Removal of Organic Micropollutants by Aerobic Activated Sludge

Thesis by

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ABSTRACT

Removal of Organic Micropollutants by Aerobic Activated Sludge

Nan Wang

The study examined the removal mechanism of non-acclimated and acclimated aerobic activated sludge for 29 target organic micropollutants (OMPs) at low concentration. The selection of the target OMPs represents a wide range of physical-chemical properties such as hydrophobicity, charge state as well as a diverse range of classes, including pharmaceuticals, personal care products and household chemicals.

The removal mechanisms of OMPs include adsorption, biodegradation, hydrolysis, and vaporization. Adsorption and biodegradation were found to be the main routes for OMPs removal for all target OMPs. Target OMPs responded to the two dominant removal routes in different ways: (1) complete adsorption, (2) strong biodegradation and weak adsorption, (3) medium biodegradation and adsorption, and (4) weak sorption and weak biodegradation. Kinetic study showed that adsorption of atenolol, methylparaben and propylparaben well followed first-order model ($R^2$: 0.939 to 0.999) with the rate constants ranging from 0.519-7.092 $h^{-1}$. For biodegradation kinetics, it was found that benzafibrate, bisphenol A, diclofenac, gemfibrozil, ibuprofen, caffeine and DEET followed zero-order model ($K_0$: 1.15E-4 to 0.0142 $µg/Lh^{-1}$, $R^2$: 0.991 to 0.999), while TCEP, naproxen, diphenhydramine, oxybenzone and sulfamethoxazole followed first-order model ($K_1$: 1.96E-4 to 0.101 $h^{-1}$, $R^2$: 0.912 to 0.996).
Inhibition by sodium azide (Na$_3$N) and high temperature sterilization was compared, and it was found that high temperature sterilization will damage cells and change the sludge charge state.

For the OMPs adaptation removal study, it was found that some of OMPs effluent concentration decreased, which may be due to the slow adaptation of the sludge or the increase of certain bacteria culture; some increased due to chromic toxicity of the chemicals; most of the OMPs had stable effluent concentration trend, it was explained that some of the OMPs were too difficult to remove while other showed strong quick adaptation.

A new module combined of sequencing batch reactor (SBR) and nanofiltration membrane filtration (NF-MBR) was developed to further study the OMPs removal and to exam the concept of compounds (CRT). The NF-MBR was proved to be a promising bioreactor, as OMPs were rejected by NF membrane which leaded to a low OMPs concentration in permeate water, the apparent removal rate was over 80% for most of the OMPs.
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<th>Abbreviation</th>
<th>Definition</th>
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<tbody>
<tr>
<td>Ae-MBR</td>
<td>Aerobic Membrane Bioreactor</td>
<td></td>
</tr>
<tr>
<td>An-MBR</td>
<td>Anaerobic Membrane Bioreactor</td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>Maximum Amount of the Compound Absorbed per Sludge</td>
<td></td>
</tr>
<tr>
<td>C0</td>
<td>Initial Concentration</td>
<td></td>
</tr>
<tr>
<td>COD</td>
<td>Chemical Oxygen Demand</td>
<td>mg/L</td>
</tr>
<tr>
<td>CODsol</td>
<td>Soluble Chemical Oxygen Demand</td>
<td>mg/L</td>
</tr>
<tr>
<td>CRT</td>
<td>Compound Retention Time</td>
<td>d</td>
</tr>
<tr>
<td>EPS</td>
<td>Extracellular Organic Substances</td>
<td></td>
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<tr>
<td>FEEM</td>
<td>Fluorescence Excitation Emission Matrices</td>
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</tr>
<tr>
<td>HRT</td>
<td>Hydraulic Retention Time</td>
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</tr>
<tr>
<td>K0</td>
<td>Zero-Order Rate Constant</td>
<td></td>
</tr>
<tr>
<td>K1</td>
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<td>Second-Order Rate Constant</td>
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</tr>
<tr>
<td>Kd</td>
<td>Distribution Coefficient</td>
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</tr>
<tr>
<td>Kf</td>
<td>Freundlich Adsorption Coefficient</td>
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</tr>
<tr>
<td>LC-OCD</td>
<td>Liquid Chromatography – Organic Carbon detection</td>
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<tr>
<td>MBR</td>
<td>Membrane Bioreactor</td>
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<tr>
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<td>Mixing Liquid Suspended Solid</td>
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<td>MQ</td>
<td>Milli-Q Water</td>
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<tr>
<td>MWCO</td>
<td>Molecular Weight Cut-Off</td>
<td>Da</td>
</tr>
<tr>
<td>NF</td>
<td>Nano Filtration</td>
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<tr>
<td>OMPs</td>
<td>Organic Micro-Pollutant</td>
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<tr>
<td>ORP</td>
<td>Oxidation Reduction Potential</td>
<td>mV</td>
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<td>q</td>
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<tr>
<td>Q</td>
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<tr>
<td>SV</td>
<td>Sludge Volume</td>
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<tr>
<td>SVI</td>
<td>Sludge Volume Index</td>
<td>mL/gTSS</td>
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<tr>
<td>TOC</td>
<td>Total Organic Carbon</td>
<td>mg/L</td>
</tr>
<tr>
<td>UASB</td>
<td>Up-Flow Anaerobic Sludge Blanket</td>
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<tr>
<td>VFA</td>
<td>Volatile Fatty Acids</td>
<td>mg/L</td>
</tr>
<tr>
<td>VLR</td>
<td>Volume Loading Rate</td>
<td>kgCOD/(m³d)</td>
</tr>
<tr>
<td>WWTP</td>
<td>Wastewater Treatment Plant</td>
<td></td>
</tr>
</tbody>
</table>

\[ \Delta_{ads}G^o \] Standard Gibbs Free Adsorption Energy
\[ \Delta_{ads}H^o \] Standard Adsorption Enthalpy
\[ \Delta_{ads}S^o \] Standard Adsorption Entropy Change
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Chapter 1. Introduction

In the recent decades, organic micropollutants contamination in water treatment has attracted great concerns [1] [2]. Traditional water treatment processes were not designed for the micropollutants removal, although some reports have demonstrated that some types of pharmaceuticals can be eliminated by conventional wastewater treatment unit, such as activated sludge. These chemicals are usually at low concentration (ng/L-µg/L) [3, 4], but they cannot be negligible as they may still course serious effect on human health and the environment. Many PPCPs possess acute toxicities similar to industrial chemicals, exhibit chronic toxicity, and exhibit ecotoxic effects principally through endocrine disruption [5]. Concern is also mounting that low level contamination by certain PPCPs may contribute to the spread of antibacterial resistance [6]. To date, more than 80 different compounds have been detected in surface and ground water worldwide. The disposal of unused medication via the toilet seems to be of minor importance but many of the pharmaceuticals applied in human medical care are not completely eliminated in the human body [2]. These micropollutants are usually released into the aquatic environment by effluents from municipal sewage treatment plants (STPs), and investigations have shown that these substances are often not eliminated during waste water treatment and also not biodegraded in the environment [2, 7, 8]. The low concentrations at which they occur in WWTPs make them difficult to remove. Mechanisms behind their treatment include biodegradation, abiotic transformations and sorption to biomass or suspended solid [9, 10]. Among these, sorption processes and biodegradation contribute the most to the micropollutants removal. However, for an efficient and complete removal of micropollutants, biotransformation or advanced
oxidation processes will be the most effective removal strategy. Although advanced oxidation processes require more capital and operation costs, they are able to oxidize many organic micropollutants, and either eliminate them completely or make them biodegradable. Since most of the wastewater treatment processes are based on biodegradation, optimizing the conditions could be a more feasible pathway [11].

1.1 The Occurrence of Micropollutants

Effluents of municipal WWTPs have been identified as a major source of emerging micropollutant [12], hormones, pharmaceuticals and personal care products (PPCPs). People in private households are either dumping drugs in normal metabolism routes or dispose expired drugs into the toilets [7, 12]. Sometimes, hospital wastewater can contribute to the load due to unregular operations. Some organic micropollutants such EDCs and PPCPs are not biodegradable in the WWTPs, and the domestic sewage will be then disposed into the natural environment. Another route for the discharge of micropollutants is by the usage of green fertilizer. When manure is used, it is very likely that the veterinary pharmaceuticals been introduced into the rivers and groundwater by runoff. The other source from agriculture is from the usage of pesticides, which has long been known. Point –source discharges by pharmaceutical plants are also released into the rivers, which is always a serious problem for the local ecology. Leakage from landfills can also contaminate waters, as some of landfills are not secure landfill [13]. Figure 1-1 shows the typical origin routes of pharmaceutical products, and Figure 1-2 shows transformation pathways of PPs.
Figure 1-1. Origin and routes of PPs[14]

Some investigations have been carried out in Austria, Brazil, Canada, Croatia, England, Germany, Greece, Italy, Spain, Switzerland, the Netherlands, and the U.S., and more than 80 compounds, pharmaceuticals and several drug metabolites have been detected in the aquatic environment [2, 15].
1.1.2 Occurrence of Pharmaceutical Residues

In the recent reports, many researchers have found new environmental effects of the PPCPs. However, because of the lack of assessment of complete data, it is difficult for researchers to fully understand the environmental effects of most PPCPs, and no one knows whether the relatively low concentrations found for PPCPs produce adverse effects on biota or whether the toxicity of complex mixtures might be totally different.
from that of individual compound [7, 16, 17]. Thus, we need more research and investigations on the effects and occurrence of micropollutants as well as reducing their generation and disposal into the environment. Fortunately, there are many research institutes and government agencies that are intensively working on the topic. The EU and the U.S. have launched research projects like EU’s Repharmawater and Poseidon and U.S. EPA projects [18, 19].

Analgesics and anti-inflammatory drugs are often prescribed in human medical care but often they are sold at higher quantities as over the counter (OTC) drugs. In Germany, the total quantities of acetaminophen (ASA) sold per year have been estimated at over 500 tons [20, 21]. Other analgesics such as diclofenac or ibuprofen are sold in Germany at an annual amount of about 75 and 180 tons respectively [21]. The concentration of ASA is rather low in the sewage effluents and surface water. Ternes et al. [8] found that the highest concentrations of salicylic, ortho-hydroxypippuric acid and gentisic acid in sewage influents are 54, 6.8 and 4.6 µg/L, respectively, and all of these three compounds were efficiently removed by municipal STPs. Another pain killer, acetaminophen is also easily degraded and removed by STPs, and seldom has acetaminophen been detected [22].

