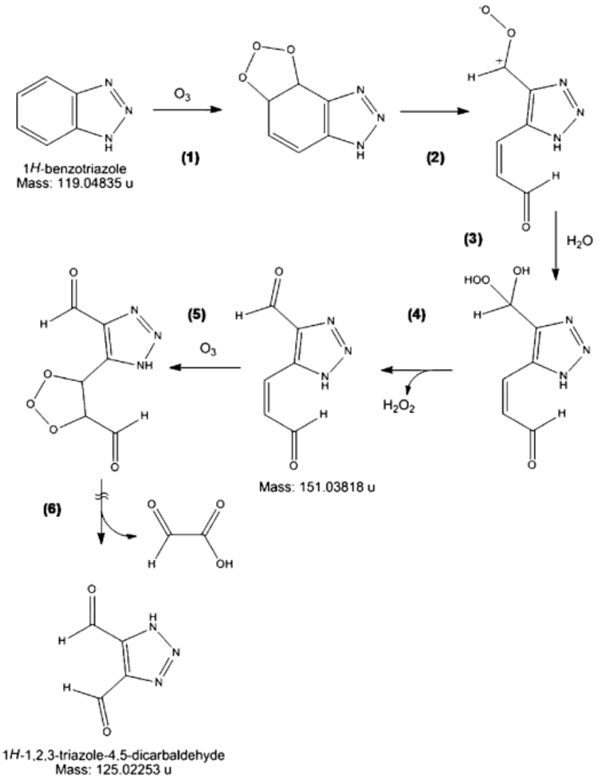


Figure D.1 Proposed ozonation pathway of benzotriazole (Mawhinney et al. 2012).

Hydrochlorothiazide

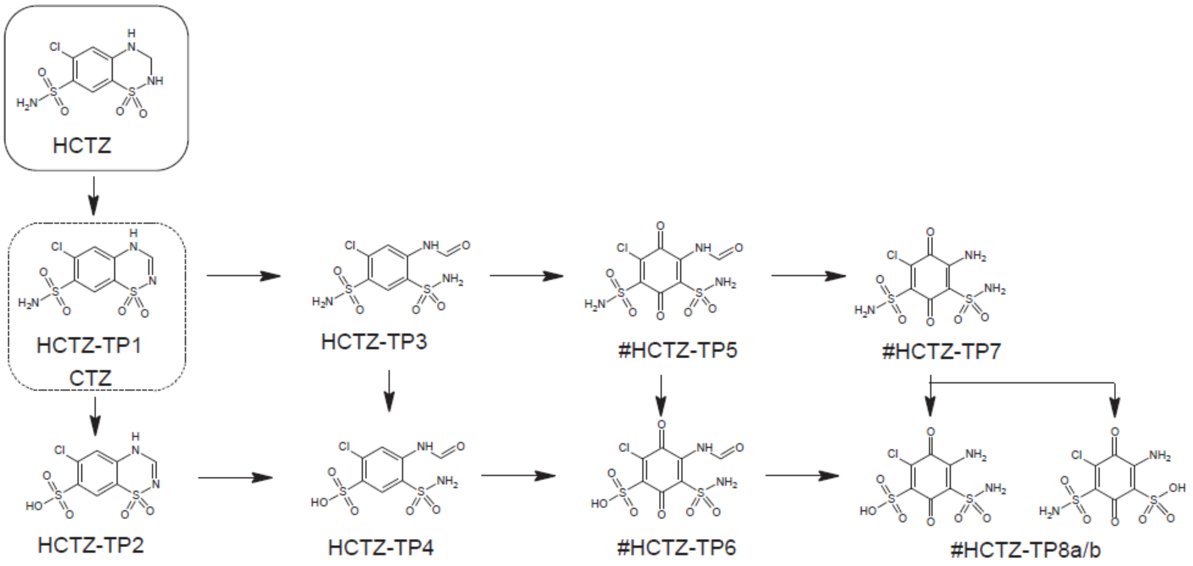


Figure D.2 Proposed ozonation pathway of hydrochlorothiazide (Borowska et al. 2016).

