Concept of Compound Retention Time for Organic Micro Pollutants in Anaerobic Membrane Bioreactor with Nanofiltration

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ABSTRACT

Concept of compound retention time for organic micro pollutants in anaerobic membrane bioreactor with nanofiltration

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Organic micropollutants (OMPs) have received more and more attention in recent years due to their potential harmful effects on public health and aquatic ecosystems, and eliminating OMPs in wastewater treatment systems is an important solution to control OMPs wastage. An innovative hybrid process, anaerobic membrane bioreactor with nanofiltration (AnMBR-NF), in which enhanced OMPs removal is possible based on the concept of compound retention time (CRT) through coupling anaerobic biodegradation and NF rejection, is proposed and examined in terms of preliminary feasibility in this study. First, NF membrane screening through sludge water dead-end filtration tests demonstrated that KOCH NF200 (molecular weight cut-off (MWCO) 200 Da, acid/base stable) performed best in organic matter rejection. Then, selected OMPs (ketobrofen and naproxen) in MQ water and a biologically treated wastewater matrix were filtered through NF200 under constant-pressure dead-end mode, with and without stirring, and several methods (contact angle, scanning electronic microscopy, Zeta potential, Fourier transform infra-red spectroscopy) were used to characterize membranes. Results show selected OMPs in MQ could be rejected (about 40%) by a clean NF200 membrane. The main rejection mechanism was initial absorption by the membrane followed by size exclusion (electric charge interaction plays a less important role). The wastewater matrix could enhance the rejection significantly (up

to 90%) because effluent organic matter (EfOM) enhanced size exclusion and electric charge interaction through blocking membrane pores and forming a gel layer as well as binding some OMPs through partitioning followed by retention by NF. Third, an anaerobic bioreactor was set up to evaluate the anaerobic biodegradability of selected OMPs. Results showed selected OMPs could be absorbed by sludge and reached equilibrium within one day, and then were consumed by anaerobic microorganism with a half life 9.4 days for ketoprofen and 11.6 days for naproxen. Finally, the CRT for selected OMPs was intensively analyzed under different hydraulic retention time (HRT), sludge retention time (SRT), sludge concentration, feed OMPs concentration, OMPs' biodegradation rate and NF rejection. Full simulations of an AnMBR-NF for domestic wastewater containing selected OMPs from start-up to steady state showed CRT would be a useful concept for assessing the biodegradation of OMPs.

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ABBREVIATIONS

AnMBR-NF	anaerobic membrane bioreactor with nano-filtration
C_f	concentration of OMPs in feed (mg/L)
C_p	concentration of OMPs in permeate (mg/L)
C_l	concentration of OMPs in liquid phase of the sludge in the reactor (mg/L)
C_s	concentration of OMPs in solid phase of the sludge in the reactor (mg/g)
C_{in}	mean concentration of OMPs in the reactor (mg/L)
CRT	compound retention time
CSTR	continuous stirred tank reactor
COD	chemical oxygen demand (mg/L)
d	day
Da	Dalton, unit for molecular weight
DOC	dissolved organic carbon
EfOM	effluent organic matters
EPS	extracellular polymeric substances
FT-IR	Fourier transform infrared spectroscopy
g	gram
h	hour
HRT	hydraulic retention time (h)
J	flux ($L/m^2/h$, LHM)

k	constant of isotherm for adsorption of OMPs onto sludge (L/g)
K	reaction constant for the bio degradations of OMPs (d^{-1})
Ket	ketoprofen
L	liter
LC-OCD	liquid chromatography with online organic carbon detector
M	molar concentration
M_s	Mass of solid in the reactor (g)
MBR	membrane bioreactor
MF	microfiltration
mg	milligram
min	minute
ml	milliliter
MPF	Melamine Phenol Formaldehyde
MQ	Milli-Q water
MWCO	molecular weight cut-off
Nap	naproxen
NF	nanofiltration
NOM	natural organic matters
OMPs	organic micro pollutants
ORP	oxidation reduction potential
Q_f	flow rate of feed (L/day)

Q_p	flow rate of permeate (L/day)
Q_s	flow rate of sludge mixture (L/day)
R_j	reaction rate
RO	reverse osmosis
s	second
SEM	scanning electron microscopy
SRT	sludge retention time (d)
MLSS	solid concentration of the mixture in the reactor (g/L)
T, t	time (s, min, h, d)
TOC	total organic carbon (mg/L)
UF	ultrafiltration
UV	ultraviolet
V	cumulative filtrate volume (ml)
V_l	volume of liquid in the reactor (L)
V_R	volume of the reactor (assume that the reactor is filled full and as a result, the volume of the mixture in the tank is V_R) (L)
WWTP	wastewater treatment plant

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Chapter I Introduction

In recent years, organic micropollutants (OMPs) have received more and more attention, especially with the rapid development of analytical methods. As we know, many organic pollutants can be present in environmental water, normally at the μg L^{-1} level or below, as a result of different sources of pollution (anthropogenic activities, including industrial chemical production or agricultural applications, or natural origin). OMPs accumulate in the aquatic environment, causing ecological risk [1], such as interferences with the endocrine system of higher organisms, microbiological resistance and accumulation in soil, plants and animals [2, 3]. OMPs can be usually classified into 3 categories: endocrine disrupting chemicals (EDC), pharmaceuticals, and mask fragrances [4, 5, 6].

1.1 Occurrence of OMPs

Most countries have the occurrence of OMPs in wastewater treatment plants, drinking water systems and even natural systems. We summarized the occurrence and concentrations of OMPs in different countries from the literature.

GREECE: EDCs were reported, e.g., nonylphenol monoethoxylate, 4-n-nonylphenol, triclosan, nonylphenol diethoxylate, and bisphenol A. For these compounds, the average concentrations in the raw and treated wastewater ranged from 0.23 to 5.76 mg/L and from 0.15 to 1.84 mg/L, respectively. The author also found that the detected EDCs were adsorbed onto suspended solids easily. In sewage sludge, the

average concentrations ranged between 0.17 and 12.3 mg/g [7].

UK: Both synthetic and natural EDCs (e.g., 17b-estradiol, estrone, and bisphenol A) were found in wastewaters from wastewater treatment plants with concentrations to several tens to hundreds ng/L [8].

FINLAND: The raw and treated sewage of sewage treatment plants in Finland contained pharmaceuticals (e.g., atenolol, acebutolol, metoprolol, norfloxacin, carbamazepine, ciprofloxacin, ofloxacin). The average concentrations in the raw and treated sewage ranged from 100 to 1060 ng/L and from 24 to 755 ng /L, respectively [9].

CHINA: Pharmaceuticals and consumer products, including antibiotics, insect repellents, antilipidemics, stimulants, anti-inflammatories, anti-hypertensives, anticonvulsants, and antipsychotics, were detected in wastewater treatment plants of Beijing, China, with concentrations of 4.4 ng/L – 6.6 mg/L and 2.2–320 ng/L in the influents and secondary effluents, respectively [10].

South Korea: The total OMPs concentrations in the influents of wastewater treatment plants ranged from 11.5 to 30.2 mg/L: acetylsalicylic acid (6.29 - 3.39 mg/L), acetaminophen (6.80 - 2.41 mg/L) and caffeine (3.37 - 1.94 mg/L), naproxen (0.714 - 0.233 mg/L), ibuprofen (1.04 - 0.225 mg/L), erythromycin-H_2O (0.730 - 0.346 mg/L), lincomycin (0.382- 0.199 mg/L), ketoprofen (0.083 - 0.061 mg/L), carbamazepine (0.288- 0.119 mg/L), mefenamic acid (0.088 - 0.049 mg/L), gemfibrozil (0.018 - 0.004 mg/L), clofibric acid (0.044 - 0.011 mg/L) and diclofenac (0.018 - 0.013 mg/L)

[11].

CANADA: As is shown in the following table, more than 10 OMPs were detected from the samples of municipal wastewater treatment plants along the Thames River and their concentration levels are at μg/L.

Table 1-1 Influent concentrations (μg/L) of OMPs in wastewater treatment plants along the Thames River, Canada

analyte, μg/L	method detection limit	median	mean
salicylic acid	0.087	14.1	13.7
ibuprofen	0.061	8.84	8.45
gemfibrozil	0.077	0.418	0.453
naproxen	0.074	5.22	5.58
ketoprofen	0.088	0.136	0.146
diclofenac	0.062	0.14	0.204
Indomethacin	0.1	0.196	0.23
Triclosan	0.031	1.86	1.93
Celestolide	0.016	0.0345	0.0372
phantolide	0.018	0.022	0.042
Traseolide	0.013	0.131	0.168
Galaxolide	0.012	1.701	2.031
Tonalide	0.0085	0.687	0.804
Estrodiol	0.005	0.0081	0.0083
Estrone	0.005	0.0302	0.0295

Source: Occurrence and reductions of pharmaceuticals and personal care products and estrogens by municipal wastewater treatment plants in Ontario, Canada [12]

USA: As indicated in the following table, more than 20 OMPs were detected from wastewater treatment processes, and their concentrations varied with time and phases. Generally, most OMPs could be absorbed by biosolids and consumed by microorganisms.

Table 1-2 OMPs concentrations for influent, effluent and bio solids samples from wastewater plants in Ohio, USA

Compound	Influent, µg/L	Effluent,µg/L	Biosolid, µg/kg
Caffeine	2.7698	0.0231	4.5241
Carbamazepine	0.0248	0.0337	5.8025
Chlortetracycline	0.0159	<LOQ	14.7471
Cimetidine	<LOQ	<LOQ	<LOQ
Ciprofloxacin	0.0635	0.1099	<LOQ
Clarithromycin	0.7242	0.6106	30.2402
Clindamycin	0.0068	0.0149	3.7175
Clofibric acid	<LOQ	<LOQ	<LOQ
Cotinine	1.5811	<LOQ	<LOQ
Diclofenac	<LOQ	0.1771	<LOQ
Diltiazem	0.0405	0.0939	12.8216
Gemfibrozil	0.4513	0.0835	<LOQ
Salicylic acid	0.6368	<LOQ	<LOQ
Sulfadimethoxine	<LOQ	0.0019	8.1467
Sulfamethazine	<LOQ	<LOQ	10.9979
Sulfamethizole	<LOQ	<LOQ	<LOQ
Sulfamethoxazole	0.0135	0.0794	<LOQ
Sulfathiazole	<LOQ	<LOQ	<LOQ
Sulfisoxazole	<LOQ	0.0119	9.1383
Tetracycline	0.0293	0.031	<LOQ

LOQ: limit of qualification

In addition, diclofenac was detected in springs with concentrations of 3.6 - 15.4 ng/L, and ibuprofen was also detected in one spring at a concentration 1.4 - 7.9 ng/L, as reported by researchers [13]. The concentrations of diclofenac detected in a groundwater (C/Co) were approximately of 1:50–250 lower than in the WWTP effluent, whereas the concentrations of ibuprofen were up to 1:1000 lower compared to the WWTP effluent. The less frequent occurrence of ibuprofen was probably due to its higher biodegradability. Mersmann et al.[14] also demonstrated that ibuprofen was

easily biodegradable under conditions of the saturated zone while diclofenac was more resistant to biodegradation. Other researchers also reported that ibuprofen was sensitive for oxidation and photodegradation [15].

1.2 Detection methods for OMPs

Gas chromatography (GC) can be used for the analysis of environmental samples which contain semi-volatile and volatile organic compounds with the advantages of good accuracy and precision, high selectivity and resolution, wide dynamic concentration range and high sensitivity [16]. Numerous applications of GC - MS (mass spectrometry) have been reported for the determination of pesticides [17], PAHs [18], as well as some multi residue procedures for the determination of priority and persistent organic pollutants [19].

Although GC–MS has proved to be a useful technique for the determination of organic compounds in environmental samples, the application of tandem mass spectrometry (MS/MS) has been considered as a much more valuable approach which allows high selectivity and low detection limits, minimizing or even removing many of the interferences. We will discuss different kinds of OMPs in details next.

A method for EDCs analysis was proposed by Zhou et al. [20]. Solid phase extraction (SPE) was used for liquid samples extraction with polymeric cartridges (Oasis HLB, 6 cc 200 mg, Waters, Ireland. The EDCs were determined by a GC (7890A, Agilent, USA) MS (5975C, Agilent, USA) system with HP-5MS (Agilent, USA) chromatographic column. Sludge samples were freeze-dried, treated by ultrasonic

extraction, and the extracted supernatant was diluted with ultrapure water to reduce the content of organic solvent for analysis of liquid samples. Some researchers also compared different methods for EDCs detections [21].

The pharmaceuticals analysis of liquid samples was also proposed by Zhou et al. . After extraction by SPE, the pharmaceuticals were analyzed by ultra performance liquid chromatography (ACQUITY, Waters, USA) - tandem mass spectrometry (Quattro Premier™ XE Mass Spectrometer, Waters, USA) coupled with reversed-phase liquid chromatography (ACQUITY UPLC™ BEH C18, Waters, USA). All the extracted solvent fractions were diluted with ultrapure water in order to reduce the fraction of the organic solvent to below 5%. The pretreated samples were then extracted by SPE and analyzed by UPLC-MS-MS [22, 23].

The concentration of musk fragrances was also determined as described by Zhou et al. . After extracted by SPE, the liquid samples were analyzed by GC (7890A, Agilent, USA) - MS (5975C, Agilent, USA). The GC column was DB-FFAP (Agilent, USA). USE was also performed prior to analysis of the sludge samples.

There is a new method developed recently [24]. A multiclass method has been developed for screening, quantification and confirmation of OMPs in water by GC - MS with a triple quadrupole analyzer. This method can be used for the determination of more than 50 compounds belonging to different chemical families, including herbicides, polychlorinated biphenyls, organochlorine and organophosphorus insecticides, polycyclic aromatics hydrocarbons, brominated diphenyl ethers, and

octyl/nonyl phenols and pentachlorobenzene, most of which are included in the list of priority substances in the framework on European Water Policy.

1.3 Treatment of OMPs

In order to reduce OMPs contamination, several treatment methods have been applied, including sorption, membrane retention, oxidation and so on. It was reported that NF/RO membranes could separate almost all of the low molecular weight organic compounds, particular pesticides from water [25, 26], indicating that membrane technology was a promising method for OMPs pollution.

1.3.1 Membrane related treatment of OMPs

Membrane related methods have been paid more attention in recent years. The membrane bio reactor (MBR) is a promising method to control OMPs, since membrane can separate OMPs and as a result, OMPs can be confined within a reactor and consumed by microbes.

MBR is a fairly new method to control OMPs, which combines a bioreactor with a membrane [27]. The obvious advantage of a MBR is that it can have specialized microorganism in the system due to the longer sludge retention time (SRT) compared with conventional wastewater treatment. In addition, the specialized microorganisms may consume OMPs which have low removal efficiencies in the conventional wastewater treatment [28].

Although microfiltration (MF) and ultra-filtration (UF) membranes cannot directly

retain OMPs molecules, they effectively reject activated sludge floc with adsorbed OMPs, and thus eliminate OMPs. Meanwhile, membranes may effectively removes nutrients, and create favorable conditions for OMPs biodegradation. Gaulke et al. [29] reported three possible degradation mechanisms of 17a-ethinylestradiol (EE2): (1) the cometabolic degradation by ammonia oxidizing bacteria, (2) the degradation by heterotrophic bacteria and (3) the abiotic nitration, which indicate that the degradation mechanisms of OMPs in WWTP might be diverse. Although the main degradation mechanism still need to be explored, Clara et al. reported the WWTP with the function of nutrient removal had better performance in eliminating OMPs [30].

Terzic et al. [31] and Radjenovic et al. [32] stated the performance of lab-scale and pilot-scale MBRs for the removal of OMPs has been well studied and proved to be better than conventional processes. David [33] also reported the application of membrane bioreactor technology for wastewater treatment and reuse in the Mediterranean region, and found that the removal efficiency of OMPs varies among different chemicals.

Christopher [34] studied the removal of organic acids by membranes and stated that that the rejection of negatively charged organic acids by NF membranes was larger than expected based on steric/size exclusions because of electrostatic repulsion between solute and membrane. The extent of rejection of the OMPs depended upon the surface charge of a membrane, the extent of deprotonation of the OMPs, and the presence of divalent cations. He pointed that increasing feed water pH could result in

an increased negative surface charge of the membrane, an increased percentage of solutes in the deprotonated state, and an increased rejection through electrostatic repulsion. His experiments showed the NF-90 and NF- 200 had similar surface charge values led to similar organic acid rejections at higher feed water pH values, although they have different MWCO values. Ibuprofen, which is an organic acid with hydrophobic properties, was found to be adsorbed to the membranes at feed water pH < p*K*a. However, at feed water pH > p*K*a, adsorption was not dominant anymore and rejection remained constant over the experiment which can be explained by electrostatic interaction. In addition, the addition of calcium ions to the feed water decreased the rejection of solutes with a MW significantly smaller than the MWCO of the membrane.

It is known that OMPs can be separated from wastewater, and many factors can influence the efficiency of separation. We can predict the rejection efficiency by the steps mentioned below by Bellona [35]. He proposed a rejection diagram for OMPs as follows:

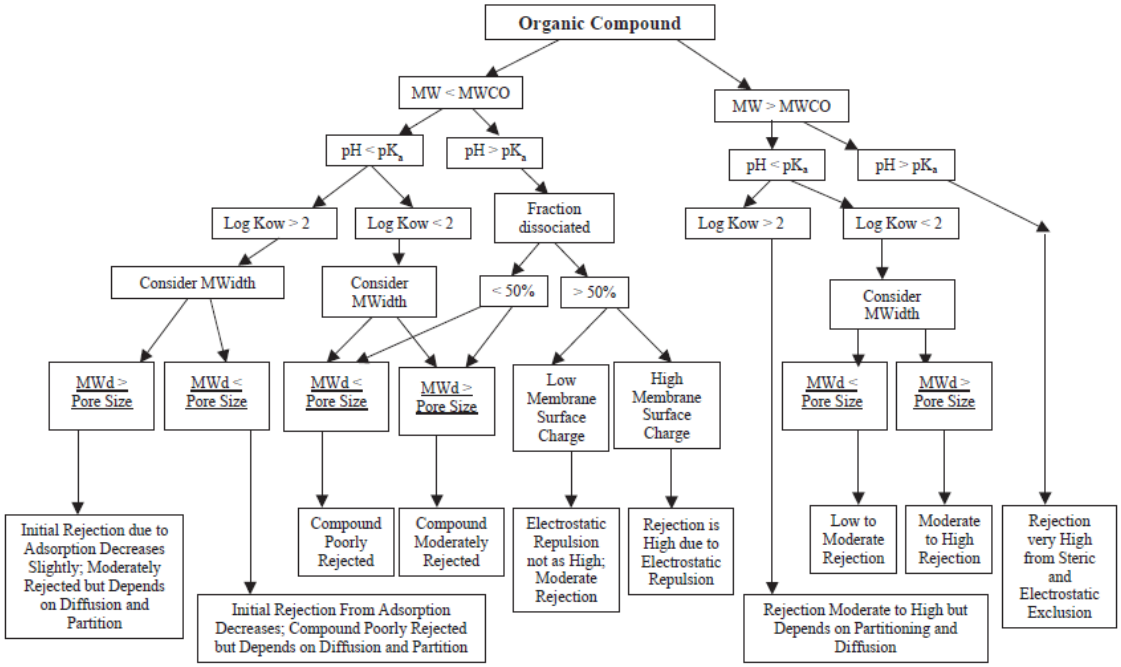


Figure 1-1 Rejection diagram of organic micro pollutants during membrane treatment based on solute and membrane properties

According to the figure above, there are some important factors for rejection: (1) molecular weight (MW), (2) molecular size (length and width), (3) acid disassociation constant (pKa), (4) hydrophobicity/hydrophilicity (logKow), and (5) diffusion coefficient (Dp). There are also some membrane properties affecting rejection, including molecular weight cut-off (MWCO), pore size, hydrophobicity/hydrophilicity (contact angle), surface charge (zeta potential), and surface morphology (roughness). In addition, feed water conditions, such as ionic strength, pH, hardness, and the presence of organic matter, was also identified as having an influence on solute rejection.