Several researches have been done to investigate the occurrence of antibacterial drugs in STPs and surface waters [23, 24]. Macrolide antibiotics (clarithromycin, dehydro-erythromycin [metabolite of erythromycin], roxithromycin, lincomycin), sulfonamides (sulfamethoxazole, sulfadimethoxine, sulfamethazine, and sulfathiazole), fluoroquinolones (ciprofloxacin, norfloxacin, and enrofloxacin), chloramphenicol, tylosin and trimethoprim have been found up to the low µg/l-level in sewage and surface water samples [15]. Penicillin and tetracyclines were not detected which was explained that
penicillin are easily hydrolyzed and tetracyclines readily precipitated with cations such as calcium and accumulate in sewage sludge or sediments [25, 26]. However, antibiotics are detected at high concentration in hospital wastewater and primary and tertiary wastewater effluents [27].

The data collected above indicate that some PhACs are originated from municipal WWTPs as they cannot be completely eliminated. Most of them are at low level concentration up to µg/L in municipal sewage and surface water. New methods to detect the PhACs are being developed to better understand their occurrence.

1.1.3 Occurrence of Endocrine Disrupting Compounds

Some pharmaceuticals have been found to be EDCs, and it has long been known that EDCs can cause unpredictable side effects especially in central nervous system [28] and hormone systems. Thus, the concern of the occurrence of EDCs is rapidly increasing. Generally, EDCs are classified as estrogenic, androgenic and thyroidal [29]. EDCs have been detected by several cities at wide ranges of concentration. The removal efficiency of different operation units is not clear, but most removal seems to be done within the activated sludge process. The removal efficiency of activated sludge is better than that of a trickling filter due to the faster rate of aerobic biodegradation.
Chapter 2. The Operation of Aerobic Activated Sludge

2.1 Introduction

The conventional activated sludge (CAS) process is the mostly widely used wastewater treatment system in the world; therefore, the study of the removal organic micropollutants (OMPs) by CAS is of vital importance. In this study, conventional aerobic activated sludge wastewater treatment was chosen for the sludge operation, and followed a classical sequencing batch reactor mode. In order to get the non-acclimated activated sludge, synthetic wastewater without any OMPs content was used as influent. After 2 weeks of operation, the effluent water reached equilibrium, and the reactor was kept operating for about 6 months. All of the parameters of the effluent reached steady state after two weeks. The sludge could be used for the studying of OMPs removal by non-acclimated aerobic activated sludge.

2.2 Setup of the aerobic activated sludge reactor

2.2.1 The setup of the reactor

The Applikon ez-control system, which is shown in Figure 2-1, was used as the reactor for the culture of non-acclimated activated sludge. Parameters like temperature, pH, DO, ORP could be controlled or monitored by the system, and influent and effluent were also control by the built-in pump. The sludge container was made of double glazing glass with a total volume of 2.4 L, the temperature could be controlled by circulating water in the glass interlayer. All of the pipes were covered with aluminum foil to inhibit the growth of algae.
2.2.2 Composition of the synthetic wastewater

The composition of the synthetic wastewater was chosen according to Nopens et al.[30]. All the chemicals are purchased from Sigma-Aldrich, which are listed in Table 2-1. The theoretical COD was 439.47 mg/L, the measured COD was around 380-410 mg/L. The possible reason for the low value was the loss of large molecules after filtration of the synthetic wastewater samples.

2.3 The operation of the reactor

2.3.1 Sludge seeding

The seeding sludge was taken from the Jeddah wastewater plant, and was filtered through 100 µm sieve.
2.3.2 Operation mode

The operation of the reactor followed a classical sequencing batch reactor mode, which is shown in Figure 2-2.

**Fill mode:** 1L synthetic waste water was filled into the reactor through the pipe, and the flow rate was 2L/h, and the filling time was 30 mins, after filling, the water reached the highest level as the F/M value.

**React mode:** Immediately after filling, the valve of pure oxygen was open, and oxygen was bubbled into the reactor under a pressure of 0.01 bar for two hours. DO was 75-81% under constant temperature of 20℃. Meanwhile, the built-in stirring started at the speed of 200 rpm.

**Settle mode:** The settling time was 2 hours, while the stirrer and aeration was stopped.

**Draw mode:** Effluent rate was also 2L/h and draw for 30 mins, the effluent was collected for further investigation.

2.3.3 Monitoring methods

During the 6 month operation of the reactor, COD, TOC, pH, DO, VFA, MLSS, MLVSS, TN, NO₃-N, NH₃-N, and other parameters were intensively monitored. All samples were filtered through Whatman 0.45 µm glass fiber filter before use.

**COD, VFA, TN, NO₃-N, NH₃-N:** Hach series parameter reagents were used to measure the above parameters. A Hach DBR 200 digital block reactor was used for digestion, and a Hach 2800 portable spectrophotometer was used to measure the samples.
TOC: Shimadzu TOC-V WP was used for the TOC measurements.

pH: pH was measured with the built-in pH meter.

MLSS: MLSS was measured using the standard method. The filters used were Whatman 0.45 µm filters, the volume used for sludge was 10 mL and for effluent was 200 mL, the drying temperature was 103-105°C.

\[ MLSS = \frac{m_1 - m_2}{V} \]  

Where,

- \( m_1 \) was the sample and filter weight,
- \( m_2 \) was the weight of the filter,
- \( V \) was the volume of the sample.

MLVSS: The mixed liquor volatile suspended solids (MLVSS) represented the population size of bacteria within the activated sludge process. Volatile suspended solids were solids that burn in a muffle furnace at 550°C for 3 hours, where the loss of volatile solids was considered bacteria. The increase of MLVSS represented an increase of bacteria population.

\[ MLSS = \frac{m_1 - m_2}{V} \]  

Where, \( m_2 \) was the sample and filter weight after burning.
SVI: SVI is the sludge volume index, which was used to measure the settling character.

SVI was the volume of the MLSS over the density of the mixed liquor suspended solids.

The settling time was set to 30 minutes in this case.

\[
SVI = \frac{\text{volume of settled solids (ml) after 30 minutes}}{\text{concentration of mixed liquor suspended solids}}
\]  

(1.3)

Table 2-1. Composition of the synthetic wastewater

<table>
<thead>
<tr>
<th>Chemical compound</th>
<th>mg/L</th>
<th>COD mg/L</th>
<th>N mg/L</th>
<th>P mg/L</th>
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<tr>
<td>Yeast</td>
<td>52.24</td>
<td>52.24</td>
<td>6.28</td>
<td>0</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>439.47</td>
<td>60.23</td>
<td>9.42</td>
<td></td>
</tr>
<tr>
<td><strong>Trace metals</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr(NO(_3))_3\cdot9H(_2)O</td>
<td>0.77</td>
<td>0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuCl(_2)\cdot2H(_2)O</td>
<td>0.536</td>
<td>0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MnSO(_4)H(_2)O</td>
<td>0.108</td>
<td>0.035</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiSO(_4)\cdot6H(_2)O</td>
<td>0.336</td>
<td>0.075</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PbCl(_2)</td>
<td>0.1</td>
<td>0.075</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnCl(_2)</td>
<td>0.208</td>
<td>0.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 2-2. Aerobic SBR operation mode

2.3.4 Operational parameters of the bioreactor

The starting parameters for the bioreactor are shown in Table 2-2. The operation was kept the same for about 6 months, and the bioreactor effluent was stable during the process.

Table 2-2. Starting parameters for the bioreactor

<table>
<thead>
<tr>
<th>MLSS (mg/L)</th>
<th>Temperature (°C)</th>
<th>Influent COD (mg/L)</th>
<th>Stirring rate (rpm)</th>
<th>DO %</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>1220</td>
<td>22±1</td>
<td>390-410</td>
<td>200</td>
<td>75-81</td>
<td>6.8-7.1</td>
</tr>
</tbody>
</table>

2.3.5 Operation monitoring parameters of the bioreactor

The effluent samples were taken and analyzed every few days. Parameters are shown in Table 2-3. COD and TOC could be removed over 95%, and 80% for organic nitrogen at most.
Table 2-3. Operational parameters of the aerobic activated sludge bioreactor

<table>
<thead>
<tr>
<th>MLSS (mg/L)</th>
<th>MLVSS (mg/L)</th>
<th>MLVSS/MLSS (%)</th>
<th>COD (mg/L)</th>
<th>TOC (mg/L)</th>
<th>Ammonia (mg/L-N)</th>
<th>Nitrate (mg/L-N)</th>
<th>TN (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2290-3390</td>
<td>1340</td>
<td>79-96</td>
<td>13.5-86.1</td>
<td>2.05-14.3</td>
<td>11.6-61.3</td>
<td>1.73-22.9</td>
<td>35.4-53.7</td>
</tr>
</tbody>
</table>

**2.4 Summary**

The aerobic activated sludge was operated for 6 months, and the effluent was stable. No OMPs were spiked into the synthetic wastewater, therefore, the sludge could be considered as “non-acclimated sludge” for OMPs, and could be used for further studies.
Chapter 3. Adsorption and Biodegradation of Organic Micropollutants by Non-acclimated Aerobic Activated Sludge

3.1 Introduction

In this chapter, the removal mechanisms of 29 selected organic micropollutants (OMPs) with different chemical and physical properties were investigated using batch reactors. The work studied the roles of adsorption, biodegradation, hydrolysis and volatilization in the removal of target OMPs, it was found that hydrolysis and volatilization effects could be considered negligible, while adsorption and biodegradation played the main roles in the process. To study the adsorption route, NaN$_3$ was used as an inhibitor, and it was demonstrated that it worked well as expected, as COD as observed not changed after the NaN$_3$ injection. The removals could be classified according to different routes: strong adsorption, strong biodegradation, both adsorption and biodegradation.

3.2 Materials and methods

3.2.1 Materials

3.2.1.1 Target organic micropollutants

We selected 29 OMPs as target for their removal in the study, and they were typical OMPs reported in the literature. The selection considered the differences between physic-chemical properties, like hydrophobicity, charge state, as well as their classification and usage.

