Separation and Purification Technology 256 (2021) 117616

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

Ozone-based regeneration of granular zeolites loaded with acetaminophen

Mingyan Fu[a,*], Mingjing He[a], Bas Heijman[a], Jan Peter van der Hoek[a,b]

[a] Delft University of Technology, P.O. Box 5048, 2600 GA Delft, the Netherlands
[b] Waternet, P.O. Box 94370, 1090 GJ Amsterdam, the Netherlands

ARTICLE INFO

Keywords:
Acetaminophen
Contaminants of emerging concern
Granular zeolites
Ozone
Regeneration

ABSTRACT

Removal of contaminants of emerging concern (CECs) 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 that limits the 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 mass of ozone dosed (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 intermediates accumulation on the long-term adsorption capacity recovery rate were also investigated. It was found that gaseous ozone did not influence the adsorption of ACE on zeolites. The adsorption capacity of ACE decreased 7% after three adsorption-regeneration cycles. This can be explained by the accumulation of undissolved intermediate breakdown products adsorbed on the granules.

1. Introduction

Contaminants of emerging concern (CECs), especially pharmaceuticals used in households and hospitals, mostly end up in the environment via municipal wastewater treatment plants (WWTPs). The accumulation of CECs can cause potential environmental and health risks [1]. Acetaminophen (ACE) is a common pharmaceutical mostly used in households to treat pain and fever. As one of the aniline analgesics 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 people's concern about its potential impact on the environment and human health [2]. However, a conventional municipal WWTP is not designed to remove the CECs [3]. For this purpose, an effective barrier is needed. The current treatment methods of CECs mainly include physical separation (adsorption and membrane technology), chemical oxidation (ozonation and advanced oxidation processes) and biodegradation. Due to the diverse properties of CECs, none of these methods can guarantee the complete removal of them [4].

Adsorption is a widely applied separation process to remove certain classes of pollutants from wastewater [5]. Activated carbons are the most commonly used adsorbents for treatment of secondary effluent to remove micropollutants [4,5]. In the last decades, hydrophobic zeolites have been evaluated as alternative adsorbents for CECs removal from wastewater [6]. 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 [6,7]. Chemical oxidation is an important technology to eliminate organic pollutants from wastewater [8]. Ozone is the most commonly used oxidant due to its strong oxidation potential [9]. Ozonation is also a conventional treatment that is applied for disinfection of drinking water [9]. Despite the advantages of ozonation, the ozone consumption is high because natural organic matter (NOM), present in the wastewater, competes with the desired target micropollutants [10]. Furthermore, harmful by-products, such as bromate, may be generated during ozone treatment [11].

After saturation with CECs, the exhausted zeolites should be regenerated. The reuse of the zeolites can avoid secondary environmental

* Corresponding author.
E-mail address: m.fu@tudelft.nl (M. Fu).

https://doi.org/10.1016/j.seppur.2020.117616
Received 23 April 2020; Received in revised form 31 July 2020; Accepted 17 August 2020
Available online 25 August 2020

problems due to the disposal of contaminated adsorbents and avoid high operational costs due to one-time use of the adsorbent. The resistance of zeolites to chemical reactions allows the adsorbents for chemical regeneration by ozone [6]. As the ozone is generated on-site, the ozone-based regeneration can be performed 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 [12]. Compared with 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 CECs. In theory, the oxidation of CECs 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 CECs from water by zeolite powders, and subsequent ozone-based regeneration is not fully studied and only a few studies are reported [13,14]. Meanwhile, there is an intrinsic drawback applying powder-form adsorbents. After the adsorption of CECs, it is difficult to remove the powder-form adsorbents from water for recycling [15]. In practical applications, the drawback can be avoided by applying fixed-bed reactors packed with granular adsorbents. However, the regeneration of zeolite granules loaded with CECs via ozone-based treatment has rarely been reported. Zhang et al reported the regeneration of zeolites loaded with 2,4,6-trichlorophenol (TCP) was effective [16]. 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 the regeneration performance was not investigated. It can be assumed that, with less water content, the gaseous ozone may diffuse into the granules faster and thus improve the 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, including water content, ozone gas flow, ozone concentration, and ozonation duration were determined. Among the variables, water content probably is the main factor that influences 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 a previous research [17]. 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 firstly 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 with size 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 h. Acetaminophen and methanol were purchased from Sigma-Aldrich, Germany.

