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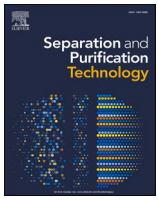

Removal of organic micropollutants from wastewater effluent: Selective adsorption by a fixed-bed granular zeolite filter followed by *in-situ* ozone-based regeneration

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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 [1]. The environmental occurrence and detection of OMPs have been studied extensively over the last two decades [2]. It has been reported that OMPs could impose adverse effects on the health of aquatic organisms and human beings [3,4]. As a result, OMPs are noticed as the representative of a directive regarding priority substances, which have been adopted in Europe since 2016 [5]. 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 [6]. 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 [7,8]. 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 [9].

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) [10]. 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 [11]. 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 [10]. 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 [12–14]. However, the degree of adsorption competition of NOM

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depends on the composition of the NOM, which varies with the type of water and ozone dosage used [10].

High-silica zeolite has been evaluated as an alternative adsorbent for the adsorption of OMPs. High-silica zeolite is hydrophobic and capable of selective 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 [15]. The structural properties of zeolite can reduce the influence of the composition of the NOM on the adsorption of OMPs. De Ridder et al. [16] studied the adsorption of nitrosamine from surface water by hydrophobic zeolite ZSM5. They indicated that NOM was effectively excluded from the zeolite pores and did not block the pores. Jiang [17] 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 [18], 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 [19]. Fixed-bed column is widely used for the industrial purpose of removing various contaminants from wastewater [20]. 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. [21] 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. [19] 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) [13]. 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 [22]. Direct ozonation thus has limited potential because its application in some WWTPs is restricted due to the formation of bromate [23]. 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 [17]. 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 [19]. 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 [17]. 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 [17].

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.

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

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 %.

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.

2.2.1. 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-μm 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 [24]. 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

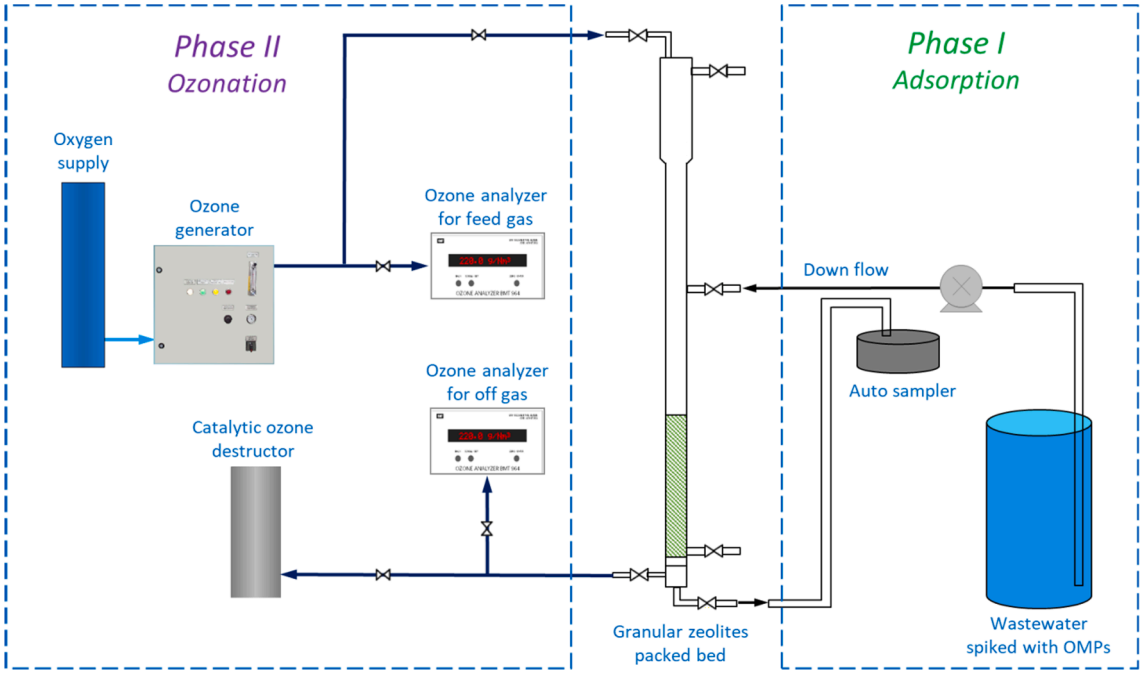

Fig. 2. Two phases setup: Phase I: zeolite granules packed column adsorption; Phase II: *in-situ* ozone-based regeneration.

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 h. The concentration of OMPs in the column effluent samples was analyzed by LC-MS.

2.2.2. 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.

2.2.3. 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 [19,25]. 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 h 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.