1.3.2 Other treatment processes for OMPs

Many other kinds of methods are applied to remove EDCs and PhACs, including, coagulation, adsorption [36. 37, 38], chlorination [39], electro-chemical oxidation [40], ozonation [41], and photo-catalytic oxidation [42, 43]. Vinod [44] used the bagasse fly ash for the removal of lindane and malathion from wastewater, finding the optimum contact time needed to reach equilibrium was 60 min. The removal of the pesticides increased with an increase in adsorbent dose and decreased with adsorbent particle size. Also, natural systems were applied for lindane pollution control [45].

1.4 Potential enhanced OMPs removal by AnMBR-NF based on CRT

Most MBRs are presently operated under aerobic conditions and there are some drawbacks for an aerobic MBR [46]. For example, it is energy intensive process since it needs enough aeration (oxygen) for the reactor and foulants can significantly reduce the flux. Theoretically, an anaerobic MBR could overcome some of these drawbacks, since there is no need for oxygen. On the other hand, anaerobic microorganism may consume some OMPs that are not easily degraded by aerobic organisms easily and an AnMBR can also produce methane, which can be collected for energy. Hence, we chose an anaerobic membrane bioreactor for OMPs control.

Our group (KAUST and UIUC) proposed an AnMBR system as follows:

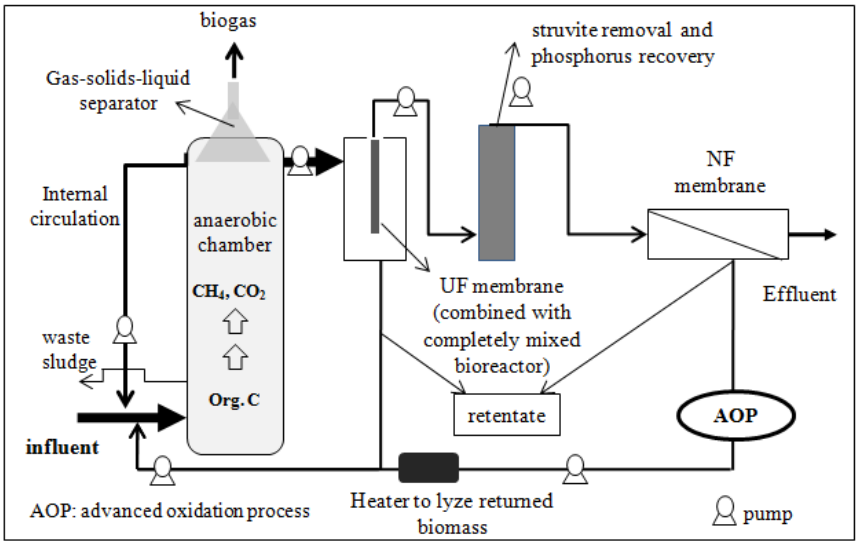


Figure 1-2 Overall schematic diagram for the AnMBR system

It consists of the following units: (1) Anaerobic bioreactor, which is the main reactor for the microorganisms and the degradation of OMPs should be within this reactor; (2) Membrane separation unit, UF used for separation of suspended biomass and NF used for separation of both biomass and OMPs only if no AOP step (it is also possible to use NF for separation of both biomass and OMPs); (3) Struvite and mineral crystallization fluidized bed reactor (FBR): It is likely that the introduction of an NF membrane can lead to the accumulation of high concentrations of rejected multi-valent ions which may lead to potential scale formation. To solve this issue, a FBR filled with quartz sand is introduced into the AnMBR system to study the efficiency of removing phosphate and magnesium as a precipitate. (4) Advanced oxidation process (AOP) unit: this approach will enable more biodegradable OMP oxidation products to be recycled back into the anaerobic reactor. Thus, the retentate of the membrane separation unit will be pumped through an AOP unit to breakdown

OMPs to a certain extent that can lead to better biodegradation in the anaerobic bioreactor.

This thesis is related with the AnMBR mentioned above and dealing with following there aspects: (1) OMPs rejection by NF membranes; (2) anaerobic biodegradation of OMPs; (3) concept of compound retention time. Details are in the following section.

1.5 Research outline

1.5.1 Research objective

The research objective is to explore the preliminary feasibility of enhanced OMPs removal based on the concept of compound retention time (CRT) through coupling anaerobic biodegradation and NF rejection.

1.5.2 Research steps

Firstly, NF selection and OMPs rejection performance were conducted after standard detection methods for selected OMPs were implemented. Mechanisms of OMPs rejection by NF membrane were studied by characterization of the membrane and solution (contact angle, zeta potential, FT-IR, SEM). Secondly, anaerobic adsorption and biodegradation tests of selected OMPs were performed in order to obtain some lab scale data for simulations. Ketoprofen and naproxen were selected as OMPs and 2 L anaerobic reactor was set up for the biodegradation of OMPs. Finally, simulations on OMPs removal were performed based on CRT under aerobic (data from the literature) and anaerobic (own data) conditions.

1.5.3 Structure of the thesis

Chapter I. Introduction: General view of the occurrence, detection methods, and control of OMPs will be discussed, followed by the necessity of the anaerobic membrane reactor with nanofiltration (AnMBR-NF) for OMPs removal.

Chapter II. Methodology: Experimental set-up, procedure, analytical methods including the detection method for ketoprofen and naproxen.

Chapter III. Rejection performance and mechanisms of selected OMPs by NF: This chapter includes short-term and long-term filtration performance, and mechanism for the rejection of OMPs. In addition, mass balance calculation and several methods (contact angle, SEM, Zeta Potential, FT-IR) were applied to explore the mechanisms of rejection.

Chapter IV. Simulation of OMPs' removal based on Compound Retention Time (CRT): CRT for selected OMPs in continuous stirred tank reactor (CSTR) was intensively analyzed under different hydraulic retention time (HRT), sludge retention time (SRT), sludge concentration, feed OMPs concentration biodegradation rate, and NF rejection. Full simulations on an AnMBR-NF for domestic wastewater containing selected OMPs from start-up to steady state are also included in this chapter as well as the experimental adsorption and biodegradation data were also included.

Chapter V: Conclusions and Suggestions: This chapter includes conclusions for the thesis and the suggestions for the further research on this topic.

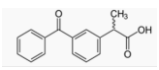
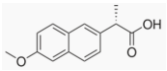
Chapter II Methodology

2.1 Selected OMPs and different matrices

The information on selected OMPs in this study is displayed in Table 2-1. Both ketoprofen and naproxen are non-steroidal anti-inflammatory drugs (NSAID). They have similar physicochemical property but different biodegradability, which will be discussed in Chapter 4. Ketoprofen is used in musculoskeletal and joint disorders and in mild to moderate pain. Naproxen is used for the treatment of primary dysmenorrhoea, rheumatoid arthritis, osteoarthritis, ankylosing, and so on [47].

The OMPs stock solutions were prepared by adding 4 to 9 mg OMP powder (solubilities of ketoprofen and naproxen are 51 and 15.9 mg/L, respectively. Source: http://www.syrres.com/what-we-do/databaseforms.aspx?) into MQ water (500 ml or 1000ml) and then stirring at 700 rpm overnight. Afterwards they were stored in a cold room (4 ^{o}C) and covered by foil to prevent degradation by light. The OMPs stock solutions were diluted with different matrixes (MQ water and/or secondary effluent) to achieve the target concentrations for experiments.

Table 2-1 Information on selected OMPs

Compound	Structure	Formula	**Usage**	**Level in wastewater**	MW	pKa	Log Kow	Company	CAS
Ketoprofen		$C_{16}H_{14}O_3$	**NSAID**	ppt-ppm	254	4.45	3.12	SIGMA	22071-15-4
Naproxen		$C_{14}H_{14}O_3$	**NSAID**	ppt-ppm	230	4.15	3.18	SIGMA	22204-53-1

NSAID：nonsteroidal anti-inflammatory drug; ppt: part per trillion, ng/L; ppm: part per million, mg/L.

The secondary effluents were from KAUST, Jeddah and Riyadh wastewater treatment plants. They were pre-filtered by a 1.2 micrometer membrane and then stored in a cold room.

Mixtures of OMPs with MQ water or secondary effluent were prepared for filtration tests. All of the solutions were kept in filtration room for more than 6 hours before experiments to make sure the temperature of solutions was the same as the room temperature, since temperature has a significant influence on filtration and membrane characteristics. The room temperature was approximately 20 ℃.

2.2 Detection methods for selected OMPs

2.2.1 UV absorbance determination

UV spectra of ketoprofen (KET), naproxen (NAP) and water were scanned by UV-2550 UV/Vis spectrophotometer (SHIMADZU) in order to find the best light absorption wavelength. As shown below, the best wavelength for naproxen (4.6 mg/L) was 230nm and for ketoprofen (5 mg/L) was 259nm. Although UV259 had the strongest adsorption by ketoprofen, there were no significant adsorption differences between UV259 and UV254 (the widely used index for aromatic organics).

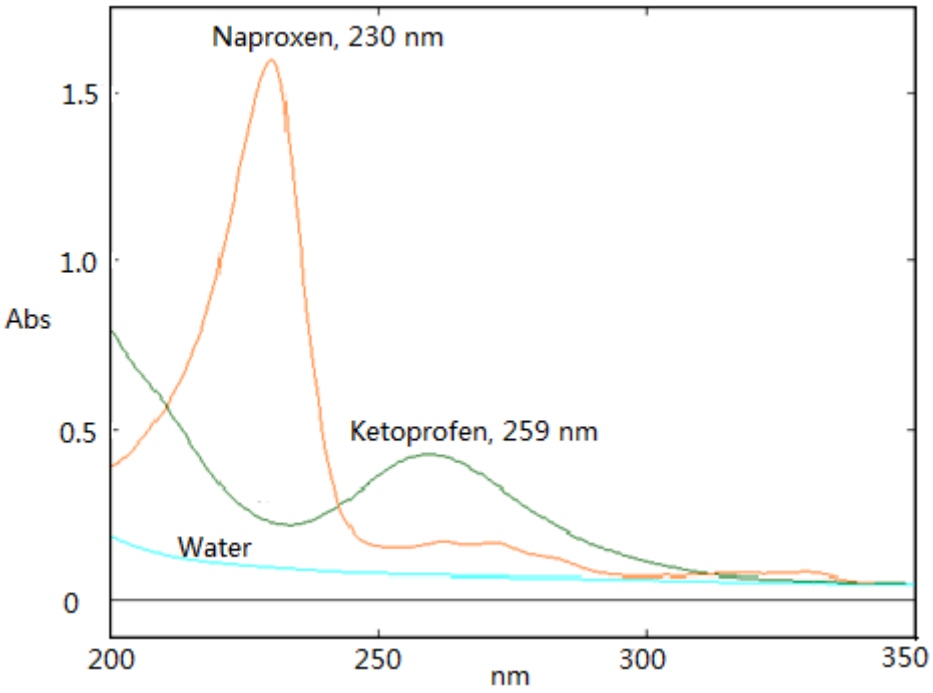


Figure 2-1 UV spectra of naproxen and ketoprofen

The concentrations of ketoprofen and naproxen were determined by HPLC-UV with UV254 and UV230, respectively. HPLC-UV is composed of Waters 2707 Auto sampler and Waters 1525 Binary HPLC pump, with the UV/Visible detector of Waters 2489 and the column of Symmetry C 18 3.5μm 4.6*75mm (Part No. WAT066224). Parameters: injection volume 50 μL, 0.4ml/min A (acetonitrile) +0.6 ml/min B (1 L water + 300 μL H_3PO4) , UV detector, symmetry C 18 column.

2.2.2 Calibration line of ketoprofen

The concentrations of ketoprofen were determined by HPLC-UV254.

The chromatograph for HPLC-UV254 for ketoprofen (about 5mg/L) is shown below (5.5 min for ketoprofen peak):

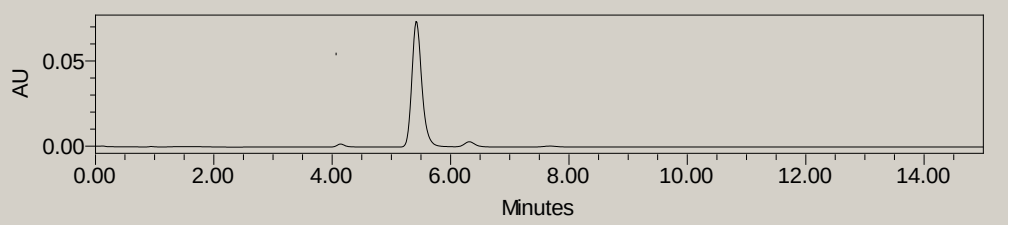


Figure 2-2 HPLC-UV 254 for ketoprofen

The peak height (H) was used to correlate ketoprofen concentration by establishing a calibration line because both peaks for ketoprofen and naproxen under UV254 cannot be separated by HPLC completely. Following is the calibration line for ketoprofen at 254nm.

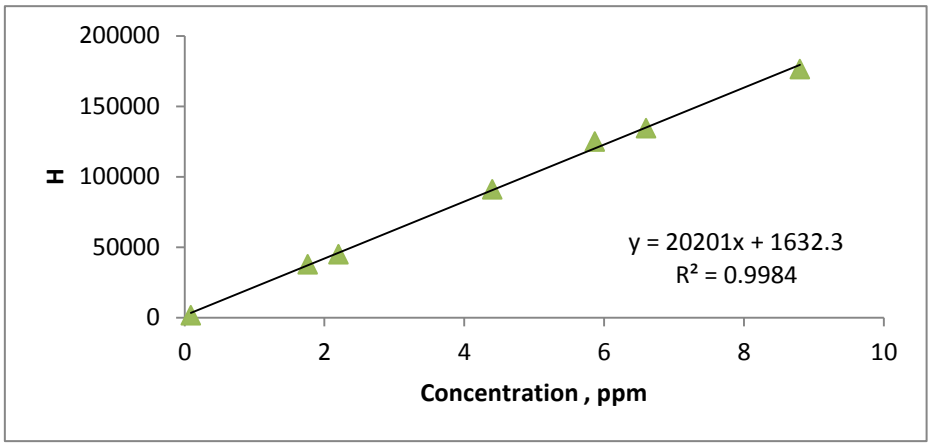


Figure 2-3 Calibration line for ketoprofen (UV254)

The relationship of H and concentration is linear in the range of 0.0275 - 5.5 mg/L.

2.2.3 Calibration line of naproxen

The figure of naproxen (4.6mg/L) determined by HPLC-UV is shown below:

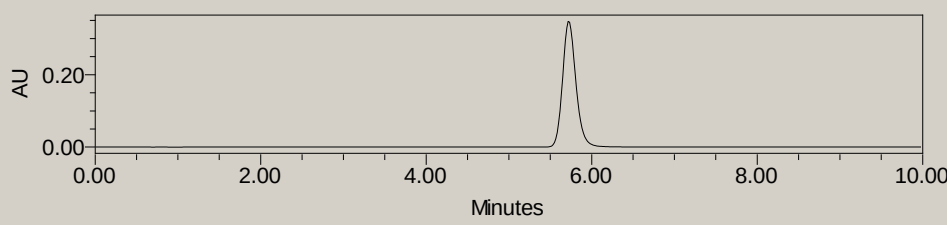


Figure 2-4 HPLC-UV230 for naproxen

The calibration line is as follows:

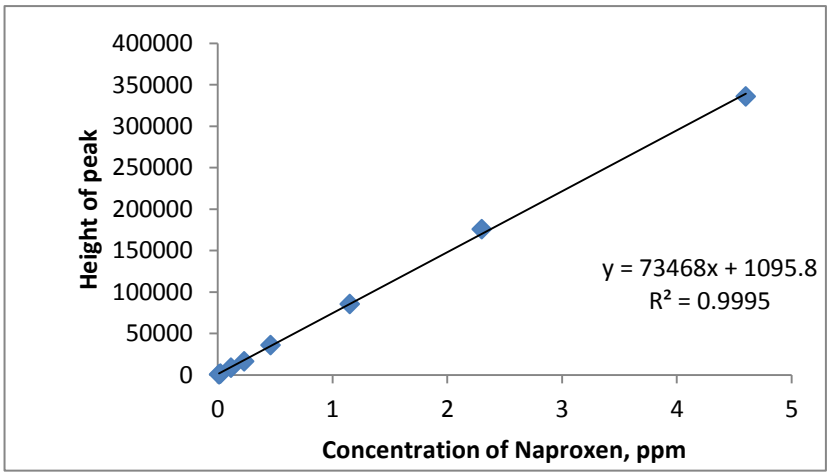


Figure 2-5 Calibration line for naproxen (UV230)

In order to make sure the HPLC procedure was suitable to measure ketoprofen and naproxen at the same time, they are mixed together and HPLC was applied, obtaining the following figures:

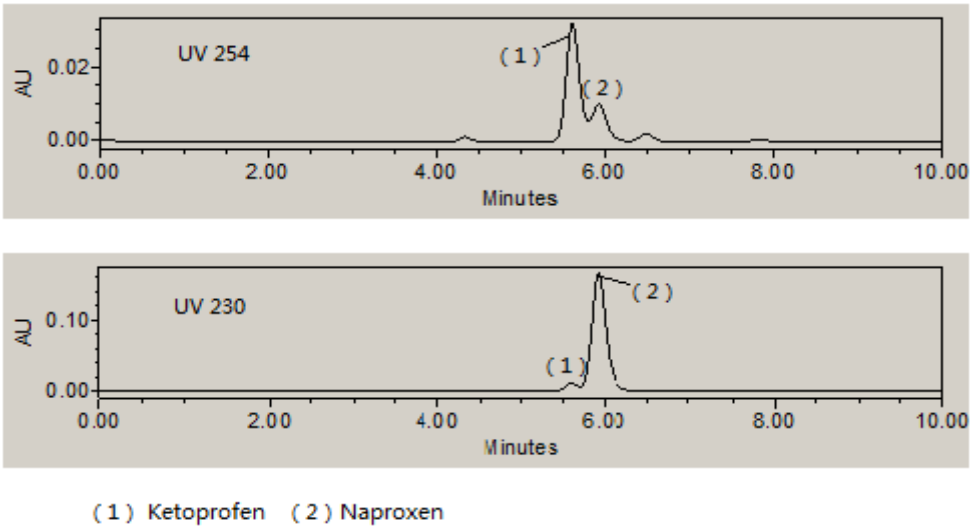


Figure 2-6 HPLC-UV for ketoprofen-naproxen mixture at UV254 (up) and UV230 (down) (Concentrations: ketoprofen about 2.5 mg/L, naproxen 2.3mg/L)

The figures indicate HPLC and its parameters are suitable for the determination of OMPs in MQ water matrix at the same time.

