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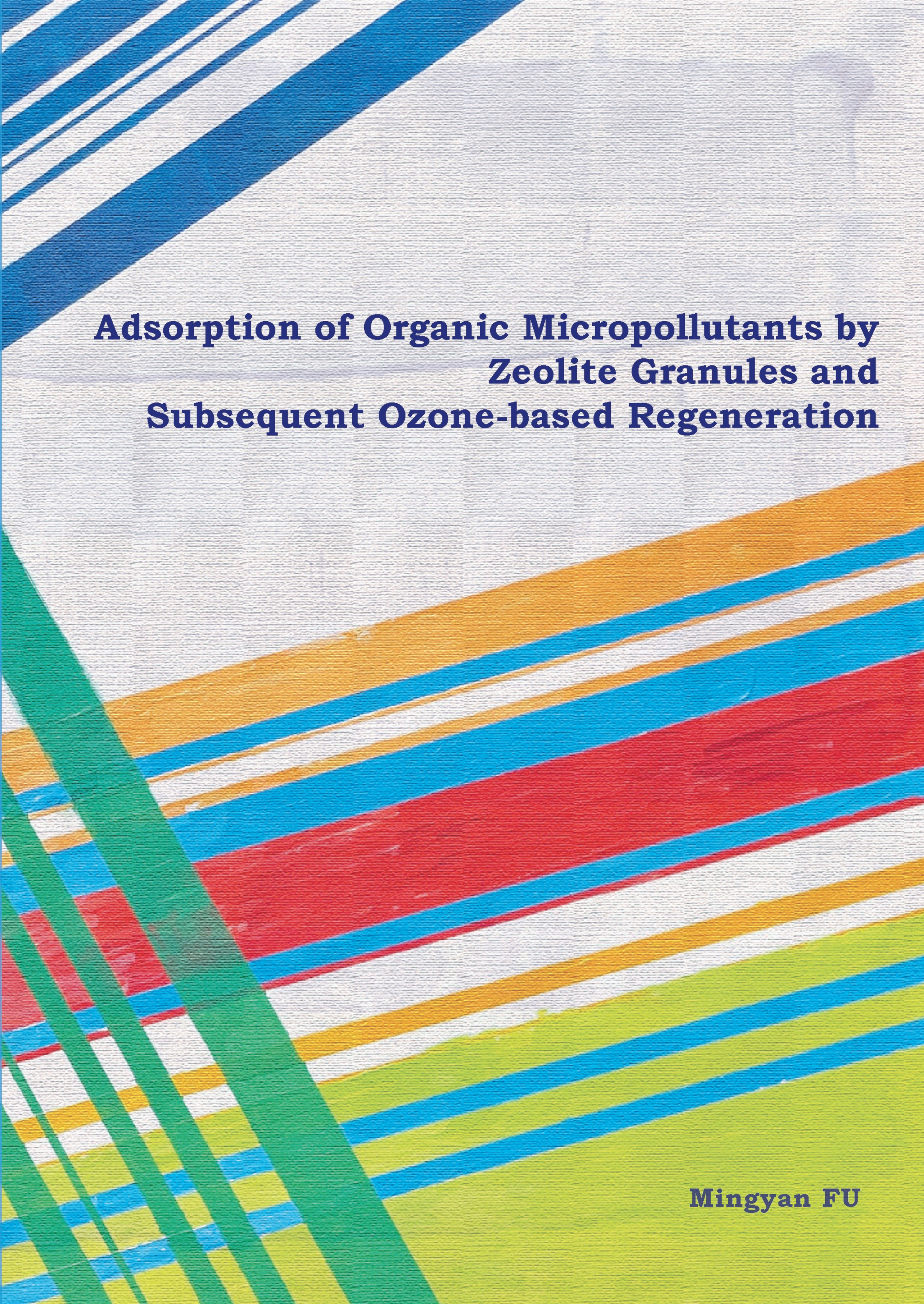

# Adsorption of Organic Micropollutants by Zeolite Granules and Subsequent Ozone-based Regeneration

**Mingyan FU**

# Adsorption of organic micropollutants by zeolite granules and subsequent ozone-based regeneration

## Dissertation

for the purpose of obtaining the degree of doctor
at Delft University of Technology
by the authority of the Rector Magnificus, prof.dr.ir. T.H.J.J. van der Hagen,
chair of the Board for Doctorates
to be defended publicly on

**Friday 12, May 2023 at 15:00 o'clock**

by

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This dissertation has been approved by the promotors.

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Acrylic paint on canvas
Mixed colours lines represent OMPs in water, Green lines represent zeolite adsorption, Dark blue lines represent ozone treatment

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# Contents

# Chapter 1

## Introduction

## 1. Research background

*Occurrence of organic micropollutants in the aquatic environment*

Organic micropollutants (OMPs) that occur in the aquatic environment at trace level, ranging from a few ng/L to several µg/L, adversely affect the health of aquatic organisms and human beings (Barbosa et al. 2016, Houtman et al. 2014, Luo et al. 2014, Pomies et al. 2013). The detection and analysis of OMPs in water bodies are challenging due to their low concentration (Luo et al. 2014). OMPs are natural and anthropogenic substances, including pharmaceuticals, industrial chemicals, personal care products, steroid hormones, surfactants, and pesticides. The representative sources and fate of OMPs are shown in Fig. 1 (Barbosa et al. 2016). Domestic wastewater is an important pathway of OMPs to water bodies. Compared to other sources and pathways, wastewater treatment plants (WWTPs) effluent is the leading cause of OMPs in surface water (Luo et al. 2014). After conventional wastewater treatment, OMPs can contaminate drinking water sources by ending up in surface water and groundwater. Then some OMPs can penetrate drinking water after drinking water treatment (Kotowska 2022). The present OMPs in surface water can be naturally attenuated, e.g. by river water dilution. The natural attenuation of OMPs is significantly affected by rainfalls in different seasons (Gómez et al. 2012). Nonsteroidal anti-inflammatory drugs (NSAIDs), carbamazepine, sulfamethoxazole and triclosan were the most frequently reported OMPs in surface water with trace concentrations at hundreds of ng per litre (Luo et al. 2014).

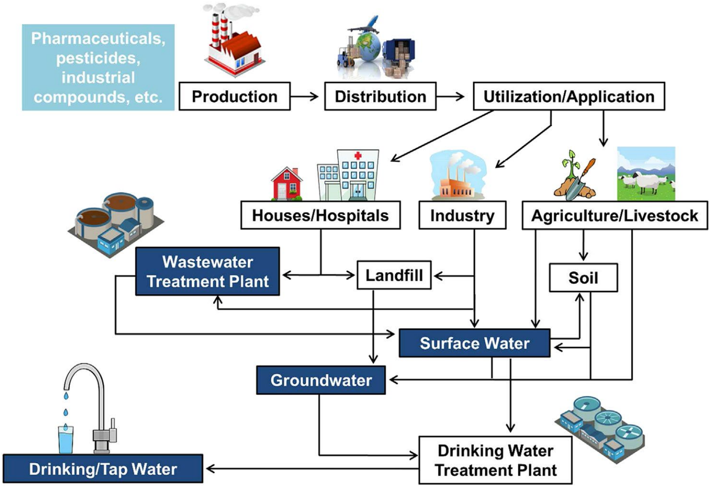


Fig.1. Sources and fate of OMPs in the environment (Barbosa et al. 2016)

*Current technologies to remove OMPs in WWTPs*

Wastewater treatment technologies used in conventional WWTPs have achieved favourable carbon, nitrogen, and phosphorous removal efficiencies. Various substances, including particulates, carbonaceous, nutrients, and pathogens, can be eliminated efficiently and consistently (Luo et al. 2014). Unfortunately, conventional WWTPs are not designed for removing OMPs (Rout et al. 2020), and the average removal efficiency ranges from 30% to 65% (Bolong et al. 2009). Hence, most OMPs pass through this barrier and can be continuously released into the surface water, increasing the eco-toxicity of the aquatic environment. The current wastewater treatment options for removing OMPs include adsorption by activated carbon, ozonation, and membrane filtration.

Activated carbon (both powdered activated carbon (PAC) and granular activated carbon (GAC)) can effectively adsorb a broad range of OMPs from water (Jiang et al. 2018). Adding PAC in post-treatment configurations or the activated sludge system is a significant application of PAC in the full-scale municipal WWTPs with efficient OMPs removal of more than 80% (Boehler et al. 2012, Luo et al. 2014). Directly dosing PAC in the activated sludge system of Papendrecht WWTP (the Netherlands) enhanced the removal of OMPs by 100%, and the ecotoxicity of the WWTP effluent was reduced by 50% (Mulder et al. 2019). Applying GAC in a post-treatment filter can ensure the adsorption of OMPs the same as with PAC, and the growth of bacteria on granules can enhance the removal of nutrients (Mulder et al. 2019). The exhausted GAC has to be off-site regenerated by thermal treatment, resulting in high operational costs and an environmental burden (high energy consumption and $CO_2$ emission) (Larasati et al. 2022). The replacement of the carbon loss in regeneration further increases the operational costs. Moreover, the adsorption of OMPs on activated carbon can be significantly reduced by the presence of natural organic matter (NOM), which can compete with OMPs for adsorption sites and block the pores of activated carbon (Loganathan et al. 2022).

Ozonation is a promising technology to considerably reduce the OMP load in WWTPs effluents, with removal efficiencies above 90% for almost all OMPs (Rout et al. 2020). Ozone can directly degrade OMPs by ozone molecules and indirectly degrade OMPs by generating hydroxyl radicals. For the OMPs resistant to ozone molecules, applying $H_2O_2$, Fenton reagent, and ultraviolet (UV) radiation can promote the formation of hydroxyl radicals. One critical issue with ozonation is that NOM fractions in wastewater can compete with OMPs to severely reduce the ozonation effectiveness (Gardoni et al. 2012). The NOM can also significantly interfere with ozone decomposition, resulting in low mineralization efficiency of OMPs (Barbosa et al. 2016). Another critical issue with ozonation is the formation of ozonation transformation products, which are generated in the incomplete mineralization of OMPs, and ozonation by-products, such as bromate converted from bromide during ozonation. Subsequent biological treatment, such as sand and GAC filtration, is necessary to remove the ozonation transformation products, reducing the ecotoxicity of the ozone-treated water (Knopp et al. 2016). However, sand filters cannot remove bromate (Zimmermann et al. 2011). Kirisits et al. (Kirisits et al. 2000) reported that the adsorption of bromate by GAC was hindered by NOM and other anions in ozone-treated water.

Membrane filtration can remove OMPs by size exclusion, adsorption onto the membrane, and charge repulsion. Many factors influence this process, including membrane process type, membrane characteristics (such as hydrophobicity), operation conditions, specific OMP characteristics and membrane fouling (Schäfer et al. 2011). Microfiltration (MF) and ultrafiltration (UF) combined with activated sludge biological treatment are widely applied as membrane reactors to treat OMPs in conventional WWTPs (Luo et al. 2014). Although the MF and UF membrane pore size is larger than the molecular size of OMPs, many OMPs can still be removed via adsorption onto the membrane by interacting with NOM (Jermann et al. 2009). However, the removal of some OMPs is limited (24-68%), including amitriptyline, carbamazepine, diazepam, fluoxetine, gemfibrozil, trimethoprim, sulfamethoxazole, diclofenac, and omeprazole (Trinh et al. 2012). Nanofiltration (NF) and reverse osmosis (RO) can partially or significantly remove most OMPs but are not an absolute barrier for OMPs, such as ibuprofen and diclofenac (Sahar et al. 2011). Complementary treatment should be considered to ensure the complete removal of some specific OMPs. Moreover, as a separation process, membrane filtration cannot degrade OMPs. After membrane filtration, the concentrated OMPs in the retentate need further treatment.

*Adsorption of OMPs on zeolite granules and oxidative regeneration*

Integrated different treatment technologies are promising to achieve efficient removal of OMPs by bridging the limitations of individually applying one technology (Rout et al. 2020). The *AdOx* technology was proposed in this context: selective adsorption of OMPs from municipal wastewater on zeolite granules and ozone-based regeneration.

In the *AdOx* technology, zeolites are selected and applied as an alternative adsorbent for activated carbon. Zeolites are porous crystalline aluminosilicates with uniform pore sizes (0.6-1.0 nm), which are smaller than the size of big NOM molecules(> 1 nm), mostly biopolymers, humic acids and building blocks. Therefore, the unique structure of zeolite can cause effective adsorption of OMPs and promisingly reduce the influence of NOM as the molecules of NOM are too large to enter the zeolite pores (Jiang 2019). In other words, NOM will not be adsorbed on zeolite. Powdered zeolites should be applied in granular form packed in fixed-bed columns for real applications, as the additional separation of powders from the treated water is problematic and costly from the engineering perspective (Bhargava et al. 2004). Several types of zeolite powders with uniform pores that nicely match the molecules of OMPs can be engineered in granular form to remove a broad range of OMPs.

Adsorbents saturated with OMPs must be regenerated to recover the adsorption capacity by integrating with oxidative treatment technology. Reusing adsorbents with effective regeneration has many advantages, such as low operational costs and no secondary environmental problems caused by the direct disposal of adsorbents. During oxidative regeneration, the adsorbed OMPs can be degraded into harmless substances. As zeolites are thermally stable at high temperatures (Zaitan et al. 2016), exhausted zeolite granules can be regenerated by various oxidative treatments, including thermal and chemical oxidation treatments. Thermal treatment is often used for regenerating exhausted activated carbon, which is operated at high temperatures to volatilize and oxidize the adsorbed OMPs (San Miguel et al. 2001). Chemical oxidation treatment applies ozonation and advanced oxidation processes (AOPs) to degrade the adsorbed OMPs. AOPs based on Fenton reactions and UV radiation are commonly applied. Chemical oxidation has the potential to regenerate the exhausted adsorbents on-site with low energy use compared to thermal treatment and no loss of material.

The *AdOx* technology applies ozonation to on-site regenerate the OMPs-loaded zeolite granules. On-site regeneration can minimize operational costs by preventing the transportation of exhausted adsorbents to the factory for thermal treatment and can reduce carbon dioxide emissions. On-site regeneration can also lead to an innovative treatment concept that is small in size. Small reactors can be applied due to the short adsorption contact time, and regeneration processes can frequently be conducted due to on-site ozone generation. As ozone is not dosed continuously to water but only applied during regeneration in a side stream, ozone dosage is potentially much less than that applied in single ozonation for wastewater treatment. The dosed ozone is only used to decompose the OMPs adsorbed on zeolite. As NOM is probably not adsorbed on zeolite, no NOM will further consume ozone during regeneration. In addition, regarding the ozonation by-products, no bromate can be expected to form in this technology because ozone is not dosed in the full stream, and zeolite does not adsorb bromide. Hence, the WWTP effluent is free of bromate.

## 2. Research outline

### *2.1 Research objective*

The *AdOx* technology aims to realize an innovative adsorption–oxidation process for OMPs removal from municipal wastewater. This integrated technology, adsorption followed by ozonation, can lead to the next generation of OMPs removal, characterized by high removal efficiencies, low costs, and low environmental impacts.

The current dissertation aims to prove two aspects. One is that the zeolite granules, containing zeolites with different pore structures, can effectively adsorb various OMPs from water. The other is that ozonation treatment can effectively regenerate zeolite granules loaded with OMPs. The current dissertation also aims to prove that this technology has the potential to be operated on a larger scale to treat real wastewater.

### *2.2 Knowledge gaps*

Based on the literature review (**Chapter 2**), the knowledge gaps were determined as follows:

a. The evaluation of the potential for various oxidative methods to degrade OMPs in the presence of zeolite granules for practical application is missing.

b. The performance of ozone-based regeneration of zeolite granules loaded with OMPs is unclear. The oxidation efficiency of OMPs adsorbed on zeolites by gaseous ozone is not known.

c. The long-term operational performance of this integrated technology to achieve an efficient on-site regeneration of OMPs-loaded zeolite granules has not been reported.

d. The effectiveness of applying this technology for treating real wastewater is not known, including the average OMPs removal percentage and the operational stability.

### *2.2 Research framework*

According to the knowledge gaps, the research questions (RQ) were formulated.

*RQ 1. What is the current knowledge about different oxidative technologies that can be applied to regenerate granular zeolites loaded with OMPs?*

**Chapter 2** comprehensively reviews different oxidative technologies to degrade OMPs in the presence of zeolite granules. The review further discusses the feasibility of applying each oxidative technology to regenerate zeolite granules. The potential of each oxidative technology for real applications is discussed.

*RQ 2. Is ozone-based regeneration efficient for regenerating zeolite granules loaded with a single OMP?*

**Chapter 3** applies acetaminophen, an organic compound that can be readily adsorbed by zeolite and easily oxidized by ozone, in demi-water for lab-scale experiments. The influence of the water content in granules on the ozonation efficiency is studied. Different ozonation conditions are applied, including ozone gas flow rate, ozone concentration, and ozonation duration. The influence of ozonation transformation products on the adsorption performance is discussed.

*RQ 3. How does the ozone-based regeneration perform with zeolite granules loaded with various OMPs?*

In **Chapter 4**, homogenous granulation by a 3D clay printer is applied. Different zeolites are added in granules for adsorbing a broad range of OMPs. The adsorption isotherms and kinetics tests are carried out in demi-water. Degradation of OMPs adsorbed on granules is achieved by flowing ozone gas into a column packed with dried granules. Seven sequential adsorption-regeneration cycles are operated to investigate the long-term performance.

*RQ 4. What is the performance of this combined technology in treating real wastewater?*

**Chapter 5** studies the performance of this combined technology to treat real wastewater spiked with eleven OMPs. Secondary effluent from WWTP Horstermeer (the Netherlands) is applied for lab-scale experiments. The technology comprises five steps: 1) selective adsorption of OMPs from wastewater in five days by a column packed with zeolite granules, 2) backwash of the column, 3) drying of the column, 4) *in-situ* regeneration of the column with gaseous ozone, 5) post-backwash of the column. The long-term tests are performed for six sequential adsorption-regeneration cycles. The influence of the cations and dissolved organic matter on the adsorption is discussed. In addition, the importance of backwash is also discussed.

**Chapter 6** gives the overall conclusions and the outlook for up-scaling tests.

# Chapter 2

## Degradation of organic micropollutants adsorbed on zeolite granules: A review

This chapter is in preparation for publication

M. Fu, B. Heijman, J.P. van der Hoek, Degradation of organic micropollutants adsorbed on zeolite granules: A review.

## Abstract

Organic micropollutants (OMPs) that occur in the aquatic environment at trace levels can cause adverse ecological effects. Significant removal of OMPs from waste streams (gasses and liquids) by advanced treatment technologies is still challenging. Integrating the adsorption of OMPs on zeolites and oxidative treatment for degrading the adsorbed OMPs is promising for efficiently removing OMPs from waste streams. This review comprehensively summarises various oxidative treatment technologies applied for degrading OMPs adsorbed on granular zeolites. The oxidative treatment technologies include thermal and chemical oxidation treatment (ozonation and advanced oxidation processes (AOPs)). AOPs based on Fenton reactions and UV radiation are commonly applied. Results of this review indicate that all the oxidative treatments combined with the adsorption of OMPs on zeolite granules can significantly remove OMPs from water and air. However, the high operational costs of thermal treatment and the radical diffusion problems of AOPs might restrict their potential for real applications. In contrast, ozonation applied in the gas phase to regenerate the exhausted zeolite granules packed column is promising for real applications. However, further research is still needed for up-scaling this process.

## 1. Introduction

The effluent of municipal wastewater treatment plants (WWTPs) is an important way of introducing organic micropollutants (OMPs) to surface water (Luo et al. 2014, Pomies et al. 2013). After conventional wastewater treatment, OMPs may end up in the aquatic environment, such as surface water and groundwater, penetrating the drinking water (Kotowska 2022). Although the OMPs concentrations range from a few ng/L to several μg/L, their presence negatively impacts water quality (Barbosa et al. 2016, Luo et al. 2014). OMPs consist of volatile organic compounds (VOCs) and other micropollutants, including natural and anthropogenic substances, which are pharmaceuticals, industrial chemicals, personal care products, steroid hormones, surfactants, and pesticides (Kotowska 2022, Luo et al. 2014). In the last decade, numerous authors have reviewed the occurrence of OMPs and their removal methods (Barbosa et al. 2016, Bolong et al. 2009, Kotowska 2022, Luo et al. 2014, Mompelat et al. 2009, Pomies et al. 2013, Tijani et al. 2013).

Conventional treatment consisting of a primary settling followed by anoxic and aerated tanks and a secondary clarifier cannot remove dissolved small organics (Bolong et al. 2009, Tijani et al. 2013). Most OMPs pass through the barrier and are continuously released into the surface water, increasing the potential of an ecotoxic effect on the aquatic environment (Pomies et al. 2013). The advanced treatment options for removing

OMPs from water and air include physical separation, chemical oxidation, and biodegradation (Luo et al. 2014). As OMPs possess diverse properties and low concentrations, applying a single treatment to achieve effective OMP removal is quite challenging. Therefore, integrated technologies should be applied to bridge the limitation of individual treatment, leading to the effective removal of all OMPs (Rout et al. 2020).

Adsorption of OMPs by activated carbon is a well-known separation process with low initial cost, high flexibility and simplicity of design, and ease of operation (Ahmaruzzaman 2008). As a separation process, adsorption cannot degrade OMPs to harmless substances. The adsorbent needs to be regenerated after a certain operational period. The following thermal treatment of exhausted activated carbon can cause a significant loss of the adsorbent, increasing operational costs. Exhausted granular activated carbon reactivation also has a high environmental impact (Mohapatra et al. 2002). Zeolites have been reported as an alternative adsorbent for OMP removal from water and air (Jiang et al. 2018). Zeolites are porous crystalline aluminosilicates with various frameworks formed by $SiO_4$ and $AlO_4$ tetrahedrons, joined together in various regular arrangements through shared oxygen atoms. The open crystal lattices in zeolites provide a uniform pore size, which makes zeolites different from activated carbon. The intracrystalline channel structure determines the intracrystalline diffusivity of the target OMP molecules. In addition, zeolites are hydrophilic but turn hydrophobic when the Si/Al molar ratio reaches 8 or 10 (Ruthven 1984). Zeolites with high Si/Al molar ratios are called high silica zeolites with high adsorption capacities of OMPs (Jiang et al. 2018, Koubaissy 2008).

Powdered adsorbents are technologically impracticable in continuous treatment processes for removing OMPs from water and air (Monneyron et al. 2003a, Sacco et al. 2018). Especially in the water-phase application, the additional separation process of removing powdered material from the treated water is difficult from the process-engineering perspective and is costly (Bhargava et al. 2004). Thus, zeolites should be applied in granular form. Various adsorption processes are applied based on the contact between adsorbents and contaminants in the adsorption system (Patel 2019). The adsorption processes include batch, continuous moving bed, continuous fixed bed (upflow or downflow), continuous fluidized bed, and pulsed bed. Among all techniques, the fixed-bed column is the most used and industrially feasible for removing various contaminants (Patel 2019). In fixed-bed adsorption, the waste stream to be treated continuously flows through a bed of adsorbents at a constant rate. The fixed-bed system is widely used for industrial purposes to treat high quantities of waste streams (Patel 2019). The separation problem of powdered zeolites can be avoided using granular zeolites in fixed-bed adsorption.

The exhausted adsorbent in the fixed-bed column must be replaced or regenerated. Reusing zeolite granules after effective regeneration can avoid high operational costs due to the one-time use of adsorbents and secondary environmental problems due to the disposal of contaminated adsorbents (Fu et al. 2021a). Integrating adsorption by zeolites and other advanced treatment processes to degrade OMPs is feasible because zeolites are thermally stable and safe to use in oxidation processes operating at high temperatures (Zaitan et al. 2016). The adsorption capacity of zeolites can be recovered by degrading the adsorbed OMPs using thermal and chemical oxidation. Thermal treatment is usually operated off-site. The adsorbed OMPs are volatilized and oxidized by heating at high temperatures (San Miguel et al. 2001). Chemical oxidation treatment includes ozonation and advanced oxidation processes (AOPs). AOPs based on Fenton reactions and UV radiation are commonly applied. Heterogeneous catalytic reactions often occur as the catalysts used in AOPs are usually in a different phase from the reactants. Several heterogeneous catalytic reactors include fixed bed reactors, tubular catalytic wall reactors, and fluidized bed reactors (Klaewkla et al. 2011). The fixed-bed adsorption column can be used as a fixed-bed reactor with a continuous gas or liquid phase flowing through a packed bed of catalysts. The fixed-bed column allows operating chemical oxidation on-site.

The current paper reviews the literature concerning the oxidative degradation of OMPs adsorbed to zeolites. Different oxidative treatment processes are shown in Fig. 1. The chemical background of different oxidative treatments is introduced. The mechanisms behind different oxidative treatments for degrading OMPs adsorbed on zeolite granules are explained. The potential knowledge gaps and drawbacks in each oxidative treatment are identified. The potential for each oxidative treatment in real future applications is discussed.

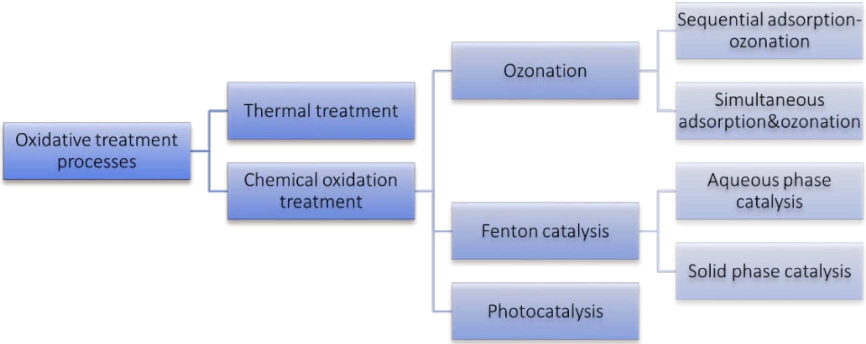


Fig. 1. Oxidative treatment processes for degrading OMPs adsorbed on zeolite granules

## 2. Thermal treatment

Thermal treatment is the most commonly practised technique for the regeneration of granular activated carbon (GAC) after saturation with organic contaminants (Guo and Du 2012, Jiang et al. 2018, Ledesma et al. 2014, Marques et al. 2017, San Miguel et al. 2001). The thermal treatment of GAC involves the pyrolytic and oxidative stages (San Miguel et al. 2001). At the pyrolytic stage, the exhausted GAC is exposed to temperatures up to 800 °C under inert conditions. At this stage, volatile organic compounds are eliminated from the pores, and less-volatile compounds are decomposed into carbonised residues which occupy some pores. The oxidative stage is a controlled gasification process of the pyrolysed carbon. At the temperature of 800 °C, carbonised residues are eliminated in a mildly oxidising atmosphere containing steam. The extent of carbon gasification determines the recovery of GAC characteristics. Process temperature and reaction time are essential parameters to be adjusted to control the extent of carbon gasification.

As synthetic zeolites remain stable during calcination at temperatures of 700 – 800 °C (Fernández-Reyes et al. 2021), thermal treatment is also a technique for regenerating zeolites. Wang et al. (Wang et al. 2006) reported the regeneration of zeolite MCM-22 after the adsorption of a basic dye, methylene blue, by high-temperature treatment. The regeneration experiments were conducted in a furnace with air. The exhausted zeolites were reactivated with a heating rate of 5 °C/min starting from room temperature to burn off the adsorbed organics. The recovery efficiency of thermal regeneration was influenced by temperature and time. High temperature and extended treatment time might cause pore collapse and result in adsorption capacity loss. The optimal temperature and time were 540 °C and 1 h, suggesting a complete recovery of the adsorption capacity.

Natural zeolites were also used for the adsorption of organics from water. Wang et al. (Wang and Zhu 2006) studied the performance of an Australian natural zeolite for the removal of basic dye from aqueous solutions. Natural zeolite loaded with dyes was regenerated at a temperature of 550 °C for 5 h. Only 60% of the adsorption capacity was recovered. High-temperature calcination can decompose the organic dyes both adsorbed on the surface and in pores to carbon oxides. However, the high temperature might change the surface functional groups and the pore structure of natural zeolites, decreasing surface area and pore volume. Thus the adsorption capacity was reduced.

Moreover, off-site thermal regeneration of exhausted adsorbents results in high operational costs, including transportation and replacement, and an environmental burden (high energy consumption and $CO_2$ emission) (Gonzalez-Olmos et al. 2013, Larasati et al. 2022, Matheickal et al. 1998).

## 3. Chemical oxidation treatment

As an alternative approach, chemical oxidation can on-site restore the adsorption capacity of zeolites by oxidizing the adsorbed organic contaminants. By sequentially or simultaneously applying adsorption and chemical oxidation, OMPs can be removed from water and air and degraded into small organic groups or fully mineralized into inorganic substances. In the field of chemical oxidation, ozonation and advanced oxidation processes (AOPs) are widely investigated for wastewater treatment (Rivera-Utrilla et al. 2013). Ozonation has two reaction mechanisms: direct ozonation by ozone molecules and advanced oxidation by hydroxyl radicals formed from ozone decomposition in water (Kasprzyk-Hordern 2003). AOPs, including Fenton catalysis and photocatalysis, are based on the generation of free radicals such as $O_2^{\bullet-}$ and $HO_2^{\bullet}$, especially hydroxyl radicals ($OH^{\bullet}$). These highly reactive species can successfully attack most organic molecules with high reaction rate constants ranging from $10^6$ to $10^9$ $M^{-1}s^{-1}$ (Rivera-Utrilla et al. 2013).

### 3.1. Ozonation

Ozone is the most commonly used oxidant in chemical oxidation because it has a high oxidation potential, it does not remain in the water, and an ozonation process can run continuously (Reungoat et al. 2007). The chemistry of ozone is complex, based on two ozone decomposition mechanisms: direct ozonation by ozone molecules and advanced oxidation by forming hydroxyl radicals in water. Direct ozonation is related to the structure of the ozone molecule. Molecular ozone can react as a dipole, an electrophilic or nucleophilic agent. Temperature, pH and concentration of organic and inorganic compounds in water influence the half-life time of molecular ozone (Kasprzyk-Hordern 2003). The ability of ozone to oxidize organic and inorganic molecules is related to its oxidation potential ($E^0 = 2.07$ V) (Kasprzyk-Hordern 2003). Advanced oxidation by ozone is via a chain reaction mechanism resulting in the generation of hydroxyl radicals ($E^0 = 2.33$ V), which is one of the most reactive free radicals and has a stronger oxidation ability than molecular ozone (Kasprzyk-Hordern 2003). Following is the five-step chain reaction of advanced oxidation by ozone (1)-(5):

$$O_3 + H_2O \rightarrow 2OH^{\bullet} + O_2 \quad (1)$$

$$O_3 + OH^- \rightarrow O_2^{\bullet-} + HO_2^{\bullet} \quad (2)$$

$$O_3 + OH^{\bullet} \rightarrow O_2 + HO_2^{\bullet} \leftrightarrow O_2^{\bullet-} + H^+ \quad (3)$$

$$O_3 + HO_2^{\bullet} \rightleftharpoons 2O_2 + OH^{\bullet} \quad (4)$$

$$2HO_2^{\bullet} \rightarrow O_2 + H_2O_2 \quad (5)$$

The process of ozonation can be used for the regeneration of OMPs-loaded zeolites. Adsorption of OMPs by zeolites can be carried out from gas streams or water solutions. Regeneration possibilities for both mentioned adsorption options are similar. Based on the literature, OMPs-loaded zeolites can be regenerated by using gaseous ozone mixed with humidified air for zeolites in the gas phase or using water-dissolved ozone for zeolites in the water phase. Based on the sequence of applying adsorption and ozonation, the OMPs removal processes can be classified into two categories: adsorption followed by ozonation (sequential adsorption – ozonation) and simultaneous adsorption and ozonation (simultaneous adsorption & ozonation).