Carbamazepine

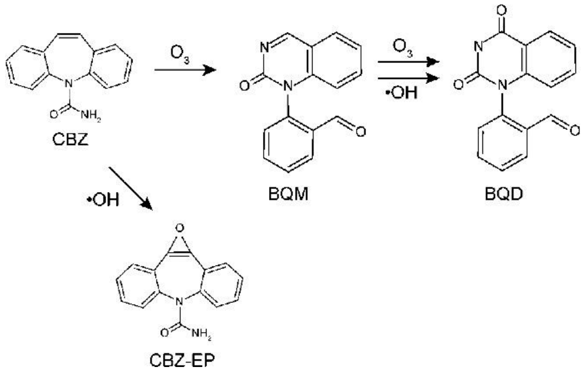
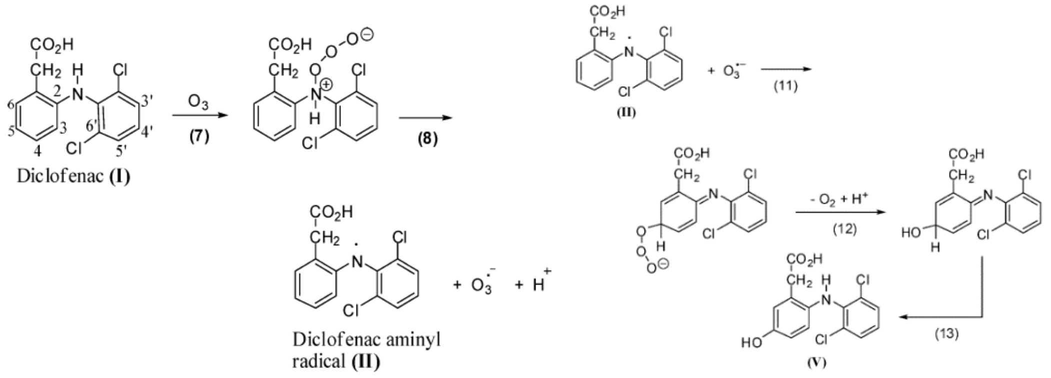


Figure D.3 Proposed transformation pathway of Carbamazepine by ozonation (Hübner et al. 2013).

Diclofenac



(a) (b)

Figure D.4 Proposed ozonation pathway of diclofenac, from (a) to (b) (Sein et al. 2008).

Sulfamethoxazole

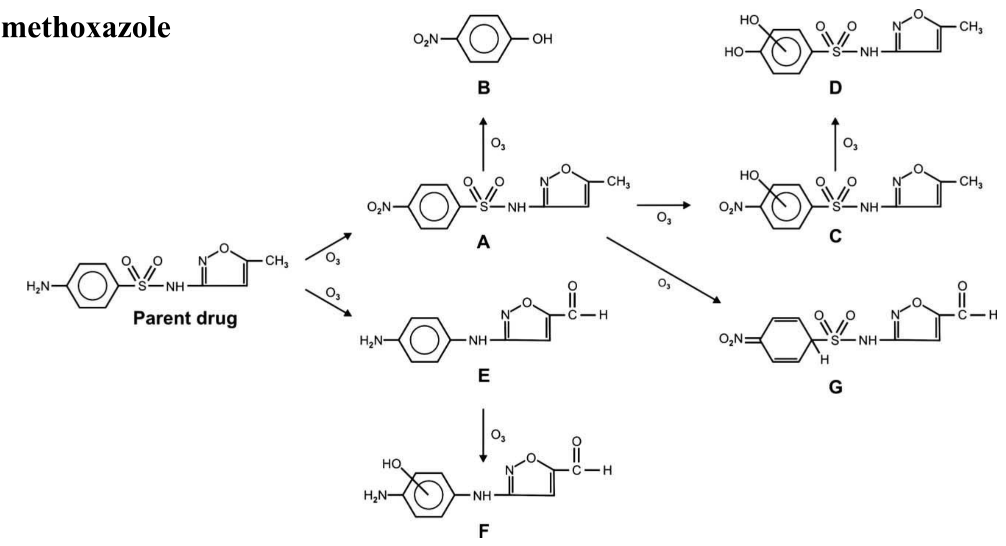


Figure D.5 Proposed ozonation pathway of sulfamethoxazole (Abellán et al. 2008)