2.2.4 Effect of wastewater matrix and pre-filtration (0.45µm)

In order to explore the effect of water matrix and pre-filtration on the determination of ketoprofen by HPLC-UV, 6 samples were prepared as indicated in the following table.

Table 2-2 Effect of wastewater matrix on the determination of ketoprofen by HPLC-UV

Sample names	H at UV254	concentration (mg/L, UV254)
1, Jeddah by 0.45	peaks at 0.5-3 min with H<0.02	
2, KAUST by 0.45	peaks at 0.5-3 min with H<0.006	
3, Jeddah+0.45+ketoprofen (2+2)	426699	2.371
4, KAUST+0.45+ketoprofen (2+2)	426101	2.368
5, KAUST+ketoprofen+0.45 (2+2)	421675	2.343
6, Ketoprofen+0.45	847556	4.711
7, Ketoprofen stock solution (5.5 mg/L)	859843	4.78

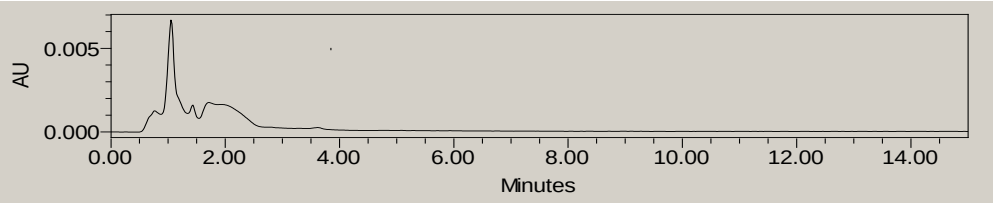
Notes: 0.45, filtered by 0.45µm glass fiber syringe filter;
2+2, 2 ml A + 2 ml B, A and B stand for secondary effluent or ketoprofen solution;
H, height of the peak
KAUST, KAUST WWTP wastewater effluent
Jeddah, Jeddah WWTP wastewater effluent

Results show that UV detection of secondary effluent (both Jeddah and KAUST) exhibited small peaks at around 0.5 - 3 min, but no peaks at 5 – 6 min, which was the range for ketoprofen and naproxen peaks. Therefore, ketoprofen in wastewater can be detected by HPLC-UV (see the first 2 experiments), and it is also applicable to naproxen.

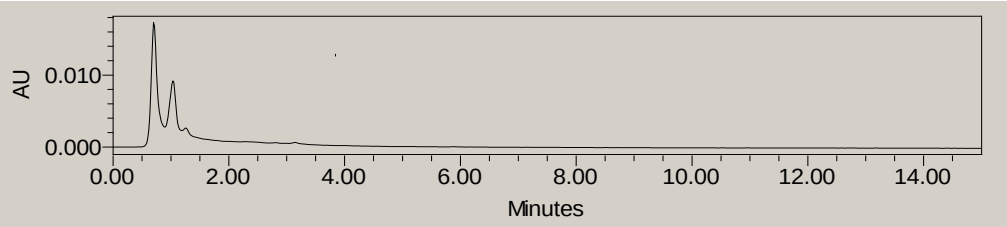
Comparing the results of concentrations of ketoprofen with and without 0.45 μm filtration (the last 2 experiments), it is clear there are no significant differences between them. In addition, based on the last test, it should be noted that concentration of ketoprofen could decrease at room temperature, since the initial concentration of the solution had been 5.5 mg/L but then changed to 4.7 mg/L (the solution was kept at room temperature exposed to the light for 3 days).

Furthermore, based on experiments 4 and 5, there is a very small loss due to the membrane filtration, less than 2%. This can be ignored in future experiments.

Wastewater HPLC-UV graphs were as follows:



(1) KAUST, UV254



(2) Jeddah, UV254

Figure 2-7 HPLC-UV for wastewater from KAUST or Jeddah WWTP

The figures above indicate there is no significant peak from 5 to 6 min, indicating the HPLC method was feasible for OMPs detection in wastewater matrix. The OMPs in the wastewater matrix were also determined by HPLC-UV, and the spectra are as follows:

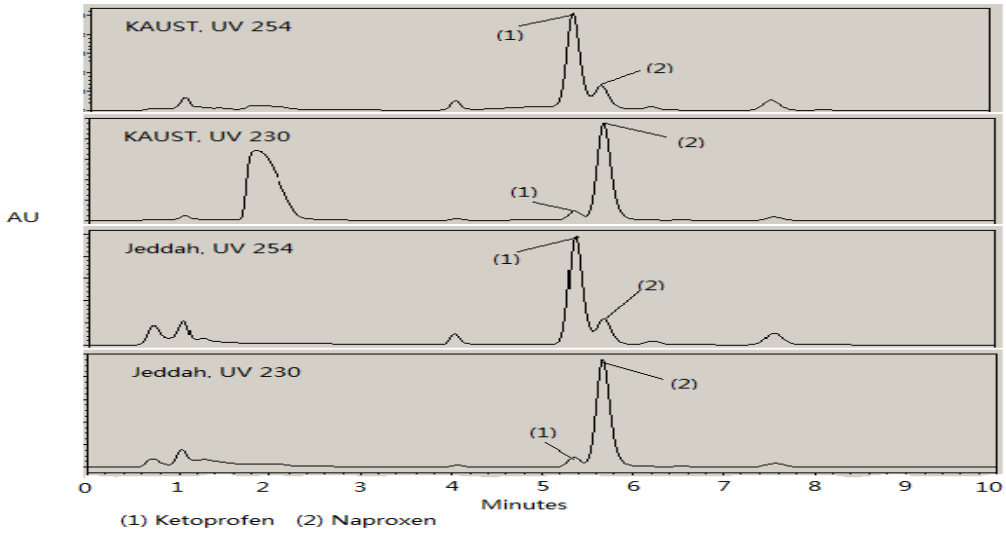


Figure 2-8 HPLC-UV for determination of ketoprofen-naproxen mixture in wastewater from KAUST or Jeddah WWTP

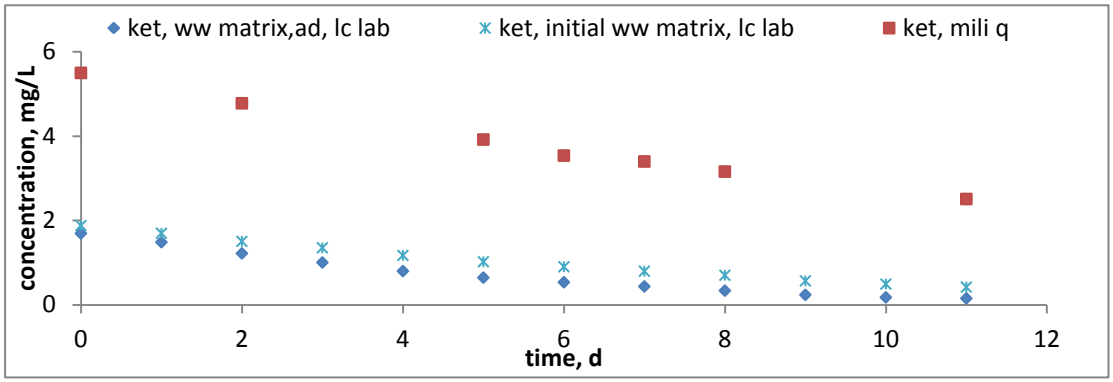
These figures demonstrate that the HPLC method for OMPs determination is indeed suitable, since HPLC can separate both peaks efficiently.

2.3 Stability and storage of selected OMPs samples

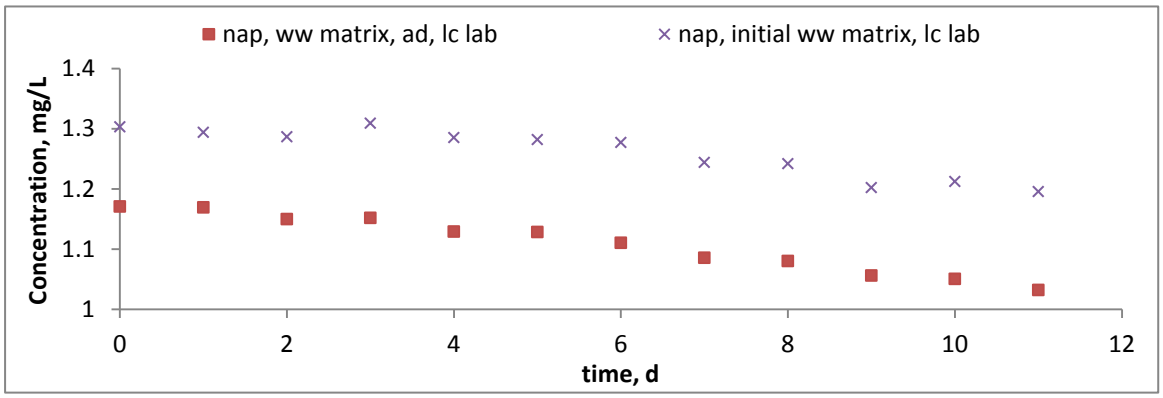
During the preparation of ketoprofen and naproxen solutions, the concentration of ketoprofen decreased quickly at room temperature exposed to the room light. However, there was no detectable decrease for the concentration of naproxen under the same conditions. In order to explore the impact of matrix and room conditions on photolysis and find a suitable way to store our stock solutions and samples, photolysis experiments were conducted.

Photolysis tests were conducted in TOC tubes (20 ml). Ketoprofen-naproxen mixture solutions in different matrix were introduced into the tubes, sealed and then placed in different labs (filtration lab or liquid chromatography lab). 1 ml samples were taken every day at the same time, and OMPs were determined by HPLC-UV.

The results are as follows:



(1) Ketoprofen



(2**) Naproxen**

Note: ket: ketoprofen;
nap: naproxen;
ww matrix, ad: the ketoprofen- naproxen mixture solution was after the adsorption experiments
initial ww matrix: the original prepared ketoprofen-naproxen mixture in wastewater matrix
lc lab: the liquid chromatography lab room
MQ: the ketoprofen was dissolved in MQ water matrix

Figure 2-9 Ketoprofen and naproxen photolysis in different matrices

It is obvious that the photolysis of ketoprofen in MQ water had a significant effect on the concentration of ketoprofen, as indicated by Figure 2-9 (1) line ket, MQ. Naproxen was much more stable than ketoprofen, and there was little decrease for naproxen in MQ water for tens of days. In other words, naproxen is not sensitive to

light radiation. However, there was some degradation when naproxen was in a wastewater matrix, which contained bacteria and other biota.

On the other hand, both of the samples were placed in the testing tubes, which were stored in the injection box for HPLC and it is found that the concentration increased slightly due to the evaporation of water, as indicated by the following data:

Table 2-3 Degradation tests in the dark environment

solution in testing tube in the injection box				
day	naproxen 4.6,mg/L	naproxen in mixture, mg/L	Ketoprofen 5.5, mg/L	Ketoprofen in mixture, mg/L
0	4.599	2.32764	3.539763	1.792659
1	4.798	2.40874	3.636864	1.847367
2	4.771	2.39796	3.536876	1.839489

Note: weak light and room temperature in the injection box of HPLC, the tube is about 1.5 mL

In conclusion, ketoprofen and naproxen should be stored in brown bottles in the fridge to stabilize the concentrations of solutions.

2.4 Filtration set-up

The membrane was placed in the filtration cell after pretreatment by MQ water. For the filtration system shown in Figure 2-10, compressed nitrogen gas was used to drive the DI water to flow through the system, including the filtration cell. Subsequently, the filtered water ran into a beaker which was on the surface of a balance. Then the balance transferred the weight data to the computer by which the flow rate of water could be calculated.

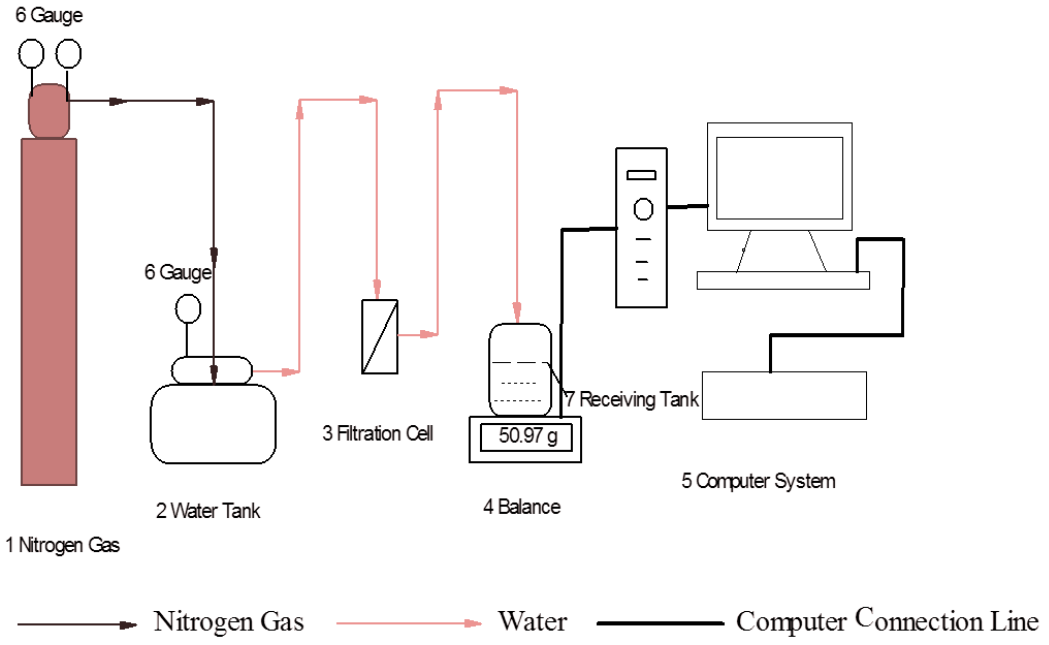


Figure 2-10 Filtration set up

An electronic balance (Mettler Toledo ML3002/01, Switzerland) was connected with a computer and the data of weight were recorded by a computer every 1 minute. In the filtration experiment, an EXCEL program was used to calculate flow rate and flux.

Cell (Amicon 8050) was used for the dead end filtration test of selected OMPs, with 5 bars as the applied transmembrane pressure. The KOCH membrane was first soaked in MQ water for 2 hours and then rinsed by MQ water.

For the filtration test, MQ water was applied to remove the residues of the membrane in order that there was low organics going into samples in the later experiments. Then, a filtration test was performed.

In the beginning of a filtration test, adsorption could be the main mechanism for OMPs rejection. Thus adsorption tests of selected OMPs onto NF membrane were also performed for the filtration tests.

50 ml solution (Ketoprofen-naproxen mixture in MQ water matrix or wastewater matrix) was introduced into a conical flask with a stir bar (350 rpm) to mix the solution well. New washed membrane samples (3.2*3.5 cm^2 for MQ water matrix; 2.8*1.2 cm^2 for wastewater matrix) were put into the flask, and then the flask was sealed. Solution samples were taken periodically and light degradation was prevented throughout all of the adsorption process. The concentrations of ketoprofen and naproxen in the samples were determined by HPLC-UV.

2.5 NF membranes

2.5.1 General information on membranes

General information the membranes tested is listed as follows:

Table 2-4 General information on membranes

Manufacturer	Material	Salt rejection/MWCO/ Reject range	Product No.	TMP (Bar)	Permeability LMH/Bar
KOCH	Acid/base stable	200 Da	770002	5	11.6
	TFC®	200 Da	8150002	5	-
	Solvent stable	250 Da	770003	5	-
	Acid/base stable	1000 Da	770007	5	>5
GE	Thin Film (TF)	98%-$MgSO_4$	DK	5	2---5
	Thin Film (TF)	96%-$MgSO_4$	DL	5	5
	Composite polyamide	1000 Da	GE	5	5.4
	Thin Film (TF)	98%-$MgSO_4$	HL	5	>5
	Cellulose Acetate (CA)	92%-Na_2SO_4	CK	5	30
DOW	Polyamide Thin-Film Composite	97% $MgSO_4$	NF270	5	9.7

2.5.2 Membrane screening

2.5.2.1 KOCH and Dow NFs

The rinsing methods, feed sludge waters, filtered volume and pressures applied for all KOCH NF membranes are given in the table below. Corresponding information for the Dow NF270 is presented as well.

Table 2-5 Test details for KOCH and Dow NF membranes

NF	Pre-treatment		Feed	Filtrated volume (ml)
	Soaking in MQ water	MQ water filtration		
KOCH A/B NF200	2h, changing water 3 times	50ml, 5bar	KAUST WWTP membranetank sludge water	33.98
KOCH TFC NF200	24h, changing water 3 times	50ml, 5bar		27.48
KOCH NF250		50ml, 5bar		21.24
KOCH NF1000		50ml, 5bar		256.74
Dow NF270		120ml, 5bar		43.96

Permeates through these NF membranes were analyzed by LC-OCD.

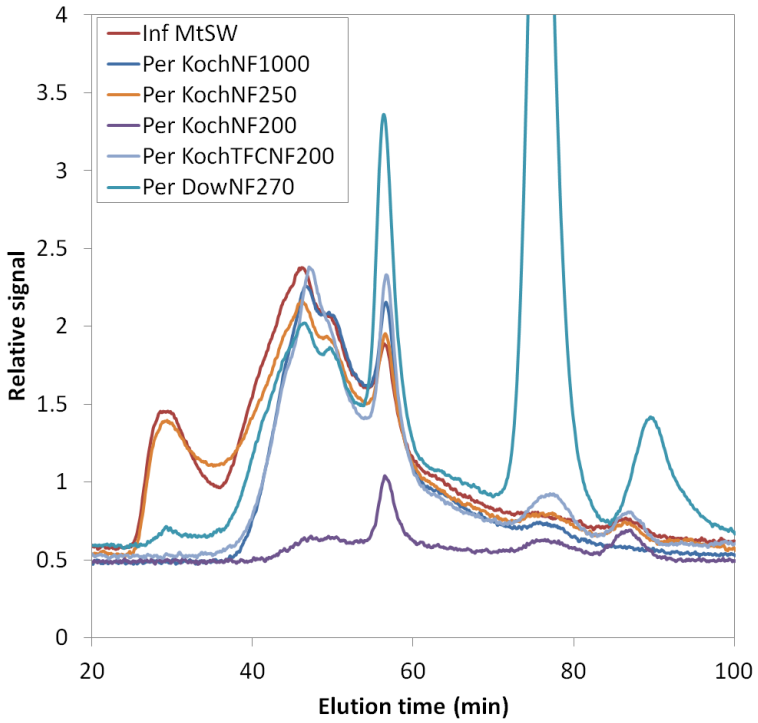


Figure 2-11 LC-OCD comparison of permeates by different NF membranes

The KOCH A/B NF200 is the only membrane has great rejection of humic substances and at the same time no obvious organic residue release from the membrane. It was used in the later filtration tests.

