Investigation into the Removal of the By-product NDMA (N-Nitrosodimethylamine) from Ozonation Process in Wastewater Treatment

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Water and Environmental Engineering
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Preface

This thesis is a conclusion of my master's project during the two years that I have spent in Water Resources Engineering at Lund University, where I had the chance to gain knowledge and experience a different life in Sweden.

To complete this thesis as well as my master's project, I have received so much kind support and generous help from my family, my friends, and my university. I am grateful to my family for their full support, otherwise, I have had no chance to study at Lund university. Here I give all my respect and appreciation to my supervisor Per Falås and my examiner Michael Cimbritz. Mr. Cimbritz offered the opportunity for me to work on such an interesting topic. Mr. Falås has shown me what an excellent teacher is like. He is patient, kind, responsible, wise, and professional. I also hold a grateful heart to Gertrude Persson and Stina Karlsson for their kind help in the laboratory. My thanks are also delivered to the staff at Sjölunda WWTP, Lundåkra WWTP and Klippan WWTP for their generous help with the experimental materials.

Finally, I feel so lucky that I met our WRE group here in Lund. I love everyone in my class and also wish them a bright future and a happy life!

Summary

In people's modern life, daily usage of artificial compounds such as active pharmaceuticals ingredients (API) is usual. These compounds are likely to end up as micropollutants in the municipal wastewater. Municipal wastewater is the major source of pharmaceuticals in the aquatic environment. These chemicals can affect the health and behavior of wildlife and the local ecological system. Thus, it is necessary to remove these compounds through WWTPs. The main mechanics of micropollutants removal during treatment processes are sorption and biological degradation.

The toxicity may increase after ozonation due to the formation of ozonation transformation products (OTPs) and oxidation by-products (OBPs). To eliminate possible negative ecotoxicological effects caused by biodegradable OTPs and OBPs generated during ozonation, an additional biological post-treatment is needed, such as sand filter, moving bed reactor and fixed bed reactor.

This study aims to investigate the degradation of the ozonation by-product, NDMA, by different biomasses (suspended and attached growth) at different redox conditions (oxic and anaerobic). Together with NDMA, three other pharmaceuticals that are commonly detected in wastewater have been also investigated in order to make a comparison with NDMA. The work on the degradation of NDMA and three pharmaceuticals with suspended and attached growth under different redox conditions resulted in several interesting observations:

① NDMA could be completely degraded under oxic redox condition by the suspended biofilm carriers.
② Higher degradation rates of NDMA and the three pharmaceuticals were observed under oxic than anoxic conditions.
③ NDMA has shown similar characteristics of degradation as diclofenac, such as in what situation it is degradable, but NDMA has been considered to be degraded at a larger percentage than diclofenac.
④ Some pharmaceuticals turned out to be easier to be degraded by suspended biofilm carriers than by activated sludge under both redox conditions.
⑤ Ibuprofen and naproxen could be fully degraded under oxic condition by both activated sludge and suspended biofilm carriers.

Table Of Contents

1. Introduction

In people's modern life, daily usage of artificial compounds such as active pharmaceuticals ingredients (API) is usual. These compounds are likely to end up as micropollutants in the municipal wastewater (Fick *et al.*, 2010; Hollender *et al.*, 2009; Richardson, 2010; Gerrity and Snyder, 2011; Huber *et al.*, 2005). Municipal wastewater is the major source of pharmaceuticals in the aquatic environment (Daughton and Ternes, 1999). These chemicals can affect the health and behavior of wildlife and the local ecological system.

Many pharmaceuticals would pass through WWTPs if there is not any process to remove them. Thus, the removal of these pharmaceuticals in WWTPs before discharge is necessary. The main mechanics of micropollutants removal during biological treatment are sorption and biological degradation (Ternes *et al.*, 2004a). Sorbed micropollutants can be removed during the removal of influent particulate matter and excess sludge, and it depends on different molecular characteristics of the micropollutants and the sorbing particulate matter. However, there are not any generally valid surrogate parameters that can describe this removal mechanism quantitively (Joss *et al.*, 2008).

Also, it shows that the degradation of pharmaceuticals through conventional activated sludge treatment (CAS) is limited. Longer sludge retention time may result in an improved degradation, but most compounds could not be degraded under a certain level (Najm and Trussell, 2001). Therefore, more advanced treatment technologies are usually recommended to achieve further removal of pharmaceuticals.

Ozonation and activated carbon treatments are two main processes responsible for micropollutants removal after centralized biological treatment. The estimated total costs of these two processes are between 0.05-0.2€ per m^3 treated water, which is economically feasible (Joss *et al.*, 2008). Ozonation is a very promising method to remove these micropollutants in WWTPs, since it has shown a high potential of oxidizing pharmaceuticals in drinking water and wastewater. Doses with 5-15 mg/L O_3 will lead to a removal of most parent pharmaceuticals except for iodinated X-ray contrast media. Besides, ozonation has an additional advantage of achieving partial disinfection (Joss *et al.*, 2008).

Ozonation may lead to the formation of toxic ozonation transformation products (OTPs) and oxidation by-products (OBPs) (Stalter *et al.*, 2010a, 2010b). To eliminate possible negative ecotoxicological effects caused by biodegradable OTPs and OBPs generated during ozonation, an additional biological post-treatment is needed, such as sand filter, moving bed reactor and fixed bed reactor (Bourgin *et al.*, 2017). Besides biological post-treatment, granular activated carbon filtration is also an alternative (Bourgin *et al.*, 2017).