2.2.4. 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 [19,25]. 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 h.

2.2.5. 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^{TM} BEH 2.1 × 50 mm, 1.7 μm particle size). The details of the LC-MS analysis are described in our previous research [19]. 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).

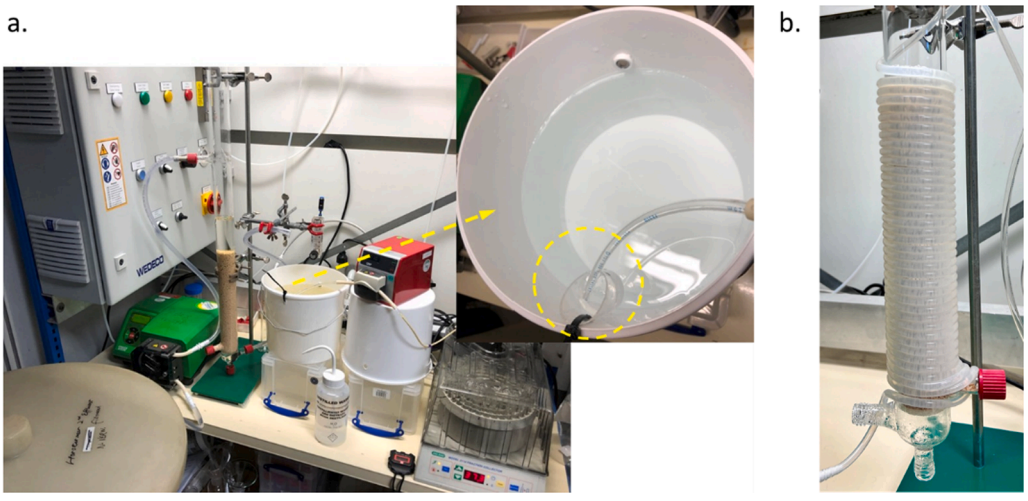

Fig. 3. Experimental setup (a. adsorption, b. drying).

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 4 h-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 [26], 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 [27]. 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 [17]. Moreover, compared to the adsorption performance of SMX in demi-water [19], the adsorption of SMX was depleted in wastewater. The low adsorption performance might be caused by NOM in wastewater [17]. 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.

3.2. Cations adsorption

Potassium, calcium and ammonium cations are exchangeable with the sodium cations on zeolite [28,29]. 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 to 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. [30] 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 [31]. 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.