2.5.2.2 GE NF membranes

Test details are summarized in Table 2-6. Permeates produced by each membrane were further analyzed. A comparison of LC-OCD results is shown below. According to the criteria of NF selection, GE DK seems the most promising choice for further study. However, the quantitative results of humic substances rejection reveal that this membrane released a significant amount of organic nitrogen in terms of humic-like substances into the solution, making it not a proper choice for further investigation.

Table 2-6 Test details for GE NF membranes

NF	Pre-treatment		Feed	Filtrated volume (ml)	Applied pressure (Bar)
	Rinsing in MQ water	Milli-Q water filtration			
GE DK	24h, Changing water 3 times	50ml, 5bar	KAUST WWTP membrane tank sludge water	79.39	5
GE DL				87.57	
GE GE				29.21	
GE HL				53.20	
GE CK				2.57	

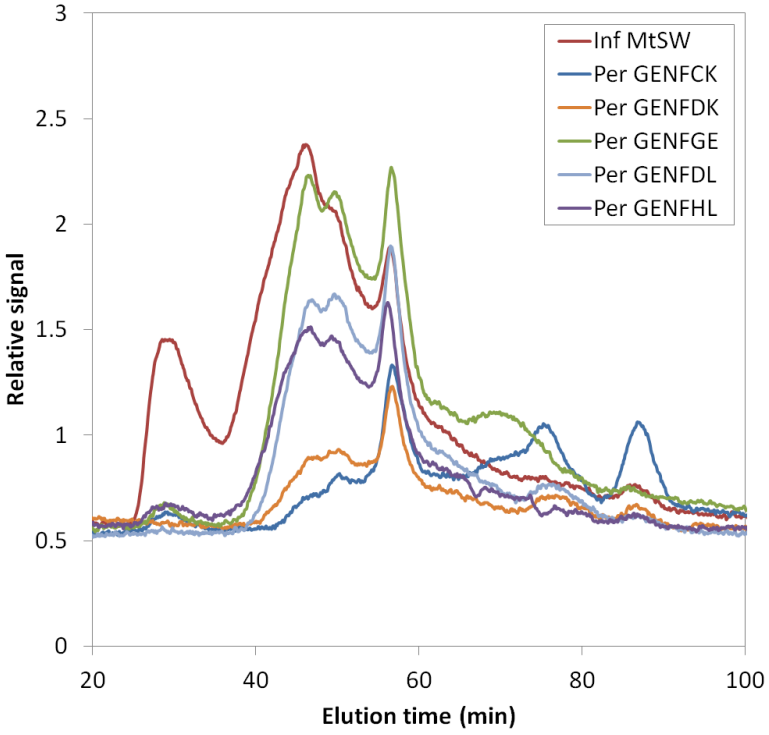


Figure 2-12 LC-OCD comparison of sludge water permeates by GE NF membrane

From the previous results, Koch NF200 worked best for organic matter removal. Thus the Kock NF 200 was chosen for OMPs rejection.

2.6 Anaerobic adsorption and biodegradation of selected OMPs

2.6.1 Adsorption

(1) Equilibrium time

100 ml of anaerobic wastewater sludge (solid content is about 30 g/L, pH = 7.8) and 100 ml OMP stock solution (concentrations of naproxen and ketoprofen are about 3 mg/L) were mixed well by a stirring bar (350 rpm) after being preheated by an oven to 36 ℃ (it is the optimum temperature for microorganisms and this temperature is the same as that in the anaerobic system). Then the mixture was stripped by nitrogen gas for several minutes in order to get rid of oxygen and sealed firmly, followed by storing of the reactor in the oven (36 ℃) for the adsorption process. 2 ml of samples were taken from the reactor periodically and OMP concentrations were determined by HPLC-UV.

(2) Adsorption isotherm

Similar with the previous experiment, different amounts of OMP stock solution and anaerobic sludge were mixed together to have different initial concentrations of OMPs in the mixture (sometimes the mixture was diluted by adding MQ water). Nitrogen stripping was applied and then the reactors were kept in the oven for more than 20 hours to make sure the equilibrium of the adsorption process reached. Finally OMP concentrations were measured by HPLC-UV.

2.6.2 Biodegradation

Biodegradation of OMPs was evaluated based on a 2 L batch reactor, in which biomass was from an anaerobic bioreactor. OMPs solution and sludge were mixed well to obtain sludge system containing ketoprofen at about 1 mg/L and naproxen at

about 1 mg/L. Nutrients and acid (to control pH) were added into the reactor periodically in order to have a well developed anaerobic environmental for the microorganism. Sludge samples were taken from the reactors every day, analyzing ketoprofen and naproxen concentrations in liquid phase of the sludge in the reactors, for the purpose of evaluating the biodegradation kinetics for ketoprofen and naproxen. The reactor was covered by aluminum foil to prevent photolysis of OMPs.

The anaerobic bioreactor had automatic control system for the temperature and stirring speed. The temperature was controlled at 35 ℃ while the stirring speed was at 100 rpm. 10-20 ml glucose or sodium acetate (200 mg COD/ml) was introduced into the system every day.

Concentrations of OMPs were measured every day with five sets of data were taken.

2.7 Analytical methods

2.7.1 Membrane characterization method

SEM: The sample of the dried membrane was coated with gold and subjected to a scanning electron microscope (Quanta 600 FEG at 5 kV) for a SEM image.

Contact angle: Contact angle was measured by an optical tension meter (KSV Theta, Finland) by the sessile drop method. A drop of 2.0 micro liter MQ water was dropped on the surface of membrane and photos were taken to measure the contact angle. Several drops of water at different locations on the membrane surface were evaluated

and the average values of contact angle were calculated. The greater the contact angle, the more hydrophobicity the membrane surface is.

Zeta potential: Zeta potential of the membrane surface was measured using a SurPASS electrokinetic analyser (Anton Paar GmbH, Graz, Austria). The zeta potential of the membrane surface was calculated from the measured streaming potential using the Fairbrother–Mastin approach [48]. All streaming potential measurements were conducted in a background electrolyte solution containing 10mM KCl. Hydrochloric acid and potassium hydroxide were used to adjust pH by means of automatic titration. The test solution was used to thoroughly flush the cell prior to the pH adjustment for each measurement. All streaming potential measurements were performed at a room temperature of approximately 20 ℃, which was monitored by the temperature probe of the instrument.

FT-IR: FTIR (Spectrum 100, PerkinElmer,U.S.) was used to determine the functional groups on the surface of membrane.

2.7.2 Solution analysis

TOC: Total organic carbon (TOC) was observed by a TOC analyzer (SHIMADZU Total Organic Carbon Analyzer (TOC-V CPN, ASI-V)) under the non-purgeable organic carbon (NPOC) mode. A mixture of 2mL sample with 4 mL of HCl acidified Milli-Q water solution was introduced into the TOC analyzer. Calibration samples were run before each experiment.

LC-OCD: LC-OCD (liquid chromatography-organic carbon detection) was developed to identify classes of organic compounds in natural water. It gives quantitative information on NOM (natural organic matter) and qualitative results regarding molecular size distribution of water impurities. A LC-OCD Model 8 (DOC-LABOR, Karlsruhe, Germany) was used. Samples should be pre-filtrated by a 1.2 μm filter and contain a DOC lower than 5 mg/L. The sample vials were cleaned sequentially by soaking in 0.1 N HCl for 1day, soaking in 0.1 N NaOH for 1day, soaking in MQ water for 1day, soaking in another MQ for 1day and drying under room temperature before use in order to keep the vials very clean. During measurement, one 0.1 N NaOH sample followed by one MQ sample were placed before and after real samples in order to clean the column. Each sample took 130 min for a complete measurement.

Chapter III Rejection performance and mechanism of selected OMPs by NF

3.1 Short term filtration of selected OMPs

3.1.1 Ketoprofen alone

Filtration of ketoprofen is described in table 3-1. The results are as follows:

Table 3-1 Ketoprofen filtration test by KOCH NF 200

Ketoprofen filtration by KOCH NF 200 (initial concentration 5.5 mg/L)						
	Concentration at time 1=1.5 h	Concentration at time 2=3 h	Concentrate in cell	Initial solution volume in the cell	Concentrate volume in the cell	Filtration time
concentration	0.056 mg/L	0.1556 mg/L	6.195 mg/L	40ml	15ml	4 h
removal efficiency	0.991	0.975	-	-	-	-

Results show that the total removal efficiencies are more than 97% (based on concentrate in the cell), which indicates that almost all of the ketoprofen was retained by the membrane. The concentration of ketoprofen in the filtration cell is slightly increased from 5.5 mg/L to 6.1 mg/L after filtration. Based on the materials balance calculation, the concentration of ketoprofen should be doubled theoretically, since the initial volume of the sample in cell was 40ml and there was only 15 ml left at last. It is clear that some of the ketoprofen was absorbed by the membrane.

3.1.2 Naproxen alone

Similar with ketoprofen filtration testing, naproxen filtration testing was conducted and the results are as follows:

Table 3-2 Naproxen filtration by KOCH NF 200

Naproxen filtration by KOCH NF 200 (initial concentration 4.6 mg/L)						
	Concentration at time 1=1.5 h	Concentration at time 2=3 h	Concentrate in cell	initial solution volume in the cell	Concentrate volume in the cell	Filtration time
concentration	0.0654 mg/L	0.2121 mg/L	4.622 mg/L	40ml	15ml	4 h
removal efficiency	0.986	0.954				

The short term removal efficiency for naproxen was also very high, above 95%, which indicates a good removal of naproxen from the MQ water matrix. However, the concentration of naproxen in concentrate is almost the same with the initial value, indicating the eliminated naproxen should be absorbed by membrane.

3.1.3 Mixture of ketoprofen and naproxen

In this section, in order to investigate whether the rejection of OMPs is table, an old membrane which had been used for above-mentioned naproxen filtration once (the results are in the previous page) was used, and at the same time check the removal efficiencies for the mixture of ketoprofen and naproxen.

First, MQ water was used for the filtration and the naproxen could be washed out with a concentration of 0.56mg/L.

Then, the ketoprofen solution and naproxen solution was mixed together with the ratio of 1:1. Similar with the filtration test, filtration efficiencies for the mixture of chemicals were explored, and the results are as follows:

Table 3-3 Ketoprofen-naproxen mixture filtration by KOCH NF 200

	concentration of ketoprofen, mg/L	concentration of naproxen, mg/L
Original	1.61428	2.2806
t1=1.5h	0.017	0.5433
t2=3h	0.119719	0.83091
Concentrate in the cell	1.8144	2.47556
removal efficiency t1	0.989469	0.761773
removal efficiency t2	0.934017	0.664355

Results show the removal efficiency for ketoprofen is above 93%. However, removal efficiency of naproxen is about 66-76%. As is shown in the long term filtration experiment, the decreasing of removal efficiency is due to the free adsorption sites becoming less and less with filtration going on.

From the short term filtration of single ketorprofen or naproxen and mixture of them, the permeate concentrations of both compounds increased with time, especially those of the mixture one, indicating the possible effects of initial adsorption. Thus the adsorption of OMPs onto membrane should be investigated, which can be seen in the next section. In addition, a long term filtration test to check the steady removal of selected OMPs should also be required to check whether the effluent concentration will decrease to stable values.

3.1.4 Adsorption of selected OMPs onto membrane

The adsorption curves of ketoprofen and naproxen in different matrix are shown as follows:

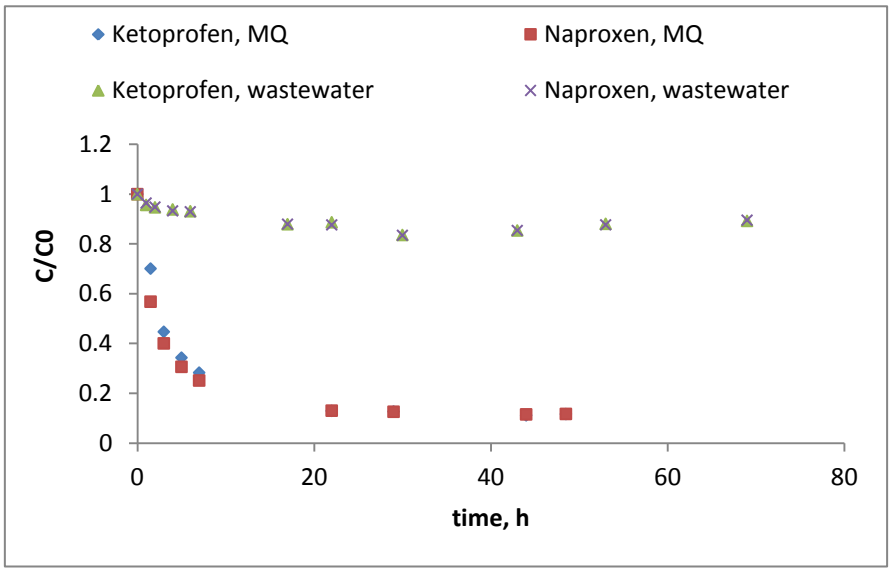


Figure 3-1 Adsorption of ketoprofen and naproxen onto the Membrane

It is obvious that the adsorption capacities of ketoprofen and naproxen in MQ water are much greater than those in wastewater matrix. In MQ matrix, the adsorption reached equilibrium at about 20 hours for both ketoprofen and naproxen, and the adsorption capacities for both OMPs are about 0.012 mg/ cm^2, but the adsorption rate for naproxen is greater than that of ketoprofen. Nevertheless, the adsorption process in wastewater matrix is not obvious, with little adsorption capacities (almost zero) for both of the OMPs.

The adsorption tests indicated the matrix of a ketoprofen-naproxen mixture has a great impact on the adsorption rate and capacity. The organic matter in wastewater can compete with OMPs to adsorb onto the membrane and at the same time, organic matter can also react with OMPs to reduce the adsorption. The organic matter may also modify membrane so that the membrane has a low capacity for adsorption of OMPs. On the other hand, ketoprofen and naproxen behave similar during the process,

and they have a similar adsorption rate and capacity. In other words, these similar molecular (containing aromatic rings and -COOH), can absorb onto the membrane by a similar mechanism.

The adsorption tests also demonstrate that the membrane has adsorption sites for OMPs, and these sites help reduce the permeate concentration of OMPs during the initial filtration process. That is also the reason why the permeate concentration of the OMPs were low during the initial filtration, and the concentration of cell concentrate was also low. Most of the OMPs were absorbed by membrane.

3.2 Long term filtration of ketprofen – naproxen mixture

3.2.1 Selected OMPs in MQ matrix and clean NF membrane

In previous experiments, the removal efficiency of OMPs decreased with time and more time is needed to determine the performance of the membrane. As a result, a continuous filtration experiment was conducted with a ketoprofen-naproxen mixture in a MQ water matrix. This experiment consisted of 8 cycles, as shown below:

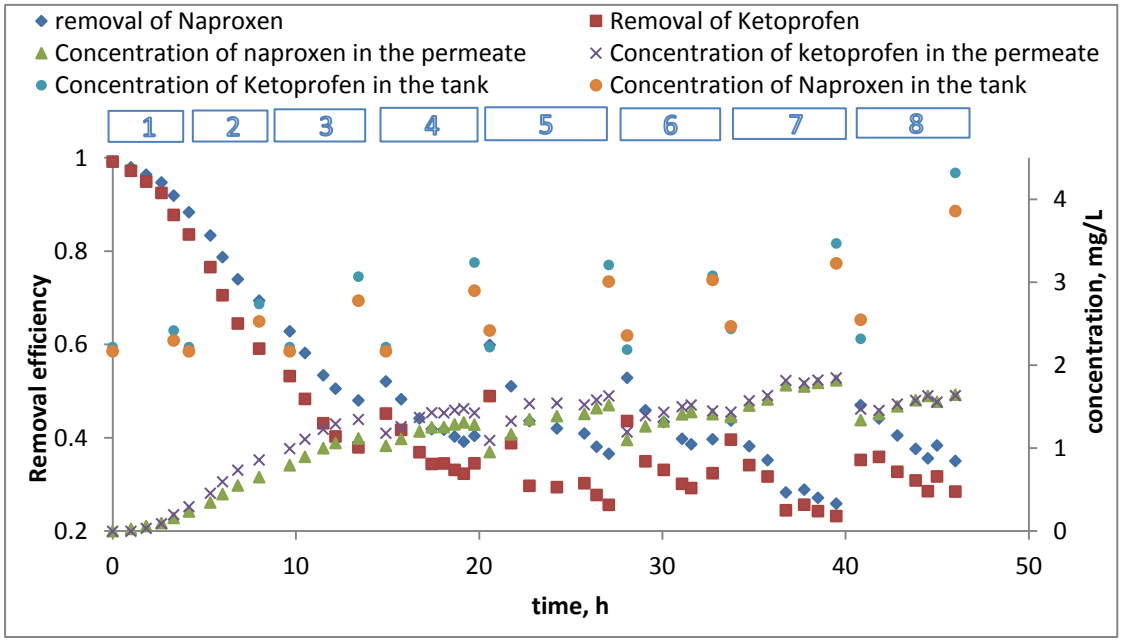


Figure 3-2 Long term filtration of OMPs in MQ water matrix (feed concentration: ketoprofen 2.22 mg/L, naproxen 2.17 mg/L)

The apparent removal efficiency ($1-C_p/C_{\text{initial concentration in the cell}}$) for the first three cycles (time 0 to 14 hour) decreased with time continuously from 99% to 40% for naproxen and from 99% to 34% for ketoprofen, and the removal efficiency reached a steady state after 14 hours. For the later cycles, the general removal efficiencies for naproxen and ketoprofen were 40% and 30%, respectively. There is always a relatively high removal at the beginning of every cycle for the last five ones, which is due to the dilution of cell concentrate. About 50 ml mixture solution was added at the beginning of each cycle and thus the cell concentrate was diluted from the previous cycle. As is well known, the more concentrated the feed, the more concentration might be detected in the permeate. Similarly, the reason for the relatively low removal of OMPs at the end of each cycle is the highly concentrated OMPs in the cell concentrate, which can

be determined by HPLC-UV at the end of each cycle. In the other words, the actual removal efficiency (1- $C_p/C_{\text{concentration in the cell at the same time with permeate}}$) should be higher than the apparent removal efficiency (1-$C_p/C_{\text{initial concentration in the cell}}$) in the figure.