These by-products involve N-Nitrosodimethylamine (NDMA) and bromate, which have turned out to be possible obstacles for a healthy environment. For example, NDMA has attracted wide attention as being highly hepatotoxic and a known carcinogen in lab animals (Tricker and Preussmann, 1991). Therefore, removal of NDMA has become a crucial issue for environmental sanitation and human hygiene.

The vapor pressure of NDMA is estimated to be relatively high at 360 Pa at 20°C (Klein, 1982). As a result of the high water solubility of NDMA, the Henry's law constant for NDMA is estimated to be low at $2.6*10^{-4}$ atm M^{-1} 20 °C (ATSDR, 1989; Mirvish *et al.*, 1976).

Therefore, volatilization from natural waters and air stripping stands few chances to remove NDMA from solution significantly. Being a small, uncharged molecule gives NDMA a poor opportunity of being removed by membranes (Mitch *et al*., 2003).

One alternative method to evaluate the removal of organic micropollutants and other organic compounds is the combined use of ^{14}C-labeled compounds and liquid scintillation counting. The method has previously been applied to assess biological degradation of diclofenac, ibuprofen and naproxen in biological incubations with carriers and biologically treated water. The possibilities of using ^{14}C-labeled NDMA for assessing the removal in contact with suspended sludge and biofilm carriers have, however, not been fully explored.

Previous studies with parent NDMA have indicated that the compound can be biodegradable in post-treatments such as sand filters and sludge carriers. By using ^{14}C-labeled NDMA, it may be possible to further track the labeled ^{14}C in order to investigate the degradation of NDMA.

1.1 Aim

This thesis aims to investigate the efficiency of the degradation of NDMA in contact with different biomasses at different redox conditions, such as oxic and anaerobic conditions. With purpose of classifying the degradation rates in different situations, experiments on NDMA will be conducted and compared together with three other micropollutants, which are ibuprofen, naproxen, and diclofenac.

2. Background

This section provides information about micropollutants, redox conditions, suspended growth, attached growth, and information about sampling wastewater treatment plants.

2.1 NDMA and investigated pharmaceuticals

For many pharmaceuticals, a significant reduction in the water phase can occur during their passage through WWTP (Golet *et al.*, 2003; Heberer, 2002; Ternes, 1998). There are usually two processes that are responsible for this reduction, which are named as sorption and biodegradation. Information regarding the sorption and biodegradation of the investigated compounds are therefore provided in this section. Figure 2.1-2.4, respectively, show the molecule formula of diclofenac, ibuprofen, naproxen and NDMA as well as the locations of labeled ^{14}C on each molecule.

2.1.1 Diclofenac

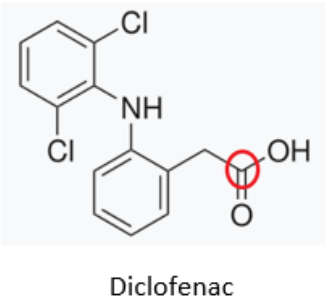


Figure 2.1. Molecule formula of diclofenac and the location of labeled ^{14}C.

Diclofenac is a nonsteroidal anti-inflammatory drug (NSAID). It has been reported to be more potent, weight for weight, than ibuprofen and naproxen in various animal models of suppressing acute and chronic inflammation, pain and hyperthermia (Todd and Sorkin, 1988).

Sorption of diclofenac has been determined that in primary sludge (K_d=459±32 L kg_{ss}^{-1}, where K_d is solid-water distribution coefficient) and in secondary sludge (K_d=16±3 L kg_{ss}^{-1}), leading to a partitioning of 5-15% to particulate matter in the influent (for sludge production ranging from 100 to 400 g_{ss} m^{-3}) and <5% in the secondary sludge (Ternes *et al.*, 2004).

Diclofenac has shown that it is very hard to be biodegraded in activated sludge system (Suarez *et al.*, 2010; Joss *et al.*, 2006; Abegglen *et al.*, 2009), but can sometimes be degraded by biofilm systems (Falås *et al.*, 2018).

2.1.2 Ibuprofen

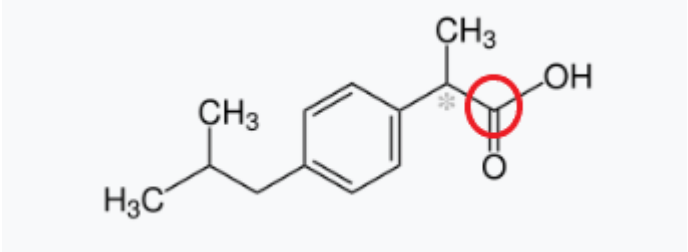


Figure 2.2. Molecule formula of ibuprofen and the location of labeled ^{14}C.

Ibuprofen is an anti-inflammatory drug that was introduced for use in human in England in 1967 and the US in 1974. It has similar anti-inflammatory properties to those of aspirin, but with less adverse effect on the stomach (Thomas and Kantor, 1979).

Ibuprofen was found to own an extremely low sorption coefficient (K_d=7.1±2.0 L kg_{ss}^{-1}, where K_d is solid-water distribution coefficient). Hence, sorption plays no significant role for the removal of it in wastewater treatment plants (Ternes *et al.*, 2004).

Ibuprofen has been proved to be rather easily biodegraded by both activated sludge and suspended biofilm carriers (Suarez *et al.*, 2010; Joss *et al.*, 2006; Falås *et al.*, 2018; Abegglen *et al.*, 2009).

