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On-site Regeneration of Acetaminophen Loaded Zeolite Granules by Applying Gaseous Ozone Based Oxidation Process

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ABSTRACT

The wide application of pesticides, pharmaceuticals and personal care products cause an increasing contamination of aquatic systems. Adsorption by zeolites is a promising process to remove target organic micro-pollutants (OMPs) selectively from water bodies. In order to have a sustainable adsorption process, restoring the adsorption capacity of the exhausted zeolites is necessary.

In this research, the gaseous O_3 based process was applied to regenerate the column packed with acetaminophen (ACE) loaded zeolite granules. The aim of this study was to investigate the regeneration performance by using the gaseous O_3 based process and the feasibility of its long-term operation. An initial concentration $200\,mgL^{-1}$ of ACE was used for the zeolite granules adsorption process. After 120 hours of loading, the gaseous O_3 based process was applied to regenerate the ACE loaded zeolite granules. It was found that an ideal ACE degradation rate of $80-100\%$ was obtained by drying the zeolite granules before the regeneration. While when the drained bed (without drying process) was applied, the ACE degradation rates were below 35% for both the gaseous O_3 and the gaseous O_3/H_2O_2 processes.

The water content of zeolite granules was the main limiting factor that affected the regeneration performance. A higher ACE degradation rate was obtained with lower water content. It was also found that adding H_2O_2 to the process enhanced the ACE degradation rate for the zeolite granules with the same water content. Nevertheless, the highest ACE degradation rate was achieved when the water content was 0% without adding H_2O_2.

Regarding the long-term regeneration, three cycles of regeneration were conducted to investigate the feasibility of long-term regeneration by using the gaseous O_3 process in dried bed. The effect of ozone on zeolite surface characteristics and the accumulation of intermediates had minor influences on the adsorption capacity restoration. Compared to the fresh zeolite, owing to the incomplete regeneration of the adsorbed ACE in the inner part of zeolite, the used zeolite granules lost 25% of the adsorption capacity in the long-term operation. Therefore, it is feasible to use gaseous O_3 process in dried bed to regenerate ACE-loaded zeolite granules from the long-term operation perspectives.

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With this thesis, this special master journey in Delft University of Technology has ended. The whole process of obtaining this master's degree has been like walking into a tunnel. I felt excited at the beginning for the country, the culture, the people and the new knowledge. While when I reached the deeper part of this tunnel, the feeling was mostly about fighting against the stress and motivating myself to finish this programme on time. Now when I can finally touch the light of the exit, the only feeling left is gratitude.

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Last but not least, I would like to express my deepest gratitude and love to my parents. They always stand behind me and make me brave enough to chase my dream.

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CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS

AC	Activated Carbon
ACE	Acetaminophen
AOC	Assimilable Organic Carbon
AOPs	Advanced Oxidation Processes
CECs	Contaminants of Emerging Concerns
DOC	Dissolved Organic Carbon
EBCT	Empty Bed Contact Time
GAC	Granular Activated Carbon
Ha	Hatta Parameter
HPLC	High pressure Liquid Chromatography
LC-MS	Liquid Chromatography–Mass Spectrometry
MBR	Membrane Bioreactor
NOM	Natural Organic Matter
OMPs	Organic Micro-pollutants
pCBA	p-chlorobenzoic acid
POPs	Persistent Organic Pollutants
qe	ACE Adsorption Equilibrium Capacity
RE	Recovery Efficiency
SEM	Scanning Electron Microscope
UH	Unsaturated Hydrocarbons
VOCs	Volatile Organic Compounds
WC	Water Content of Zeolite Granules
WWTP	Wastewater Treatment Plant

1 INTRODUCTION

1.1 BACKGROUND

Due to the wide application of pesticides, pharmaceuticals and personal care products, the increasing contamination of these organic micro-pollutants (OMPs) in aquatic systems has become one of the key environmental issues that threaten public health [Schwarzenbach et al., 2006; Luo et al., 2014]. Acetaminophen (ACE; $C_8H_9NO_2$), also known as paracetamol, is a drug that is commonly applied for mitigating fever and other minor pain. Because of the frequent purchase of ACE over the counter, ACE has become one of the most prevalent pharmaceuticals in treated wastewater [Wu et al., 2012]. In this study, ACE is selected as the model organic pollutant for the whole research.

To date, tertiary wastewater treatment is the most effective method to remove and degrade OMPs in wastewater, which can avoid the ending up and accumulation of OMPs in aquatic environment [Luo et al., 2014; Jiang et al., 2018]. Advanced oxidation processes (AOPs), adsorption by activated carbon (AC) and biodegradation are common treatment methods to remove OMPs from water bodies effectively. Apart from these convention single process, integrating pre-ozonation or nanofiltration with granule activated carbon (GAC) can also effectively reduce the OMPs contamination [Heijman and Hopman, 1999]. However, these technologies cannot selectively remove the organic matters from water bodies, which result in higher cost and lower removal efficiency due to the existence of natural organic matter (NOM). Besides, in terms of practical application, treatment for the total flow is required, resulting in high chemicals (e.g. ozone or H_2O_2) or energy consumption (e.g. photochemical AOPs) for the overall OMPs removal process.

Based on the batch experiments done by published studies, it was found that the selective adsorption by zeolites is a promising process to decontaminate target OMPs [Damjanović et al., 2010; Wang and Peng, 2010; Zhang et al., 2014]. As zeolites have uniform pore sizes, the target OMPs can be adsorbed selectively and the competition from NOM would be minimized [De Ridder et al., 2012; Jiang et al., 2018]. However, the adsorbed pollutants cannot be degraded through the adsorption process and the toxicity of the pollutants are still remained. Therefore, the loaded adsorbents are needed to be regenerated to restore the adsorption capacity and to remove the toxicity of the adsorbed pollutants to the environment.

Thermal calcination is a common method to regenerate the used adsorbents, which requires high energy input [Lee et al., 2011]. In this case, owing to the stable chemical composition and the resistance of zeolites to chemical reaction, chemical oxidation (e.g. AOPs and ozonation) was found as a possible alternative regeneration process to regenerate the OMPs-loaded zeolites [Zhang et al., 2016]. Powerful oxidants (e.g. hydroxyl radical $OH\cdot$) are utilized to oxidize and degrade the adsorbed organic matters in zeolites. Besides, compared to directly use chemical oxidation in water phase, integrating chemical oxidation and adsorption is a more efficient method to concentrate the target pollutant first by adsorption and then degrade it through chemical oxidation, hence less chemicals are demand for the oxidation process [Alsbaiee et al., 2016].

According to the study done by Ikhlaq et al. [2018], ozonation (an oxidation process by only O_3) with presence of zeolite powder was found that can remove OMPs from water bodies effectively through non-radical process in batch mode. However, the ozonation process in water phase has several limiting factors, such as the high energy consumption for ozone generation due to the low water solubility of ozone [Oturan and Aaron, 2014]. In this case, applying gaseous O_3 is an alternative option to regenerate OMPs-loaded zeolites. Besides, gaseous O_3 was already found to regenerate volatile organic compounds (VOCs) loaded zeolites effectively in air purification industry [Zaitan et al., 2016]. Nevertheless, using gaseous O_3 to on-site regenerate ACE-loaded zeolite granules is rarely reported in the published studies. Therefore, it is interested to investigate the regeneration efficiency of the gaseous O_3 based process to ACE-loaded zeolite granules.

In an ozonation process, there are two different oxidation mechanisms that by ozone molecules and/or the generated $OH\cdot$. Skoumal et al. [2006] stated that the process with only O_3 was hardly to completely and effectively mineralize ACE to CO_2 and H_2O due to the formation of carboxylic acid intermediates. For this reason, the impact of intermediates accumulation on the long-term operation of zeolite granules is also meaningful to be studied. Besides, the impact of gaseous O_3 on zeolite itself is also interested to be discussed in long-term study. Moreover, it was found that dosing hydrogen peroxide (H_2O_2) to the ozonation process can enhance the oxidation potential and mineralization rate [Von Gunten, 2003]. Therefore, determination of the effect of H_2O_2 on the gaseous O_3 based regeneration process is deserved to be investigated.

Considering the practical application, using packed zeolite granules column can eliminate the post filtration process from applying zeolite powder. Based on the published studies, most researches on OMPs adsorption and zeolite regeneration made use of zeolite powder in batch mode. There are seldom researches on zeolite granules packed column adsorption and on-site regeneration by chemical oxidation.

In this study, the objective was to obtain the regeneration performance for ACE-loaded zeolite granules by using the gaseous O_3 based process, and to understand the kinetics of reactions.

1.2 KNOWLEDGE GAPS AND RESEARCH OBJECTIVES

Based on the state of the art illustrated in Section 1.1, there are several knowledge gaps to be investigated and further discussed:

1) Researches on the gaseous O_3 based process to on-site regenerate OMPs-loaded zeolite granules are rarely reported.
2) The effectiveness of the gaseous O_3 based process on regeneration of OMPs-loaded zeolite granules under different operation conditions is unknown.
3) Methods to define the regeneration performance of zeolite granules are not fully investigated from present studies.
4) The feasibility of long-term on-site regeneration of OMPs-loaded zeolite granules by using the gaseous O_3 process is seldom studied.

According to the stated knowledge gaps, the major research objective is:

Determination of the regeneration efficiency and effectiveness of acetaminophen loaded zeolite granules by the gaseous O_3 based process, to achieve a high number of operation cycles without loss of adsorption capacity.

1.3 RESEARCH QUESTIONS AND APPROACHES

Based on the state of the art mentioned in Section 1.1, the following four research questions are formulated to meet the research objective stated in Section 1.2.

1) How to define the regeneration performance of zeolite granules?
2) How effective is the gaseous O_3 based process for regeneration of ACE-loaded zeolite granules regeneration?
3) What are the effects of different operation conditions on ACE-loaded zeolite granules regeneration processes?
4) What is the feasibility of long-term regeneration for ACE-loaded zeolite granules by gaseous O_3?

To answer the research questions, two research approaches were applied, which were literature review and laboratory research.

Literature Review:

A literature review, presented in Chapter 2, was firstly carried out for the experiment preparation and the understanding of basic mechanisms. As the research continued, the collected experiment data were analyzed and explained based on the literature to ensure the theoretical stringency of the results.

Laboratory Research:

To accomplish the research objectives and to obtain first-hand data, three stages of experiments were conducted:

Stage I: *Experiment setup and define the effectiveness of regeneration by the gaseous O_3 process.*

In this stage, the experiment setups were built based on published literature and the pre-experiments conducted by Mingyan FU (phD candidate, TU Delft). The methods to define ACE degradation rates and the remained adsorption capacity of zeolite granules were defined. Besides, the regeneration effectiveness with applying the gaseous O_3 based process was examined. In this stage, the tested regeneration processes included 1) the gaseous O_3 only process in drained bed; 2) the gaseous O_3/H_2O_2 process in drained bed and 3) the gaseous O_3 only process in dried bed. Research questions (1) and (2) could be answered after completing *Stage I.*

Stage II: *Investigate the effects of different operation conditions on acetaminophen-loaded zeolite granules regeneration process.*

It was expected that research question (3) can be explained in the second stage. Different operation conditions for the regeneration process were studied, including: 1) O_3 flow rate; 2) O_3 concentration; 3) H_2O_2 concentration; 4) water content of zeolite granules.

Regarding the water content of zeolite granules, when the granules are completely dry (water content = 0%), the reaction with gaseous ozone is in gas-solid phase. When the granules are wet, the reaction would be in gas-liquid-solid phase. The theoretical background of the reaction mechanisms difference between these two phases is introduced in Section 2.3.2.

Stage III: *Examine the feasibility of long-term on-site regeneration for acetaminophen loaded zeolite granules through the gaseous* O_3 *only process.*

In the third stage, research question (4) can be determined. The long-term experiment was conducted with the operation conditions selected from the results of *Stage II*. The same zeolite granules packed column was operated for three cycles to understand the change of restored adsorption capacity after long-term operation. The effect of ozone on zeolite granules and the effect of intermediates accumulation were studied respectively.

All the detailed setups for *Stage I-III*, experimental materials and methods are given in Chapter 3.

2 LITERATURE REVIEW

2.1 ORGANIC MICRO-POLLUTANTS (OMPS)

Organic micro-pollutants (OMPs), also known as one type of contaminants of emerging concerns (CECs), are persistent anthropogenic chemicals that occur in natural water bodies with very trace levels (i.e. $ng - \mu g\, L^{-1}$) [Cotruvo, 1985; Cotruvo and Eaton, 2018]. OMPs include pesticides, pharmaceuticals and personal care products. Due to the unregulated and continuous release, OMPs became widespread in the aquatic environment. The accumulation of OMPs and the related by-products can cause potential environmental and health risks, such as interfacing endogenous hormone systems and bacterial resistance [Gavrilescu et al., 2015]. In Europe, Environmental Quality Standard *Directive 2008/105/EU* in the field of water policy amended by *Directive 2013/39/EU* was launched to highlight the need of developing innovative water treatment technologies to remove the priority substances including OMPs from water bodies.

2.2 CURRENT TECHNOLOGIES TO REMOVE ORGANIC MICRO-POLLUTANTS (OMPS)

Currently, the common options for OMPs removal can be divided into three types: 1) physical methods: adsorption and membrane process; 2) chemical methods: ozonation and advanced oxidation processes (AOPs); 3) biological methods: membrane bioreactor (MBR). According to the review done by Luo et al. [2014], OMPs that have complex structure (e.g. polycyclic compounds and compounds with long side chains) have lower bio-availability and can be hardly removed by biological treatment. Physical and chemical treatment methods were proved able to remove OMPs effectively. Nevertheless, the possible formation of intermediates and by-products as well as the high investment are the major concerns of physical and chemical methods [Schwarzenbach et al., 2006]. Due to the diverse physicochemical properties (e.g. hydrophobicity) of a wide range of OMPs, the removal performance by one method is limited. Therefore, detailed studies on different OMPs fate are needed to define the optimum treatment method and hence minimize the pollution to the receiving aquatic systems.

2.2.1 Adsorption

Activated carbon (AC) is the most widespread method to remove OMPs by adsorption but with several drawbacks. For instance, to restore the adsorption capacity of exhausted AC, the regeneration process is energy intensive through thermal calcination [Jiang et al., 2018]. In addition, the OMPs removal efficiency would be lower with the presence of natural organic matter (NOM) and it required new carbon addition after regeneration due to the loss from thermal regeneration [Luo et al., 2014; Alsbaiee et al., 2016]. In this case, zeolite is an alternative option which has a stable chemical composition and uniform pore size to adsorb target pollutants selectively and minimize the competition of NOM.

Zeolites are aluminosilicate based porous materials that are constructed with a 3-dimensional structure, the hydrophobicity of zeolites surface is decided by Si/Al ratio which can be adjusted for different target OMPs [Damjanović et al., 2010; Zhang et al., 2016]. The framework of SiO_4 and AlO_4 can be placed in different structures with various pore opening sizes, such as BEA with $5.6 \times 5.6\ \dot{A}$ and FAU with $7.4 \times 7.4\ \dot{A}$ [Jiang et al., 2018]. Due to larger van der Waals force between OMPs and zeolites surface, OMPs with molecular size similar to the zeolites pore size have better removal efficiency, which is also called "Close-fit mechanism" [De Ridder et al., 2012]. Therefore, pollutants such as NOM with sizes larger than zeolites pore sizes cannot be adsorbed. Considering the selective adsorption ability of zeolites, mixing different types of zeolites is a feasible method to remove wide range of OMPs from water.

Oxygen and acidic sites (i.e. Brønsted and Lewis acidic sites) are two main adsorption sites for zeolites [Jiang et al., 2018]. Research done by Valdés et al. [2014] found that weak base aromatic OMPs (e.g. toluene and benzene) can form hydrogen bonds through interacting with Brønsted acid sites and can therefore be adsorbed. For aromatic compounds, the hydrogens of the aromatic ring have affinity to the oxygen sites (basic sites) of zeolites, and can thus enhance the adsorption energy [Koubaissy et al., 2011].

2.2.2 Membrane Separation

Nanofiltration (NF) has been considered as an effective pressure-driven filtration process to remove OMPs from water bodies with a promising purification performance [Hilal et al., 2004]. Besides, Kimura et al. [2003] illustrated that the hydrophobic OMPs and NOM would be adsorbed onto the membrane surface at the beginning of the operation before the membrane were saturated. However, the study done by Laîné et al. [2003] indicated that the presence of NOM in water caused bio-fouling of the membrane. The reversible and irreversible organic fouling could cause the decline of membrane flux [Virkutyte, 2010]. In this case, a regular chemical cleaning is required to remove the reversible fouling and restore part of the flux, which would increase the operation cost for the overall purification process.

2.2.3 Chemical Oxidation

Chemical oxidation processes such as ozonation and advanced oxidation processes (AOPs) are efficient and promising methods to degrade persistent organic pollutants (POPs) by the generated powerful oxidation agents [Oturan and Aaron, 2014]. As presented in Figure 2.1, the possible points for applying chemical oxidation processes are indicated [Ikehata et al., 2006].

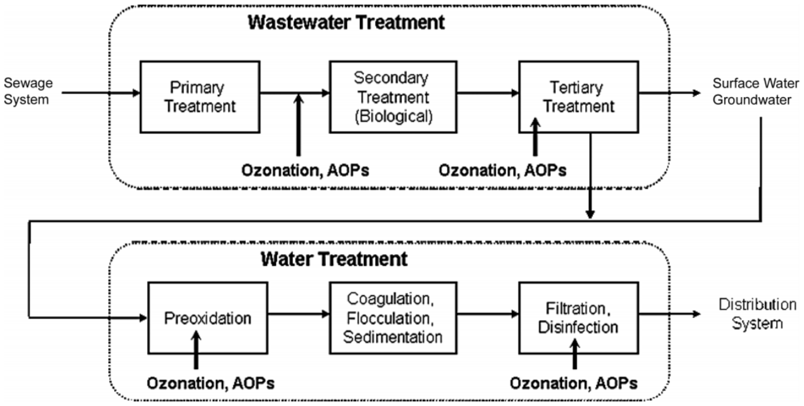


Figure 2.1: Possible Points to Apply Chemical Oxidation for the Degradation of OMPs [Ikehata et al., 2006]

Ozonation in water phase is a conventional process for the purpose of disinfection and OMPs removal in wastewater treatment plant (WWTP) [Von Gunten, 2003]. The dissolved O_3 gas is able to oxidize the OMPs by ozone molecules and/or the generated $OH\cdot$ [Acero and Von Gunten, 2001]. More detailed information on ozone-based oxidation process is given in Section 2.3.2.

With respect to AOPs, the on-site generated hydroxyl radical ($OH\cdot$) is the most common oxidizing agent in AOPs that can decontaminate water effectively without selectivity [Chiron et al., 2000]. The AOPs can be divided into four types: 1) chemical AOPs e.g. Fenton and

O_3/H_2O_2); 2) photochemical AOPs (e.g. O_3/UV and H_2O_2/UV); 3) sonochemical AOPs (e.g. ultrasound) and 4) eletrochemical AOPs (e.g. electro-Fenton) [Oturan and Aaron, 2014]. Among the AOPs types, no extra energy is required for chemical AOPs and the chemicals are relatively cheap.

Compared to ozonation, AOPs have better oxidation ability without selectivity. The oxidation potential of O_3 molecules ($E_v = 2.07\,V$) is smaller than that of $OH\cdot$ ($E_v = 2.86\,V$), which indicates that $OH\cdot$ is a more powerful oxidant to degrade organic compounds with higher kinetics rate [Von Gunten, 2003]. Apart from the oxidation ability, ozone molecules is a selective oxidation agent that the ozone-resistant compounds (e.g. halogenated compounds and surfactants) can be hardly degraded [Von Gunten, 2003; Ikehata et al., 2006]. In this case, applying AOPs such as O_3/H_2O_2, O_3/UV and O_3 (pH $\geqslant$ 8) are more feasible to remove a wide range of OMPs including the ozone-resistant one by the enhanced regeneration of $OH\cdot$.

2.2.4 Membrane Bioreactor (MBR)

Membrane bioreactor (MBR) is a treatment process that integrating activated sludge treatment with membrane process (microfiltration or ultrafiltration). The removal mechanisms by applying MBR are mainly biodegradation and sorption onto sludge surface [Virkutyte, 2010]. The operation temperature, pH, aerobic or anaerobic environment and water matrix can all affect the OMPs removal performance by applying MBR [Kovalova et al., 2012]. Besides, the OMPs with less hydrophobicity have better bioavailability to be utilized by sludge matrix [Luo et al., 2014]. Nevertheless, MBR process can hardly remove the OMPs with fused aromatic rings or chlorine groups, which are recalcitrant compounds for biodegradation [Alvarino et al., 2018].

2.2.5 Pre-ozonation and Granules Activated Carbon (GAC) Filtration

Both ozonation and granules activated carbon (GAC) filtration can remove a wide range of OMPS. However, the removal performance varies and depends on the characteristics of OMPs (e.g. hydrophobicity). GAC filtration has less effective removal performance for the hydrophilic OMPs [Luo et al., 2014]. while with applying ozonation, the organic matters can be degraded to assimilable organic carbon (AOC), which can be easily adsorbed [Van Der Hoek et al., 1999]. Apart from that, with integrating pre-ozonation and GAC filtration, the competition effect from NOM can be mitigated by the ozonation process. After the ozonation process, the polarity, the biodegradability and the size of NOM can be changed, which could significantly enhance the operation lifetime of the GAC filter. [Heijman and Hopman, 1999]. However, there are several limiting factors of this treatment method, such as ozonation of the total flow is required and the thermal regeneration process for the used GAC has a high energy demand.