2.2. Adsorption

The adsorption isotherms of ACE by zeolites were studied in batch mode at 20 °C. 200 mg/L ACE solution was prepared with demineralized water. Varied amounts of high-silica zeolite Beta powders were dosed into 100 mL prepared ACE solution. After reaching equilibrium (48 h), samples were taken and filtered over 0.2 μm polycarbonate syringe filters. To obtain ACE loaded granular zeolites for regeneration, first the zeolite had to be loaded. 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 ACE solution was prepared with demiwater. The empty bed contact time was 11 min. The feed flow rate was 0.74 m/h. The adsorption process was running for 120 h. Samples were taken from the outflow at different time intervals. ACE concentration in the samples were measured by HPLC.

2.3. Ozone-based regeneration

Ozone-based regeneration was carried out using ozone in the gas phase. Gaseous ozone was introduced to the column packed with zeolite granules. Two types of columns, made from glass, were used for these experiments. The small column was 10 mm in diameter and 25 cm in length. 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 the 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 destructed by a catalytic ozone destructor before venting out. Ozonation set-up 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. 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 the water film on the granules, the loaded granules were firstly 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 before drying but after draining the water in between the particles 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 (0.04 m/s in the column). The experiments were stopped after 30 min. The total mass of ozone dosed was 2160 mg. To investigate the influence of gas flow and ozone concentration, two sets of experiments were conducted. Loaded granules were completely dried in the oven at 60 °C overnight to avoid the influence of water films on granules. The total mass of ozone dosed was constant by changing the exposure time for all of the experiments. The reason for this is that ozonation efficiency depends on the ozone consumption during the reaction [18]. 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 mass of ozone dosed 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) in the gas phase. A gas flow of 0.2 L/min was applied, and the total mass of ozone dosed was 540 mg in all experiments by varying the duration. Before and after each regeneration experiment, approximately 0.2 g of granules was sampled and ground into powders and put into 100 mL pure methanol for 30 min to extract the remaining ACE (extraction efficiency 80%, taken 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

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

Type	Pore opening size (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[a] (μmol/g)	LAS[b] (μmol/g)	Reference
Beta	6.6 * 7.7 5.6 * 5.6	516	351	0.3022	0.1557	286	16	7	Jiang et al. [17]

[a] Brønsted acid sites.
[b] Lewis acid sites.

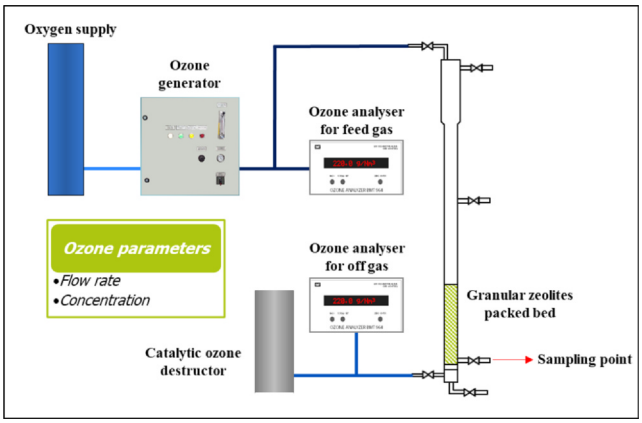

Fig. 1. Experimental setup of big column experiments.

efficiency was calculated according to the remained and initial ACE mass in the granules.

2.3.2. Big column tests

To upscale the ozone-based regeneration process, a big column (4 cm in diameter, 1 m in length) was applied. 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 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 in the column).

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 to the column.

During the regeneration, approximately 0.2 g of granules were taken from the sampling point at different time for ACE extraction. The ACE regeneration efficiency was calculated. The sampling process took 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. Then, in the drained-bed experiments, the samples were taken after backwash of the column by demiwater. 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 ACE solution was lead through the column at an empty bed contact time of 11 min for 120 h. 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 in the column) and an ozonation duration of 7.5 h. 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 concentration of ACE 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 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 by 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 in the column) 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.

2.4. Analytical procedure

The concentrations of ACE in both demi-water and methanol were measured by a HPLC system (SHIMADZU 74909) equipped with a Kinetex 2.6 μm C18 column. 50 μL of each sample was injected to 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 found to be 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 about that 15% bentonite was added to the granules as binders, the maximum adsorption capacity of granular zeolites should be around 90 mg/g.