Metoprolol

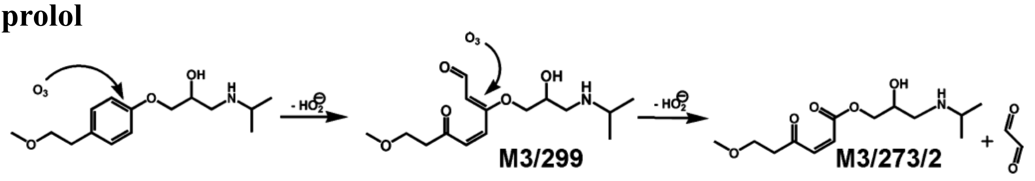


Figure D.6 Proposed Oxidation Reaction Pathway of Metoprolol (Benner et al. 2009).

Trimethoprim

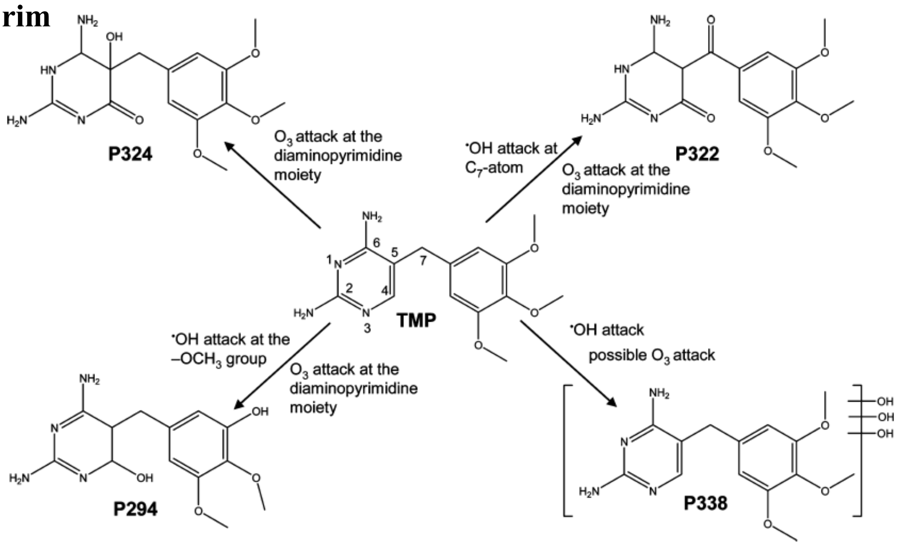


Figure D.7 Degradation mechanism of ozonation of trimethoprim (Radjenovic et al. 2009).