2.3 REGENERATION METHODS FOR ZEOLITES

To date, there are four types of regeneration methods to restore the adsorption capacity of adsorbents, including thermal, chemical, microbiological and vacuum regeneration. With respect of microbiological regeneration, long-lasting time (i.e. $10-15$ days) is needed for the biodegradation process and the regeneration efficiency is not stable [Salvador et al., 2015b]. Regarding the vacuum regeneration, the desorption process is occurred by exposing the adsorbents to a vacuum source, which is mostly applied for gaseous stream (e.g. CO_2) separation or VOC recovery and not feasible for the regeneration of OMPs-loaded absorbent [Hedin et al., 2013; Salvador et al., 2015b]. In this case, this section will mainly address another two common regeneration methods, which are thermal and chemical oxidation regeneration.

2.3.1 Thermal Regeneration

To regenerate the exhausted adsorbents, thermal regeneration is widely applied for restoring the adsorption capacity of adsorbents, including zeolites and activated carbon (AC) [Lee et al., 2011]. Currently, hot inert gases, water and steam are applied within thermal regeneration methods. The classification of thermal regeneration pathways can be divided into three types: 1) thermal desorption that breaks the interactions between adsorbent and adsorbate without decomposing the pollutants; 2) thermal desorption and decomposition that degrades only part of the adsorbate and accumulates residue in the adsorbent; 3) gasification that decomposes all the adsorbate to CO_2 and H_2O [Liu et al., 1987].

Although thermal regeneration can restore the adsorption capacity of adsorbents effectively, all the mentioned methods require high energy inputs to achieve a high temperature (i.e. $800-900°C$) for thermal calcination [Salvador et al., 2015a]. Considering the relatively stable condition of zeolites under high temperature, significant losses of adsorbents during thermal calcination can be neglected.

2.3.2 Ozone Based Regeneration

In an ozonation process (O_3 only), the oxidation mechanisms can react by ozone molecules and/or generated $OH\cdot$, which are mainly dependent on the phases of ozone (i.e. gas- or liquid-phase) and water matrix [Acero and Von Gunten, 2001].

Ozonation in Gaseous phase

In gas-phase, the non ozone-resistant OMPs can be oxidized by ozone directly to CO_2, H_2O and by-products. The mixture of ozone and oxygen passes through solid phase OMPs and is partially adsorbed on the zeolite surface. The reaction rate of ozonation in gas-phase is mainly affected by several conditions: 1) ozone flow rate; 2) ozone concentration and 3) temperature [Poznyak et al., 2019]. Gas-phase ozonation is mostly applied to eliminate the volatile organic compounds (VOCs) in industrial or indoor environments for air purification [Chao et al., 2007; Alejandro et al., 2014; Poznyak et al., 2019].

The organic compounds with double bonds, aromatic rings and non-protonated amines react with ozone molecules directly [Von Gunten, 2003]. The research done by Weschler and Shields [1996] illustrated that $OH\cdot$ can be activated when gaseous ozone reacts with unsaturated hydrocarbons through Equation 2.1. The produced $OH\cdot$ can react with the intermediate and generate stable function groups, such as carbonyl (-C=O) and carboxylate (-COOH) [Weschler, 2000].

$$\mathrm{O_3} + \mathrm{UH} \longrightarrow \text{intermediates} \longrightarrow OH\cdot + \text{by}-\text{products} \tag{2.1}$$

where UH is unsaturated hydrocarbons.

In terms of the gaseous ozonation on zeolites, gaseous ozone could be adsorbed on the surface of zeolites and decompose into O_2 and $OH\cdot$ at Lewis acid sites [Alejandro et al., 2014]. The activated $OH\cdot$ reacts with the adsorbed OMPs at Brønsted acid sites, thus can regenerate the OMPs-loaded zeolites [Valdés et al., 2014]. However, when there is insufficient generated $OH\cdot$ to decompose all the intermediates, the ozone-resistant compounds are hardly degraded by ozone molecules.

Ozonation in liquid phase

Ozone is widely applied for disinfection, oxidation and decoloration in drinking water treatment. In liquid phase, both ozone molecules and $OH\cdot$ take effect to oxidize the organic or inorganic compounds [Poznyak et al., 2019]. The half-life time of ozone in water takes seconds to several hours and depends on the characteristic of the water matrix, such as the alkalinity, the pH level and the concentration of

NOM [Hoigné, 1998]. The major product of ozone decomposition is $OH\cdot$. It was found that both adding hydrogen peroxide (H_2O_2) and increasing pH (pH $\geqslant$ 8) can shorten the ozone half-life time and activate more $OH\cdot$, hence ozonation with pH $\geqslant$ 8 is also considered as an AOP [Von Gunten, 2003]. In liquid phase, the ratio constant of $OH\cdot$ and ozone concentration ($R = [\mathrm{OH}\cdot]/[\mathrm{O_3}]$) ranges from 10^{-7} to 10^{-9} ($molL^{-1}/molL^{-1}$) and depends on different water matrix [Elovitz et al., 2000].

When gaseous ozone is applied for a liquid reactor, the ozonation process is in liquid phase. Nevertheless, the types of reactor determine the gas transfer rate and hence affect the dissolved ozone concentration in liquid phase. In this case, the concept of *Hatta parameter* (Ha) is introduced. Ha is a parameter that is used for selecting a gas-liquid reactor, Ha shows the ratio of gas diffusion and mass transfer of gas through liquid film. Different types of reactors have various Ha number, that are independent from the dimension of reactor [van Swaaij and Versteeg, 1992]. When Ha is large, the time needed for gas diffusion in liquid phase is more than the reaction time, and more gas will be consumed in liquid film than the gas flux can be transferred through the liquid film. Compared to agitated reactor and bubble reactor ($Ha < 0.3$), packed bed column has a higher Ha value ($Ha > 3$), which means that the concentration of gas (i.e. ozone) will drop significantly in the liquid film and less gas can be transferred through the liquid films [Poznyak et al., 2019]. Therefore, with applying the packed zeolite column reactor, less amount of gaseous ozone can be transferred through the liquid films that surrounded the zeolite granules.

Ozonation with Hydrogen Peroxide

By adding H_2O_2, O_3 can be decomposed into $OH\cdot$ faster as shown in Equation 2.2, and $OH\cdot$ has a higher oxidation potential to remove O_3 resistant compounds, such as oxalic acid [Oturan and Aaron, 2014; Skoumal, 2009].

$$\mathrm{H_2O_2} + 2\,\mathrm{O_3} \longrightarrow 2\,\mathrm{OH}\cdot + 2\,\mathrm{O_2} \tag{2.2}$$

However, the research done by Acero and Von Gunten [2001] found that the effect of adding H_2O_2 for accelerating single ozonation also depends on the concentration of dissolved organic carbon (DOC) in water. When the DOC concentration is low ($< 1\,mgL^{-1}$), adding H_2O_2 can greatly enhance the oxidation through AOPs. Nevertheless, when the DOC concentration is high ($> 3\,mgL^{-1}$), the $OH\cdot$ generation rate is same as the O_3 decomposition rate. Consequently, adding H_2O_2 cannot accelerate the oxidation process significantly.

2.4 ACETAMINOPHEN AND RELATED INTERMEDIATES BY OZONE-BASED OXIDATION

Acetaminophen (ACE; $C_8H_9NO_2$, 151.16 $gmol^{-1}$), also known as paracetamol, is freely soluble in ethanol and methanol [O'Neil, 2006]. The solubility of ACE in different solvents at 20°C is summarized in Table 2.1 [Granberg and Rasmuson, 1999]. Due to the high solubility, the zeolite column can be loaded quickly by the high concentration ACE solution. The chemical structure of ACE is shown in Figure 2.2. ACE is widely found in water bodies with trace concentrations that amount up to 6 $\mu g L^{-1}$ in Europe and up to 10 $\mu g L^{-1}$ in the US [Ternes, 1998; Till et al., 2003]. Under room temperature, ACE is very stable under dry conditions. It was found out that the hydrolysis reaction rate of ACE increases significantly when temperature is above 70°C [Koshy and Lach, 1961]. The degradation rate of ACE shows the positive temperature dependence at different pH [Gilpin and Zhou, 2004].

Table 2.1: Summary of ACE Solubility in Different Common Solvents at 20°C [Granberg and Rasmuson, 1999].

Type of Solvent	Solubility (g ACE/kg Solvent)
Water	12.78
Methanol	297.81
Ethanol	190.61
Acetonitrile	23.10
Acetone	88.09

According to the research done by Skoumal [2009], assuming that ideally ACE can be mineralized completely by single ozonation, the overall stoichiometry reaction would be Equation 2.3, that 1 g of ACE needs 2.86 g of ozone to be completely decomposed to CO_2 and H_2O.

$$\mathrm{C_8H_9NO_2} + 9\,\mathrm{O_3} \longrightarrow 8\,\mathrm{CO_2} + 3\,\mathrm{O_2} + 4\,\mathrm{H_2O} + \mathrm{NO_3}^- + \mathrm{H}^+ \quad (2.3)$$

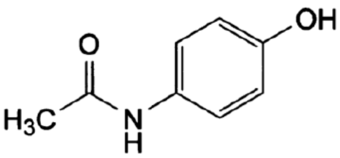


Figure 2.2: Chemical Structure of Acetaminophen

The suggested mineralization pathways of ACE by single ozonation and catalyzed ozonation are shown in Appendix Figure A.1. It can be seen that single ozonation has a low mineralization rate for ACE due to the high stability of the formed carboxylic acid intermediates, which are hardly decomposed by ozone molecules [Centellas et al., 2006]. Besides, NH_4^+ and NO_3^- ions are released during the mineralization process as inorganic ions.

The octanol-water coefficients (Log K_{ow}) for acetaminophen and the related intermediates stated in Appendix Figure A.1 are summarized in Table 2.2 [Villaescusa et al., 2011; EuropeanChemicalsAgency, 2019]. Log K_{ow} is a measure of the characterization of chemicals regarding their hydrophobicity or polarity, which can be measured by a high pressure liquid chromatography (HPLC) system [Moldoveanu and David, 2015]. Chemical that has a higher Log K_{ow} shows more hydrophobicity and hence has better adsorption potential [Luo et al., 2014]. The value of Log K_{ow} is related to the measuring retention time in a HPLC system. With regard to the reverse phase HPLC system with polar mobile phase, the hydrophilic compounds with smaller Log K_{ow} are eluted earlier than the hydrophobic compounds with higher Log K_{ow}, which can be calculated by Equation 2.4 [OECD, 2004].

$$Log\mathrm{K}_{ow} = \mathrm{a} + \mathrm{b} \times Log\frac{t_R - t_0}{t_0} \tag{2.4}$$

where Log K_{ow} is the octanol-water coefficient, a and b are the tested linear regression coefficients, t_R is the retention time in HPLC column and t_0 is the dead time of HPLC column.

Table 2.2: Summary of Octanol-water Coefficients for Acetaminophen and related Intermediates

Name of Compounds	Log K_{ow}	Reference
Acetaminophen	0.46	[Villaescusa et al., 2011]
Hydroquinone	0.59	[EuropeanChemicalsAgency, 2019]
p-benzoquinone	$0.1 - 0.3$	
Acetamide	0.3	
Glycolic Acid	0.3	
Glyoxylic Acid	$-1.4 - -0.7$	
Fumaric Acid	$-4.02 - 0.47$	
Oxalic Acid	-1.7	

2.5 OTHER OMPS BY OZONE-BASED OXIDATION

According to the review done by [Luo et al., 2014], acetaminophen is classified as a OMP with high removal efficiency, while many OMPs are classified as poorly removed compounds, such as atrazine. The degradation kinetics of several typical poorly removed OMPs by O_3 molecules and $OH\cdot$ are summarized in Table 2.3 [Von Gunten, 2003]. As can be seen from Table 2.3, these selected OMPs can be hardly degraded by only O_3 molecules. Nevertheless, when the oxidation process is dominated by $OH\cdot$, the oxidation can react very quickly. As mentioned in Section 2.2.3, the halogenated compounds are resistant to ozone, which agrees with the degradation rate of bromoform listed in Table 2.3. Therefore, applying $OH\cdot$ by AOPs to degrade the ozone-resistant compounds is more feasible.

Table 2.3: Summary of Degradation Kinetics of Selected OMPs by O_3 molecules and $OH\cdot$ [Von Gunten, 2003]

Name of Compounds	$k_{O_3}(M^{-1}s^{-1})$	$k_{OH\cdot}(M^{-1}s^{-1})$
Atrazine	6	3×10^9
Carbofuran	620	7×10^9
Benzene	2	7.9×10^9
Bromoform	0.2	1.3×10^8
Trichloroethene	17	2.9×10^9

3 MATERIALS AND METHODS

3.1 MATERIALS

The zeolite used in this study was a high-silica BEA zeolite (HSZ-980HOA; pore opening size $6.6 \times 6.5 \dot{A}$, accessible area $1220.45\, m^2 g^{-1}$) supplied by Tosoh Corporation, Europe. The chemical composition of the BEA zeolite is $HO \cdot Al_2O_3 \cdot xSiO_2 \cdot nH_2O$ ($x = 500$). The zeolite granules applied in this research were prepared by mixing BEA zeolite powder with bentonite (15% by weight, Sigma-Aldrich). The zeolite granules (diameter $2\, mm$; length $4 - 5\, mm$) were sintered at $850°C$ for 2 hours.

The chemical reagents used in this research are acetaminophen (ACE; $98 - 102\%$ purity; powder) and pure methanol of technical grade that was purchased from Sigma-Aldrich, Germany.The applied hydrogen peroxide (H_2O_2; 30%) was purchased from Merck KGaA, Germany.

3.2 METHODS

The flowchart of the general experimental design is shown in Figure 3.1, and consists of three sections: 1) ACE adsorption by zeolite granules packed column, 2) zeolite granules regeneration and 3) zeolite extraction to measure the degradation rate of ACE.

With regard to the regeneration section, three stages of experiments were planned as mentioned in Section 1.3. The detailed experimental conditions for each set of different stages can be found in Appendix C.

3.2.1 Adsorption

The ACE adsorption process was conducted in a column with diameter 4 cm and length 1 m under $20°C$, the schematic diagram of the experiment setup for ACE adsorption is illustrated in Figure 3.2. High concentration of ACE solution (i.e. $200\, mgL^{-1}$) was transported to the vertical column from the top with feed flow rate of $15.4\, mLmin^{-1}$ ($1.23\, cmmin^{-1}$). The empty bed contact time (EBCT) of the column

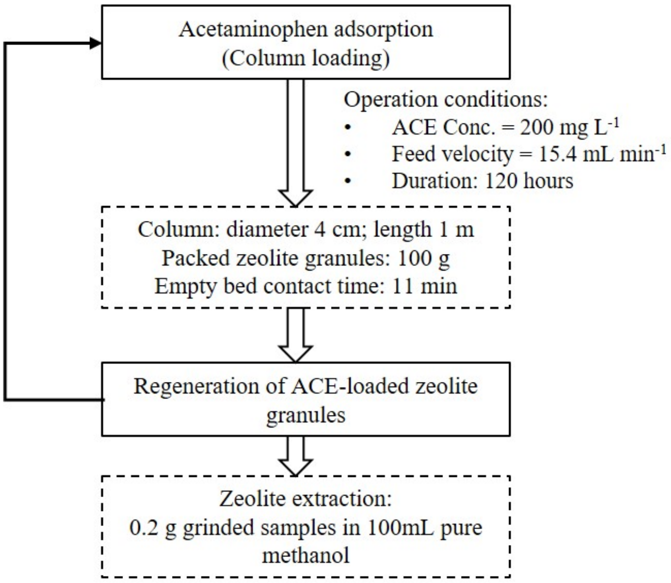


Figure 3.1: Flowchart of General Experiment Design

was 11 minutes. The ACE concentration in the feed flow was measured everytime after filling the bucket to ensure the same inflow concentration. The outlet flow was sampled with different time intervals at the discharge point during 120 hours. The ACE concentration in both feed and outlet flow was measured by a high performance liquid chromatography (HPLC), more details on the ACE analysis are given in Section 3.2.4. A picture of the experimental setup for the ACE adsorption is shown in Appendix Figure B.1a.

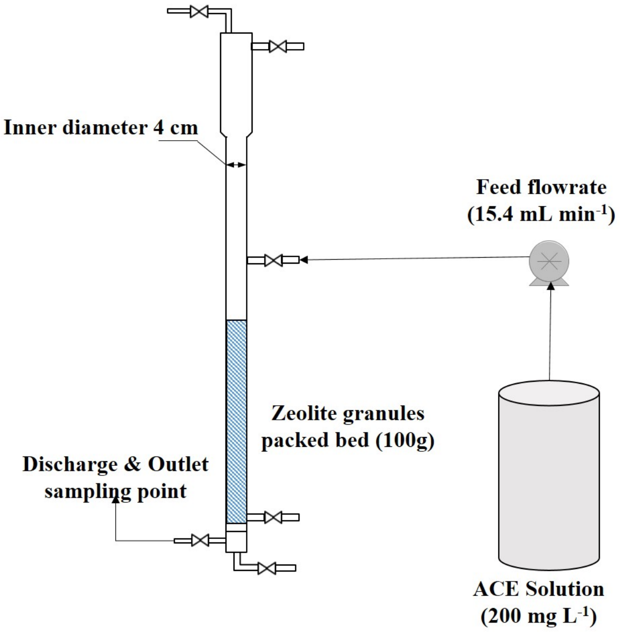


Figure 3.2: Experimental Setup for ACE Adsorption by Zeolite Granules Packed Column

To have more clear comparison between the restored adsorption ability of each process, the adsorption capacity of the column after each regeneration test was determined in accordance with the integration equation of Equation 3.1. The integrated area between the ACE concentrations of feed solution curve and outflow solution curve is the amount of adsorbed ACE.

$$M_{ACE} = Q \int_0^t (C_{in} - C_{out})dt \qquad (3.1)$$

where M_{ACE} is the mass of adsorbed ACE in the column (mg); Q is the ACE solution feed flow rate (i.e. 15.4 $mLmin^{-1}$; 1.23 $cmmin^{-1}$); t is the operation time ($hour$); C_{in} and C_{out} are the inlet and outlet ACE concentration (mgL^{-1}).

3.2.2 Regeneration

Two types of columns were applied for the regeneration experiments. *Column I* has the same size as the column that was used for the adsorption process in Section 3.2.1, 100 g of ACE-loaded zeolite granules were packed into *Column I*. *Column II* (diameter 10 mm, length 25 cm, glass) was applied to test different operation conditions in a smaller scale setup, 5 g of ACE-loaded zeolite granules were packed into the column. The schematic diagrams for *Column I* and *Column II* are given in Figure 3.3 and Figure 3.4 respectively.

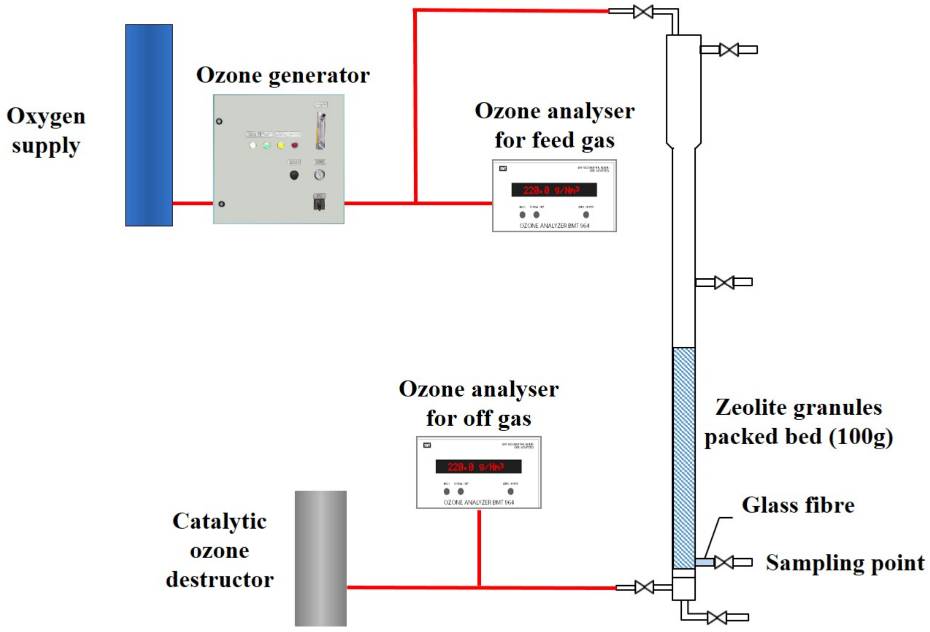


Figure 3.3: Experimental Setup ACE-loaded Zeolite Granules Regeneration in *Column I*

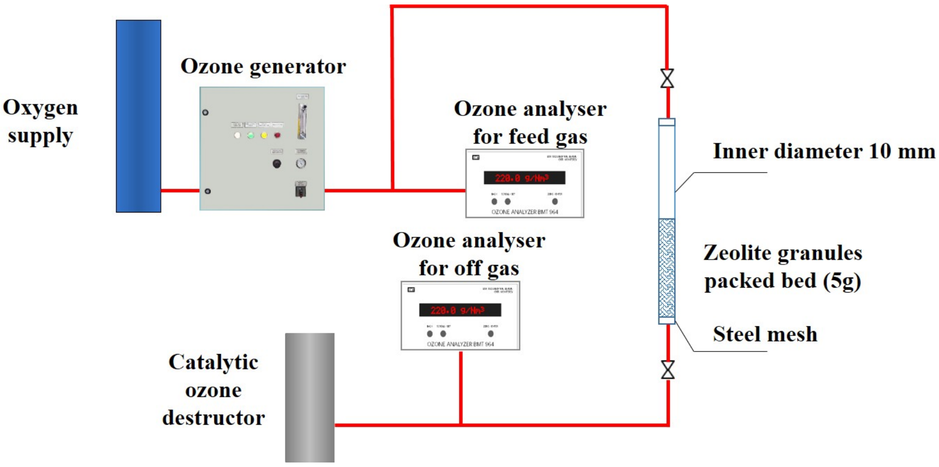


Figure 3.4: Experimental Setup ACE-loaded Zeolite Granules Regeneration in *Column II*

In this research, ozone was generated from a commercial ozone generator by liquid oxygen under room temperature. The supply pressure of the ozone is 0.5 bar, the ozone concentration and flow rate were adjusted under different experimental conditions. At the inlet and outlet points of the column, gaseous samples were taken and measured by two ozone analysers to obtain the ozone concentration in the gas streams. The unused ozone in the outlet gas was destructed to oxygen by a catalytic column and then was discharged safely.