Acesulfame, atrazine, caffeine, DEET, TCEP, TCPP, TDCPP, were purchased from Fluka (USA), amitriptyline, atenolol, benzafibrate, bisphenol A, carbamazepine, clofibric acid,
diclofenac, dilatin, diphenhydramine, gemfibrozil, ibuprofen, methylparaben, oxybenzone, trimethoprim were purchased from Sigma-Aldrich (USA), and iopromide, naproxen, propylparaben, sucralose were purchased from the U.S. Pharmacopeial Convention. Isotopes of acesulfame, carbamazepine, naproxen, sulfamethoxazole, trimethoprim were purchased from Toronto Research Chemicals, isotopes of amitriptyline, atenolol, bisphenol A, caffeine, dilatin, diphenhydramine, gemfibrozil, ibuprofen, methylparaben, propylparaben were purchased from CDN, isotopes of atrazine, ibuprofen were purchased from Fluka, and isotopes of benzafibrate, clofibrate acid, oxybenzone, primidone, TCEP were purchased from Cambridge Isotope Laboratories. All stock solutions were prepared in methanol with a concentration of 1000 mg L\(^{-1}\), and stored at -20 °C. Table 3-1 shows a summary of target OMPs and their physico-chemical properties, and the structures of the target OMPs could be found in Appendix A.

3.2.1.2 Other chemicals and materials
The synthetic waste water followed the recipe which was described in Chapter 2. Sodium azide, which was used to inhibit the sludge biodegradation, was purchased from Sigma-Aldrich (USA). All of the selected OMPs have been found in municipal water treatment plants [2, 4, 5, 31-38]. As the acclimation of sludge can influence the degradation of OMPs at trace concentration, the sludge used had been running without OMPs for 6 months, which can ensure the sludge was in non-acclimated stages for OMPs.
### Table 3-1. Summary of target organic micropollutants and their physic-chemical properties.

<table>
<thead>
<tr>
<th>Compound</th>
<th>CAS</th>
<th>use</th>
<th>Formula</th>
<th>MW g/mol</th>
<th>$K_{i}$ atm$m^2$/mol</th>
<th>log $K_{ow}$</th>
<th>pKa</th>
<th>Kd L/kg S</th>
<th>Charge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acesulfame</td>
<td>33665-90-6</td>
<td>Sweetener</td>
<td>C$_4$H$_9$NO$_4$S</td>
<td>163.15</td>
<td>9.63E-009</td>
<td>-1.33</td>
<td>60</td>
<td>2686</td>
<td>+</td>
</tr>
<tr>
<td>Amitriptyline</td>
<td>50-48-6</td>
<td>Antibiotic</td>
<td>C$<em>{20}$H$</em>{17}$N</td>
<td>277.41</td>
<td>6.85E-008</td>
<td>9.4</td>
<td>9.6</td>
<td>35</td>
<td>+</td>
</tr>
<tr>
<td>Atenolol</td>
<td>29122-68-7</td>
<td>Beta-blocker</td>
<td>C$<em>{14}$H$</em>{22}$N$_2$O$_3$</td>
<td>266.34</td>
<td>1.37E-018</td>
<td>0.16</td>
<td>2.61</td>
<td>60</td>
<td>N</td>
</tr>
<tr>
<td>Atrazine</td>
<td>1912-24-9</td>
<td>Pesticide</td>
<td>C$_3$H$_4$ClN$_3$</td>
<td>215.68</td>
<td>2.36E-009</td>
<td>1.7</td>
<td>60</td>
<td>2686</td>
<td>+</td>
</tr>
<tr>
<td>Bezafibrate</td>
<td>41859-67-0</td>
<td>Fibrate</td>
<td>C$<em>{19}$H$</em>{21}$ClNO$_4$</td>
<td>361.83</td>
<td>2.12E-015</td>
<td>4.25</td>
<td>60</td>
<td>60</td>
<td>N</td>
</tr>
<tr>
<td>Bisphenol A</td>
<td>80-05-7</td>
<td>EDS</td>
<td>(CH$_3$)$_2$C(PO$_3$H)$_2$</td>
<td>228.29</td>
<td>1.01E-011</td>
<td>3.32</td>
<td>2.57</td>
<td>3.18</td>
<td>N</td>
</tr>
<tr>
<td>Caffeine</td>
<td>58-08-2</td>
<td>Stumulant</td>
<td>C$<em>9$H$</em>{10}$N$_2$O$_2$</td>
<td>194.19</td>
<td>3.58E-011</td>
<td>-0.07</td>
<td>10.4</td>
<td>&lt;30</td>
<td>N</td>
</tr>
<tr>
<td>Carbamazepine</td>
<td>298-46-4</td>
<td>Anticonvulsant</td>
<td>C$<em>{15}$H$</em>{12}$N$_2$O</td>
<td>236.28</td>
<td>1.08E-010</td>
<td>2.45</td>
<td>15.96</td>
<td>50, 36</td>
<td>N</td>
</tr>
<tr>
<td>Clofibric acid</td>
<td>882-09-7</td>
<td>Fibrates</td>
<td>C$<em>{10}$H$</em>{14}$O$_5$CO$_2$H</td>
<td>214.65</td>
<td>2.19E-008</td>
<td>2.57</td>
<td>3.18</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DEET</td>
<td>134-62-3</td>
<td>Insect Repellent</td>
<td>CH$_3$C$_6$H$_2$CON(C$_3$H$_3$)$_2$</td>
<td>191.28</td>
<td>2.08E-008</td>
<td>2.18</td>
<td>9.68</td>
<td>42</td>
<td>N</td>
</tr>
<tr>
<td>Diclofenac</td>
<td>15307-86-5</td>
<td>NSAID</td>
<td>C$<em>{14}$H$</em>{13}$ClNO$_2$</td>
<td>296.16</td>
<td>4.73E-012</td>
<td>4.51</td>
<td>4.15</td>
<td>&lt;30</td>
<td>-</td>
</tr>
<tr>
<td>Dilantin</td>
<td>57-41-0</td>
<td>Anticonvulsants</td>
<td>C$<em>{15}$H$</em>{16}$N$_2$O$_2$</td>
<td>252.28</td>
<td>1.02E-011</td>
<td>2.47</td>
<td>8.33</td>
<td>81, 45</td>
<td>-</td>
</tr>
<tr>
<td>Diphenhydramine</td>
<td>58-73-1</td>
<td>Antihistamine</td>
<td>C$<em>{17}$H$</em>{23}$NO</td>
<td>255.36</td>
<td>3.7E-009</td>
<td>3.27</td>
<td>8.98</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Gemfibrozil</td>
<td>25812-30-0</td>
<td>Fibrates</td>
<td>C$<em>{15}$H$</em>{23}$O$_3$</td>
<td>250.34</td>
<td>1.19E-008</td>
<td>4.77</td>
<td>4.42</td>
<td>45, 30</td>
<td>N</td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>15687-27-1</td>
<td>NSAID</td>
<td>C$<em>{13}$H$</em>{16}$O$_2$</td>
<td>206.29</td>
<td>1.5E-007</td>
<td>3.97</td>
<td>4.91</td>
<td>&lt;30</td>
<td>-</td>
</tr>
<tr>
<td>Iopromide</td>
<td>73334-07-3</td>
<td>Contrast medium</td>
<td>C$<em>{18}$H$</em>{14}$I$_3$N$_3$O$_8$</td>
<td>791.12</td>
<td>1.02E-008</td>
<td>-2.05</td>
<td>10.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Methylparaben</td>
<td>99-76-3</td>
<td>Paraben</td>
<td>C$<em>{6}$H$</em>{11}$O$_3$</td>
<td>152.15</td>
<td>2.16E-008</td>
<td>1.96</td>
<td>3.08</td>
<td>&lt;30</td>
<td>-</td>
</tr>
<tr>
<td>Naproxen</td>
<td>22204-53-1</td>
<td>NSAID</td>
<td>C$<em>{14}$H$</em>{23}$O$_3$</td>
<td>230.27</td>
<td>3.39E-010</td>
<td>3.18</td>
<td>4.15</td>
<td>&lt;30</td>
<td>-</td>
</tr>
<tr>
<td>Oxybenzone</td>
<td>131-57-7</td>
<td>Sunscreens</td>
<td>C$<em>{14}$H$</em>{13}$O$_3$</td>
<td>228.25</td>
<td>1.5E-008</td>
<td>3.79</td>
<td>45.30</td>
<td>45, 30</td>
<td>N</td>
</tr>
<tr>
<td>Primidone</td>
<td>125-33-7</td>
<td>Anticonvulsant</td>
<td>C$<em>{12}$H$</em>{14}$N$_2$O$_2$</td>
<td>218.26</td>
<td>1.94E-010</td>
<td>0.91</td>
<td>11.50</td>
<td>30</td>
<td>N</td>
</tr>
<tr>
<td>Propylparaben</td>
<td>94-13-3</td>
<td>Paraben</td>
<td>C$<em>{10}$H$</em>{13}$O$_3$</td>
<td>180.21</td>
<td>6.37E-009</td>
<td>3.04</td>
<td>60</td>
<td>60</td>
<td>N</td>
</tr>
<tr>
<td>Sucrose</td>
<td>56038-13-2</td>
<td>Sweetener</td>
<td>C$<em>{12}$H$</em>{13}$Cl$_2$O$_8$</td>
<td>397.64</td>
<td>3.99E-019</td>
<td>-1.00</td>
<td>3.08</td>
<td>30</td>
<td>N, -</td>
</tr>
<tr>
<td>Sulfamethoxazole</td>
<td>723-46-6</td>
<td>Antibiotic</td>
<td>C$<em>{16}$H$</em>{11}$N$_2$O$_3$S</td>
<td>253.28</td>
<td>6.42E-013</td>
<td>0.89</td>
<td>6.16</td>
<td>&lt;30</td>
<td>N, -</td>
</tr>
<tr>
<td>TCEP</td>
<td>115-96-8</td>
<td>Flame Retardant</td>
<td>C$<em>{6}$H$</em>{15}$O$_8$P</td>
<td>285.49</td>
<td>3.29E-006</td>
<td>1.44</td>
<td>65</td>
<td>-</td>
<td>N, +</td>
</tr>
<tr>
<td>TCPP</td>
<td>13674-84-5</td>
<td>Flame Retardant</td>
<td>C$<em>{6}$H$</em>{15}$Cl$_2$O$_4$P</td>
<td>327.57</td>
<td>2.02E-005</td>
<td>2.59</td>
<td>60</td>
<td>60</td>
<td>N</td>
</tr>
<tr>
<td>TDCPP</td>
<td>13674-87-8</td>
<td>Flame Retardant</td>
<td>C$<em>{13}$H$</em>{15}$ClO$_4$P</td>
<td>430.91</td>
<td>7.36E-008</td>
<td>3.65</td>
<td>65</td>
<td>65</td>
<td>N, +</td>
</tr>
<tr>
<td>Trimethoprim</td>
<td>738-70-5</td>
<td>Antibiotic</td>
<td>C$<em>{14}$H$</em>{18}$N$_2$O$_3$</td>
<td>290.32</td>
<td>2.39E-014</td>
<td>0.91</td>
<td>7.12</td>
<td>119, 193</td>
<td>N, +</td>
</tr>
</tbody>
</table>