2.1.3 Naproxen

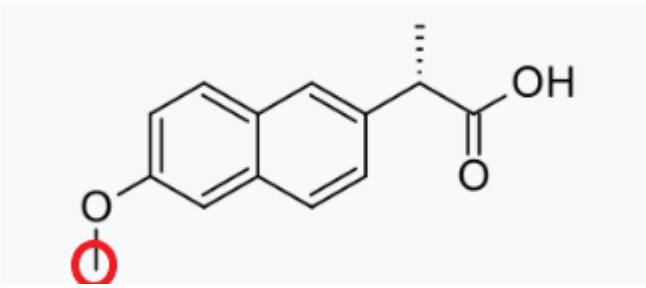


Figure 2.3. Molecule formula of naproxen and the location of labeled ^{14}C.

Naproxen is a nonsteroidal anti-inflammatory drug (NSAID) that is used in painful and inflammatory rheumatic and also some specific nonrheumatic conditions (Todd and Clissold, 1991).

The sorption coefficient K_d of naproxen is 6.5±1.4 L kg_{ss}^{-1} according to previous studies. Therefore, sorption is not the dominant mechanism to remove naproxen in wastewater treatment processes (Zhang *et al.*, 2017).

Previous study has indicated that naproxen is quite easily degraded by both activated sludge and biofilm carriers (Suarez *et al.*, 2010; Joss *et al.*, 2006; Falås *et al.*, 2018; Abegglen *et al.*, 2009).

2.1.4 Previous studies on the degradation of Dic, Ibu, and Nap

In earlier researches, these three pharmaceuticals have shown different performance of being degraded during conventional activated sludge process. Under anoxic condition, ibuprofen showed a degradation percentage of 37 ± 26, while naproxen and diclofenac showed degradation percentages of 9 ± 13 and 2 ± 5 respectively. Under aerobic condition, ibuprofen and naproxen indicated good degradation percentages, which were 95 ± 4 and 86 ± 5 respectively. However, diclofenac gave a degradation percentage of 22 ± 28, which was less than the other two pharmaceuticals (Suarez et al., 2010).

2.1.5 NDMA

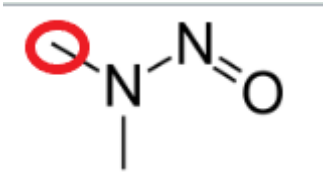


Figure 2.4. Molecule formula of NDMA and the location of labeled ^{14}C.

N-Nitrosodimethylamine (NDMA) is a member of a family of extremely potent carcinogens, N-nitrosamines (U.S. EPA, 2002). It has drawn people's attention by appearing in food, polluted air and even drinking water. According to a survey of NDMA that was done in California drinking water, NDMA did not only occur in the areas proximal to facilities that used UDMH-based fuels, but also was detected in the process of chlorine disinfection in drinking water and wastewater, especially in those regions where the chlorinated wastewater effluent was used for aquifer recharge (Mitch, *et al.*,2003). Although NDMA formation is commonly considered to be related to chloramination, recent studies have shown direct NDMA formation also occurs during ozonation (Andrzejewski *et al.*, 2008). NDMA has also appeared in dried municipal sewage sludge that has been used for agricultural fertilizer, but the NDMA here might have been formed from biologically mediated nitrosation during anaerobic digestion (Brewer *et al.*, 1980; ATSDR, 1989).

NDMA is not an emerging contaminant even if it has raised ecotoxicological concerns. Toxicologists have studied nitrosamines about their influence on health since 1960s. The biggest concern about NDMA is its widespread occurrence over different aspects that are related to people's daily life, for example, in food and consumer product, especially beer, meats cured with nitrite, tobacco smoke, and rubber products including baby bottle nipples (IARC, 1978). During 1970s, NDMA was detected even in air and water near industrial factories, and it was suggested by some researchers that NDMA formed in the atmosphere could be responsible for the rising urban cancer rates (Shapley, 1976).

2.2 Advanced treatment of organic micropollutants

Ozonation and activated carbon treatment are proposed as main alternatives for micropollutants removal after centralized biological treatment. The estimated total costs of these two processes are between 0.05-0.2€ per m^3 treated water, which has been considered economically feasible. Ozonation is a very promising method to remove these micropollutants in WWTPs, since it has shown a high potential of oxidizing pharmaceuticals in drinking water and wastewater. Doses with 5-15 mg/L O_3 will lead to a removal of most parent pharmaceuticals except for iodinated

X-ray contrast media. Besides, ozonation has an additional advantage of achieving partial disinfection (Joss *et al.*, 2008).

2.3 Biological post-treatment

Toxicity in wastewater has shown a trend to decrease again after biological post-treatment because of the biodegradability of the toxic ozonation transformation products (OTPs) and oxidation by-products (OBPs) (Stalter *et al.*, 2010a, 2010b). To eliminate possible negative ecotoxicological effects caused by biodegradable OTPs and OBPs generated during ozonation, an additional biological post-treatment is needed, such as sand filter, moving bed reactor and fixed bed reactor (Bourgin *et al.*, 2017).

2.4 Formation of NDMA during chemical oxidation

Previous knowledge on the formation of NDMA during chemical oxidation through chloramination and ozonation is summarized in this section.

2.4.1 NDMA formation during chloramination

In 1989, a survey of 145 drinking water treatment plants was prompted in Ohsweken, Ontario in Canada due to the rising concentrations of NDMA in treated drinking water (Jobb *et al.*, 1994; MOE, 1998). It showed that the concentrations in the treated drinking water from most drinking water treatment plants were less than 5 ng/L, while some were over 9 ng/L. In another similar survey conducted in 2001 by California Department of Health Services, the results indicated that 3 of the 20 chloraminated supplies contained NDMA concentrations exceeding 10 ng/L, although none of the 8 drinking water treatment plants which only used free chlorine disinfection exhibited NDMA concentrations above 5 ng/L. Most samples contained less than 10 ng/L NDMA, but 1 of the 4 drinking water treatment plants that employed anion exchange treatment also contained NDMA concentrations more than 10 ng/L (Tomkins *et al.*, 1995; Tomkins and Griest, 1996).