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

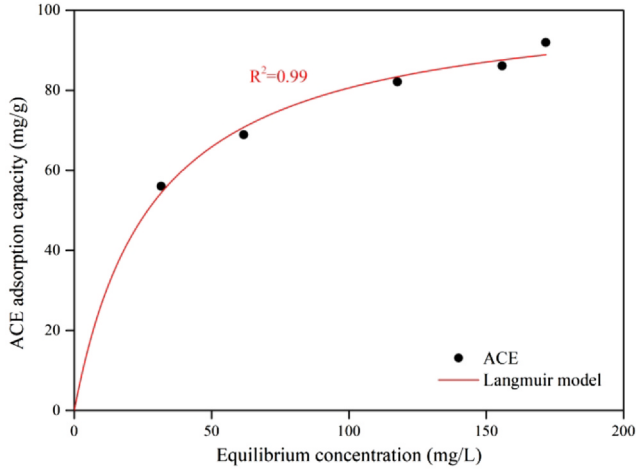

Fig. 2. The adsorption isotherms of ACE by Beta zeolite, Langmuir model fitting.

Table 2
Isotherm constants for ACE adsorption by Beta zeolite.

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

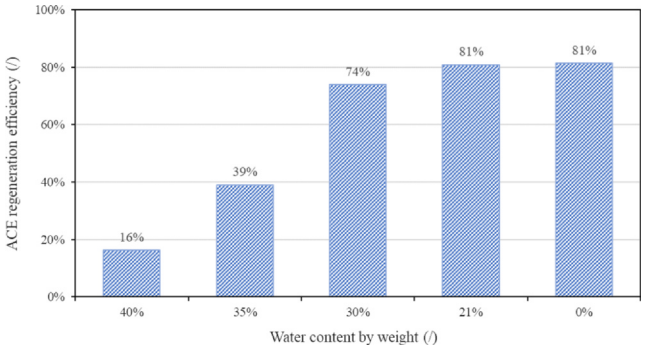

Fig. 3. The influence of water content in granules on the ACE regeneration efficiency of 2160 mg ozone dose.

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 were both 81%. It was remarkable that when the granules were partially dried (water content 30%), the ACE regeneration efficiency was 74%, which was close to the level of regeneration efficiency of totally dried granules. 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 the time. Compared with the off-gas ozone concentration at 35% water content, the off-gas ozone concentration at 30% water content was lower. 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 releasing in the reaction between ozone and ACE could further dry the granules. Along with the time increase, the used gas could also transport the water from the granules. Thus, the degradation of ACE was promoted. This 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 in the regeneration of granules with 0% water content. After regeneration, the remained ACE and generated substances in the granules were extracted by pure methanol, and samples were taken and analysed with HPLC. 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 indicates the presence of an intermediate product generated by ozonation. This intermediate had a longer retention time than ACE in the chromatographic column. Therefore, it is probably more apolar compound compared to ACE. According to the ACE degradation pathway [19], there is 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 the 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.

The influence of gas flow and ozone concentration on ACE regeneration efficiency are shown in Figs. 6 and 7, respectively. It can be seen that the ACE regeneration efficiency decreased from 95% to 56% as the gas flow rate increased from 0.2 to 0.8 L/min. Furthermore, the ACE regeneration efficiency decreased from 74% to 46% as the concentration increased from 50 to 150 mg/L. The total dosing of ozone was constant in these experiments. Therefore, at a higher gas flow or gas concentration, the exposure time is shorter. Considering the ozonation duration was longer at low gas flow rate and 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 completely degradation of ACE can be reached if the ozonation duration is long enough.

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 Figs. 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 a level of 82 mg/L after running for 3 h. The degradation of ACE only happened when the ozone dispersed in the water films on granules. The ACE regeneration efficiency was below 10%. These results suggest that drained-bed regeneration is not effective to regenerate granules. By comparison, in dried-bed regeneration, as shown in Fig. 9, the ozone concentration in the off-gas increased after 3 h. The ACE regeneration efficiency reached 100% after introducing ozone to the dried-bed column for 6 h. 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 increase of regeneration efficiency happened earlier than that of ozone concentration in off-gas, 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 the top to the bottom in the packed column. A yellowish layer was generated along with a formation of water vapour (near the layer) and a heat