Propranolol

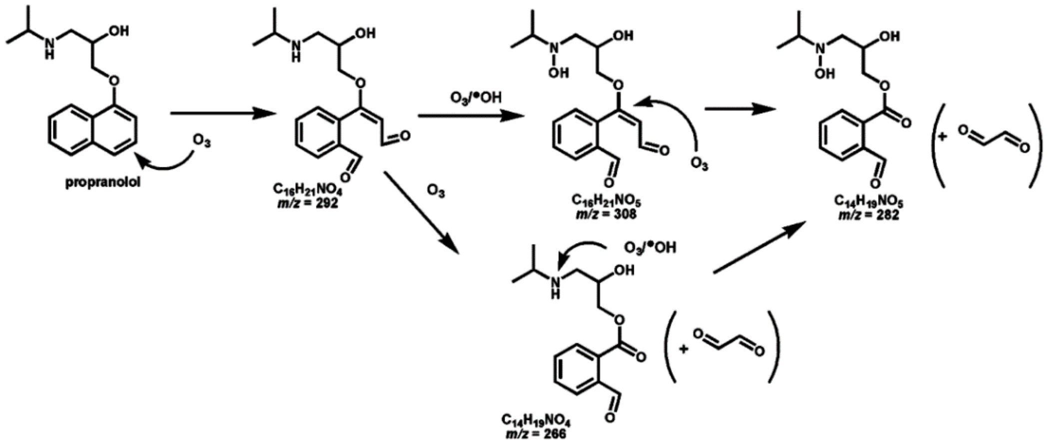
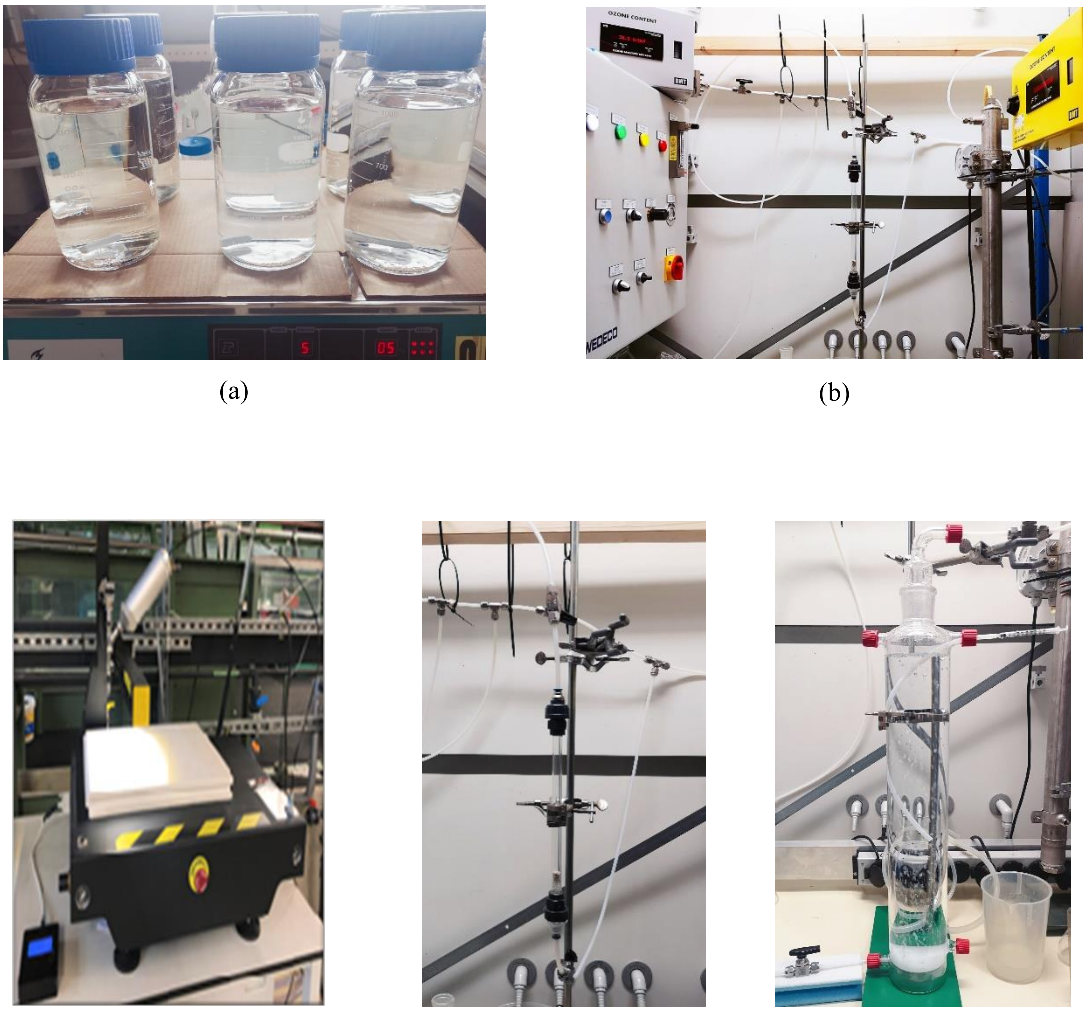


Figure D.8 Reaction scheme for the oxidation of propranolol (Benner 2009).