### 3.1.1. Sequential adsorption – ozonation

*Gas-phase*

In this process, gaseous ozone is introduced into the column packed with exhausted zeolite granules. Zeolite acts as an adsorbent and concentrator for OMPs from gas streams or water solutions. After a fixed adsorption time, ozone gas was introduced to the column packed with loaded zeolite granules for the degradation of OMPs. Gas organic pollutants mainly include hazardous air pollutants, such as VOCs, typically generated in chemical industries (Kotowska 2022).

Monneyron et al. (Monneyron et al. 2007) reported complete mineralization of VOCs by applying gaseous ozone to regenerate the fixed-bed column (80 mm in diameter) packed with saturated high-silica zeolite granules. Zeolite FAU granules (3 mm in diameter) and zeolite ZSM-5 granules (1.5 mm in diameter) were used for the adsorption of VOCs. The inflow ozone gas conditions were 4.2 L/min (0.01 m/s) and 0.018 g $O_3$/L. The regeneration efficiency was 95% for the zeolite ZSM-5 and 75% for the zeolite FAU because the reactivity of ZSM-5 and FAU was different in contact with ozone. Water in the ozonated air could accelerate the oxidation of VOCs as hydroxyl radicals were generated in the presence of humidity and trapped in the zeolite.

Serguei Alejandro et al. (Alejandro et al. 2014) investigated the influence of zeolite chemical surface characteristics on the ozonation regeneration of natural zeolite saturated with toluene. 50 g of natural zeolite granules (ingredients: 53% clinoptilolite, 40% mordenite and 7% quartz; granular size 0.3-0.425 mm) were packed in a fixed-bed column (45 mm in diameter). Natural zeolite was modified by acid treatment using HCl (2.4 mol/L), single ion exchange modification using ammonium sulphate (0.1 mol/L), and double ion exchange modification. After the adsorption phase, toluene was decomposed by ozone (4.5 L/min (0.05 m/s), 24.3 g $O_3$/L) in the column. The highest recovery of adsorption capacity was 57% for the zeolite only modified with acid. The acid modification increased the zeolite microporosity and thus led to an increase in adsorption capacity. Ozone reaction with multilayer adsorbed toluene increased reactor temperature, resulting in thermal desorption of oxidation transformation products. Fourier-transform infrared spectra results suggested that a surface reaction mechanism could occur among toluene molecules adsorbed at Bronsted acid sites and surface active oxygen species generated after ozone decomposition at Lewis acid sites.

Hicham Zaitan et al. (Zaitan et al. 2016) applied synthetic zeolites ZSM-5 (granular size 1.5 mm) as an adsorbent for toluene removal. This research studied the adsorption followed by ozone oxidation in a fixed-bed reactor (80 mm in diameter and 200 mm in length) packed with 150 g of ZSM-5 granules. The regeneration step was performed using a humidified gaseous ozone stream (0.4 L/min (0.001 m/s), 0.018 g $O_3$/L, and 60% relative humidity). The results indicated that the ZSM-5 had an excellent adsorption capacity recovery (92%-99%) in five adsorption-ozonation cycles. Notably, the oxidation products that detected ecotoxicity were only $CO_2$ and $H_2O$. The toluene mineralisation factor reached between 75% and 85%, which could be related to the three-dimensional structure of the zeolite framework with interconnected channels and the proximity between the pores. These structure properties allowed surface contact between toluene and ozone (Alejandro et al. 2014). The ozone and toluene consumption ratio was nearly equal to the stoichiometric ratio of $O_3/C_7H_8$ in the gaseous reaction. A surface reaction could occur when the ozone in the gas phase diffused through the gas film close to the zeolite surface and contacted the adsorbed toluene in the pores of zeolites. This result was in agreement with the previous studies (Alejandro et al. 2014, Chao et al. 2007), assuming that both toluene and ozone gas could be adsorbed onto the surface of zeolites, followed by ozone reaction with adsorbed toluene in the vicinity of the zeolite surface.

Other studies reported the regeneration performance of directly introducing gaseous ozone into the column packed with zeolite granules that were dried after the adsorption of OMPs from water. Zhang et al. (Zhang et al. 2016) introduced gaseous ozone into a column (30 mm in diameter and 130 mm in length) packed with dried granules that had adsorbed trichlorophenol (TCP) in batch mode. The ozonation regeneration performance of high-silica FAU zeolite granules (1.6-2.5 mm in diameter) was evaluated. Ozone conditions were 0.3 L/min (0.007 m/s) and 0.02 g $O_3$/L. The stoichiometric mass ratio of ozone and TCP was 0.36 g $O_3$/g TCP. The applied ozone dosage in this study was approximately 1.2 ± 0.3 g $O_3$/g TCP (approximately three times higher than the stoichiometric mass ratio). This value was much lower than the ozone consumption (between 21.6 and 11.4 g $O_3$/g TCP at pH = 2 and 7.5, respectively) in the direct ozone gas dosing into the water to remove TCP (Graham et al. 2003). This study also suggests applying zeolites with mesopores (approx. 4 nm) and macropores (approx. 1 μm) to remove large OMPs from water.

Fu et al. (Fu et al. 2021a) reported a significant influence of the water content in high-silica zeolite BEA granules (2 mm in diameter and 4-5 mm in length) on regeneration performance. The zeolite granules were first saturated with acetaminophen in column adsorption tests. Gaseous ozone was introduced to the column (10 mm in diameter) packed with zeolite granules at 0.8 L/min (0.04 m/s) and 0.09 g $O_3$/L. The recovery of adsorption capacity was 81% for the granules with 0% water content (by weight), whereas it was only 16% for the granules with 40% water content. Lower water content was beneficial for the mass transfer of ozone and thus promoted the reaction of ozone with OMPs (Zhang et al. 2016). Ozonation transformation products did not influence the adsorption performance in three adsorption-regeneration cycles. Fu et al. (Fu et al. 2021b) further reported that gaseous ozone could effectively regenerate the dried granules when the ozonation duration was long enough. Various OMPs were adsorbed on high-silica zeolite granules (mixture of zeolite MOR and BEA, granular size 1 mm in diameter and 2-3 mm in length). The gaseous ozone conditions were 0.2 L/min (0.01 m/s) and 0.03 g $O_3$/L. Longer ozonation duration resulted in better diffusion of ozone gas into the inner pores of zeolites, leading to complete degradation of OMPs.

*Water-phase*

Typically, a practical ozone bubbling system applies water-dissolved ozone to treat OMPs in wastewater. In the sequential adsorption – ozonation process, OMPs are first adsorbed by zeolite granules, after which the exhausted column is regenerated by introducing ozone dissolved in water into the fixed-bed column packed with zeolite granules, and the adsorbed OMPs are degraded. Sagehashi et al. (Sagehashi et al. 2005b) reported that the adsorption of 2-methylisoborneol (MIB) onto high silica zeolite USY granules (granular size 0.5 mm) led to a significant enhancement of the MIB decomposition rate in the ozonation process. An ozone solution was prepared by bubbling ozone gas into distilled water. Zeolite samples were washed with $NH_4Cl$ solution and rinsed well with distilled water before use to avoid the rapid decomposition of water-dissolved ozone in water. OMPs were oxidized both by molecular ozone and hydroxyl radicals. Under certain ozonation conditions (0.07 mg $O_3$/L in water), the concentration of hydroxyl radicals was assumed to be proportional to the dissolved molecular ozone concentration.

### 3.1.2. Simultaneous adsorption & ozonation

*Gas-phase*

In this process, gaseous ozone is introduced into the zeolite granules packed column together with the air pollutants, mainly VOCs. Chao et al. (Chao et al. 2007) studied the performance of a combined ozone and zeolite system for the degradation of gaseous toluene. Hydrophilic FAU zeolite granules (granular size 3-5mm) were applied as a favourable adsorbent for toluene. The removal efficiency of 1.5 g/m$^3$ toluene was more than 90% by combined adsorption on zeolite and simultaneously ozonation (0.006 g $O_3$/L and 0.35 m/s), while about 25% only by just adsorption on zeolite without ozone gas dosing. Atomic oxygen generated from ozone decomposition on the Lewis acid sites in zeolite can react with toluene and thus enhance the removal efficiency.

*Water-phase*

In this process, water-dissolved ozone was applied to degrade the OMPs in water simultaneously with the presence of zeolite granules in a column. The ozonation process proceeds either by bubbling gaseous ozone or injecting ozone-dissolved water into the column when the water stream containing OMPs is simultaneously injected. Zeolite granules are used as an adsorptive concentrator of water-dissolved ozone and OMPs, resulting in a significant increase in reaction rate (Fujita et al. 2004b).

Fujita et al. (Fujita et al. 2004b) reported a significant increase in the oxidative decomposition rate of trichloroethene (TCE) in the presence of high silica zeolite ZSM-5 granules (granular size 0.35-0.5 mm) packed in a column (10 mm in diameter). Nearly 75% of TCE was decomposed in seconds when the introduced ozone concentration in water was low at 1.5 mg/L. They proposed that the decomposition of TCE was attributed to the direct ozonation of TCE by ozone molecules. The TCE decomposition was related to the adsorptive concentration of both ozone and TCE on high silica zeolites. More hydrophobic zeolites can adsorb more ozone and TCE, leading to a higher TCE decomposition. This study affirmed that TCE inside zeolites was effectively and quickly decomposed before adsorptive saturation.

Valdes et al. (Valdes et al. 2009b) reported that the overall methylene blue (MB) removal rate was enhanced in simultaneous adsorption/oxidation (ozone oxidation combined with zeolite adsorption) compared to individual adsorption and ozonation processes. Natural zeolite mordenite granules (granular size 0.60-0.85 mm) were packed in a fixed-bed column. The capacity of the ozone generator was 5 g $O_3$/h. Saturated ozone water was prepared by bubbling gaseous ozone in a tank containing 1 L of deionized water. After that, the MB stock solution was injected into the tank, and the mixed solution was recirculated through the fixed-bed column. The increase in MB removal rate was attributed to the fact that zeolite could provide a contact place for MB and ozone, thus promoting the formation of radicals through the decomposition of aqueous ozone by the hydroxyl groups on the zeolite surface. In addition, the acid-treated natural zeolite had a higher kinetic rate of MB removal than the untreated one. Acid treatment could increase the Lewis acid sites on the zeolite surface, promoting aqueous ozone decomposition and resulting in better MB removal (Valdes et al. 2009a).

Reungoat et al. (Reungoat et al. 2010b) reported that the nitrobenzene (NB) decomposition rate in ozone oxidation was enhanced in the presence of high-silica zeolite FAU granules (3 mm in diameter, 7.5 mm in length). Zeolite granules were packed in a column (6 cm in diameter, 20 cm in length) as adsorbents. The experiments were carried out in a continuous flow condition. NB solution was continuously injected into the column with simultaneous ozone bubbling (0.6 L/min and 0.03 g $O_3$/L). Before the ozonation process, zeolite granules were loaded with NB to limit adsorption during ozonation experiments. The enhancement of the NB oxidation was possibly attributed to the micropore concentration effect that both ozone and NB were adsorptively concentrated on zeolite (Fujita et al. 2004b, Sagehashi et al. 2005b). Moreover, the silanol groups formed on the defects of zeolite during the dealumination treatment might be responsible for the catalytic decomposition of ozone in the gas phase (Monneyron et al. 2003b). A higher ozone decomposition rate possibly enhanced the oxidation of NB and its by-products.

Ikhlaq et al. (Ikhlaq et al. 2014, Ikhlaq and Kasprzyk-Hordern 2017) reported a semi-continuous experimental setup to remove VOC from aqueous solutions. The experiments were carried out by injecting a VOC-saturated solution into a column (3.1 cm in diameter, 70 cm in length) packed with 5 g of hydrophobic zeolite ZSM-5 granules and simultaneously bubbling ozone gas into the column by a ceramic sparger. The VOC-saturated solution was recirculated in the column at a flow rate of 15 mL/min for 30 min. They found that zeolite ZSM-5 performed a catalytic effect on promoting surface reactions between the OMPs and aqueous ozone adsorbed on zeolite. Furthermore, the catalytic ozonation proceeded via direct oxidation by molecular ozone, leading to the generation of chlorides during the oxidation of chlorinated VOCs. In addition, the decomposition of VOCs was more effective by the more hydrophobic zeolites.

### 3.1.3. Discussion

In the last two decades, the removal of OMPs, either from water or gas phases, has been promoted by the combined application of ozone and zeolite (mainly hydrophobic zeolite). The degradation of OMPs by ozonation is enhanced in the presence of zeolite. Meanwhile, ozonation can recover the adsorption capacity of zeolite, leading to a promising sustainable application of zeolite. However, many controversies appeared regarding the understanding of the ozonation mechanism. From the literature, some reported that zeolites could decompose gaseous ozone to form active species on the zeolite surface. In contrast, others suggest that zeolites acted more as adsorbents for aqueous ozone and OMPs to facilitate surface reactions.

In the research on gas-phase ozonation, some findings indicated that hydrophilic and hydrophobic zeolites could decompose ozone, yielding reactive oxygen species. The ozone decomposition was attributed to the strong Lewis acid sites on the zeolite surface (Alejandro et al. 2014, Brodu et al. 2013, Chao et al. 2007). Besides, hydrophobic zeolites can adsorb gaseous ozone by the weak Lewis acid surface sites (Brodu et al. 2013). Ozone decomposition on hydrophobic zeolites can be considered a thermo-catalytic effect controlled by local ozone concentration and temperature at the micropore scale (Monneyron 2007). In the presence of humidity, more hydroxyl radicals were trapped, leading to a higher mineralization rate (Monneyron 2007, Monneyron et al. 2003b). Both the OMPs and ozone were adsorbed on the zeolite surface, thus promoting a surface reaction between OMPs and the reactive oxygen species, leading to the oxidation of OMPs (Zaitan et al. 2016).

In the research on water-phase ozonation, some findings reported that hydrophilic zeolites could promote aqueous ozone decomposition. The decomposition of aqueous ozone (ozone dissolved in water) was attributed to the Lewis acid sites on the zeolite surface (Valdes et al. 2009b, Valdés et al. 2012). The modified hydrophilic zeolites after acid treatment, in which aluminium could be expulsed, had an increase in strong acid sites. The strong Lewis acid sites could increase aqueous ozone decomposition by acting as initiators and/or promoters of radical chain reactions (Valdes et al. 2009a). Similarly, Kusuda et al. (Kusuda et al. 2013) reported that the hydrophilic zeolites with high alkali cation contents possessed high catalytic activity for aqueous ozone decomposition, whereas the hydrophobic zeolites had almost no catalytic activity for aqueous ozone decomposition. The type of metal cations in the hydrophilic zeolite structure significantly influenced the aqueous ozone decomposition. Moreover, the hydrophobic zeolites did promote the decomposition of OMPs in the ozonation process by adsorptive concentrating both ozone and OMPs on the zeolite surface (Fujita et al. 2004b, Fujita et al. 2005, Reungoat et al. 2010b, Sagehashi et al. 2005b). The ozonation proceeded via direct reactions of molecular ozone and OMPs on the zeolite surface (Ikhlaq et al. 2013, 2014).

To date, no up-scaling studies of this combined technology have been reported. A unified mechanism of the ozonation processes in the presence of zeolite in the gas and water phases is still lacking in the literature. Further study about the process mechanism and attempts to up-scale this combined technology is recommended. Moreover, removing OMPs from the water phase requires considering the influence of natural organic matter

(NOM) in the aquatic environment. Simultaneously adding ozone and OMPs-containing water to the zeolite column is not an optimum option because much ozone might be consumed by NOM, leading to high operational costs. Adsorption followed by ozonation is highly recommended. After the adsorption and enrichment of OMPs from water on the zeolite column, the dosing ozone is only dedicated to decomposing the adsorbed OMPs, leading to a high ozonation efficiency.

### 3.2. Fenton catalysis

Advanced oxidation processes (AOPs) utilize the generation of hydroxyl radicals for degrading organic pollutants. Hydroxyl radicals are powerful and non-selective oxidants, which may eventually lead to complete mineralization. The efficient use of hydroxyl radicals should be considered to minimize the loss of radicals. Zeolites, as an efficient adsorbent, could be used for selective adsorption and enrichment of OMPs, and promote the efficiency of the following AOPs.

Fenton reagent, a combination of hydrogen peroxide and a ferrous salt, is successfully used for the degradation of organic pollutants as an AOP technology (Doocey and Sharratt 2004). The Fenton reaction used in wastewater treatment is effective against many hazardous organic pollutants in water (Mackuľak et al. 2015). The Fenton reaction can completely degrade contaminants to harmless compounds, such as $CO_2$, water and inorganic salts. Fenton reaction can cause the dissociation of the oxidant and the generation of hydroxyl radicals which attack and decompose the organic compounds (Neyens and Baeyens 2003). Fenton reactions are based on the following mechanism (Eqs. (6)–(9) (Gonzalez-Olmos et al. 2011)):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet \tag{6}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HOO^\bullet \tag{7}$$

$$Fe^{3+} + HOO^\bullet \rightarrow Fe^{2+} + H^+ + O_2 \tag{8}$$

$$OH^\bullet + H_2O_2 \rightarrow H_2O + HOO^\bullet \tag{9}$$

The Fenton-like reaction uses various iron compounds, including iron complexes with organic ligands or solid iron oxides and iron species immobilized on solid supports. It is widely assumed that the active oxidant in these processes is $OH^\bullet$. However, the free radicals mechanism has been questioned repeatedly, and alternative mechanisms have been proposed that involve hypothetical transients other than $OH^\bullet$ (Gogate and Pandit 2004). Two reaction pathways of Fenton chemistry have been proposed: a radical pathway, which involves the generation of $OH^\bullet$, and a non-radical pathway in which the reaction between $H_2O_2$ and iron species produces ferryl ions ($FeO^{2+}$, an oxidizing Fe(IV) species). The generated ferryl ions become the active intermediate species in a Fenton-like reaction (Gonzalez-Olmos et al. 2011). The ferryl ions are generated based on the following mechanism (Eqs. (10)–(11) (Bray and Gorin 1932)):

$$Fe^{2+} + H_2O_2 \rightarrow FeO^{2+} + H_2O \tag{10}$$

$$FeO^{2+} + H_2O_2 \rightarrow Fe^{2+} + H_2O + O_2 \tag{11}$$

Due to the different reaction pathways, Fenton catalysis regeneration of zeolites loaded with OMPs can be divided into two categories, aqueous phase catalysis (homogeneous Fenton catalysis) and solid phase catalysis (heterogeneous Fenton catalysis). Aqueous phase catalysis applies the Fenton reagent, $H_2O_2$ combined with dissolved iron salts. Solid phase catalysis utilizes a Fenton-like reaction in which iron species are immobilized on zeolites (Doocey and Sharratt 2004).

### 3.2.1. Aqueous phase catalysis

Doocey et al. (Doocey and Sharratt 2004) reported that the adsorption of chlorinated phenols on hydrophobic zeolite followed by oxidation of saturated zeolite by applying the Fenton reagent was possible. Sequential adsorption and regeneration aim to prevent the influence of some scavengers present in water. The scavengers, such as sodium sulphate and acetone, can react with radicals generated by the Fenton reagent, resulting in the low-efficient use of radicals. Hydrophobic zeolite Beta was applied in granular form (granular size 0.18-0.25 mm), packed in a column (5 mm in diameter, 50 mm in length). The regeneration of the saturated zeolite was carried out by simultaneously pumping $H_2O_2$ and $Fe^{2+}$ solutions at pH 3 to the exhausted column in up-flow mode. They found that 60-65% of the theoretical chloride expectation was achieved before flow problems (clogging) occurred. Applying a larger column with the zeolite in a micro-granule form was expected to avoid flow problems.

### 3.2.2. Solid phase catalysis

In heterogeneous Fenton catalysis, transition metals (mainly Fe and Cu) were immobilized on zeolite by hydrothermal synthesis (Ribera et al. 2000) or ion exchange process (Pirngruber et al. 2006). The iron species on zeolite could be in various forms because of different synthesis routes and iron content. The iron species can be (a) substituted iron atoms in the framework, (b) isolated iron ions or oxygen-bridged binuclear iron species on ion-exchange sites, (c) small iron clusters in the pores, (d) large iron clusters on zeolite surface (Gonzalez-Olmos et al. 2013). The formation of the reactive species (hydroxyl radicals and ferryl species) is ascribed to the isolated mononuclear and binuclear iron species at the ion-exchange sites on the zeolite surface (Gonzalez-Olmos et al. 2011, Gonzalez-Olmos et al. 2013).

Doocey et al. (Doocey et al. 2004) reported the regeneration of iron-loaded zeolites through the degradation of the adsorbed chlorinated phenols by *in-situ* Fenton oxidation. The iron-loaded zeolites acted as catalysts in the advanced oxidation process. Higher iron loading might result in higher catalytic activity for the decomposition of $H_2O_2$. The iron leaching degree from the Fe-zeolite was low, indicating that the decomposition of $H_2O_2$ was not because of the leaching iron. Column tests were carried out in a stainless steel column (10 mm in diameter and 125 mm in length) packed with 3.8 g of Fe-Beta zeolite granules (1 mm in diameter and 3 mm in length). The Fe-zeolite granules packed in the column could be regenerated by circulating $H_2O_2$ at pH 3.5 and 3 mL/min for three days. The zeolite crystallinity remained the same after three regeneration cycles, indicating that the structure of zeolite was not affected during Fenton oxidation.

Gonzalez-Olmos et al. (Gonzalez-Olmos et al. 2013) studied the regeneration of iron-loaded hydrophobic zeolites by heterogeneous Fenton-like reactions. Although the ion-exchange capacity of the hydrophobic zeolites was low (≤ 0.09 wt %), the active catalysis was sufficient to degrade the adsorbed MTBE. The characterization of iron-loaded ZSM-5 zeolites indicated that a small fraction of $Fe^{(III)}{}_xO_y$ clusters were loaded on zeolite in the ion-exchange procedure. The $Fe^{(III)}{}_xO_y$ clusters were attributed to high redox reactivity (Zecchina et al. 2007). Additional pre-treatment (calcination at 550 °C for 5 h) of the Fe-zeolite might change the loaded iron species, leading to an increase in the catalytic activity of Fe-zeolite. Column tests were carried out in a small vertical glass column (0.4 cm in diameter, 2 cm in length) packed with 0.2 g Fe-zeolite granules (granular size 0.25–0.63 mm). The Fe-zeolite granules were regenerated by recirculating $H_2O_2$ through the packing bed at 0.8 mL/min during 48-72 h using a 100-250 mL reservoir with 2-5 g/L $H_2O_2$. The optimal pH conditions in the regeneration solutions were neutral or slightly acidic. The adsorption breakthrough curves of MTBE did not significantly change in three cycles, and a high degree of mineralization (76%) was achieved at the end of the third cycle.

Shahbazi et al. (Shahbazi et al. 2014) studied using iron-loaded zeolites as adsorbents and heterogeneous Fenton-like catalysts to remove the non-ionic surfactant TX-100 from water. Under identical reaction conditions, the catalytic activity of hydrophobic zeolite Beta for $H_2O_2$ decomposition was lower than that of natural zeolite because the iron loading on natural zeolite was higher than the iron loading on zeolite Beta. In contrast, the TX-100 oxidation activity of zeolite Beta was higher than that of natural zeolite. The higher oxidation activity of Fe-zeolite Beta can be explained by the combined effect of better adsorption of the target compound and more preferable iron species (isolated iron species of low nuclearity). Column adsorption/oxidation experiments were carried out in a glass column (4 mm in diameter and 90 mm in bed height) packed with

0.5 g of Fe-Beta granules (granular size 0.25–0.63 mm). 1.2 L of the aqueous solution with 0.3 g/L of TX-100 was treated by the column at a flow rate of 0.3-0.4 mL/min in up-flow mode. Two cycles of adsorption and regeneration were performed. The column was regenerated by flushing $H_2O_2$ at varied conditions through the column. The regeneration lasted for 135-169 h. The degree of mineralization was 85% and 68% for the first and second cycles, respectively. The iron leaching was 7% and 4% of the total iron loading on zeolite for the first and second cycles, respectively.

Cabrera-Codony et al. (Cabrera-Codony et al. 2017) reported an evaluation of iron-loaded hydrophobic zeolite BEA as a recyclable adsorbent/catalyst for the removal of biogas siloxanes in dynamic adsorption cycles. A stream with a siloxane concentration of 3 g/m$^3$ was introduced to a glass column (7 mm in diameter) packed with 0.25 g of zeolite granules (granular size 0.2-0.4 mm). After the adsorption tests, the granules were transferred to glass reactors filled with 100 mL $H_2O_2$ at varying concentrations for 24 h for the Fenton-like reactive regeneration. The regeneration efficiency of Fe-zeolite decreased from 100% in the first cycle to 50% in the fourth cycle. The $H_2O_2$ decomposition rate dropped significantly, and the conversion degree of $H_2O_2$ decreased from 38% in the first to 8% in the fifth cycle. The decrease in the regeneration efficiency and the catalytic activity of Fe-zeolite was due to the accumulation of oxidation by-products formed during the Fenton-like reaction. The oxidation by-products could block the adsorption sites for the siloxanes and the reactive catalytic sites for the $H_2O_2$ decomposition, thus affecting both the adsorption and regeneration processes.

### 3.2.3. Discussion

The aqueous phase Fenton catalysis (homogeneous catalysis) is ineffective in regenerating OMPs-loaded Fe-zeolite granules. In contrast, the solid phase Fenton-like catalysis (heterogeneous catalysis) performs well in the regeneration process. The ineffective regeneration by homogeneous Fenton reaction is because the lifetime of the reactive species (hydroxyl radicals formed from the decomposition of $H_2O_2$) is too short to allow diffusion into the pore structure of zeolite to react with the adsorbed OMPs (Gonzalez-Olmos et al. 2013).

In the heterogeneous Fenton-like reactive regeneration, only the OMPs that enter the zeolite pores can be degraded by the reactive species, which are ferryl species and hydroxyl radicals. The hydroxyl radicals are formed from the decomposition of $H_2O_2$ at the iron sites in the inner zeolite pores. They have a too-short lifetime to diffuse within or out of the pore structure into the bulk solution. If the target OMPs cannot enter the inner pores of Fe-zeolite, only a low proportion of iron species on the external surface of zeolite can be accessible (Shahbazi et al. 2014). Furthermore, the active catalytic sites (acid sites and iron species) in the inner pores might be blocked by the oxidation by-products formed during the Fenton-like reaction, resulting in a reduction of the catalytic activity, affecting the performance of both the adsorption and regeneration processes (Cabrera-Codony et al. 2017). Besides the possible reduced catalytic activity, several other aspects are worth discussing concerning the heterogeneous Fenton-like regeneration. The pH conditions in the regeneration solutions should be adjusted to a neutral or acidic range (Gonzalez-Olmos et al. 2013). Additional chemicals should be added in real applications to adjust the pH conditions. The duration of the Fenton-like reactive regeneration appears to be long, running for 2 to 5 days in the lab-scale experiments from the literature. The long regeneration duration might increase the operational costs of the whole process in real applications. Moreover, although iron leaching was reported at a low level in the lab-scale experiments, iron leaching in long-term tests in real applications might lead to sludge formation and reduce the catalytic activity.

### 3.3. Photocatalysis

Photodegradation of organic pollutants occurs upon exposure to sunlight, including direct and indirect photodegradation (Gruchlik et al. 2018). Direct photodegradation occurs when the OMP molecules absorb radiation from the solar light, followed by bond breaking, leading to degradation. The molecular structure of OMPs determines the capability to absorb radiation. Indirect photodegradation is promoted by reactive species generated by natural photosensitisers in natural water (Gruchlik et al. 2018). Most pharmaceuticals can absorb luminous radiation as they generally contain aromatic rings, heteroatoms, and some functional groups that can facilitate photodegradation (Rivera-Utrilla et al. 2013).

Photocatalytic reactions mediated by photocatalysts can enhance the photodegradation of OMPs. The photocatalytic reaction is an AOP technology to eliminate OMPs by reactive species (hydroxyl radicals) without generating harmful products (Nezamzadeh-Ejhieh and Khorsandi 2014). Photocatalysis processes are based on the electronic excitation of semiconductors caused by absorbing UV light (Areerachakul et al. 2007). Hydroxyl radicals are generated upon excitation with UV light ($\lambda < 380$ nm) (Bhargava et al. 2004). Semiconductors (e.g. $TiO_2$ and ZnO) have been used as photocatalysts and found to be effective in removing refractory compounds (Kabir et al. 2006). Photo-induced electrons ($e^-$) and positive holes ($h^+$) are produced from $TiO_2$ upon exposure to UV light (Eq. (12)). The charged species can further generate free reactive radicals (Eqs. (13) and (14)). The positive holes ($h^+$) are highly oxidizing species that dominate in the degradation of OMPs (Chu and Wong 2004).

$TiO_2 + h^+ \rightarrow TiO_2 (e^- + h^+)$ (12)

$h^+ + OH^- \rightarrow OH^\bullet$ (13)

$e^- + O_2 \rightarrow {}^\bullet O_2$ (14)

The removal of OMPs using photocatalysts is achieved via two mechanisms: adsorption on the surface of semiconductors and oxidation. The adsorption usually occurs faster than photocatalytic oxidation (Liu et al. 2014). However, the insufficient adsorption properties of semiconductors limit their applications. Applying zeolites as support for semiconductors can enhance photocatalytic performance. This strategy can combine the adsorption properties of zeolites with the photocatalytic properties of semiconductors (Nezamzadeh-Ejhieh and Khorsandi 2014). Some studies have been reported on the regeneration of semiconductor-immobilized zeolite powders for the degradation of adsorbed OMPs (Aziz and Kim 2017, Liu et al. 2014). However, the regeneration of zeolite granules has received little attention.

Monneyron et al. (Monneyron et al. 2003a) reported a co-treatment of industrial VOC (1-butanol) using adsorption and photocatalytic oxidation by $TiO_2$-zeolite catalysts. High-silica zeolite (FAU and ZSM-5) granules (2 mm in diameter, 5 mm in length) were used to support $TiO_2$. Both adsorption and irradiation experiments were carried out in a continuous flow annular reactor, which was 15 cm in length, 3mm in optical path length, and 60 $cm^3$ in total volume. 2 g of $TiO_2$-zeolite granules were packed in the annular space with a fixed-bed height of 1 cm. A mercury medium-pressure UV lamp was positioned in the internal cylinder. Shifting from adsorption to oxidation process was done by turning the UV lamp on once the adsorption breakthrough was achieved. The 1-butanol inlet concentration ranged between 0.3 and 5 $g/m^3$ and remained unchanged during irradiation. Adsorption and photocatalysis simultaneously occurred during irradiation. The final adsorption/photocatalysis steady-state was evaluated instead of a complete regeneration which may not be easy to determine because of the complex mechanisms involved. At an inlet concentration of 0.55 $g/m^3$, the degradation of 1-butanol was above 90%, and a partial regeneration of 30% was found in three consecutive cycles using $TiO_2$-zeolite FAU. However, the degradation of 1-butanol using $TiO_2$-zeolite ZSM-5 was lower under identical conditions. The degradation was different because of the different framework structures of zeolite FAU and ZSM-5. The intracrystalline diffusion was faster in FAU than in ZSM-5. FAU has a larger mesoporous volume than ZSM-5. The adsorption strength of zeolites was a decisive parameter of the photodegradation rate.

