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

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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. In this study, the regeneration performance of well-tailored granular zeolites loaded with OMPs was evaluated. 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 fully restore their adsorption capacity. For the low adsorbing OMPs, the regeneration efficiency reached 60% after 60 min of ozonation. Interestingly, their recovered adsorption capacities firstly decreased and subsequently increased along with the ozonation duration. The dramatically 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 7 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 for the production of drinking water from surface water in the last decades. OMPs comprise pharmaceuticals, plant protection products, personal care products, and industrial chemicals. Many enter the aquatic environment via municipal wastewater treatment plants (WWTPs) [1]. OMPs occur in water bodies at trace levels (between few ng/L and several μg/L). The low concentration both increases the difficulties of detection and analysis, and also brings challenges for wastewater treatment [2]. Municipal WWTPs are designed to control a wide range of substances, including particulates, carbonaceous substances, nutrients and pathogens. These substances can be efficiently and consistently eliminated [2]. However, traditional WWTPs are not specifically designed for the removal of OMPs [3], and the average removal efficiency ranges from 30% to 65% [4]. 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 [1–9]. OMPs are becoming a severe threat to the aquatic life as it is associated with many negative effects, such as short-term and long-term toxicity, endocrine disrupting effects and antibiotic resistance of microorganisms [10]. 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 removal of OMPs from wastewater [11].

Adsorption is an effective technology to remove OMPs. Activated carbons are widely used as adsorbents to treat municipal wastewater [12,13]. Currently, ozonation followed by granular activated carbon filtration is applied to remove pharmaceuticals from municipal treatment effluents [12]. 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 [14]. As an alternative, oxidative technologies, especially ozonation, are promisingly able to regenerate the exhausted adsorbents [15]. However, ozone can attack and destroy the structure of activated carbons [16]. Thus, ozonation is not suitable for 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 the wastewater

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

Type	Pore opening size[a] (Å * Å)	Surface area (m^2/g)	Micropore surface area (m^2/g)	Pore volume (cm^3/g)	Micropore volume (cm^3/g)	Si/Al ratio (XRF)	BAS[b] (μmol/g)	LAS[c] (μmol/g)	Reference
BEA	6.6 * 7.7 5.6 * 5.6	516	351	0.3022	0.1557	286	16	7	Jiang et al. [29]
MOR	6.5 * 7.0 2.6 * 5.7	431	360	0.2687	0.1606	113	52	8	Jiang et al. [29]
MFI	5.1 * 5.5 5.3 * 5.6	359	199	0.5341	0.0891	42	142	40	Jiang et al. [29]

[a] Two channel systems are interconnected at right angles (Baerlocher et al. [28].
[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 pH 5.8[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%.

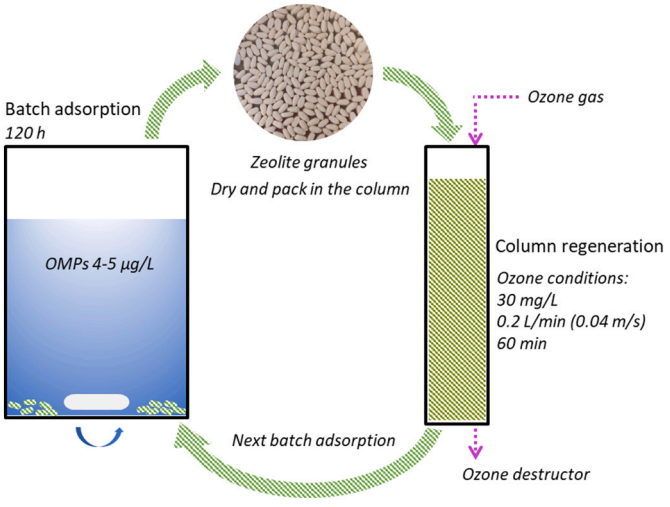

Fig. 1. Sequential adsorption-regeneration procedure.

containing natural organic matters (NOM) [17,18]. Moreover, ozonation can effectively regenerate zeolites after adsorption of OMPs without changing their structure properties [19].