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

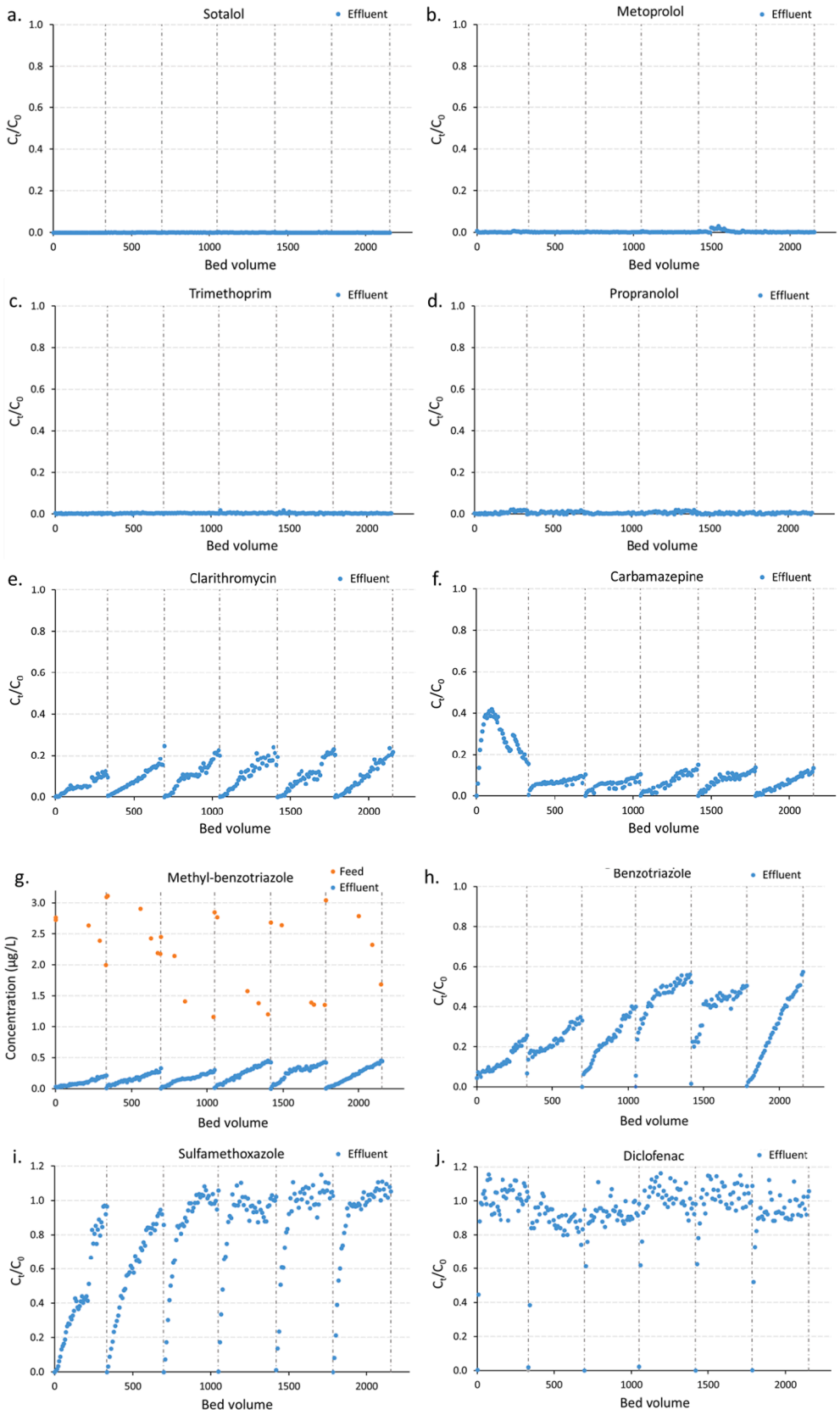

Fig. 4. Adsorption breakthrough curves of OMPs in six cycles. (a. SOT, b. MP, c. TMP, d. PRO, e. CLA, f. CBZ, g. MeBT, h. BT, i. SMX, j. DIC).

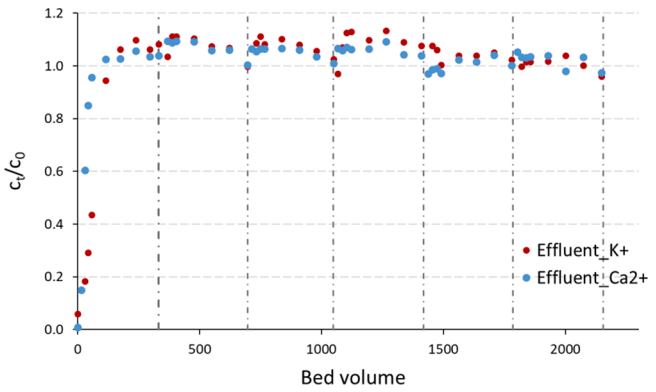

Fig. 5. Adsorption breakthrough curves of potassium and calcium ions in six cycles.

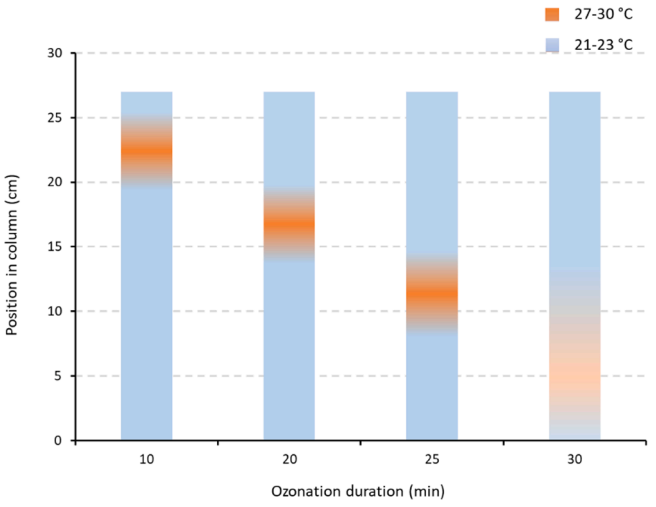

Fig. 6. Heat release zone movement in the column during ozone-based regeneration.

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.

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.