Bhargava et al. (Bhargava et al. 2004) designed and constructed a pilot-scale photocatalytic reactor packed with a new hybrid photocatalyst for phenol degradation. The photocatalyst was synthesized by impregnating high-silica zeolite and $TiO_2$ powders into the caverns of sintered porous glass beads (approximately 0.5 mm). The photoreactor was an annular photocatalytic batch reactor with recirculation. The reaction chamber was 81 cm in height, with an optical path length of 4 cm. A mercury medium-pressure UV lamp was placed in the centre axis of the reactor. The reactor was applied for liquid dual-mode, which consisted of adsorption in fixed-bed mode and simultaneous photocatalysis in fluidized-bed mode. The maximum adsorption capacity of phenol on the catalyst was 2 mg/g. Higher catalyst loading in the reactor might increase the backscattering of UV light, resulting in a reduced degradation rate. The degradation rate could be enhanced by increasing the superficial velocity in fluidization. The improved fluidization at high velocities could increase the frequency of the catalyst movement to the irradiation zone. The optimum conditions were $TiO_2$ loading at 2.81 $kg/m^3$ and a superficial velocity at 2.3 cm/s. The pilot-scale photoreactor presented a potential for industrial application.

Olga Sacco et al. (Sacco et al. 2018) reported a combination of adsorption and photocatalysis to remove caffeine from aqueous solutions using ZnO-loaded high silica zeolite ZSM-5 granules (granular size 1.2-2 mm). The experiments were carried out in a cylindrical photoreactor (2.6 cm in diameter and 9 cm in length). The caffeine solution was continuously recirculated in the reactor. The initial caffeine concentration and the ZnO-zeolite granules packing amount were 25 mg/L and 17.5 g, respectively. The reactor was irradiated with UV lamps (wavelength of 365-370 nm) that surrounded the external surface of the reactor. The adsorption tests were conducted in dark conditions. The simultaneous adsorption and photocatalytic tests were conducted by turning on the UV lamps. The ZnO-zeolite and unloaded-zeolite had the same caffeine removal efficiency (approximately 60%) in the individual adsorption tests. The caffeine removal was higher than 94% after 120 min simultaneous adsorption/photocatalysis in five successive cycles. The photocatalytic oxidation could degrade the caffeine adsorbed on the ZnO-zeolite surface, leading to the recovery of the adsorption capacity.

### 3.3.1. Discussion

In heterogeneous photocatalytic oxidation, the contact among reactants, photons, and catalysts should be maximized. The contact is decisively influenced by the characteristics of mixing and flow conditions. When applying a fixed-bed reactor, the irradiated proportion on the catalyst is limited to a thin layer, and a significant reactor volume is needed (Bhargava et al. 2004). Applying continuous stirred tanks or fluidized-bed photoreactors can enhance contact efficiency, even if the operational costs are significantly high. Increasing the flow rate can improve the exposure frequency of the catalyst to irradiation, resulting in an enhanced reaction rate (Bhargava et al. 2004).

Since the UV light cannot penetrate the catalysts, the photodegradation might only happen on the semiconductor-loaded zeolite granules surface (Biomorgi et al. 2010). The radicals generated on the catalyst surface need to diffuse into the pores to further react with the adsorbed OMPs. In most of the studies, adsorption and photocatalysis were simultaneously operated. This process might not be suitable for the removal of OMPs from waste streams (both aqueous and gas phases) that consist of natural background organics because the energy consumption by UV lamps for the degradation of background organics might be extremely high. In addition, since the degradation efficiency of OMPs adsorbed on zeolites is highly dependent on the structure properties of zeolites (Monneyron et al. 2003a), specific zeolites might have to be selected for removing specific OMPs.

## 4. Conclusions and outlook

Many research efforts have been contributed to evaluating the degradation of OMPs from water and air by integrating granular zeolite adsorption and oxidative treatment processes. Progressive developments have been achieved in different oxidation technologies. However, limitations still exist and hinder the potential for real applications. The main characteristics of different technologies and related challenges in future research are as follows:

1. As thermal treatment has to be applied off-site, the operational costs are expected to be high. However, as zeolites are thermally stable, the loss of adsorbents in thermal treatment might be minor compared to that of activated carbon. The thermal treatment process has the potential to be optimized to reduce the cost.

2. A specific mechanism to explain the ozonation in the gas and water phase in the presence of zeolites needs further research. The catalytic roles played by different types of zeolites should be determined. The adsorptive/catalytic properties of zeolites are essential for optimising the ozonation process. In addition, sequential adsorption and ozonation are frequently used to remove VOCs from the gas phase, and simultaneous adsorption and ozonation are commonly used to remove OMPs from the water phase. Furthermore, the adsorption of OMPs from the water phase followed by gas-phase ozone regeneration has the potential for wastewater treatment in real applications, but it still needs further research.

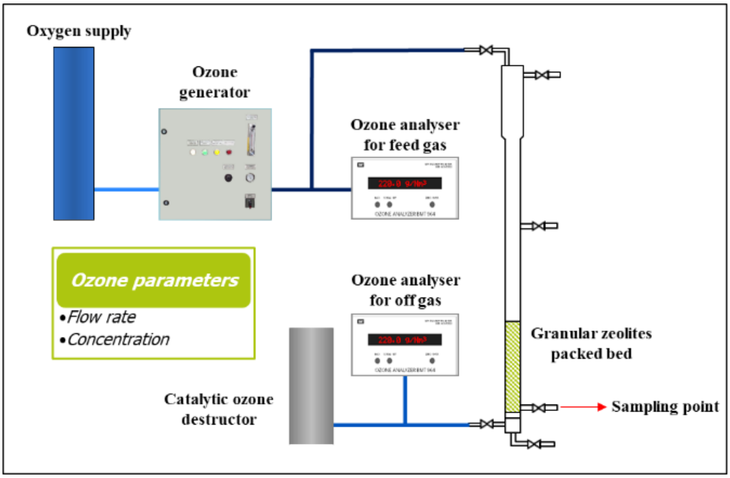
3. Heterogeneous Fenton catalysis initiated by the iron species immobilized on zeolite is more effective in regenerating zeolite granules than homogeneous Fenton catalysis. However, several parameters, such as pH conditions and

initial $H_2O_2$ concentrations, must be optimized to achieve optimal removal performance. Furthermore, after adding hydrogen peroxide, it needs time for the $H_2O_2$ to diffuse into zeolite to contact the immobilized iron species to generate oxidative radicals. As the lifetime of the radicals is too short, they cannot diffuse within the pores of zeolite to degrade the adsorbed OMPs. Thus, the oxidation efficiency might be limited. In addition, iron leaching in a long-term operation needs further research.

4. Photocatalytic oxidation of OMPs initiated by UV light irradiation on the semiconductor-loaded zeolite often simultaneously occurs with the adsorption of OMPs on zeolite. Selecting zeolites with specific structures to adsorb specific OMPs is essential, as the photodegradation efficiency of OMPs is highly dependent on the adsorption properties of OMPs on zeolite. The irradiation proportion on granules packed in the column significantly influences the oxidation efficiency. As UV light cannot penetrate granules, oxidation of OMPs by generating radicals only occurs on the surface of granules. Although applying fluidized-bed reactors can enhance the exposure frequency of the catalyst to irradiation, leading to a higher degradation rate, the operational costs are relatively high.

# Chapter 3

## Ozone-based regeneration of granular zeolites loaded with acetaminophen



This chapter is based on

M. Fu, M. He, B. Heijman, J.P. van der Hoek, Ozone-based regeneration of granular zeolites loaded with acetaminophen, Separation and Purification Technology 256 (2021) 117616.

## Abstract

Removal of organic micropollutants (OMPs) from municipal wastewater is becoming more and more important. On-site regeneration of exhausted adsorbents can be the key to practical applications. In this study, ozone-based regeneration of granular zeolites loaded with acetaminophen (ACE) was investigated. The adsorption capacity of ACE was 90 mg/g. After adsorption and breakthrough in column tests, granular zeolites were drained and dried for regeneration. Water content in granules is the main factor limiting regeneration performance by affecting the gaseous ozone transfer rate. Ozone-based regeneration of fully dried granular zeolites (0% water content) is the most efficient, whereas fully wet granules (40% water content) have poor regeneration efficiency. Various ozone concentrations and gas flow rates were applied. With the same total ozone dose (900 mg), the regeneration efficiency increased by increasing the ozonation duration up to 50 min. The longer the regeneration time, the deeper the gaseous ozone can diffuse into the inner pores of zeolites to decompose the adsorbed ACE. The effect of gaseous ozone on the adsorption capacity of zeolites and the effect of the accumulation of the intermediates on the long-term adsorption capacity recovery rate was also investigated. It was found that gaseous ozone did not influence the adsorption of ACE on zeolites. The adsorption capacity of ACE decreased by 7% after three adsorption-regeneration cycles. This decrease can be explained by the accumulation of undissolved intermediate breakdown products adsorbed on the granules.

## 1. Introduction

Organic micropollutants (OMPs), especially pharmaceuticals used in households and hospitals, mostly end up in the environment via municipal wastewater treatment plants (WWTPs). The accumulation of OMPs can cause potential environmental and health risks (Gavrilescu et al. 2015). Acetaminophen (ACE) is a common pharmaceutical used in households to treat pain and fever. As one of the aniline analgesic drugs, ACE is widespread used today. Since ACE is often purchased from pharmacies, it has become one of the most prevalent pharmaceuticals in treated wastewater. The frequent occurrence has raised concerns about its potential impact on the environment and human health (Wu et al. 2012). However, a conventional municipal WWTP is not designed to remove the OMPs (Bolong et al. 2009). For this purpose, an effective barrier is needed. The current treatment methods of OMPs mainly include physical separation (adsorption and membrane technology), chemical oxidation (ozonation and advanced oxidation processes) and biodegradation. Due to the diverse properties of OMPs, none of these methods can guarantee the complete removal of them (Luo et al. 2014).

Adsorption is a widely applied separation process to remove certain classes of pollutants from wastewater (Ahmaruzzaman 2008). Activated carbons are the most commonly used adsorbents for treating secondary effluent to remove micropollutants (Ahmaruzzaman 2008, Luo et al. 2014). In the last decades, hydrophobic zeolites have been evaluated as alternative adsorbents for OMPs removal from wastewater (Jiang et al. 2018). Zeolites are porous crystalline aluminosilicates with various frameworks formed by $SiO_4$ and $AlO_4$ tetrahedrons connected by oxygen atoms. This crystalline structure gives zeolites a uniform pore size, making zeolites different from other microporous adsorbents. Pore sizes are in the range of a few Å, allowing small molecules (e.g. pharmaceuticals) to enter the solid frame and excluding large molecules (especially natural organic matter), thus making zeolites selective adsorbents (De Ridder et al. 2012, Jiang et al. 2018). Chemical oxidation is an important technology to eliminate organic pollutants from wastewater (Ikehata et al. 2006). Ozone is the most commonly used oxidant due to its strong oxidation potential (Rodríguez et al. 2008). Ozonation is also a conventional treatment applied for the disinfection of drinking water (Rodríguez et al. 2008). Despite the advantages of ozonation, ozone consumption is high because natural organic matter (NOM), present in the wastewater, competes with the desired target micropollutants (Gardoni et al. 2012). Furthermore, harmful by-products, such as bromate, may be generated during ozone treatment (Sagehashi et al. 2005a).

After saturation with OMPs, the exhausted zeolites should be regenerated. Reusing the zeolites can avoid secondary environmental problems due to the disposal of contaminated adsorbents and high operational costs due to the one-time use of the adsorbent. The resistance of zeolites to chemical reactions allows the adsorbents for chemical regeneration by ozone (Jiang et al. 2018). The ozone-based regeneration can be performed on-site as the ozone is generated on-site. Compared with off-site regeneration by thermal methods, on-site regeneration will probably be less expensive due to the absence of costs for transportation and replacement (Gonzalez-Olmos et al. 2013). Compared with the direct oxidation of wastewater effluent, there are two advantages:

- As the NOM is not adsorbed on zeolites, the dosed ozone is only used for oxidizing the adsorbed OMPs. In theory, the oxidation of OMPs by ozone is more efficient.
- Ozone-based regeneration is operated in a side stream, and thus possible oxidation by-products are not produced in the main stream, and no by-products will end up in the effluent.

The removal of OMPs from water by zeolite powders, and subsequent ozone-based regeneration has not been fully studied, and only a few studies have been reported

(Reungoat et al. 2007, Zhang et al. 2014). Meanwhile, there is an intrinsic drawback to applying powder-form adsorbents. After the adsorption of OMPs, it is difficult to remove the powder-form adsorbents from water for recycling (Sacco et al. 2018). In practical applications, this drawback can be avoided by applying fixed-bed reactors packed with granular adsorbents. However, the regeneration of zeolite granules loaded with OMPs via ozone-based treatment has rarely been reported. Zhang et al. reported that the regeneration of zeolites loaded with 2,4,6-trichlorophenol (TCP) was effective (Zhang et al. 2016). The ozone consumption in regeneration was approximately 10 times lower than that of the ozonation in bulk water at neutral pH. In the study, the zeolites were dried before regeneration. Dried adsorbents could be beneficial for the mass transfer of ozone and thus promote the reaction of ozone with TCP. However, the influence of the water content in granules on regeneration performance was not investigated. It can be assumed that, with less water content, the gaseous ozone may diffuse into the granules faster, thus improving regeneration efficiency. Optimal applied ozone conditions (ozone gas flow, ozone concentration and ozonation duration) were also missing.

Furthermore, the regeneration of zeolite granules loaded with ACE has not yet been reported. Therefore, the first objective of this study was to investigate the adsorption isotherms of ACE onto zeolites. Secondly, the ozone-based regeneration variables were determined, including water content, ozone gas flow, ozone concentration, and ozonation duration. Among the variables, water content is probably the main factor influencing regeneration performance by limiting the gaseous ozone transfer rate in granules. The degradation pathway of ACE on granules was discussed. Finally, the long-term effects (multiple adsorption-regeneration cycles in sequence) were investigated. The effect of gaseous ozone on zeolites and the effect of the accumulation of intermediates on the long-term adsorption capacity recovery were discussed.

## 2. Materials and Methods

### *2.1. Materials*

High-silica zeolite Beta (HSZ-980HOA) was supplied by Tosoh Corporation, Japan. Its chemical formula is $HO \cdot Al_2O_3 \cdot xSiO_2 \cdot nH_2O$ (x = 500). The characterization of high-silica zeolite Beta was studied in previous research (Jiang et al. 2020). The structural and chemical characteristics of high-silica zeolite Beta are listed in Table 1. The granulation procedure is part of this research. Beta zeolite powders were mixed uniformly with bentonite (15% by weight, Sigma-Aldrich). After adding water to the mixture, the mixed paste was extruded out in stripe form by an extruder. Then the extruded stripes were cut into small granules of 2 mm in diameter and 4-5 mm in length. After drying in the oven at 105 °C overnight, the granules were transferred to a furnace and sintered under

850 °C for 2 hours. Acetaminophen and methanol were purchased from Sigma-Aldrich, Germany.

Table 1. The structural and chemical characteristics of high-silica zeolite Beta

| Type | Pore opening size (Å*Å) | Surface area ($m^2/g$) | Micro-pore surface area ($m^2/g$) | Pore volume ($cm^3/g$) | Micro-pore volume ($cm^3/g$) | Si/Al ratio (XRF) | BAS[a] (μmol/g) | LAS[b] (μmol/g) | Reference |
|---|---|---|---|---|---|---|---|---|---|
| Beta | 6.6*7.7<br>5.6*5.6 | 516 | 351 | 0.3022 | 0.1557 | 286 | 16 | 7 | Jiang et al. (Jiang et al. 2020) |

[a] Brønsted acid sites

[b] Lewis acid sites

### *2.2. Adsorption*

*Batch tests*

The adsorption isotherms of ACE by zeolite powders were studied in batch mode at 20 °C. 200 mg/L of the ACE solution was prepared with demi-water. Different amounts of high-silica zeolite Beta powders were added to 100 mL of the prepared ACE solution in several glass bottles. After reaching equilibrium (48 h), samples were taken and filtered over 0.2 μm polycarbonate syringe filters.

*Column tests*

Column adsorption tests were conducted to obtain ACE-loaded granular zeolites for regeneration. The ACE adsorption was conducted in a column (4 cm in diameter, 1 m in length). 100 g of granular zeolites were packed in the column. 200 mg/L of the ACE solution was prepared with demi-water. The empty bed contact time was 11 min. The feed flow rate was 0.74 m/h. The adsorption process ran for 120 hours. Column effluent samples were taken at different time intervals.

### *2.3. Ozone-based regeneration*

Ozone-based regeneration was carried out by applying ozone in the gas phase. Gaseous ozone was introduced to the column packed with zeolite granules. Two types of glass columns were used for the experiments. The small column was 10 mm in diameter and 25 cm in length, and the big column was 4 cm in diameter and 1 m in length. Ozone equipment was provided by Wedeco (Xylem Water Solutions Herford, GmbH). Ozone was produced from pure oxygen with an ozone generator (Modular 4 HC, with a nominal ozone production of 4 g/h). Two ozone analysers (BMT 964, Messtechnik, GmbH) were used to measure in-gas and off-gas ozone concentrations. The off-gas was treated by a catalytic ozone destructor before venting out. Ozonation setup was installed inside a fume hood at room temperature.

### *2.3.1. Small column tests*

To optimize the regeneration conditions, 5 g of granular zeolites saturated with ACE was transferred into a small column. The ozone/oxygen gas mixture was directly introduced in the column from top to bottom at various ozone concentrations and gas flow rates. To investigate the influence of water content in granules, the drained ACE-loaded granules were dried in the oven at 60 °C. After different time intervals, different water contents (0%, 21%, 30% and 35% by weight) were reached. The water content of the drained granules (fully wet) was 40% by weight. The regeneration conditions were set at an ozone concentration in the gas phase of 90 mg/L and a gas flow of 0.8 L/min (0.17 m/s). The experiments lasted for 30 min. The total ozone dose was 2160 mg. To investigate the influence of gas flow and ozone concentration, two sets of experiments were conducted. The ACE-loaded granules were completely dried in the oven at 60 °C overnight to avoid the influence of water content in granules. The total ozone dose was constant by changing the exposure time to ozone for all experiments. Ozonation efficiency depends on ozone consumption during the reaction (Poznyak et al. 2019). One set of experiments was conducted at various ozone gas flow rates (0.2, 0.4, 0.6 and 0.8 L/min). An ozone concentration in the gas phase was set at 90 mg/L, and the total ozone dose was 900 mg in all experiments by varying the duration. The other set of experiments was conducted at various ozone concentrations (50, 90, 120 and 150 mg/L). A gas flow of 0.2 L/min was applied, and the total ozone dose was 540 mg in all experiments by varying the duration. Before and after each regeneration experiment, approximately 0.2 g of granules was sampled, ground into powders, and put into 100 mL pure methanol for 30 min to extract the remaining ACE (extraction efficiency 80%, taking into account in the calculations). ACE concentration in methanol was measured with HPLC and represented the amount of ACE on the zeolite. The ACE regeneration efficiency was calculated according to the remaining and initial ACE mass in the granules.

### *2.3.2. Big column tests*

A big column (4 cm in diameter, 1 m in length) was applied to upscale the ozone-based regeneration process. The experimental setup is shown in Fig. 1. After adsorption, which was conducted with 100 g of granular zeolites in the packed column, the regeneration was carried out in both the drained bed (40% water) and dried bed (0% water) by introducing gaseous ozone from top to bottom. The regeneration conditions were set at an ozone concentration in the gas phase of 90 mg/L and a gas flow of 0.8 L/min (0.01 m/s).

The drained-bed experiments were conducted after backwash. During the backwash, the not adsorbed ACE was flushed away. In the regeneration, ozone only reacted with the ACE adsorbed on granules. Before dried-bed experiments, the granules were transferred out of the column and dried in the oven at 60 °C overnight. After drying, the granules were packed back into the column.

During the regeneration, approximately 0.2 g of granules were taken from the sampling point at different time intervals for ACE extraction. The ACE regeneration efficiency was calculated. The sampling process lasted for 15 min. The sampling port is shown in Fig. 1. Before sampling, oxygen was introduced to the column to vent out the residual gaseous ozone. In the drained-bed experiments, the granule samples were taken after the backwash of the column by demi-water. During the backwash, the granules in the column were mixed uniformly, whereas, in the dried-bed experiments, the granules were taken directly from the sampling port without backwash.

### *2.3.3. Long-term adsorption-regeneration tests*

Three cycles of adsorption and regeneration were conducted. 100 g of granular zeolites were packed in the big column (4 cm in diameter, 1 m in length). In the adsorption phase, 200 mg/L of the ACE solution flowed through the column at an empty bed contact time of 11 min for 120 hours. Dried-bed regeneration was carried out. The regeneration conditions were set at an ozone concentration in the gas phase of 90 mg/L, a gas flow of 0.8 L/min (0.01 m/s) and an ozonation duration of 7.5 hours. Samples were taken before and after regeneration. The adsorption capacity recovery rate was applied to define the long-term adsorption-regeneration performance. At the start of the experiment and after each regeneration cycle, adsorption capacity measurements were conducted. 0.7 g of granules were taken, dried and ground into powders for batch adsorption tests by adding the powders to 1 L, 200 mg/L ACE solution and stirring for 5 days to reach the adsorption equilibrium. Samples were taken from the solution once per day and analysed by HPLC to determine the ACE concentration in the water. The adsorption capacity recovery rate was calculated by:

$$R = \frac{q_{en}}{q_{e0}} \times 100\%$$

Where R is the recovery rate (%); $q_{en}$ is the adsorption capacity of granules after the $n^{th}$ regeneration (mg/g); $q_{e0}$ is the adsorption capacity before the long-term test (mg/g).

### *2.3.4. Effect of ozone on adsorption capacity*

To investigate the effect of gaseous ozone on the ACE adsorption capacity of zeolites, 5 g of fresh granules were treated with gaseous ozone for one, two and three times without adsorption in between. The ozone conditions for each time were set at an ozone concentration in the gas phase of 90 mg/L, a gas flow of 0.8 L/min (0.01 m/s) and an ozone treatment duration of 30 min. The adsorption capacity of fresh granules and the granules after each gaseous ozone treatment were measured. The adsorption experiments were conducted the same as the adsorption capacity measurement in long-term tests. The samples were taken and measured with HPLC.

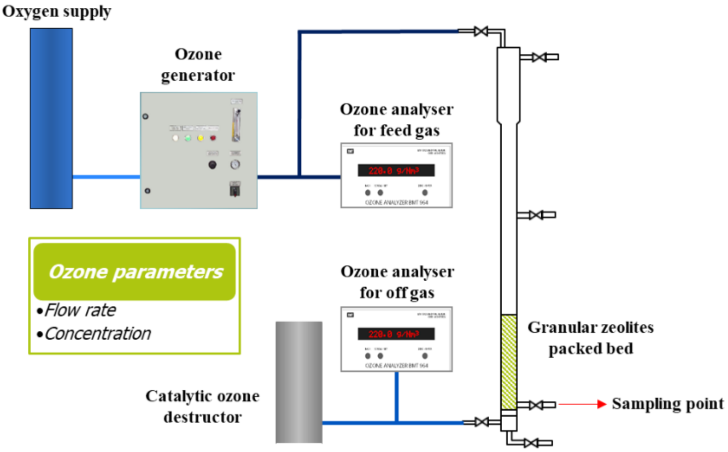


Fig. 1. Experimental setup of big column experiments

## *2.4. Analytical procedure*

The concentrations of ACE in both demi-water and methanol were measured by an HPLC system (SHIMADZU 74909) equipped with a Kinetex 2.6 µm C18 column. 50 µL of each sample was injected into the column. The flow rate of the elution, which was prepared with 40% acetonitrile and 60% ultrapure water, was set at 0.6 mL/min. The oven temperature was 40 °C. ACE in the elution was detected by a UV detector at the wavelength of 215 nm. LOD and LOQ were 20 µg/L and 100 µg/L, respectively.

## 3. Results and Discussion

### *3.1. Adsorption isotherms*

The adsorption isotherms of ACE by zeolites were interpreted with the Langmuir model (Fig. 2). All the isotherm constants are listed in Table 2. Results indicated that the adsorption of ACE correlated well with the Langmuir model. The maximum adsorption capacity obtained from the Langmuir model fitting was 104 mg/g. Considering that 15% bentonite was added to the granules as binders, the maximum adsorption capacity of granular zeolites should be around 90 mg/g.

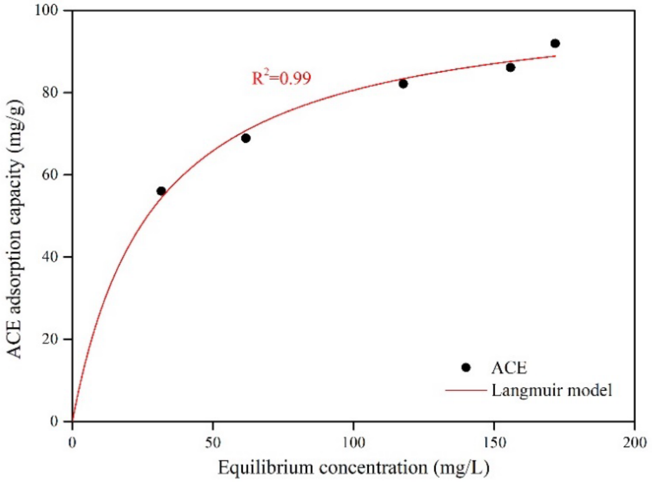


Fig. 2. The adsorption isotherms of ACE by Beta zeolite, Langmuir model fitting

Table 2. Isotherm constants for ACE adsorption by Beta zeolite

| OMP | Langmuir model | | |
|---|---|---|---|
| | $K_L$ (L/mg) | $Q^0_{max}$ (mg/g) | $R^2$ |
| ACE | 0.035 | 104 | 0.99 |

### *3.2. Influence of water content, ozone gas flow and ozone concentration on regeneration efficiency*

The influence of water content in granules on the ACE regeneration efficiency of 2160 mg of ozone exposure is shown in Fig. 3. The ACE regeneration efficiency increased from 16% to 81% when the water content decreased from 40% to 0% (percentage by weight). 40% is the water content in wet granules after draining the column. The ACE regeneration efficiency was only 39% at 35% water content. However, the regeneration efficiency at 30% water content was almost double, reaching 74% when only an additional 5% of water was removed. The ACE regeneration efficiency of granules with 0% and 21% water content was 81%. It was remarkable that when the granules were partially dried (water content 30%), the ACE regeneration efficiency was 74%, close to the regeneration efficiency level of totally dried granules. The ozone concentration of in-gas and off-gas against time at various water contents is shown in Fig. 4. The ozone concentration in the off-gas increased along with time. The off-gas ozone concentration at 30% water content was lower than that at 35% water content. It indicated that more ozone was consumed. When only 5% more water was removed, more outer space in granules was dry, and the gaseous ozone could easily diffuse into the granules to degrade the adsorbed ACE. Meanwhile, the heat released in the reaction between ozone and ACE could further dry the granules. Thus, the degradation of ACE was promoted. This assumption may explain the doubled regeneration efficiency at 30% water content compared to 35% water content. It suggests that the water content significantly influenced the ACE degradation on granules. Furthermore, there was a significant difference between the ozone consumption of granules with 0% and 21% water content. More ozone (approximately 900 mg, calculated from the blue area) was consumed to regenerate granules with 0% water content. After regeneration, the remained ACE and generated substances in the granules were extracted by pure methanol. HPLC peaks of the samples extracted from the granules with 0% and 21% water contents are shown in Fig. 5. In contrast to Fig. 5b (21% water content), a broad peak was observed at the retention time of 2.8 min in Fig. 5a (0% water content). It indicated the presence of an intermediate product generated in ozonation. This intermediate had a longer retention time than ACE in the chromatographic column. Therefore, it was probably a more apolar compound compared to ACE. According to the ACE degradation pathway (Skoumal et al. 2006), only one apolar compound, benzoquinone, formed during ozonation. HPLC peaks of only ACE and benzoquinone are shown in Fig. 5c. Benzoquinone had a peak at a retention time of 2.4 min. It might be possible that a mixture of benzoquinone-type intermediates was generated during the regeneration of granules with 0% water content.

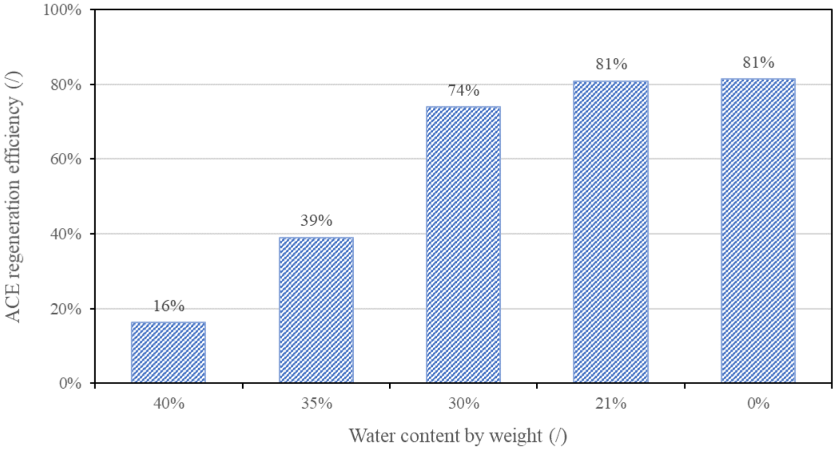


Fig. 3. The influence of water content in granules on the ACE regeneration efficiency of 2160 mg ozone dose

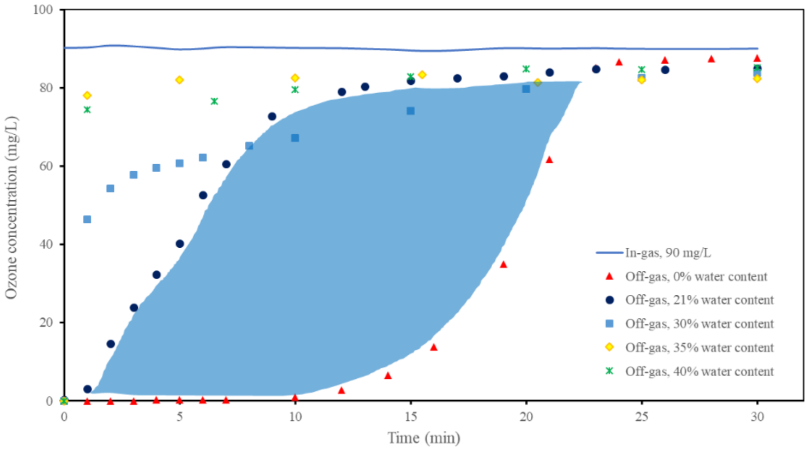


Fig. 4. Ozone concentration of in-gas and off-gas as a function of time under different water content

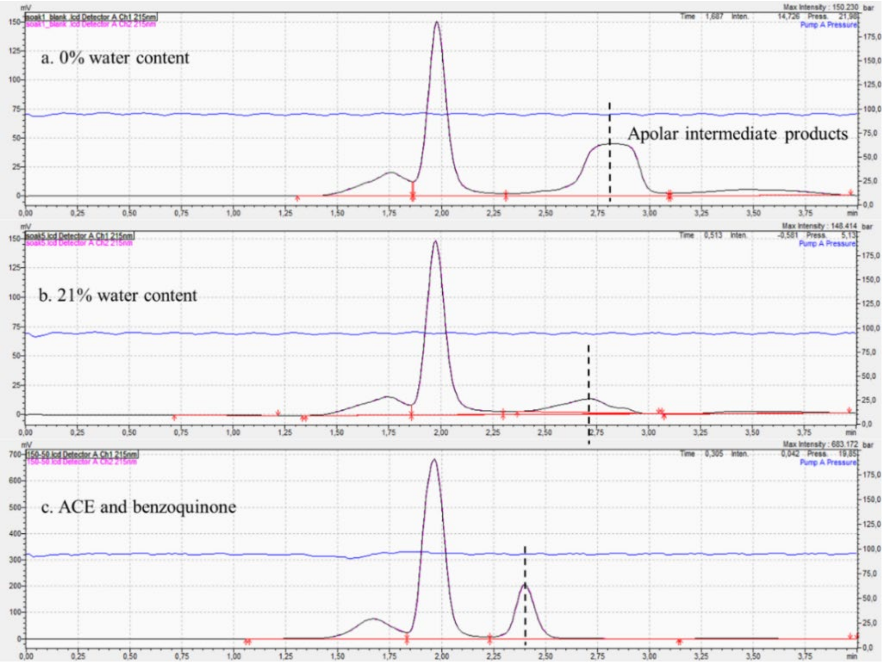


Fig. 5. HPLC peaks: a. extraction from granules with 0% water content; b. extraction from granules with 21% water content; c. samples of ACE and benzoquinone prepared with methanol

The influence of gas flow and ozone concentration on ACE regeneration efficiency is shown in Fig. 6 and 7, respectively. It can be seen that the ACE regeneration efficiency decreased from 95% to 56% as the ozone gas flow rate increased from 0.2 to 0.8 L/min. Furthermore, the ACE regeneration efficiency decreased from 74% to 46% as the ozone concentration increased from 50 to 150 mg/L. The total ozone dose was constant in these experiments. Therefore, the exposure time was shorter at a higher gas flow or gas concentration. Considering the ozonation duration was longer at a low ozone gas flow rate and ozone concentration, it can be inferred that ozone had more time to diffuse into the inner pores of zeolites. Therefore, more ACE adsorbed on granules was degraded. This result suggests that a complete degradation of ACE can be reached if the ozonation duration is long enough.