Appendix E: Experimental set-ups



(a) (b)

(c) (d) (e)

Figure E Experimental set-ups in laboratory: (a) adsorption batch experiments; (b) ozonation set-ups (c) 3D clay printer for granulation (d) small column for zeolite granules regeneration in the gas phase (e) ozone bubbling tank for ozonation in the water phase

Appendix F: Detection limits of OMPs in LC-MS Measurement

Table F LOQ (method detection limits) of target OMPs in LC-MS measurement

OMPs	LOQ (μgL^{-1})
Carbamazepine	0.1
Diclofenac	0.1
Benzotriazole	0.1
Methyl-benzotriazole	0.05
Hydrochlorothiazide	1
Sulfamethoxazole	0.5
Metoprolol	0.05
Sotalol	0.1
Trimethoprim	0.01
Propranolol	1
Clarithromycin	0.5

Appendix G: Supplementary results

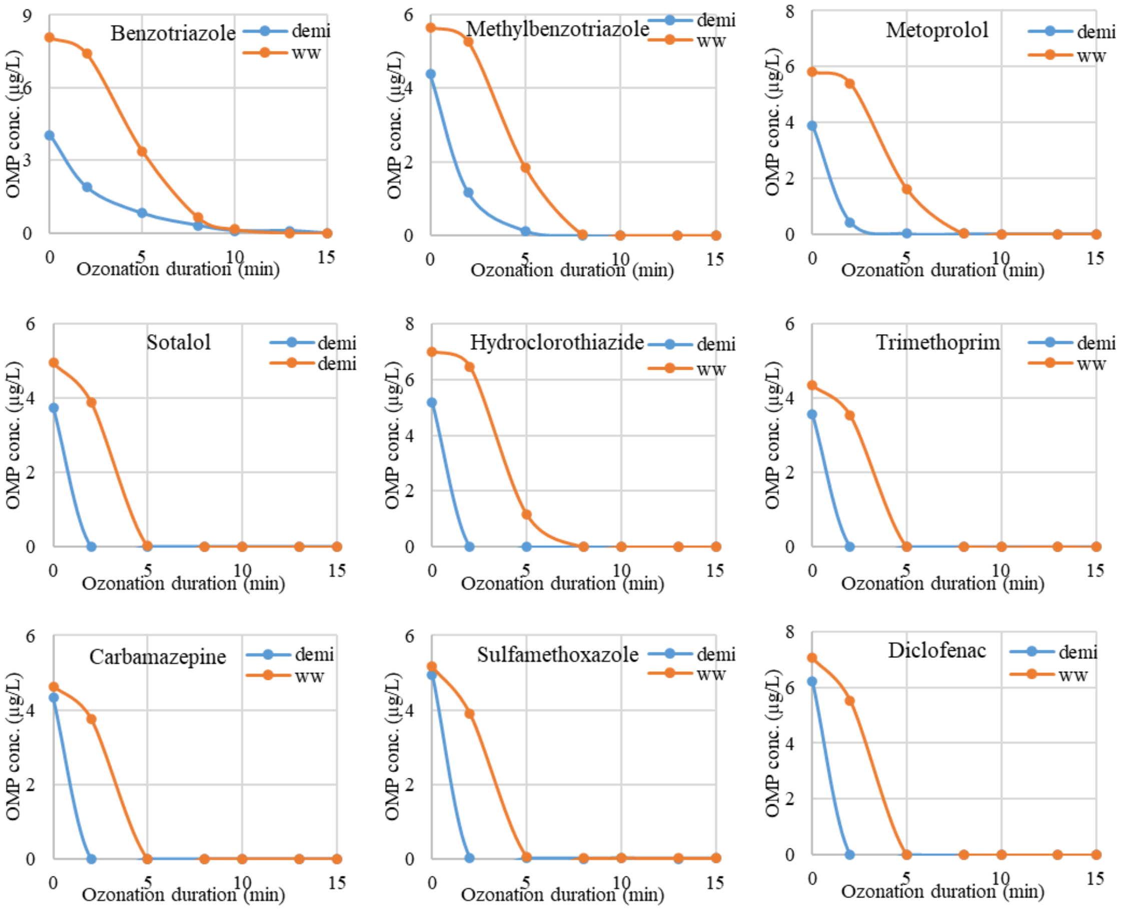


Figure G.1 OMP degradation over time in spiked-demieralised water and spiked-wastwater. (Ozone conditions: concentration = 30 mgL^{-1}; flow rate = 0.2 $Lmin^{-1}$; duration = 30min)