* Source: http://www.syres.com/what-we-do/databaseforms.aspx?id=386. ** Kd from John et. al. [39], which was based on the adsorption by CAS. c + positively charged, - negatively charged, N neutral.
3.2.1.3 Analytical methods

For every single sample, solid phased extraction was used to purify them, and a Dionex™ Autotrace™ 280 solid-phase extraction instrument and Oasis® cartridges were applied for the process. All samples have been spiked with 100 µg/L standard isotopes, except TCPP and TDCPP, the method was following the EPA method 8270, and the steps were as follows:

**Activation of sorbent**: conditioned cartridge with 5.0 mL of MTBE and methanol into solvent waste and water into aqueous waste, separately;

**Application of samples**: loaded 50 mL into cartridge, original sample was 1.0 mL and diluted to 50 mL;

**Removal of interfering compounds**: rinsed cartridge with 5.0 mL of waste into aqueous waste, dried cartridge with 5.0 mL of methanol;

**Elution of analytes**: washed cartridge with 5.0 mL of methanol and 5.0 mL of 10% methanol with MTBE separately, and collected 5.0 mL fraction into sample tube using methanol, and 5.0 mL 10% methanol with MTBE separately.

The concentration of target OMPs were measured using Agilent Technology 1260 module coupled with AB SCIEX QTRAP 5500 mass spectrometer (Applied Biosystems, Foster City, CA). The LC unit consists of a degasser, a binary pump, an autosampler and an LC column and the injection volume was 10 µL.
The operation of the LC was separated into positive and negative mode for different OMPs, and the detailed process was as following, and the MS information can be found in the Appendix B.

**Mobile phase for ESI +**: 4 mM ammonium formate in water containing 0.1% formic acid (A) and 4mM Ammonium formate in methanol containing 0.1% formic acid (B). Flow rate of 800 µL/min as follows: 90% A held for 0.5 min, then stepped down to 50% at 0.51 min and decreased linearly to 5% at 8 min. It is held at 5% for 6 mins, then stepped up to 90% A for an equilibration step of 4 min, giving a total run time of 18 mins.

**Mobile phase for ESI-**: 2mM ammonium acetate in water (A) and 2mM Ammonium acetate in methanol (B). Flow rate of 800 µL/min as follows: 90% A held for 0.5 min, then stepped down to 60% at 0.51 min and decreased linearly to 5% at 8 min. It was held at 5% till 11 min, then decreased linearly to 90% A in 3 min followed by a 4 min equilibration step at 90% A, resulting in a total run time of 18 mins.

3.2.2 Adsorption and biodegradation experiments

The MLSS in the bioreactor was 3000 mg/L when the batch experiment began. In the batch test, eight 250 ml Erlenmeyer flasks with 200 ml mixed liquor were run simultaneously at 20 °C for a week following the four treatments (reactor1, reactor2, reactor3, and reactor4) shown in Table 3-2. The removal routes for OMPs in the activated sludge process were considered to be biodegradation (B), adsorption (A), volatilization (V), and hydrolysis (H). For reactor1, a and b were duplicated reactors in which all of the removal routes will occur. For reactor2 and reactor3, biodegradation was inhibited by NaN₃ and high temperature sterilization, respectively. For reactor4, activated sludge was not added, therefore, only
self-degradation according to hydrolysis and volatilization can occur. According to the results and assumption, biodegradation and adsorption was based on the differences of different reactor results as follows:

\[ removal_B = removal_{R1} - removal_{R2,R3} \]  
\[ removal_A = removal_{R2,R3} - removal_{R4} \]  

All reactors were covered with aluminum foil to void possible photolysis. OMPs were spiked with a methanol stock solution mixture containing 1 mg/mL of each OMPs, and final OMPs concentrations in the batch reactors were 100 µg/L. The high concentration in the stock was planned to avoid increasing the COD by methanol stock. Synthetic wastewater as described in Chapter 2, and activated sludge was taken just after the fill mode in the bioreactors, therefore, COD was kept same as the bioreactor influent. Pure oxygen was used for aeration with a pressure of 0.1 MPa, and DO in the batch reactors was around 80% at 20 °C. Stirring was supplied by magnetic stirrers at 350 rpm. Samples were taken from the batch reactor at the following times: 0, 0.25, 0.5, 1, 2, 5, 12, 24, 36, 48, 72, 96, 120, 144, 168h, respectively. The collected samples will be first centrifuged at 4000 G for 10 minutes, and then filtered through 0.45µm glass fiber filter. The filter was cleaned by M.Q. water and injected air to squeeze out the liquid. The first 1 mL filtrate was discarded, and the following was collected in a glass centrifuge tubes. All of the samples were carried out in duplicate, and a control sample without sludge was also prepared under the same condition to determine if there was a loss of OMPs. The whole design sketch is shown in Figure 3-1.
Table 3-2. Batch experiment design

<table>
<thead>
<tr>
<th>reactor No.</th>
<th>activated sludge&lt;sup&gt;a&lt;/sup&gt;</th>
<th>wastewater OMPs&lt;sup&gt;b&lt;/sup&gt;</th>
<th>0.1% NaN&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt;</th>
<th>aeration&lt;sup&gt;d&lt;/sup&gt;</th>
<th>high temperature sterilization</th>
<th>removal routes</th>
</tr>
</thead>
<tbody>
<tr>
<td>AeR1a</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>B+A+(V+H)&lt;sup&gt;f&lt;/sup&gt;</td>
</tr>
<tr>
<td>AeR1b</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>B+A+(V+H)</td>
</tr>
<tr>
<td>AeR2a</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>B+A+(V+H)</td>
</tr>
<tr>
<td>AeR2b</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>B+A+(V+H)</td>
</tr>
<tr>
<td>AeR3a</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>A+(V+H)</td>
</tr>
<tr>
<td>AeR3b</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>A+(V+H)</td>
</tr>
<tr>
<td>AeR4a</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>V+H</td>
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<tr>
<td>AeR4b</td>
<td>-</td>
<td>+</td>
<td>+</td>
<td>+</td>
<td>-</td>
<td>V+H</td>
</tr>
</tbody>
</table>

<sup>a</sup> MLSS was 2000mg/L.  
<sup>b</sup> OMPs stock concentration was 1000mg/L, spiking concentration was 100µg/L.  
<sup>c</sup> NaN<sub>3</sub> was used to inhibit the sludge biodegradation activity.  
<sup>d</sup> Pure Oxygen was used for aeration, DO was around 6.4-7.3 mg/L at 20 ºC.  
<sup>e</sup> + indicated with or added, - indicated without or not added.  
<sup>f</sup> B-biodegradation, A-adsorption by NaN<sub>3</sub> or high temperature sterilization inhibition, (V+H) volatilization and hydrolysis

Figure 3-1. Design of removal of OMPs test steps
3.2.3 Sorption equilibrium time determination

Design of reactor 2 was applied to find the sorption equilibrium time. Samples were taken at 0, 24, 48h, respectively. OMPs concentration was checked, and the equilibrium time was determined.

3.2.4 Sorption isotherms

Design of reactor 2 was also applied in the determination of sorption isotherms after the equilibrium time was determined (48h was set as the sorption equilibrium time). The sorption isotherms were conducted using 1, 10, 50, and 100 µg/L OMPs. The injection volumes of the OMPs were the same to keep same COD in each reactor, stocks with different concentration were prepared, and the spiking volumes are shown in Table 3-3.

<table>
<thead>
<tr>
<th>Stock Concentration</th>
<th>1 µg/L</th>
<th>5 µg/L</th>
<th>10 µg/L</th>
<th>50 µg/L</th>
<th>100 µg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume Injected</td>
<td>20uL</td>
<td>20uL</td>
<td>20uL</td>
<td>20uL</td>
<td>20uL</td>
</tr>
</tbody>
</table>

3.3 Mechanism models

3.3.1 Adsorption models

Three isotherms including the Freundlich, linear, and Langmuir isotherms were applied to describe the sorption equilibrium. During the sorption experiments, OMPs concentration in the liquid phase were used to determined their partitioning into the sludge as follows:

\[
q_{eq} = \frac{C_0 - C_{eq}}{M}
\]  

(2.3)
Where \( q_{eq} \) is the OMPs partition into the sludge, \( C_0 \) is the initial concentration of OMPs, \( C_{eq} \) is the residual OMPs concentration, and \( M \) is the concentration of the sludge.

Models are described as follows:

**Freundlich model:**

\[
q_{eq} = K_f C_{eq}^{1/n}
\]

(2.4)

Where \( q_{eq} \) (mg/g) is the equilibrium amount OMPs that adsorbed onto the sludge, \( k_f \) is the Freundlich adsorption coefficient, \( C_{eq} \) is the equilibrium concentration of OMPs in the liquid phase, and \( 1/n \) is the measurement of nonlinearity. Freundlich isotherm can be interpreted into linear form:

\[
\log q_{eq} = \log K_f + \frac{1}{n} \log C_{eq}
\]

(2.5)

**Linear model:**

When \( 1/n \) is 1, the Freundlich model can be described in linear form:

\[
q_{eq} = K_d C_{eq}
\]

(2.6)

Where \( K_d \) (L mg\(^{-1}\)) is the distribution coefficient.