The experiments for the regeneration process were divided into three stages. For each stage of regeneration, the methods for each experimental section are included respectively: 1) the sampling process, 2) the water content of zeolite granules, 3) the hydrogen peroxide concentration of zeolite granules and 4) inflow ozone concentration and flow rate.

Stage I

Experiment setup and define the effectiveness of regeneration through gaseous O_3 *only process and gaseous* O_3/H_2O_2 *process respectively.*

In *Stage I*, *Column I* was applied for testing the effectiveness of regeneration. The effectiveness of regeneration by applying 1) gaseous O_3 process with drained bed; 2) gaseous O_3/H_2O_2 process with drained bed and 3) gaseous O_3 process with dried bed was tested to investigate if the ozone based regeneration process is feasible to regenerate the ACE-loaded zeolite granules column.

Sampling Process during Regeneration:

Regarding the *Stage I* regeneration conducted in Column I, the ozonation process was suspended for 15 minutes to take samples during regeneration. Within the defined time interval, oxygen (0.5 bar) was firstly introduced to dilute the ozone in the column for safety concern, then the column was back washed by deionized water to mix well the zeolite granules. After that, approximately 0.2 g of zeolite granules were taken from the sampling point and then oxygen (0.6 bar) was introduced again to drain the retained water from the column.

The ACE degradation rate (R_{ACE}) were applied to determine the regeneration performance of the selected process. R_{ACE} was determined by Equation 3.2 to Equation 3.4. Equation 3.9 was applied in Equation 3.2 to calculate E.

$$\mathrm{m_{ACE}} = \mathrm{C}_t \cdot \mathrm{V/E} \tag{3.2}$$

$$\mathrm{q}_t = \mathrm{m_{ACE}}/(\mathrm{m_{sample}} - \mathrm{m_{ACE}}) \tag{3.3}$$

$$\mathrm{R_{ACE}} = 1 - (\mathrm{q}_t/\mathrm{q}_0) \cdot 100\% \tag{3.4}$$

where m_{ACE} is the estimated adsorbed ACE amount in zeolite granules (mg), C_t is the tested ACE concentration in methanol (mgL^{-1}), V is the volume of methanol used for extraction (L), E is the expected extraction percentage from the theoretical adsorption amount (%), m_{sample} is the sample weight (g), R_{ACE} is the ACE degradation rate (%), q_t is the adsorbed ACE by the zeolite granules (mgg^{-1}) after regeneration of duration t and q_0 is the initial adsorbed ACE by zeolite granules without regeneration (mgg^{-1}).

Water Content of Zeolite Granules:

In this stage, the water content of zeolite granules was adjusted to achieve drained bed and dried bed. The water contents of zeolite granules were determined by Equation 3.5. After the adsorption process stated in Section 2.2.1, the zeolite granules were back washed with deionized water and transferred out of the column. The effect of the backwash process to the adsorbed ACE concentration can be neglected, this part of the experiment results are shown in Appendix D. The water content of the zeolite granules before drying (drained bed) was around 40%. It was assumed that for the dried bed, all the water content of zeolite granules was removed (water content = 0%) after drying at 60°C for 20 hours.

$$\mathrm{WC} = ((\mathrm{m_{wet}} - \mathrm{m_{dry}})/\mathrm{m_{dry}}) \cdot 100\% \tag{3.5}$$

where WC is the water content of zeolite granules (%), m_{wet} is the weight of zeolite with water (g) and m_{dry} is the weight of dried zeolite (g).

Hydrogen Peroxide Concentration of Zeolite Granules:

In *Stage I*, to conduct the gaseous O_3/H_2O_2 process with drained bed, hydrogen peroxide (H_2O_2) solution was involved by replacing the deionized water for the backwash in the sampling process. As shown in Figure 3.5, $2\,L$ of H_2O_2 solution with initial concentration of $100\,mgL^{-1}$ was used for the backwash process each time that a 5-minute continuous flow ($400\,mLmin^{-1}$; $0.32\,cmmin^{-1}$) was introduced from the bottom of the column. In this case, H_2O_2 was retained in the zeolite pores. Same bottle of solution was used for the whole process, the initial and the after H_2O_2 concentrations were measured.

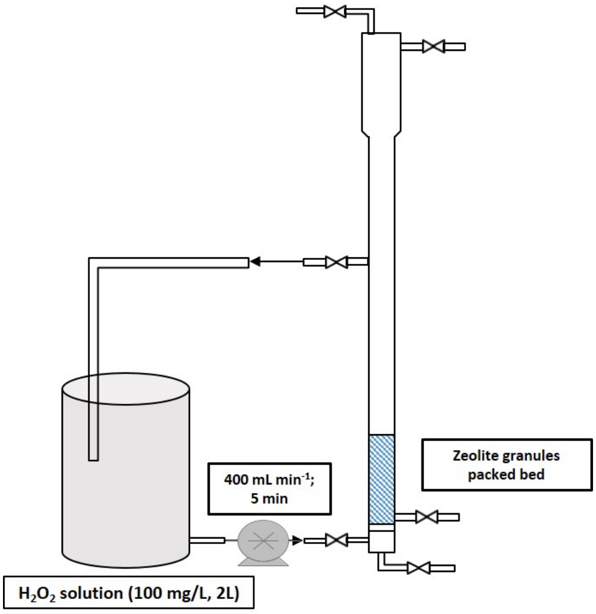


Figure 3.5: Schematic Experiment Setup for Regeneration with Hydrogen Peroxide in *Column I*

Inflow Ozone Concentration and Flow Rate:

The inflow ozone concentration and flow rate can be controlled by the ozone generator. The ozone concentration measurement range for inflow gas is $0 - 300\,mgL^{-1}$, and $0 - 100\,mgL^{-1}$ for outflow gas. The flow rate up-limit is $1\,Lmin^{-1}$.

The superficial ozone flow rate was determined by Equation 3.6

$$V_s = \frac{V_{O_3}}{0.25 \cdot \pi \cdot d_{column}} \tag{3.6}$$

where V_s is the superficial flow rate at the top surface of zeolite granules ($mmin^{-1}$) and d_{column} is the diameter of the column (m).

Stage II

Investigate the effects of different operation conditions on acetaminophen-loaded zeolite granules regeneration process.

In *Stage II*, to test the effects of different operation conditions on the ACE degradation rate, *Column II* with smaller scale (with 5 g of zeolite granules packed) was applied. Different experimental conditions for the regeneration process were studied, including: 1) O_3 flow rate; 2) O_3 concentration; 3) H_2O_2 concentration; 4) water content of zeolite granules.

Sampling Process during Regeneration:

As only 5 g of ACE-loaded zeolite granules were packed in *Column II*, there was no sampling process during the regeneration process in *Column II*. Approximately 0.2 g of zeolite granules were taken before and after the regeneration. The ACE degradation rate was calculated by Equation 3.2 to Equation 3.4.

Water Content of Zeolite Granules:

Same as *Stage I*, the ACE-loaded zeolite granules were dried at 60°C for 20 hours to achieve 0% of water content by assumption. The water content of zeolite granules was determined by Equation 3.5. To investigate the influence of the water film on the granules, the dried zeolite granules were soaked into deionized water for 30 minutes and dried by oven at 60°C for different time intervals to obtain different water contents (i.e. 0%, 20%, 30%, 35% by weight). It was found that after 30 minutes of soaking, around 0.06 mg of ACE (0.3 % of total adsorbed ACE) was dissolved into water, which can be neglected in the calculation.

Hydrogen Peroxide Concentration of Zeolite Granules:

To investigate the effect of H_2O_2 concentration on the regeneration process, the ACE-loaded zeolite granules were dried at 60°C for 20 hours to achieve 0% of water content by assumption. After that, 5 g of dried ACE-loaded zeolite granules were soaked into different concentrations (i.e. 0, 50, 100, 200, 300 and 600 mgL^{-1}) of H_2O_2 solution (i.e. 100 mL) for 30 minutes.

Inflow Ozone Concentration and Flow Rate:

In *Stage II*, to investigate the effect of ozone concentration and ozone flow rate, the total inflow dosage of ozone was 900 mg to partially decompose ACE as calculated based on Equation 2.3. The total inflow dosage of ozone was calculated by Equation 3.7. The superficial ozone flow rate was determined by Equation 3.6.

$$\mathrm{D}_{\mathrm{O}_3} = t \cdot \mathrm{C}_{\mathrm{O}_3} \cdot \mathrm{V}_{\mathrm{O}_3} \tag{3.7}$$

where D_{O_3} is the inflow dosage of ozone (mg), t is the duration of regeneration (min), C_{O_3} is the inflow concentration of ozone (mgL^{-1}), and V_{O_3} is the inflow flow rate of ozone ($Lmin^{-1}$).

Stage III

Examine the feasibility of long-term on-site regeneration for acetaminophen loaded zeolite granules through the gaseous O3 only process.

In *Stage III*, the long-term experiment was conducted in *Column I* with the operation conditions selected from the results of *Stage I-II*. Gaseous O_3 only process with dried bed (*Column I*; 100 g of zeolite granules packed) was applied for the long-term regeneration experiments. The same zeolite granules packed column was operated for three cycles to understand the change of the restored adsorption capacity after long-term operation. The effect of ozone on zeolite granules and the effect of intermediates accumulation were studied respectively.

Sampling Process during Regeneration:

In *Stage III*, the long-term regeneration tests were conducted in *Column I*. Samples were taken before and after the regeneration. 0.5 g and 0.7 g of samples after regeneration were taken, ground and put into 1 L ACE solution (200 mgL^{-1}) respectively to examine the restored adsorption capacity. 1.5 mL of samples were taken once per day for 5 days to analyse the remained ACE concentration in solution. The recovery efficiency (RE) was calculated by Equation 3.8 to obtain the percentage of restored adsorption capacity after regeneration.

$$\mathrm{RE} = \mathrm{q}_{e(n)} / \mathrm{q}_{e(0)} \cdot 100\% \tag{3.8}$$

where RE is the recovery efficiency (%), $q_{e(n)}$ is the adsorption capacity of zeolite granules after n cycles of regeneration (mgg^{-1}) and $q_{e(0)}$ is the initial adsorption capacity before long-term regeneration (mgg^{-1}).

Water Content of Zeolite Granules:

As dried bed was applied in *Stage III*, the ACE-loaded zeolite granules were dried at 60°C for 20 hours to achieve 0% of water content by assumption.

Hydrogen Peroxide Concentration of Zeolite Granules:

As the regeneration process was gaseous O_3 only process with dried bed, no H_2O_2 was applied in this stage.

Inflow Ozone Concentration and Flow Rate:

Same inflow ozone concentration and flow rate were applied in *Stage III*, the parameters were set based on the results of *Stage I-II*. Gaseous ozone with flow rate of $0.8\,Lmin^{-1}$ ($63.7\,cmmin^{-1}$) and concentration of $90\,mgL^{-1}$ were applied.

3.2.3 Extraction

To obtain the ACE degradation rate in the regeneration process, extraction tests were conducted to measure the amount of ACE that remained in the zeolites granules. Compared to the equilibrium adsorption tests, extraction required less time to obtain the regeneration performance from a series of samples. Besides, the degradation efficiency of ACE through the regeneration processes can be directly obtained through the extraction.

Based on the pre-experiments shown in Appendix E, it was found that methanol is better for ACE extraction and measurement, a duration of 30 minutes is enough for the extraction. Approximately $0.2\,g$ of the zeolite granules were sampled and ground into powder, then put into $100\,mL$ pure methanol for 30 minutes to extract the ACE from zeolites. After first extraction, the zeolite powder was filtrated and put into another $100\,mL$ pure methanol for 30 minutes to obtain second extraction. The extraction process was conducted by a shaker as shown in Figure B.1d at 20°C to mix well the extraction solution. The results of the extraction tests by using other organic solvents (i.e. ethanol and acetonitrile) are also given in Appendix E.

Additionally, controlled equilibrium adsorption tests were conducted to calculate the actual adsorption capacity of zeolite granules, which were compared with the results of extractions to obtain the expected extraction percentage (E) by Equation 3.9. $0.5\,g$ of zeolite granules were put into $1\,L$ ACE solution ($200\,mgL^{-1}$). $1.5\,mL$ of samples were taken once per day for 14 days to analyse the remained ACE concentration in solution. After the ACE concentration in the solution reached equilibrium, the ACE-loaded zeolite granules were dried and ground, then put into 250 mL of pure methanol to do extraction twice.

$$E = \frac{\mathrm{m_{extractedACE}}}{\mathrm{m_{adsorbedACE}}} = \frac{\mathrm{C_t} \cdot \mathrm{V_{methanol}}}{(\mathrm{C_0} - \mathrm{C_e}) \cdot \mathrm{V_{ACE}}} \tag{3.9}$$

where $m_{extractedACE}$ is the amount of first ACE extraction by methanol, $m_{adsorbedACE}$ is the amount of ACE adsorbed by zeolite granules, C_t is the tested ACE concentration in methanol (mgL^{-1}), $V_{methanol}$ is the volume of methanol that used for extraction (i.e. 0.25 L), C_0 is the initial concentration of ACE solution (i.e. 200 mgL^{-1}), C_e is the equilibrium concentration of ACE solution after adsorption (mgL^{-1}) and V_{ACE} is the volume of ACE solution (i.e. 1 L).

The expected extraction percentage (E) calculated from test results as listed in Table 3.1 was around 80%, which was used for determining the ACE degradation rate (R_{ACE}) in this study. The detailed data for adsorption and extraction tests are given in Appendix E.

Table 3.1: Extraction for ACE Fully Loaded Zeolite Granules

Items	Symbols	Value	Unit
Initial ACE Conc.	C_0	200.4	mgL^{-1}
Equilibrium ACE Conc.	C_e	152 ± 2	mgL^{-1}
Volume of ACE Solution	V_{ACE}	1	L
Tested ACE Conc. in Methanol (1^{st})	C_t	39.09	mgL^{-1}
Volume of Methanol	$V_{methanol}$	0.1	L

3.2.4 Analysis of Acetaminophen

The concentration of ACE in water samples and methanol samples were determined by a HPLC system (SHIMADZU 74909) equipped with a Kinetex 2.6 μm column. The ACE was monitored with a UV detector (wavelength 254 nm). Acetonitrile was used for the mobile phase in the reverse phase HPLC system. A series of standard solution of ACE with different concentrations in water and methanol were prepared to obtain the calibration curves as given in Appendix F. The calibration curves can transfer the peak area of HPLC to the actual concentration of ACE in solution.

4 RESULTS AND DISCUSSIONS

4.1 RESULTS OF STAGE I

In the first stage, the effectiveness of regeneration by applying 1) gaseous O_3 process with drained bed; 2) gaseous O_3/H_2O_2 process with drained bed and 3) gaseous O_3 process with dried bed was tested to investigate if the ozone based regeneration process is feasible to regenerate the ACE-loaded zeolite granules column.

4.1.1 Gaseous O_3 Process with Drained Bed

The regeneration tests were conducted with two different flow rates of ozone: 0.2 and 0.8 $Lmin^{-1}$ (15.9 $cmmin^{-1}$ and 63.7 $cmmin^{-1}$). The ozone concentration in the inlet gas was 90 mgL^{-1}. The water content of zeolite granules was 40% after draining the water from the column by pressurized air (0.6 bar). The zeolite granules were surrounded by water films. In this case, the regeneration process was conducted in gas-liquid-solid phase so that the ozone gases first dissolved into the surrounding water films and then reacted with the adsorbed ACE on zeolite.

The concentrations of ozone in the inlet and outlet gases against time with different flow rates were plotted in Figure 4.1. *Column I* has around 1.99 L of dead volume filling with air. The required time for the outlet ozone to achieve half of the inflow concentration (90 mgL^{-1}) was 9.95 minutes for 0.2 $Lmin^{-1}$ (15.9 $cmmin^{-1}$) ozone flow rate and 2.49 minutes for that of 0.8 $Lmin^{-1}$ (63.7 $cmmin^{-1}$). It can be seen that a higher flow rate required less time to reach the equilibrium concentration of the outlet ozone compared to the one with a lower ozone flow rate. Besides, larger gaps between equilibrium outlet and inlet ozone concentrations were observed for the one with lower ozone flow rate. It is suggested that more time was needed for ozone with lower flow rate to mix with the air in the empty space, meanwhile part of the ozone would be decomposed in the air due to the short half-life time.

The results for regeneration performance by the low flow rate (i.e. 0.2 $Lmin^{-1}$; 15.9 $cmmin^{-1}$) gaseous O_3 process with drained bed were

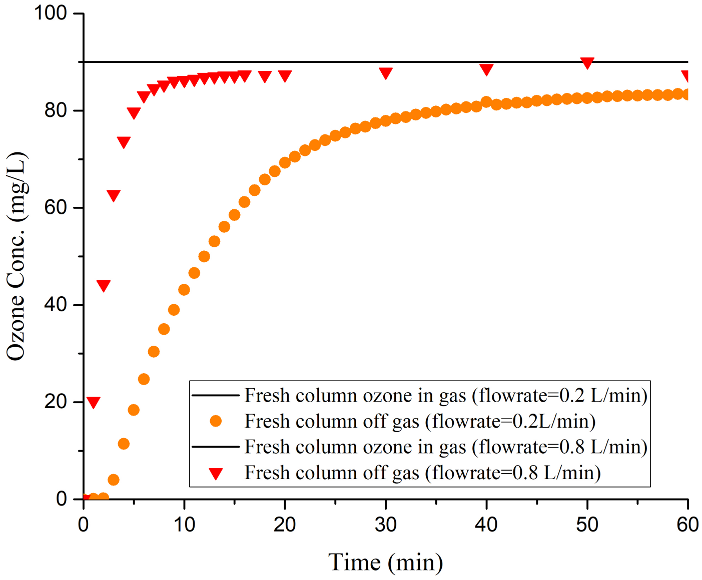
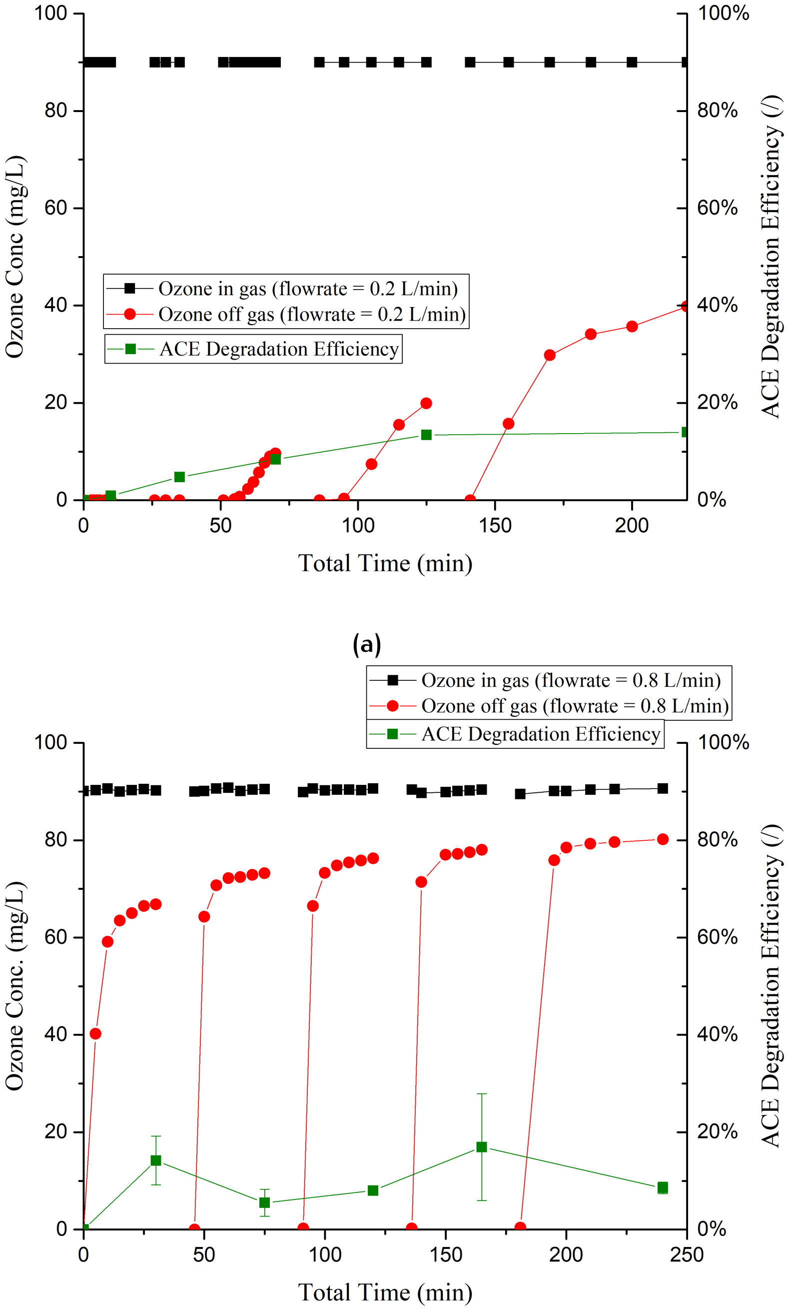


Figure 4.1: The Concentrations of O_3 in Inlet and Outlet Gas with Different Flow Rates in Fresh Column I (ozone conc. = $90\,mgL^{-1}$; zeolite water content = 40%)

shown in Figure 4.2a. Samples were taken during the regeneration which suspended the reaction around 15 minutes each time. The overall effective ozonation time was 180 minutes. At the beginning of the regeneration, ozone was hardly detected in the outlet gas, which can be explained by the ozone dissolution in the water films and the decomposition in the air due to the instability. As the process continued, an increasing amount of ozone was measured and reached around $40\,mgL^{-1}$ at the end of the process. By applying the low flow rate of ozone, the ACE degradation efficiency had a steady and minor increase that achieved 17% after 180 minutes of regeneration.