Table G.1 $gO_3/gDOC$ in wastewater ozone bubbling tests

Time(min)	gO3/gDOC
2	0.10
5	0.57
8	1.25
10	1.79

Table G.2 Specific calculation in ozone bubbling teste

$D_{O_3} = t \cdot C_{O_3} \cdot V_{O_3}$	$D_{\text{total } O_3}$	180mg
$D_{\text{dissolved } O_3} = D_{O_3} - V_{O_3} \int_0^t C_{O_3\text{\_outflow\_without OMP}} \, dt$	$D_{\text{dissolved } O_3}$	51.65mg
$D_{\text{reacted } O_3} + D_{\text{self-decomposed } O_3} = D_{O_3} - D_{\text{dissolved } O_3}$	$D_{\text{reacted } O_3} + D_{\text{self-decomposed } O_3}$ (in demi)	5.57mg
	$D_{\text{reacted } O_3} + D_{\text{self-decomposed } O_3}$ (in ww)	50.7 mg

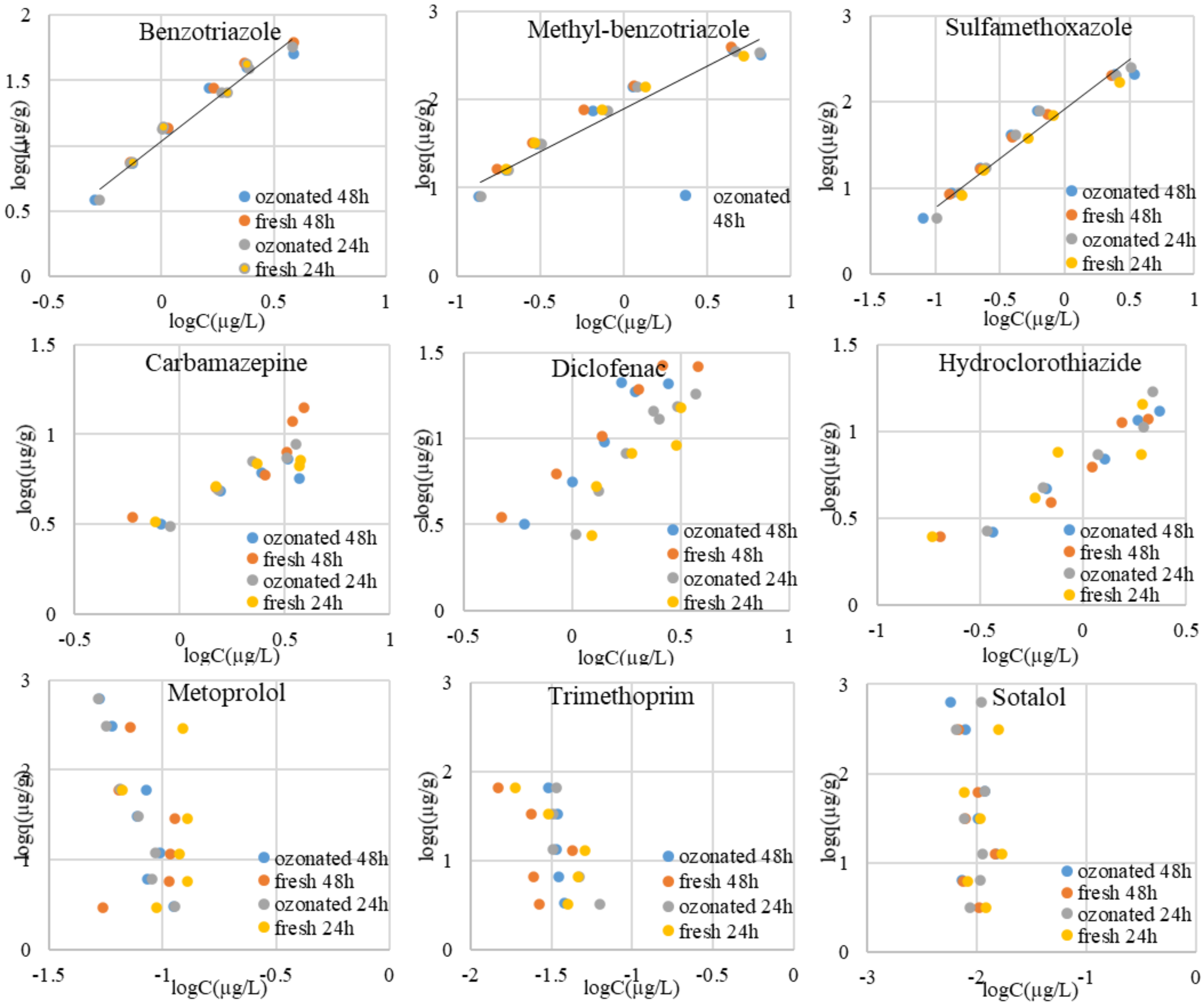


Figure G.2 24h and 48h adsorption isotherms of 9 OMPs over fresh and ozonated zeolite powders in spiked-deminerlised water. (OMP initial concentration was spiked at 4 µgL^{-1}; zeolite dosage is from 0 to 1000 mgL^{-1})

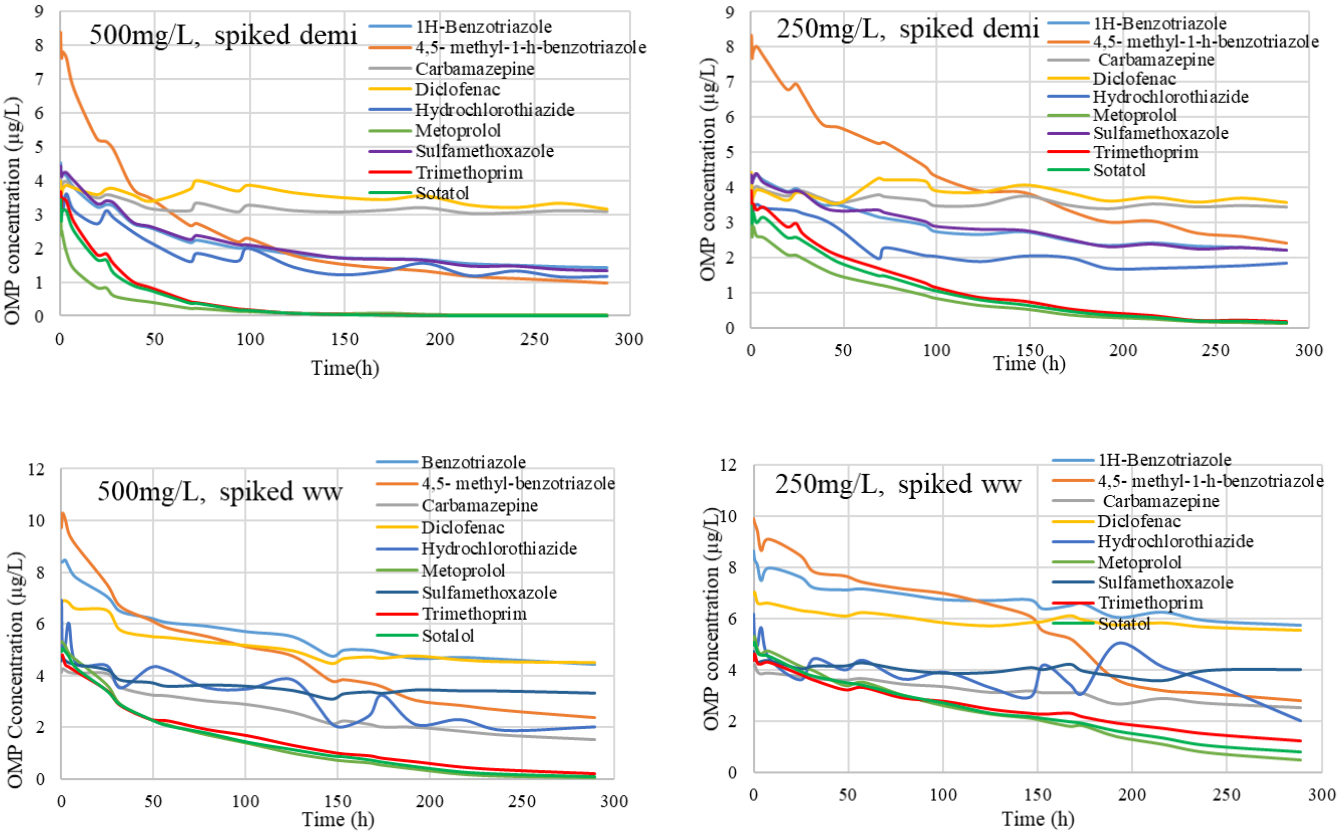


Figure G.3 The adsorption kinetics of 9 OMPs over mixed zeolite granules in spiked-demineralised water and spiked-wastewater (OMP initial concentration was spiked at 4 μgL^{-1}; zeolite dosage was 250 or 500 mgL^{-1})

Table G.3 Standard Deviations (*SD*) of regeneration duration determination experiments in triplication.