Comparing to drinking water treatment plants, there usually are relatively higher concentrations of NDMA in the effluent from conventional and advanced wastewater treatment plants. And NDMA often exists in the raw sewage prior to the chlorination. As a result of the removal processes during secondary treatment, the effluent before chlorination often contains NDMA less than 20 ng/L, while some industrial input can lead to a higher concentration of NDMA (Mitch, *et al.*, 2003). And chlorination would usually form 20-100 ng/L NDMA in the secondary wastewater effluent (Mitch and Sedlak, 2002). In wastewater recycling plants that receive secondary wastewater effluent, NDMA concentration may increase by around 30-50 ng/L in microfiltration effluent due to the chlorination process before the membrane to prevent biological growth.

2.4.2 NDMA formation during ozonation

As the shortage of potable water has been a significant issue in more and more communities, the reuse of wastewater for increasing overall water supply has been considered (Marti *et al.*, 2015). Ozonation is an efficient method for treating pathogens and trace organic contaminants that it becomes a very promising treatment technology for potable water reuse applications

(Marti *et al.*, 2015). However, NDMA, a by-product during ozonation, could be a barrier in this field.

Ozonation of aqueous solutions of dimethylamine (DMA) could lead to the formation of NDMA. The yield of this reaction is below 0.4% in relation to DMA, but it increases with increasing pH. And other variables that can control the yield of reaction are contact time, ozone/DMA ratio and radical scavengers. Thus, NDMA is often produced as a by-product of ozonation in wastewater treatment, which can be formed in a specific and common range of ozone/DMA ratios. Since NDMA can be formed directly from the reaction of monochloramine with DMA, and drinking water and wastewater usually contain DMA or related compounds as well as ammonia, NDMA should be considered as a potential by-product of disinfection (Andrzejewski *et al.*, 2008).

2.5 Suspended and attached growth

Biological treatment systems for wastewater treatment can generally be divided into suspended and attached growth systems. Activated sludge is the most frequently applied suspended growth process and the MBBR technology is a frequently applied biofilm technique.

2.5.1 Activated sludge process

The activated sludge process is the most widely applied biological wastewater treatment method (Gernaey *et al.*, 2004). Most wastewater treatment plants have used it as a core part of the treatment processes. In the activated sludge process, microbial biomass in suspension (the activated sludge) is used to remove pollutants (Gernaey *et al.*, 2004). With different designs, activated sludge treatments are not only able to remove organic carbon substances, but also able to achieve both biological nitrogen (N) removal and biological phosphorus (P) removal (Gernaey *et al.*, 2004). Since the suspended activated sludge process is the most widely used biological treatment at municipal WWTPs, technical and operational solutions that can improve micropollutant removal in this process are highly desirable (Falås *et al.*, 2013). Previous studies have shown that upgrading of high loaded activated sludge processes to nitrogen removal through enlargement of the treatment basin enhances removal of some micropollutants (Andersen *et al.*, 2003; Schaar *et al.*, 2010)

2.5.2 MBBR

Moving Bed Biofilm Reactor (MBBR) which is now broadly used around the world, was introduced around 30 years ago. It has been successfully operated in urban and some industrial wastewater treatment plants (Rusten *et al.*, 2006). MBBRs are designed to offer the advantages of the biofilm process without its drawbacks. Besides, MBBRs also reduces channeling and clogging. The purpose of MBBR was adopting the best features of biofilter processes as well as those of activated sludge in one reactor (Rusten *et al.*, 2006). Comparing with conventional activated sludge process, it is more compact, and it has stable removal efficiency and simplicity of operation.

The removal of micropollutants in a Moving Bed Biofilm Reactor process has previously been investigated under aerobic and anaerobic conditions (Torresi *et al.*, 2019). The experiments showed that aerobic conditions could enable degradation of several

micropollutants, while the anaerobic conditions resulted in lower removal efficiencies (Torresi *et al.*, 2019).

2.6 Redox conditions

Wastewater treatment processes for Nitrification/denitrification applies various redox conditions. To enable oxidation of ammonia oxygen is required for the oxidation to nitrate. To convert nitrate to nitrogen gas, anoxic conditions are applied where nitrate is used as an electron acceptor during the degradation of organic carbon sources.

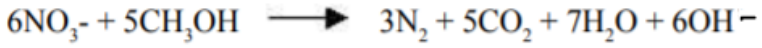
Nitrification is a two-step process during which ammonium is firstly converted to nitrite by bacteria, such as *Nitrosomonas*, and bacteria, such as *Nitrobacter*, then complete the conversion of nitrite to nitrate. These reactions are always coupled and proceed rapidly to the nitrate form, hence nitrite levels at any time are usually low.

Denitrification is performed with nitrate as electron acceptor by heterotrophic microorganisms using organic carbon.

Chemical formulas:

- Nitrification equation:

- Denitrification equation:



2.7 Liquid scintillation counting

Liquid scintillation counting is the measurement of radioactive activity of a sample material which uses the technique of mixing the active material with a scintillation liquid, and counting the resultant photon emissions. In liquid phase, once ^{14}C is decayed, beta radiation is unleashed, which can induce light pulses in the scintillation liquid, and then liquid scintillation counter records the number of light pulses per minute. When $^{14}CO_2$ is formed during the reaction, it is trapped in a strong base for liquid scintillation counting later.