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 high ratio of Si/Al was capable to highly concentrate the ozone dissolved in water [20]. This property was able to promote the removal of trichloroethene, 2-methylisoborneol and

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

ibuprofen during simultaneously injections of both ozone-dissolved water and pollutant feed water to a zeolite packed column [21–23]. Reungoat et al. [24] found that zeolites with 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. [19] 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 for application in practice, 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 8 cycles by using FAU granular zeolites and an ozone bubbling system [15]. However, this study was carried out in semi-batch mode. This study proposed an interesting

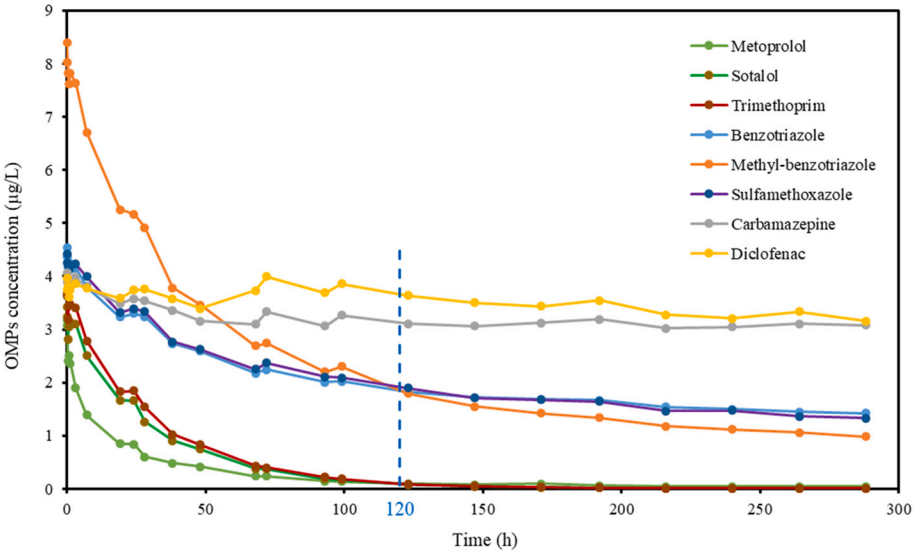

Fig. 2. The concentrations of OMPs as a function of loading time (initial concentration of OMPs at 4–5 μg/L, zeolite granules dosage at 0.5 g/L).

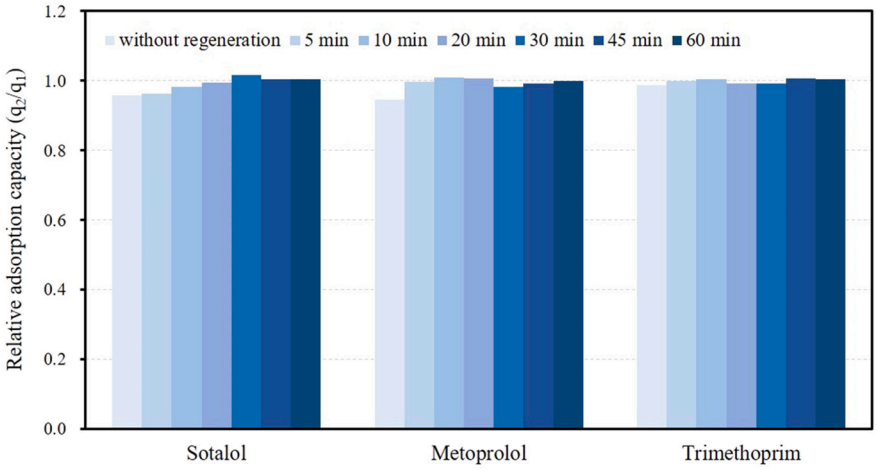

Fig. 3. Regeneration performance of high adsorbing OMPs (SOT, MP, and TMP) after varying ozonation durations.