OMPs	without regeneration	5min	10min	20min	30min	45min	60min
Carbamazepine (CBZ)	0.095	0.077	0.085	0.025	0.144	0.067	0.082
Diclofenac (DIC)	0.116	0.029	0.025	0.107	0.121	0.124	0.016
Hydrochlorothiazide (HCTZ)	0.047	0.040	0.117	0.144	0.168	0.075	0.100
Benzotriazole (BTA)	0.145	0.021	0.144	0.055	0.073	0.083	0.145
Methyl-benzotriazole (MBTA)	0.238	0.067	0.019	0.234	0.068	0.007	0.039
Sulfamethoxazole (SMX)	0.171	0.010	0.035	0.001	0.049	0.036	0.150
Sotalol (SOT)	0.084	0.036	0.031	0.004	0.046	0.032	0.003
Metoprolol (MP)	0.051	0.010	0.040	0.009	0.071	0.015	0.044
Trimethoprim (TMP)	0.060	0.013	0.073	0.008	0.090	0.013	0.010

Table G.4 Relative Standard Deviations (*RSD*) of regeneration duration determination experiments in triplication.

OMPs	without regeneration	5min	10min	20min	30min	45min	60min
Carbamazepine (CBZ)	100%	16%	23%	10%	80%	15%	14%
Diclofenac (DIC)	53%	6%	3%	34%	45%	18%	2%
Hydrochlorothiazide (HCTZ)	48%	8%	3%	52%	6%	1%	3%
Benzotriazole (BTA)	6%	5%	15%	15%	19%	7%	10%
Methyl-benzotriazole (MBTA)	27%	3%	20%	7%	8%	8%	15%
Sulfamethoxazole (SMX)	9%	4%	4%	0%	4%	3%	0%
Sotalol (SOT)	6%	1%	7%	1%	8%	1%	1%
Metoprolol (MP)	17%	1%	4%	0%	5%	4%	13%
Trimethoprim (TMP)	6%	1%	4%	1%	7%	1%	5%

Table G.5 Relative Standard Deviations (*RSD*) of 4 cycles of adsorption-regeneration experiments in triplication

OMPs	1st	2nd	3rd	4th
Carbamazepine (CBZ)	23%	33%	66%	49%
Diclofenac (DIC)	70%	21%	34%	80%
Benzotriazole (BTA)	6%	10%	6%	3%
Methyl-benzotriazole (MBTA)	8%	9%	5%	4%
Sulfamethoxazole (SMX)	7%	13%	3%	1%
Sotalol (SOT)	3%	6%	1%	1%
Metoprolol (MP)	3%	5%	1%	1%
Trimethoprim (TMP)	4%	8%	1%	2%

Table G.5 Relative Standard Deviations (*RSD*) of 4 cycles of single adsorption experiments in triplication

OMPs	1st	2nd	3rd	4th
Carbamazepine (CBZ)	91%	100%	100%	72%
Diclofenac (DIC)	100%	100%	100%	93%
Benzotriazole (BTA)	24%	41%	16%	23%
Methyl-benzotriazole (MBTA)	27%	21%	16%	18%
Sulfamethoxazole (SMX)	11%	18%	9%	13%
Sotalol (SOT)	17%	4%	16%	15%
Metoprolol (MP)	18%	6%	18%	17%
Trimethoprim (TMP)	17%	6%	15%	19%

Appendix H: Cleaning procedures

The procedure of cleaning all glass, stirring bars and bottle caps involved in experiments:

1) Rinse with 0.1mg/L HCL solution to remove inorganic pollutants.
2) Rinse with Ethanol Absolute solution 2 times to remove organic pollutants.
3) Rinse with soapy water.
4) Rinse with demineralised water.
5) Place overhead in a large box which is covered with paper wipes for drying.