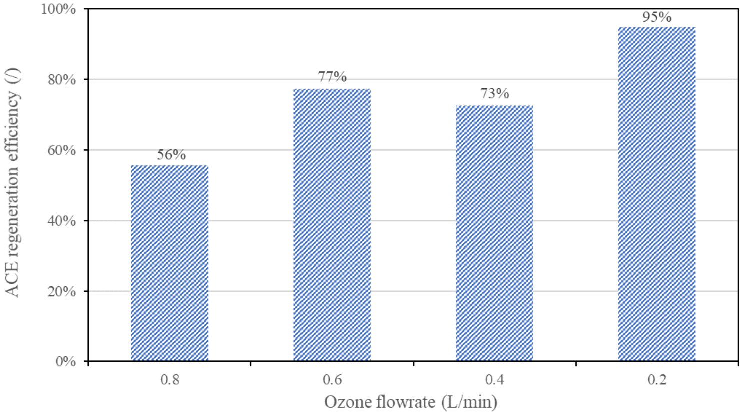


Fig. 6. The influence of gas flow on ACE regeneration efficiency of 900 mg ozone dose

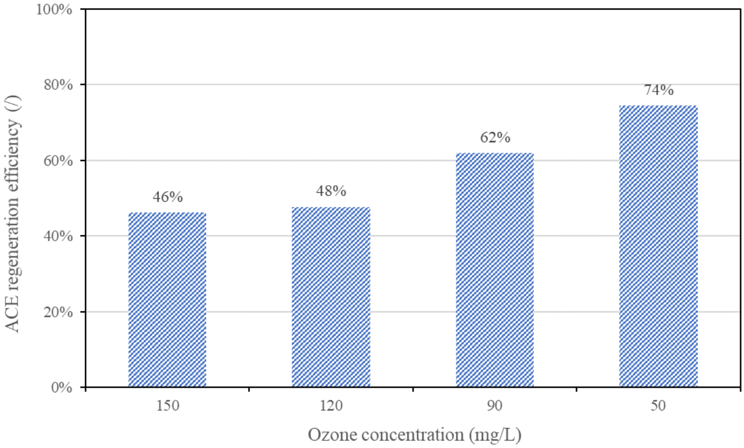


Fig. 7. The influence of ozone concentration on ACE regeneration efficiency of 540 mg ozone dose

### *3.3. Influence of drained-bed and dried-bed regeneration on regeneration efficiency and intermediate product formation*

Ozone concentrations in in-gas and off-gas as a function of time for drained-bed and dried-bed regeneration tests are shown in Fig. 8 and 9, respectively. The concentration difference between in-gas and off-gas is contributed by the decay of ozone, the dissolving of ozone in the water films on granules, and the consumption of ozone by the ACE adsorbed on granules. In addition, the ACE regeneration efficiency as measured by extraction is shown. The breaks are the sampling time interval, approximately 15 min.

The ozone concentration in the off-gas in the drained-bed test (Fig. 8) increased rapidly and reached 82 mg/L after running for 3 hours. The degradation of ACE only occurred when ozone diffused into the water films on granules. The ACE regeneration efficiency was below 10%. These results suggest that drained-bed regeneration is not effective in regenerating granules. By comparison, in dried-bed regeneration, as shown in Fig. 9, the ozone concentration in the off-gas increased after 3 hours. The ACE regeneration efficiency reached 100% after introducing ozone to the dried-bed column for 6 hours. When ACE in granules was decomposed completely, the ozone concentration in the off-gas increased rapidly and approached the level of the in-gas concentration (90 mg/L). The regeneration efficiency increased earlier than the increase of the off-gas ozone concentration because after decomposing all the ACE, more ozone was consumed for the degradation of intermediates. The reaction phenomenon of dried-bed regeneration is presented in Fig. 10. The degradation of ACE adsorbed on granules by ozone occurred layer by layer from top to bottom in the packed column. A yellowish layer was generated along with a formation of water vapour (near the layer) and a heat release (around 60 °C) during the reaction of ozone and ACE. When the yellowish layer moved to the sampling point at the bottom of the column (Fig. 10c, ozonation duration 3 h), the ACE regeneration efficiency started increasing (as shown in Fig. 9). According to the ACE degradation pathway (Skoumal et al. 2006), its degradation is initiated by the attack of ozone on C(4)-position forming hydroquinone with the release of acetamide. Further oxidation of hydroquinone generates benzoquinone. In consecutive steps, this product is degraded to a mixture of glyoxylic acid, ketomalonic acid and maleic acid. The mixture is converted into oxalic acid as the ultimate product. In the degradation pathway, benzoquinone is the only intermediate with a yellowish colour. Therefore, when the yellowish layer disappeared, the degradation of ACE came to the next step. This phenomenon matched well with the results of the small column tests. These results indicated that dried-bed regeneration could effectively degrade the ACE adsorbed on zeolite granules. It is worth mentioning that there was no desorption during regeneration, which was confirmed by the same removal efficiency in the first 2 h (Fig. 9). The mass of ACE extracted from the samples by methanol was the same.

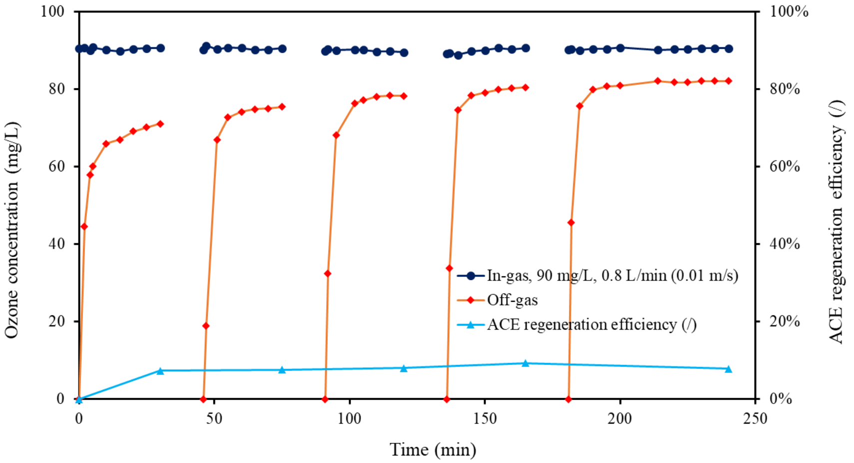


Fig. 8. Ozone concentration in in-gas and off-gas along time and ACE regeneration efficiency at each sampling point from the drained-bed regeneration test in a big column

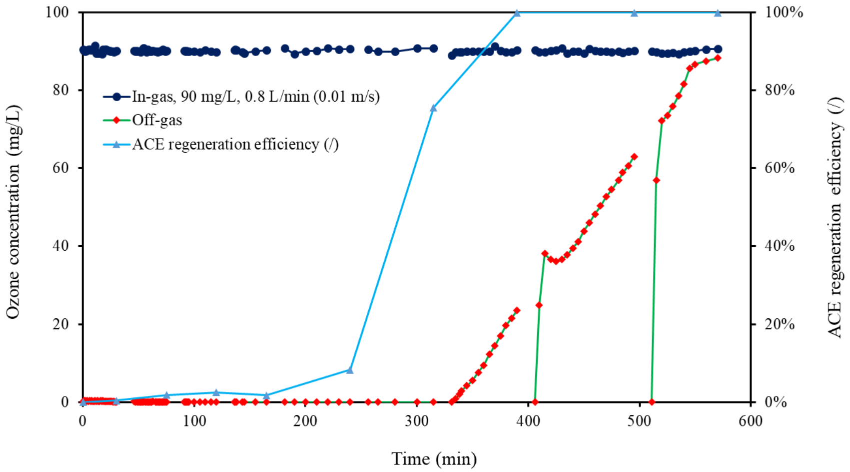


Fig. 9. Ozone concentration in in-gas and off-gas along time and ACE regeneration efficiency at each sampling point from the dried-bed regeneration test in a big column

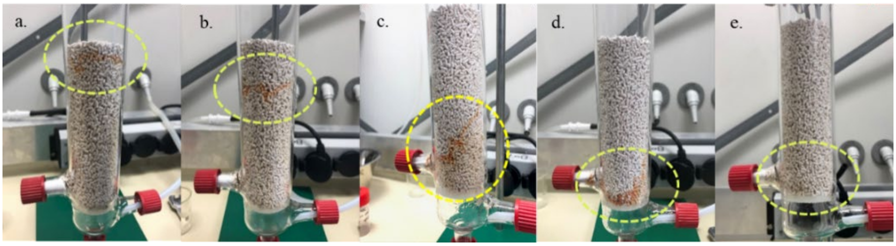


Fig. 10. Experimental phenomenon in dried-bed regeneration at different runtime: a. 3 min; b. 45 min; c. 3 h; d. 4 h; e. 7.5 h. (ozone gas flow from top to bottom)

### *3.4. Influence of adsorption-regeneration cycles on adsorption capacity*

ACE adsorption capacity recovery decreased by 7% from 93% to 86% after three adsorption-regeneration cycles with ozone (Fig. 11). A hypothesis may be that some undissolved intermediates generated from an incomplete degradation remained in the granules. After that, the accumulation of the undissolved intermediate breakdown products adsorbed on the granules resulted in a slight decrease in the recovery rate after each regeneration cycle. The adsorption capacity of fresh granules and the granules after sequential gaseous ozone treatment cycles is shown in Fig. 12. ACE adsorption capacity only decreased by 3% from 91 mg/g to 88 mg/g. This result indicated that gaseous ozone did not influence the adsorption of ACE on zeolite granules.

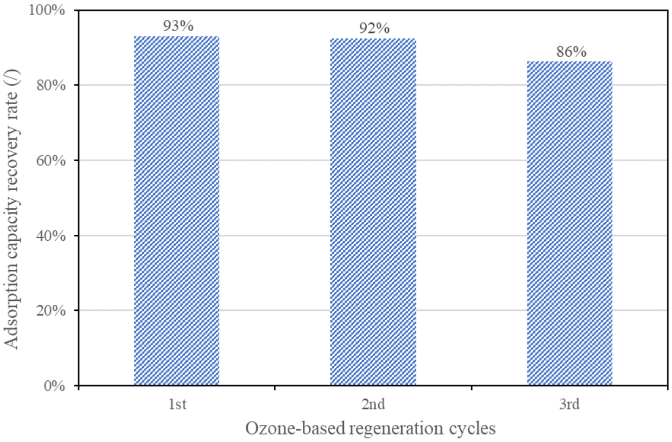


Fig. 11. ACE adsorption capacity recovery rate after each ozone-based adsorption-regeneration cycle

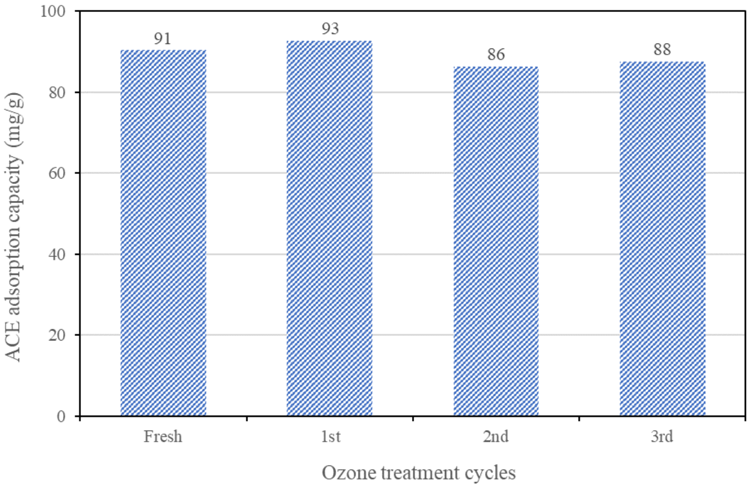


Fig. 12. ACE adsorption capacity of fresh granules and the granules after sequential gaseous ozone treatments

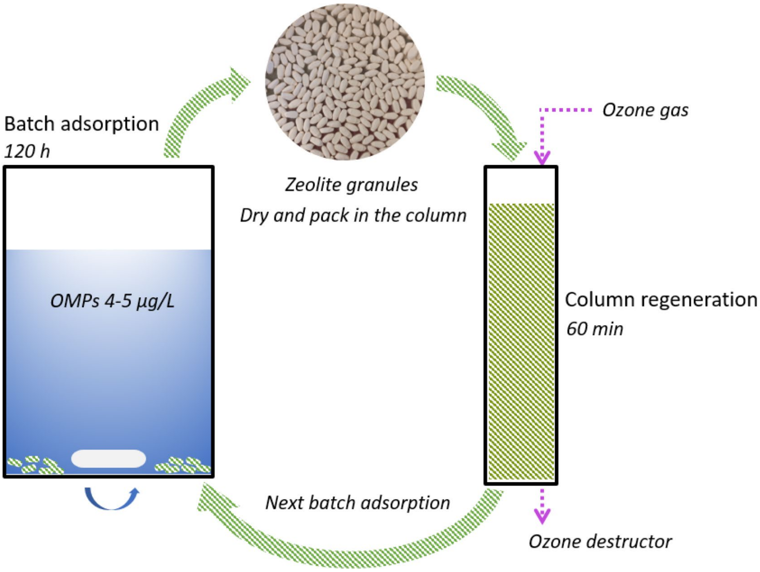
## 4. Conclusions

This study investigated the regeneration of granular zeolites loaded with ACE by applying gaseous ozone. The conclusions derived from this study are:

- Ozone-based regeneration of totally dried zeolite granules (0% water content) is more efficient than fully wet granules (collected directly after draining the column, 40% water content).
- At the same total ozone dose (g/h), longer ozonation duration results in higher regeneration efficiency. If the ozonation duration is long enough, the adsorbed ACE can be degraded completely.
- Gaseous ozone does not influence the adsorption capacity of zeolites for ACE. The accumulation of intermediates in granules has a minor influence on the adsorption capacity recovery in the long run.
- Since ACE is an easy organic compound, which can be easily degraded by ozone, further research should be carried out with different OMPs. Moreover, the study on a complex wastewater matrix is also of great interest for practical applications.

# Chapter 4

## Removal of organic micropollutants by well-tailored granular zeolites and subsequent ozone-based regeneration



This chapter is based on

M. Fu, J. Wang, B. Heijman, J.P. van der Hoek, Removal of organic micropollutants by well-tailored granular zeolites and subsequent ozone-based regeneration, Journal of Water Process Engineering 44 (2021) 102403.

## Abstract

Advanced technologies to remove organic micropollutants (OMPs) from municipal wastewater have gained much attention over the last decades. Adsorption by zeolites is one of these technologies. This study evaluated the regeneration performance of well-tailored granular zeolites loaded with OMPs. The selected OMPs were categorized into three groups due to the adsorption performance: high, medium and low adsorbance. Gaseous ozone was directly applied to regenerate dried zeolite granules at an ozone concentration of 30 mg/L and a gas flow rate of 0.2 L/min (0.04 m/s). For the high- and medium-adsorbing OMPs, 45 min of ozonation was long enough to restore their adsorption capacity fully. For the low-adsorbing OMPs, the regeneration efficiency reached 60% after 60 min of ozonation. Interestingly, their recovered adsorption capacities first decreased and subsequently increased along with the ozonation duration. The dramatic decrease was most probably due to the presence of the transformation products generated from the ozonation of some selected OMPs. In seven sequential adsorption-regeneration cycles, the adsorption capacity for 75% of the selected OMPs was fully recovered at an ozonation duration of 60 min in each regeneration. The assumed accumulation of the ozonation transformation products only influenced the adsorption of low-adsorbing OMPs in seven cycles.

## 1. Introduction

The presence of organic micropollutants (OMPs) in the aquatic environment has become an increasing problem for the quality of aquatic ecosystems and the production of drinking water from surface water in the last decades. OMPs occur in water bodies at trace levels (between a few ng/L and several µg/L), comprising pharmaceuticals, plant protection products, personal care products, and industrial chemicals. Many enter the aquatic environment via municipal wastewater treatment plants (WWTPs) (Loos et al. 2013). The low concentration both increases the difficulties of detection and analysis, and also brings challenges for wastewater treatment (Luo et al. 2014). The conventional municipal WWTPs are designed to control various substances, including particulates, carbonaceous substances, nutrients and pathogens. These substances can be efficiently and consistently eliminated (Luo et al. 2014). However, traditional WWTPs are not designed to remove OMPs (Rout et al. 2020), and the average removal efficiency ranges from 30% to 65% (Bolong et al. 2009). Thus, many of the OMPs pass through the wastewater treatment processes. The occurrence of OMPs and their fate and removal from wastewater were reviewed in many studies in the last decades (Ahmed et al. 2017, Barbosa et al. 2016, Bolong et al. 2009, Loos et al. 2013, Luo et al. 2014, Mompelat et al. 2009, Pomies et al. 2013, Reemtsma et al. 2006, Rout et al. 2020). OMPs are becoming a severe threat to aquatic life as it is associated with many adverse effects, such as short-term and long-term toxicity, endocrine disrupting effects and antibiotic resistance of microorganisms (Fent et al. 2006). For this reason, the Dutch Ministry of Infrastructure and Water Management lists 11 compounds as target substances to monitor the effectiveness of novel treatment technologies for removing OMPs from wastewater (Ministry of Infrastructure and Water Management 2020).

Adsorption is an effective technology to remove OMPs. Activated carbons are widely used as adsorbents to treat municipal wastewater (Beijer et al. 2017, Reungoat et al. 2010a). Currently, ozonation followed by granular activated carbon filtration is applied to remove pharmaceuticals from municipal treatment effluents (Reungoat et al. 2010a). After the adsorbent is exhausted, it has to be regenerated or replaced to regain the adsorption capacity. Thermal reactivation is commonly used to regenerate exhausted activated carbons (Narbaitz and McEwen 2012). As an alternative, oxidative technologies, especially ozonation, can potentially regenerate the exhausted adsorbents (Zhang et al. 2014). However, ozone can attack and destroy the structure of activated carbons (Valdés et al. 2002). Thus, ozonation is not suitable for the regeneration of activated carbons. Recently, hydrophobic zeolites were evaluated as alternative adsorbents. Their structure with uniform small pores (a few Å) makes them attractive for selective uptake of OMPs from wastewater containing natural organic matter (NOM) (De Ridder et al. 2012, Jiang et al. 2018). Moreover, ozonation can effectively regenerate zeolites after the adsorption of OMPs without changing their structure properties (Ma et al. 2019).

However, a limited number of studies are available, and they all focus on the regeneration of powdered zeolites by ozone in the water phase. ZSM-5 zeolite with a high ratio of Si/Al could highly concentrate the ozone dissolved in water (Fujita et al. 2004a). This property promoted the removal of trichloroethene, 2-methylisoborneol and ibuprofen during simultaneous injections of ozone-dissolved water and pollutant-feed water to a zeolite-packed column (Fujita et al. 2004b, Ikhlaq et al. 2014, Sagehashi et al. 2005b). Reungoat et al. (Reungoat et al. 2007) found that zeolites with a higher ratio of Si/Al had a better removal of nitrobenzene. They obtained a complete removal of nitrobenzene in the presence of powdered zeolites during ozonation in semi-batch mode. Ma et al. (Ma et al. 2019) obtained a 97% recovery of the adsorption of sulfamethoxazole on powdered ZSM-5 in sequential adsorption and ozonation regeneration.

Considering that powdered zeolites have difficulties in practical application, granular zeolites should be investigated. The use of granular material in fixed-bed reactors is a well-known technology in water treatment. Unfortunately, these studies are rarely reported. Some studies reported about applying ozone in the water phase. An effective adsorption of trichlorophenol was kept in eight cycles by using FAU granular zeolites and an ozone-bubbling system (Zhang et al. 2014). However, this study was carried out in semi-batch mode. This study proposed a hypothesis that the intermediates formed in ozonation might influence the adsorption capacity of trichlorophenol. Unfortunately, further identification was missing to prove this hypothesis. Simultaneously applying adsorption and ozonation in a fixed bed column packed with FAU granules enhanced the removal performance of nitrobenzene (Reungoat et al. 2010b). A study by Zhang et al. [26] reported sequential adsorption-regeneration, in which ozone was applied in the gas phase. The regeneration process was carried out in a column packed with dried zeolite granules. The granules consisted of only one type of zeolite, FAU. The adsorption capacity of trichlorophenol on FAU granules noticeably increased in three adsorption-regeneration cycles (Zhang et al. 2016). An intensive interaction of ozone and zeolite was hypothesized. Our previous study found that the adsorption capacity of acetaminophen on FAU granules was effective in three cycles (Fu et al. 2020). This study revealed that lower water content in granules significantly increased the ozone-based regeneration performance, applying ozone in the gas phase.

The current study aimed to evaluate the regeneration performance of well-tailored zeolite granules loaded with OMPs. In this study, for the first time, a mixture of three types of zeolites was prepared in granular form and applied to adsorb a broad range of OMPs from water. After adsorption, ozone-based regeneration was conducted in the gas phase instead of the water phase, as commonly applied. This process setup, using zeolites in the form of granules and ozone in the gas phase, is promisingly applicable in water technology practice. Before applying for the treatment of real wastewater, this study was a proof of principle starting with demi-water. Eleven OMPs requested by the Dutch Ministry of Infrastructure and Water Management (Ministry of Infrastructure and Water Management 2020) were applied in the current study, including sotalol, metoprolol, propranolol, trimethoprim, clarithromycin, sulfamethoxazole, benzotriazole, methyl-benzotriazole, carbamazepine, diclofenac, and hydrochlorothiazide.

The objectives of this study were first to study the adsorption performance of the selected OMPs on zeolite granules by conducting adsorption isotherms and kinetics tests, secondly to determine the optimum loading duration, thirdly to assess the regeneration performance at varying ozonation durations, fourthly to discuss the influence of the ozonation transformation products on the adsorption capacity, and finally to study the change in adsorption capacity for the selected OMPs in seven sequential adsorption-regeneration cycles at the optimum loading and regeneration duration for an overall evaluation of the long-term performance.

## 2. Materials and Methods

### *2.1. Zeolite adsorbents*

High silica zeolite powders were supplied by Tosoh Corporation, Japan. The chemical composition is $HO\cdot Al_2O_3\cdot xSiO_2\cdot nH_2O$. Three types of synthetic zeolites with different framework structures were applied in this research. They were Beta (BEA), Mordenite (MOR), and ZSM-5 (MFI), respectively. Their framework structure was illustrated by Baerlocher et al. (Baerlocher et al. 2007). Different from natural zeolites, which are mostly hydrophilic with a low Si/Al ratio, synthetic high-silica zeolites are evaluated as feasible adsorbents to uptake OMPs (Jiang et al. 2018, 2020). Zeolite with a higher ratio of Si/Al was efficient in adsorbing OMPs (Reungoat et al. 2007). The characterizations of the selected high silica zeolites were studied in a previous study by our research group (Jiang et al. 2020). Their chemical characteristics are listed in Table 1.

Granular zeolites were produced by a 3D clay printer supplied by VormVrij. Zeolite powders of BEA, MOR, and MFI were mixed uniformly with a mass ratio of 1:1:1. Bentonite (Sigma-Aldrich), as a binder, was added at 15% by weight. After adding demi-water, the uniformly mixed paste was packed in the cartridge of the 3D clay printer. The paste was extruded out in grain form as pre-programmed in the software. The size of the granules was 1 mm in diameter and 2-3 mm in length. After that, the granules were sintered at 950 °C for 2 hours to enhance the mechanical strength.

### *2.2. Organic micropollutants*

All the OMPs were purchased from Sigma-Aldrich. As propranolol, clarithromycin, and hydrochlorothiazide in the demi-water samples were poorly quantified, the other eight OMPs were the target OMPs in the current study. Their physicochemical and structural properties are listed in Table 2.

### *2.3. Adsorption tests*

All the adsorption tests were carried out in batch mode at 20 °C. Before the adsorption tests, eight selected OMPs were spiked to demi-water at 4-5 µg/L. The effect of ozone on the adsorption behaviour of zeolites was studied. The detailed ozone treatment procedure is described in section 2.4.

#### *2.3.1. Determination of the effect of ozone on adsorption*

2 g of fresh granules were packed in a column, which was 10 mm in diameter and 25 cm in length. The granules were treated with gaseous ozone for 1 hour at an ozone concentration of 90 mg/L and a flow rate of 0.8 L/min (0.16 m/s). After gaseous ozone

treatment, various amounts (ranging from 0 to 1 g/L) of fresh and ozone-treated granules were added to several 1 L glass bottles. The granules were pulverized in the bottles before adding 1 L prepared OMPs solution to obtain equilibrium adsorption in a short time. The solutions were stirred at 200 rpm for 48 hours to obtain equilibrium adsorption. Before and after adsorption, water samples were taken and measured with LC-MS to determine the concentrations of OMPs.

#### *2.3.2. Determination of optimum loading duration*

0.5 g of fresh granules were dosed into 1 L prepared OMPs solution to determine the optimum loading duration. The solution was stirred at 100-120 rpm for 288 h. At this low stirring rate, the full granules remained at the bottom of the bottle while only the solution was moving in the bottle. The low stirring rate was set to prevent any abrasion of the granules during adsorption. Water samples were taken at different time intervals. The concentrations of OMPs in the samples were measured with LC-MS.

### *2.4. Ozone-based regeneration*

Ozone-based regeneration tests were carried out in a column packed with zeolite granules loaded with OMPs, using the optimum loading duration determined as described in section 2.3.2. Gaseous ozone was introduced in down-flow mode in the column. The column size was 10 mm in diameter and 25 cm in length. An ozone setup supplied by Wedeco (Xylem Water Solutions Herford, GmbH) was installed in a fume hood. An ozone generator (Modular 4 HC) produced ozone from pure oxygen. The maximum ozone production was 4 g/h. Two ozone analysers (BMT 964, Messtechnik, GmbH) were applied to monitor the ozone concentration of the feed gas and the outflow. The experimental setup was illustrated in our previous research (Fu et al. 2020). The regeneration performance was determined by comparing the OMPs loading on zeolite granules before and after regeneration. The OMPs loading was measured in a limited amount of adsorption time derived from section 2.3.2.

#### *2.4.1. Optimum ozonation duration*

The adsorption before regeneration was conducted by adding 0.5 g of fresh zeolite granules to 1 L prepared OMPs solution. The adsorption process was run for the same duration as the optimum loading duration obtained from section 2.3.2. After adsorption, the granules were dried overnight at 50 °C in the oven. Dried granules were packed in the column for regeneration. Varying ozonation durations from 0 to 60 min were applied. The gaseous ozone conditions were set at an ozone concentration of 30 mg/L and a gas flow rate of 0.2 L/min (0.04 m/s). After regeneration, the granules were collected for the second adsorption with the same procedure to obtain the loading. Water samples were taken before and after each adsorption. The concentrations of OMPs in the samples were measured with LC-MS.

### 2.4.2. Ozonation transformation products

To further study the influence of the ozonation transformation products remaining in the granules, pure methanol was applied to extract the possible transformation products from the granules used for different ozonation durations. After the second adsorption, the granules were dried at 50 °C in the oven overnight. Dried granules were then pulverized and added to 100 mL pure methanol. After stirring for 120 h, liquid samples were taken and analysed with LC-MS.

### 2.4.3. Long-term adsorption-regeneration

The long-term regeneration performance was evaluated in seven sequential adsorption-regeneration cycles. The sequential adsorption-regeneration procedure is shown in Fig. 1. In each adsorption-regeneration cycle, the adsorption procedure was performed the same as aforementioned in section 2.4.1. The regeneration procedure lasted for 60 min with a total ozone dose of 0.36 g/h. The gaseous ozone conditions were set the same as described in section 2.4.1. Water samples were taken before and after each adsorption. The concentrations of OMPs in the samples were measured with LC-MS. All the adsorption and regeneration tests were conducted in triple.

### 2.4.4. Calculations

Relative adsorption capacity (Rq) was introduced to represent the regeneration performance. It was calculated by:

$$\mathrm{Rq} = q_n / q_1$$

where $q_n$ (μg/g) was the loading of the granules after a fixed time in the nth adsorption; $q_1$ (μg/g) was the loading of the fresh granules after a fixed time in the first adsorption. When the Rq reached 1, it indicated that the regeneration was successful and the adsorption capacity of zeolite granules was fully restored.

Table 1. Structural and chemical characteristics of three types of high silica zeolites

| Type | Pore opening size[a] (Å*Å) | Surface area (m²/g) | Micro-pore surface area (m²/g) | Pore volume (cm³/g) | Micro-pore volume (cm³/g) | Si/Al ratio (XRF) | BAS[b] (μmol/g) | LAS[c] (μmol/g) | Reference |
|---|---|---|---|---|---|---|---|---|---|
| BEA | 6.6*7.7<br>5.6*5.6 | 516 | 351 | 0.3022 | 0.1557 | 286 | 16 | 7 | Jiang et al. (Jiang et al. 2020) |
| MOR | 6.5*7.0<br>2.6*5.7 | 431 | 360 | 0.2687 | 0.1606 | 113 | 52 | 8 | Jiang et al. (Jiang et al. 2020) |
| MFI | 5.1*5.5<br>5.3*5.6 | 359 | 199 | 0.5341 | 0.0891 | 42 | 142 | 40 | Jiang et al. (Jiang et al. 2020) |

[a] Two channel systems are interconnected at right angles (Baerlocher et al. 2007).