Figure 4.2b presents the results for the regeneration performance with a high flow rate (i.e. $0.8\,Lmin^{-1}$; $63.7\,cmmin^{-1}$) gaseous O_3 process with drained bed. It was found that when applying the high flow rate, the concentration of outlet ozone increased rapidly after the regeneration started. At the end of the regeneration, the outlet ozone concentration reached $80\,mgL^{-1}$. A steady improvement for ACE degradation efficiency could not be observed during the regeneration process. The ACE degradation efficiency fluctuated between 2 % and 17 %. Compared to the ACE degradation rate by applying a high ozone flow rate, the regeneration process with a low ozone flow rate had a slight higher ACE degradation rate. As can be seen in Figure 4.1, the retention time of the high flow rate ozone in the column was shorter than that of the short flow rate ozone. Therefore, the



(a)

(b)

Figure 4.2: Regeneration by Gaseous O_3 with Different O_3 Flow Rates. (a) ozone flow rate = $0.2\,Lmin^{-1}$ ($15.9\,cmmin^{-1}$); ozone conc. = $90\,mgL^{-1}$; zeolite water content = 40%. (b) ozone flow rate = $0.8\,Lmin^{-1}$ ($63.7\,cmmin^{-1}$); ozone conc. = $90\,mgL^{-1}$; zeolite water content = 40%.

contact time between zeolite water films and ozone was shorter and less ozone can be diffused into the water to degrade the ACE. In addition, the fluctuation of the ACE degradation rate for the high flow rate process can also be explained by the short retention time. As the oxidation was not homogeneous distributed, the sampled zeolite granules might have variable outcomes of ACE degradation rates after the mixing process.

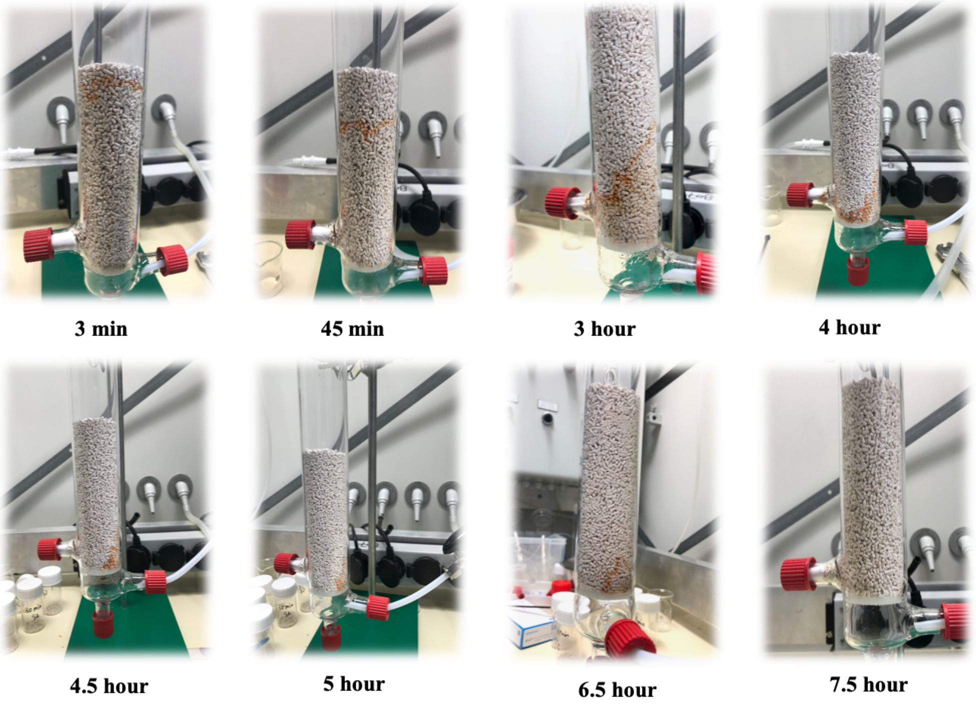
The regeneration performance of the gaseous O_3 process with either a high or low ozone flow rate in drained bed was not ideal. Considering the relatively low diffusivity of ozone in water (i.e. $1.74 \times 10^{-5} cm^2 s^{-1}$; 20°C), it is suggested that the water films surrounding the zeolite granules limited the diffusion of ozone gas to the inner pores of zeolites, only the ACE that was adsorbed on the zeolite surface was able to be degraded [Zhou and Smith, 2000]. Moreover, the results of low ACE degradation rates is also in accordance with what was mentioned in Section 2.3.2, which stated that the Ha number of packed bed reactor is relatively high. In this case, the concentration of ozone in water films will drop significantly due to the oxidation reaction with ACE on zeolite surface, thus less ozone flux can reach the ACE adsorbed in the inner pores [Poznyak et al., 2019].

Additionally, according to the trends of ozone concentration in the outlet gas that are shown in both Figure 4.2a and Figure 4.2b, it was found that each time after restarting the ozonation process, the ozone concentration in the outlet gas increased faster than last time and achieved a higher ending concentration each time. It may also illustrate that in both regeneration processes, only a small amount of ozone was utilized for the ACE degradation and only the ACE from zeolite surface was involved into the reaction. The rest of the ozone gas might directly flow out from the gap between zeolite granules and the column glass wall due to the low diffusivity of ozone in water.

4.1.2 Gaseous O_3 only process with dried bed

The gaseous O_3 only process with drained bed as mentioned in Section 4.1.1 was not effective to regenerate ACE-loaded zeolite granules due to the poor ozone gas transfer rate through the surrounding water films. In this case, to exclude the effect of water film and maximize the ozone gas transfer rate, the ACE-loaded zeolite granules were dried (water content = 0%) at 60°C for more than 20 hours. The regeneration experiment was conducted with $0.8\,Lmin^{-1}$ ($63.7\,cmmin^{-1}$) and $90\,mgL^{-1}$ ozone in dried bed. The reaction was in gas-solid phase so that the ozone gas was able to directly diffuse into the zeolite pores and react with the adsorbed ACE.

During the regeneration, it was found that there was an orange colored area at the top surface of the packed zeolite granules. As the reaction continued, the layer moved down with releasing heat, the measured temperature of glass wall was around 60°C. Besides, it was observed that a circle of small water drops had formed on the column glass wall, surrounding the orange layer. The photos of the reactions progress are presented in Figure 4.3. As these phenomena occurred layer by layer from the top, no mixing was conducted during the sampling processes to avoid disturbing the reactions.



3 min **45 min** **3 hour** **4 hour**

4.5 hour **5 hour** **6.5 hour** **7.5 hour**

Figure 4.3: Experiment Photos for Gaseous O_3 only Process with Dried Bed: ozone flow rate = $0.8\,Lmin^{-1}$ ($63.7\,cmmin^{-1}$); ozone conc. = $90\,mgL^{-1}$; zeolite water content = 0%

The ozone concentrations in the inlet and outlet gases as well as the ACE degradation efficiency are presented in Figure 4.4. It can be noticed that the time of no ACE degradation rate corresponded well with the time at which the orange layer appears near the sampling point as shown in Figure 4.3. When the orange layer reached the sampling point (i.e. reaction time of 3 hour in Figure 4.3), 8% of ACE degradation efficiency was obtained (i.e. total time of 240 minutes in Figure 4.4). When the orange layer moved downward from the the sampling point, the ACE could not be detected by HPLC and the corresponding ACE degradation rates were 100%. However, according to the measured peaks in HPLC as shown in Appendix G, the generated intermediates had a similar retention time as ACE, the measured peak area of ACE was merged with that of the generated intermediates. In this case, when the concentration of ACE in the extraction was smaller than that of the intermediates, the peak of ACE was hardly

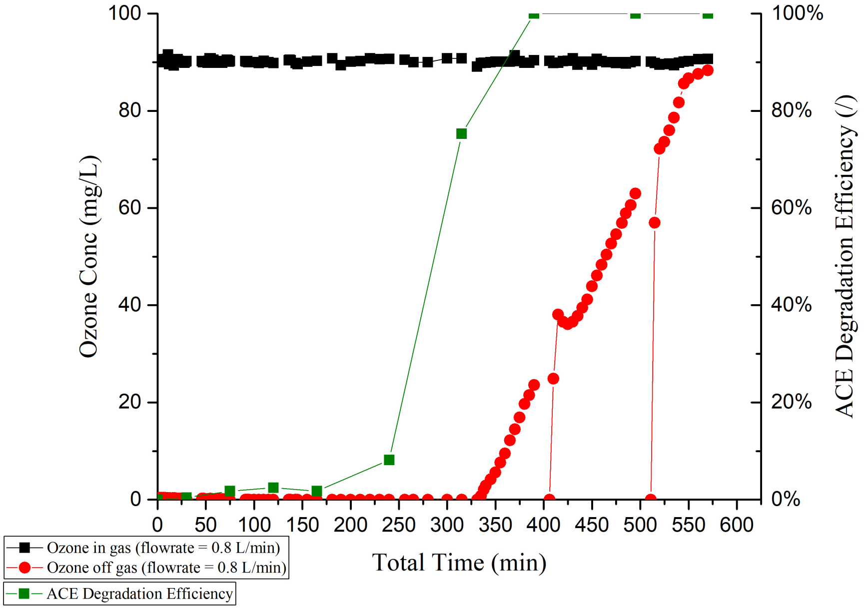


Figure 4.4: Regeneration by Gaseous O_3 with High O_3 Flow Rate: ozone flow rate = $0.8\,Lmin^{-1}$ ($63.7\,cmmin^{-1}$); ozone conc. = $90\,mgL^{-1}$; zeolite water content = 0%

measured. Hence, even though the peak of ACE cannot be measured by HPLC, the ACE degradation efficiency cannot be defined as 100%, but the ACE concentration was relatively low to be hardly detected. According to the suggested ACE mineralization pathway stated in Figure A.1, the orange compound was suggested to be p-benzoquinone which is the compound from the generated intermediates that has orange color [EuropeanChemicalsAgency, 2019]. The appearance of the orange layer can indicate the ACE degradation progress in the column.

In addition, it was found that after the orange layer turned back to normal zeolite color, the measured total peak areas in HPLC still had a slight decline of 8%. It is suggested that p-benzoquinone was degraded to secondary intermediates. As the compounds of the generated intermediates were not defined, the exact concentrations of the related intermediates could not be identified. It is suggested that the overall mineralization of ACE and its by-products were still reacting. According to the measured peaks in HPLC shown in Figure G.1, the total HPLC peak area of the extracted samples in 7.5-hour regeneration had a small decline (i.e. 8%) compared to that of 5-hour of regeneration, which suggested that the degradation rate of the generated intermediates was relatively low. Hence, it is suggested that the ozone gas was not able to decompose the intermediates effectively which can agree with the finding from the literature review in Section 2.3.2.

According to the trends of the ozone outlet gas concentration, it was found that the first 3 hours of the regeneration, there was almost no ozone to be detected in the outlet gas, all the ozone was consumed to decompose the adsorbed ACE. As the ACE degradation rate started to increase, ozone started to be measured in the outlet gas and steadily reached to proximity of the inlet ozone concentration level. It is suggested that during the steady ozone concentrations increasing period, the generated intermediates were oxidized by ozone slowly. It was assumed that the regeneration process was completed when the difference of inlet and outlet ozone concentrations was within $5\,mgL^{-1}$ according to the results from Figure 4.1. The effect of generated intermediates on long-term operation will be discussed in Section 4.3.

4.1.3 Gaseous O_3/H_2O_2 process with drained bed

Figure 4.5 shows the regeneration performance by the gaseous O_3/H_2O_2 process with drained bed. As shown in Figure 4.5, the ozone concentrations in the outlet gas had similar increase trends to the regeneration by gaseous O_3 with drained bed, thus it was assumed the ozone consumption for these two processes was the same. $2\,L$ H_2O_2 solution with initial concentration of $100\,mgL^{-1}$ was used for backwash the column during the sampling process. After five times of the backwash, the residual concentration of H_2O_2 decreased to $65.75\,mgL^{-1}$. It can be seen that 34% of ACE degradation rate was achieved after 3-hour ozonation in the presence of H_2O_2 with drained bed. With the addition of H_2O_2 better regeneration performance can be achieved compared to that with gaseous O_3 only (i.e. 17% of ACE degradation rate). The enhancement of ACE degradation rate supports the theories stated in Section 2.3.2 that adding H_2O_2 can activate more $OH\cdot$ and increase the oxidation potential for the reaction [Von Gunten, 2003]. Therefore, more ozone can be decomposed to $OH\cdot$ by reaction Equation 2.2. The activated $OH\cdot$ has a better ability to oxidize ACE with higher degradation kinetics.

However, the presence of water films was still the dominant limiting factor for improving the ACE degradation rate to the same level as the gaseous O_3 only process with drained bed. It is suggested that the generated $OH\cdot$ was hardly diffused into the zeolite pores due to the high Ha value of packed bed reactor and less gas diffusion rate [Poznyak et al., 2019].

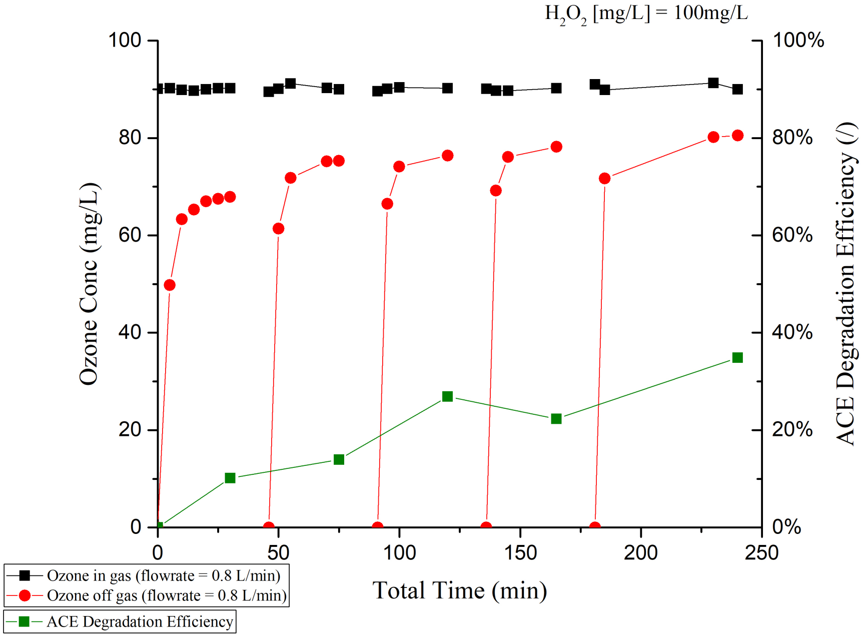


Figure 4.5: Regeneration by Gaseous O_3/H_2O_2 with High O_3 Flow Rate: ozone flow rate = $0.8\,Lmin^{-1}$ ($63.7\,cmmin^{-1}$); ozone conc. = $90\,mgL^{-1}$; H_2O_2 initial conc. = $100\,mgL^{-1}$; zeolite water content = 40%)

4.1.4 Column Adsorption Performance of Stage I

In *Stage I*, the column was reloaded with ACE solution for the experiment of the next round of regeneration. The adsorption capacity of the column after different regeneration processes is shown in the adsorption breakthrough curve in Figure 4.6. When the outflow ACE concentration of the column reaches the inflow concentration, it is assumed that the column was fully loaded. The integrated area between the ACE concentrations of feed curve and outflow curve indicates the amount of adsorbed ACE. The calculated adsorbed ACE amount in the column by using Equation 3.1 is summarized in Figure 4.7.

As shown in Figure 4.6 and Figure 4.7, the adsorption capacity recovery of the column was not ideal by applying the processes with drained bed. With respect to the column regenerated by the processes with drained bed, the adsorption ability was similar for different processes due to the uncompleted regeneration. As shown in Figure 4.6, the column treated by the regeneration process with dried bed achieved similar adsorption trends to that with fresh bed. However, according to the calculated adsorbed ACE amount, 100% of recovery of the adsorption capacity after the regeneration process of gaseous O_3 with dried bed cannot be obtained.

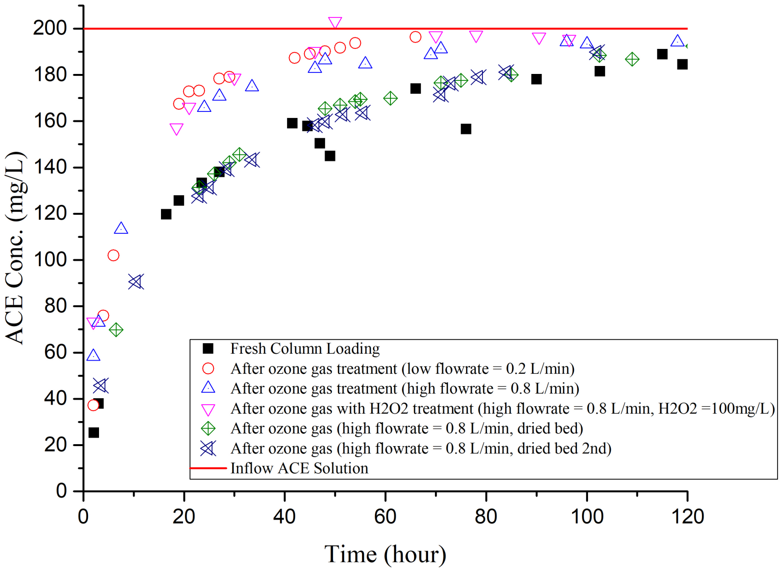


Figure 4.6: Column Adsorption Performance after Regeneration Processes in Stage I (ACE conc. = 200 mgL^{-1}).

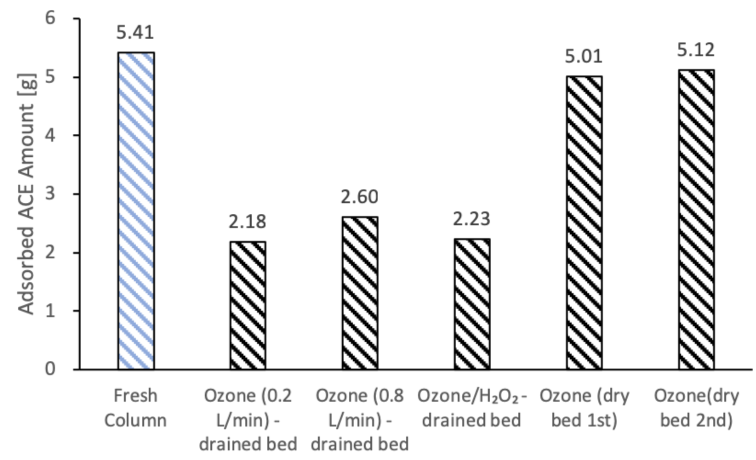


Figure 4.7: Adsorbed ACE amount after Regeneration Processes in Stage I (ACE conc. = 200 mgL^{-1}).

4.2 RESULTS OF STAGE II

Based on the results given in Section 4.1, although adding H_2O_2 was found able to slightly enhance the ozonation in drained bed, the overall regeneration performance by gaseous O_3/H_2O_2 with drained bed was not ideal as the presence of water films limited the oxidants diffusion. It was found that with implementing the dried zeolite bed, the adsorbed ACE was effectively decomposed and can hardly be detected in the extraction solution. Therefore, it is interesting to investigate the effect of water content of zeolite granules, ozone flow rate, ozone concentration on the regeneration performance. Besides, the effect of H_2O_2 concentrations with different water contents was also meaningful to be studied to understand the combination effect of ozone diffusion and H_2O_2 concentrations to the regeneration performance.