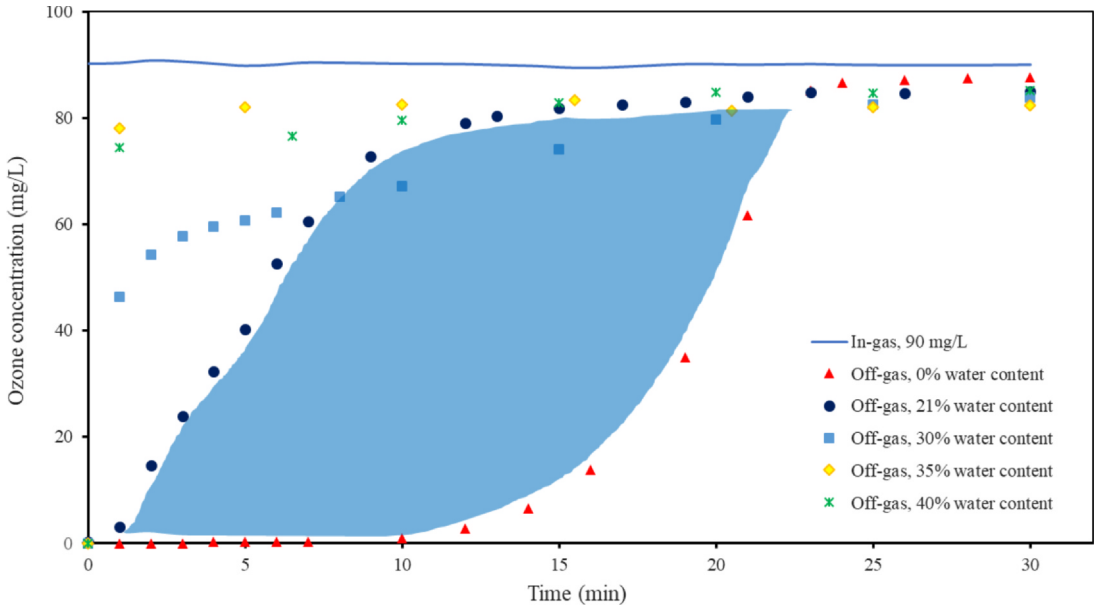

Fig. 4. Ozone concentration of in-gas and off-gas as a function of time under different water content.