[b] Brønsted acid sites

[c] Lewis acid sites

Table 2. Physicochemical and structural properties of the selected OMPs

| Name | Molecular formula | CAS | | Molecular weight (g/mol) | pKa[a] | Charge at pH5.8[a] | Min. projection radius (Å)[a] | Max. projection radius (Å)[a] | Application |
|---|---|---|---|---|---|---|---|---|---|
| Sotalol (SOT) | $C_{12}H_{20}N_2O_3S$ | | 27948-47-6 | 272 | 9.43 | + | 4.21 | 7.94 | Betablocker |
| Metoprolol (MP) | $C_{15}H_{25}NO_3$ | | 51384-51-1 | 267 | 9.67 | + | 4.39 | 10.07 | |
| Trimethoprim (TMP) | $C_{14}H_{18}N_4O_3$ | | 738-70-5 | 290 | 7.16 | + | 4.97 | 6.95 | Antibiotic |
| Sulfamethoxazole (SMX) | $C_{10}H_{11}N_3O_3S$ | | 723-46-6 | 253 | 6.16 | -/0[b] | 5.4 | 5.88 | |
| Benzotriazole (BT) | $C_6H_5N_3$ | | 95-14-7 | 119 | 9.04 | 0 | 3.66 | 4.12 | Corrosion inhibitors |
| Methyl-benzotriazole (MeBT) | $C_7H_7N_3$ | 4-MeBT | 29878-31-7 | 133 | 9.29 | 0 | 4.05 | 4.43 | |
| | | 5-MeBT | 136-85-6 | 133 | 9.12 | 0 | 3.82 | 4.67 | |
| Carbamazepine (CBZ) | $C_{15}H_{12}N_2O$ | | 298-46-4 | 236 | 15.96 | 0 | 4.48 | 5.76 | Anti-epileptic |
| Diclofenac (DIC) | $C_{14}H_{11}Cl_2NO_2$ | | 15307-86-5 | 296 | 4 | - | 4.62 | 6.34 | Analgesics/Anti-inflammatories |

[a] Estimated by Chemicalize Platform; +, positively charged; -, negatively charged; 0, neutral

[b] Negatively charged and neutral SMX molecules simultaneously existed at pH 5.8, the contribution of negatively charged form is 30 %

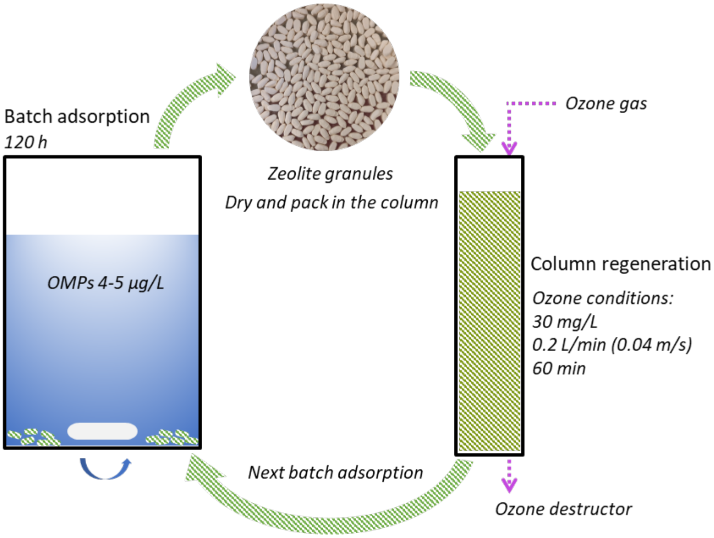


Fig. 1. Sequential adsorption-regeneration procedure

### 2.5. LC-MS analysis

All the samples were filtered over 0.2 µm polycarbonate syringe filters before analysis. The OMPs in demi-water and methanol were analysed by a UPLC-MS/MS system (Waters, ACQUITY UPLC I-Class, Xevo TQ-S micro fitted with the ESI) equipped with a C18 column (ACQUITY UPLC™ BEH 2.1 x 50 mm, 1.7 µm particle size). The elution flow rate was set at 0.35 mL/min with 95% ultrapure water acidified with 0.1% formic acid and 5% acetonitrile. The oven temperature was 40 °C. MS provides specific and sensitive detection of multiple OMPs. The compounds are ionized first and separated based on their mass-to-charge ratios (*m/z*). The mass spectrum at each retention time point provides the molecular mass and structural information. An internal standard (IS) for each OMP was added in equal amounts to the calibration standards (0.0025 - 10 µg/L) and unknown samples. By adding an IS for quantitation, the measurement variations can be corrected, and then the accuracy of the results is improved (Tan et al. 2012). Limits of detection (LOD) and quantitation (LOQ), and the retention time for each compound are listed in Table 3.

Table 3. LOD, LOQ and retention time for each OMP in LC-MS analysis

| OMPs | LOD (μg/L) | LOQ (μg/L) | Retention time (min) |
|---|---|---|---|
| Sotalol (SOT) | 0.017 | 0.05 | 1.28 |
| Metoprolol (MP) | 0.017 | 0.05 | 2.21 |
| Trimethoprim (TMP) | 0.003 | 0.01 | 2.10 |
| Sulfamethoxazole (SMX) | 0.003 | 0.01 | 2.31 |
| Benzotriazole (BT) | 0.003 | 0.01 | 2.13 |
| Methyl-benzotriazole (MeBT) | 0.003 | 0.01 | 2.29 |
| Carbamazepine (CBZ) | 0.017 | 0.05 | 2.50 |
| Diclofenac (DIC) | 0.017 | 0.05 | 2.91 |

## 3. Results and Discussion

### *3.1. Determination of loading duration*

The decrease of the concentrations of eight selected OMPs as a function of time is shown in Fig. 2. The eight OMPs were categorized into three groups by their removal efficiencies after 288 h adsorption. SOT, MP, and TMP were the high-adsorbing OMPs with removal efficiency above 99 %. BT, MeBT, and SMX were the medium-adsorbing OMPs. For BT and SMX, their removal efficiencies were around 70 %. For MeBT, its removal efficiency was 88 %. The adsorption isotherms of the medium-adsorbing OMPs were interpreted with the Freundlich model (Fig. S1, Supplementary Information). CBZ and DIC were the low-adsorbing OMPs. Their removal efficiencies were around 20 %. For the high-adsorbing OMPs, their concentrations decreased from around 4 μg/L to 0 μg/L after 120 h. They were adsorbed faster than the other two categories. For the medium-adsorbing OMPs, the adsorption equilibrium was reached after 250 h. The concentration of MeBT at the start was around 8 μg/L, as the same amounts of 4-MeBT and 5-MeBT were spiked in the solution. The LC-MS recognized them as the same compound. The low-adsorbing OMPs were slightly removed. The concentration of CBZ decreased from 4 μg/L to 3 μg/L after 120 h, while the concentration of DIC decreased from 4 μg/L to 3.2 μg/L after 240 h. It indicated that all the high-adsorbing OMPs were completely removed after 120 h of adsorption. The concentrations of the medium-adsorbing OMPs still decreased slowly after 120 h, while the concentrations of the low-adsorbing OMPs remained constant. The results suggest that the loading duration applied in the adsorption tests to indicate regeneration performance is appropriate around 120 h. If the loading duration was shorter than 120 h, 50 h for instance, the uptake of OMPs was still in the rapid adsorption zone. The relative adsorption capacity for the high- and medium-adsorbing OMPs would be estimated high, as there were many remaining available adsorption sites. If the loading duration was longer than 120 h, 200 h for instance, the relative adsorption capacity for the target OMPs would most likely be close to 1 because the same loading of OMPs could be reached in a long adsorption duration with a slower adsorption rate in the second loading process after regeneration. In both cases, the regeneration performance could not be well determined.

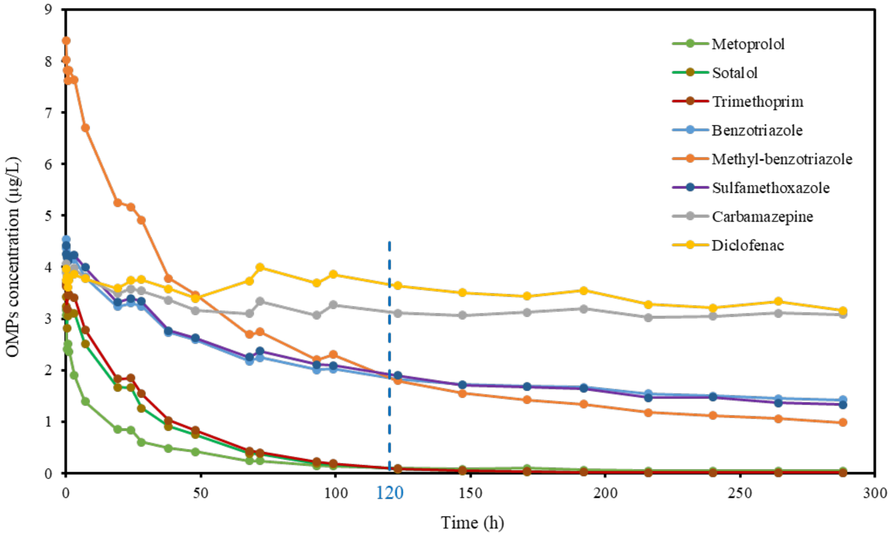


Fig. 2. The concentrations of OMPs as a function of loading time
(initial concentration of OMPs at 4-5 μg/L, zeolite granules dosage at 0.5 g/L)

### *3.2. Optimum ozone-based regeneration duration*

The regeneration performance of zeolite granules loaded with OMPs at different ozonation durations is shown in Fig. 3 – 5. It is worth mentioning that gaseous ozone did not affect the adsorption capacity of OMPs on zeolite (Table S1, Supplementary Information). Our previous study also found the same results (Fu et al. 2020). For the high-adsorbing OMPs, their relative adsorption capacities (Rq) remained 1 after all ozonation durations (Fig. 3). It indicated that many adsorption sites were available on zeolites for the high-adsorbing OMPs. Therefore, when no regeneration was applied, the Rq could also reach 1. The Rq of the medium-adsorbing OMPs gradually increased along with the ozonation duration (Fig. 4). The Rq of BT and MeBT increased from 0.64 at 0 min ozonation to 1 at 45 min ozonation, while the Rq of SMX increased from 0.84 at 0 min ozonation to 1 at 30 min ozonation. The results indicated that 45 min of ozonation was long enough for the zeolite granules to restore the adsorption capacity of the high- and medium-adsorbing OMPs.

For the low-adsorbing OMPs, the Rq reached around 0.6 at 60 min ozonation (Fig. 5a). Interestingly, the Rq of CBZ reached 0.56 at 5 min ozonation and dramatically decreased from 0.56 to 0.24 at 20 min ozonation. Subsequently, the Rq increased to 0.59 at 60 min ozonation. A similar pattern was found for DIC. The Rq of DIC reached 0.63 at 5 min ozonation, decreased to 0.31 at 30 min ozonation, and eventually reached 0.63 at 60 min ozonation. To further study the influence of the ozonation duration, the regeneration performance of the adsorption of only CBZ, instead of a mixture of OMPs, is shown in Fig. 5b. The Rq of CBZ increased from 0.15 to 0.7 at 10 min ozonation, and remained around 0.53 at 20 min ozonation. The assumption for the tendency of CBZ in Fig. 5b was that at a short ozonation duration (10 min), the adsorption sites on zeolites for CBZ were released, but not completely. This assumption was due to the rapid reaction of ozone and the double bond in CBZ (Mcdowell et al. 2005). Meanwhile, many transformation products containing quinazoline groups were generated during the ozonation of CBZ (Hübner et al. 2014). The ozonation transformation products of CBZ adsorbed on zeolites and/or the not long enough ozonation duration may result in a low Rq around 0.5 after 60 min ozonation.

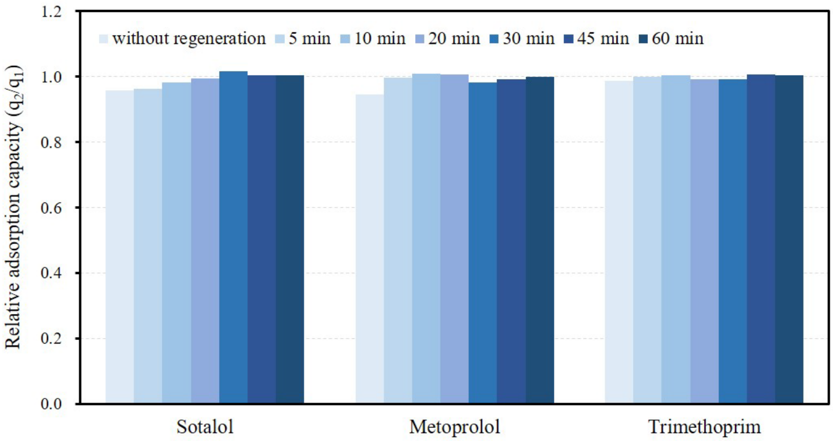


Fig. 3. Regeneration performance of high-adsorbing OMPs (SOT, MP, and TMP) after varying ozonation durations

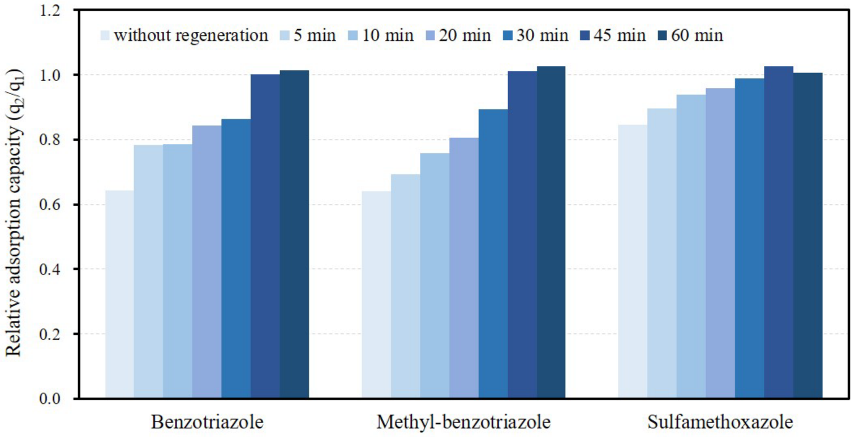


Fig. 4. Regeneration performance of medium-adsorbing OMPs (BT, MeBT, and SMX) after varying ozonation durations

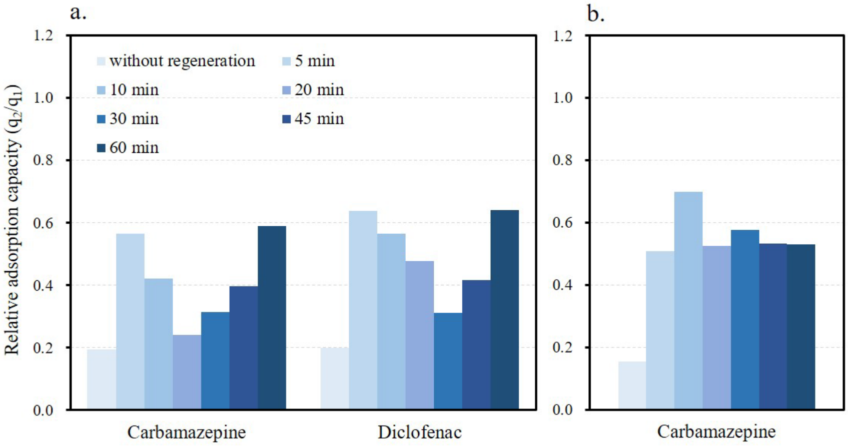


Fig. 5. Regeneration performance of low-adsorbing OMPs (CBZ and DIC) after varying ozonation durations. (a. adsorption of various OMPs; b. adsorption of only CBZ)

### *3.3. Influence of ozonation transformation products*

Furthermore, it can be hypothesized that the decrease of Rq from 5 min to 20 min (Fig. 5a) was caused by the adsorption of transformation products generated in the ozonation of all eight OMPs, which competed with CBZ for adsorption sites. Subsequently, the Rq increased along with the decomposition of the ozonation transformation products at longer ozonation durations. The results suggest that a longer ozonation duration of at least 60 minutes is needed for the granules to restore the adsorption capacity of the low-adsorbing OMPs.

In addition, the total ion chromatogram (Fig. S2, Supplementary Information) was acquired over a mass range of $m/z$ 50 – 400 in positive ion mode for the liquid samples after methanol extraction. The peak curves in Fig. S2 were processed by subtracting the total ion chromatogram of fresh zeolite granules. After comparing all the peaks of the curves after different ozonation durations, the most interesting aspect of the data was at the retention time of 3.35 min. Along with the increase of the ozonation duration, the peak intensity at 3.35 min started to increase after 5 min ozonation and reached the highest level at 20 min ozonation. After 20 min ozonation, the peak intensity decreased until 45 min ozonation. This trend was reversely corresponding to the Rq changes of CBZ (Fig. 5a). The mass spectrums at the retention time of 3.35 min are shown in Fig. S3 (Supplementary Information). Three ozonation transformation products were selected from the peaks. Their abbreviations were P213, P218, and P274, respectively. The numbers refer to their $m/z$ obtained from the ESI(+)-MS analysis. The intensity of the three products after different ozonation durations are shown in Fig. 6. At 20 min ozonation, the intensity of all three products reached the highest level. For P274, its intensity increased after 5 min ozonation and decreased after 20 min ozonation. It is possible to hypothesize that the formation of P213, P218, and P274 might influence the adsorption capacity of CBZ after different ozonation durations (Fig. 5a). Moreover, P274 might contain M273 [$C_{13}H_{24}NO_5^+$], which was identified as an oxidation product formed in the ozonation of metoprolol (Benner and Ternes 2009, Tay et al. 2013). P274 might also contain DIC_p_273.9813_16.4, which was identified as a transformation product of diclofenac (Gulde et al. 2021). It is worth mentioning that metoprolol is one of the high-adsorbing OMPs, and diclofenac is the other low-adsorbing OMP. Identifications of P213 and P218 were not found in the literature. Thus, it can be further hypothesized that the ozonation transformation products formed in the ozone reaction with OMPs other than CBZ might influence the adsorption capacity of CBZ after different ozonation durations (Fig. 5a).

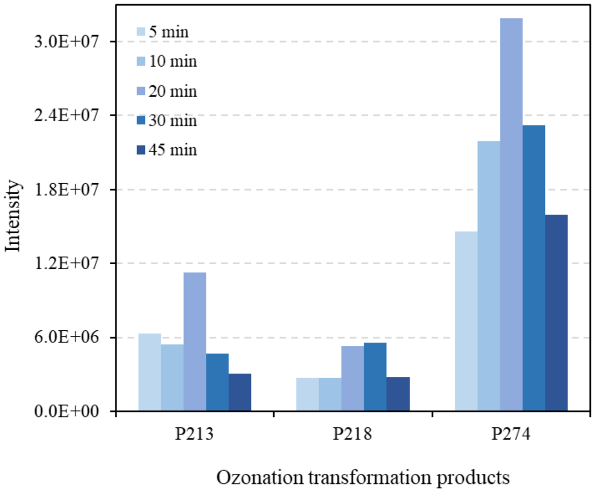
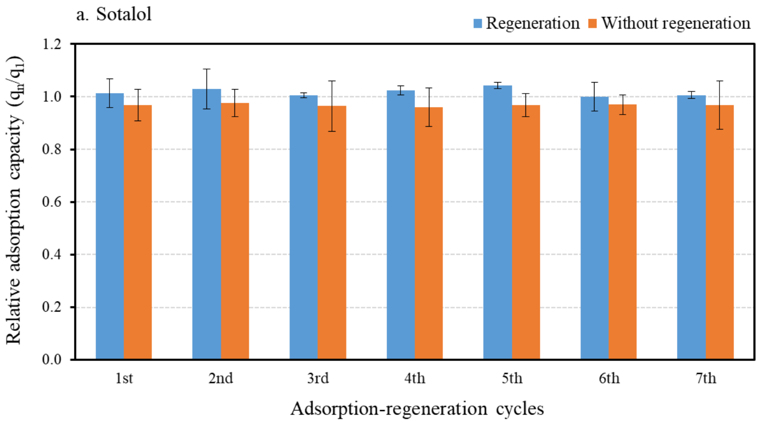


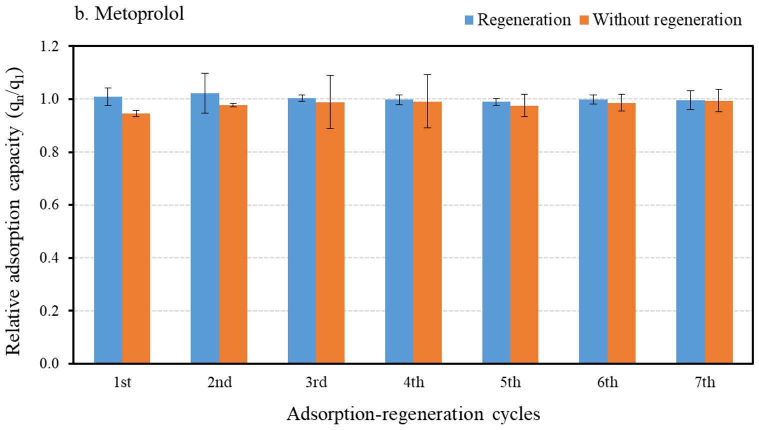
Fig. 6. The intensity of the ozonation transformation products (P213, P218, and P274) after different ozonation durations at the retention time of 3.35 min

### *3.4. Long-term adsorption-regeneration performance*

The regeneration performance of the high-adsorbing OMPs in seven adsorption-regeneration cycles is shown in Fig. 7. The Rq was constant at 1 after 60 min of ozonation in seven cycles, and the Rq without regeneration was also approaching 1 in each cycle. The difference in the Rq between regeneration and without regeneration was smaller than 0.05 for each cycle. The average adsorption capacities were 6.31, 5.99, and 7.07 μg/g for SOT, MP, and TMP, respectively. The results indicated that huge amounts of adsorption sites for the high-adsorbing OMPs were present in the zeolites. Therefore, the Rq can reach 1 after seven cycles even without regeneration. For the medium-adsorbing OMPs, the Rq with regeneration remained at 1 in seven cycles, while the Rq without regeneration gradually decreased in seven cycles (Fig. 8). After seven cycles without regeneration, the Rq of BT decreased from 0.66 to 0.44 (Fig. 8a); the Rq of MeBT decreased from 0.61 to 0.5 (Fig. 8b); and the Rq of SMX decreased from 0.83 to 0.62 (Fig. 8c). The adsorption capacities of fresh granules were 4.85, 6.5, and 4.01 μg/g for BT, MeBT, and SMX, respectively. The results indicated that the adsorption sites for the medium-adsorbing OMPs were gradually occupied in seven cycles when no regeneration was applied. Whereas after ozone-based regeneration, the adsorption capacity was fully recovered. The Rq of the low-adsorbing OMPs without regeneration in seven cycles was lower than 0.2 (Fig. 9). By comparison, the Rq of CBZ was almost constant at 0.6 after regeneration in seven cycles (Fig. 9a). The Rq of DIC decreased from 0.61 to 0.29 in seven cycles (Fig. 9b). The adsorption capacities of fresh granules were 1.9 and 1.07

μg/g for CBZ and DIC, respectively. A hypothesis was that the accumulation of ozonation transformation products in the granules resulted in the decrease of Rq. The results indicated that the adsorption capacity of the low-adsorbing OMPs was partially restored after ozone-based regeneration. Thus, it suggests that 60 min of ozonation is not long enough to recover the adsorption capacity along with the increase of the adsorption-regeneration cycles.





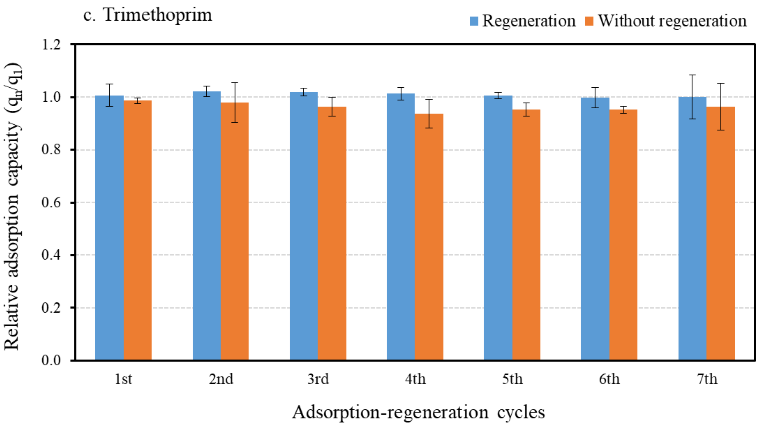
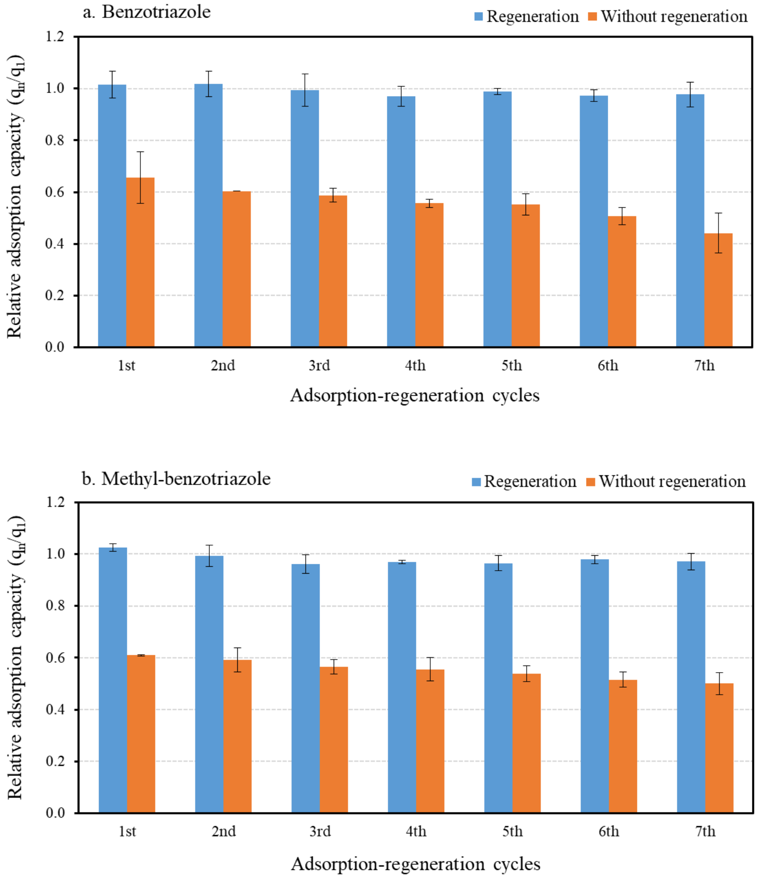


Fig. 7. Regeneration performance of high-adsorbing OMPs in 7 adsorption-regeneration cycles (60 min ozonation; a. SOT, b. MP, c. TMP)



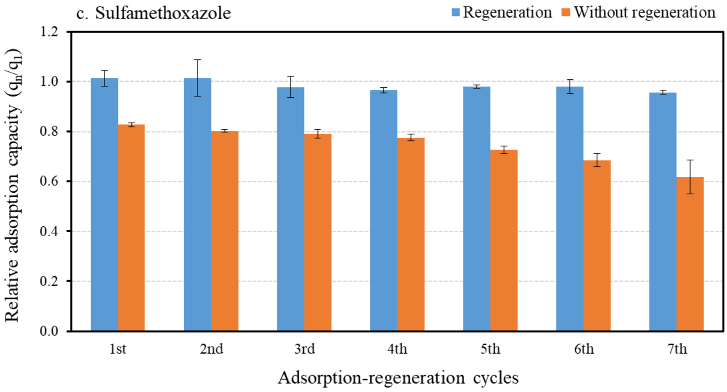
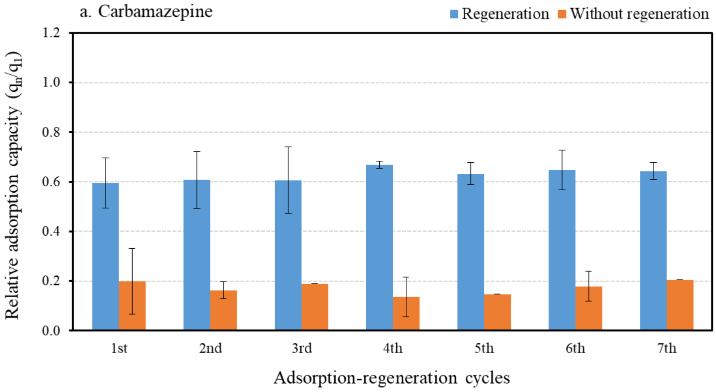


Fig. 8. Regeneration performance of medium-adsorbing OMPs in 7 adsorption-regeneration cycles (60 min ozonation; a. BT, b. MeBT, c. SMX)



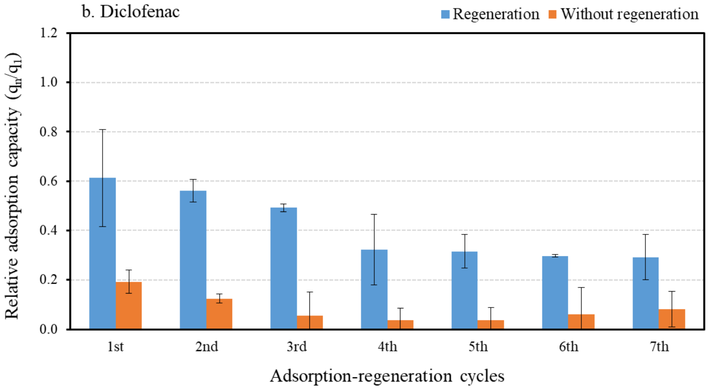


Fig. 9. Regeneration performance of low-adsorbing OMPs in 7 adsorption-regeneration cycles (60 min ozonation; a. CBZ, b. DIC)

## 4. Conclusions and outlook

Granular zeolites containing three types can effectively remove a broad range of OMPs from demi-water by adsorption. Regeneration of dried zeolite granules loaded with OMPs by gaseous ozone is efficient. Adsorption by granular zeolites followed by regeneration with ozone in the gas phase offers possibilities to apply this process in practice. Specific transformation products generated in the ozonation of some selected OMPs might compete with the low-adsorbing OMPs for adsorption sites. Thus, their adsorption capacities dramatically decreased in a short ozonation duration. Along with the increase of the ozonation duration, their adsorption capacities can be recovered. 60 min of ozonation was long enough to fully recover the adsorption capacity of most target OMPs. The adsorption capacity of six out of eight selected OMPs was completely restored in seven cycles. The accumulation of transformation products might only influence the adsorption capacity of diclofenac in seven cycles. Further studies should focus on real wastewater to scale up this process.

## Supplementary Information

The adsorption performance of the selected OMPs by both fresh and ozone-treated zeolite granules (pulverized) is listed in Table S1. The selected OMPs were categorized into three groups by their removal efficiencies at zeolite granule dosages of 0.1 g/L. The adsorption isotherms of the medium-adsorbing OMPs were interpreted with the Freundlich model (Fig. S1). The isotherm constants shown in Table S1 were from the ozone-treated granules.