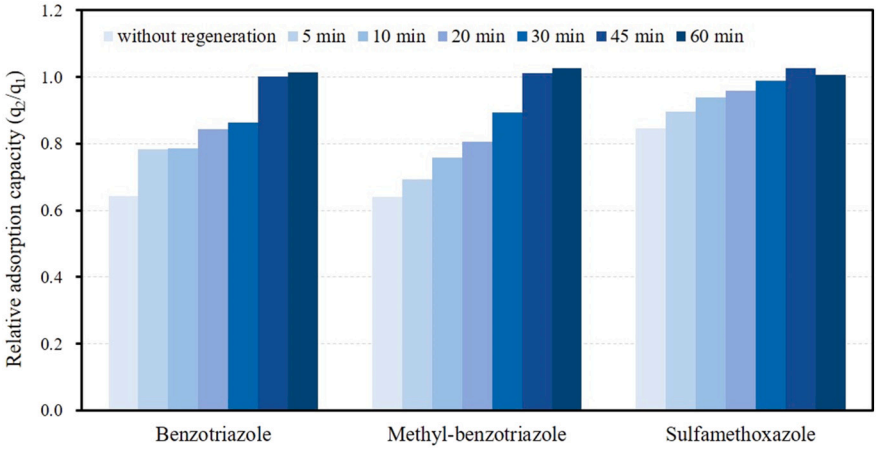

Fig. 4. Regeneration performance of medium adsorbing OMPs (BT, MeBT, and SMX) after varying ozonation durations.

hypothesis that the intermediates formed in ozonation might influence the adsorption capacity of trichlorophenol. Unfortunately, further identification was missing to prove this hypothesis. By simultaneously applying adsorption and ozonation in a fixed bed column packed with FAU granules, the removal performance of nitrobenzene was enhanced [25]. A study of Zhang et al. [26] reported about sequential adsorption-

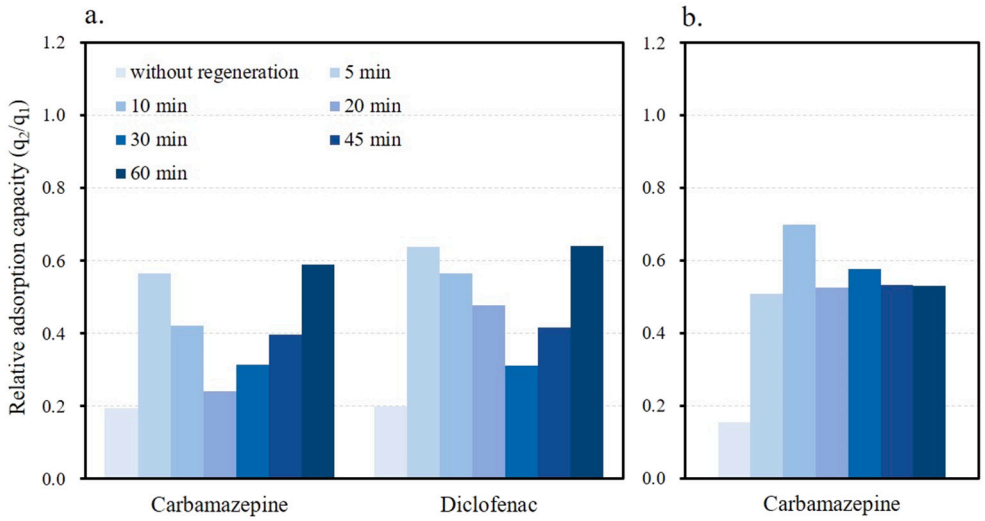

Fig. 5. Regeneration performance of low adsorbing OMPs (CBZ and DIC) after varying ozonation durations. (a. adsorption of various OMPs; b. adsorption of only CBZ).