Column II packed with $5\,g$ of ACE-loaded zeolite granules was applied in *Stage II*. The concentration of O_3 in inlet and outlet gases of the fresh column is shown in Figure H.1. The calculated dead volume for *Column II* is $0.01\,L$ and the time needed to reach half equilibrium concentration is $0.9\,s$ with a gas flow rate of $0.8\,Lmin^{-1}$ ($10.2\,m\,min^{-1}$). Therefore, the decay of ozone within the column can be neglected due to the short retention time.

4.2.1 Effect of Water Contents of Zeolite Granules

The initial water content of the zeolite granules was 40%, only the retained water was drained by pressurized air ($0.6\,bar$) and no drying process was conducted. Through the drying process at 60°C, the water films between zeolite granules were removed and achieved different levels of water contents. The photos of zeolite granules with different water contents are shown in Figure 4.8.

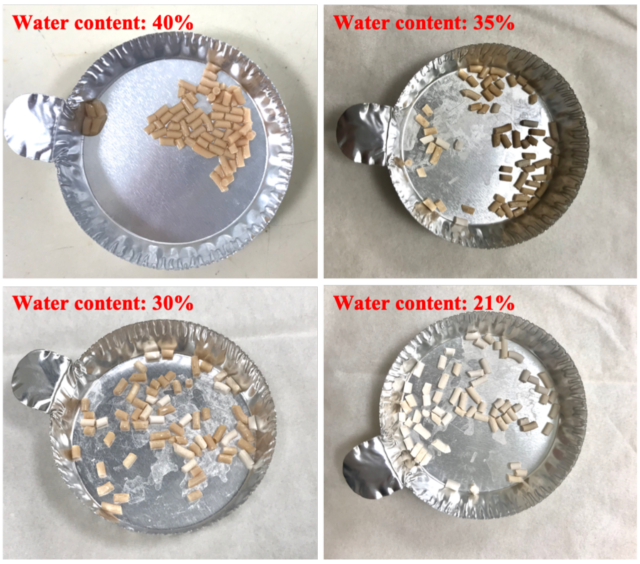
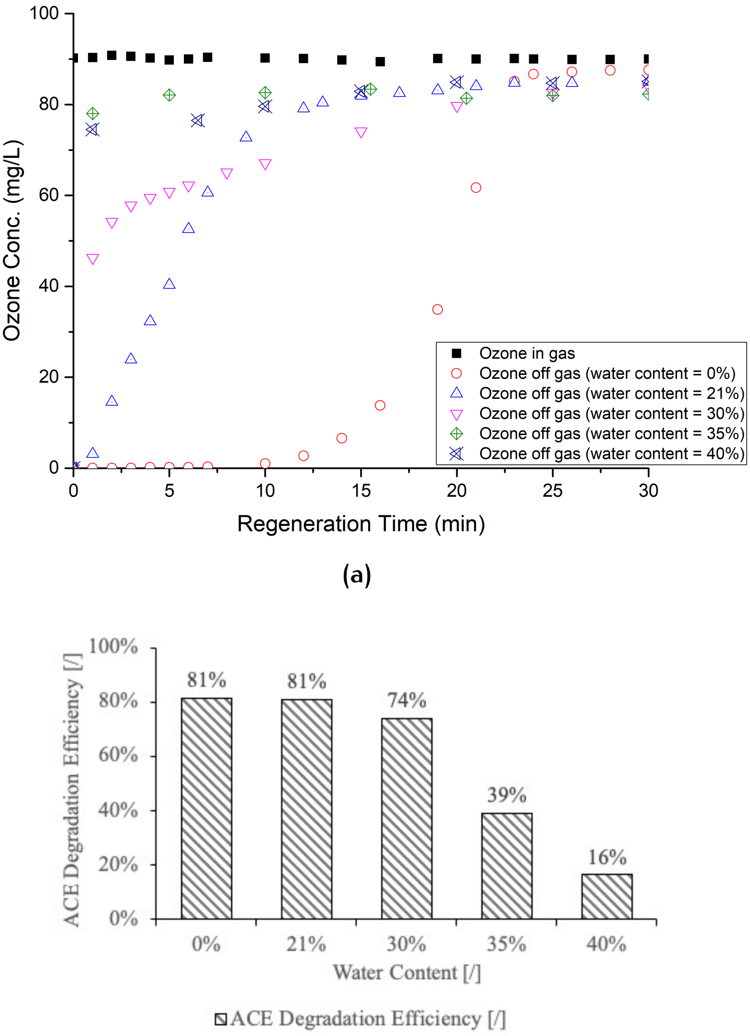


Figure 4.8: Photos of Zeolite Granules ($0.5\,g$ dry weight) with Different Water Contents

The effect of water contents of zeolite granules to the regeneration performance was examined. It can be seen from Figure 4.9a that lower water contents consumed more ozone during the regeneration as the ozone concentration in the outlet gas had a smaller increase rate and more area between ozone inlet gas and outlet gas curves can be observed in the figure. As presented in Figure 4.9b, decreasing the water contents (by weight) of zeolite significantly enhanced the ACE degradation efficiency. It was observed that the ACE degradation efficiency was improved from 16% to 81% by decreasing the water contents from 40% to 21%. Nevertheless, no significant enhancement of ACE degradation rate can be observed by changing water contents from 21% to totally dry (i.e. water content = 0%).



(a)

(b)

Figure 4.9: Effect of Water Content of Zeolite Granules on Regeneration Performance by applying the Gaseous O_3 only Process (ozone flow rate = $0.8\,Lmin^{-1}$ ($10.2\,m\,min^{-1}$); ozone conc. = $90\,mgL^{-1}$; duration = $30\,min$). (a) The Concentrations of O_3 in Inlet and Outlet Gas. (b) ACE Degradation Efficiency with Different Water Contents of Zeolite Granules.

It is suggested that the water contents of zeolite granules would affect the ozone gas transfer rate from ozone gas to the adsorbed ACE, thus the ozone consumption as well as the ACE degradation efficiency would be affected. The gas transfer rate was determined by several terms as expressed by Equation 4.1 [Benjamin and Lawler, 2013]. J_L is the flux determined by the gas and liquid characteristics which are the same in this case. Therefore, the main reasons that affect the ozone gas transfer rate would be the changing of interface thickness and the interfacial area between ozone gas and water films. Through the drying process, the water films between zeolite granules were removed, which increased the interface area between water films and ozone gas. Besides, the thickness of the water films from both outside and inner pores of zeolites was decreased. Hence, more ozone can be diffused into the inner pores of zeolites to oxidize the adsorbed ACE.

$$\mathrm{r}_{gt} = \mathrm{J}_L \frac{A}{V_R} \tag{4.1}$$

where r_{gt} is the gas transfer rate, J_L is the flux into liquid phase, A is the interfacial area and V_R is the reactor volume.

It is interesting to observe in Figure 4.9 that although more ozone was consumed when the water content was 0%, the ACE degradation rate was the same when the water contents were 21% and 0%. It can be explained by the measured HPLC peaks as shown in Figure 4.10, the results indicated that higher amounts of intermediates were detected from the regenerated zeolites with 0% water content. The detected intermediates had a longer retention time in the reverse phase HPLC. According to the mineralization of ACE pathway in Figure A.1 and the K_{ow} value in Table 2.2, the regenerated intermediate is suggested to be hydroquinone which is the only related apolar intermediate that has longer retention time than ACE in the reverse phase HPLC. As hydroquinone is the secondary intermediate, less hydroquinone was generated with 21% of water content due to the lower ozone consumption.

4.2.2 Effect of O_3 Flow Rate

To investigate the effect of ozone flow rate, the experiments were conducted with the same total ozone inflow dosage of 900 mg and concentration of 90 mgL^{-1} to ensure that the ACE degradation was not completed and thus can observe the regeneration performance difference between each flow rate. Dry ACE-loaded zeolite granules (i.e. water content = 0%) were used to exclude the effect of water films, the reactions were in gas-solid phase. To obtain the same dosage, the regeneration duration was calculated by Equation 3.7. In Figure 4.11,

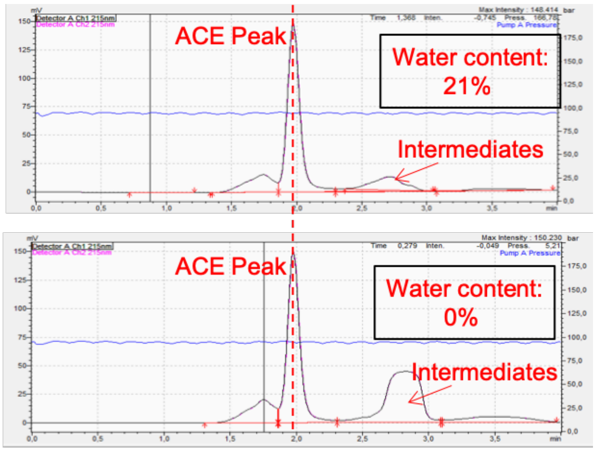


Figure 4.10: Measured HPLC peaks for Gaseous O_3 Regenerated Zeolite Granules with Water Contents 21% and 0%

a declination of the ACE degradation rate can be found with increasing ozone flow rate. The ACE degradation rate dropped down from 95% at 0.2 $Lmin^{-1}$ to 56% (2.5 $m\,min^{-1}$) at 0.8 $Lmin^{-1}$ (10.2 $m\,min^{-1}$). The similar ACE degradation rates of around 75% were found for 0.4 $Lmin^{-1}$ and 0.6 $Lmin^{-1}$. The trends of ozone inlet and outlet concentrations can be found in Figure H.2.

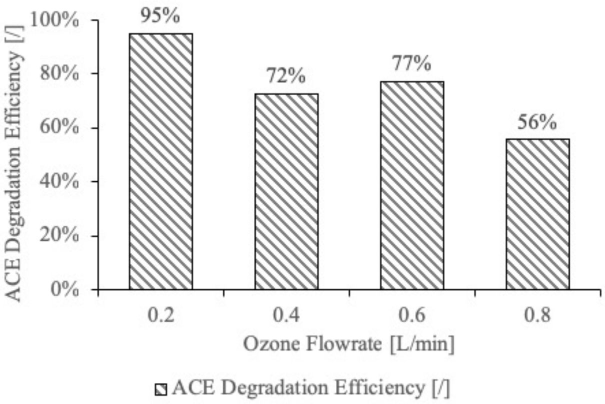


Figure 4.11: ACE Degradation Efficiency with Different Ozone Flow Rates by applying the Gaseous O_3 only Process in Dried Bed (ozone inflow dosage = 900 mg; ozone conc. = 90 mgL^{-1}; duration: 50 min of 0.2 L/min (2.5 $m\,min^{-1}$); 25 min of 0.4 L/min (5.1 $m\,min^{-1}$) ; 16.67 min of 0.6 L/min (7.6 $m\,min^{-1}$); 12.5 min of 0.8 L/min (10.2 $m\,min^{-1}$); water content = 0%).

The observed results can probably be explained by the gas transfer mechanisms. Since the concentration of ozone for each test was the same, the concentration difference was negligible. According to the theories stated by Benjamin and Lawler [2013], if the gas stays at the interface for a longer time, the gas can have a longer diffusion distance to the inner pores of zeolite granules and the gas concentration in the interfacial layer will be higher. From microenvironment scale on the zeolite surface, the localized gas flux for each unit interfacial area would not be affected by the ozone gas flow rate. In this case, it is suggested that the enhancement of ACE degradation by decreasing the ozone flow rate was mainly from the increasing regeneration duration.

4.2.3 Effect of O_3 Concentration

Figure 4.12 shows the effect of ozone inflow concentration on the regeneration process, the same ozone dosage (i.e. $900\,mg$) was applied with a different duration. The trends of ozone inlet and outlet concentrations can be found in Figure 4.12. It can be seen that $90\,mgL^{-1}$ was the optimum ozone concentration with 95% of ACE degradation rate. With an ozone dosage increasing from $50\,mgL^{-1}$ to $90\,mgL^{-1}$, enhancement of ACE degradation can be observed with increasing ozone dosage. Nevertheless, opposite phenomena were found when the ozone concentration was above $90\,mgL^{-1}$.

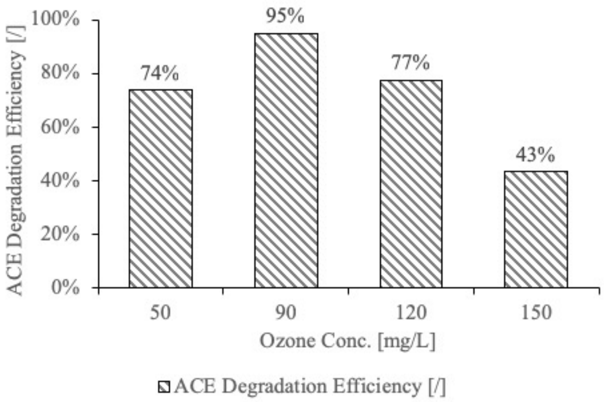


Figure 4.12: ACE Degradation Efficiency with Different Ozone Concentrations by applying the Gaseous O_3 only Process in Dried Bed (ozone inflow dosage = $900\,mg$; ozone flow rate = $0.2\,Lmin^{-1}$ ($2.5\,m\,min^{-1}$); duration: $90\,min$ of $50\,mgL^{-1}$; $50\,min$ of $90\,mgL^{-1}$; $37.5\,min$ of $120\,mgL^{-1}$; $30\,min$ of $150\,mgL^{-1}$; water content = 0%).

It might be explained that the limiting factor of ACE degradation was the concentration of ozone. When the ozone concentration was below $90\,mgL^{-1}$, the low concentration ozone was hardly able to diffuse into the zeolite pores to decompose the adsorbed ACE. When the required ozone concentration for gas diffusion was reached, the ACE decomposition rate would be independent of ozone concentration due to the limited Lewis acid sites on zeolite surface and the limiting factor for the reaction would be the ozone transfer rate [Fujita et al., 2004; Howe et al., 2013; Alejandro et al., 2014; Bourgin et al., 2017]. In this case, when ozone concentration was above 90 mgL^{-1}, the factor that limited the ACE degradation rate would be the regeneration duration.

4.2.4 Effect of H_2O_2 without O_3 Dosage

To investigate the effect of H_2O_2 on the ACE degradation rate, the inflow ozone was replaced by oxygen with the same flow rate (i.e. 0.8 $Lmin^{-1}$; 10.2 $m\,min^{-1}$). The ACE-loaded zeolite granules were soaked in H_2O_2 solution (i.e. 100 mgL^{-1}; 100 mL) for 30 minutes. After 30 minutes of regeneration by gaseous oxygen with drained bed, only 0.8% of ACE was removed which can be explained by the fact that the ACE on the zeolite surface was dissolved into the solution during the soaking process. Without dosing ozone, ACE was hardly decomposed by only H_2O_2.

4.2.5 Effect of H_2O_2 Concentration under Different Water Contents

As stated in *Stage I*, the limiting factor of the regeneration performance of gaseous O_3/H_2O_2 was the water contents of zeolite granules. In this section, the experiments were conducted under different water contents (i.e. 30%, 35% and 40% by weight) with varying H_2O_2 concentrations (i.e. $50 - 600\,mgL^{-1}$). When the water content was 35%, the enhancement of ACE degradation efficiency from 39% to 76% was obtained at a H_2O_2 concentration of 300 mgL^{-1} as shown in Figure 4.13. Further increases of H_2O_2 concentration did not cause better ACE degradation efficiency, a drop of ACE degradation efficiency to 50% was observed at 600 mgL^{-1} of H_2O_2. It is suggested that a high concentration of H_2O_2 might lead to an overdose effect, the additional H_2O_2 plays as a free radical quencher to consume the activated $OH\cdot$ by Equation 4.2 [Oturan and Aaron, 2014]. The trends of ozone concentrations in inlet and outlet gases for water content 35% can be found in Appendix Figure H.5.

$$\mathrm{H_2O_2} + OH\cdot \longrightarrow \mathrm{HO_2} + \mathrm{H_2O} \tag{4.2}$$

With regard to the performance of gaseous O_3/H_2O_2 with zeolite water contents of 40% and 30%, it was found that under water content of 40%, increasing the concentrations of H_2O_2 from 50 mgL^{-1} to 600 mgL^{-1} lead to a minor enhancement on the ACE degradation efficiency $(3 - 5\%)$. The reason could be that without the drying process, the water films surrounding the zeolite granules limited the diffusion of ozone to activate $OH\cdot$ for oxidizing the adsorbed ACE. When the water content was decreased to 30%, it can be seen that the improvement of ACE degradation efficiency by adding H_2O_2 was not significant. It is suggested that due to the lower water content (i.e. 30%), less H_2O_2 compounds can be retained within the zeolite granules. Besides, the ACE degradation rate without adding H_2O_2 with water content of 30% was already satisfying (around 75%), the room for further enhancement was limited. The results of ACE degradation rates and trends of ozone inlet and outlet concentrations for water content 30% and 40% can be found in Appendix Figure H.6 and Appendix Figure H.4.

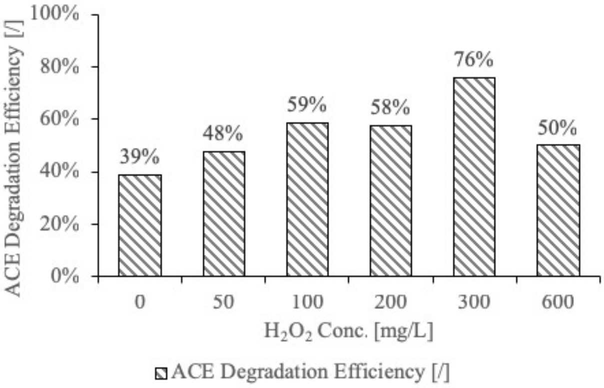


Figure 4.13: Stage II: ACE Degradation Efficiency with O_3/H_2O_2 under Water Content of 35% (ozone flow rate = 0.8 $L min^{-1}$ (10.2 $m\,min^{-1}$) ; ozone conc. = 90 mgL^{-1}; duration: 30 min).

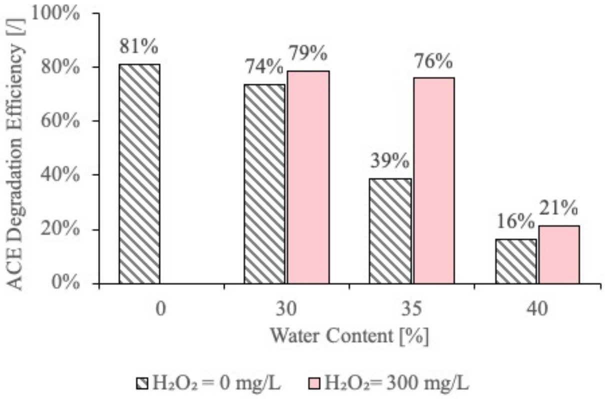


Figure 4.14: Stage II: Summary of ACE Degradation Efficiency with O_3/H_2O_2 under Different Water Content (ozone flow rate = 0.8 $L min^{-1}$ (10.2 $m\,min^{-1}$) ; ozone conc. = 90 mgL^{-1}; duration: 30 min).

A concentration of 300 mgL^{-1} H_2O_2 was selected to compare the ACE degradation efficiency between gaseous O_3/H_2O_2 process and gaseous

O_3 only process under different zeolite water contents. No H_2O_2 solution can be dosed when the water content was 0%. As present in Figure 4.14, the addition of H_2O_2 effectively enhanced the ACE degradation when the zeolite granules contained water, the most effective enhancement was observed at water content of 35%. However, dry zeolite without dosing H_2O_2 still achieved the best ACE degradation rate. In this case, it can concluded that reducing the zeolite water content is the most effective method to improve the ACE degradation rate by gaseous O_3. With decreasing the water content from 40% to 35%, 79% of ACE degradation rate was achieved by adding H_2O_2 with 300 mgL^{-1}.

4.3 RESULTS OF STAGE III

According to the current studies, two main factors are suggested that affect the long-term adsorption performance of zeolite granules. The two factors are the change of zeolite surface characteristic by ozone and the intermediates accumulation in the zeolite pores.

4.3.1 Long-term Effect of Gaseous O_3 on Fresh Zeolite Granules

A pre-experiment was conducted by using methylene blue as the color change of solution can be measured easily. The pre-experiment was applied to compare the adsorption performance between fresh zeolite and fresh zeolite treated by ozone as shown in Appendix I. It was found that ozone treated zeolite had less adsorption capacity for methylene blue. However, different organic compounds have various characteristics on adsorption, the detailed mechanisms are not involved in this research. Nevertheless, based on the pre-experiment, it is interested to investigate the effect of ozone on zeolite itself.

The effect of gaseous ozone on the fresh zeolite granules were investigated for three cycles of operation. Each cycle the fresh zeolites were treated by ozone (0.8 $Lmin^{-1}$; 63.7 $cmmin^{-1}$; 90 mgL^{-1}) for 30 minutes. After that, to obtain the recovered adsorption capacity, the adsorption equilibrium tests were conducted with 0.5 g of samples in ACE solution (200 mgL^{-1}; 1 L) for 7 days. The results of using 0.7 g samples are presented in Figure H.8.

The results of tested ACE adsorption equilibrium capacity (q_e) are shown in Figure 4.15. It can be seen that the gaseous ozone process had minor abatement on the ACE adsorption capacity. Therefore, it is suggested that the ozonation process might have minor effect on the pore size and surface characteristic of zeolite for ACE adsorption due to the stable chemical composition of zeolite.