The mechanism for the rejection of OMPs by an NF membrane should be one or several of the followings: (1) adsorption mechanism, which is the dominant mechanism at the early stage; (2) sieving mechanism, which is accomplished by a membrane having a smaller pore size than the target compounds; (3) electrostatic interaction, which relies on relative charge interaction; (4) factors related to NF operation conditions [49]. Other filtration experiments and surface characteristics were applied to study which mechanism(s) is (are) dominant for OMPs rejection in our research. As is shown in the adsorption experiments, the membrane has a good adsorption capacity for OMPs in the MQ water. Meanwhile, the cell concentrate of the first 2 cycles was less concentrated, but removal data shows most of the OMPs were removed from the mixture. That is to say, the majority of OMPs should be absorbed by the membrane in the first 2 cycles. For the last 5 cycles, the high concentrations of OMPs in the cell concentrate indicate the rejection of OMPs should be attributed to sieving (size exclusive) and electrostatic interaction. Zeta potential determination will be applied later to classify the importance of charge interaction. On the other hand, operating conditions will influence the rejection of OMPs, such as feed water quality, trans-membrane pressure, etc. The organic matter matrix for feed water will be discussed next.

3.2.2 Selected OMPs in wastewater matrix and clean NF membrane

For the purpose of determining the impact of organic matter on the filtration of OMPs, a wastewater (secondary effluent) matrix for the feed ketoprofen-naproxen mixture was studied, as shown below:

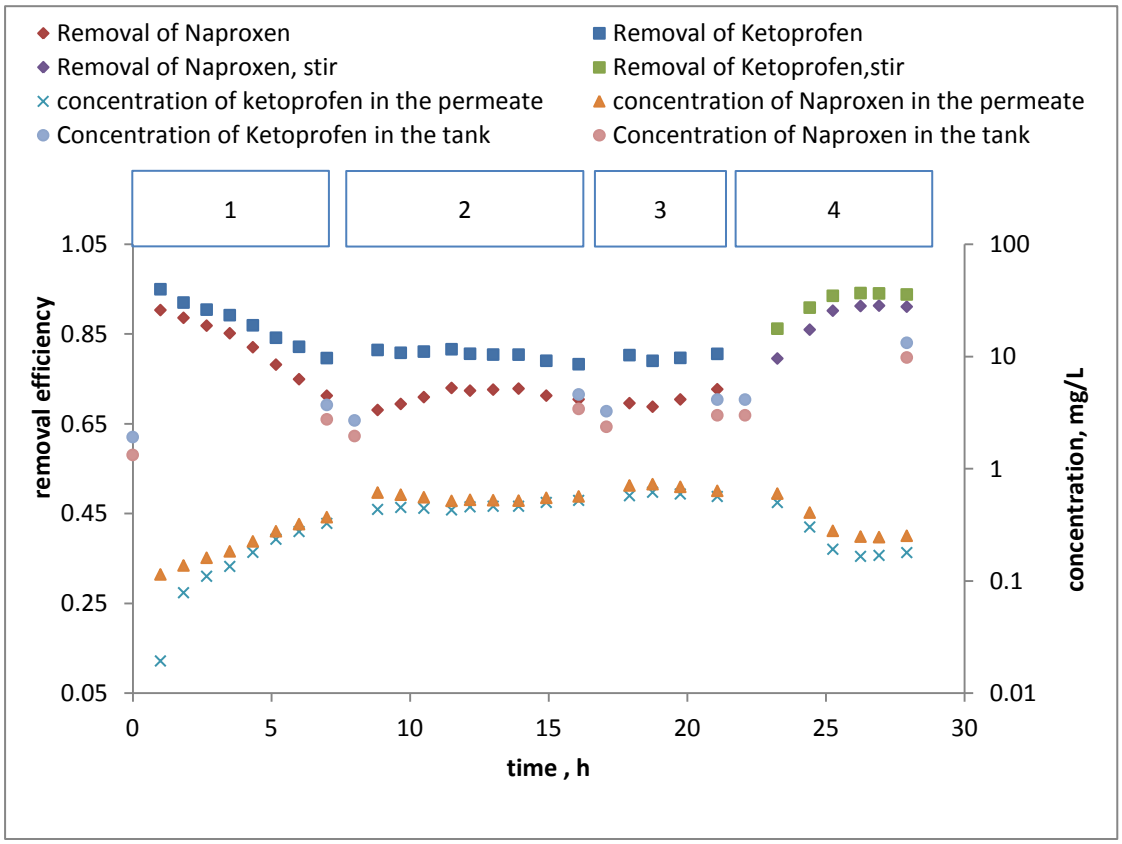


Figure 3-3 Long term filtration of OMPs in wastewater matrix

There are 4 cycles in the figure above. The apparent removal efficiencies ($1-C_p/C_{\text{initial concentration in the cell}}$) decrease from more than 90% for both of the OMPs to 80% for ketoprofen and 70 % for naproxen, but remain almost the same during the following two cycles (time 9 hour to 21 hour). After stirring at 125 rpm (as indicated in the last cycle, time 22 hour to 28 hour), the removal efficiencies increase up to

more than 90%. The explanation is that the stirring broke up the concentration polarization layer which was close to the surface of membrane and mixed the solution well, so that the concentration of OMPs over the membrane surface decreased and thus the permeate contained less OMPs. In previous experiments without stirring, it was found that the concentration at the bottom of the cell was much higher than that at the top or in the middle of the cell, indicating there is a concentration polarization layer formed during the filtration mainly due to the sieving effects. To achieve better removal efficiency, stirring was applied for our later experiments.

Comparing Cycle 3 with Cycle 4, it is clear that the concentration polarization layer did not help for the retention of OMPs. On the contrary, the concentration polarization layer decreased the removal efficiency since it increased the concentration over the membrane. Theoretically, the concentration polarization layer may form a gel layer and become a foulant on the surface of the membrane. In terms of fouling, stirring can also reduce the fouling potential and prolong the membrane filtration.

Compared with filtration in the MQ matrix, the increase of removal efficiency can be attributed to matrix effects. The wastewater matrix contains various organic compounds, such as humic acids, proteins and polysaccharides, some of which can bind with OMPs (discussed in the mass balance section later) followed by rejection by NF due to size exclusion and as a result enhance the removal efficiencies. Meanwhile, organic matters from wastewater can also absorb onto the membrane, competing with OMPs, which can be concluded from the phenomenon that the concentration in cell

concentrate for the first cycle was more concentrated than that of filtration in the MQ matrix. Organic matter and OMPs may adsorb to similar adsorption sites. The absorbed organic matter in/on the membrane could block membrane pores/modify the surface of membrane by forming a gel layer (see SEM figures later), which may enhance the rejection of OMPs by size exclusion.

3.2.3 Selected OMPs mixtures in MQ water matrix with fouled NF membrane

In order to classify the role of wastewater matrix enhancing the rejection percentage of OMPs during the process of filtration, another experiment was conducted: first, a secondary effluent (TOC about 8 mg/L) was filtered through the membrane for two cycles (one cycle is about 50 ml solution), allowing a foulant to form on or in the membrane; second, a ketoprofen-naproxen mixture in a MQ water matrix was applied for the filtration process with stirring applied. The concentrations of ketoprofen and naproxen in the permeate were determined by HPLC-UV periodically.

The removal efficiencies of OMPs are shown in the following figure:

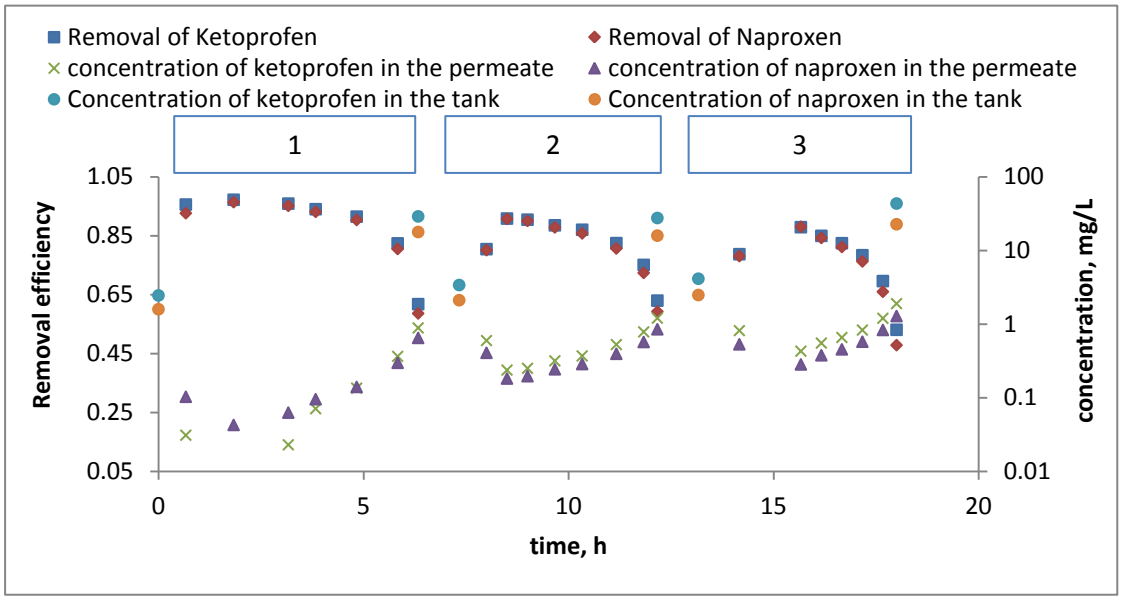


Figure 3-4 Long term filtration of wastewater, following by filtration of OMPs in MQ water

There are three cycles in the figure and each cycle was about 6 hours. Generally, the apparent removal efficiency ($1-C_p/C_{\text{initial concentration in the cell}}$) of both OMPs was similar because of their similar molecular properties. All three cycle showed a similar trend of removal efficiencies, which increased during the first stage of filtration and then decreased during later stages. The apparent removal efficiencies decreased down to 60% at the end of the cycle. The decreasing efficiencies are due to the increasing concentrations of OMPs in the cell concentrate, which had concentraions of OMPs more that 10 times those of the initial cell sollution for filtration. As we know, high concentrations of feed solution may result in higher concentration of permeate. As a result, the actual removal efficiencies should be much greater than the efficiencies here. The low removal efficiency of the first point of the second and third cycles might be attributed to the OMPs adsorbed by membrane and OMPs residued in the exit tube from the previous cycle. OMPs in the cell are always highly concentrated at

the end of the cycle, which would be diluted by the feed of the next cycle, causing the OMPs concentration in the cell to be less than the previous period of filtration, and as a result increasing the apparant removal efficiency. However, the efficiency decreased again due to the concentrated OMPs in the cell.

Compared with the removal efficiencies achieved by filtration of the ketoprofen-naproxen mixture in MQ water, rejection are higher after fouling of the membrane occurred. Only about 30 % of OMPs removal was achieved by the membrane in MQ water, versus more than 60% removal in this experiment. However, the apparant removal efficencies are lower than those of filtration of the ketoprofen-naproxen mixture in a wastewater matrix (more than 90%), indicating the organic matter in wastewater enhances the rejection of OMPs greatly, gives that organic matter can bind with OMPs. Thus OMPs can be distributed in the wastewater matrix between water and organic matter, which can be rejected easily by the NF membrane. That is to say, the partitioning of OMPs plays an important role in the rejection of OMPs in the watewater matrix. Theoritically, the effect of partitioning can be calculated by K_{ow} at the the testing pH (it was 7.8 in the filtration of OMPs in the wastewater matrix), but the values found in the literature were not tested at that pH. More research should be conducted for K_{ow} to calculate the importance of partitioning effect. On the other hand, there is no effect of partitioning for the filtration of OMPs in MQ water, even though the membrane had been fouled. That is why the rejection of OMPs in the wastewater matrix is highest.

3.2.4 Flux variation of filtration

In our three groups of filtration experiments, the flux of each cycle varied with time, as shown below:

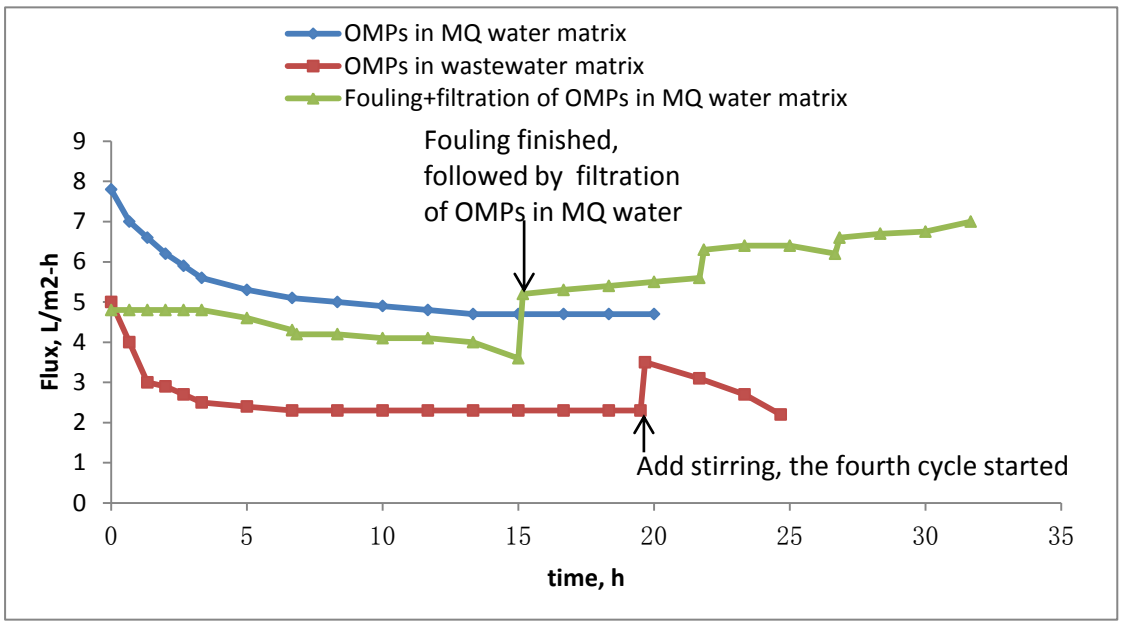


Figure 3-5 Flux variation of long term filtration

For flux of filtration in MQ water, the flux declines from 7.5 to 5 L/m^2-h slowly from time 0 to 400 min, and remains the same value until the end of the experiment. It appears that the changing of cycles does not affect the flux, even though there are 4 cycles shown in this figure.

The flux during wastewater matrix filtration was studied over 5 cycles: the first 3 cycles were for filtration of the ketoprofen-naproxen mixture in a wastewater matrix without stirring, and the last 2 cycles were for a similar filtration with stirring (125 rpm). Without stirring, the flux decreased sharply from 5 to 2.5 L/m^2-h within 80 min and declined slowly to 2 L/m^2-h until the end of the cycle 3. The fourth cycle (time

1100 min to 1500 min) showed flux of 3.5 L/m^2-h initially which decreased to 3 L/m^2-h slowly.

For flux during filtration of wastewater and OMPs in a MQ water matrix, first two cycles for secondary effluent wastewater filtration, which shows flux decreased from 5 to 3.5 L/m^2-h slowly (the sharp drop at 400 min was due to a refill of wastewater); and the last three cycles (from time 900 min on) for a ketoprofen-naproxen mixture during MQ water matrix filtration, which shows an increasing flux from 5 to 7 L/m^2-h. It is obvious that changing the filtration matrix can have an influence on flux, which can be deduced by time 900 min.

To summarize, an organic matter matrix has a significant influence on flux and can decrease the flux when there is no stirring, but the flux can increase again when providing stirring. Pure water can clean the membrane even with forward washing, and as a result, the membrane flux can increase to the value achieved by MQ water filtration.

3.3 Rejection mechanism of selected OMPs by NF membrane

3.3.1 Mass balance of selected OMPs during long-term filtration

In order to study the removal mechanism and the fate of OMPs, mass balance calculations were done as follows:

Table 3-4 Mass balance calculation of long term filtraion

	Ketoprofen S0, mg/L	ketoprofen Sf, mg/L	Naproxen S0, mg/L	naproxen Sf, mg/L	V0, ml	Vf, ml	mean removal efficiency	
							ket	nap
MQ,1	2.22	2.42	2.17	2.30	60	15	0.94	0.96
MQ,2	2.22	2.74	2.17	2.53	60	15	0.71	0.79
MQ,3	2.22	3.07	2.17	2.78	60	15	0.45	0.55
MQ,4	2.22	3.24	2.17	2.90	60	12	0.37	0.44
MQ,5	2.22	3.21	2.42	3.01	60	11	0.33	0.45
MQ,6	2.19	3.08	2.36	3.03	60	11	0.34	0.43
MQ,7	2.44	3.47	2.47	3.23	60	10	0.29	0.33
MQ,8	2.32	4.32	2.55	3.86	60	9	0.32	0.40
ww, 1	1.92	3.71	1.33	2.76	55	19	0.87	0.82
ww, 2	2.70	4.60	1.96	3.42	55	18	0.80	0.71
ww, 3	3.26	4.14	2.37	3.00	55	20	0.80	0.70
ww, 4	4.14	13.27	3.00	9.82	55	10	0.92	0.88
Fouling+MQ,1	2.45	29.00	1.59	17.80	55	4	0.88	0.87
fouling+MQ,2	3.39	27.60	2.11	15.90	55	5	0.82	0.81
fouling+MQ,3	4.13	43.40	2.48	22.70	55	3	0.76	0.75

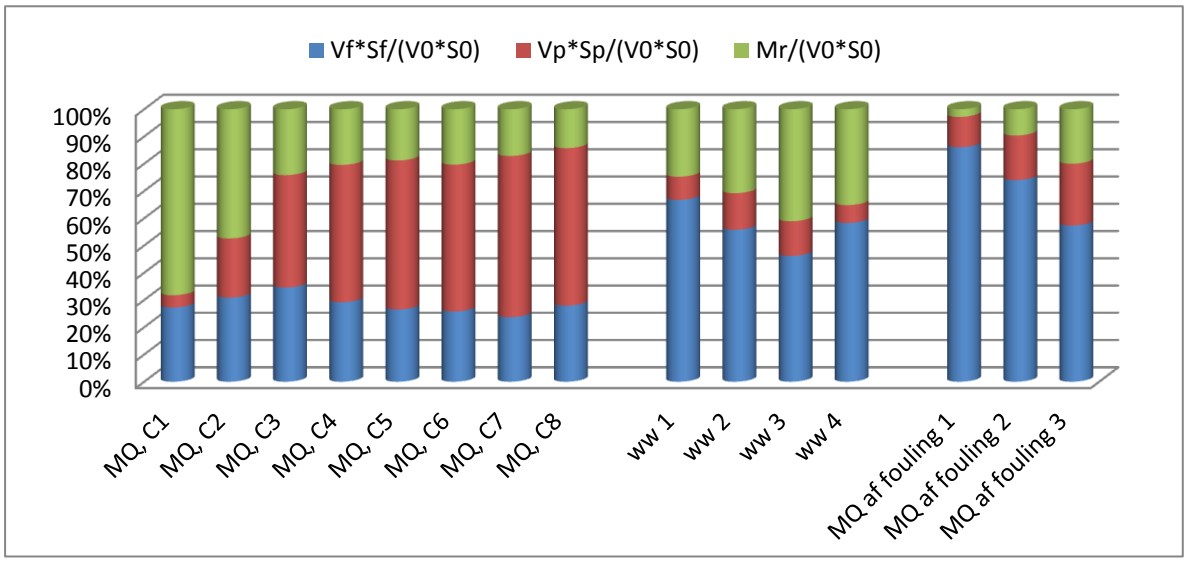
Note:

(1) S0: initial concentration in cell; Sf, final concentration in cell concentrate; V0: initial solution volume in cell; Vf: final solution volume in cell.