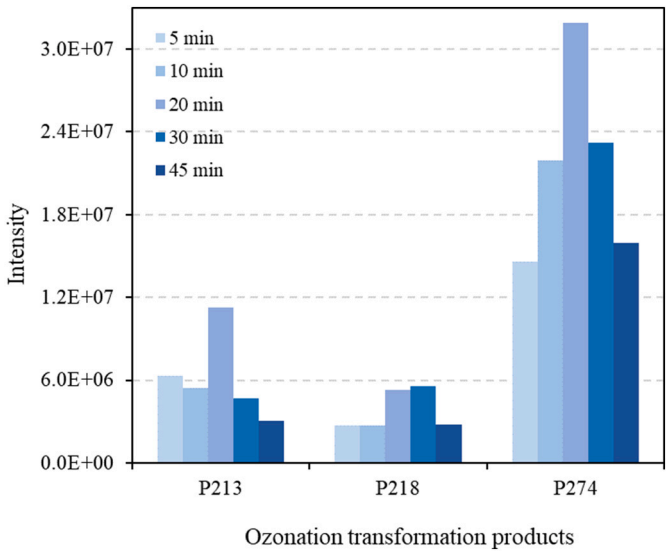

Fig. 6. The intensity of the ozonation transformation products (P213, P218, and P274) after different ozonation durations at the retention time of 3.35 min.

regeneration, in which ozone was applied in the gas phase. The regeneration process was carried 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 [26]. 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 3 cycles [27]. 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 set-up, 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. Eight OMPs were selected from the list requested by the Dutch Ministry of Infrastructure and Water Management [11]: sotalol, metoprolol, trimethoprim, sulfamethoxazole, benzotriazole, methyl-benzotriazole, carbamazepine, and diclofenac, respectively.

The objectives of this study were firstly 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. [28]. Different from natural zeolites, which are mostly hydrophilic with low Si/Al ratio, synthetic high-silica zeolites are evaluated as good adsorbents to uptake OMPs [18,29]. Zeolite with higher ratio of Si/Al was more efficient to adsorb OMPs [24]. The characterizations of the selected high silica zeolites were studied in a previous study done by our research group [29]. 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 firstly 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. Thereafter, the granules were sintered at 950 °C for 2 h to enhance the mechanical strength.