**Langmuir model:**

\[
q_{eq} = \frac{QbC_{eq}}{1 + bC_{eq}}
\]

(2.7)
Where Q is the binding strength, b is the maximum amount of the compound absorbed per sludge. Langmuir model can also be transform into a linear form:

\[
\frac{C_{eq}}{q_{eq}} = \frac{1}{Qb} + \frac{C_{eq}}{Q}
\]  

(2.8)

3.3.2 Adsorption kinetic models

Lagergren model which is a pseudo-first order rate equation was used to simulate the adsorption kinetics:

\[
\frac{dq}{dt} = K_i (q_{eq} - q)
\]  

(2.9)

\[
\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t
\]  

(2.10)

3.3.3 Biodegradation kinetic models

Three kinetic models were applied to simulate the results for biodegradation, which were zero-order, first-order, and second-order models.

Zero-order:

\[
\frac{dC}{dt} = -k_0 \iff C_t = C_0 - k_0 t
\]  

(2.11)

First-order:

\[
\frac{dC}{dt} = -k_1 C \iff C_t = C_0 e^{-k_1 t}
\]  

(2.12)

Second-order:
\[
\frac{dC}{dt} = -k_2 C^2 \Leftrightarrow C_t = C_0 / (1 + C_0 k_2 t)
\]  
(2.13)

Where, \( C_0 (\mu g/L) \) is initial concentration of the OMPs;

\( C_t (\mu g/L) \) is concentration of the OMPs at time \( t \);

\( K_0 (\mu g \cdot L^{-1} \cdot h^{-1}) \), \( K_1 (h^{-1}) \) and \( K_2 (L \cdot \mu g^{-1} \cdot h^{-1}) \) are the zero-order, first-order, second-order rate constant separately

### 3.4 Result and discussion

Due to the complexity of the sludge composition, the results for the removal of OMPs by different groups varied greatly. It was difficult to separate biodegradation and biosorption\([41]\), though NaN\(_3\) was spiked to inhibit the sludge activity.

#### 3.4.1 Hydrolysis and volatilization

In the control groups, no obvious changes of OMPs concentration was found, therefore, the removal by hydrolysis and volatilization was ignored in the study. This result could be explained by the low Henry’s constants, relative high molecular weight and polarized functional groups (Table 3-1 and Appendix A); several other groups also found the same conclusion that the removal by hydrolysis and volatilization could be ignored [39, 41-44].

#### 3.4.2 The biodegradation inhibition by NaN\(_3\)

Many studies had employed NaN\(_3\) to inhibit the aerobic sludge activities by paralyzing cytochrome oxidase so that OMPs would not be bio-decomposed, which biodegradation would not work in the process [41, 42]. Li et al. [42] had proposed to use caffeine to exam
the inhibition ability. It was based that caffeine was easy to be degraded by microbes while hard to be adsorbed by sludge. In their studies, caffeine was biodegraded completely within 10 hours without adsorption. Judging from our result (see Figure 3-2), caffeine was not adsorbed but the degradation was also not obvious. This was due to the differences between the sludge rather than the weak biodegradation ability, as other target OMPs like bisphenol A and naproxen were found to be biodegraded well. Therefore, caffeine was not a perfect indicator in our study, and we choose COD changes as a parameter in this case. COD of the samples taken at 0h and 168h was measured, and the result is shown in Table 3-4. The 58.6% removal in reactor 1 indicated that biodegradation was occurring, while there was not much change in other reactors. In reactor 3, the COD was much higher than the others; this was because of the cell rupture during sterilization, which brought the intracellular substances into the liquid phase. The results indicated that NaN₃ could inhibit the sludge in our study, as COD associated with the synthetic wastewater was easier biodegraded by the activated sludge than OMPs, while there were not much COD changes when NaN₃ was spiked into the reactors. Therefore, the OMPs removal in reactor 2 was chosen to calculate the biodegradation in this study.

Table 3-4. COD changes between 0h and 168h in the adsorption and biodegradation experiment

<table>
<thead>
<tr>
<th></th>
<th>Reactor 1</th>
<th>Reactor 2</th>
<th>Reactor 3</th>
<th>Reactor 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>0h COD (mg/L)</td>
<td>355</td>
<td>147</td>
<td>473</td>
<td>773</td>
</tr>
<tr>
<td>168h COD (mg/L)</td>
<td>147</td>
<td>473</td>
<td>484</td>
<td>710</td>
</tr>
<tr>
<td></td>
<td>444</td>
<td>446</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.5 Adsorption and biodegradation of OMPs by aerobic activated sludge

3.5.1 Isotherms

It was found that many OMP like methylparaben, propylparaben, and atenolol could be well adsorbed by activated sludge. However, it was hard to determine the isotherm due to three reasons: OMPs like methylparaben and propylparaben were totally adsorbed within few hours; therefore, the equilibrium sorption amount could not be decided. Other OMPs like diclofenac, and sulfamethoxazole were continually been adsorbed by the sludge rather than reaching equilibrium, therefore, the sorption equilibrium time we used was not
applicable in the case. Therefore, the sorption equilibrium curves will be not presented in this study.

### 3.5.2 Difficult to remove OMPs

It was found that acesulfame, clofibric acid, dilatin, iopromide, primidone, sucralose, TCPP, TDCPP and trimethoprim were not removed by aerobic activated sludge, part of results corresponded to the result by other groups [45, 46]. It was easy to explain that there was not much adsorption for those OMPs as they reflected negative or neutral charges, which would be electrostatic repulsed, the result was in agreement with the $K_d$ value in Table 3-1, as Joss et al. [47] proposed that the adsorption could be ignored when $K_d$ was lower than 300 L/kg SS. In addition, due to the high molecular weight as well as stable structures of the OMPs, they were hard to be biodegraded by the sludge. TCPP and TDCPP were the typical chemicals that were difficult to remove by aerobic activated sludge as chlorine was high in their structures. Moreover, the bacteria culture may not be adapted to certain chemicals, as the sludge was cultured as non-acclimated sludge for OMPs.

### 3.5.3 OMPs adsorption by aerobic activated sludge

Typical OMPs was selected to be presented for their adsorption properties in this section, and the information for the other OMPs can be found in the appendix.

It was found that in reactor2 that the adsorption of atrazine, sulfamethoxazole, amitriptyline, and TCEP kept being adsorbed by sludge. For atrazion, naproxen, and TCEP, the apparent sorption equilibrium were reached at more than one days, shown in [42] which was not in agreement with the Lagergren model, which usually uses 3-6 hours as the equilibrium time. The same phenomenon was observed by Yu et al. [48]. The adsorption for
sulfamethoxazole was following a zero-order model, and \( K_{p0} \) was 0.00265 mgL\(^{-1}\)h\(^{-1}\) \((R^2: 0.999)\). In general, the zero-order kinetics were not applicable in adsorption processes as the adsorption should reach equilibrium at a certain time with the desorption processes. This phenomena could be explained that the sorption process of sulfamethoxazole was a two-step process adsorption, in the first step, the adsorption was quick which was not related to the sulfamethoxazole concentration; and then in the second step, while the sorption points was taken, the sorption slowed down, and finally reach equilibrium. Further study is needed to study the process as shown in Figure 3-4.
Figure 3-3. The removal of atrazine by aerobic activated sludge. A total removal, B adsorption curve

Figure 3-4. The removal of sulfamethoxazole by aerobic activated sludge. A total removal, B zero order simulation curve
For OMPs like atenolol, methyparaben, and propylparaben, the complete adsorption occurred within 8 hours. Zero order and first order kinetics was applied to simulate the processes. Propylparaben was firstly fitted with the zero-order model, and the $R^2$ was 0.416, while $R^2$ for first order model was 0.999, therefore, first-order adsorption model was selected, as shown in Figure 3-5. The analysis of the other OMPs was done with the same method, i.e. choosing the model with higher $R^2$ value, and the results is shown in Table 3-5. The strong adsorption of atenolol could be explained by its positive charge, as the sludge exhibited a negative charge, the electrostatic attraction made the adsorption process stronger than other routes. Methylparaben and propylparaben were also positively charged, and their adsorption was found to be quicker than atenolol. The reason for this phenomenon was their phenolic group, which may also enhance the adsorption process.

### 3.5.4 Adsorption differences between NaN₃ and high temperature sterilization inhibition

For the study of adsorption of OMPs by aerobic activated sludge, different inhibition methods have been applied by different groups; among them, NaN₃ and high temperature sterilization were the most commonly used methods. The advantage of NaN₃ is it will not damage the cells, while its inhibition ability is effective for aerobic sludge. However, the addition of NaN₃ will isolate the mechanism for target compounds [49]. The advantage of high temperature sterilization inhibition is it could guarantee the total inhibition of the sludge, while it could break the cells which provide new sorption points, and change the sludge charge as well. It was found that there were no more adsorption of atenolol and atrazine after high temperature sterilization, noting that electrostatic attraction played main role in the adsorption of atrazine, the phenomena could be explained by the change of
sludge charge. Methylparaben and propylparaben were not detected in the high temperature sterilization experiment, which made it difficult for further analysis. For the other OMPs, no obvious change was found in this case.