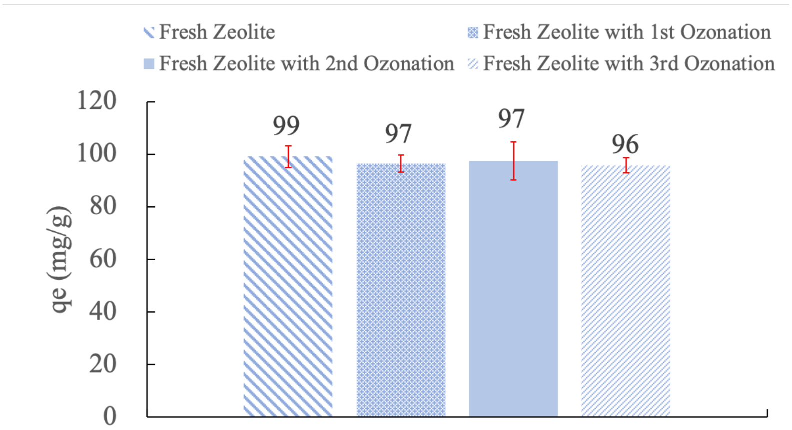


Figure 4.15: Stage III: Long-term Effect of Gaseous O_3 on Fresh Zeolite Granules - Adsorption Capacity Test ((Zeolite = $0.5\,g$; ACE solution = $1\,L$; ACE conc. = $200\,mgL^{-1}$).

4.3.2 Long-term Regeneration by Gaseous O_3 with Dried Bed Zeolite Granules

The long-term regeneration by gaseous O_3 with dried bed was tested for three cycles as shown in Figure 4.16. The column loading adsorption performance after each cycle regeneration was present in Figure H.7. Each cycle of regeneration, the zeolite granules packed column was treated by ozone ($0.8\,Lmin^{-1}$; $63.7\,cmmin^{-1}$; $90\,mgL^{-1}$) for 7.5 hours until the ozone concentrations difference in inlet and outlet gases was less than $5\,mgL^{-1}$. $0.5\,g$ of samples were taken for the ACE adsorption equilibrium tests (ACE solution: $200\,mgL^{-1}$; $1\,L$). The results of using $0.7\,g$ samples are presented in Figure H.9.

In this experiment, because of the limited fresh zeolite granules, the zeolite granules utilized for the long-term test were the mixture of the used zeolite granules from previous experiments and then regenerated by O_3 with dried bed for 7.5 hours. Compared to the q_e result of fresh zeolites of $99.05\,mgg^{-1}$, around 25% of adsorption capacity was lost due to the incomplete regeneration. The q_e of the zeolites applied for the long-term tests was $74.25\,mgg^{-1}$. According to the extraction tests, $18.93\,mgg^{-1}$ was extracted from the regenerated zeolite granules, which also agreed with the adsorption tests results that the lost of adsorption capacity was caused by the incomplete decomposition of ACE. It is suggested that the ACE adsorbed in the inner part of zeolite granules was hardly to be oxidized by ozone due to the long

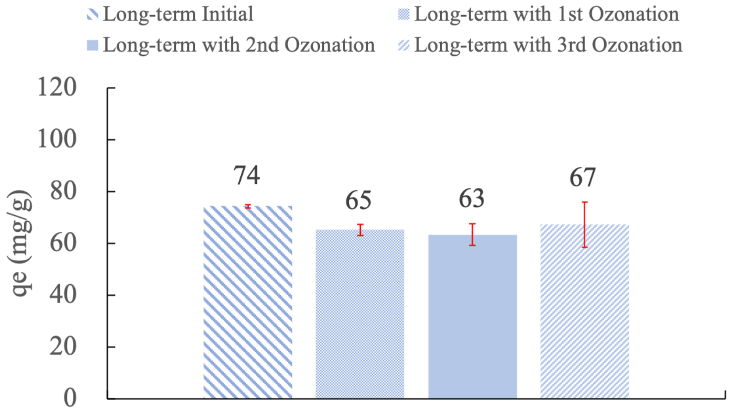


Figure 4.16: Stage III: Recovered Adsorption Capacity by Long-term Gaseous O_3 Regeneration with Dried Bed Zeolite Granules (Zeolite = 0.5 g; ACE solution = 1 L; ACE conc. = 200 mgL^{-1}; ozone flow rate = 0.8 $Lmin^{-1}$ (63.7 $cmmin^{-1}$); ozone conc. = 90 mgL^{-1}; duration: 7.5 hour).

diffusion distance. Therefore, although the ozone concentrations in inlet and outlet gases achieved the same level at the end of the regeneration process, the adsorbed ACE was hardly completely degraded.

As can be seen in Figure 4.16, the restored ACE adsorption capacity decreased 10.4% after three cycles of regeneration for the test with dosing 0.5 g of regenerated zeolite granules. It is suggested that only the presence of water insoluble intermediates had a negative impact on the adsorption capacity recovery of zeolite granules. As the regenerated zeolite granules were soaked overnight and back washed before next round of ACE loading, it was found that most of the intermediates generated from the regeneration process were dissolved into the soaking water and backwash water.

In Figure 4.17, after 20 hours of soaking, the generated intermediates with lower K_{ow} value were dissolved into water. It is suggested that the generated reaction by-products which have lower K_{ow} such as oxalic acid and glyoxylic acid are able to dissolve into water easily, thus the adsorption capacity would not be affected. However, some intermediates that have less water solubility would stay in the zeolite pores, hence the adsorption capacity would have a minor decrease (i.e. around 7.5 mgg^{-1}. Besides, according to the results of the effect of backwash shown in Appendix D, it can also found that the intermediates concentration decreased by increasing the times of backwash process. The final intermediates of the gaseous O_3 process were suggested to be carboxylic acid which has high water solubility. Thus by applying the backwash process before adsorption, it is suggested that the generated carboxylic acid would dissolve into the backwash water. In this case, the overall impact by the intermediates accumulation could have minor impact on the long-term operation.

Apart from that, it was observed that due to the backwash process and the long-term operation, part of the zeolite granules were broken into smaller size granules or powder. It might lead to higher adsorption kinetics, but due to the smaller granule size, the mounted glass filter that held the zeolites was easily blocked which increased the operation difficulty.

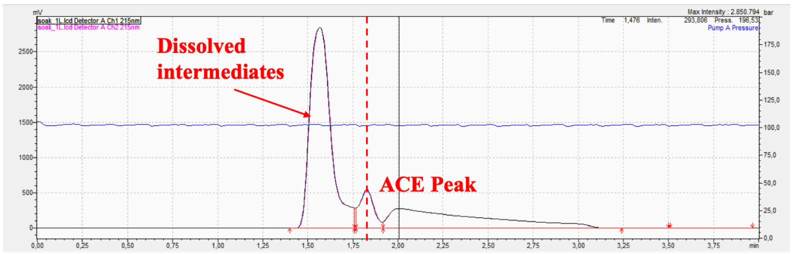


Figure 4.17: Stage III: HPLC Measured Peaks for the Soaking Water of Regenerated Zeolite Granules (Soaking water: 1 L; Duration: 20 hours.

5 RESEARCH LIMITATIONS AND SUGGESTIONS

Based on the conducted experiments, several limitations of this research are stated below. Besides, the corresponding suggestions are given to improve the current methodology and future research.

5.1 SELECTION OF MODEL OMPS

In this research, ACE was selected as the model OMPs for the whole experiment. ACE is considered as a easy degradable organic compounds, which can be degraded by ozone directly. Therefore, the performance enhancement by adding H_2O_2 was not significant, and ideal regeneration performance was achieved for ACE-loaded zeolite column. However, there are some OMPs that are resistant to ozone that can only be degraded by $OH\cdot$ effectively as mentioned in Section 2.5 (e.g. Atrazine). In this case, the suggested regeneration process by applying the gaseous O_3 only with dried bed might not have an ideal regeneration performance for the zeolite column loaded with persistent OMPs. Hence, the gaseous O_3/H_2O_2 process is worthwhile to be investigated for a wider range of OMPs removal.

Moreover, in this research, only one compound was studied, the combination effect of different OMPs during the regeneration process is not clear. In this case, understanding the regeneration mechanisms for different OMPs in one column would be a challenge for the further investigation.

5.2 ADSORPTION

In this research, a high concentration of ACE (i.e. $200\,mgL^{-1}$) was applied for the feed solution to load the zeolite granules column. Hence, the adsorption breakthrough point occurred at the start of the process, and the precise adsorption capacity difference between each process was hardly distinguished from the column adsorption breakthrough curve. However, the actual ACE concentration or other OMPs in wastewater are in the range of $ng - \mu gL^{-1}$, the breakthrough point will occur later with a more clear difference between each regeneration process. Therefore, applying real wastewater for the adsorption experiment is meaningful for the future research.

Additionally, as can be seen from the batch experiment for the ACE loading, it required more than 7 days to achieve the adsorption equilibrium. The expected time for the column to achieve fully loaded would be around 1 to 2 months. However, due to the time limitation, a duration of 120 hours was applied for the column adsorption process. It was assumed that the column reached equilibrium, and the adsorption duration was the same each time to reduce the errors by adsorption process. Regarding the future research, it is suggested to take the samples after adsorption process each time and conduct an adsorption equilibrium test to understand the remained adsorption capacity of the zeolite granules.

5.3 REGENERATION

Stage I:

In the first stage, as the optimum method to regenerate the column was still in the investigation progress, the column cannot be fully regenerated by the regeneration process. For instance, only 17% of ACE can be degraded by using the gaseous O_3 in drained bed process. In this case, due to the insufficient fresh zeolite granules, the used zeolite granules without fully regeneration were applied again for the next round experiment. In this case, after the 120-hour of adsorption, it was assumed that the initial status of ACE-loaded zeolite granules for each regeneration process was the same.

Stage II:

In the second stage, with respect to the experiments that investigated the effect of H_2O_2 concentration on the regeneration performance, the exact amount of H_2O_2 that remained in the zeolite granules was hardly defined. Hence, it can only be discussed based on the controlled soaking process in this research. In the future research, it is recommended to investigate a method that can define the amount of H_2O_2 retained in the zeolite granules and hence can calculate the precise H_2O_2 consumption during the reaction.

In this stage, mainly the operation conditions for the ACE degradation rate were examined, more experiments need to be designed to understand the detailed mechanisms of the degradation. For instance, p-chlorobenzoic acid (pCBA) (a $OH\cdot$ scavenger) can be used to understand the exposure ratio of $OH\cdot$ and ozone to the overall reaction [Acero and Von Gunten, 2001]. However, due to the research scope limitation, the method of utilizing pCBA to the process should be investigated in future research.

Stage III:

In the third stage, as the mechanisms of the gaseous O_3/H_2O_2 process were not clear at this stage, only the gaseous O_3 process was conducted for the long-term regeneration tests. Besides, due to time limitation of the project, only three cycles of operation were conducted. It is suggested to conduct a long-term regeneration with around ten cycles in future research.

In addition, the surface characteristic change of zeolite granules after gaseous O_3 process was defined by the equilibrium adsorption batch experiments. Due to the research scope limitation and the budget limitation, the porosity test for the zeolite granules was not conducted. In future research, it is suggested to conduct porosity tests and scanning electron microscope (SEM) tests to have more in-depth understanding of the effect of ozone on the surface characteristic of zeolite granules.

5.4 EXTRACTION

In this research, the extraction was conducted with $0.2\,g$ sample in $100\,mL$ of pure methanol. Although methanol has the highest solubility for ACE (i.e. 297.81 g ACE/kg Methanol) so that the adsorbed ACE amount is far below the saturation point, the ACE dissolving equilibrium can still have a small difference for the zeolite granules with different amounts of adsorbed ACE. Therefore, in this research, it was assumed that the percentage of first extraction was the same for all the zeolite granules.

5.5 INTERMEDIATES ANALYSIS

In this research, due to the research scope limitation, the concentrations of the generated intermediates were not investigated. The ACE mineralization rates by using different regeneration processes cannot be compared. In the future research, using liquid chromatography–mass spectrometry (LC-MS) is suggested to test the generated intermediates by different processes. Hence, the ACE mineralization pathway by different ozone based regeneration processes can be obtained.

5.6 SUGGESTIONS FOR PRACTICAL APPLICATIONS

According to the results stated in Chapter 4, there are two possible strategies for potential practical application: 1) gaseous O_3 process with dried bed; 2) gaseous O_3/H_2O_2 process with 35% of water content.

Gaseous O_3 Process with Dried Bed:

Although satisfying regeneration performance can be obtained by applying gaseous O_3 process with dry bed, drying the ACE-loaded zeolite would be an energy consuming process. In this case, an energy saving method is proposed to reduced the energy consumed for the drying process. During the regeneration process, amount of heat was released due to the oxidation reaction. The air within the column was heated up to 60°C. Therefore, the released heat can be utilized to dry another column for the next round regeneration.

To understand the amount of energy that can be saved, an approximate calculation was conducted as shown in Table 5.1 with several assumptions.

It is assumed that: 1) the temperature of the heated air that can be used is 50°C (assuming 10°C lost during the transportation of hot air); 2) 50% of the heat energy (energy utilization efficiency) can be utilized for the drying process of the next column; 3) the hot air flow rate for the drying process is the same of the ozone in-gas flow rate (i.e. $0.8\,Lmin^{-1}$).

As calculated in Table 5.1, $40.038\,g$ of water is needed to be removed by the drying process, which requires $13.389\,kJ$ of energy. By reusing the released heat, around 33.1% of column can be dried. In this case, for a column with $100\,g$ of zeolite granules, $8.959\,kJ$ of energy can be saved. In practical, for a column with $1000\,kg$ of zeolite granules, $37\,kWh$ of energy can be saved.

Gaseous O_3/H_2O_2 Process with 35% of Water Content:

With applying the gaseous O_3/H_2O_2 process with 35% of water content, only 5% of water needs to be removed when the water content of zeolite granules drained bed is 40%. Compared to the process with

Table 5.1: Approximate Calculation for Saved Energy by Gaseous O_3 Process with Dried Bed

Parameter	Value	Unit
Zeolite weight	100	g
Heat capacity of water	4.180	kJ/kg K
Heat capacity of air	1.005	kJ/kg K
Air density	1.225	g/L
Room temperature	20	°C
Hot air temperature from reaction	50	°C
Initial water content	40	%
Dried water content	0	%
Adsorbed ACE amount	95	mg
Dried water amount	40.038	g
Required energy for drying process	13.389	kJ
Assumed energy efficiency of using hot air	50	%
Required air amount	888.140	g
Air flow rate	0.8	L/min
Required time for drying process	22.666	hour
Regeneration duration of one column	7.500	hour
Percentage of dried column	33.089	%
Saved energy	8.959	kJ

dry bed, only 12.5% of the energy for complete drying is required. However, the cost is added from dosing H_2O_2 to the process. Besides, the mechanisms of gaseous O_3/H_2O_2 process are not fully understood at present, more detailed studies on the operation conditions need to be conducted.

6 OVERALL DISCUSSIONS AND CONCLUSIONS

6.1 OVERALL DISCUSSION FOR RESULTS OF STAGE I–III

According to the conducted experiments, the listed research questions can be answered below:

1) **How to define the regeneration performance of zeolite granules?**
In this research, there were two methods applied to define the regeneration performance, including extraction and adsorption equilibrium test. By conducting the extraction tests, around 80% of the organic compounds in the zeolite was able to be dissolved into methanol by the first extraction. The ACE degradation rate of the reaction was calculated based on the extracted ACE concentration from zeolite granules. Besides, through the extraction, the generation of intermediates could be approximately understood based on the ACE degradation pathway and the K_{ow} value. By conducting the adsorption equilibrium test, the q_e was be obtained to understand the restored adsorption capacity of the zeolite granules.

2) **How effective is the gaseous O_3 only process and the gaseous O_3/H_2O_2 process on ACE-loaded zeolite granules regeneration respectively?**
It was found that with applying the gaseous O_3 process, an ideal performance was obtained in dried bed with around $80 - 100\%$ of ACE degradation rate. However, when drained bed was used, the ACE degradation rates of both the gaseous O_3 process and the gaseous O_3/H_2O_2 process were below 35%. The presence of water films between zeolite granules was the main limiting factor to improve the ACE rate.

3) **What are the effects of different operation conditions on ACE-loaded zeolite granules regeneration processes?**
It was found that the water content of zeolite granules had the most significant effect on the regeneration performance, higher ACE degradation rates were obtained for the zeolite with lower water contents.

Aside from that, the concentrations and the flow rates of ozone had less influence on the ACE degradation rates with the same ozone inflow dosage. In this case, the regeneration duration was the dominant factor to determine the performance of ACE degradation. With respect of the effect of the H_2O_2 concentration, a initial concentration of 300 mgL^{-1} was found that achieved the optimum ACE degradation rate. An overdose effect was observed under a high concentration of H_2O_2 (i.e. 600 mgL^{-1}). By dosing H_2O_2 to the ozonation process, the ACE degradation rate was enhanced for the zeolite granules with the same water content.

4) **What is the feasibility of long-term regeneration for ACE-loaded zeolite granules by gaseous O_3?**
Regarding the long-term regeneration test, 3 cycles of operation were conducted. It was found that both ozone and intermediates accumulation had minor influences (i.e. 2.8%-14.7%) on the adsorption capacity. The incomplete decomposition for the adsorbed ACE in the inner part of the zeolites was the major reason that affect the adsorption capacity of the used zeolite granules. Apart from that, part of the zeolite granules were broken into smaller sizes, which increased the possibility of the blockage of the mounted glass plate. In this case, although the adsorption capacity was hardly recovered completely, with appropriate operation to reduce the breaking of the zeolite granules, it is still feasible to have long-term operation for ACE-loaded zeolite granules regenerated by the gaseous O_3 process in dried bed.

6.2 CONCLUSIONS

In this research, the regeneration performance of the ACE-loaded zeolite granules by applying the gaseous O_3 based process was investigated. The long-term regeneration by the gaseous O_3 process in dried bed was tested. The conclusions drawn from this study are listed below:

1) Extraction by methanol is a feasible method to define the ACE degradation rate and the intermediates generation from the regeneration process. 80% of the organic compounds can be extracted into the methanol solution.

2) Compared to the regeneration performance in drained bed of zeolite granules, the dried bed one achieved ideal regeneration performance with around $80-100\%$ of ACE degradation rate. The ACE degradation rates for both the gaseous O_3 process and the gaseous O_3/H_2O_2 process in drained bed were below 35%.

3) The water content of zeolite granules was the main factor that affected the regeneration performance. The water films between granules limited the diffusion of ozone to react with the adsorbed ACE. Higher ACE degradation rates were obtained with lower water contents of zeolite granules. 81% of ACE degradation rate was obtained with 0% of water content.

4) Adding H_2O_2 is able to enhance the ACE degradation rate for the zeolites with the same water content. The optimum condition was found at $300\, mgL^{-1}$ of H_2O_2 and 35% of water content, and 79% of ACE degradation rate was achieved with this condition.

5) It is feasible to have long-term regeneration for ACE-loaded zeolite granules by the gaseous O_3 process in dried bed. The effects of ozone on the zeolite surface characteristics and the intermediates accumulation had minor influences on restoring adsorption capacity of zeolite granules. The incomplete decomposition of ACE which was adsorbed in the inner part of the granules caused a lost of 25% of adsorption capacity compared to that of the fresh zeolite granules.