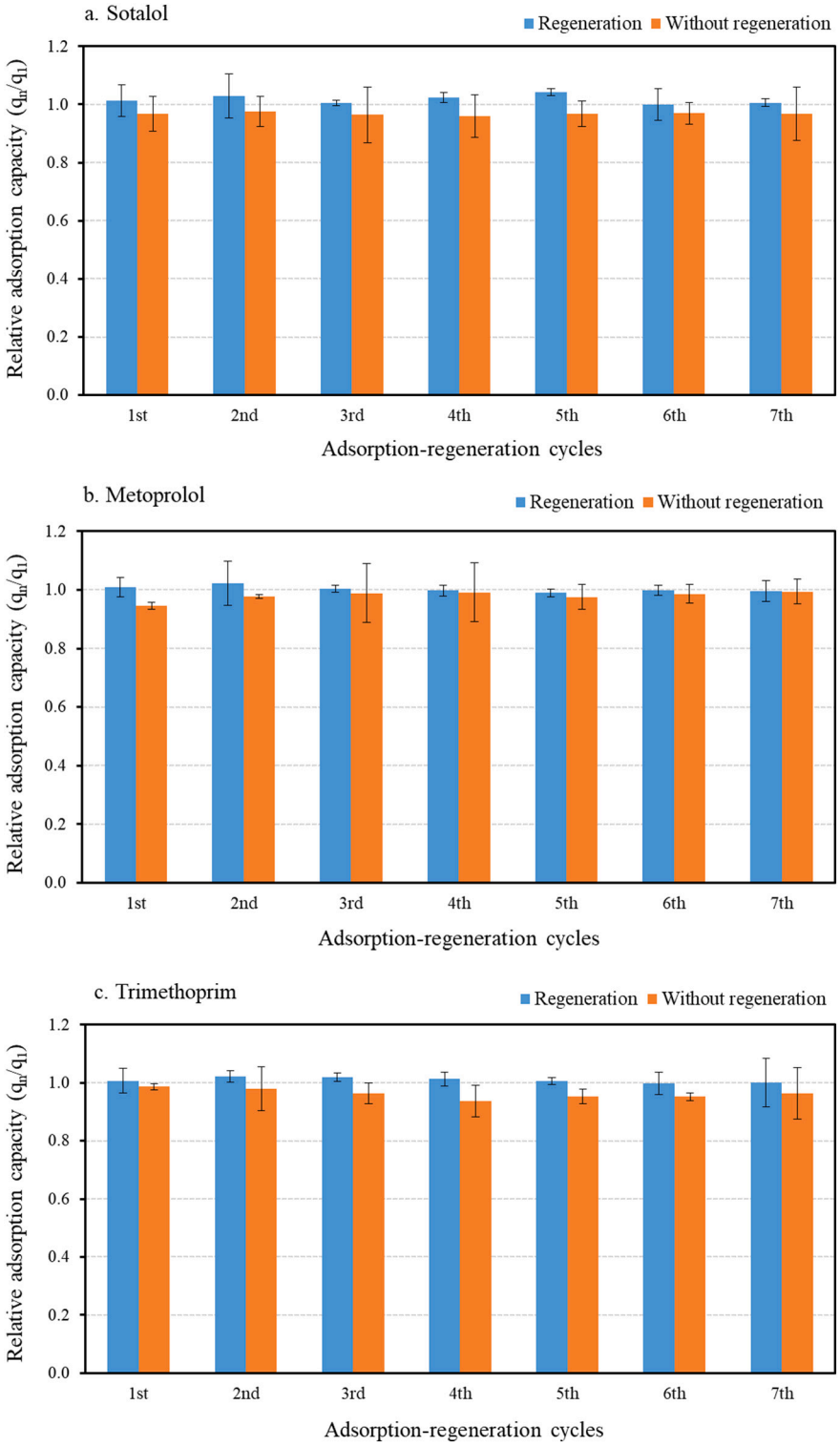

Fig. 7. Regeneration performance of high adsorbing OMPs in 7 adsorption-regeneration cycles (60 min ozonation; a. SOT, b. MP, c. TMP).

2.2. Organic micropollutants

All the selected OMPs were purchased from Sigma-Aldrich. 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. Prior to 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 by gaseous