Table S1. The adsorption performance of the selected OMPs

| OMPs | Removal efficiency[a] | | Adsorption performance | | |
|---|---|---|---|---|---|
| | Fresh | Ozone-treated | | | |
| Sotalol (SOT) | 99% | 99% | High adsorption | | |
| Metoprolol (MP) | 98% | 98% | | | |
| Trimethoprim (TMP) | 99% | 99% | | | |
| | | | Medium adsorption (Freundlich Model) | | |
| | | | $K_F$, (mg/g)/(mg/L)$^n$ | n | $R^2$ |
| Benzotriazole (BT) | 62% | 63% | 11.21 | 1.31 | 0.96 |
| Methyl-benzotriazole (MeBT) | 93% | 92% | 89.23 | 1.02 | 0.98 |
| Sulfamethoxazole (SMX) | 91% | 91% | 99.40 | 1.16 | 0.97 |
| Carbamazepine (CBZ) | 18% | 18% | Low adsorption | | |
| Diclofenac (DIC) | 49% | 51% | | | |

[a] The removal efficiency of OMPs at zeolite granule dosages of 0.1 g/L

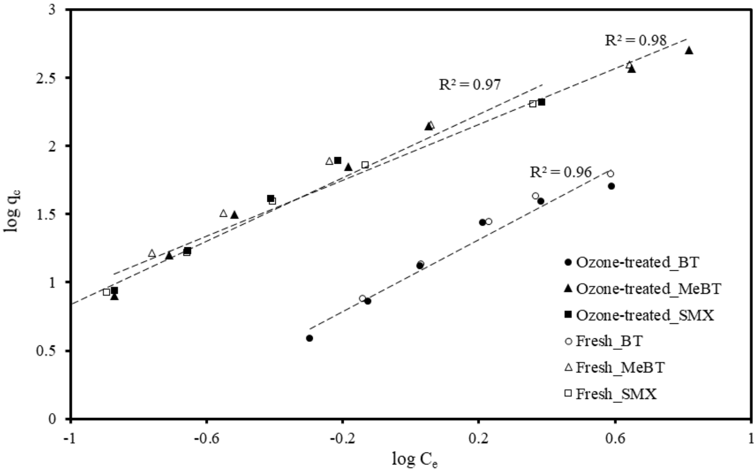


Fig. S1. Adsorption isotherms of medium-adsorbing OMPs (BT, MeBT, and SMX) on fresh and ozone-treated zeolite granules (pulverized), Freundlich model fitting

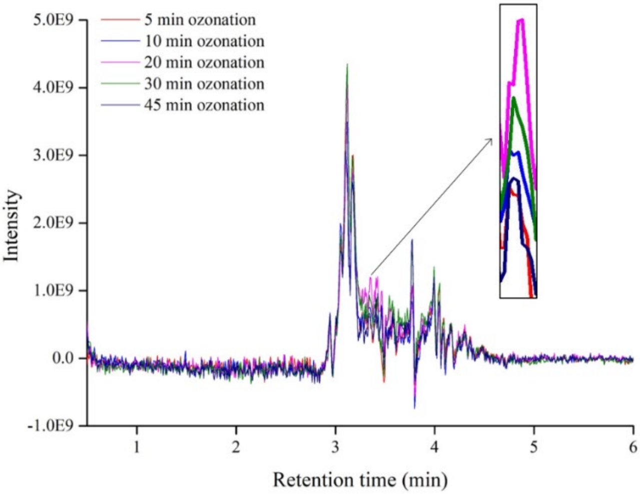


Fig. S2. Total ion choromatogram acquired over a mass range of *m/z* 50 – 400 in positive ion mode. Liquid samples taken after methanol extraction of granules treated by varying ozonation durations.

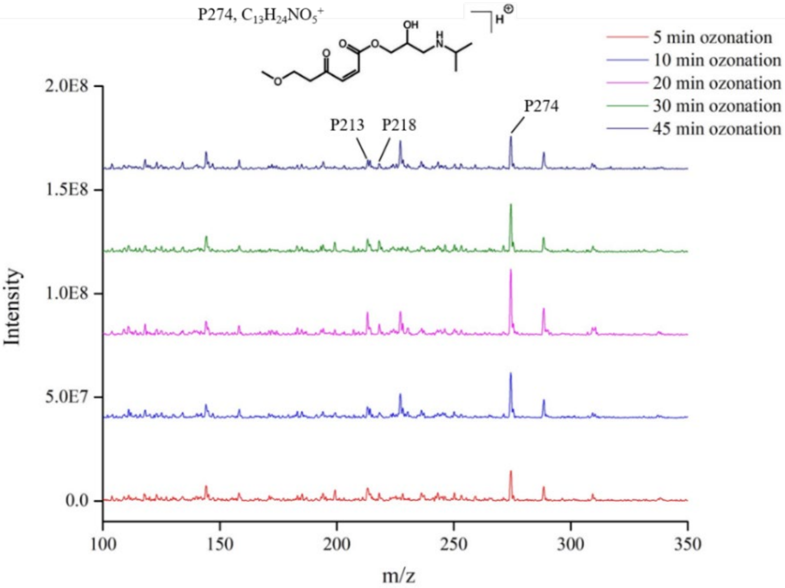
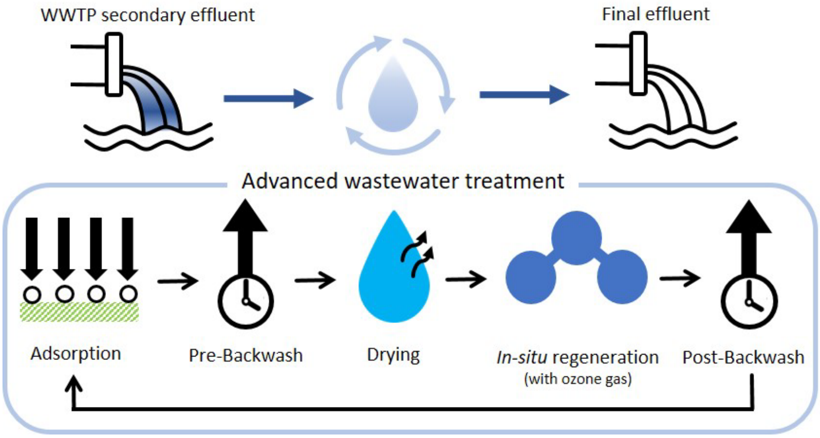


Fig. S3. Mass spectrums aquired in ESI(+)-MS at the rention time of 3.35 min

# Chapter 5

## Removal of organic micropollutants from wastewater effluent: selective adsorption by a fixed-bed granular zeolite filter followed by *in-situ* ozone-based regeneration



This chapter is based on

M. Fu, B. Heijman, J.P. van der Hoek, Removal of organic micropollutants from wastewater effluent: Selective adsorption by a fixed-bed granular zeolite filter followed by *in-situ* ozone-based regeneration, Separation and Purification Technology 303 (2022) 122303.

## Abstract

Organic micropollutants (OMPs) that occur in the aquatic environment are an emerging concern. Adsorption by granular zeolites and regenerating exhausted zeolites by gaseous ozone is an innovative and advanced treatment technology for removing OMPs from wastewater treatment plant (WWTP) effluent. In this study, WWTP effluent spiked with eleven OMPs at 4-5 μg/L was treated by this combined technology, which included five steps in each cycle. The five steps comprised 1) selective adsorption of OMPs from WWTP effluent for five days by a zeolite granules fixed-bed column, 2) pre-backwash of the column, 3) drying of the column, 4) *in-situ* regeneration of the column with gaseous ozone 5) post-backwash of the column. The removal efficiency of eight OMPs (sotalol, metoprolol, propranolol, trimethoprim, clarithromycin, carbamazepine, methyl-benzotriazole, and benzotriazole) reached between 70% and 100% in six cycles. The adsorption of sulfamethoxazole and diclofenac was less favourable. In each cycle, less than 8% of dissolved organic carbon (DOC) was removed from the WWTP effluent. The effect of the natural organic matter (NOM) on the adsorption of OMPs was negligible. Ozone consumption during regeneration was reduced by around 70% by increasing pre-backwash duration from 30 min to 1 h. Ozonation directly with ozone gas can effectively regenerate the zeolite granules in the column under low ozone consumption.

## 1. Introduction

Organic micropollutants (OMPs) occur in surface water with conventionally treated wastewater (Luo et al. 2014). The environmental occurrence and detection of OMPs have been studied extensively over the last two decades (Rout et al. 2020). It has been reported that OMPs could impose adverse effects on the health of aquatic organisms and human beings (Barbosa et al. 2016, Houtman et al. 2014). As a result, OMPs are noticed as the representative of a directive regarding priority substances, which have been adopted in Europe since 2016 (Kern 2014). The Dutch Ministry of Infrastructure and Water Management has listed eleven guide compounds to monitor the removal effectiveness of OMPs in advanced wastewater treatment technologies (Ministry of Infrastructure and Water Management 2020). The guide compounds are sotalol, metoprolol, propranolol, trimethoprim, clarithromycin, sulfamethoxazole, methyl-benzotriazole, benzotriazole, carbamazepine, diclofenac, and hydrochlorothiazide. They are selected from two categories of OMPs, namely pharmaceuticals and industrial chemicals (Reemtsma et al. 2010, Rivera-Utrilla et al. 2013). The removal efficiency for at least 7 of the 11 guide substances is required to be above 70% in every 24-hour or 48-hour flow rate proportional sample (Mulder et al. 2019).

The most widely used technologies for advanced wastewater treatment in full-scale operation to reduce OMPs are oxidation of OMPs by ozone to harmless substances and adsorption of OMPs by activated carbon, which is either powdered activated carbon (PAC) or granular activated carbon (GAC) (Loganathan et al. 2022). The efficiencies of ozonation and adsorption are significantly influenced by natural organic matter (NOM) in wastewater. Ozonation for OMP removal from wastewater is energy- and cost-intensive due to the competition between NOM and OMPs (van Gijn et al. 2021). OMPs adsorption can be reduced by NOM because of competition for adsorption sites on activated carbon and blockage of activated carbon pores with large molecules of NOM (Loganathan et al. 2022). By combining ozonation and adsorption (ozonation followed by adsorption of oxidized products and unoxidized NOM and OMPs onto activated carbon), the removal of OMPs was more efficient than using these treatments individually (Altmann et al. 2014, Beijer et al. 2017, Bourgin et al. 2018). However, the degree of adsorption competition of NOM depends on the composition of the NOM, which varies with the type of water and ozone dosage used (Loganathan et al. 2022).

High-silica zeolite has been evaluated as an alternative adsorbent for the adsorption of OMPs. High-silica zeolite is hydrophobic and capable of selectively adsorbing OMPs from water containing NOM because zeolite possesses uniform micropores that allow small molecules of OMPs to enter and exclude large molecules of NOM (Jiang et al. 2018). The structural properties of zeolite can reduce the influence of the composition of the NOM on the adsorption of OMPs. De Ridder et al. (De Ridder et al. 2012) studied the adsorption of nitrosamine from surface water by hydrophobic zeolite ZSM-5. They indicated that NOM was effectively excluded from the zeolite pores and did not block the pores. Jiang (Jiang 2019) reported that NOM did not influence the adsorption of positively charged OMPs from drinking water treatment plant effluent by high-silica zeolite MOR and MFI. The majority of the NOM was excluded by zeolite in the adsorption of OMPs. Since the NOM composition in wastewater treatment plant (WWTP) effluent is more complex than that in surface water and drinking water treatment effluent (Shi et al. 2021), it is crucial to evaluate the adsorption performance of OMPs from real WWTP effluent by high-silica zeolite. However, this evaluation has not been reported yet.

Granular zeolites need to be engineered from a range of powdered zeolites and packed in a fixed-bed column for practical applications (Fu et al. 2021b). Fixed-bed column is widely used for the industrial purpose of removing various contaminants from wastewater (Patel 2019). On-site regeneration of OMPs-loaded granular zeolites by ozonation is an approach to *in-situ* oxidizing the adsorbed OMPs into harmless substances, leading to the recovery of adsorption capacity. As most NOM fractions are expected not to be adsorbed, ozone is only used for degrading adsorbed OMPs. Thus, the ozone dose can be expected to be lower than the dose in applying ozone treatment individually. Zhang et al. (Zhang et al. 2016) reported that the adsorption capacity of trichlorophenol on granular zeolite FAU increased after regeneration with gaseous ozone. The ozone dose highly depended on the adsorbed mass of trichlorophenol and was ten times lower than that in direct ozonation. Fu et al. (Fu et al. 2021b) reported that the adsorption of eight OMPs from OMPs-spiked demi-water by zeolite granules was efficient, and the regeneration of OMPs-loaded zeolite granules by gaseous ozone was effective and stable in seven adsorption-regeneration cycles. However, the adsorption experiments reported in the literature were all conducted in batch mode, and an on-site ozonation regeneration was not realized. Fixed-bed column tests are more representative of evaluating the adsorption and on-site ozonation regeneration performance on zeolite granules and have not been reported yet.

Moreover, the direct ozonation process on WWTP effluent can yield harmful oxidation by-products, such as bromate (from the oxidation of bromide in effluent) (Bourgin et al. 2018). In the Netherlands, risks limits for bromate have been determined to be 1 μg/L for both surface water and drinking water intake points in 2022 (RIVM 2021). Direct ozonation thus has limited potential because its application in some WWTPs is restricted due to the formation of bromate (Soltermann et al. 2016). A possible advantage of applying adsorption of OMPs from the WWTP effluent by a zeolite filter followed by oxidation of the OMPs adsorbed on the zeolite is preventing the formation of bromate. Because bromide in the WWTP effluent is not adsorbed by zeolite, ozone only reacts with the adsorbed OMPs in the regeneration cycle. Ozone is not in contact with the WWTP effluent containing bromide. Hence, the WWTP effluent is free of bromate.

In the current study, we applied a zeolite granules fixed-bed column for selective adsorption of OMPs from municipal WWTP effluent and subsequently *in-situ* oxidative regeneration of the exhausted column by gaseous ozone in a side stream. The *in-situ* regeneration, in which the exhausted zeolite granules remain in the column and are regenerated with ozone gas on-site, avoids transport of the adsorbent to a regeneration plant off-site and allows short running times of the zeolite column with frequent regeneration on-site. The primary goal of the current research was to study the removal performance of eleven guide OMPs (requested by the Dutch Ministry of Infrastructure and Water Management) from the secondary effluent of WWTP Horstermeer (the Netherlands) in long-term adsorption-regeneration operations. The combined technology included column adsorption, pre-backwash of the column, drying of the column, *in-situ* oxidative regeneration of the exhausted column by gaseous ozone, and post-backwash of the column.

## 2. Materials and Methods

### *2.1 Zeolite, OMPs, and WWTP effluent*

Synthetic high-silica zeolites were applied to produce granules in the current study. Beta (BEA) and Mordenite (MOR) types of zeolites were selected for OMP removal based on the batch experimental results reported in a previous study (Jiang 2019). Powdered zeolites were purchased from Tosoh Corporation, Japan. The characteristics of zeolites are listed in Table S1. Zeolite granules used in the current study were prepared in the lab, and the granulation details are described in our previous publication (Fu et al. 2021b). In the current study, powdered zeolite BEA and MOR were added with a mass ratio of 1:1. Bentonite (Sigma-Aldrich) was added as a binder at 15% by weight. Granules were printed using a 3D clay printer purchased from VormVrij, the Netherlands. After sintering at 950 °C for 2 h, the mechanical strength of the granules was enhanced for application. The shape of the granules resembled rice grains (Fig. 1). Each granule was 1 mm in diameter and 3 mm in length.

All eleven OMPs used in the current study were purchased from Sigma-Aldrich. Their physicochemical and structural properties are listed in Table 1. In the pore structures of zeolite BEA and MOR, two-channel systems were interconnected at right angles. The pore opening size was 6.6 Å × 7.7 Å / 5.6 Å × 5.6 Å and 6.5 Å × 7.0 Å / 2.6 Å × 5.7 Å for BEA and MOR, respectively. The positive- and neutral-charged OMPs with molecular sizes smaller than the pore opening in two dimensions can be adsorbed by zeolite (Jiang 2019). Clarithromycin is an OMP with the largest molecular size on the list. Its molecular size is larger than the pore opening in three dimensions. It was hypothesized that clarithromycin might be adsorbed on the external surface of zeolite (Jiang 2019).

WWTP Horstermeer consists of a primary settling followed by two anoxic tanks, an aerated tank, and a secondary clarifier. WWTP effluent was sampled from the secondary clarifier in WWTP Horstermeer. The yearly average concentrations in the secondary effluent of WWTP Horstermeer are listed in Table S2. The pH of the secondary effluent was around 7. Different charged forms of the OMPs present in water at pH 7 are listed in Table 1.

Table 1. Physicochemical and structural properties of the target OMPs

| Name | Molecular formula | | CAS | Molecular weight (g/mol) | pKa | Charge at pH7[a] | Min. projection radius (Å)[a] | Max. projection radius (Å)[a] | Application |
|---|---|---|---|---|---|---|---|---|---|
| Sotalol (SOT) | C12H20N2O3S | | 27948-47-6 | 272 | 9.43 | + | 4.21 | 7.94 | Betablocker |
| Metoprolol (MP) | C15H25NO3 | | 51384-51-1 | 267 | 9.67 | + | 4.39 | 10.07 | |
| Propranolol (PRO) | C16H21NO2 | | 13013-17-7 | 259 | 9.67 | + | 4.66 | 7.41 | |
| Trimethoprim (TMP) | C14H18N4O3 | | 738-70-5 | 290 | 7.16 | +/0[b] | 4.97 | 6.95 | Antibiotic |
| Clarithromycin (CLA) | C38H69NO13 | | 81103-11-9 | 747 | 9 | + | 7.73 | 8.47 | |
| Sulfamethoxazole (SMX) | C10H11N3O3S | | 723-46-6 | 253 | 6.16 | - | 5.4 | 5.88 | |
| Methyl-benzotriazole (MeBT) | C7H7N3 | 4-MeBT | 29878-31-7 | 133 | 9.29 | 0 | 4.05 | 4.43 | Corrosion inhibitors |
| | | 5-MeBT | 136-85-6 | 133 | 9.12 | 0 | 3.82 | 4.67 | |
| Benzotriazole (BT) | C6H5N3 | | 95-14-7 | 119 | 9.04 | 0 | 3.66 | 4.12 | |
| Carbamazepine (CBZ) | C15H12N2O | | 298-46-4 | 236 | 15.96 | 0 | 4.48 | 5.76 | Anti-epileptic |
| Diclofenac (DIC) | C14H11Cl2NO2 | | 15307-86-5 | 296 | 4 | - | 4.62 | 6.34 | Analgesics/Anti-inflammatories |
| Hydrochlorothiazide (HCTZ) | C7H8ClN3O4S2 | | 58-93-5 | 297 | 9.09 | 0 | 4.13 | 5.67 | Thiazide diuretic |

[a] Estimated by Chemicalize Platform; +, positively charged; -, negatively charged; 0, neutral

[b] Positively charged and neutral TMP molecules simultaneously existed at pH 7, the contribution of positively charged form is around 50 %

Fig. 1. Printed zeolite granules (after sintering at 950 °C)

### 2.2 Technological process

The process of this technology included two phases in each cycle. The phases were: adsorption and regeneration (including pre-backwash, drying, *in-situ* regeneration, and post-backwash). The setup of two main phases (adsorption and ozonation) is schematically shown in Fig. 2.

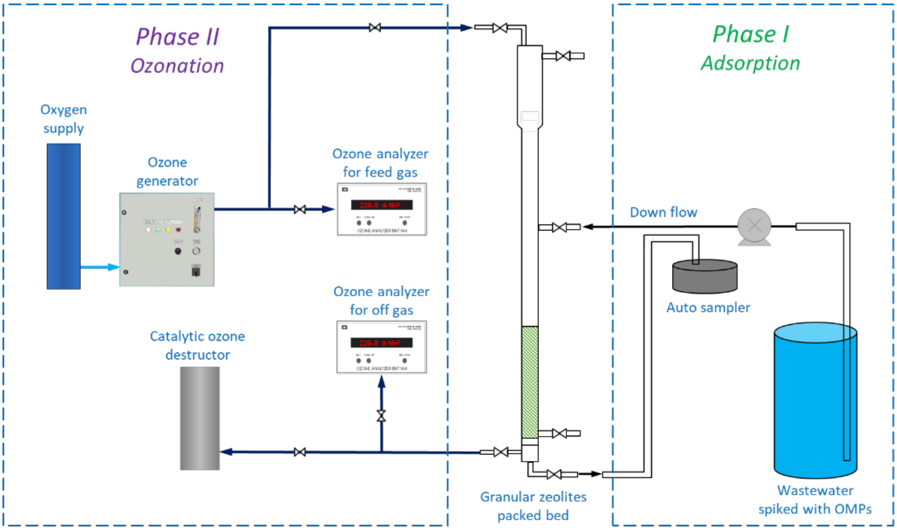


Fig. 2. Two phases setup:
Phase I: zeolite granules packed column adsorption; Phase II: *in-situ* ozone-based regeneration

*Adsorption*

Phase I (adsorption) is shown in Fig. 2. WWTP effluent was collected from WWTP Horstermeer. Before each adsorption, the sampled WWTP effluent was pre-filtrated with 1-micron cartridge filters to exclude the suspended solids and most bacteria. The feed wastewater for column adsorption was prepared by spiking 11 OMPs to the pre-filtrated WWTP effluent at 4-5 μg/L. The feed wastewater was stored in a 160 L volume tank. 200 g of zeolite granules were packed in a column (4 cm in diameter, 1 m in length). The packing length was 27 cm, resulting in a bed volume of 0.34 L. The feed wastewater was pumped into the column in down-flow mode. In the down-flow mode adsorption, suspended substances that remained in wastewater might clog the column. The subsequent backwash was operated up-flow to remove the clogging substances. Empty bed contact time (EBCT) is a critical process parameter for filtration, e.g. for GAC filters. The breakthrough point of individual OMP is highly dependent on EBCT. An EBCT of 20 to 30 min is recommended as a minimum for a GAC filter design to guarantee an effective adsorption performance (Fundneider et al. 2021). Corresponding to the GAC filtration, the EBCT of the zeolite filter was 20 min in the current study. The adsorption kinetics of the target OMPs by zeolite granules is discussed in the Supplementary Information. The flow rate was 1.02 L/h. Approximately 120 L of wastewater was treated during a 5 days adsorption period. A picture of the adsorption setup is shown in Fig. 3a. A small collector (yellow circle) was prepared to collect the column effluent. Column effluent samples were automatically taken from the small collector every 3 hours. The concentration of OMPs in the column effluent samples was analyzed by LC-MS.

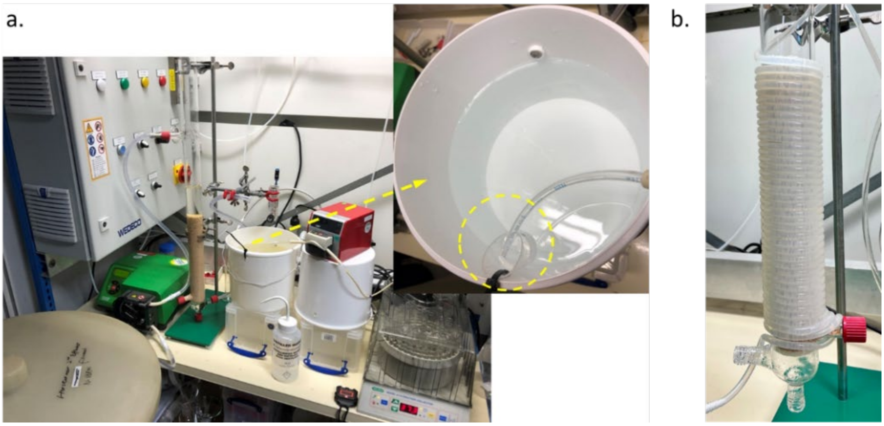


Fig. 3. Experimental setup (a. adsorption, b. drying)

*Pre-backwash*

After adsorption, the column was backwashed. The purpose of the pre-backwash was to remove the clogging substances in the filter and reduce the biofilm formed on the surface of granules. The column effluent in the bucket shown on the top right in Fig. 3a was used for backwash. Identical to GAC filtration, backwash intensity is an important process parameter. Around 8 L of the column effluent was recirculated at a flow rate of around 1.4 L/min to backwash the column. Bed fluidization was at an expansion of 100%. Air was not injected during the backwash. The duration of the pre-backwash was from 30 min to 1 h. At the end of the pre-backwash process, the column was backwashed with demi-water without recirculation to refresh the column.

*Drying*

Before regeneration, the column was fully dried on-site. The ozone mass transfer rate in air is much faster than in water. Our previous studies reported that gaseous ozone could effectively regenerate dried granules (Fu et al. 2021a, Fu et al. 2021b). The drying setup is shown in Fig. 3b. The column was tightly wound by soft tubings with 80 °C hot water recirculating inside. The recirculation flow rate was around 0.9 L/min. Compressed air was introduced from top to bottom in the column at a flow rate of 6-10 L/min (0.08-0.13 m/s). The drying process lasted for 7 hours to fully dry the granules. The drying efficiency as a function of time is shown in Fig. S4. The drying performance is discussed in the Supplementary Information.

*In-situ regeneration*

Ozone-based regeneration was applied on-site. Gaseous ozone was directly introduced to the dried-bed column in down-flow mode. Phase II (ozonation) is shown in Fig. 2. The ozone setup (ozone generator and ozone gas sensors) was supplied by Wedeco (Xylem Water Solutions Herford, GmbH) and its details were described in our previous research (Fu et al. 2021a, Fu et al. 2021b). Gaseous ozone conditions were set at a concentration of 90 mg/L and a gas flow rate of 0.8 L/min (0.01 m/s). *In-situ* regeneration lasted for 5 hours.

*Post-backwash*

After regeneration, the column was backwashed again. The purpose of the post-backwash was to mix the granules homogeneously in the column for sampling by fluidizing the bed. Bed fluidization was at an expansion of 100%. Air was not injected during the backwash. Around 8 L of demi-water was recirculated at around 1.4 L/min for 30 min. After post-backwash, the column was ready for the next cycle of adsorption.

### *2.3 Determination of regeneration performance in batch tests*

After post-backwash, 1 g of granules were taken from the port above the bottom of the column. The sampled granules were pulverized for a batch adsorption test to determine the regeneration performance. 0.5 g of pulverized granules were added to 1 L of feed wastewater (spiked with 11 OMPs at 4-5 μg/L, same source as the column influent in the adsorption cycle) for 5 days of adsorption. Fresh granules were pulverized and applied in a blank test with feed wastewater. All batch experiments were conducted in duplicate. Water samples in the batch adsorption tests were taken before and after adsorption. The concentration of OMPs in the water samples was analyzed by LC-MS. Relative adsorption capacity (Rq) was used to represent the regeneration performance. The Rq was the ratio of the adsorption capacity of the granules after regeneration compared with the fresh granules.

### *2.4 Analysis*

All the water samples were filtered over 0.2 μm polycarbonate syringe filters and analyzed by a UPLC-MS/MS system (Waters, ACQUITY UPLC I-Class, Xevo TQ-S micro fitted with the ESI) equipped with a C18 column (ACQUITY UPLC™ BEH 2.1 × 50 mm, 1.7 μm particle size). The details of the LC-MS analysis are described in our previous research (Fu et al. 2021b). Briefly, the elution flow rate was 0.35 mL/min with 95% ultrapure water acidified with 0.1% formic acid and 5% acetonitrile. Internal standards for each OMP were added to the samples for quantitation. Limits of detection (LOD) and quantitation (LOQ) for each OMP are listed in Table S3. As hydrochlorothiazide in the samples was poorly quantified, the other 10 OMPs were targeted in the current study. The concentration of potassium, calcium, and ammonium ions in the column influent and effluent samples was analyzed by ion chromatography (IC, 883 Basic IC plus, Metrohm). The concentration of dissolved organic carbon (DOC) in the column influent and effluent samples was analyzed by a total organic carbon analyzer (TOC-$V_{CPH}$, SHIMADZU).

## 3. Results and Discussion

### *3.1 Overall removal performance*

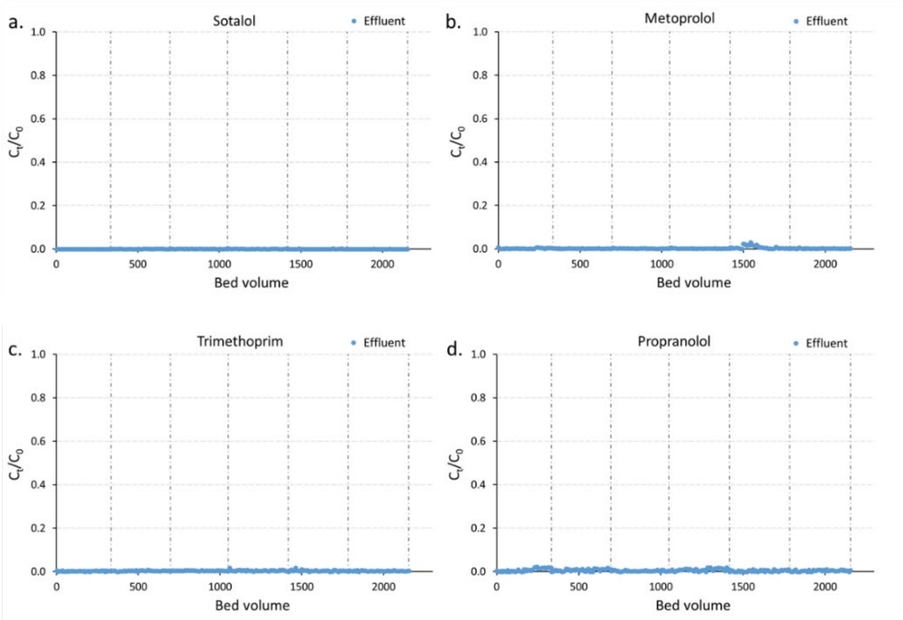
The target 10 OMPs (without HCTZ) could be categorized into three groups (high-, medium-, and low-adsorbing, Table S4). The adsorption kinetics of the target OMPs on zeolite granules is shown in Fig. S1. The adsorption isotherms of the target OMPs were interpreted with the Freundlich model (Fig. S2). The OMPs categorization and the isotherm constants are listed in Table S4. The breakthrough curves as a function of bed volume in six cycles for the target OMPs are shown in Fig. 4. Each adsorption cycle lasted for around 360 bed volumes in five days. The vertical axis in Fig. 4a-f and 4h-j represents the ratio of the column effluent concentration to influent concentration, $C_t/C_0$. The vertical axis in Fig. 4g shows the column effluent and influent concentration.

For SOT, MP, TMP, and PRO, their overall removal efficiencies derived from the breakthrough curve of each OMP were approaching 100% in six cycles (Fig. 4a-d). The concentration of these four OMPs in the column effluent samples was still lower than the limits of quantification in LC-MS after 5 days of adsorption. It indicated that zeolite granules possessed high adsorption capacity for these four OMPs. Furthermore, due to the rapid reaction of ozone with these four OMPs (Abegglen et al. 2009), the subsequent ozonation can further release the adsorption sites on zeolite.

For CLA, CBZ, and MeBT, the average removal efficiency of each OMP in six cycles was higher than 85% (Fig. 4e-g). Their concentrations in the column effluent increased along with the bed volume. The adsorption performance was stable in six cycles. For CLA, the $C_t/C_0$ ratio at the adsorption endpoint reached 0.12 in the first cycle, increased to 0.25 in the second cycle, and remained constant at 0.25 in the rest cycles (Fig. 4e). For CBZ, the $C_t/C_0$ ratio in the first cycle increased to 0.4 at 72-116 bed volumes and subsequently decreased to 0.16 at the endpoint (Fig. 4f). In the subsequent five cycles, the $C_t/C_0$ ratio at the endpoint remained at 0.16. This trend might be caused by the cations present in wastewater. Further discussion is in Section 3.2. For MeBT, the red dots represent the influent concentration, and the blue dots represent the effluent concentration. The influent concentration decreased along with the running time (Fig. 4g). The concentration decrease was probably because of the biodegradation of 5-MeBT in wastewater, whereas 4-MeBT is non-degradable in wastewater with active biomass (Abu-Dalo et al. 2018). In the current study, both 4-MeBT and 5-MeBT were spiked in wastewater, and LC-MS analyzed 4-MeBT and 5-MeBT as one compound. For BT, the $C_t/C_0$ ratio at the endpoint in the fourth cycle reached a higher level of 0.56 (Fig. 4h). The average removal efficiency decreased from 87% in the first cycle to 60% in the fourth cycle and remained at 70% in the last two cycles. The results indicated that the adsorption capacity of BT was partially recovered and decreased in the first four cycles. It can be reasonably inferred that the adsorption sites for BT in the inner part of the granules were gradually occupied in the first four cycles. However, the inner part might not be regenerated entirely due to the limited ozone diffusion depth in granules under the applied experimental conditions. After four cycles, the adsorption performance of BT was stable, indicating that the adsorption sites in the outer part of the granules might be released entirely.