<table>
<thead>
<tr>
<th>OMPs</th>
<th>$K_{pl}(h^{-1})$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atenolol</td>
<td>0.764</td>
<td>0.939</td>
</tr>
<tr>
<td>Methylparaben</td>
<td>0.519</td>
<td>0.988</td>
</tr>
<tr>
<td>Propylparaben</td>
<td>7.092</td>
<td>0.999</td>
</tr>
</tbody>
</table>

Table 3-5. First-order adsorption kinetics rate constants of target OMPs

![Graph](image1)

**Figure 3-5.** The removal of propylparaben by aerobic activated sludge. A total removal, B first-order simulation curve

3.5.5 OMPs biodegradation by aerobic activated sludge

For most target OMPs, biodegradation was the main removal route [41, 50, 51]. Zero-order and first-order reaction were the main removal kinetics for the experiment. The result are
shown in Table 3-6 and Table 3-7. Benzafibrate, bisphenol A, diclofenac, gemfibrozil, ibuprofen, caffeine, and DEET fit the zero-order biodegradation kinetics. Ibuprofen was completely removal by both adsorption and biodegradation, Nakada et al. [52] found the same result. Although Yu et al. [41] gave a first-order kinetics of biodegradation/sorption reaction (\(K_{BDS}=0.88d^{-1}, R^2=0.955\)), and the constants we simulated was close as reported (\(K_{BDS}=0.252d^{-1}, R^2=0.953\)), the biodegradation curve followed zero-order kinetics, as shown in Figure 3-6. The biodegradation kinetics of sulfamethoxazole, TCEP, naproxen, diphenhydramine, and oxybenzone followed the first-order model. The biodegradation of naproxen was not high, which was in agreement with Nakada et al.[52]. The possible explanation was the lower hydrophobicity (\(\log K_{ow}<3\)) of amide-type pharmaceuticals. Joss et al [47] found that removal of selected pharmaceuticals was mainly due to biological transformation and varied insignificantly (carbamazepine< 10%, ibuprofen>90%), which corresponded to our result; they also proposed that when the sorption coefficient was below 300 L/kg, adsorption could be ignored. Table 3-8 showed the removal comparison between the literature and our study, and it was found that CAS was effective for the removal of certain OMPs, however, the result varies significantly between different groups, and few literatures have reported the mechanisms behind the removal. Therefore, the selection of so many OMPs in different classifications was meaningful not only in providing data, but also for the study of mechanisms of OMPs removal.

<table>
<thead>
<tr>
<th>OMPs</th>
<th>(K_0(\mu g/L \cdot h^{-1}))</th>
<th>(R^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzafibrate</td>
<td>0.0033</td>
<td>0.999</td>
</tr>
<tr>
<td>Bisphenol A</td>
<td>0.01416</td>
<td>0.991</td>
</tr>
<tr>
<td>Diclofenac</td>
<td>2.02E-4</td>
<td>0.999</td>
</tr>
<tr>
<td>Gemfibrozil</td>
<td>1.15E-4</td>
<td>0.999</td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>0.00491</td>
<td>0.993</td>
</tr>
<tr>
<td>Caffeine</td>
<td>0.00713</td>
<td>0.991</td>
</tr>
<tr>
<td>DEET</td>
<td>5.41E-4</td>
<td>0.997</td>
</tr>
</tbody>
</table>
Table 3-7. First –order biodegradation kinetics model parameters

<table>
<thead>
<tr>
<th>OMPs</th>
<th>$K_1$(h$^{-1}$)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCEP</td>
<td>1.96E-4</td>
<td>0.996</td>
</tr>
<tr>
<td>Naproxen</td>
<td>0.0101</td>
<td>0.912</td>
</tr>
<tr>
<td>Diphenhydramine</td>
<td>0.00128</td>
<td>0.916</td>
</tr>
<tr>
<td>Oxybenzone</td>
<td>0.00142</td>
<td>0.900</td>
</tr>
<tr>
<td>Sulfamethoxazole</td>
<td>3.518E-4</td>
<td>0.955</td>
</tr>
</tbody>
</table>

Figure 3-6. Simulation of removal ibuprofen by aerobic activated sludge. A first-order removal kinetics by sorption and biodegradation, B zero-order biodegradation kinetics

3.6 Summary

In this chapter, experiment was designed to study the removal mechanism of OMPs by aerobic activated sludge. It was found that biodegradation and adsorption were the main removal routes, while volatilization and hydrolysis could be ignored in the process. NaN$_3$ proved to be an effective inhibitor for the aerobic bacteria, and the comparison between the inhibitions by NaN$_3$ and high temperature sterilization proved electrostatic attraction played an important role in the adsorption process. Target OMPs responded to the two
dominant removal routes in different ways: (1) complete adsorption by atenolol, methylnparaben and propylparaben, (2) strong biodegradation and weak adsorption by benzafibrate, bisphenol A, diphenhydramine, ibuprofen, naproxen, and oxybenzone, (3) medium biodegradation and adsorption by amitriptyline and sulfamethoxazole, and (4) weak sorption and weak biodegradation by atrazine, DEET, diclofenac, gemfibrozil, TCEP, and trimethoprim. Kinetic study showed that adsorption of atenolol, methylnparaben and propylparaben well followed first-order model ($R^2$: 0.939 to 0.999) with the rate constants ranging from 0.519-7.092 h$^{-1}$. For biodegradation kinetics, it was found that benzafibrate, bisphenol A, diclofenac, gemfibrozil, ibuprofen, caffeine and DEET followed zero-order model ($K_0$: 1.15E-4 to 0.0142 µg/Lh$^{-1}$, $R^2$: 0.991 to 0.999), while TCEP, naproxen, diphenhydramine, oxybenzone and sulfamethoxazole followed first-order model ($K_1$: 1.96E-4 to 0.101 h$^{-1}$, $R^2$: 0.912 to 0.996).
<table>
<thead>
<tr>
<th>OMPs</th>
<th>Literature</th>
<th>Biodegradation removal rate %</th>
<th>method</th>
<th>Total removal rate %</th>
<th>method</th>
<th>Batch test</th>
<th>Biodegradation removal rate %</th>
<th>Total removal rate %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amitriptyline</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>61</td>
<td>88</td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Atrazine</td>
<td>n.d.</td>
<td>n.d.</td>
<td>92.2[56]</td>
<td>Batch</td>
<td>Batch</td>
<td>50</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Bezafibrate</td>
<td>100[54]</td>
<td>Batch</td>
<td>100[54]</td>
<td>Batch</td>
<td></td>
<td>55</td>
<td>63</td>
<td></td>
</tr>
<tr>
<td>Bisphenol A</td>
<td>n.d.</td>
<td>n.d.</td>
<td>&lt;20[57]</td>
<td>SBR, lab scale</td>
<td>n.d.</td>
<td>62</td>
<td>97</td>
<td></td>
</tr>
<tr>
<td>Carbachazepine</td>
<td>n.d.</td>
<td>n.d.</td>
<td>98.9[56]</td>
<td>Batch</td>
<td></td>
<td>&lt;5</td>
<td>n.d.</td>
<td></td>
</tr>
<tr>
<td>Carbamazepine</td>
<td>n.d.</td>
<td>n.d.</td>
<td>19.2–46.2[52]</td>
<td>WWTP, full scale</td>
<td>n.d.</td>
<td>51</td>
<td>66</td>
<td></td>
</tr>
<tr>
<td>Clofibric acid</td>
<td>26–30[58]</td>
<td>Lab columns</td>
<td>98.9[56]</td>
<td>Batch</td>
<td></td>
<td>10</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>DEET</td>
<td>n.d.</td>
<td>n.d.</td>
<td>98.9[56]</td>
<td>MBR, lab scale</td>
<td>n.d.</td>
<td>63</td>
<td>89</td>
<td></td>
</tr>
<tr>
<td>Diclofenac</td>
<td>34–38[58]</td>
<td>Lab columns</td>
<td>96.3[60]</td>
<td>SBR, lab scale</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dilantin</td>
<td>n.d.</td>
<td>n.d.</td>
<td>98.9[56]</td>
<td>Batch</td>
<td></td>
<td>10</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>Diphenhydramine</td>
<td>n.d.</td>
<td>n.d.</td>
<td>98.9[56]</td>
<td>Batch</td>
<td></td>
<td>53</td>
<td>93</td>
<td></td>
</tr>
<tr>
<td>Gemfibrozil</td>
<td>&gt;99[48]</td>
<td>Batch</td>
<td>96.3[60]</td>
<td>Lab columns</td>
<td>n.d.</td>
<td>43</td>
<td>49</td>
<td></td>
</tr>
<tr>
<td>Ibuprofen</td>
<td>n.d.</td>
<td>n.d.</td>
<td>97.8[56]</td>
<td>Batch</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Iopromide</td>
<td>86-97[61]</td>
<td>Batch</td>
<td>100[60], 48.8[60], 33.0[56]</td>
<td>Lab columns</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
</tr>
<tr>
<td>Methyrapbaben</td>
<td>n.d.</td>
<td>n.d.</td>
<td>41[63]</td>
<td>MBR, pilot scale</td>
<td></td>
<td>43</td>
<td>49</td>
<td></td>
</tr>
<tr>
<td>Naproxen</td>
<td>60[54], 80[48]</td>
<td>Batch</td>
<td>98.9[56]</td>
<td>Batch</td>
<td></td>
<td>~100</td>
<td>~99</td>
<td></td>
</tr>
<tr>
<td>Oxybenzone</td>
<td>n.d.</td>
<td>n.d.</td>
<td>98.9[56]</td>
<td>Batch</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Primidone</td>
<td>n.d.</td>
<td>n.d.</td>
<td>98.9[56]</td>
<td>Batch</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propy/lparaben</td>
<td>n.d.</td>
<td>n.d.</td>
<td>98.9[56]</td>
<td>Batch</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sucralose</td>
<td>n.d.</td>
<td>n.d.</td>
<td>98.9[56]</td>
<td>Batch</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfamethoxazole</td>
<td>n.d.</td>
<td>n.d.</td>
<td>98.9[56]</td>
<td>Batch</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TCEP</td>
<td>n.d.</td>
<td>n.d.</td>
<td>98.9[56]</td>
<td>Batch</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TCPP</td>
<td>n.d.</td>
<td>n.d.</td>
<td>98.9[56]</td>
<td>Batch</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TDCPP</td>
<td>n.d.</td>
<td>n.d.</td>
<td>98.9[56]</td>
<td>Batch</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>n.d.</td>
<td>n.d.</td>
<td>98.9[56]</td>
<td>Batch</td>
<td></td>
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</table>
Chapter 4. The Adaptation of Removal of Organic Micropollutants by Aerobic Activated Sludge

4.1 Introduction

For many of the target OMPs, they do not always exist in wastewater. Some of the OMPs can be classified as emerging organic micropollutants. It is important to research the changes of removal ability of those OMPs in non-acclimated and acclimated sludge. It was found that for some OMPs, the removal had been enhanced during the adaptation, which showed an OMPs concentration decrease in the effluent water; for most of the OMPs, the OMPs concentration stayed the same, which could be explained by quick adaptation or the culturing time is too short for obvious adaptation. A noticeable result was found that some of the OMPs showed a decrease trend of removal ability.