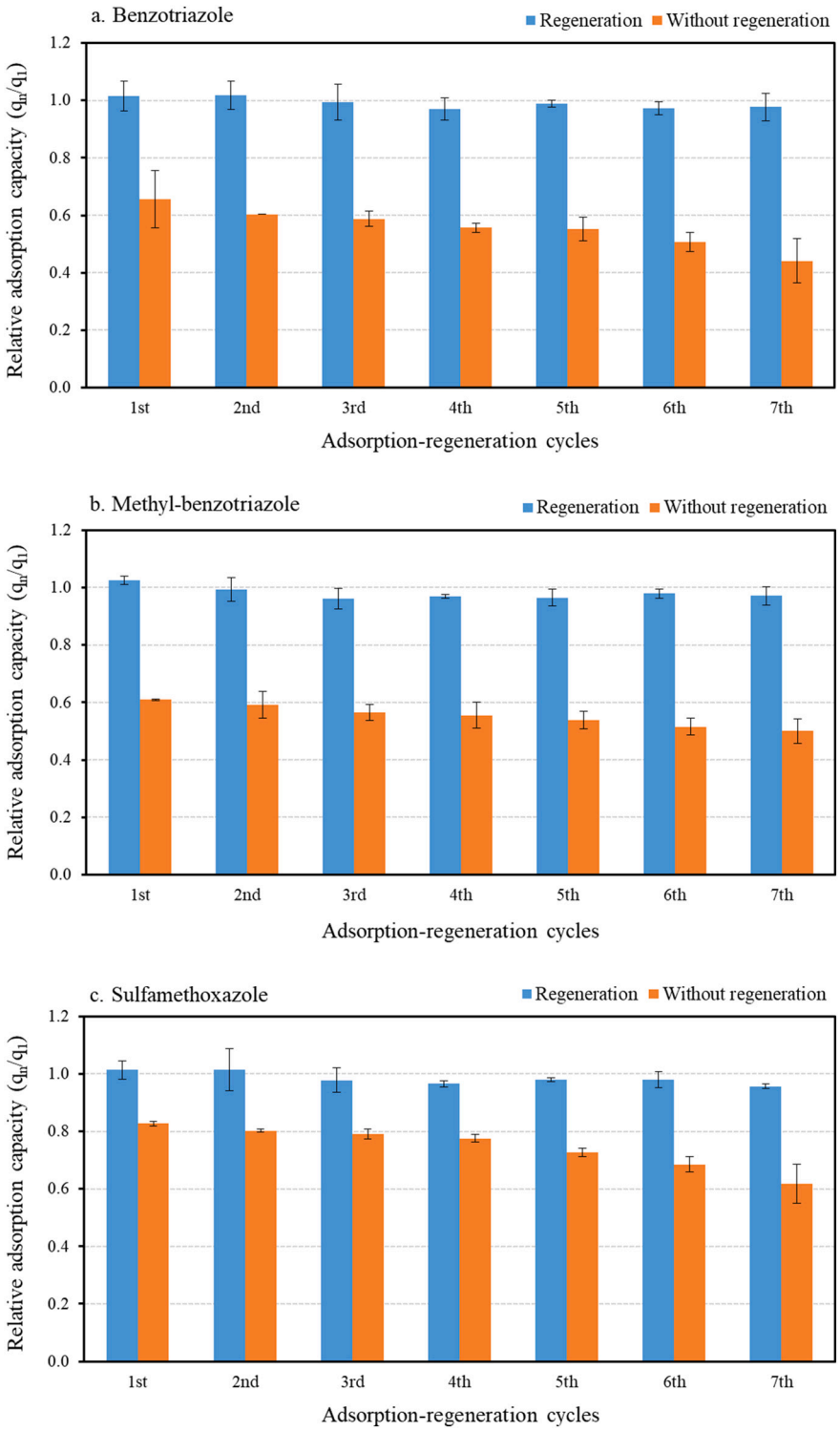

Fig. 8. Regeneration performance of medium adsorbing OMPs in 7 adsorption-regeneration cycles (60 min ozonation; a. BT, b. MeBT, c. SMX).

ozone for 1 h 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. To obtain equilibrium adsorption in a short time, the granules were pulverized in the bottles before adding 1 L prepared OMPs solution. The solutions were stirred at 200 rpm for 48 h 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*

To determine the optimum loading duration, 0.5 g of fresh granules were dosed to 1 L prepared OMPs solution. 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. This was 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.