For SMX, in the first two cycles, its removal efficiency reached around 50%. Whereas, starting from the third cycle, its removal efficiency was reduced to 15% and remained stable at 15% in the last two cycles (Fig. 4i). For DIC, the average removal efficiency was lower than 5% in six cycles (Fig. 4j). The low removal efficiencies of SMX and DIC was caused by the fact that both OMPs were present in wastewater in negatively charged forms. For BEA and MOR types of zeolites, the adsorption capacity of negatively charged OMPs is considerably lower than that of positively charged OMPs (Jiang 2019). Moreover, compared to the adsorption performance of SMX in demi-water (Fu et al. 2021b), the adsorption of SMX was depleted in wastewater. The low adsorption performance might be caused by NOM in wastewater (Jiang 2019). Small NOM fractions might compete with SMX for the adsorption sites on zeolite.

In addition, the breakthrough curves of the medium-adsorbing OMPs could be improved by optimization of flow conditions (including EBCT), column and granule geometry. However, the optimization was not within the scope of the current study. This study aimed to examine the reproducibility of the adsorption behaviour after several regeneration cycles. Further investigation should also be performed to address the effect of small NOM fractions on the adsorption performance of OMPs. The results also indicated that *in-situ* regeneration efficiently recovered the adsorption capacity of the target OMPs to comply with the required removal efficiency of 70% for at least 7 of the 11 guide substances.



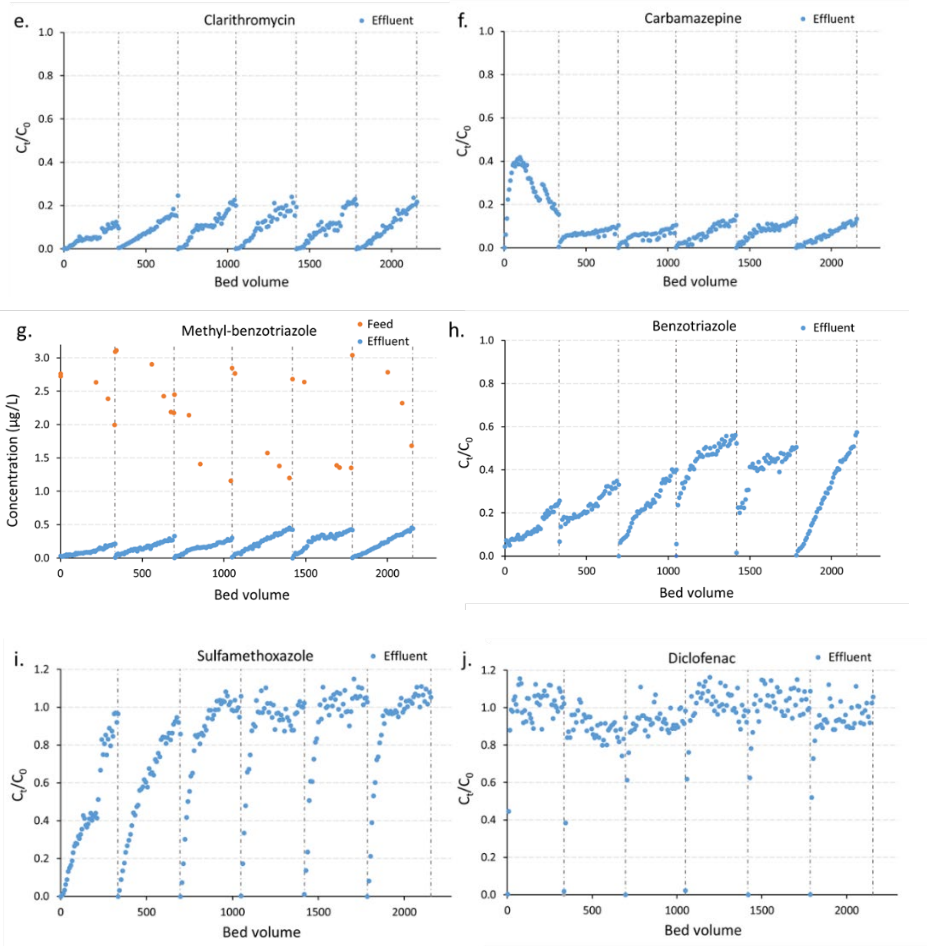


Fig. 4. Adsorption breakthrough curves of OMPs in six cycles
(a. SOT, b. MP, c. TMP, d. PRO, e. CLA, f. CBZ, g. MeBT, h. BT, i. SMX, j. DIC)

### *3.2 Cations adsorption*

Potassium, calcium and ammonium cations are exchangeable with the sodium cations on zeolite (Langwaldt 2008, Ruthven 1984). The initial concentration of ammonium ions in the column adsorption influent was lower than the limits of quantification in the ion chromatograph. Thus, potassium and calcium ions were the target cations in the current study. In six cycles, the initial concentration of potassium and calcium ions varied from 8-25 mg/L and 30-60 mg/L, respectively. The initial concentrations varied because of different sampling times from WWTP Horstermeer. The breakthrough curves of potassium and calcium ions in six cycles are shown in Fig. 5. The vertical axis represents the ratio of column effluent concentration to influent concentration, $C_t/C_0$. The red and blue dots represent the $C_t/C_0$ ratio of potassium and calcium ions in the column effluent samples. The $C_t/C_0$ ratio of potassium and calcium ions increased to 0.94 and 1.03 at 116 bed volumes. Subsequently, the $C_t/C_0$ ratio of both cations remained at approximately 1 in the remaining bed volumes. The results indicated that zeolite granules were saturated with potassium and calcium during the first cycle. The estimated maximum adsorption capacity of the potassium and calcium was approximately 0.9 and 2.0 mg/g, respectively. It can be indicated that potassium and calcium ions were possibly removed from wastewater by the limited ion-exchange property of high-silica zeolite, especially of the MOR type. Similarly, the study of Doekhi-Bennani et al. (Doekhi-Bennani et al. 2021) reported that high-silica zeolite MOR could simultaneously remove ammonium ions and sulfamethoxazole from water.

Comparing the breakthrough curves of cations with the breakthrough curve of CBZ (Fig. 4f), in the first cycle, a fast breakthrough of CBZ happened before 72-116 bed volumes, and the adsorption capacity of CBZ occurred a sudden increase starting from 116 bed volumes. In contrast, in the subsequent five cycles, the breakthrough performance of CBZ remained stable. An enhancement of the adsorption of CBZ was observed when the zeolite granules were saturated with potassium and calcium ions. A similar observation was reported in the adsorption of CBZ on a metal-organic framework MIL-53(Al), with enhancement adsorption of CBZ by the potassium ions adsorbed on the adsorbent (Sompornpailin et al. 2021). However, the effect of cations on the adsorption of OMPs by zeolite has not been reported in the literature. Further investigation is recommended to address the effect of cations on the adsorption performance of OMPs.

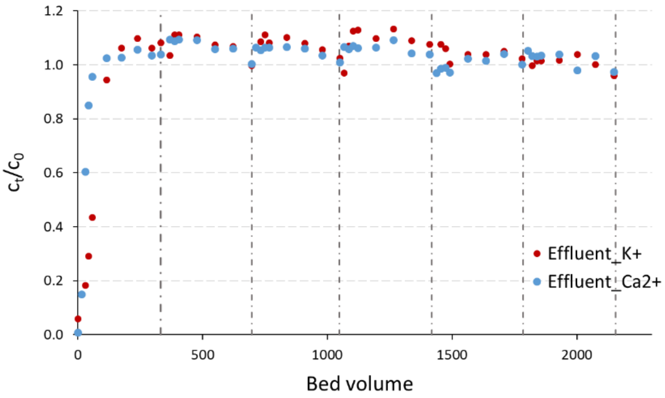


Fig. 5. Adsorption breakthrough curves of potassium and calcium ions in six cycles

### *3.3 Regeneration performance*

During the *in-situ* regeneration with ozone gas, real-time temperature measurement on the external wall of the glass column was realized by applying an infrared thermometer. The movement of the heat release zone in the column during regeneration is shown in Fig. 6. The red area represents the heat release zone with a temperature of 27-30 °C, while the blue area represents the normal zone in the column with a temperature of 21-23 °C. At 10 min regeneration, the heat release zone was at the top of the column, around 21-24 cm. At 20 and 25 min regeneration, the zone moved downward to 14-18 cm and 9-12 cm, respectively. At 30 min regeneration, the zone moved down to the bottom, and the heat was spreading. This phenomenon indicated that the reaction of ozone with the target OMPs adsorbed on zeolite granules was very fast and happened immediately after contact. The released heat might be recovered and reused for column drying in real applications.

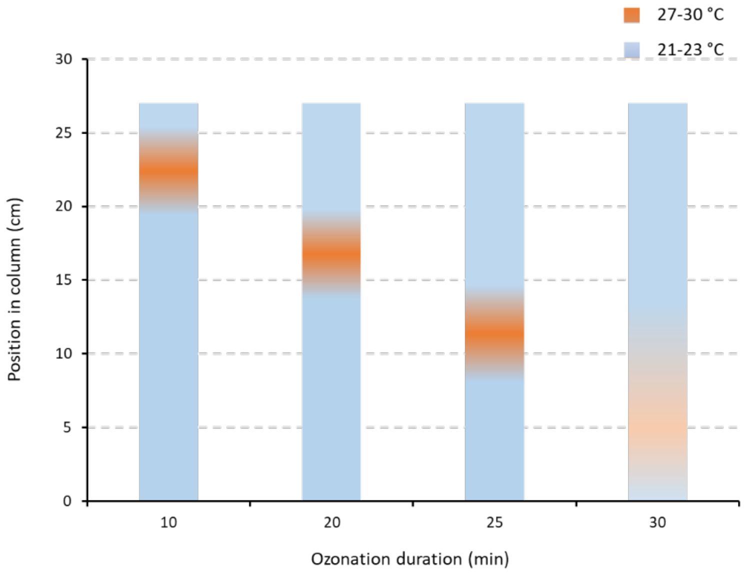


Fig. 6. Heat release zone movement in the column during ozone-based regeneration

The relative adsorption capacity (Rq) of six OMPs after each regeneration cycle is shown in Fig. 7. The adsorption capacities of the fresh granules were 17.8, 6.8, 3.5, 6.8, 2.6, and 3.9 μg/g for CLA, CBZ, MeBT, BT, SMX, and DIC, respectively. The Rq of CLA reached 0.8 in the first cycle and remained constant at 0.6 in the rest cycles. The error bar of CLA decreased in six cycles. It can be hypothesized that the decrease of the error bar was attributed to the ozonation transformation products that remained in the granules. In the first few cycles, the adsorption sites located at the inner part of the granules were gradually occupied by the adsorbed CLA, and the ozonation transformation products formed during regeneration probably remained in the granules, resulting in a significant fluctuation of Rq. The Rq of CBZ reached 0.9 in the first cycle and subsequently decreased to 0.7 in the second cycle and remained at 0.6 in the rest cycles. Corresponding to the results in Fig. 4f, the Rq value of 0.9 might be caused by the effect of cations. The high Rq suggests that there were still many adsorption sites available on the zeolite granules for the adsorption of CBZ. The Rq of MeBT reached 0.6 in the first cycle, decreased to 0.5 in the third cycle, and remained at 0.75 in the last three cycles. The experiments with the granules from the first three and last three cycles were conducted in separate batches of adsorption. The biodegradation of 5-MeBT might be slightly different as the wastewater for different batch experiments was sampled at different times from WWTP Horstermeer. Thus, the Rq of MeBT in the last three cycles was higher than that in the first three cycles. The Rq of BT decreased from 0.6 in the first cycle to 0.3 in the fourth cycle and remained at 0.3 in the last two cycles. The Rq of SMX decreased from 0.2 to 0.1 in six cycles, while the Rq of DIC decreased from 0.15 to 0 in six cycles. The large error bars of SMX and DIC further proved the poor adsorption performance of both OMPs. The results corresponded well with the results shown in Fig. 4.

In addition, the Rq values did not reach 1 after different regeneration cycles, indicating that the adsorption capacity of the granules after regeneration was lower than that of the fresh granules. In the batch adsorption experiments, all the granules were used in pulverized form to obtain fast equilibrium adsorption, leading the inner part of the granules to be exposed to the OMPs in wastewater. However, the inner part of the regenerated granules might not be regenerated to a full extent as ozone diffusion depth to the inner part of granules might have a limitation under the applied experimental conditions. After a few cycles, the Rq values remained stable, the adsorption sites were gradually occupied by the OMPs, and the regeneration by gaseous ozone occurred in the outer space inside granules. For the medium-adsorbing OMPs (CLA, CBZ, MeBT and BT), the adsorption sites in the outer part of the granules might be adequate for their removal. Further research into mass transfer kinetics and granule size is strongly recommended.

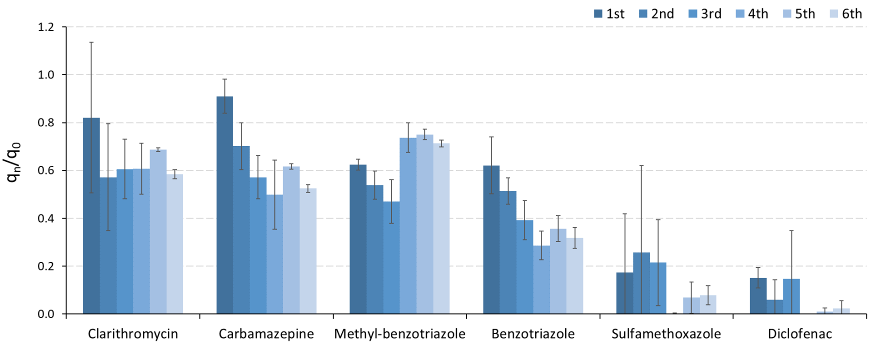


Fig. 7. The relative adsorption capacity of the target OMPs after regeneration in six cycles

### *3.4 Ozone consumption and the importance of backwash*

During the *in-situ* regeneration, ozone concentration in the inflow and outflow was monitored. The ozone concentration as a function of ozonation duration is shown in Fig. 8. In all six cycles, the ozone concentration of the off-gas started to increase from 0 at 10 min and reached equilibrium at around 120 min. A decrease in the ozone equilibrium concentration of the off-gas was observed in the second cycle. Thus the ozonation duration was extended from 3 to 5 h for the remaining cycles. The varying durations of pre-backwash may cause the varying equilibrium concentration of off-gas in different cycles. Before the 1st, 2nd, 3rd, and 5th regeneration, the pre-backwash duration lasted for 30 min, while before the 4th and 6th regeneration, the pre-backwash duration lasted for 1 h. A longer backwash duration can wash out most of the biofilm formed on granules (Simpson 2008). Less microbial biomass on granules means less organic matter to oxidize. Therefore, less ozone was consumed during the ozonation process. In the 4th and 6th regeneration, an estimated ozone consumption was approximately 3 g. In the 3rd and 5th regeneration, an estimated ozone consumption was approximately 11.4 g. The difference in the ozone consumption between the 4th and 6th regeneration, and the 3rd and 5th regeneration, was around 8 g (blue pattern-filled area in Fig. 8). It indicated that the ozone consumption could be reduced by approximately 70% by increasing the duration of the pre-backwash from 30 min to 1 h. As the adsorption of OMPs performed stable in six cycles (Section 3.1), pre-backwash duration might only influence the ozone consumption and not the regeneration efficiency. Ozonation was still effective under low ozone consumption. Further investigation into the optimization of the pre-backwash is recommended.

In addition, the concentration of OMPs in the backwash water influent and effluent was monitored. Column effluent from the adsorption cycle was applied for the pre-backwash, and demi-water was applied for the post-backwash. The high-adsorbing OMPs (SOT, MP, TMP, and PRO) concentrations in the pre-backwash influent and effluent were relatively low because of their high adsorption capacities on zeolite. The low-adsorbing OMPs (SMX and DIC) concentrations did not increase from the pre-backwash influent to effluent. As they were both saturated in the column, the pre-backwash influent and effluent concentrations were equal to those in the column influent during the adsorption cycle. For the medium-adsorbing OMPs (CLA, CBZ, MeBT, and BT), taking BT as an example, its concentration increased by 13-20% from the pre-backwash influent to effluent in each cycle. The concentration increase was attributed to the presence of the feed wastewater (column influent during the adsorption cycle) in the pre-backwash effluent. Before the pre-backwash process, the column was drained. The feed wastewater that remained on granules was flushed out with the backwash water, resulting in a concentration increase of BT. The results indicated that the OMPs desorption effect during the pre-backwash process was negligible. During the post-backwash process, large amounts of tiny bubbles were flushed out from granules. The bubbles might contain $CO_2$ generated in the mineralization of OMPs and trapped in the pores of zeolite granules. The target OMPs were not detected in the post-backwash effluent. Furthermore, the post-backwash process can be expected to remove the ozonation transformation products from the granules after regeneration in case they are produced during the regeneration cycle. The detection and identification of the ozonation transformation products generated in regeneration were not within the scope of the current study. Further investigation on the occurrence and fate of the ozonation transformation products in this technology is recommended.

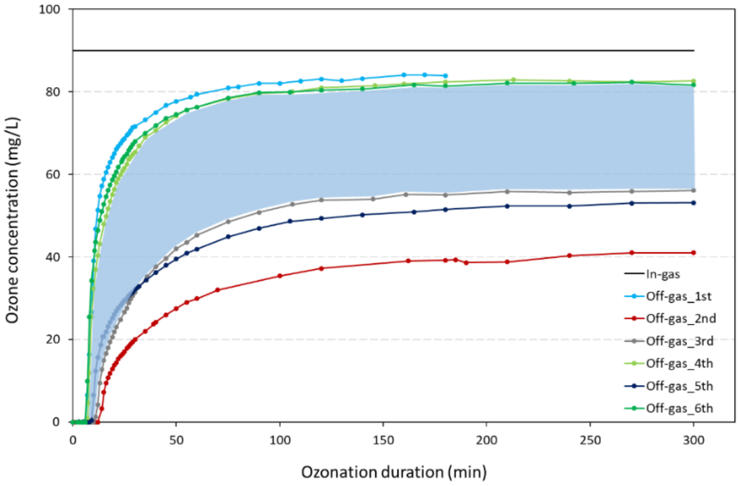


Fig. 8. Ozone concentration of in-gas and off-gas as a function of time

### *3.5 DOC removal*

The ratio of the concentration of DOC in the column effluent and influent in six cycles is shown in Fig. 9. The column effluent samples were taken from the column effluent tank after 5 days of adsorption. The average DOC value of the column influent was 8.8 mg/L. The DOC ratio was 0.97 in the first adsorption and decreased to 0.93 in the second adsorption. Subsequently, the DOC ratio remained at 0.92 in the remaining four cycles. On average, less than 8% of DOC was removed from wastewater. It was considerably low compared to the DOC removal by a GAC filter, which could remove 70% of DOC from wastewater in 6 to 10 consecutive days (Sounthararajah et al. 2016, van der Aa et al. 2011). Less DOC adsorbed on granules results in less ozone consumption by DOC. Thus, ozonation for OMP oxidation was more efficient as no ozone was used for the oxidation of DOC.

Moreover, the DOC value represents the proportion of NOM fractions in wastewater. Caltran et al. (Caltran et al. 2020) reported that over 97% of NOM was rejected by a ceramic membrane with a pore size of 0.9 nm. As the pore size of the zeolites used in the current study was between 0.6 and 1.0 nm (Table S1), the majority of NOM fractions could be expected not to be able to enter the zeolite pores and to be adsorbed. The DOC ratio obtained in six cycles proved that zeolite granules could hardly adsorb NOM fractions. The marginal decrease of the DOC was possibly due to two aspects. One aspect was that zeolites could adsorb small molecules of NOM fractions. The other aspect was that forming the biofilm on the surface of granules could consume NOM fractions. In the subsequent processes, the adsorbed small NOM fractions could be oxidized by ozonation, and the biofilm could be effectively removed by the backwash and ozonation processes. Therefore, the removal efficiency of the DOC was constantly low in six cycles.

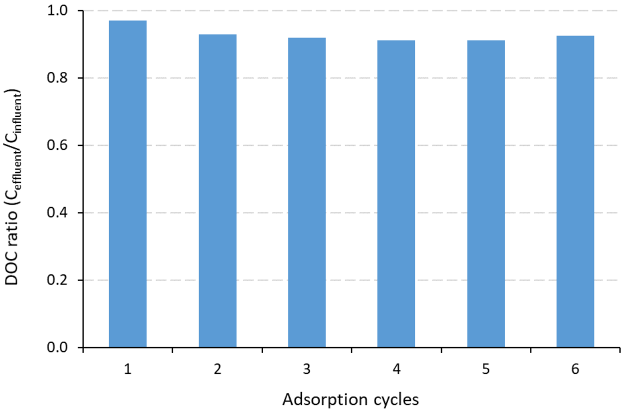


Fig. 9. DOC ratio of the effluent and influent in six cycles

## 4. Conclusions and outlook

The primary goal of the current research was to study the OMPs removal performance from WWTP effluent by a zeolite granules fixed-bed column followed by *in-situ* regeneration by gaseous ozone. The granular zeolite column can selectively and effectively adsorb the target OMPs from WWTP effluent under continuous flow conditions in six adsorption-regeneration cycles. For SOT, MP, TMP, and PRO, the removal efficiency was approaching 100%. For CLA, CBZ, and MeBT, the removal efficiency was above 85%. For BT, the removal efficiency was around 70%. The adsorption of SMX and DIC was less favourable than the other OMPs due to their negatively charged occurrence in wastewater. Potassium and calcium ions might enhance the adsorption of CBZ. In addition, DOC removal was less than 8%. The effect of most NOM fractions on the adsorption of OMPs was negligible. Further research about the effect of small NOM fractions and cations on the adsorption of OMPs by zeolite granules is recommended. The *in-situ* regeneration with ozone gas was efficient in recovering the adsorption capacity of the zeolite filter. The pre-backwash process was essential in reducing ozone consumption during regeneration. A longer duration of pre-backwash can remove the majority of the biofilm formed on the zeolite granules. Thus, less ozone was consumed by the biofilm in regeneration.

## Supplementary Information

Table S1. Structural and chemical characteristics of zeolites selected for granulation

| Type | Pore opening size[a] (Å*Å) | Surface area ($m^2/g$) | Micro-pore surface area ($m^2/g$) | Pore volume ($cm^3/g$) | Micro-pore volume ($cm^3/g$) | Si/Al ratio (XRF) | BAS[b] (μmol/g) | LAS[c] (μmol/g) | Reference |
|---|---|---|---|---|---|---|---|---|---|
| BEA | 6.6*7.7<br>5.6*5.6 | 516 | 351 | 0.3022 | 0.1557 | 286 | 16 | 7 | Jiang et al. (Jiang et al. 2020) |
| MOR | 6.5*7.0<br>2.6*5.7 | 431 | 360 | 0.2687 | 0.1606 | 113 | 52 | 8 | Jiang et al. (Jiang et al. 2020) |

[a] Two channel systems are interconnected at right angles (Baerlocher et al. 2007)

[b] Brønsted acid sites

[c] Lewis acid sites

Table S2. The yearly average concentrations in the secondary effluent of WWTP Horstermeer

| Composition (mg/L) | 2021 | 2020 | 2019 | 2018 | 2017 |
|---|---|---|---|---|---|
| COD | 31 | 30 | 32 | 32 | 32 |
| N-Kj | 3 | 2.8 | 2.6 | 2.2 | 2.2 |
| $NH_4^+$ | 1.47 | 1.28 | 0.97 | 0.62 | 0.54 |
| $NO_3^-$ | 4.6 | 5.8 | 5.4 | 4.7 | 4.2 |
| $NO_2^-$ | 0.12 | 0.11 | 0.09 | 0.1 | 0.1 |
| NOx | 4.7 | 5.9 | 5.5 | 4.8 | 4.3 |
| N-tot | 7.8 | 8.8 | 8.1 | 7.1 | 6.5 |
| P-tot | 0.37 | 0.44 | 0.38 | 0.34 | 0.37 |
| P-ortho | 0.09 | 0.19 | 0.16 | 0.15 | 0.16 |
| TSS | 5.3 | 6.2 | 5.6 | 15.7 | 6.2 |

Table S3. LOD, LOQ and retention time for each OMP in LC-MS analysis

| OMPs | LOD (μg/L) | LOQ (μg/L) | Retention time (min) |
|---|---|---|---|
| Sotalol (SOT) | 0.017 | 0.05 | 1.96 |
| Metoprolol (MP) | 0.017 | 0.05 | 2.28 |
| Trimethoprim (TMP) | 0.003 | 0.01 | 2.18 |
| Propranolol (PRO) | 0.033 | 0.10 | 2.47 |
| Clarithromycin (CLA) | 0.167 | 0.50 | 2.56 |
| Carbamazepine (CBZ) | 0.017 | 0.05 | 2.58 |
| Methyl-benzotriazole (MeBT) | 0.003 | 0.01 | 2.38 |
| Benzotriazole (BT) | 0.003 | 0.01 | 2.24 |
| Sulfamethoxazole (SMX) | 0.003 | 0.01 | 2.41 |
| Diclofenac (DIC) | 0.017 | 0.05 | 3.01 |

Table S4. The adsorption performance of the target OMPs

| Adsorption performance | OMPs | Removal efficiency (%)[a] | Freundlich model fitting | | |
|---|---|---|---|---|---|
| | | | $K_F$, (μg/g)/(μg/L)$^n$ | n | $R^2$ |
| High | Sotalol (SOT) | 99.1 | 24.68 | 0.39 | 0.93 |
| | Metoprolol (MP) | 99.7 | 290.47 | 0.89 | 0.92 |
| | Trimethoprim (TMP) | 98.8 | 18.61 | 0.44 | 0.97 |
| | Propranolol (PRO) | 99.8 | 40.42 | 0.32 | 0.91 |
| Medium | Clarithromycin (CLA) | 91.5 | 22.60 | 1.29 | 0.99 |
| | Carbamazepine (CBZ) | 79.1 | 6.02 | 0.84 | 0.93 |
| | Methyl-benzotriazole (MeBT) | 85.6 | N/A | N/A | N/A |
| | Benzotriazole (BT) | 52.3 | 3.07 | 0.81 | 0.98 |
| Low | Sulfamethoxazole (SMX) | 34.5 | N/A | N/A | N/A |
| | Diclofenac (DIC) | 45.7 | 1.03 | 1.70 | 0.97 |

[a] The removal efficiency of OMPs at zeolite granule dosages of 0.5 g/L

Table S5. The adsorption kinetics constants of the target OMPs

| OMPs | MW (g/mol) | Kinetic constant, *k* (1/s)[a] | |
|---|---|---|---|
| | | GAC[b] | zeolite granules |
| Benzotriazole | 119 | 3.78E-06 | 4.28E-06 |
| Carbamazepine | 236 | 1.69E-06 | 2.04E-06 |

[a] Pseudo-first-order fitting

[b] Granular activated carbon (GAC) applied in the O3GAC project (Liu 2017)

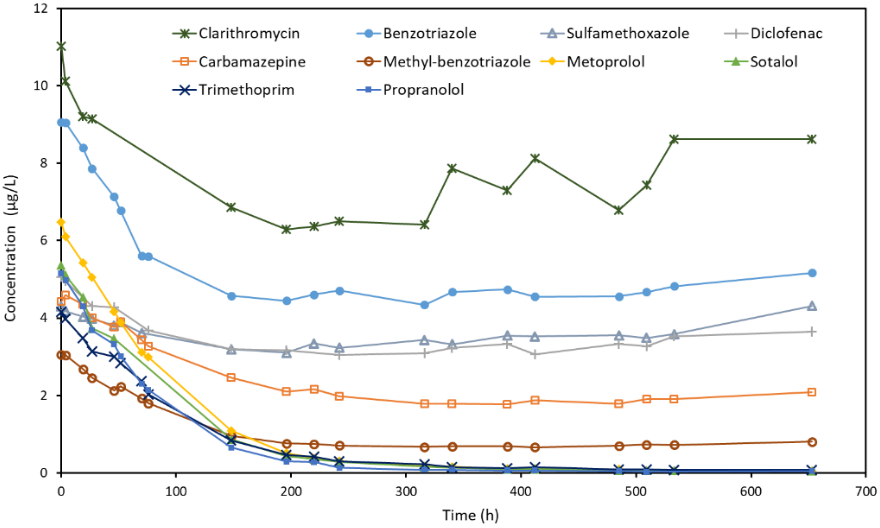


Fig. S1. Adsorption kinetics of the target OMPs on zeolite granules

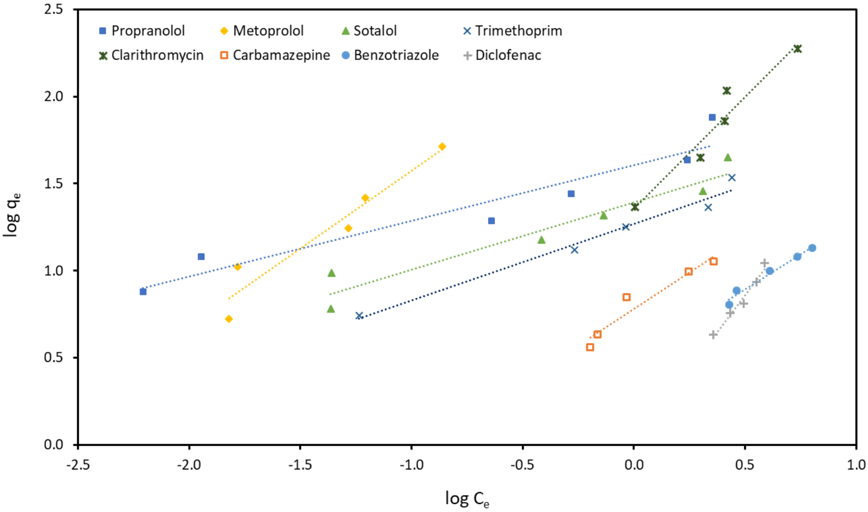


Fig. S2. Adsorption isotherms of the target OMPs on zeolite granules, Freundlich model fitting

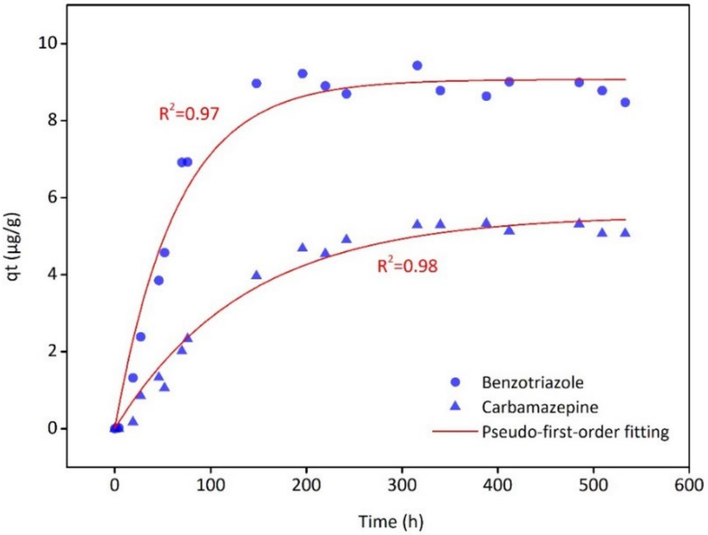


Fig. S3. Effect of time on the adsorption of benzotriazole and carbamazepine, pseudo-first-order fitting

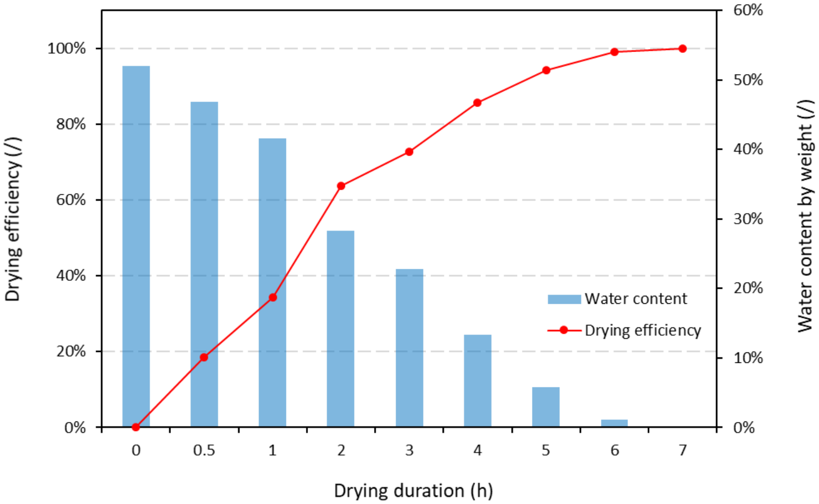


Fig. S4. Drying efficiency and water content by weight as a function of drying time

*Adsorption kinetics and isotherms*

The adsorption kinetics of the target OMPs by zeolite granules in OMPs-spiked wastewater (described in Section 2.3) was studied in batch mode at 20 °C. 0.5 g of fresh granules were added to 1 L of OMPs-spiked wastewater in a glass bottle. The solution was stirred at 100-120 rpm for 27 days. A low stirring rate was applied to avoid any abrasion of granules during adsorption. Water samples were collected at different time intervals.