3. Materials and methodology

To evaluate and compare the removal of NDMA and three pharmaceuticals in contact with suspended sludge and biofilm carriers, four sets of experiments were performed. The experimental conditions are summarized in table 3.1 and detailed in this section.

Table 3.1. Combinations of biomasses and redox conditions for each pharmaceutical.

Biomass / Redox condition	Activated sludge	Suspended biofilm carriers
Anaerobic	Bottle 1	Bottle 2
Oxic	Bottle 3	Bottle 4

3.1 Biomasses

Biomass and wastewater for the experiments were collected from full-scale wastewater treatment plants. Oxic carriers were collected from Klippan WWTP, anaerobic carriers from Sjölunda WWTP, suspended sludge from Lundåkra WWTP and effluent wastewater from Lundåkra WWTP.

3.2 NDMA and selected pharmaceuticals

Diclofenac, Ibuprofen, Naproxen and NDMA were ^{14}C-labeled to enable degradation studies through liquid scintillation counting and CO_2-trapping.

3.3 Experimental set-up

Experiments were designed to investigate degradation of NDMA and other three pharmaceuticals with suspended and attached growth under different redox conditions (table 3.1). Batch experiments were performed, with the individual compounds at a radiation level of 0.1 µCi/L. Each compound was incubated in 4 bottles with 150 mL wastewater. Biomass was added as suspended sludge or carrier-biofilms to a target concentration of 1.7 g/L. Then experiments were performed either under oxic condition or anaerobic condition with suspended biofilm carriers or activated sludge. In total, there were 16 bottles being taken care of during the whole experiment.

In the anaerobic experiment oxygen was depleted in the reactor prior to experiment. In order to do this, the effluent wastewater that was going to be used in anaerobic condition was bubbled with N_2 gas for 12 hours before and for 5 minutes after being transported into the bottles to remove the oxygen. Nitrate was added as electron acceptor in the anaerobic bottles to reach a concentration of NO_3-N was 200 mg/L at the beginning of the experiment.

pH of it was adjusted to 7 by adding $H_2PO_4^-$ or NaOH. The amount of biomass in the sludge was measured as suspended solids, SS, according to SS-EN 872:2005. The amount of biofilm on the carriers was measured in three triplicates before and after biofilm removal. Results from the biomass measurements are summarized in Table 3.2.

Table 3.2. Measurement and Calculation of Biomass Amount.

Biomass	Number of carriers	Sludge Volume (mL)	Amount of Biofilm per carrier (g/carrier)	Total Water volume (mL)	Biomass Concentration (g/L)
Suspended biofilm carriers (oxic)	3	-	0.0847	150	1.7
Suspended biofilm carriers (anaerobic)	33	-	0.0077	150	1.7
Activated sludge (oxic)	-	30	-	150	1.7
Activated sludge (anaerobic)	-	30	-	150	1.7

3.4 Sampling

The way of monitoring the degradation of pharmaceuticals was to measure the radioactivity of the radiation-labeled ^{14}C in the liquid and gas inside the 16 bottles respectively. In order to trap the CO_2 that is released in the bottle, a tube with NaOH solution in it was set inside the bottle. After starting the experiment for 30 minutes, samples of liquid in each bottle were collected. And after 1h, 2h, 3h, 4h, 6h, 8h, 12h, 24h, 30h, 48h, 72h, 96h, 120h, samples of both liquid and gas were collected respectively. For liquid, 1 mL sample was collected, and for gas, 0.5 mL sample was collected.

Only samples of liquid were centrifuged in a centrifuger right after being collected, and the purpose was to separate the pharmaceuticals and biomass so that the reaction was stopped. Then 0.5 mL of the liquid supernatant after centrifuged were transported out for the liquid scintillation counting measurement later.

3.5 Liquid scintillation counting

^{14}C analysis of the samples from liquid phase and the CO_2 trap was conducted by using this method. Samples (0.4 mL from liquid phase and 0.2 mL from CO_2 trap) were pipetted into vials together with 1.6 mL and 1.8 mL scintillation liquid (Hionic-Flour, PerkinElmer). Samples were measured in a liquid scintillation counter (4910 TR, PerkinElmer) after mixing for 5 minutes for each (Falås *et al.*, 2018). By using liquid scintillation counting method, the ^{14}C can be detected either in the samples from liquid phase (the compound remains undegraded) or in the samples from CO_2 trap (the compound has been degraded).

3.6 Wastewater treatment plants

The wastewater treatment plants that were sourced for biomass or wastewater are briefly described in this section.

3.6.1 Sjölunda WWTP

Sjölunda wastewater treatment plant takes care of domestic wastewater from around 330 000 inhabitants and also from some industries (VA SYD, 2017). The received wastewater first passes through a sieve and an aerated grit chamber, where iron-based coagulant is added (VA SYD, 2017). Smaller particulate matter and phosphorous can be precipitated here. There is a clarifier following the grit chamber and an activated sludge system locates after it for BOD removal (VA SYD, 2017). The activated sludge is separated by a sedimentation basin before the water flows into a nitrifying trickling filter (VA SYD, 2017). The water then continues into an anoxic Moving Bed Biofilm Reactor for denitrification (VA SYD, 2017). The final stage is flotation in which process particulate material is removed from the wastewater before the water can be discharged into Öresund (VA SYD, 2017).