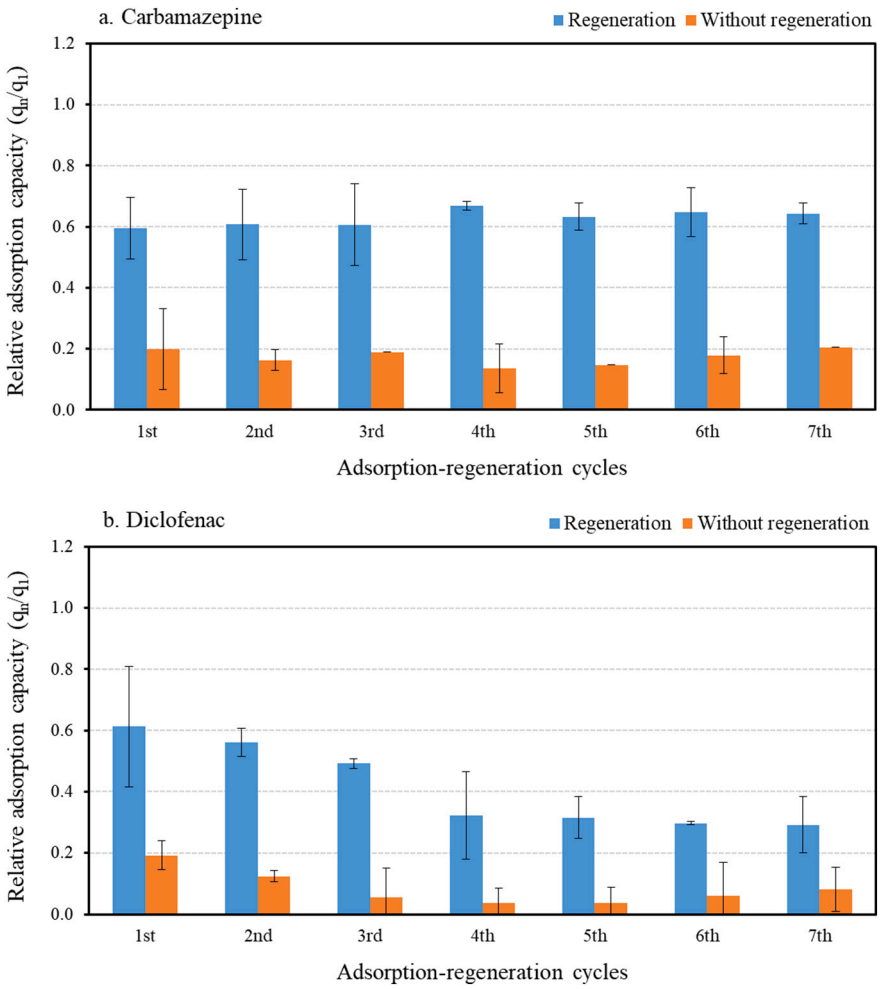

Fig. 9. Regeneration performance of low adsorbing OMPs in 7 adsorption-regeneration cycles (60 min ozonation; a. CBZ, b. DIC).

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 size of the column was 10 mm in diameter and 25 cm in length. An ozone set-up 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 set-up was illustrated in our previous research [27]. 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 at 50 °C in the oven overnight. 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 that were used for different ozonation durations. The granules were dried at 50 °C in the oven overnight after the second adsorption. 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:

$$Rq = q_n/q_1$$

where q_n (μg/g) was the loading of the granules after a fixed time in the n^{th} 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.

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 × 50 mm, 1.7 μm particle size). The flow rate of the elution 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 a 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 amount to both the calibration standards (0.0025–10 μg/L) and unknown samples. By adding an IS for quantitation, the variations of the measurement can be corrected, and then the accuracy of the results is improved [30]. Limits of detection (LOD) and quantitation (LOQ), and the retention time for each compound are listed in Table 3.

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. Their removal efficiencies were 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 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 for the indication of regeneration performance is considered 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 be most likely 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.

3.2. Optimum ozone-based regeneration duration

The regeneration performance of zeolite granules loaded with OMPs at different ozonation durations is shown in Figs. 3–5. It is worth mentioning that gaseous ozone did not affect the adsorption capacity of OMPs on zeolite (Table S1, Supplementary Information). The same results were also found in our previous study [27]. For the high adsorbing OMPs, their relative adsorption capacities (Rq) remained 1 after all ozonation durations (Fig. 3). It indicated that there were many adsorption sites 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 was due to the rapid reaction of ozone and the double bond in CBZ [31]. Meanwhile, many transformation products containing quinazoline groups were generated during the ozonation of CBZ [32]. 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.

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 min 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 intensity of the peak 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 the 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 [33,34]. P274 might also contain DIC_p_273.9813_16.4, which was identified as a transformation product of diclofenac [35]. 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 reaction of ozone with the OMPs other than CBZ might influence the adsorption capacity of CBZ after different ozonation durations (Fig. 5a).

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 of 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 7 cycles even without regeneration. For the medium adsorbing OMPs, the Rq with regeneration remained at 1 in 7 cycles, while the Rq without regeneration gradually decreased in 7 cycles (Fig. 8). After 7 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 7 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 7 cycles was lower than 0.2 (Fig. 9). By comparison, the Rq of CBZ was almost constant at 0.6 after regeneration in 7 cycles (Fig. 9a). The Rq of DIC decreased from 0.61 to 0.29 in 7 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.

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 the majority of OMPs. The adsorption capacity of six out of eight selected OMPs was completely restored in 7 cycles. The accumulation of transformation products might only influence the adsorption capacity of diclofenac in 7 cycles. Further studies should focus on real wastewater to scale up this process.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jwpe.2021.102403.

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