(2) MQ, filtration of ket-nap mixture in MQ water matrix; ww, filtration of ket-nap mixture in wastewater water matrix; fouling + MQ, filtration of ket-nap mixture in MQ water matrix after fouling process by wastewater; the number after these abbreviations stands for the cycle order.

(3) mean removal efficiency: the mean of all removal efficiency for each cycle.

There are three long-term filtrations as discussed earlier, and each filtration contains several cycles. The mean removal efficiency of OMPs in a wastewater matrix is much higher than that in MQ water, without a significant difference with that of fouling+MQ. Based on the data of the above table, the fate of OMPs was summarized in the following four figures.

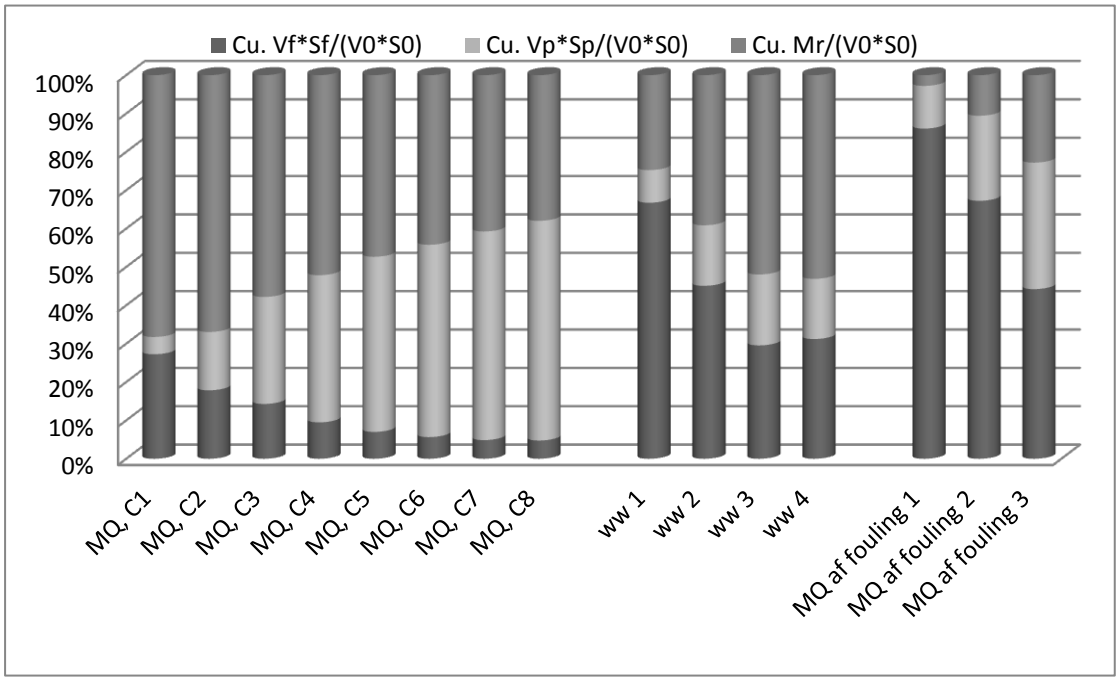


Vf*Sf/(V0*S0), the ratio of ketoprofen left in cell concentrate to the initial total value in the cell for each cycle;

Vp*Sp/(V0*S0), the ratio of ketoprofen in the permeate to the initial total value in the cell for each cycle;

Mr/(V0*S0), the ratio of ketoprofen in/on membrane to the initial total value in the cell for each cycle;

Figure 3-6 Ratio of amount of ketoprofen in cell concentrate, permeate and membrane to the total amount for each cycle

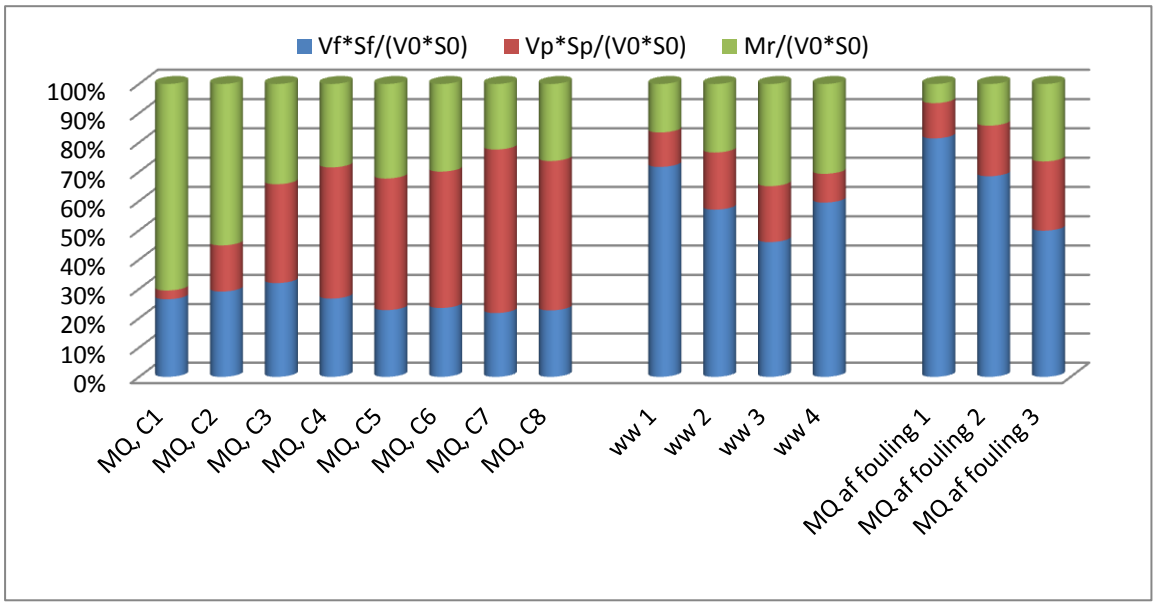


Cu, Vf*Sf/(V0*S0), the ratio of cumulative ketoprofen left in cell concentrate to the total value in the cell;

Cu, Vp*Sp/(V0*S0), the ratio of cumulative ketoprofen in the permeate to the total value in the cell;

Cu, Mr/(V0*S0), the ratio of cumulative ketoprofen in/on membrane to the total value in the cell;

Figure 3-7 Ratio of cumulative amount of ketoprofen in cell concentrate, permeate and membrane to the total amount for each cycle

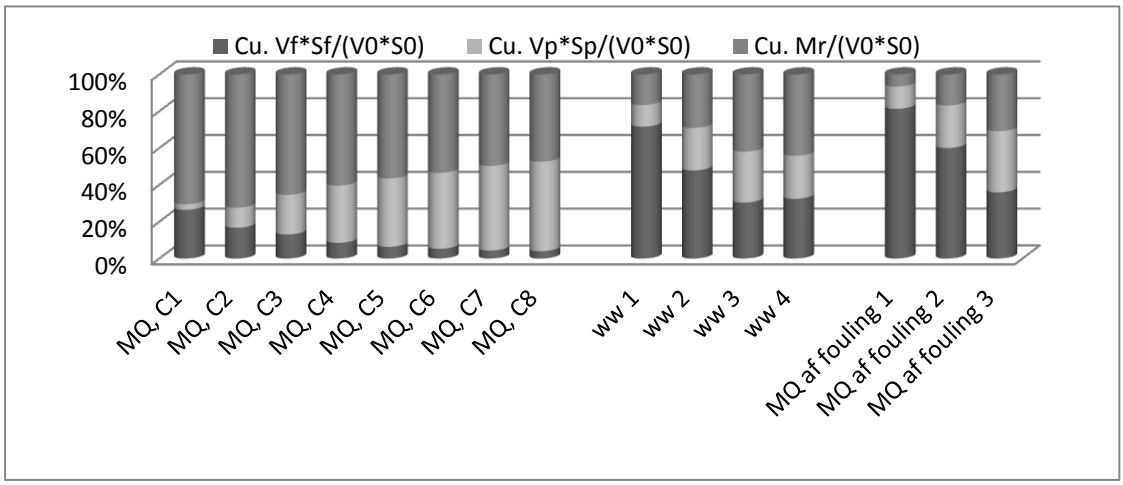


Vf*Sf/(V0*S0), the ratio of naproxen left in cell concentrate to the initial total value in the cell for each cycle;

Vp*Sp/(V0*S0), the ratio of naproxen in the permeate to the initial total value in the cell for each cycle;

Mr/(V0*S0), the ratio of naproxen in/on membrane to the total value in the cell for each cycle;

Figure 3-8 Ratio of amount of naproxen in cell concentrate, permeate and membrane to the total amount for each cycle



Cu, Vf*Sf/(V0*S0), the ratio of cumulative naproxen left in cell concentrate to the total value in the cell;

Cu, Vp*Sp/(V0*S0), the ratio of cumulative naproxen in the permeate to the total value in the cell;

Cu, Mr/(V0*S0), the ratio of cumulative naproxen in/on membrane to the total value in the cell;

Figure 3-9 Ratio of cumulative amount of naproxen in cell concentrate, permeate and membrane to the total amount for each cycle

The initial OMPs in the cell should have three fates during the filtration: the first is the cell concentrate, which can be considered the rejection by size exclusion and electric interaction; the second is the membrane, which can be regarded as rejection by membrane adsorption and deposition on membrane surface due to concentration polarization caused by OMPs alone or OMPs binding on organic matter; and the third is the permeate, which can indicate the overall system performance for OMPs rejection. The sum of the ratios of the three components to the total OMPs amount (V0*S0) is 1.

As can be seen from Figure 3-6 and 3-8, for filtration in MQ water, the amount of OMPs in the concentrate remains 20 - 30 % of the total initial amount of OMPs for the filtration in a MQ water matrix, but that of the permeate increased from 5 % to 50 %, which is consistent with the previous discussion. As a result, the percentage of OMPs in the membrane decreased, due to the decreasing free adsorption sites for OMPs.

For filtration in a wastewater matrix (ww 1-3 in the figure 3-6 and 3-8, without stirring), the OMPs in permeate remain about 10 % and 20 % of the total amount for ketoprofen and naproxen, respectively, indicating the overall performance remains stable. However, the percentage in the membrane is increasing, and it is the same value as the one in the concentrate at “ww 3” in the figure. On the other hand, both of the overall removal efficiencies increased when stirring was provided (see ww 4 in the figures).

Comparing “ww 1-3” with “MQ c1-c3” in figure 3-6 and 3-8, the ratios of OMPs in the concentrate are significantly greater, indicating that size exclusion and electrostatic repulsion are much greater in the wastewater matrix for OMPs removal. The zeta potential will be discussed later regarding electrostatic repulsion.

The bars for filtration in a MQ matrix after fouling have a similar trend with different values, and the reason has been discussed before.

For filtration in MQ water (see figure 3-7 and 3-9), the values of cumulative Vf*Sf/V0*S0 decrease from 25 % to less than 5%, but remain stable for the last 2 cycles. That is to say, the increasing rate for OMPs in the concentrate cannot catch up with the increasing rate of total OMPs because of the limited rejection by size exclusion and charge interaction for filtration of OMPs in a MQ water matrix.

For filtration in a wastewater matrix (see Figures 3-7 and 3-9), the trend is similar with the single cycle in figure 3-6 and 3-8. The ratio of cumulative OMPs in the permeate to the total amount was decreasing when there was no stirring (first three cycles), indicating the removal of OMPs was decreasing. Meanwhile, the ratio of cumulative OMPs in the concentrate to the total amount was decreasing, but the ratio of OMPs in the membrane was increasing (please note that this value is calculated as one minus the other two ratios). To the best of our knowledge, there might be two possible reasons: (1) the filtration solution can wash out the organic matters, which was absorbed by the membrane in the previous cycle, and as a result create some possible adsorption sites for OMP molecules; (2) OMPs reacted with organic matters

in the wastewater matrix and then were retained by membrane because those molecules are large enough to be rejected by NF. Both of the possible paths result in the increase of the ratio of OMPs associated with the membrane (on the surface or in the pores inner part of the membrane). After applying stirring (ww 4 in figure 3-7 and 3-9), the ratio of cumulative OMPs in the permeate to the total amount slightly decreased, leading the other two ratios increased, because the concentration polarization layer was less important in this cycle. These two possible reasons can also explain the increase of cumulative OMPs ratios in the membrane.

3.3.2 Characteristics of membrane before and after filtration

3.3.2.1 Contact angle

Contact angle is an important parameter for the hydrophobic/hydrophilic property of the membrane surface, and the macroscopic interaction between OMP molecules and the groups on the surface of membrane can be predicted by this method. The contact angles of membranes under different conditions were measured in our research, and the table below shows the results:

Table 3-5 Contact Angle of membrane surface

Description of membrane	Contact angle, degree
New membrane without washing	8—13
New membrane washed one time (rinse) and dried for one day	22---27
New membrane washed twice (rinse) and dried	for 1 day 17 (not dry enough); 2 days: 25—27
New membrane by stirring washing for several hours (more than 4)	31—33
New membrane after rinse and socked in water for more than 5 hours and dried for several days	43
Membrane after filtration of mixture of naproxen and ketoprofen in MQ water matrix	44---49
Membrane after (1) filtration of naproxen (2) filtration of mixture in MQ water	39—42
Membrane after adsorption of mixture	39---40
Membrane after filtration of mixture of naproxen and ketoprofen in wastewater Matrix	68 (fringe of the membrane has 52-54 degree contact angle)
Membrane after filtration of ketoprofen for 8 Cycles and dried for several days	77-78
membrane for wastewater fouling followed by ketoprofen-naproxen mixture filtration	53-58

It is clear that the new membrane from the manufacture has the lowest contact angle, indicating that it is the most hydrophilic membrane among all the samples. Nevertheless, the surface of the membrane became more and more hydrophobic after further intensive washing. The reason is there is a hydrophilic organic solution on the surface of membrane which decreases the contact angle of membrane, and it can be rinsed off of the membrane easily by water.

The membrane after filtration of a ketoprofen-naproxen mixture in a wastewater matrix has a higher value of contact angle than those of the membrane for adsorption and filtration in a MQ matrix. Organic matter in the wastewater accounts for the higher value of contact angle. The organic matter in wastewater has both hydrophilic

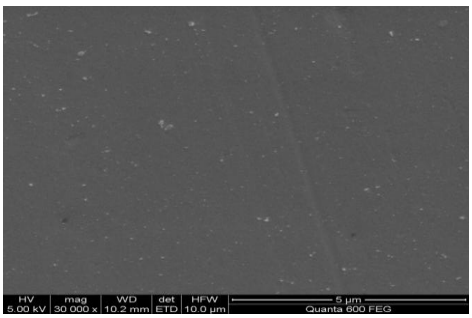
and hydrophobic parts and during the filtration process, organic matter can foul the membrane surface, perhaps leaving hydrophobic components on the membrane, increasing the contact angle.

As has been discussed, washing the membrane and filtration with the membrane (either in a MQ water matrix or wastewater matrix) result in increasing contact angle. Both of these processes enhance the rejection of ketoprofen and naproxen, since they are mainly partially ionized hydrophilic molecules, which can be repelled by hydrophobic groups on the surface of membrane according to the theory of "similarity and intermiscibility".

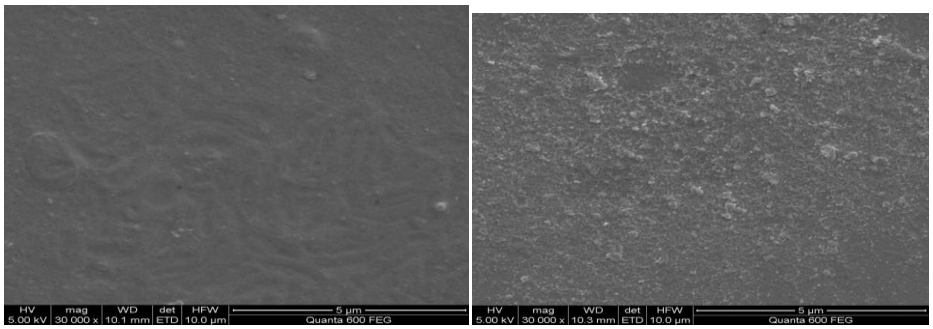
It is interesting to note that the value of contact angle varies from the interior side to exterior of the membrane after filtration of a ketoprofen-naproxen mixture in wastewater matrix, indicating the fouling layer of the membrane is not homogeneous.

3.3.2.2 SEM

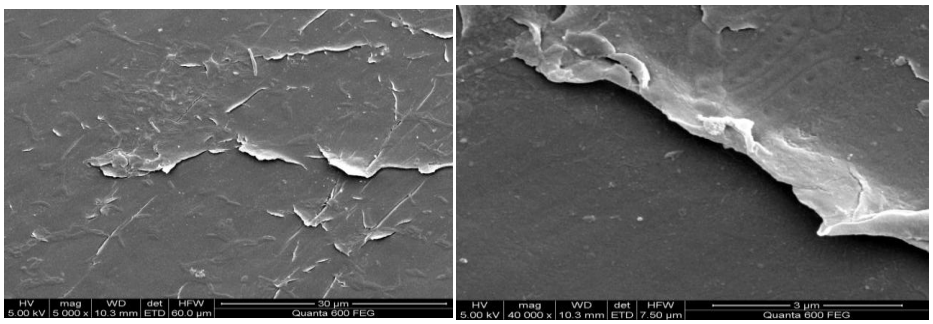
In order to study the morphology of the membrane after different filtration conditions, SEM was applied for the membrane samples, as follows (four groups of SEM figures):



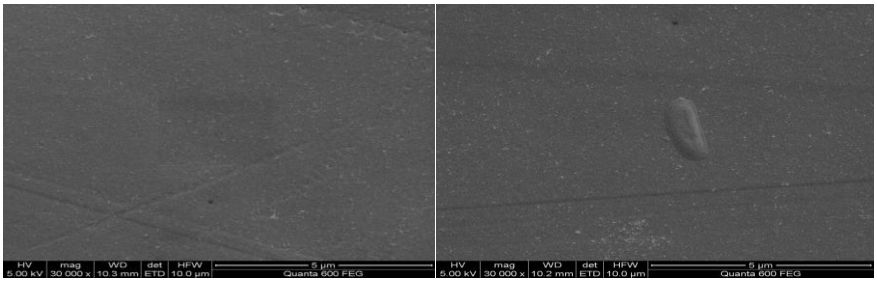
(1) New membrane



(2) after filtration of ketoprofen-naproxen mixture, Left: wastewater matrix; right: MQ water matrix



(3) Membrane after Fouling + filtration of ketoprofen-naproxen mixture in MQ water matrix



(4) after adsorption of ketoprofen-naproxen mixture, left: MQ matrix; right: wastewater matrix

Figure 3-10 SEM of membrane surface

Picture 1 shows the surface of new membrane, which is an asymmetric NF membrane with a smooth surface.