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

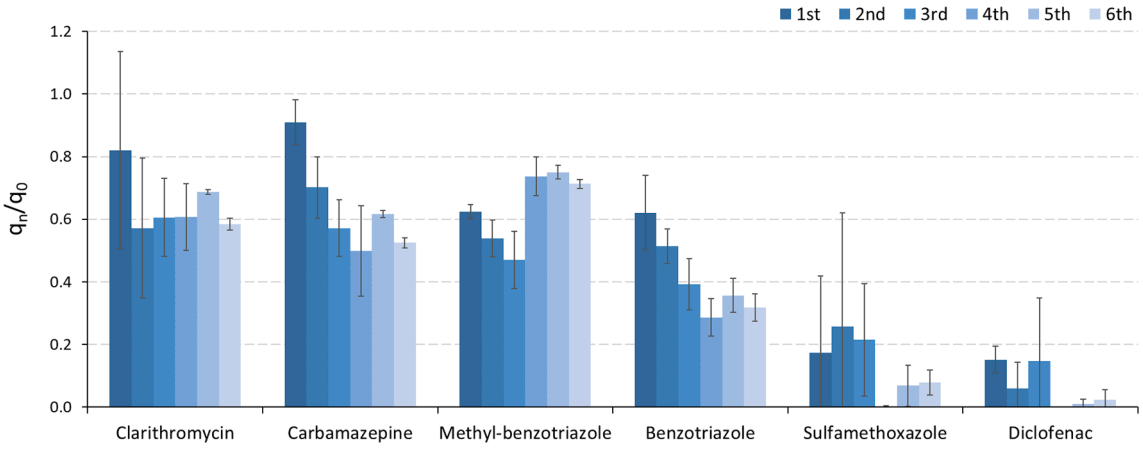

Fig. 7. The relative adsorption capacity of the target OMPs after regeneration in six cycles.

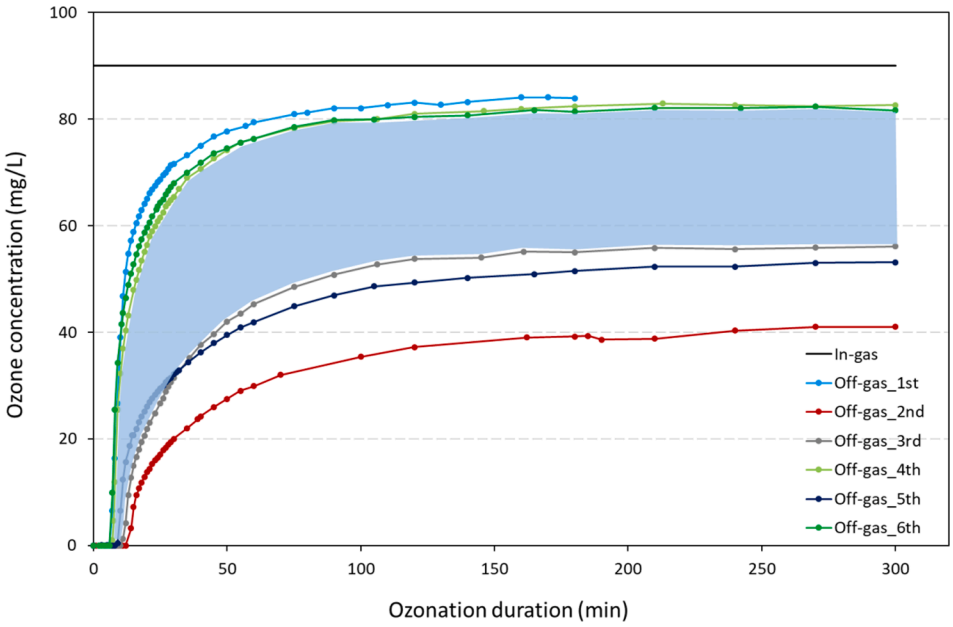

Fig. 8. Ozone concentration of in-gas and off-gas as a function of time.

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 [32]. 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 stably 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.

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

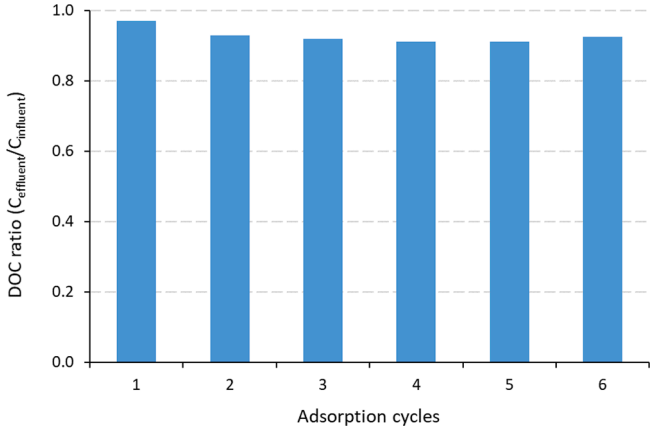

Fig. 9. DOC ratio of the effluent and influent in six cycles.

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 [33,34]. 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. [35] 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.

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.

Authors statement.

Mingyan Fu: Conceptualization, Methodology, Validation, Data Curation, Writing - Original Draft, Writing - Review & Editing.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2022.122303.

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