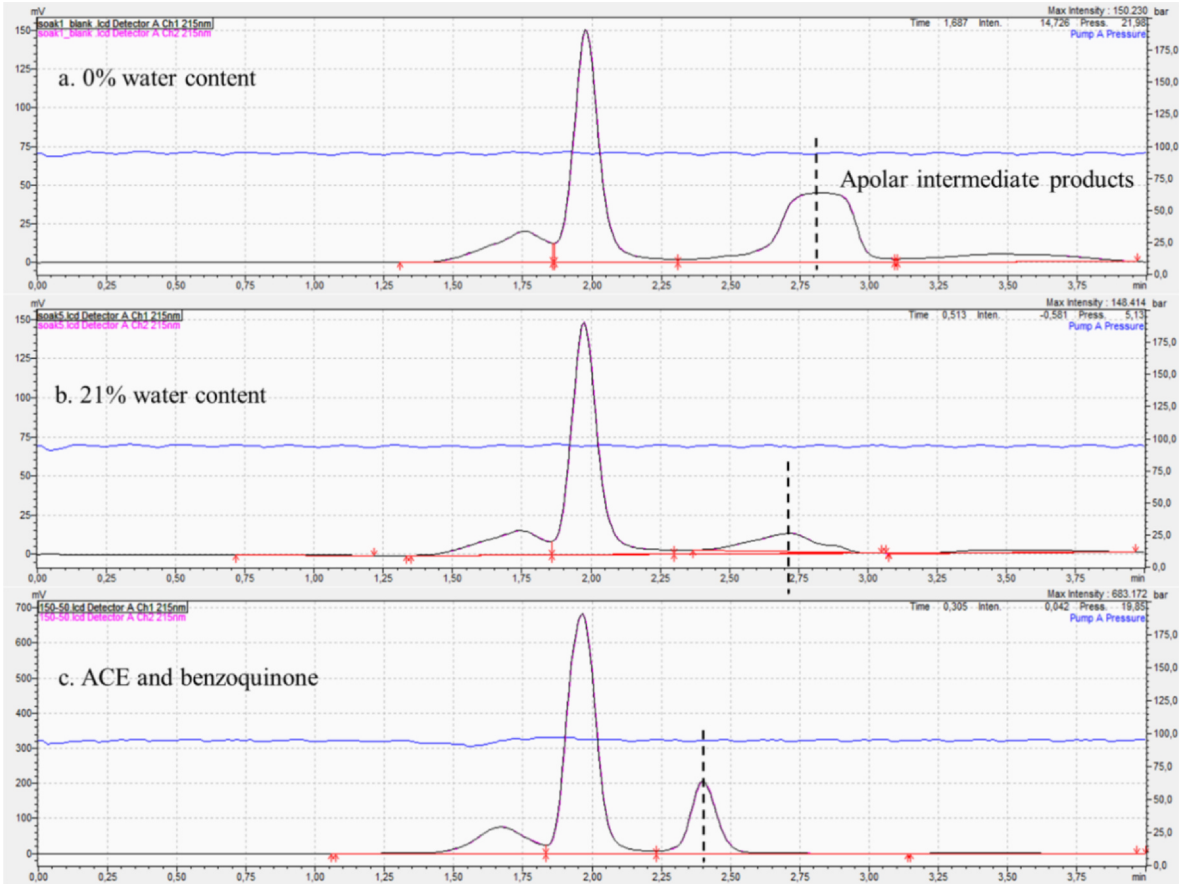

Fig. 5. HPLC peaks: a. extraction from granules with 0% water content; b. extraction from granules with 21% water content; c. samples of ACE and benzoquinone prepared with methanol.

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 [19], its degradation is initiated by the attack of ozone on C(4)-position forming hydroquinone with release of acetamide. Further oxidation of hydroquinone generates benzoquinone. This product is degraded to a mixture of glyoxylic acid, ketomalonic acid and maleic acid in consecutive steps. The mixture is converted into oxalic acid as the ultimate product. In the degradation pathway, benzoquinone is the only intermediate with yellowish colour. Therefore, when the yellowish layer disappeared, the degradation of ACE came to

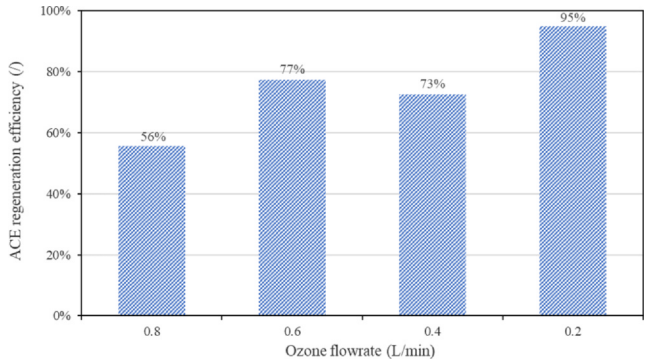

Fig. 6. The influence of gas flow on ACE regeneration efficiency of 900 mg ozone dose.

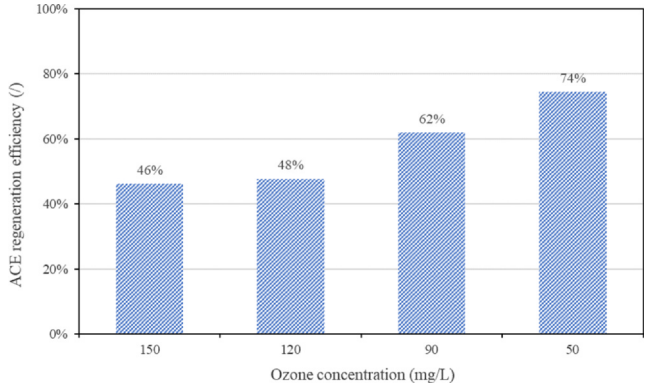

Fig. 7. The influence of ozone concentration on ACE regeneration efficiency of 540 mg ozone dose.

the next step. This phenomenon matches well with the results of the small column tests. These results also indicated that dried-bed regeneration was effective to degrade the ACE on 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.

3.4. Influence of adsorption-regeneration cycles on adsorption capacity

ACE adsorption capacity recovery rate 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 were remained in the granules. Thereafter, 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.