4.2 Materials and methods

Right after the OMPs removal mechanism experiment, 10 µg/L OMPs stock was spiked into the synthetic wastewater every day, and the OMPs concentration was monitored. After two months of operation, the sludge was taken, and the removal mechanism experiment was repeated again to check if the removal rate constants were changed.

Materials were the same as described in Chapter 2 and Chapter 3, the operation of SBR reactor was described in Chapter 2, and the OMPs concentration measure methods and OMPs removal mechanism experiment design was described in Chapter 3.
4.3 Results and discussion

After two months of monitoring, the effluent OMPs concentration data were collected, and the trend of the concentration changes were shown in table 4-1.

<table>
<thead>
<tr>
<th>decrease</th>
<th>increase</th>
<th>stable</th>
<th>not decided</th>
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<td>Benzafibrate</td>
<td>Gemfibrozil</td>
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<td>Sulfamethoxazole</td>
</tr>
<tr>
<td>Iopromide</td>
<td>TDCPP</td>
<td>Dilantin</td>
<td>TCEP</td>
</tr>
<tr>
<td>Naproxen</td>
<td></td>
<td>Diphenhydramine</td>
<td>TCPP</td>
</tr>
</tbody>
</table>

4.3.2 Decreasing trend

A decreasing trend indicated positive adaptation of OMPs by the activated sludge. Biodegradation played the most important role in the enhancement of the removal ability. Bisphenol A, ibuprofen and naproxen showed quick adaptation (Figure 4-1 and Figure 4-2). The batch test results proved this phenomenon, and it was found the removal rate was increased. Diclofenac showed slower adaptation and the removal adaptation of iopromide was even lower, see Figure 4-3. As described in Chapter 3, diclofenac showed weak sorption and biodegradation, and iopromide was found to be a difficult to remove compound. The results indicated that the initial removal ability was an important parameter in the adaptation, the stronger it is, the quicker it will be adapted.
Figure 4-1. (A) removal trend of bisphenol A. (B) removal of bisphenol A by non-acclimated and acclimated activated sludge.

Figure 4-2. (A) removal trend of ibuprofen. (B) removal of ibuprofen by non-acclimated and acclimated activated sludge.
4.3.3 Increasing trend

Atenolol, atrazine, carbamazepine TDCPP and trimethoprim showed an increasing trend of adaptation during the two months operation, see Figure 4-4 and appendix. Note that atenolol and trimethoprim were positively charged, and were well adsorbed by the negatively charged sludge, they showed a low concentration in the effluent at the beginning. The atenolol concentration kept low for about 30 days and then began to increase; this was due to the large amount of sorption points for atenolol. Adsorption played the most important role in the removal process (completely absorbed within 10 hours at 100 µg/L), after the adsorption reached equilibrium, i.e., sorption points were fully occupied, no more atenolol absorbed, and the effluent concentration began to increase. Trimethoprim
concentration showed the same trend as atenolol concentration, however, the adsorption process was not as fast as that of atenolol, therefore, the initial concentration was not as low as atenolol. The equilibrium concentration reached the influent concentration, which indicated there was not biodegradation as well.

![Figure 4-4. Removal trend of atenolol (A) and trimethoprim (B)](image)

**4.3.4 Stable trend**

The stable trend could be classified into two situations. It was obvious that for the difficult to remove compounds, the effluent concentration would stay the same as the influent concentration during the operation. clofibric acid, gemfibrozil, primidone, and TCPP fit this situation, the batch removal test also proved the results, see Figure 4-5. Although benzafibrate and caffeine were found to be biodegradable compound they showed no removal in the operation, this was probably due to the bacteria culture changes, in which the bacteria that could remove the compounds was eliminated in the competition,
see Figure 4-5. In another situation, the effluent concentration was lower than the influent concentration, see Figure 4-6. This could be explained by either a quick adaptation, which made the decrease trend not obvious, or the removal ability stayed the same during the operation. What’s more, it was easy to draw the conclusion that the lower the effluent concentration, the stronger the removal ability. Therefore, the removal ability order by activated sludge from strong to weak was DEET, diphenhydramine, oxybenzone, sulfamethoxazole, TCEP, and dilatin. The strong removal of diphenhydramine, oxybenzone, and sulfamethoxazole was proven in Chapter 3. The strong removal of DEET may be caused by the quick adaptation.

Figure 4-5. Removal trend of clofibric acid (A) and bezafibrate (B)
Figure 4-6. Removal trend of DEET, clofibric acid, oxybenzone, sulfamethoxazole, TCEP and dilatin

### 4.4 Summary

The adaptation trend was examined in different ways, typically: decreasing, increasing, stable. For the decrease situation, the reason was a positive adaptation, which enhanced the sludge removal ability, and the adaptation time was corresponded to the initial removal ability. What is more, the increasing trend was mainly caused by strong absorption by the sludge, once the sorption points were occupied; the compound concentration began to increase. Finally, the stable trend occurred whether no removal or quick adaptation removal. The lower the stable concentration was, the stronger the removal ability was.
Chapter 5. Concept of Compound Retention Time in Aerobic Nanofiltration Membrane Bioreactor

5.1 Introduction

Membrane bioreactor (MBR), which is combined of biological treatment and membrane separation, has got a rapid growth in both domestic and industrial wastewater treatment and reuse in recent years due to its significant advantages over conventional activated sludge process such as better effluent quality and less footprint. However, the microfiltration (MF) and ultrafiltration (UF) membrane widely used in membrane bioreactor cannot reject OMPs due to their much higher pore size or molecular weight cut-off (MWCO) than OMPs (see Figure 5-1). In order to enhance OMPs removal, nanofiltration (NF) is a promising alternative to MF/UF in MBR as it can effectively reject the OMPs with molecular weight over its MWCO,. A NF module was connected to the former SBR reactor to form an aerobic nanofiltration membrane bioreactor for one month operation in this study. The rejection of OMPs by NF would increase their retention time in the bioreactor,. Based on the concept of hydraulic retention time (HRT) and sludge retention time (SRT), the concept of compound retention time (CRT) for OMPs in the aerobic nanofiltration membrane bioreactor was proposed and analyzed in this chapter. The overall performance of OMPs removal was also discussed.
5.1 Materials and methods

5.1.1 Materials and devices

Dow NF 90 membrane, Sartorius TE Precision Balance TE6101, Sterlitech Sepa CF II Membrane Cell System, and all the other materials and devices were described in Chapter 2 and Chapter 3.

![Membrane separation processes overview](image)

Figure 5-1. Membrane separation processes overview[65]

5.1.2 Methods

The experiment design was shown in Figure 5-2. The system was combined with a bioreactor and a membrane filtration system. As the bioreactor was running in SBR mode,
the hybrid system was named nanofiltration sequencing batch membrane bioreactor (NF-SB-MBR). The operation of the SBR was the same as described in Chapter 2, 4 L synthetic wastewater with 10 µg/L OMPs was added into the reactor daily. The effluent was collected daily and its OMPs concentration was treated as OMPs concentration in the bioreactor, \( C_{in} (\mu g/L) \). And then, the collected effluent (4 L) from the bioreactor was filtered by Dow NF90 membrane in Sterlitech crossflow membrane cell system. Transmembrane pressure (TMP) was kept at 10 bar. Permeate was collected in a tank on an electronic balance connected to a computer for recording permeate weight with time continuously, and thus permeate flux was calculated. The filtration process was stopped when 2 L permeate was obtained. The NF permeate was sampled, and its OMPs concentration was treated as permeate concentration, \( C_{p} (\mu g/L) \). The NF concentrate was collected and used to make the synthetic wastewater. The actual daily treated wastewater volume was 2 L, and thus the HRT was 1 d. The each OMP dosage was 40 µg/d and the same as the previous SBR operation, which resulted in the average influent concentration of 20 µg/L. The OMPs concentration measurement was the same as in Chapter 3.
Figure 5-2. Schematic diagram of aerobic nanofiltration membrane bioreactor (The bioreactor was running in SBR mode, SBR effluent was sampled as $C_{in}$ and filtered by NF membrane in a constant-pressure crossflow membrane cell, the permeate was collected and sampled as the final effluent ($C_p$), and the concentrate was back to the SBR.)

5.2 Model development

Analogous to the definition of SRT, CRT could be defined as (5.1).

$$CRT = \frac{C_{in}V_R}{C_pQ_p + C_{in}Q_s}$$

(5.1)

Where $V_R$ is reactor volume (L), $Q_p$ is NF permeate flow (L/d), $C_p$ is NF permeate OMP concentration ($\mu$g/L), $Q_s$ is sludge discharge flow (L/d), $C_{in}$ is the average OMP concentration in reactor ($\mu$g/L). All the sludge was rejected by the membrane, and no waste sludge was discharged during the operation. Therefore, (5.1) could be simplified as follow:

$$CRT = \frac{C_{in}V_R}{C_pQ_p} = \left(\frac{C_{in}}{C_p}\right)HRT$$

(5.2)
NF rejection rate \( a \) was defined as as (5.3),

\[
a = 1 - \frac{C_p}{C_{in}}
\]  

(5.3)

And overall removal rate \( R \) was

\[
R = 1 - \frac{C_p}{20}
\]  

(5.4)

For OMPs biodegradated by the first-order kinetics, the degradation rate \( R_1 \) is defined as (5.5)

\[
R_1 = -\frac{dC_{in}}{dt} = K_1 C_{in}
\]  

(5.5)

When CRT reached steady state, i.e. \( C_p \) and \( C_{in} \) were stable, we can assume \( R_1 \) is stable in this case, \( R_1 \) can be written as (5.6)

\[
R_1 = \frac{1}{HRT} \left( C_f - C_p \right)
\]  

(5.6)

From (5.5) and (5.6), we can deduce the first-order reaction rate under steady state,

\[
K_1 = \frac{1}{HRT \times C_{in}} \left( C_f - C_p \right)
\]  

(5.7)

Same method can be applied in the first-order reaction, which

\[
R_0 = -\frac{dC_{in}}{dt} = K_0 = \frac{1}{HRT} \left( C_f - C_p \right)
\]  