Picture 2 shows the membrane surface covered with a layer of organic matter, including some microorganisms after filtration of the ketoprofen-naproxen mixture in a wastewater matrix, while the other membrane is covered with some white compounds which seem like crystals after the filtration of ketoprofen-naproxen mixture in MQ water.

Picture 3 shows the morphology of the membrane after wastewater fouling and filtration of ketoprofen-naproxen mixture in MQ water. It is clear that the organic matter layer was patchy on the surface of the membrane. Some microorganisms can be observed under the layer of organic matter.

Picture 4 shows the membrane after the adsorption of ketoprofen-naproxen mixture, both in MQ water and wastewater matrix. This membrane is even much smoother than new membrane.

Generally speaking, the organic matter from the wastewater can foul the membrane surface and/or the membrane pores which may enhance the rejection of ketoprofen and naproxen by sieving effects, and the fouling layer of organic matter may also adsorb some ketoprofen and naproxen.

3.3.2.3 Zeta potential analysis

Zeta potential is a very important physicochemical property for the solution and

membrane surface. Colloids or particles in solution remain stable when the absolute value of zeta potential is high, and particles may collide with one other to form aggregate, when the absolute value is low. Similarly, zeta potential of a membrane surface also indicates the property of surface charge. Generally speaking, the higher the pH, the more negative the surface of the membrane.

The Figure 3-11 shows the zeta potential for the KOCH 200 after different processes. The new membrane has an isoelectric point of pH 6.8, above which, the surface of the membrane gains negative charges due to the dissociation of OH (indicated by FT-IR). At a pH of less than 6.8, the surface of the membrane has positive charges because NH, or NH_2 can carry H^+. However, the membrane had a lower isoelectric point value of pH 6 after it was rinsed by MQ water. As discussed before, the new membrane has a protecting solution on the surface.

All the membranes used in the experiments were rinsed by MQ water, so take the zeta potential of the washed membrane as the reference. In the filtration of a ketoprofen-naproxen mixture in MQ water, the pH is around 5.5, indicating the zeta potential of the membrane is +1 mV (slightly positive charged). However, the pH of the ketoprofen-naproxen mixture in a wastewater matrix is 7.8, and the zeta potential for the membrane surface is -10 mV, more negative than that in a MQ water matrix. Both of ketoprofen and naproxen contain carboxyl groups, which can ionize at neutral or basic pH, resulting in negative charged OMP molecules. As is well know, particles with the same charge can repel one other. As a result, the higher the pH, the more negative the surface of the membrane and the larger the electrostatic repulsion force

between the membrane and OMP molecule, leading to a high rejection of OMPs by membrane. This is one reason why OMPs in wastewater have higher rejection. In a MQ water matrix, the electrostatic interaction is weak, since the membrane surface carries a low positive charge.

The membrane surface contains more negative charges after filtration of the ketoprofen-naproxen in a wastewater matrix, and the zeta potential remains at about -20 mV from pH 5.5 to pH 9. Wastewater contains much organic matter with a negative charge (discussed later), and those molecules can enhance the negative surface charge of the membrane, and pH has little impact on the zeta potential after filtration.

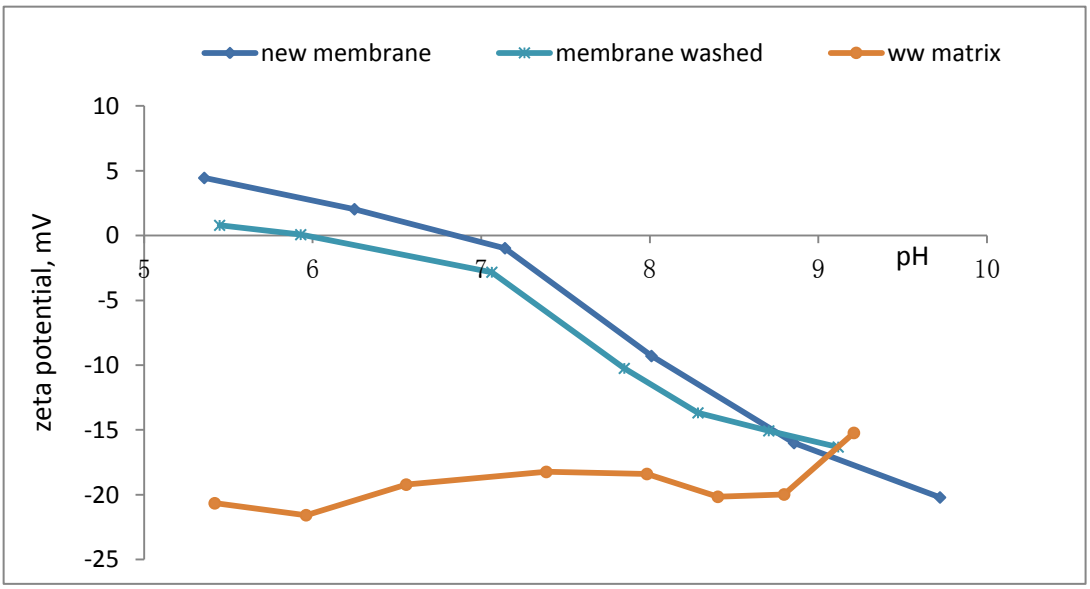


Figure 3-11 zeta potential for membranes under different conditions

Zeta potential of the feed solution was also tested. OMPs have little influence but wastewater components can lower the zeta potential considerably. The ketoprofen-naproxen in MQ water system has a zeta potential of - 0.5 mV, and in

wastewater it is -10 mV. Even though the major contribution of zeta potential is from organic matter in wastewater, a high absolute value of zeta potential on the membrane result in high rejection of OMPs, since OMPs can absorb on to or bind with the organic matter and they can be rejected together by size exclusion and electric repulsion. That is to say, charge interaction can enhance the performance of a membrane for OMPs rejection in a wastewater matrix.

3.3.2.4 FT-IR analysis

In order to study the functional groups associated with the membrane surface and the interaction of OMPs or organic matter with the membrane, FT-IR analyses were conducted.

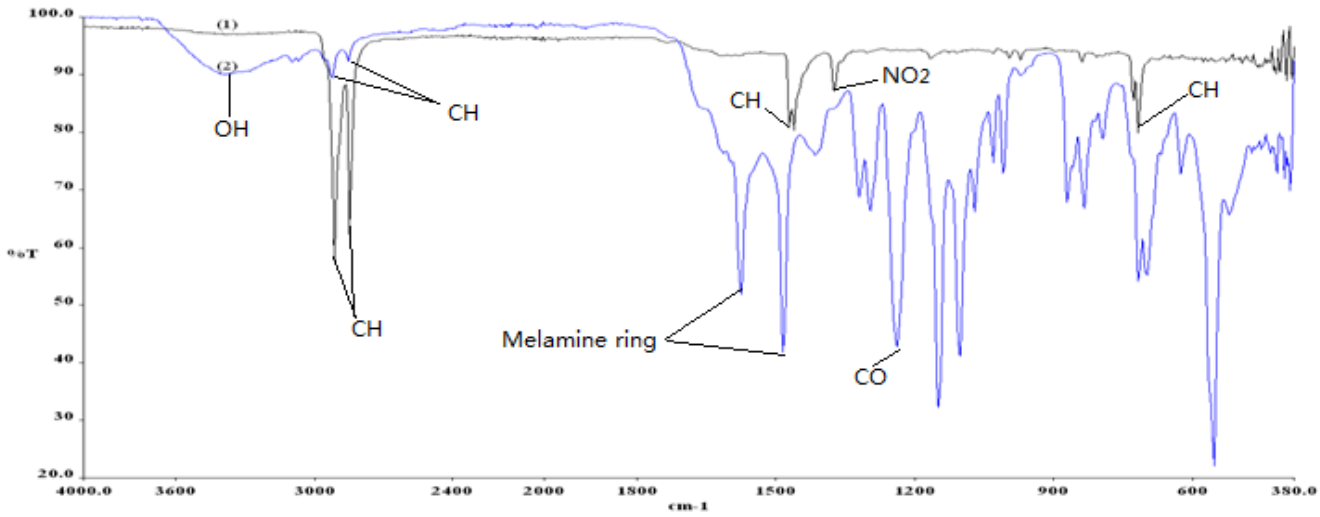
The table below shows the relationship between wave number, functional group type, and vibration type. This table can help us with analysis of FT-IR spectra.

Table 3-6 Functional groups and their FT-IR spectra responses

Wave number （cm^{-1}）	Vibration type	Functional type
3200-3400	Stretching vibration of OH	OH into polymeric compounds
2936-2916	Asymmetric stretching vibration of CH_2	
2843-2863	Symmetric stretching vibration of CH_2	
1700-1725	Strecthing Variation of C=O (shoulder)	Carboxylic acids
1650-1670	Stretching variation of C=O	Carboxylic acids
1640-1660	Stretching variation of C=O and C-N (amide Ⅰ)	Proteins（Peptidic bond）
1615-1540	Asymmetric stretching vibration of NO_2	
1550-1560	Stretching variation of C-N and deformation vibration of N-H (amide Ⅱ)	Proteins（Peptidic bond）
1445-1485	Deformation vibration of CH_2	
1400-1410	Stretching vibration of C=O	Carboxylates
	Deformation vibration of OH	Alcohols
1390-1320	Symmetric stretching vibration of NO_2	
1240	Deformation vibration of C=O	Carboxylic acids
1040-1070	Stretching vibration of OH	
<1000	Fingerprint zone	
	Several bands visible	Phosphate or sulphur functional groups, or $-(CH_2)_n-$, n>4

The figure below shows the FT-IR spectra of active and support layers for the new membrane. The active layer contains Melamine Phenol Formaldehyde (MPF). Peaks at 3400, 1400, 1000 cm^{-1} show the existence of OH and peaks at 1600, 1500 cm^{-1},

indicating that there are melamine rings in the active layer of the membrane. In addition, peak at 1500 cm also shows evidence of NH. In summary, the active layer contains functional groups of OH, NH, NH_2 aromatic rings and melamine rings. On the other hand, the FT-IR spectra of the support layer is much simpler, CH groups can be identified by peaks at 2900, 2800, 1400 and 700 cm^{-1}, and there may be some NO_2 groups, but much less than CH since the peak for NO_2 is weak. Hence, the support layer of the membrane should be hydrophobic and contains much CH and a little NO_2. That is why the support layer can absorb OMPs easily.



Note: new membrane: (1) support layer (2) active layer

Figure 3-12 FT-IR of KOCH NF 200

Chapter IV Simulation of OMPs' removal based on Compound Retention Time (CRT)

Generally, wastewater is treated in a continuous flow reactor, similar to a continuous stirred tank reactor (CSTR) in chemical engineering. In order to develop the concept of compound retention time (CRT), and simulate the concentrations of OMPs for unsteady state and steady state, 3 ideal reactors were designated: (1) a CSTR without any membrane; (2) a membrane bioreactor without any sludge wastage; (3) a membrane bioreactor with sludge wastage.

4.1 CSTR without membrane

4.1.1 Description of CSTR

An ideal CSTR for wastewater treatment is as follows:

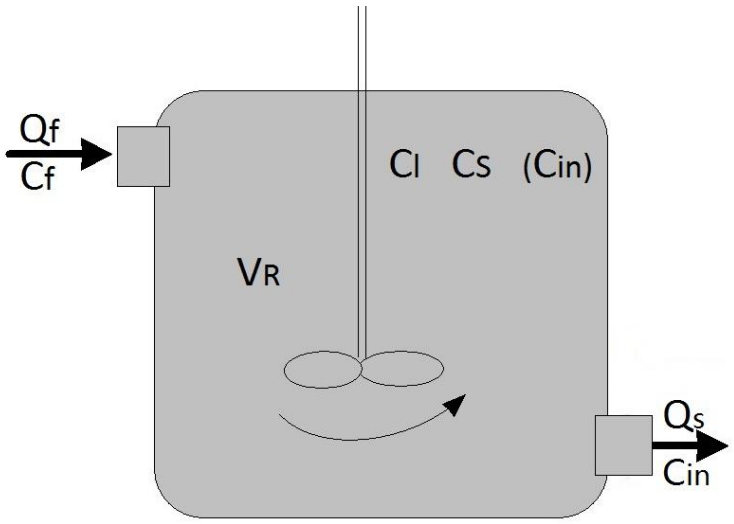


Figure 4-1 Set up for CSTR

In this CSTR, the flow rate of the influent equals to that of effluent, and the liquid-

solid mixture is homogenous anywhere within the reactor, with no dead zone. Ignoring the air in the tank, OMPs can distribute into liquid and solids in the reactor. The components in the effluent are the same as those in the CSTR at steady state. Here are definitions of the abbreviations in the figure:

C_f—concentration of OMPs in feed, mg/L

C_l—concentration of OMPs in liquid phase of the sludge in the reactor, mg/L

C_s—concentration of OMPs in solid phase of the sludge in the reactor, mg/g

C_{in}—mean concentration of OMPs in the reactor (all phases), mg/L

Q_f—flow rate of feed, L/day

Q_s—flow rate of sludge, L/day

V_l—volume of liquid in the reactor, L

M_s—Mass of solids in the reactor, g

V_R—volume of the reactor (assume that the reactor is fully filled and as a result, the volume of the mixture in the tank is V_R), L

MLSS—solid concentration of the mixture in the reactor, g/L

k— linear partitioning coefficient of isotherm for adsorption of OMPs onto sludge, L/g

K—reaction constant for the degradation of OMPs by microorganism in the reactor, d^{-1}

R_a—apparent removal of compounds ($R_a=C_l/C_f$)

R_j—reaction rate for first order reaction, mg/L-d

HRT—hydraulic retention time, days. ($HRT=V_R/Q$)

CRT—compound retention time, days

Generally, MLSS is about 5-20 g/L or 0.5-2% (v/v), the volume of sludge can be considered the same as the volume of liquid phase of sludge.

Relevant equations for the reactor are:

$$V_l = V_R \quad (4.1)$$

$$M_s = MLSS \times V_R \quad (4.2)$$

$$C_s = k \times C_l \quad (4.3)$$

$$C_{in} = \frac{C_l \times V_l + C_s \times M_s}{V_R} = \frac{C_l \times V_R + k \times C_l \times MLSS \times V_R}{V_R}$$

$$\Rightarrow C_{in} = (1 + k \times MLSS) \times C_l \quad (4.4)$$

The overall mass balance equation is:

$$Q_f C_f = Q_s C_{in} + \frac{dC_{in}}{dt} V_R - R_j V_R \quad (4.5)$$

In equation (4.5), the value of R_j should be negative for reactant. The steady state and unsteady state will be analyzed later.

4.1.2 CSTR under steady state

For steady state, there should be no change for the concentrations of OMPs in the reactor. And the volume and components of the mixture in the reactor should be unchanged. As a result:

$$\frac{dC_{in}}{dt} V_R = 0 \quad (4.6)$$

$$Q_f = Q_s = Q(\text{constant}) \quad (4.7)$$

So the mass balance equation reduces to:

$$QC_f = QC_{in} - R_j V_R \quad (4.8)$$

Analyzing this equation by the fundamental equations:

$$\frac{QC_f}{V_R} = \frac{QC_{in}}{V_R} - R_j \quad (4.9)$$

$$\frac{C_{in}}{V_R/Q} - \frac{C_f}{V_R/Q} - R_j = 0 \quad (4.10)$$

$$\frac{C_{in}}{HRT} - \frac{C_f}{HRT} - R_j = 0 \quad (4.11)$$

$$\frac{1}{HRT}(C_{in} - C_f) - R_j = 0 \quad (4.12)$$

(Note HRT = SRT in this CSTR)

Assume that the degradation of OMPs is first order, so:

$$R_j = KC_l \quad (4.13)$$

Similar to SRT, the compound retention time for the compound in the reactor is as follows:

$$CRT = \frac{C_{in}V_R}{C_{in}Q} = HRT = SRT \quad (4.14)$$

The equation above indicates that the compound retention time is the same as hydraulic retention time and sludge retention time. HRT and SRT have influence on the biodegradation degree of OMPs

4.1.3 General analysis of CSTR

The overall mass balance can be converted to:

$$\frac{dC_{in}}{dt} + \left(\frac{1}{HRT} - \frac{K}{1 + k \times MLSS}\right) C_{in} = \frac{C_f}{HRT} \quad (4.15)$$

The result is:

$$C_{in} = \frac{c}{b}\left(1 - e^{-bt}\right) \quad (4.16)$$

$$b = \left(\frac{1}{HRT} - \frac{K}{1 + k \times MLSS}\right) (K < 0 \; for \; consumption) \quad (4.17)$$

$$c = \frac{C_f}{HRT} \quad (4.18)$$

And the maximum value of C_{in} can be calculated according to the following equation:

$$C_{in,max} = \frac{c}{b} \quad (4.19)$$

According to equation (4.4), the maximum value of C_l can be calculated as follows:

$$C_{l,max} = \frac{C_{in,max}}{1 + k \times MLSS} = \frac{c}{b(1 + k \times MLSS)} \quad (4.20)$$

The apparent removal can be calculated as:

$$R_a = 1 - \frac{C_p}{C_f} \quad (4.21)\ (C_p = C_l \text{ in the CSTR})$$

Based on the literature, OMPs are listed in the following table. The order of the compounds is based on the first order reaction constant "K" (in red). The first order reaction constants are increasing from No.1 (mefenamic acid) to No.17 (acetaminophen).