4. Conclusions

The aim of this study was to investigate 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 of drained granules (40% water content).
- A higher total ozone dose (g/h) results in a higher regeneration efficiency. A complete degradation of adsorbed ACE can be reached if the ozonation duration is long enough.
- 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.
- Considering that ACE is an easy organic compound, which can be easily degraded by ozone, further research should be carried out with different organic micropollutants. Moreover, the study on a complex wastewater matrix is also of great interest for practical applications.

CRediT authorship contribution statement

Mingyan Fu: Conceptualization, Methodology, Validation, Data curation, Writing - original draft, Writing - review & editing. **Mingjing He:** Validation, Data curation. **Bas Heijman:** Supervision, Writing -

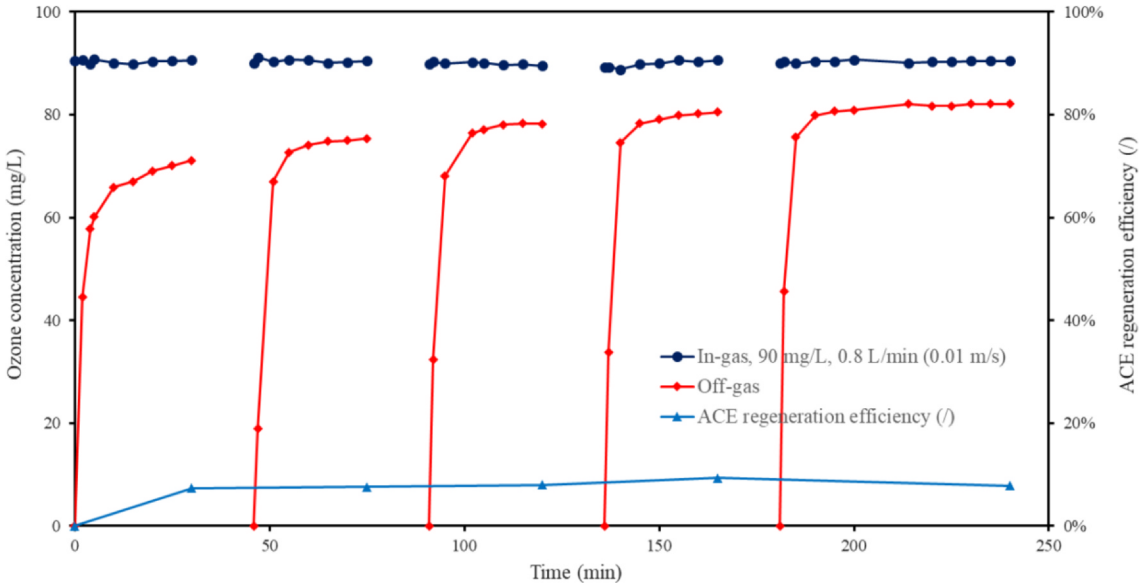

Fig. 8. Ozone concentration in in-gas and off-gas along time and ACE regeneration efficiency at each sampling point from the drained-bed regeneration test in a big column.