The adsorption isotherms of the target OMPs by zeolite granules in OMPs-spiked wastewater (described in Section 2.3) was studied in batch mode at 20 °C. Different amounts of zeolite granules (0, 10, 20, 50, 100, 200, 300, 500, 800, and 1000 mg) were added to 1 L of OMPs-spiked wastewater in several 1 L glass bottles. The solution was stirred at 100-120 rpm for 14 days to obtain adsorption equilibrium. Water samples were collected before and after adsorption.

All the water samples were filtered over 0.2 µm polycarbonate syringe filters for LC-MS analysis.

The decrease in the concentrations of the target OMPs as a function of time is shown in Fig. S1. The adsorption of all target OMPs reached equilibrium after 14 days (340 h). After reaching equilibrium, the target OMPs could be categorized into three groups by their removal efficiencies. The three groups of OMPs are listed in Table S4. The effect of time on the adsorption capacity of benzotriazole and carbamazepine was selected for pseudo-first-order fitting (Fig. S3). The kinetic constants of benzotriazole and carbamazepine by GAC and zeolite granules are listed in Table S5. The kinetic constants were related to the molecular weight of the specific OMPs. The kinetic constants of zeolite granules were approaching those of GAC. The results indicated that zeolite granules might have similar kinetic behaviour to GAC.

*Drying of the column*

Zeolite granules were dried at 105 °C overnight and packed into the column used in the current study. Dried granules were soaked in demi-water overnight. After draining the column, the column was tightly wound by soft tubings with 80 °C hot water recirculating inside. The recirculation flow rate was around 0.9 L/min. Compressed air was introduced from top to bottom in the column at a flow rate of 8 L/min (0.1 m/s). The drying process lasted for 7 hours. The mass of the empty column was measured. As granules were not transferred out of the column during drying, the sum mass of the granules and the column was measured after different time intervals. The mass change determined the drying efficiency. The drying efficiency ($D$) and water contents ($w$) in granules were calculated by:

$$D = \frac{mt - md}{m0 - md} \times 100$$

$$w = \frac{mt - md}{mt} \times 100$$

where $mt$ is the mass of the granules after different drying time intervals (g); $md$ is the mass of the fully-dried granules (g); $m0$ is the mass of the granules after draining the column (g).

The temperature of the compressed air venting out of the column (monitored at the bottom port) reached 50-60 °C. The drying efficiency and water content by weight as a function of drying time are shown in Fig. S4. The drying efficiency increased along with the time and reached 99.9% after 7 h of drying. The water content by weight in granules was 52% for drained granules and decreased to 0.1 % after 7 h of drying. The results indicated that the granules were fully dried after the drying process.

# Chapter 6

## Conclusions and outlook

This chapter comprises the main conclusions of the dissertation and the outlook for future research.

## 1. Main Conclusions

The current dissertation adopted a step-by-step method to investigate the feasibility of applying innovative technology to remove OMPs from water, combining the adsorption of OMPs from water on zeolite granules and the regeneration of OMPs-loaded zeolite granules with gaseous ozone. The main conclusions corresponding to the research questions (*RQ*) are as follows.

*RQ 1. What is the current knowledge about different oxidative technologies that can be applied to regenerate granular zeolites loaded with OMPs?*

**Chapter 2** reviewed the current oxidative treatment technologies to degrade the OMPs adsorbed on zeolite granules, including thermal and chemical oxidation treatment. Chemical oxidation treatment applies ozonation and advanced oxidation processes (AOPs). AOPs are based on the generation of oxidative radicals in Fenton reactions and UV radiation. This review indicated that the oxidative treatment technologies combined with the adsorption of OMPs on zeolite granules could significantly remove OMPs from the environment. However, the drawbacks of thermal treatment and AOPs might restrict their application for practice. The operational costs of thermal treatment are relatively high. Although the oxidative radicals generated in different AOPs are strong oxidants, the degradation of OMPs is limited because radicals cannot diffuse within the pores of zeolite to degrade OMPs. The operational conditions need to be optimized to achieve better degradation efficiency. In contrast, ozone molecules can effectively degrade OMPs via direct ozonation in the presence of zeolite granules. The adsorption of OMPs on zeolite can enhance the ozonation efficiency. Hence, this review further recommended that applying ozonation to regenerate the zeolite granules loaded with OMPs might be a promising technology for removing OMPs from water.

*To answer RQ 2, 3 and 4, the sequence of the experimental work was designed based on the complexity of the water matrix in lab-scale experiments.*

*RQ 2. Is ozone-based regeneration efficient for regenerating zeolite granules loaded with a single OMP?*

**Chapter 3** studied the removal of acetaminophen from demi-water. Acetaminophen is one of the prevalent pharmaceuticals in treated wastewater. It can be favourably adsorbed by zeolite and easily degraded by ozone. After the adsorption breakthrough in the column tests, zeolite granules were regenerated directly by gaseous ozone. Water content in granules significantly influenced the regeneration performance. Ozone-based regeneration of totally dried granules (0% water content by weight) is more efficient than drained granules (40% water content). More ozonation transformation products were generated during the regeneration of totally dried granules, indicating that the degradation of the adsorbed acetaminophen can proceed further when no water is present in the granules. Moreover, at the same total ozone dose (g/h), longer ozonation duration results in higher regeneration efficiency. The adsorption performed stable in three cycles with only a 7% decrease in the adsorption capacity.

*RQ 3. How does the ozone-based regeneration perform with zeolite granules loaded with various OMPs?*

**Chapter 4** investigated the removal of various OMPs from demi-water. The target OMPs were spiked into demi-water at 4-5 μg/L for lab experiments. The granulation method of zeolite was developed by applying a 3D clay printer. The zeolite granules containing three zeolites can effectively adsorb OMPs. The target OMPs were categorized into three groups based on the adsorption performance at the granule dosage of 0.1 g/L in batch experiments. The groups were low-, medium-, and high-adsorbing OMPs. The regeneration of dried granules loaded with various OMPs by gaseous ozone was efficient. The adsorption performance of the low-adsorbing OMPs, carbamazepine and diclofenac, was probably influenced by the ozonation transformation products in 30 min of ozonation duration. 60 min of ozonation duration was long enough to fully recover the adsorption capacities of the medium- and high-adsorbing OMPs on zeolite granules. The regeneration performed stable in seven cycles. In the long-term operation, the accumulation of ozonation transformation products might only influence the adsorption of diclofenac. Thus, applying longer ozonation duration was recommended to promote the regeneration efficiency of specific OMPs.

*RQ 4. What is the performance of this combined technology in treating real wastewater?*

**Chapter 5** studied the performance of the combined *AdOx* technology to treat real wastewater spiked with eleven OMPs at 4-5 μg/L. Secondary effluent from WWTP Horstermeer (the Netherlands) was applied for lab-scale experiments in this last research stage. In six cycles, the granular zeolite filter could selectively and effectively adsorb the target OMPs from wastewater under continuous flow conditions. The on-site regeneration with gaseous ozone could efficiently recover the adsorption capacity of the dried zeolite filter. As the adsorption behaviour of the target OMPs in different cycles was reproducible, the regeneration performance was stable in long-term operation. The removal efficiency of eight OMPs (sotalol, metoprolol, propranolol, trimethoprim, clarithromycin, carbamazepine, methyl-benzotriazole, and benzotriazole) reached between 70% and 100%. The adsorption of sulfamethoxazole and diclofenac was not favourable because these two OMPs were negatively charged in wastewater. As only less than 8% of DOC was removed from wastewater, the effect of most NOM fractions in wastewater on the adsorption of the target OMPs was negligible. The backwash after adsorption was essential to remove the biofilm formed on the granules. Increasing the backwash duration from 30 min to 1 h could reduce the ozone consumption during regeneration by around 70%. In addition, the potassium and calcium ions might enhance the adsorption of carbamazepine.

## 2. Originality and innovation

The original contribution of the current dissertation to knowledge is establishing a new barrier for OMPs occurring in wastewater by advanced integrated technology, adsorption followed by ozonation. In the last decades, the detection efficiency and accuracy for OMPs are improving with the development of analytical equipment. More OMPs are detected at low concentrations due to better analytical detection methods, and the presence of OMPs even at low concentrations leads to public concerns because the OMPs may adversely affect human health. Many post-treatment technologies to remove OMPs from water are on the verge of breakthroughs, such as oxidative techniques (ozone, UV, AOP), adsorbents (powdered activated carbon, granular activated carbon, cyclodextrine), and membrane filtration. However, these technologies are insufficiently proven to apply to large-scale WWTPs. By learning through implementation, this current study provides a new option for practical application to protect water bodies from OMP contamination. This new barrier in the current research is a complementary technology to the traditional WWTPs and can be easily added to existing WWTPs.

Zeolite can selectively adsorb OMPs from wastewater in the presence of NOM. In regeneration, ozone is only dosed for degrading the adsorbed OMPs. The ozone dosage in this technology is promisingly lower than that in directly applying ozone to treat wastewater. On-site regeneration leads to significant savings in footprint and investment costs compared to conventional off-site regeneration. The short running time of adsorption and frequent ozone-based regeneration can bring more application flexibility at acceptable costs. Furthermore, one bonus advantage of this technology is that no bromate is formed while applying ozone. Bromate is a harmful oxidation by-product formed in direct ozonation of wastewater. The current bromate standard for surface water is strictly regulated in the Netherlands at 1 μg/L. In the current technology, as bromide in wastewater is not adsorbed by zeolite and ozonation occurs in a side stream, the dosed ozone is not in contact with bromide to form bromate. Thus, the WWTP effluent is free of bromate.

## 3. Extended research

*Adsorption*

Future fundamental research should be carried out to address the unfavourable adsorption of some specific OMPs. In the current dissertation, three OMPs require further attention: carbamazepine, sulfamethoxazole, and diclofenac. The adsorption of carbamazepine in demi-water is not favourable. However, its adsorption in wastewater is probably enhanced because of the presence of cations. The mechanism of this enhancement is still unclear and needs further investigation to accommodate this integrated technology to different water matrices. The adsorption of sulfamethoxazole and diclofenac is not favourable, as both are negatively charged in demi-water and wastewater. The negatively charged form of sulfamethoxazole contributes only 30% in demi-water with a pH of 5.8, whereas the negatively charged form of sulfamethoxazole is above 90% in wastewater with a pH of 7. Larger amounts of the negatively charged form of sulfamethoxazole result in lower adsorption of sulfamethoxazole in wastewater than in demi-water. How to improve the adsorption of negatively charged OMPs on zeolite granules? High-silica zeolite is negatively charged because of the presence of aluminium atoms. Electrostatic repulsion arises between the negatively charged OMPs and the zeolite surface. The adsorption of the negatively charged OMPs might be improved by modifying zeolite to a neutral-charged form to avoid electrostatic repulsion.

Apart from the OMPs on the list given in this dissertation, perfluorinated compounds (PFAS) are becoming the top priority pollutants discussed widely in public. PFAS are widely used in various industries, such as textiles, household products, and food processing. PFAS is persistent in the aquatic environment, and its presence in drinking water can lead to serious health effects (Hussain et al. 2022). Current PFAS regulations impose threshold PFAS concentrations in tap water, surface water and wastewater (Parliament and Union 2020). The four PFAS in the assessment from the European Food Safety Authority (EFSA) focuses on perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), perfluorononanoic acid (PFNA), and perfluorohexane sulfonic acid (PFHxS). Besides, the new European Drinking Water Directive applies a list of 20 PFAS (in Annex III) with a limit value of 100 ng/L (0.1 μg/L) for the sum of these 20 PFAS compounds (Parliament and Union 2020). All-silica zeolite Beta has been reported as an adsorbent with high affinity and selectivity for PFOS and PFOA, leading to an effective removal from water (Van den Bergh et al. 2020). As PFAS is negatively charged in wastewater at pH 7, applying all-silica zeolite might improve the adsorption of negatively charged OMPs.

Furthermore, a comprehensive understanding of the adsorption mechanism for specific OMPs should be gained. Unfortunately, this understanding is not within the scope of the current dissertation. Jiang et al. (Jiang et al. 2018) reported a review regarding the adsorption mechanism of OMPs on zeolite. The structural properties and hydrophobicity of zeolite significantly influence the adsorption of OMPs. The adsorption sites on zeolite, including oxygen and acid sites, may promote the adsorption of specific OMPs. Silanol groups existing on the local defects formed in the dealumination of zeolite can facilitate the adsorption of hydrophilic OMPs. This dissertation provides a feasible option to treat a broad range of OMPs by blending different zeolites into granules. More options would be available by selecting different zeolites for practical application based on the adsorption mechanism.

*Regeneration*

In the current dissertation, ozone can effectively degrade the target OMPs, leading to stable adsorption performance in sequential cycles. However, not all OMPs are completely degraded by ozone, forming some transformation products. The occurrence of the ozonation transformation products needs further investigation. The ozonation process might be optimised by understanding the degradation pathways of certain OMPs. Moreover, some OMPs cannot be degraded by ozone molecules, such as PFAS. How to promote ozonation effectiveness to the OMPs that are resistant to ozone? Would adding hydrogen peroxide be an option? Ozone can generate hydroxyl radicals in the presence of hydrogen peroxide. Taking advantage of the high oxidative radicals can promote the degradation of the OMPs on zeolite. The mass transfer kinetics in zeolite granules with a specific granular size is strongly recommended for this case. Would applying specific zeolite that can promote catalytic ozonation be an option? Ikhlaq et al. (Ikhlaq and Kasprzyk-Hordern 2017) reported that hydrophobic zeolite ZSM-5 catalysed surface reactions between the OMPs and ozone adsorbed on zeolite, leading to the generation of chlorides during the oxidation of chlorinated OMPs. If adding a zeolite that can play a catalytic role in granules, the degradation of the ozone-resistant OMPs might be improved.

## 4. Pilot-scale prospect

The proof-of-practice tests at the lab scale were finalized with promising results, sufficiently supporting this technology to step into the up-scale research level. A small pilot-scale test applying this technology to remove OMPs from wastewater will soon be launched at the WWTP Leiden-Noord. From the practical application perspective, a pilot scale is vital to achieving technology breakthroughs. Many uncertainties must be addressed in the pilot-scale test to upgrade the technological levels in the next decade.

The optimizations of the operational conditions will be achieved in the pilot-scale tests. The running conditions include the contact time in the adsorption column, the state and duration of the backwash, the drying condition of the column, and the ozonation parameters. As the post-backwash water might contain some ozonation transformation products, the occurrence and fate of the ozonation transformation products in the post-backwash water should be investigated. Besides, the eco-toxicity of the post-backwash water is also recommended for testing. In addition, the granulation was carried out by a 3D clay printer at the lab. The production capacity of granules cannot meet the need for a larger scale. A connection with zeolite companies is recommended to address the supply of zeolite granules for practical applications. The main parameters in selecting suitable zeolites are the adsorption capacity of specific OMPs and the granular size (length and diameter). Furthermore, the mechanical strength of the granules in a long-term operation will be studied in the pilot-scale tests. Based on the results from the pilot plant, this advanced integrated technology will be further evaluated, and the possibility of applying this technology on a demonstration installation scale will be determined.

# Summary

Organic micropollutants (OMPs) that occur in the aquatic environment at trace levels are emerging concerns to society. Domestic wastewater is an important source. OMPs end up in surface water and groundwater via conventional municipal wastewater treatment plants (WWTPs), penetrating drinking water. Comprising pharmaceuticals, personal care products, pesticides, industrial chemicals, and other compounds, OMPs are persistent in water and can lead to adverse effects on human health under long-term exposure. As WWTPs are not designed to remove OMPs, various post-treatment technologies have been developed to remove OMPs from wastewater effluents over the last decades, including activated carbon adsorption, ozonation, and membrane filtration. However, the performance of these technologies is significantly influenced by natural organic matter (NOM). In the combined application of ozonation and activated carbon adsorption, the operational costs and the environmental impact are relatively high because of the off-site thermal treatment of the exhausted carbon. The *AdOx* technology aims to establish a new barrier by applying sequential adsorption and oxidation to remove OMPs from municipal wastewater effectively. As an alternative adsorbent for activated carbon, zeolite possesses uniform pores (0.6-1.0 nm) that appropriately match the molecules of OMPs. This uniform framework can potentially exclude the large molecules of most NOM fractions in wastewater. This innovative technology, selective adsorption of OMPs on zeolite granules followed by on-site ozone-based regeneration of the granules loaded with OMPs, can lead to the next generation of OMPs removal, characterized by high removal efficiencies, low costs, and low environmental impacts.

The research questions were determined based on an extensive literature review: What is the current knowledge about different oxidative technologies that can be applied to regenerate granular zeolites loaded with OMPs? Is ozone-based regeneration efficient for regenerating zeolite granules loaded with a single OMP? How does the ozone-based regeneration perform with zeolite granules loaded with various OMPs? What is the performance of this combined technology in treating real wastewater? The answers to each research question are given below.

The extensive review summarized the current oxidative technologies (thermal treatment and chemical oxidation treatment) to degrade OMPs in the presence of zeolite granules. Ozonation and advanced oxidation processes (AOPs, based on Fenton reactions and UV radiation) are commonly applied as chemical oxidation treatment. All these oxidative technologies can significantly remove OMPs from the environment when combined with zeolite granules that can effectively adsorb OMPs. However, the drawbacks of thermal treatment and AOPs might hinder their practical applications.

Thermal treatment has relatively high operational costs because zeolite granules need to be transported to a factory to recover the adsorption capacity of OMPs. The off-site thermal regeneration consumes high energy, thus increasing operational costs. The high carbon dioxide emissions can bring environmental issues. AOPs are based on the generated oxidative radicals to degrade OMPs. When applying AOPs to degrade the OMPs adsorbed on granules, the generation of radicals and the diffusion of radicals into granules might confront issues. In heterogeneous Fenton reactions, the added hydrogen peroxide needs time to diffuse into granules, contacting the immobilized iron species and generating radicals. The radicals are only generated on the active catalytic sites. As the lifetime of the radicals is too short, they cannot diffuse within the pores to degrade OMPs. In UV radiation, the irradiation proportion of the zeolite granules loaded with semiconductors significantly influences oxidation efficiency. Since the semiconductors only form the oxidative radicals on the granular surface, the degradation of the adsorbed OMPs in the inner part of the granules might not be sufficient. In ozonation, the dosed ozone can degrade the OMPs adsorbed on zeolite granules via direct oxidation by molecular ozone. Although the catalytic role of zeolite in ozonation needs further investigation, among the oxidative technologies, ozonation is recommended as a promising way to regenerate zeolite granules loaded with OMPs.

The aim was to develop a new barrier to remove OMPs from municipal WWTPs effluent. The sequence of the lab-experimental research was designed based on the complexity of the water matrix. How to apply ozone in the regeneration process is needed to be determined at the beginning of the research. Based on the literature and our preliminary results, ozone should be applied in the gas phase to regenerate the exhausted granules packed in a column.

The lab experiments began with removing a single OMP, acetaminophen, from demi-water. Acetaminophen is commonly consumed in households for treating pain and fever. It is one of the prevalent pharmaceuticals in treated wastewater. Another reason for selecting acetaminophen as the target OMP is that it can be favourably adsorbed by zeolite and easily degraded by ozone. Gaseous ozone was applied to regenerate the zeolite granules, which were saturated with acetaminophen in column adsorption tests. Granular water content was the main factor limiting regeneration performance as the ozone mass transfer rate in air is much fast than in water. The regeneration efficiency of the fully-dried granules (0% water content by weight) was 81%, whereas the totally-wet granules (collected directly after draining the column, 40% water content) was only 16% (Fig. 1). At the same total ozone dose (g/h), longer ozonation could lead to higher regeneration efficiency as ozone gas could diffuse into the inner pores of zeolite to decompose the adsorbed acetaminophen. The slight decrease of 7% in the adsorption capacity of acetaminophen in three cycles might be caused by the accumulation of ozonation transformation products in granules.

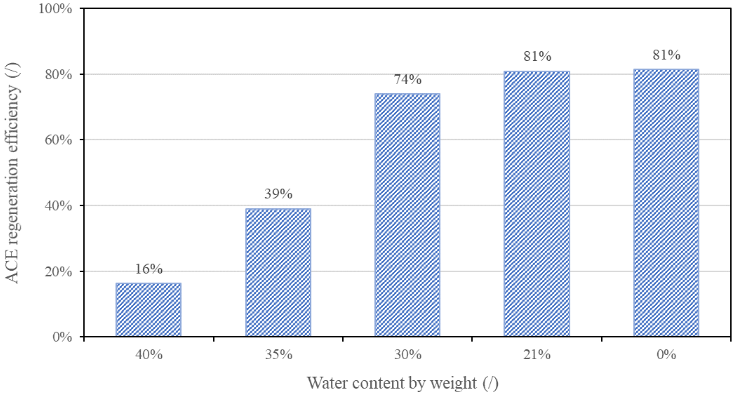


Fig. 1. The influence of water content in granules on acetaminophen regeneration efficiency

The subsequent lab experiments were conducted to study the removal of various OMPs from demi-water. The Dutch Ministry of Infrastructure and Water Management has listed eleven guide OMPs to monitor the removal effectiveness of OMPs in advanced wastewater treatment technologies, including sotalol, metoprolol, propranolol, trimethoprim, clarithromycin, sulfamethoxazole, methyl-benzotriazole, benzotriazole, carbamazepine, diclofenac, and hydrochlorothiazide. The guide substances come from pharmaceuticals and industrial chemicals. The removal efficiency for at least 7 of 11 OMPs should be above 70% in every 24- or 48-hour flow rate propositional sample. Hence, the target OMPs were spiked into demi-water at 4-5 μg/L for lab experiments. As propranolol, clarithromycin, and hydrochlorothiazide in the demi-water samples were poorly quantified, the other eight OMPs were the target OMPs in this research stage. The zeolite granulation method was developed in this research stage by applying a 3D clay printer with three zeolites blended into granules to remove OMPs. The target OMPs were categorized into low-, medium-, and high-adsorbing OMPs, based on the adsorption performance at the granule dosage of 0.1 g/L in batch experiments. The sequential adsorption-regeneration procedure is shown in Fig. 2. The regeneration of dried granules loaded with various OMPs was efficient by applying ozone gas. The adsorption of the low-adsorbing OMPs, carbamazepine and diclofenac, might be significantly influenced by the specific ozonation transformation products generated in the degradation of specific target OMPs in short ozonation running time (30 min). 60 min of ozonation at the applied conditions (Fig. 2) was long enough to fully recover the adsorption capacities of the medium- and high-adsorbing OMPs on zeolite granules. 75% of the adsorption capacity of the target OMPs remained fully recovered in seven cycles.

The accumulation of ozonation transformation products might only influence the adsorption of diclofenac. Therefore, a longer ozonation duration was recommended to promote the regeneration efficiency of the low-adsorbing OMPs.

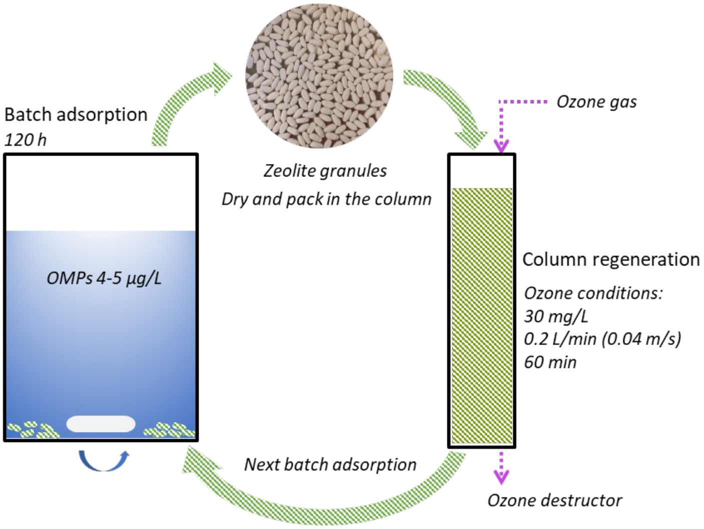


Fig. 2. Sequential adsorption-regeneration procedure

In the last research stage, the performance of applying this advanced technology to treat real wastewater was studied. Eleven OMPs were spiked at 4-5 µg/L in the secondary effluent collected from WWTP Horstermeer (the Netherlands) for lab experiments. The treatment process was divided into five steps: 1) selective adsorption of OMPs from wastewater in five days by a column packed with zeolite granules, 2) backwash of the column, 3) drying of the column, 4) on-site regeneration of the column with gaseous ozone, 5) post-backwash of the column (Fig. 3). In six sequential adsorption-regeneration cycles, the zeolite filter effectively adsorbed the target OMPs from wastewater under continuous flow conditions. The on-site regeneration of the dried zeolite filter with gaseous ozone could efficiently recover the adsorption capacity of the target OMPs. As the adsorption behaviour of OMPs in different cycles was reproducible, the regeneration performance was stable in long-term running. The removal efficiency of eight OMPs (sotalol, metoprolol, propranolol, trimethoprim, clarithromycin, carbamazepine, methyl-benzotriazole, and benzotriazole) reached between 70% and 100% in six cycles. The adsorption of sulfamethoxazole and diclofenac was not favourable, as both OMPs were negatively charged in wastewater. The electrostatic repulsion between the negatively charged OMPs and the zeolite surface might hinder the adsorption of the negatively charged OMPs. In six cycles, less than 8% of dissolved organic carbon (DOC) was removed from wastewater, indicating that the effect of the natural organic matter (NOM) on the adsorption of the target OMPs is negligible. Moreover, the backwash step after the adsorption process was essential to this technology. The ozone consumption in the subsequent regeneration process was reduced by 70% when the backwash duration was increased from 30 min to 1 h. In addition, the potassium and calcium ions in wastewater might enhance the adsorption of carbamazepine. The effect of cations on the adsorption of specific OMPs requires further investigation.

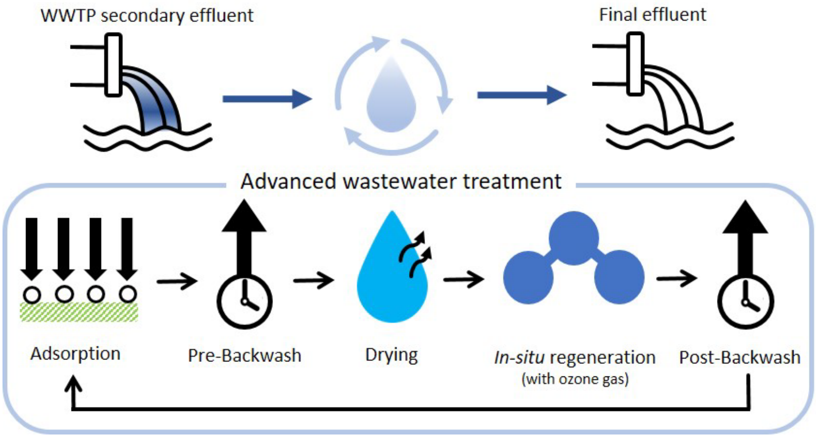


Fig. 3. Advanced wastewater treatment process

A pilot-scale test should be the next step to achieve a breakthrough of this advanced technology. The results from this dissertation are promising to support this technology to step into the next level. In this case, a small pilot-scale test will soon be launched in WWTP Leiden-Noord to upgrade the technology level. The optimizations of various operational conditions will be done on pilot plant scale, including the contact time of the column adsorption, the condition and duration of the backwash, the drying condition of the column, and the ozonation conditions. Furthermore, the study of the eco-toxicity of the backwash water after regeneration is recommended, as the backwash water might contain some ozonation transformation products. Besides, the mechanical strength of the applied granules should be monitored. The working lifetime of the granules determines the adsorbent replacement frequency, thus influencing the operational costs. The technology will be further evaluated for practical application based on the pilot-scale test results.

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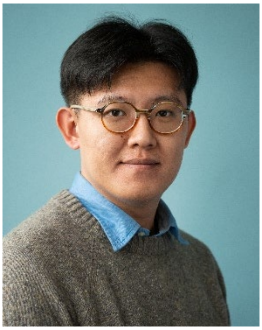
# Curriculum vitae



Mingyan Fu was born on June 16th 1990, in Anshan, China. After finishing his Bachelor's degree in 2013 at Yanshan University, Qinhuangdao, China, he continued studying synthesizing nanomaterials as adsorbents to remove radioactive contaminants from water at Yanshan University. In 2016, he obtained his Master of Engineering in Environmental Science. From October 2017 till now, he performed a PhD research in the *AdOx* project under the supervision of Prof. dr. ir. Jan Peter van der Hoek and Dr. ir. Bas Heijman at Delft University of Technology, Delft, the Netherlands. He studied the adsorption of organic micropollutants by zeolite granules and subsequent ozone-based regeneration. The results are presented in this dissertation. The outcome of his study supports upscaling the *AdOx* technology to pilot scale. All the experimental-related results have been published in peer-reviewed journals. The *AdOx* project won the Water Innovation Prize 2021, the Netherlands, in the category 'Healthy water and a healthy soil' as an essential step forward in drug removal.

# List of publications

## *Publications contained in this dissertation*

**Fu, M.,** He, M., Heijman, B. and van der Hoek, J.P. (2021a) Ozone-based regeneration of granular zeolites loaded with acetaminophen. Separation and Purification Technology 256, 117616.

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## *Other publications*

Doekhi-Bennani, Y., Leilabady, N.M., **Fu, M.,** Rietveld, L.C., van der Hoek, J.P. and Heijman, S.G.J. (2021) Simultaneous removal of ammonium ions and sulfamethoxazole by ozone regenerated high silica zeolites. Water Research 188, 116472.

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## *Conference presentations*

Poster presentation, III Summer School of the European PhD school on advanced oxidation processes, Alcoi, June 3rd – 7th, 2019

Poster presentation, 6th BENELUX Conference IWA Young Water Professional, Luxemburg, February 12th – 14th, 2020

Full-platform oral presentation, 5th International Conference on Ecotechnologies for Wastewater Treatment, Online, June 21st – 25th, 2021

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