3.6.2 Lundåkra WWTP

Lundåkra wastewater treatment plant receives domestic wastewater from about 40 000 inhabitants. The wastewater is first treated by a series of mechanical treatments including sieves and a grit chamber, which is followed by two sedimentation basins. The biological treatment is functioning subsequently by an activated sludge process with a BioDenipho configuration for biological nitrogen and phosphorous removal. The final part of the treatment process is a chemical treatment. In this part, a coagulant is added into the water to sediment phosphorous before the water is released into Öresund (NSVA, 2017).

3.6.3 Klippan WWTP

Klippan wastewater treatment plant is connected with about 13 000 PE. Incoming wastewater is mainly domestic wastewater, which is treated mechanically through screening, grit removal and sedimentation. The following activated sludge treatment consists of an anoxic part followed by an oxic part, where carriers are used in one compartment. The carrier fill-ratio in the carrier compartment is 40% (Falås *et al.*, 2018).

4. Results and discussion

In this section, the results from the batch experiments with ^{14}C-labeled diclofenac, ibuprofen, naproxen and NDMA are presented and possible reasons for the observed outcomes are also discussed. Figure 4.1-4.4, respectively, show the percentages of ^{14}C partitioning of diclofenac, ibuprofen, naproxen and NDMA in samples from liquid phase and CO_2 traps.

4.1 Diclofenac

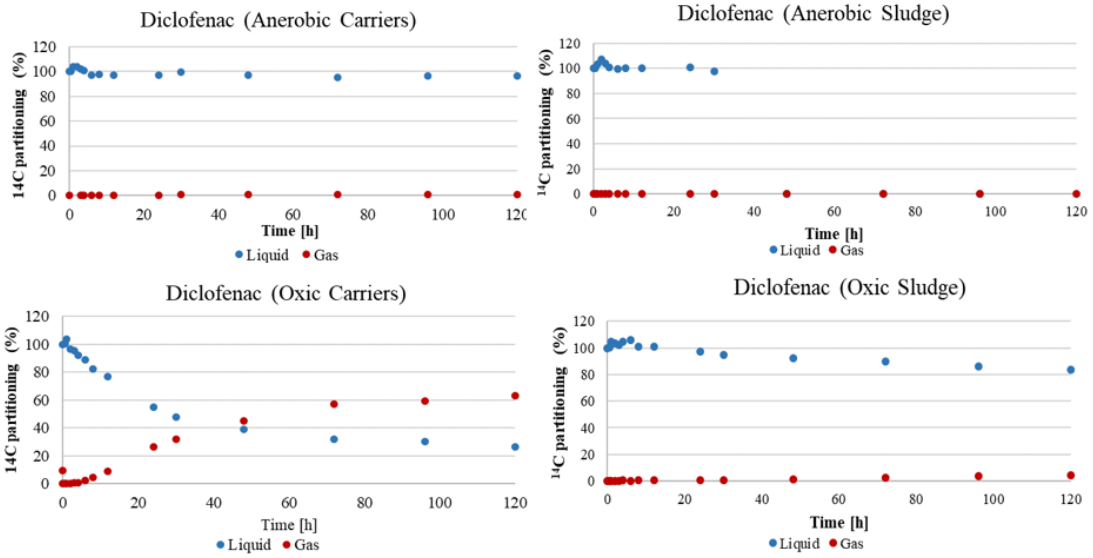


Figure 4.1. Percentage of ^{14}C partitioning of diclofenac in samples from liquid phase and CO_2 trap.

Previously diclofenac has been observed too hard to be biodegraded in activated sludge systems, but possible to degrade in biological systems with carriers. During the reaction with activated sludge, diclofenac showed no removal under both redox conditions. With oxic carriers, on the other hand, degradation of diclofenac could be observed. Part of the radio-labeled carbon did however remain in the liquid phase at the end of the experiment. The degradation experiment with diclofenac and activated sludge under anaerobic condition could not be completed, as the bottle broke during the experiment. Nonetheless by referencing previous studies as well as analyzing the data before 30h, diclofenac can be considered to be undegradable with anaerobic sludge.

4.2 Ibuprofen

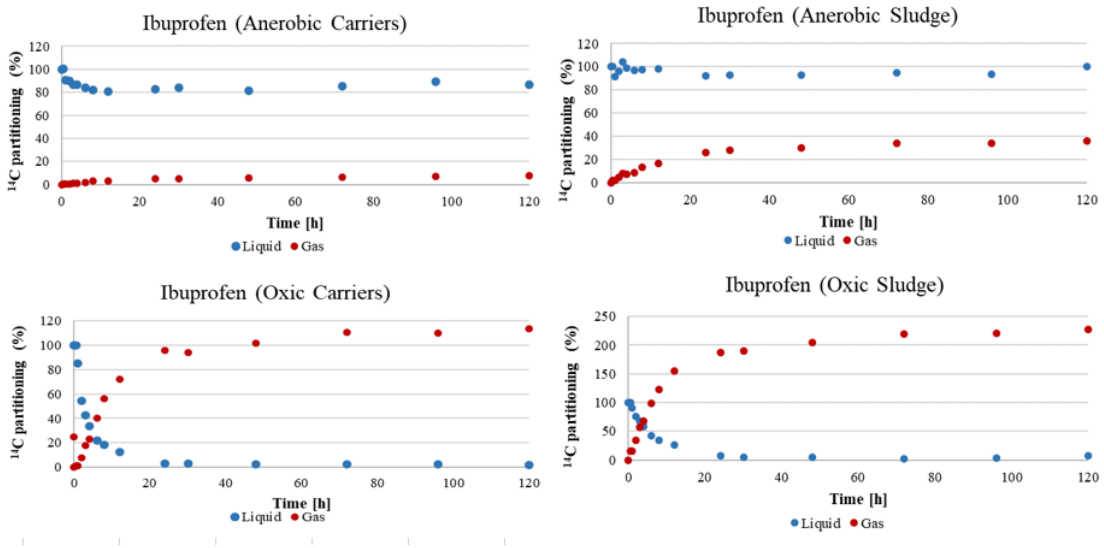


Figure 4.2. Percentage of ^{14}C partitioning of ibuprofen in samples from liquid phase and CO_2 trap.