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A APPENDIX: MINERALIZATION PATHWAY OF ACETAMINOPHEN

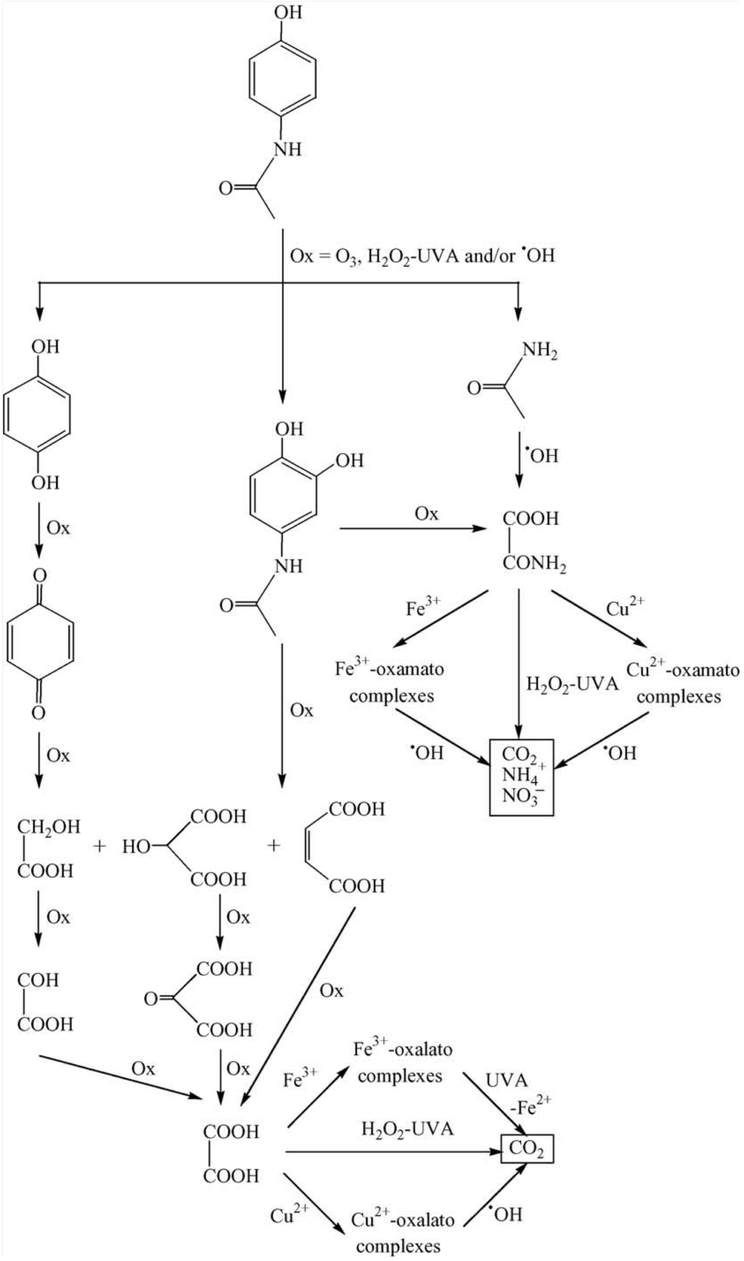
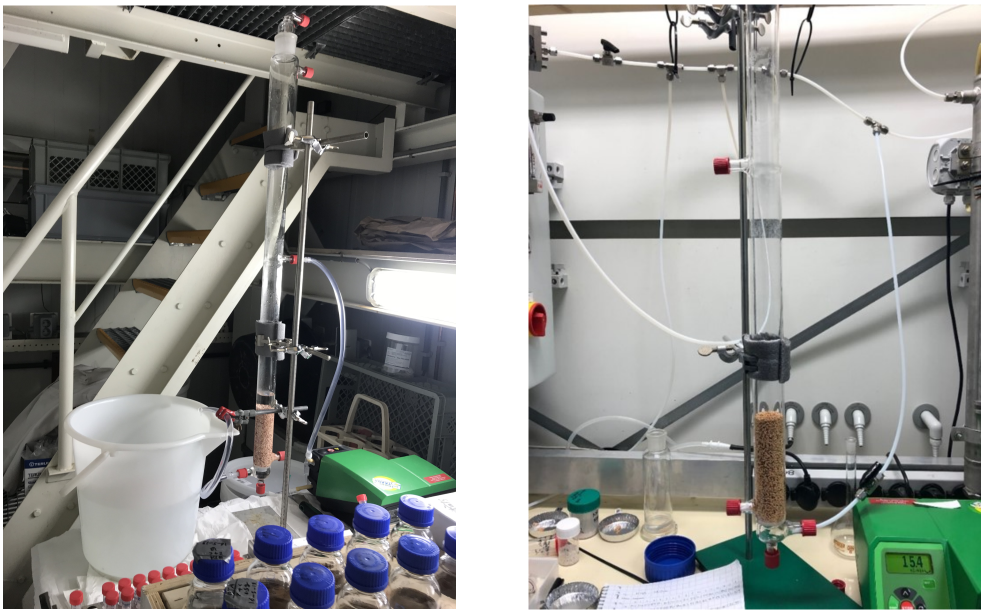


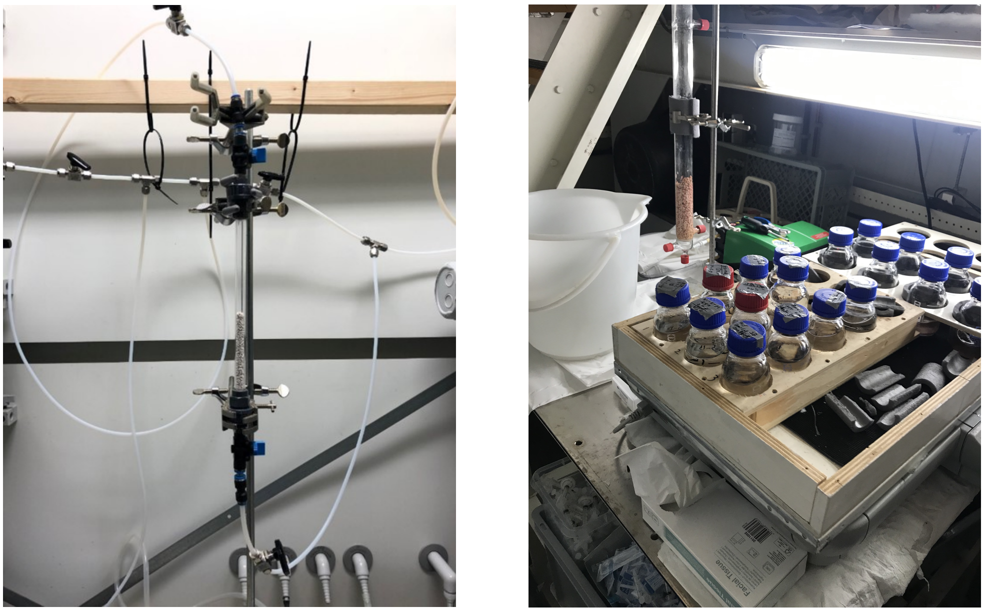
Figure A.1: Suggested Mineralization Pathways of Acetaminophen by Single Ozonation and Catalyzed Ozonation [Centellas et al., 2006]

B APPENDIX: EXPERIMENT SETUP IN LABORATORY



(a) Experiment Setup for Column Adsorption

(b) Experiment Setup for Regeneration in *Column I*



(c) Experiment Setup for Regeneration in *Column II*

(d) Experiment Setup for Extraction Shaker

Figure B.1: Experiment Setup in Laboratory

C APPENDIX: DETAILED EXPERIMENTAL CONDITIONS FOR STAGE I-II

Table C.1: Detailed Experimental Conditions for Stage I

Stage I Experiment Summary				
Experiment Set	O3		Zeolites	H2O2 (mg/L)
	Flowrate (L/min)	Conc. (mg/L)		
1	0.2	90	Drained	/
2	0.8	90	Drained	/
3	0.8	90	Dried	/
4	0.8	90	Drained	100

Table C.2: Detailed Experimental Conditions for Stage II

Stage II Experiment Summary				
Experiment Set	Tested Condition	Value	Unit	Controlled Parameters
1	Blank (fresh zeolites)			Ozone: (90mg/L; 0.8L/min; 30min); H2O2: (0mg/L); Water Content (0%).
2	Water Content	0	%	Ozone: (90mg/L; 0.8L/min; 30min); H2O2: (0mg/L).
		40	%	
		35	%	
		30	%	
		21	%	
3	Ozone Flowrate	0.8	L/min	Ozone: (90mg/L; 900mg inflow dosage); H2O2: (0mg/L); Water content (0%).
		0.6	L/min	
		0.4	L/min	
		0.2	L/min	
4	H2O2 Conc.	50	mg/L	Ozone: (90mg/L; 0.8L/min; 30min); Water Content (40%).
		100	mg/L	
		200	mg/L	
		300	mg/L	
		600	mg/L	
5	Ozone Conc.	50	mg/L	Ozone: (0.2L/min; 900mg inflow dosage); H2O2: (0mg/L); Water Content (0%).
		90	mg/L	
		120	mg/L	
		150	mg/L	
6	Effect of H2O2 only, without ozone dosage			Oxygen (0.8L/min; 30min); H2O2: (100mg/L); Water Content (40%).
7	H2O2 Conc.	50	mg/L	Ozone: (90mg/L; 0.8L/min; 30min); Water Content (35%).
		100	mg/L	
		200	mg/L	
		300	mg/L	
		600	mg/L	
8	H2O2 Conc.	50	mg/L	Ozone: (90mg/L; 0.8L/min; 30min); Water Content (25%).
		100	mg/L	
		200	mg/L	
		300	mg/L	
		600	mg/L	

D APPENDIX: EFFECT OF BACKWASH TO EXPERIMENTS

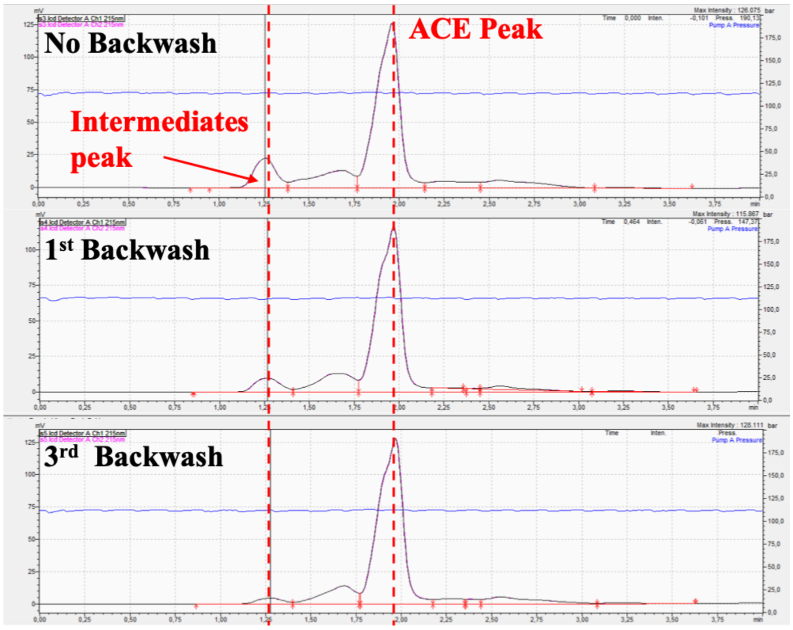


Figure D.1: The Measured HPLC Peaks for the Effect of Backwash after regeneration

E APPENDIX: RESULTS OF EXTRACTION TESTS

Due to the long duration for zeolite granules to reach adsorption equilibrium (more than 5 weeks), the samples used for the pre-experiment of extraction tests were prepared by ir. Mingyan Fu (phD student, TU Delft). Based on the ACE adsorption equilibrium tests conducted by ir. Mingyan Fu, the suggested q_e for the samples was $90\,mgg^{-1}$.

E.1 SOLVENT SELECTION

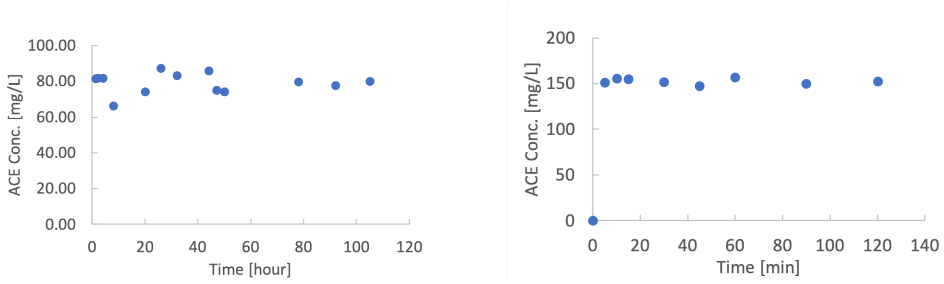
Three types of organic solvent were used to obtain the optimum extraction results, including methanol, ethanol and acetonitrile. As shown in Table E.1, methanol achieved the highest first extraction percentage of 81%.

Table E.1: Summary of Extraction Results by Different Solvents

Solvent	Methanol	Acetonitrile	Ethanol
Volume [L]	0.1		
Sample Weight [g]	0.1281	0.1231	0.2021
Theoretical Conc. [mg/L]	105.77	101.64	166.87
Extracted Conc. [mg/L]	85.85	76.41	128.78
Standard Deviation [mg/L]	5.68	2.89	8.83
First Extraction Percentage [/]	81%	75%	77%

E.2 EXTRACTION DURATION

According to the results shown in Figure E.1, the ACE concentrations reached equilibrium after 5 minutes. To ensure the equilibrium is reached in the experiment, the duration of extraction process is 30 minutes.



(a) (b)

Figure E.1: Extracted ACE Concentration against Time by Methanol: (a) Duration of 120 hours; sample weight = 0.1281 g; Methanol: 0.1 L; (b) Duration of 2 hours; sample weight = 0.2061 g; Methanol: 0.1 L.

E.3 SECOND EXTRACTION

It was found that 80% of ACE was extracted by the first extraction, a second extraction was conducted to ensure the ACE can be completely extracted. The solution of first extraction was filtered, the filtered powder was rinsed by deionized water and put into 0.1 L of methanol again for second extraction. As shown in fig:second extraction, the adsorbed ACE can be completely extracted by the twice extraction in methanol.

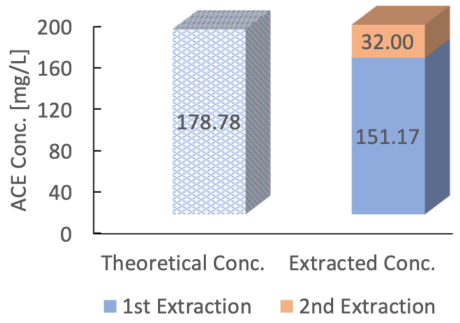


Figure E.2: Second ACE Extraction Test by Methanol: Sample weight = 0.2061 g; Methanol: 0.1 L.

F APPENDIX: HPLC CALIBRATION CURVES FOR ACETAMINOPHEN

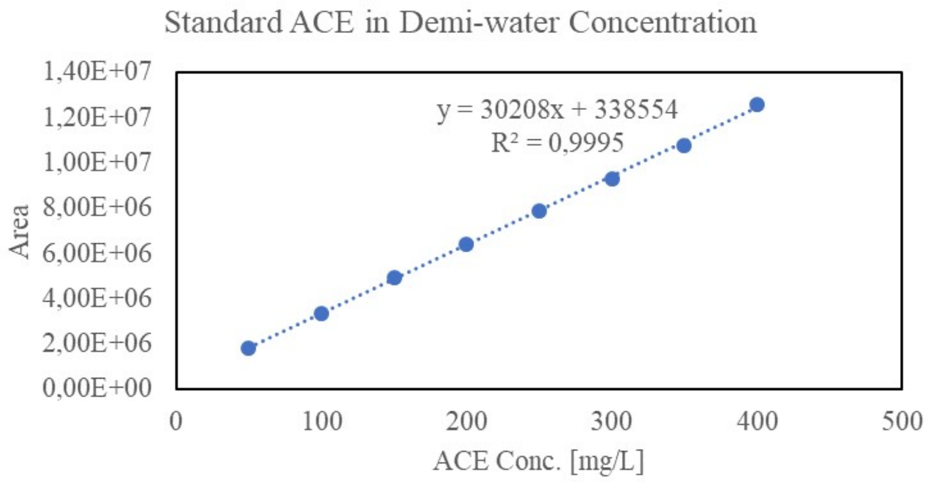


Figure F.1: HPLC Calibration Curves for Acetaminophen in Demi-water

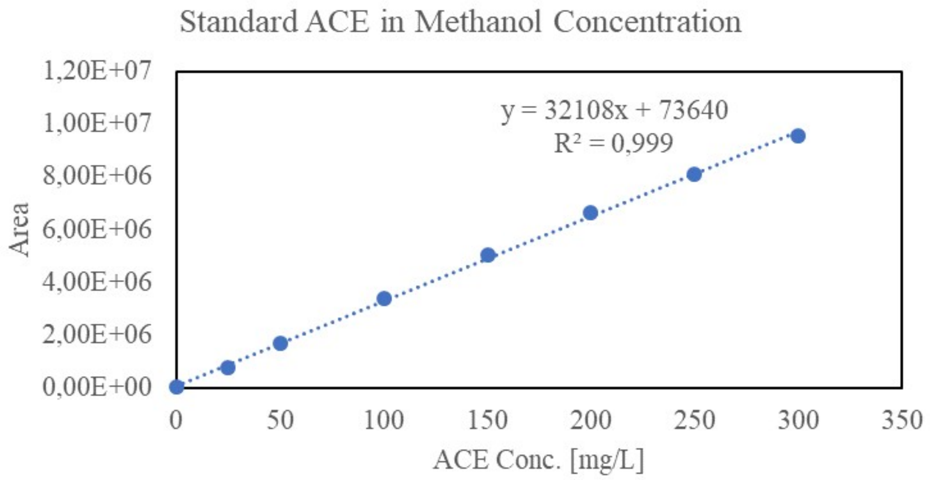
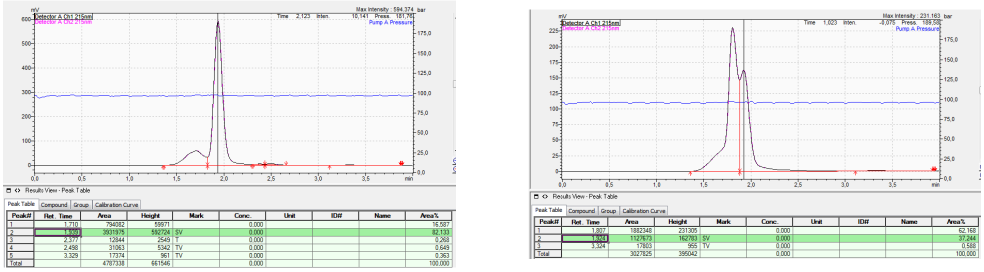


Figure F.2: HPLC Calibration Curves for Acetaminophen in Methanol

G APPENDIX: MEASURED HPLC FIGURES

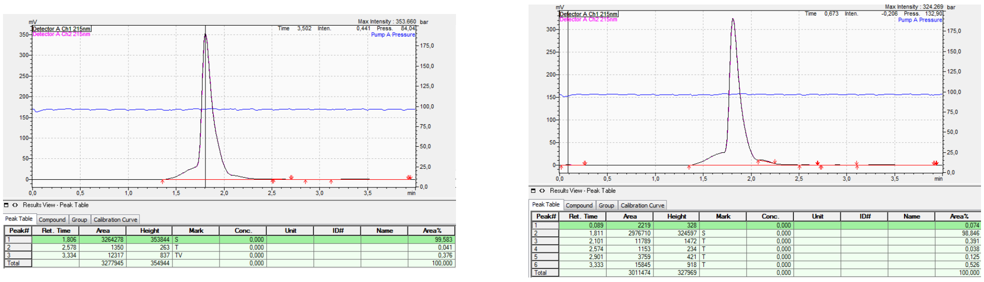


Peak#	Ret. Time	Area	Height	Mark	Conc.	Unit	ID#	Name	Area%
1	1,710	794082	59971		0,000				16,587
2	1,939	3931975	592724	SV	0,000				82,133
3	2,377	12844	2549	T	0,000				0,268
4	2,498	31063	5342	TV	0,000				0,649
5	3,329	17374	961	TV	0,000				0,363
Total		4787338	661546		0,000				100,000

(a) HPLC Figure of 3-hour Reaction

Peak#	Ret. Time	Area	Height	Mark	Conc.	Unit	ID#	Name	Area%
1	1,807	1882348	231305		0,000				62,168
2	1,924	1127673	162783	SV	0,000				37,244
3	3,324	17803	955	TV	0,000				0,588
Total		3027825	395042		0,000				100,000

(b) HPLC Figure of 4-hour Reaction



Peak#	Ret. Time	Area	Height	Mark	Conc.	Unit	ID#	Name	Area%
1	1,806	3264278	353844	S	0,000				99,583
2	2,578	1350	263	T	0,000				0,041
3	3,334	12317	837	TV	0,000				0,376
Total		3277945	354944		0,000				100,000

(c) HPLC Figure of 5-hour Reaction

Peak#	Ret. Time	Area	Height	Mark	Conc.	Unit	ID#	Name	Area%
1	0,089	2219	328		0,000				0,074
2	1,811	2976710	324597	S	0,000				98,846
3	2,101	11789	1472	T	0,000				0,391
4	2,574	1153	234	T	0,000				0,038
5	2,901	3759	421	T	0,000				0,125
6	3,333	15845	918	T	0,000				0,526
Total		3011474	327969		0,000				100,000

(d) HPLC Figure of 7.5-hour Reaction

Figure G.1: Measured HPLC Peak Figures for Stage I: Regeneration by Gaseous O_3 with Dried Bed. (O_3 flow rate = $0.8\,Lmin^{-1}$; O_3 conc. = $90\,mgL^{-1}$; zeolite water content = 0%).

H APPENDIX: ADDITIONAL EXPERIMENT RESULTS

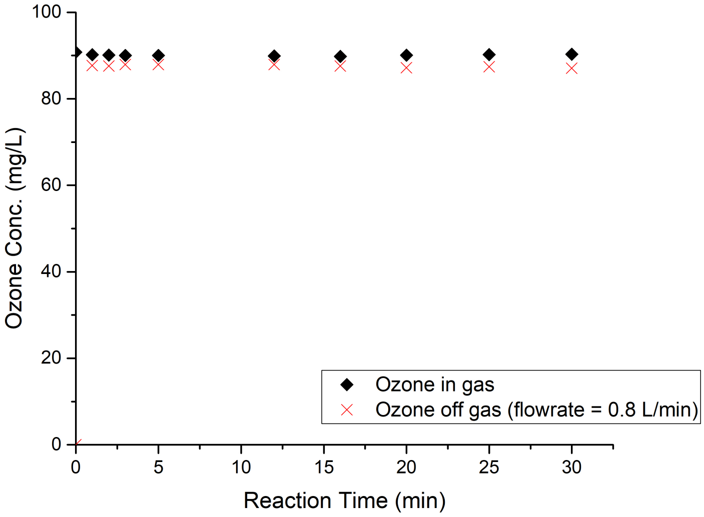


Figure H.1: The Concentrations of O_3 in Inlet and Outlet Gas in Fresh Column II (ozone conc. = 90 mgL^{-1}; ozone flow rate = 0.8 $Lmin^{-1}$ zeolite water content = 0%)

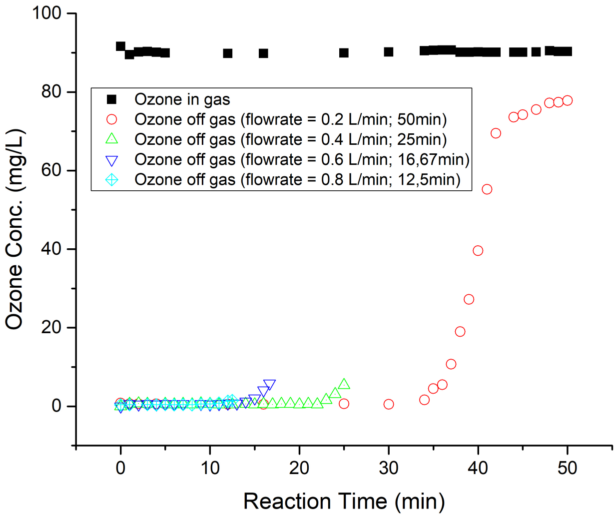


Figure H.2: The Concentrations of O_3 in Inlet and Outlet Gas with Different Ozone Flow Rate by applying the Gaseous O_3 only Process (ozone inflow dosage = $900\,mg$; ozone conc. = $90\,mgL^{-1}$; duration: $50\,min$ of $0.2\,L/min$; $25\,min$ of $0.4\,L/min$; $16.67\,min$ of $0.6\,L/min$; $12.5\,min$ of $0.8\,L/min$).