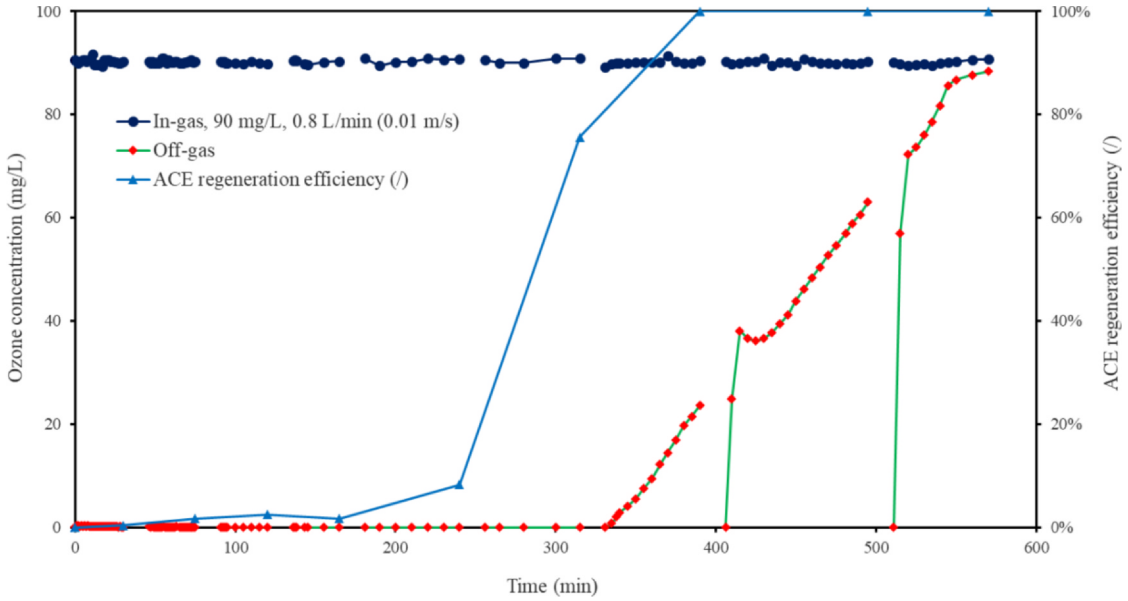

Fig. 9. Ozone concentration in in-gas and off-gas along time and ACE regeneration efficiency at each sampling point from the dried-bed regeneration test in a big column.

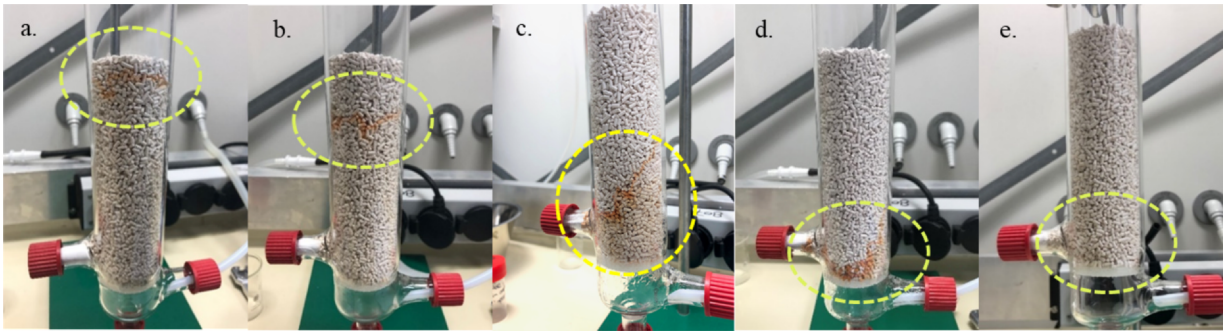

Fig. 10. Experimental phenomenon in dried-bed regeneration at different runtime: a. 3 min; b. 45 min; c. 3 h; d. 4 h; e. 7.5 h. (Ozone gas flow was from top to bottom.)

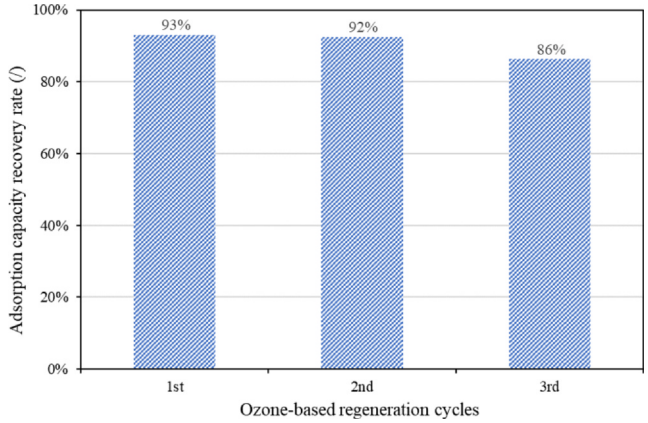

Fig. 11. ACE adsorption capacity recovery rate after each ozone-based adsorption-regeneration cycle.

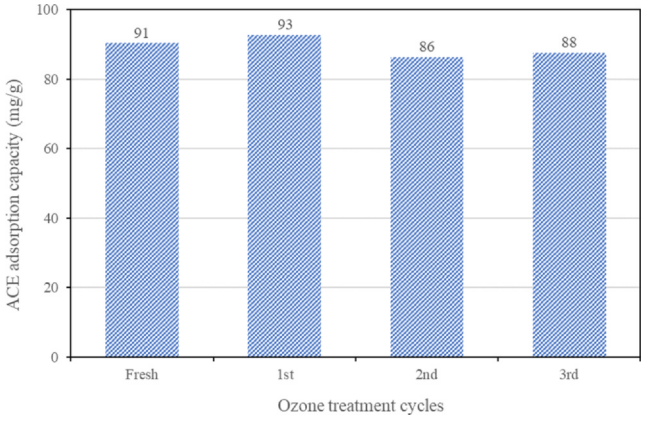

Fig. 12. ACE adsorption capacity of fresh granules and the granules after sequential gaseous ozone treatments.

review & editing. **Jan Peter van der Hoek:** Supervision, Writing - review & editing.