It has been proved that ibuprofen can be rather easily biodegraded by both activated sludge and suspended biofilm carriers. The experiments with ibuprofen and activated sludge or suspended biofilm carriers under oxic conditions resulted in a complete degradation of ibuprofen. Much slower degradation, if any, was observed under anaerobic conditions with the two biomasses. As indicated in Figure 4.2, the degradation of ibuprofen by activated sludge under oxic condition, resulted in a 200% formation of $^{14}CO_2$, but the reason for this remains unclear.

4.3 Naproxen

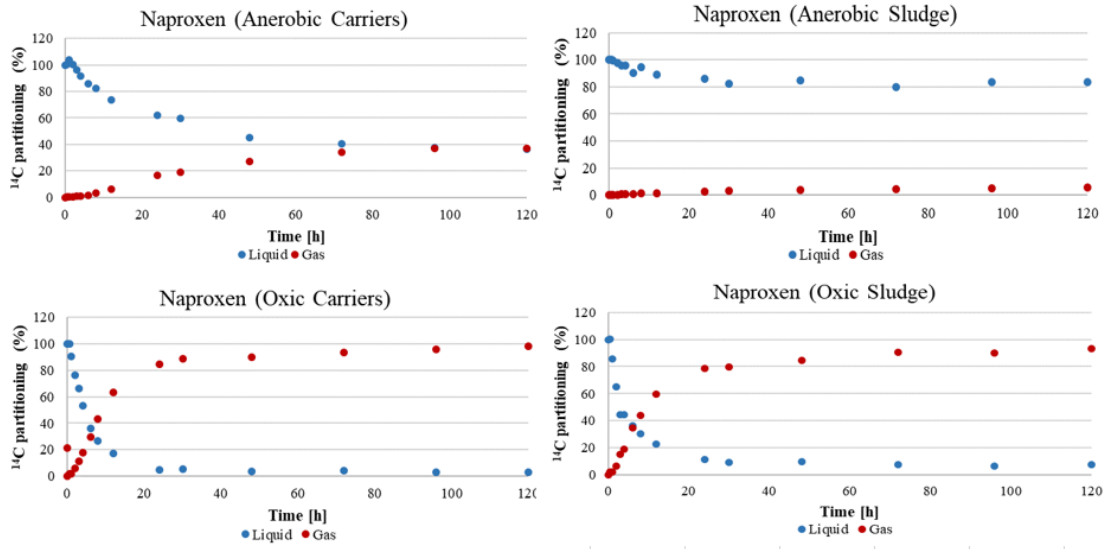


Figure 4.3. Percentage of ^{14}C partitioning of naproxen in samples from liquid phase and CO_2 trap.

Naproxen has been observed to be rather easily degradable by activated sludge and carriers. Generally, naproxen showed almost same degradation patterns as those of ibuprofen under different situations. Rapid and full degradation of naproxen occurred under oxic condition with activated sludge and suspended biofilm carriers. However, under anaerobic condition, naproxen showed no trend of being degraded by activated sludge, while some degradation could be observed with suspended biofilm carriers under anaerobic condition.

4.4 NDMA

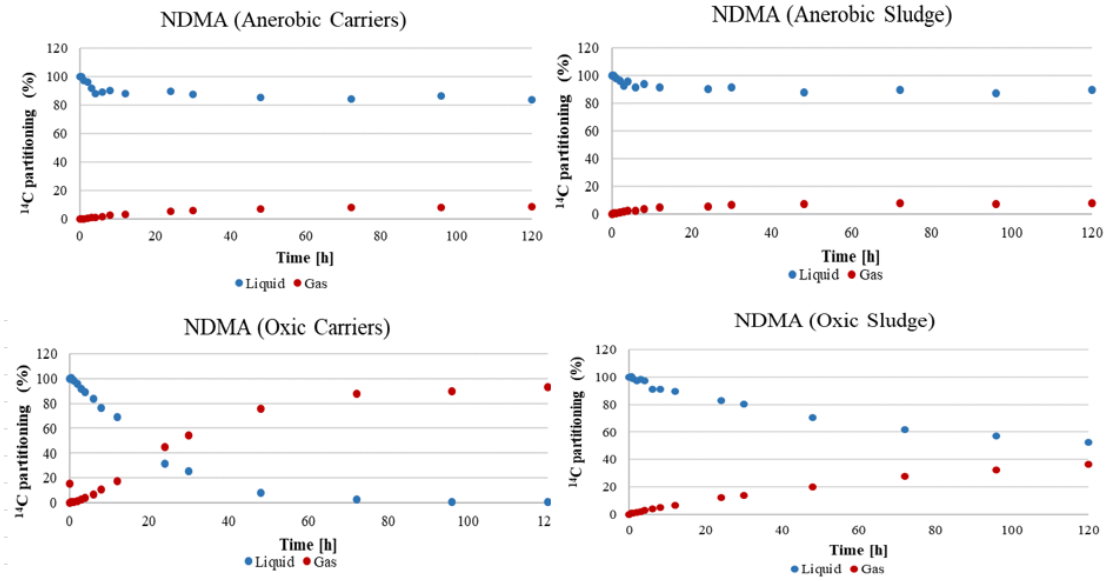


Figure 4.4. Percentage of ^{14}C partitioning of NDMA in samples from liquid phase and CO_2 trap.