(5.8)
5.3 Results and discussion

For some compounds including acesulfame, caffeine, clofibric acid, diclofenac, dilatin, gemfibrozil, iopromide and sulcralone, there were 1-3 times higher concentrations in the bioreactor than in the feed, indicating their significant accumulation in the bioreactor due to the effective rejection by NF membrane. These OMPs were found nearly no or very little removal in previous study. As an example, the concentration in the bioreactor (Cn) and the permeate (Cp), the NF rejection and the overall removal, and CRT changes of acesulfame were shown in Figure 5-3. The information of other compounds could be found in Appendix E. It was found CRT was highly dependent on NF rejection rate. The higher the rejection rate was the higher CRT was (Figure 5-4). The permeate concentration of bisphenol A at stable time (20 days later) was lower than the influent concentration. Take consideration of the high removal by activated sludge, it can be predicted that the removal bisphenol A was enhance during the operation (Figure 5-5). Amtripline was a readily removable compound, and the effluent concentration kept stable and low, see Figure 5-6. The high CRT (around 200d), which was caused by high rejection rate may contribute to the removal process. Figure 5-8 shows the permeate concentration of target OMPs, most of them are under 4 µg/L except acesulfame, caffeine, clofibric acid, diclofenac, dilatin, gemfibrozil, iopromide and sulcralone, of which the concentration in the bioreactor were increased. The overall removal rate was over 80% for most of the OMPs. The result indicates the NF-MBR is promising for removal of the selected compounds. Naproxen was well biodegradable and difficult adsorbed compound, and the biodegradation followed first-order reaction kinetic (K1=0.0101 h⁻¹). The operational parameters of naproxen in NF-SB-MBR are shown in Figure 5-7. CRT was stable after 20 days, using (5.7) the first-order
reaction constant is 0.0704 h\(^{-1}\), which is much higher than the starting value. It indicates the biodegradation was greatly enhanced during the operation. For OMPs followed zero-order reaction, like bisphenol A and benzafibrate, CRT kept decreasing, therefore, zero-order reaction constant was not calculated in this study. The decreasing of CRT indicates OMPs concentration in the bioreactor was greatly decrease, as the permeate concentration was stable.

Figure 5-3. \(C_{\text{in}}\), \(C_{\text{p}}\) and CRT changes of acesulfame in NF-SB-MBR operation
Figure 5-4. Relation between CRT and rejection rate in aceulfame

Figure 5-5. $C_{\text{in}}$, $C_p$ and CRT changes of bisphenol A in NF-SB-MBR operation
Figure 5-6. \( C_\text{in} \), \( C_\text{p} \) and CRT changes of amtrimline in NF-SB-MBR operation

Figure 5-7. \( C_\text{in} \), \( C_\text{p} \) and CRT changes of naproxen in NF-SB-MBR operation
Figure 5-8. Permeate concentration of target OMPs after NF.
Chapter 6. Conclusions and Suggestion

6.1 Conclusions

A typical aerobic non-acclimated activated sludge was cultured by SBR mode for 6 months. OMPs removal mechanisms were studied using the sludge by a batch test. Hydrolysis and volatilization could be ignored in the removal process, but adsorption and biodegradation were the main routes. For compounds like methylparaben, adsorption was the only removal mechanism due the strong electrostatic attraction, while for compounds like bisphenol A, biodegradation removal surpassed the adsorption removal. For most of compounds, adsorption and biodegradation occurred simultaneously. The adsorption and biodegradation mechanism were explained, and proper models were used to simulate the kinetics. What is more, NaN₃ was an effective inhibitor for aerobic sludge. The inhibition between NaN₃ and high temperature sterilization was compared, and NaN₃ inhibition was suggested to be a better approach in this study.

The removal of OMPs by non-acclimated and acclimated activated sludge was compared. It was found that the bioreactor effluent OMPs concentration showed three trends: decreasing, increasing, and stable. The decreasing trend suggested an adaptation of the sludge, the stronger initial removal, the quicker it could reach new equilibrium. The increasing trend was mainly caused by strong adsorption, in which the OMPs concentration was very low before the sorption points were fully occupied. The stable trend could be classified into two situations: no removal and quick removal. For the latter situation, the stable OMPs concentration suggested the removal ability: low concentration indicated strong removal.
The stable concentrations were compared, and the result corresponded to the batch test results.

A novel NF-SB-MBR operation was proposed and operated. Several OMPs concentration in the bioreactor were found to increase intensively, which suggested good rejection by NF membrane. CRT was related to rejection rate, high rejection rate indicated long CRT.

**6.2 Suggestions**

In the adaptation test, molecular biology analysis is needed. The results will give information of bacteria culture changes and explain the adaptation phenomena.

A batch test of the removal kinetic after the NF-SB-MBR was conducted to find if there is enhancement of the removal ability when CRT was longer.

The adsorption mechanism was not yet fully understood. Usually, the adsorption was related to extracellular polymeric substance (EPS), yet few studies have studied the role of EPS in adsorption in CAS, and an EPS extraction method need to be developed and evaluated.

The same study could be applied to anaerobic sludge.
References


Appendix A: The structure of target OMPs

- Acesulfame
- Amitriptyline
- Atenolol
- Atrazine
- Bezafibrate
- Bisphenol A
- Caffeine
- Ibuprofen
- Iopromide
- Methyparaben
- Naproxen
- Oxybenzone
- Primidone
- Propylparaben
Carbamazepine

Sucralose

Clofibric acid

Sulfamethoxazole

DEET

TCEP

Diclofenac

TCPP

Dilantin

TDCPP

Diphenhydramine

Trimethoprim

Gemfibrozil
Appendix B: MS parameter

ESI+ mode

<table>
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<th>Compound</th>
<th>Retention time (min)</th>
<th>Precursor ion (m/z)</th>
<th>Product ion (m/z)</th>
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### ESI- mode

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Appendix C: Removal of target OMPs in batch aerobic activated sludge reactor

Adsorption and biodegradation of amitriptyline by aerobic activated sludge

Adsorption and biodegradation of atenolol in aerobic activated sludge

Adsorption simulation curve of atenolol by aerobic activated sludge

Removal curves of atrazine by aerobic activated sludge
removal curves of benzafibrate by aerobic activated sludge

biodegradation simulation curve of benzafibrate by aerobic activated sludge

removal curves of bisphenol A by aerobic activated sludge

biodegradation simulation curve of bisphenol A by aerobic activated sludge
removal curves of caffeine by aerobic activated sludge

removal curves of diclofenac by aerobic activated sludge

adsorption simulation curve of diclofenac by aerobic activated sludge

biodegradation simulation curve of diclofenac by aerobic activated sludge
removal curves of diphenhydramine by aerobic activated sludge

adsorption simulation curve of diphenhydramine by aerobic activated sludge

removal curves of ibuprofen by aerobic activated sludge

biodegradation simulation curve of ibuprofen by aerobic activated sludge
removal curves of methylparaben by aerobic activated sludge by aerobic activated sludge

adsorption simulation curve of methylparaben by aerobic activated sludge

removal curves of naproxen by aerobic activated sludge by aerobic activated sludge

biodegradation simulation curve of naproxen by aerobic activated sludge
removal curves of oxybenzone by aerobic activated sludge by aerobic activated sludge

biodegradation simulation curve of oxybenzone by aerobic activated sludge

removal curves of propylparaben by aerobic activated sludge by aerobic activated sludge

adsorption simulation curve of propylparaben by aerobic activated sludge
removal curves of sulfamethoxazole by aerobic activated sludge by aerobic activated sludge

adsorption simulation curve of sulfamethoxazole by aerobic activated sludge

biodegradation simulation curve of sulfamethoxazole by aerobic activated sludge Sulfamethoxazole

removal curves of TCEP by aerobic activated sludge by aerobic activated sludge
adsorption simulation curve of TCEP by aerobic activated sludge
Appendix D: Removal trend of target OMPs in aerobic activated sludge bioreactor

Removal trend of acesulfame in aerobic activated sludge bioreactor

Removal trend of atenolol in aerobic activated sludge bioreactor

Removal trend of atrazine in aerobic activated sludge bioreactor

Removal trend of benzophenone in aerobic activated sludge bioreactor
Removal trend of bezafibrate in aerobic activated sludge bioreactor

Removal trend of bisphenol A in aerobic activated sludge bioreactor

Removal trend of caffeine in aerobic activated sludge bioreactor

Removal trend of carbamazepine in aerobic activated sludge bioreactor
Removal trend of clofibric acid in aerobic activated sludge bioreactor

Removal trend of DEET in aerobic activated sludge bioreactor

Removal trend of diclofenac in aerobic activated sludge bioreactor

Removal trend of dilantin in aerobic activated sludge bioreactor
Removal trend of diphenhydramine in aerobic activated sludge bioreactor

Removal trend of fluoxetine in aerobic activated sludge bioreactor

Removal trend of gemfibrozil in aerobic activated sludge bioreactor

Removal trend of ibuprofen in aerobic activated sludge bioreactor
Removal trend of iopromide in aerobic activated sludge bioreactor

Removal trend of naproxen in aerobic activated sludge bioreactor

Removal trend of oxybenzone in aerobic activated sludge bioreactor

Removal trend of promidone in aerobic activated sludge bioreactor
Removal trend of sucralose in aerobic activated sludge bioreactor

Removal trend of sulfamethoxazole in aerobic activated sludge bioreactor

Removal trend of TCEP in aerobic activated sludge bioreactor

Removal trend of TCPP in aerobic activated sludge bioreactor
Removal trend of TDCPP in aerobic activated sludge bioreactor

Removal trend of trimethoprim in aerobic activated sludge
Appendix E: $C_{in}$, $C_p$ and CRT changes in NF-SB-MBR operation

$C_{in}$, $C_p$ and CRT changes of caffeine in NF-SB-MBR operation

$C_{in}$, $C_p$ and CRT changes of clofibric acid in NF-SB-MBR operation
$C_{\text{in}}$, $C_p$ and CRT changes of diclofenac acid in NF-SB-MBR operation

$C_{\text{in}}$, $C_p$ and CRT changes of dilatinate acid in NF-SB-MBR operation
C<sub>in</sub>, C<sub>p</sub> and CRT changes of gemfibrozil in NF-SB-MBR operation

C<sub>in</sub>, C<sub>p</sub> and CRT changes of iopromide in NF-SB-MBR operation
C<sub>in</sub>, C<sub>p</sub> and CRT changes of sulcralose in NF-SB-MBR operation