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.

Acknowledgement

This research is financially supported by NWO, the Netherlands Organization for Scientific Research. The authors acknowledge the

China Scholarship Council for supporting Mingyan Fu.

References

[1] M. Gavrilescu, et al., Emerging pollutants in the environment: present and future challenges in biomonitoring, ecological risks and bioremediation, New Biotechnol. 32 (1) (2015) 147–156.

[2] S. Wu, L. Zhang, J. Chen, Paracetamol in the environment and its degradation by microorganisms, Appl. Microbiol. Biotechnol. 96 (4) (2012) 875–884.

[3] N. Bolong, et al., A review of the effects of emerging contaminants in wastewater and options for their removal, Desalination 239 (1–3) (2009) 229–246.

[4] Y. Luo, et al., A review on the occurrence of micropollutants in the aquatic environment and their fate and removal during wastewater treatment, Sci. Total Environ. 473–474 (2014) 619–641.

[5] M. Ahmaruzzaman, Adsorption of phenolic compounds on low-cost adsorbents: A review, Adv. Colloid Interface Sci. 143 (1–2) (2008) 48–67.

[6] N. Jiang, et al., High-silica zeolites for adsorption of organic micro-pollutants in water treatment: A review, Water Res. 144 (2018) 145–161.

[7] D.J. De Ridder, et al., Zeolites for nitrosamine and pharmaceutical removal from demineralised and surface water: mechanisms and efficacy, Sep. Purif. Technol. 89 (2012) 71–77.

[8] K. Ikehata, N. Jodeiri Naghashkar, M. Gamal El-Din, Degradation of aqueous pharmaceuticals by ozonation and advanced oxidation processes: a review, Ozone Sci. Eng. 28 (6) (2006) 353–414.

[9] A. Rodríguez, et al., Ozone-based technologies in water and wastewater treatment, Emerging Contaminants from Industrial and Municipal Waste, Springer, 2008, pp. 127–175.

[10] D. Gardoni, A. Vailati, R. Canziani, Decay of ozone in water: a review, Ozone Sci. Eng. 34 (4) (2012) 233–242.

[11] M. Sagehashi, et al., Adsorptive ozonation of 2-methylisoborneol in natural water with preventing bromate formation, Water Res. 39 (16) (2005) 3900–3908.

[12] R. Gonzalez-Olmos, et al., Hydrophobic Fe-zeolites for removal of MTBE from water by combination of adsorption and oxidation, Environ. Sci. Technol. 47 (5) (2013) 2353–2360.

[13] J. Reungoat, et al., Adsorption of nitrobenzene from water onto high silica zeolites and regeneration by ozone, Sep. Sci. Technol. 42 (7) (2007) 1447–1463.

[14] Y. Zhang, et al., Adsorption of trichlorophenol on zeolite and adsorbent regeneration with ozone, J. Hazard. Mater. 271 (2014) 178–184.

[15] O. Sacco, V. Vaiano, M. Matarangolo, ZnO supported on zeolite pellets as efficient catalytic system for the removal of caffeine by adsorption and photocatalysis, Sep. Purif. Technol. 193 (2018) 303–310.

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

[17] N. Jiang, et al., Adsorption of triclosan, trichlorophenol and phenol by high-silica zeolites: Adsorption efficiencies and mechanisms, Sep. Purif. Technol. 235 (2020) 116152.

[18] T.I. Poznyak, I. Chairez Oria, A.S. Poznyak, Chapter1 - Ozonation as main method for organic contaminants degradation in three different phases: liquid, solid, and gaseous, in: T.I. Poznyak, I. Chairez Oria, A.S. Poznyak (Eds.), Ozonation and Biodegradation in Environmental Engineering, Elsevier, 2019. pp. 3–23.

[19] M. Skoumal, et al., Mineralization of paracetamol by ozonation catalyzed with Fe^{2+}, Cu^{2+} and UVA light, Appl. Catal. B 66 (3–4) (2006) 228–240.