NDMA, showed higher degradation rates under oxic condition than under anaerobic condition. Under oxic redox condition, it was fully degraded by the suspended biofilm carriers from Klippan WWTP, while a degradation of 50% degradation was observed for the activated sludge from Lundåkra WWTP. Limited degradation of NDMA was observed under anaerobic condition with suspended biofilm carriers from Sjölunda WWTP and activated sludge from Lundåkra WWTP.

4.5 Comparison of results

Higher removal rates were observed during oxic conditions than anaerobic conditions. Among the investigated compounds only naproxen was significantly degraded under anaerobic conditions, whereas the other compounds seemed to require oxygen for their degradation. Overall, ibuprofen, naproxen and diclofenac have all shown same results of being degraded by activated sludge as in earlier research, where oxic condition has been indicated to be more suitable for pharmaceuticals to be degraded. Both suspended biofilm carrier and activated sludge were able to fully degrade ibuprofen and naproxen under oxic conditions at a relatively fast rate.

Higher removal of the investigated micropollutants was generally observed for the biofilm carriers than the suspended sludge. The most pronounced difference was observed for

diclofenac. Diclofenac was not degraded by the suspended sludge, while it could be degraded by the suspended biofilm carriers under oxic redox condition. A clear difference was also observed for NDMA. These observations suggest that biofilm treatment with oxic conditions could be beneficial for biological post-treatments after ozonation when NDMA needs to be targeted.

NDMA was degraded at a pretty constant rate within the first 25 hours under oxic condition with suspended biofilm carriers, and then the reaction slowed down until NDMA was fully degraded after 60 h. Under the same conditions with suspended biofilm carriers, diclofenac showed a similar degradation trend as NDMA, while the final degradation percentage of diclofenac, which is around 70%, is smaller than that of NDMA.

Comparing the different biomasses, the suspended biofilm carriers from Klippan WWTP could degrade all the investigated pharmaceuticals, while the activated sludge from Lundåkra WWTP only could degrade ibuprofen and naproxen. However, the suspended biofilm carriers from Sjölunda WWTP and the activated sludge from Lundåkra WWTP, which were investigated under anaerobic condition, have turned out to be almost unable to degrade the pharmaceuticals.

The experiments also show the time scale of the degradation processes. It takes around 100 hours for diclofenac to be degraded at 70%. Ibuprofen as well as naproxen both need more than 20 hours to be completely degraded. And a complete degradation of NDMA requires about 70 hours. Overall, it usually takes more than 20 hours for the pharmaceuticals to be completely degraded (or at a large percentage), which is not feasible for the wastewater treatment plants to operate. The common hydraulic retention time (HRT) for each basin during the treatment process is only several hours, so there is a huge difference between the experiment results and reality. Therefore, to conduct these degradation processes in a real wastewater treatment plant still needs improvements about the degradation rates of these pharmaceuticals, which could remain as a future challenge.

5. Conclusion

The work on the degradation of NDMA and three pharmaceuticals with suspended and attached growth under different redox conditions resulted in the following observations:

- Oxic condition has turned out to be more suitable for the degradation of ibuprofen, naproxen, diclofenac and NDMA.
- Ibuprofen and naproxen could be fully degraded under oxic condition by both activated sludge and suspended biofilm carriers but were hardly degradable under anaerobic condition.
- NDMA could be completely degraded under oxic redox condition by the suspended biofilm carriers.
- NDMA and diclofenac could be degraded at higher rates with suspended biofilm carriers than with activated sludge under oxic conditions.
- NDMA showed similar characteristics of degradation as diclofenac, with no degradation under anaerobic conditions and higher degradation with suspended biofilm carriers than suspended sludge under oxic conditions.

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7. Appendix

7.1 Popular science summary

NDMA, a carcinogen in wastewater, has been degraded during lab experiments

N-Nitrosodimethylamine (NDMA) is a member of extremely potent carcinogens (compounds that can induce cancer) which has been detected in environmental water body, and thus can further affect people's health. However, it has recently been proved that NDMA can be degraded during wastewater treatment processes.

Carcinogens have widely drawn people's attention by appearing in food, polluted air and even in drinking water. NDMA is one of them, and it can be formed during drinking water and wastewater treatment processes.

The experiments aim to investigate the degradation of NDMA in wastewater. In order to assess the degradation level, three other common pharmaceuticals, which are diclofenac, ibuprofen and naproxen, were also tested. For each compound, 4 sets of experiment were conducted in different conditions. Each compound respectively reacted with two kinds of biomasses under the conditions with enough oxygen or with less oxygen. The results have shown that NDMA can be completely degraded under aerobic conditions, that is with sufficient amounts of oxygen.

The results of these experiments have shown a possible way to remove NDMA in wastewater in order to protect our aquatic environment as well as ourselves. With the proper type of biomass, preferably from a biofilm process, and optimum operational conditions in terms of oxygen levels, NDMA can be degraded.

However, in lab, a satisfying degradation of NDMA could need a pretty long time, which is not realistic to be applied in real wastewater treatment plants. Therefore, one future challenge could be looking for a method to raise the degradation rate of NDMA in order to apply this technique in wastewater treatment plants in reality.