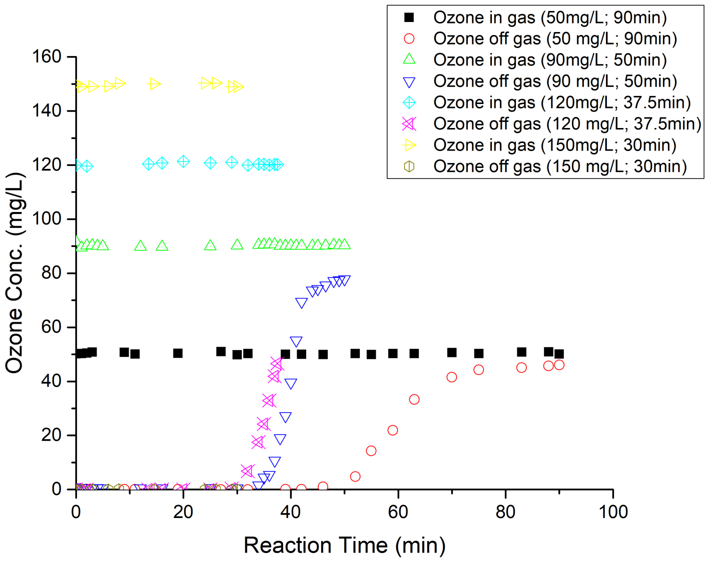
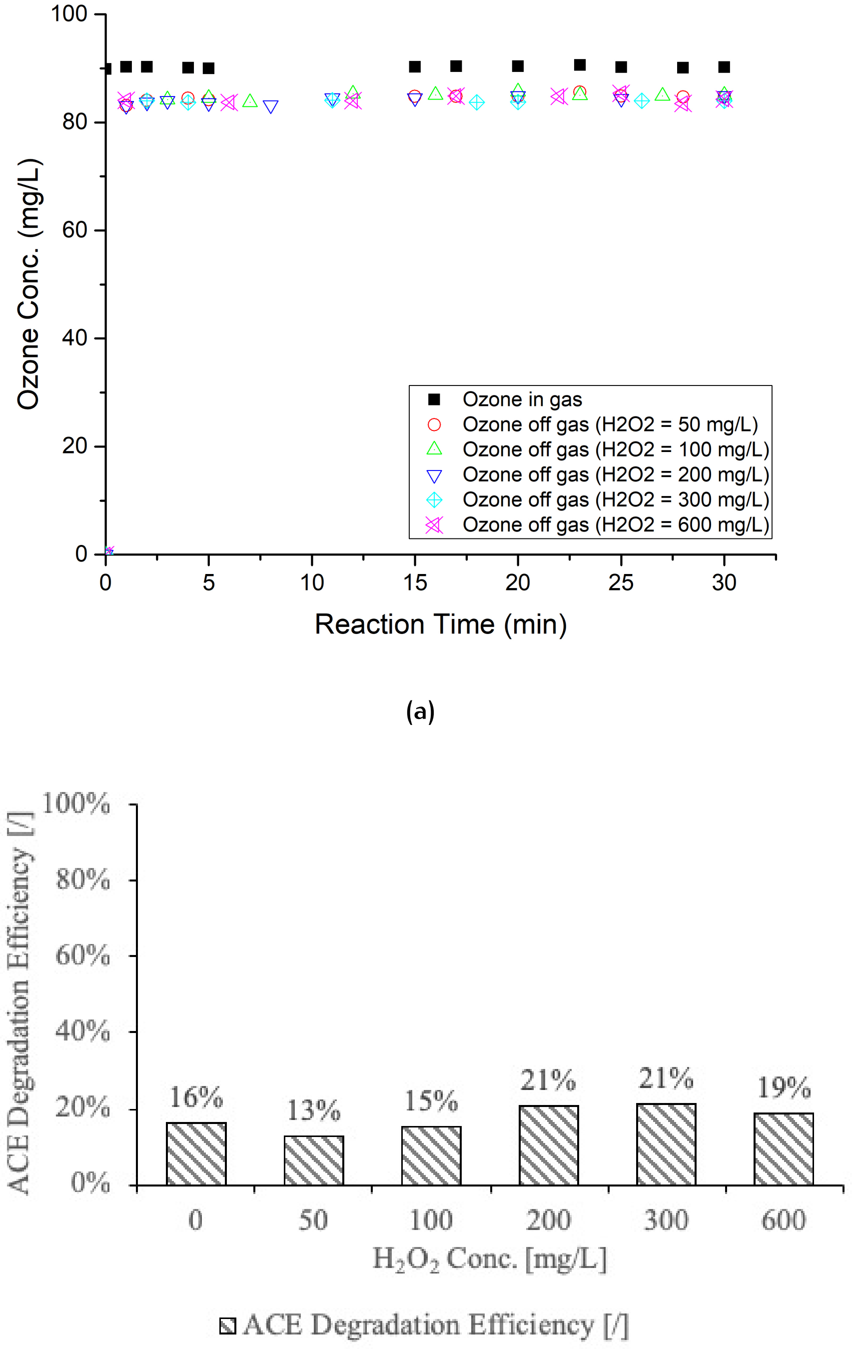


Figure H.3: The Concentrations of O_3 in Inlet and Outlet Gas with Different Ozone Concentrations by applying the Gaseous O_3 only Process (ozone inflow dosage = $900\,mg$; ozone flow rate = $0.2\,Lmin^{-1}$; duration: $90\,min$ of $50\,mgL^{-1}$; $50\,min$ of $90\,mgL^{-1}$; $37.5\,min$ of $120\,mgL^{-1}$; $30\,min$ of $150\,mgL^{-1}$; water content = 0%).



(a)

(b)

Figure H.4: Stage II: ACE Removal Efficiency with O_3/H_2O_2 under Water Content of 40% (ozone flow rate = 0.8 $Lmin^{-1}$; ozone conc. = 90 mgL^{-1}; duration: 30 min). (a) The Concentrations of O_3 in Inlet and Outlet Gas. (b) ACE Removal Efficiency with O_3/H_2O_2 under Water Content of 40%.

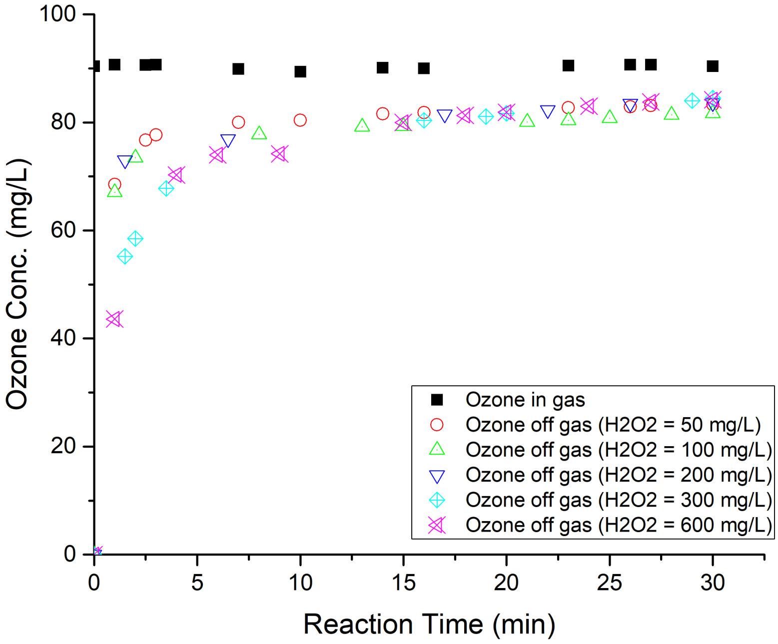
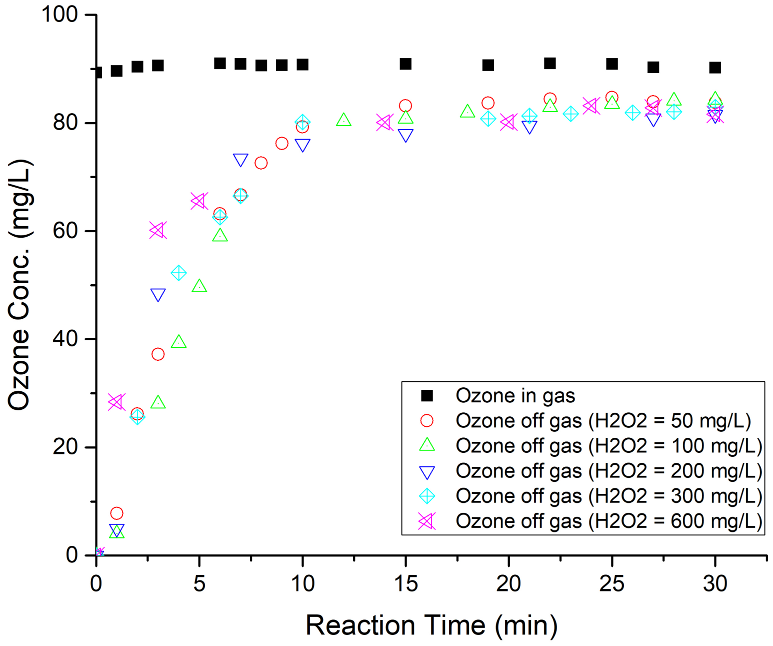
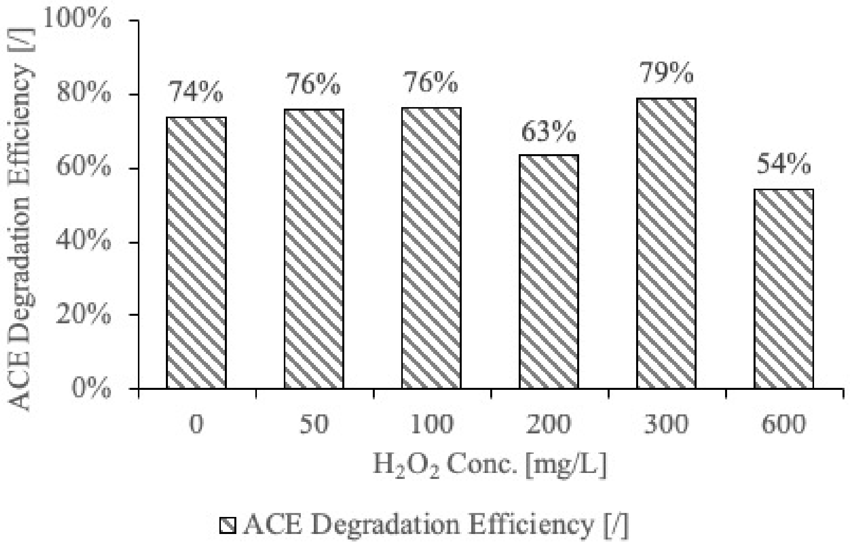


Figure H.5: The Concentrations of O_3 in Inlet and Outlet Gas in Fresh Column II (ozone flow rate = $0.8\,Lmin^{-1}$; ozone conc. = $90\,mgL^{-1}$; duration: $30\,min$)



(a)



(b)

Figure H.6: Stage II: ACE Removal Efficiency with O_3/H_2O_2 under Water Content of 30% (ozone flow rate = $0.8\,Lmin^{-1}$; ozone conc. = $90\,mgL^{-1}$; duration: $30\,min$). (a) The Concentrations of O_3 in Inlet and Outlet Gas. (b) ACE Removal Efficiency with O_3/H_2O_2 under Water Content of 30%.

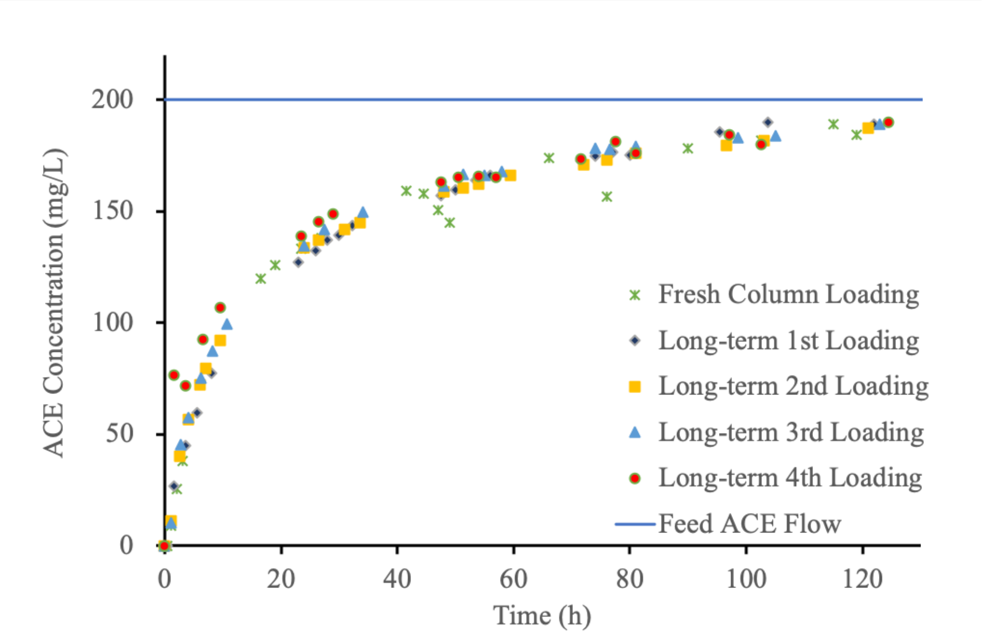


Figure H.7: Stage III: Column Adsorption Performance after Regeneration Processes (ACE conc. = 200 mgL^{-1})

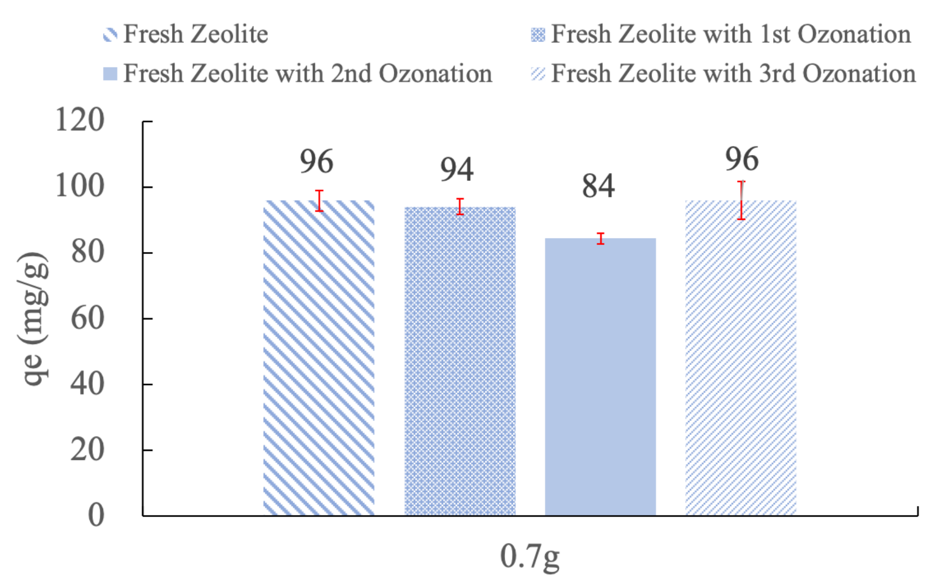


Figure H.8: Stage III: Long-term Effect of Gaseous O_3 on Fresh Zeolite Granules (Zeolite = 0.7 g; ACE solution = 1 L; ACE conc. = 200 mgL^{-1})

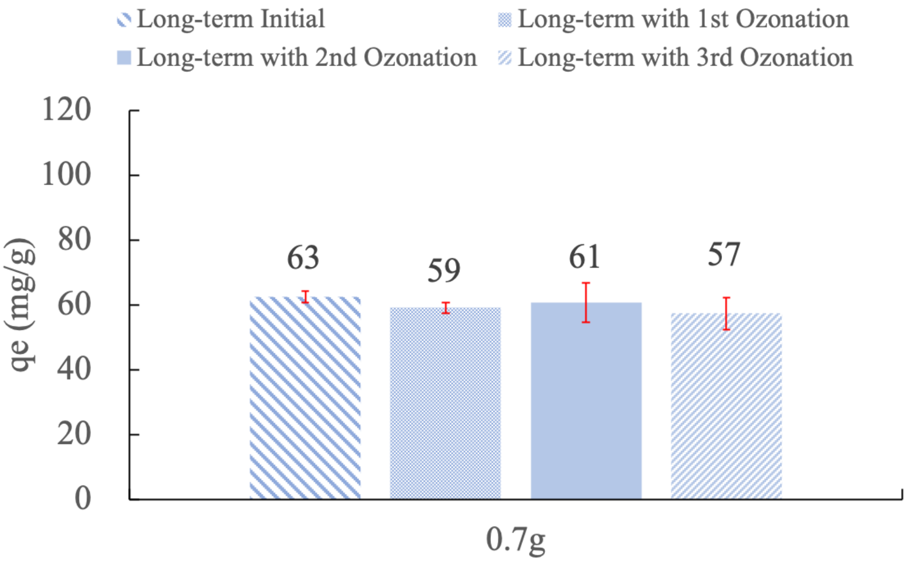


Figure H.9: Recovered Adsorption Capacity by Long-term Gaseous O_3 Regeneration with Dried Bed Zeolite Granules - Additional Test (Zeolite = 0.7 g; ACE solution = 1 L; ACE conc. = 200 mgL^{-1})

I APPENDIX: PRE-EXPERIMENT OF METHYLENE BLUE ADSORPTION TEST

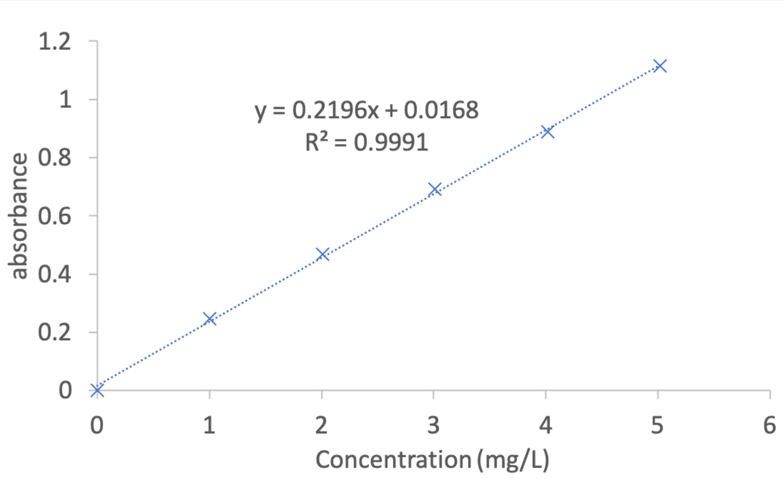


Figure I.1: Calibration of Methylene blue Solution

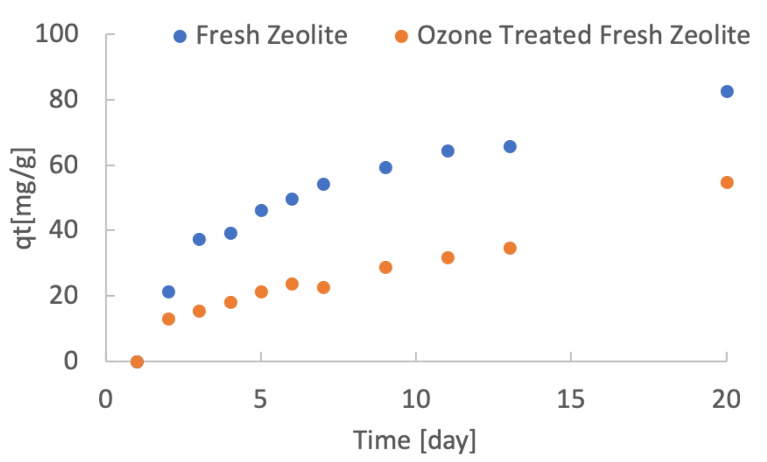


Figure I.2: Methylene blue Adsorption Test: Sample weight = 0.588 g; Methylene blue conc.= 250 mgL^{-1}.