Table 4-1 Compound information for OMPs

No	Compound	MW	pKa	Log Kow	K, d-1	k, L/g	Classification
1	Mefenamic acid	241.3	3.73(a), 4.2(b)	5.12(b)	0.00744(a)	0.02(a)	A non-steroidal anti-inflammatory drug used to treat pain
2	Carbamazepine	236.3	13.94(a)	2.45(c)	0.0144(a), 0.012-0.0076(d)	0.000085(a)	Anti-epileptic
3	Ibuprofen	206.3	4.41(a)	3.97(e)	0.036(a)	0.000093(a)	A nonsteroidal anti-inflammatory drug (NSAID)
4	Indomethacin	357.8	3.96(a), 4.5(b)	4.27(b)	0.0384(a)	0.00012(a)	A non-steroidal anti-inflammatory drug commonly used to reduce fever, pain, stiffness, and swelling

5	17a-Ethinylestradiol (EE2)	296.4	10.5(f)	3.67(c)	0.046(g)	0.014(g)	Synthetic hormone
6	Ketoprofen	254.3	4.45(e)	3.12(e)	0.05(e), 0.979(h)	0.0056(e)	Anti-phlogistic
7	Ifenprodil	325	9.34, 9.99, (a), 9.6(h)	3.90(b)	0.0504(a)	0.031(a)	Selective inhibitor of the NMDA receptor
8	Sulfamethazine	278.3	2.07, 7.65(e)	0.19(e)	0.06(e)	0.013(e)	Sulfonamide antibacterial
9	Atenolol	266.3	9.16, 13.88(a)	0.16(b)	0.0816(a)	0.0013(a)	β-blockers
10	Propranolol	259.3	9.14, 13.84(a)	3.48(b)	0.144(a)	0.0022(a)	A sympatholytic non-selective beta blocker
11	Naproxen	230.3	4.15(e)	3.18(e)	0.16(e)	0.015 (e)	Nonsteroidal anti-inflammatory drug (NSAID)
12	4-Octylphenol (4-OP)	206.3	10.3 (i)	-	0.210(g)	0.084(g)	Surfactant degradation product
13	Sulfamethoxazole	253.3	1.85, 5.60(e)	0.89(e)	0.32(e)	0.032(e)	Sulfonamide bacteriostatic antibiotic
14	Bisphenol A (BPA)	228.3	9.6-10.2(f)	3.32(c)	0.433 (g)	0.008(g)	Component of plastics
15	4-Nonylphenol (4-NP)	220.4	10.7(i)	5.76(c)	0.433 (g), 0.03-0.04(j)	0.998(g)	Surfactant degradation product
16	17ß-Estradiol (E2)	272.4	-	4.01(c)	0.462(g)	0.012(g)	Steroid hormone
17	Acetaminophen	151.2	9.38(e)	0.46(e)	1.09(e), 0.336(a)	0.036(e) 0.01(a)	Over-the-counter analgesic (pain reliever) and antipyretic (fever reducer).

(a) Hiroshi Yamamoto (2009)[50]
(b) website: http://www.syrres.com/what-we-do/databaseforms.aspx?id=386[51]
(c) Wenchao Xue (2010)[52]
(d) Lam (2004)[53]
(e)Tsung-Hsien Yu, (2011)[54]
(f) Lesley Joseph (2011)[55]
(g) Guang-Guo Ying (2008)[56]
(h) Stuart J. Khan (2004)[57]
(i) Qingxiang Zhou (2011)[58]

(j) Sally Brown (2009) [59]

As can be seen from the table, there may be several reaction or adsorption constants for one compound since different experimental conditions result in different reaction rates. The first one of the constants for every compound will be used for the simulations.

Assume the parameters for the CSTR are as follows: the initial concentrations of OMPs in the reactor are 0 mg/L, MLSS = 10 g/L, HRT = SRT= 1 d, feed concentrations of OMPs are all 0.1 mg/L.

Based on equations (4.16-21), the concentrations of OMPs and apparent removal efficiency can be calculated and summarized in the following table:

Table 4-2 Summary for CSTR

No	Compound	K, d-1	k, L/g	b	c	C_{inmax}, mg/L	C_{lmax}, mg/L	Ra
1	Mefenamic acid	0.00744	0.02	1.0062	0.1	0.099	0.083	0.172
2	Carbamazepine	0.0144	0.000085	1.014388	0.1	0.099	0.098	0.015
3	Ibuprofen	0.036	0.000093	1.035967	0.1	0.097	0.096	0.036
4	Indomethacin	0.0384	0.00012	1.038354	0.1	0.096	0.096	0.038
5	17a-Ethinylestradiol (EE2)	0.046	0.014	1.040351	0.1	0.096	0.084	0.157
6	Ketoprofen	0.05	0.0056	1.047348	0.1	0.095	0.090	0.096
7	Ifenprodil	0.0504	0.031	1.038473	0.1	0.096	0.074	0.265
8	Sulfamethazine	0.06	0.013	1.053097	0.1	0.095	0.084	0.160
9	Atenolol	0.0816	0.0013	1.080553	0.1	0.093	0.091	0.086
10	Propranolol	0.144	0.0022	1.1409	0.1	0.088	0.086	0.142
11	Naproxen	0.16	0.015	1.13913	0.1	0.088	0.076	0.237

12	4-Octylphenol (4-OP)	0.21	0.084	1.11413	0.1	0.090	0.049	0.512
13	Sulfamethoxazole	0.32	0.032	1.242424	0.1	0.080	0.061	0.390
14	Bisphenol A (BPA)	0.433	0.008	1.400926	0.1	0.071	0.066	0.339
15	4-Nonylphenol (4-NP)	0.433	0.998	1.039435	0.1	0.096	0.009	0.912
16	17ß-Estradiol (E2)	0.462	0.012	1.4125	0.1	0.071	0.063	0.368
17	Acetaminophen	1.09	0.036	1.801471	0.1	0.056	0.041	0.592

Note: b and c are calculated from equations (4.17-18), and the maximum values of C_{in} and C_l are the same as those in steady state. K, k, Ra stand for the first order reaction constant, linear adsorption coefficient and apparent removal efficiency, respectively. (The apparent removal can be calculated as:$R_a = 1 - \frac{C_p}{C_f}$ (4.21))

To explore the effect of reaction constant and adsorption coefficient, a figure is obtained as follows:

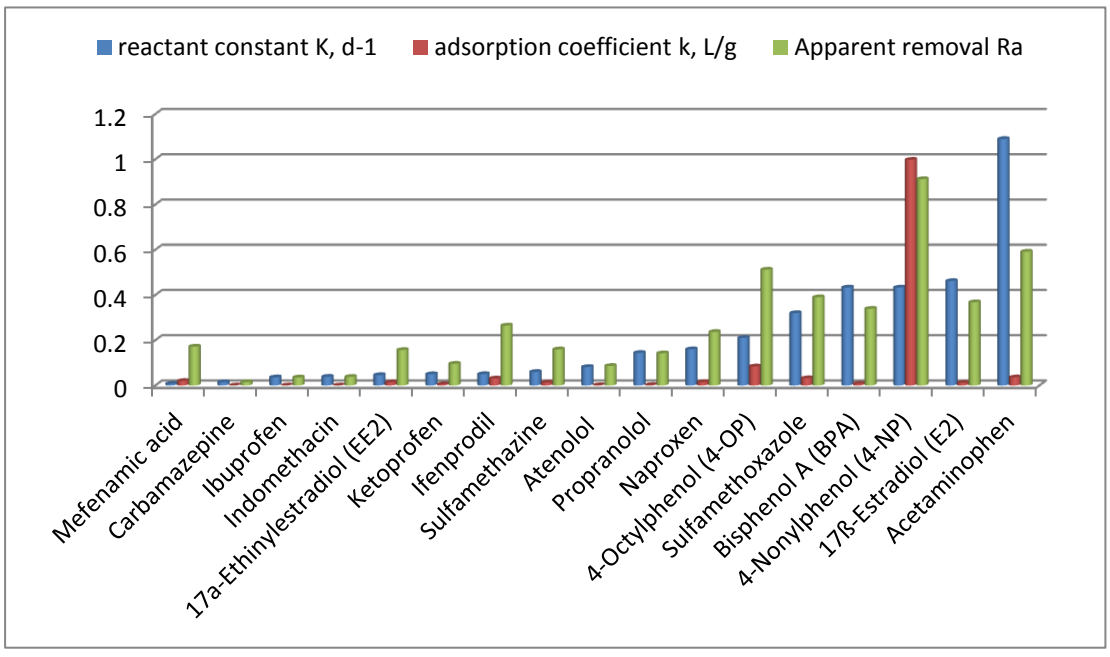


Figure 4-2 Effect of reaction and adsorption constant on apparent removal efficiency of OMPs

It is clear that different reaction and adsorption constants result in different extents of apparent removal. Generally speaking, the greater the reaction constant, the more the apparent removal. However, 4-NP has the highest apparent removal efficiency but its reaction constant is not the greatest, which indicates adsorption constant also affect the apparent removal. Most of the OMPs in the figure can be removed from the wastewater less than 50 %, showing CSTR is not sufficient for the OMPs control.

4.2 Membrane bioreactor without any sludge wastage (SRT=+∞)

4.2.1 Description of the reactor (SRT=+∞)

An ideal membrane reactor for wastewater treatment without sludge wastage is shown below.

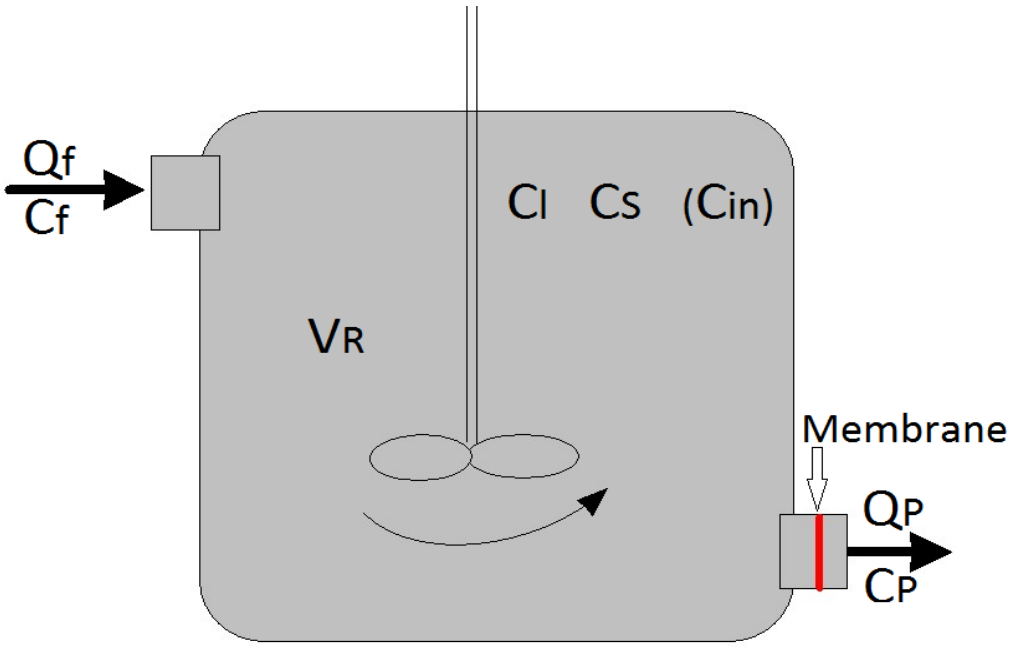


Figure 4-3 Set up for wastewater treatment reactor without sludge wastage

In this reactor, the flow rate of the influent equals to that of effluent, and the liquid-

solid mixture is homogenous anywhere within the reactor, with no dead zone. Ignoring the air in the tank, OMPs can distribute into liquid and solids in the reactor. Here are definitions of the abbreviations in the figure:

a—membrane rejection rate for OMPs (a = 0 – 1)

b'—equation (4.32)

C_f—concentration of OMPs in feed, mg/L

C_p—concentration of OMPs in permeate, mg/L

C_l—concentration of OMPs in liquid phase of the sludge in the reactor, mg/L

C_s—concentration of OMPs in solid phase of the sludge in the reactor, mg/g

C_{in}—mean concentration of OMPs in the reactor (all phases), mg/L

Q_f—flow rate of feed, L/day

Q_p—flow rate of permeate, L/day

V_l—volume of liquid in the reactor, L

M_s—Mass of solids in the reactor, g

V_R—volume of the reactor (assume that the reactor is fully filled and as a result, the volume of the mixture in the tank is VR), L

MLSS—solid concentration of the mixture in the reactor, g/L

k— linear partitioning coefficient of isotherm for adsorption of OMPs onto sludge, L/g

K—reaction constant for the degradation of OMPs by microorganism in the reactor, d^{-1}

R_a—apparent removal of compounds ($R_a=C_l/C_f$)

R_j—reaction rate for first order reaction, mg/L-d

HRT—hydraulic retention time, days. (HRT=V_R/Q)

CRT—compound retention time, days

Generally, MLSS is about 5-20g/L or 0.5-2% (v/v), the volume of sludge can be considered the same as the volume of liquid phase of sludge.

Relevant equations for the reactor are:

$$V_l = V_R \quad (4.1)$$

$$M_s = MLSS \times V_R \quad (4.2)$$

$$C_s = k \times C_l \quad (4.3)$$

$$C_{in} = \frac{C_l \times V_l + C_s \times M_s}{V_R} = \frac{C_l \times V_R + k \times C_l \times MLSS \times V_R}{V_R}$$

$$\Rightarrow C_{in} = (1 + k \times MLSS) \times C_l \quad (4.4)$$

$$C_p = f(C_l) = aC_l = \frac{a}{1+k\times MLSS} \times C_{in} \quad (0 \le a \le 1) \quad (4.22)$$

Equation (4.22) is very important, since it indicates the rejection of OMPs by the membrane. Ideally, C_p could be 0, but in the real reactor, the C_p = 0 -1 C_l. ”a” is the rejection coefficient for membrane (different from apparent removal efficiency). Generally, RO membrane and tight NF membrane have good rejection of OMPs, especially for big pesticide molecules [60, 61, 62, 63], with rejection more than 90%. And fouling membrane may enhance the rejection of OMPs [64]. In the simulations, 90% was chosen as the OMPs rejection by NF membrane (a=0.1).

The overall mass balance equation is:

$$Q_f C_f = Q_p C_p + \frac{dC_{in}}{dt} V_R - R_j V_R \quad (4.23)$$

In equation (4.6), the value of R_j should be negative for reactant (degradation). The steady state and unsteady state will be analyzed later.

4.2.2 CRT under steady state

For steady state, there should be no change for the concentrations of OMPs in the reactor. And the volume and components of the mixture in the reactor should be unchanged. As a result:

$$\frac{dC_{in}}{dt}V_R = 0 \quad (4.6)$$

$$Q_P = Q_f = Q(\text{constant}) \quad (4.7)$$

So the mass balance equation reduces to:

$$QC_f = QC_p - R_j V_R \quad (4.24)$$

Analyzing this equation by the fundamental equations:

$$\frac{QC_f}{V_R} = \frac{QC_p}{V_R} - R_j \quad (4.25)$$

$$\frac{C_p}{V_R/Q} - \frac{C_f}{V_R/Q} - R_j = 0 \quad (4.26)$$

$$\frac{C_p}{HRT} - \frac{C_f}{HRT} - R_j = 0 \quad (4.27)$$

$$\frac{1}{HRT}(C_P - C_f) - R_j = 0 \quad (4.28)$$

Assume that the degradation of OMPs is first order, so:

$$R_j = KC_l \quad (4.13)$$

Similar to SRT, the compound retention time for the compound in the reactor is as follows:

$$CRT = \frac{C_{in}V_R}{C_p Q} = \left(\frac{C_{in}}{C_p}\right)HRT = \frac{(1 + k \times MLSS)HRT}{a} \quad (4.29)$$

4.2.3 General analysis

It takes time for a real reactor to reach steady state. Simulations of unsteady state are

displayed in this section.

To solve equation (4.6), the equation can be converted into the following form:

$$\frac{dC_{in}}{dt} + \frac{1}{1 + k \times MLSS}\left(\frac{Q_p \times a}{V_R} - K\right) C_{in} = \frac{Q_f \times C_f}{V_R} \quad (4.30)$$

The result is:

$$C_{in} = \frac{c}{b'}\left(1 - e^{-b't}\right) \quad (4.31)$$

$$b' = \frac{1}{1 + k \times MLSS}\left(\frac{Q_p \times a}{V_R} - K\right)$$

$$= \frac{1}{1 + k \times MLSS}\left(\frac{a}{HRT} - K\right) (K < 0\ for\ consumption) \quad (4.32)$$

$$c = \frac{Q_f \times C_f}{V_R} = \frac{C_f}{HRT} \quad (4.18)$$

And the maximum value of C_{in} can be calculated according to the following equation:

$$C_{in,max} = \frac{c}{b'} \quad (4.33)$$

According to equation (4.4), the maximum value of C_l can be calculated as follows:

$$C_{l,max} = \frac{C_{in,max}}{1 + k \times MLSS} = \frac{c}{b'(1 + k \times MLSS)} \quad (4.34)$$

The apparent removal is:

$$R_a = 1 - \frac{C_p}{C_f} \quad (4.21)$$

4.2.3.1 Effect of adsorption and biodegradation constants

Degradation is related with reaction rate. Choose the same 17 compounds listed in table 4-1 and analysis the removal efficiencies.

Assume the parameters for the reactor are as follows: the initial concentrations of OMPs in the reactor are 0 mg/L, $C_p = 0.1 * C_l$ (this is for the NF rejection), MLSS = 10 g/L, HRT = 1 d, feed concentrations of OMPs are all 0.1 mg/L.

Table 4-3 summary for MBR without sludge wastage

No	Compound	K, d-1	k, L/g	b'	c	C_{inmax}, mg/L	C_{lmax}, mg/L	Ra	CRT
1	Mefenamic acid	0.00744	0.02	0.089533	0.1	1.117	0.093	0.069	12
2	Carbamazepine	0.0144	0.000085	0.114303	0.1	0.875	0.087	0.126	10.0085
3	Ibuprofen	0.036	0.000093	0.135874	0.1	0.736	0.074	0.265	10.0093
4	Indomethacin	0.0384	0.00012	0.138234	0.1	0.723	0.072	0.277	10.012
5	17a-Ethinylestradiol (EE2)	0.046	0.014	0.12807	0.1	0.781	0.068	0.315	11.4
6	Ketoprofen	0.05	0.0056	0.142045	0.1	0.704	0.067	0.333	10.56
7	Ifenprodil	0.0504	0.031	0.114809	0.1	0.871	0.066	0.335	13.1
8	Sulfamethazine	0.06	0.013	0.141593	0.1	0.706	0.063	0.375	11.3
9	Atenolol	0.0816	0.0013	0.179269	0.1	0.558	0.055	0.449	10.13
10	Propranolol	0.144	0.0022	0.238748	0.1	0.419	0.041	0.590	10.22
11	Naproxen	0.16	0.015	0.226087	0.1	0.442	0.038	0.615	11.5
12	4-Octylphenol (4-OP)	0.21	0.084	0.168478	0.1	0.594	0.032	0.677	18.4
13	Sulfamethoxazole	0.32	0.032	0.318182	0.1	0.314	0.024	0.762	13.2
14	Bisphenol A (BPA)	0.433	0.008	0.493519	0.1	0.203	0.019	0.812	10.8
15	4-Nonylphenol (4-NP)	0.433	0.998	0.048543	0.1	2.060	0.019	0.812	109.8
16	17ß-Estradiol (E2)	0.462	0.012	0.501786	0.1	0.199	0.018	0.822	11.2
17	Acetaminophen	1.09	0.036	0.875	0.1	0.114	0.008	0.916	13.6

(The apparent removal can be calculated as:$R_a = 1 - \frac{C_p}{C_f}$ (4.21))

Comparing the values of C_{in}, Mefenamic acid, and Carbamazepine tend to be accumulated in the reactor easily since they have low biodegradation constants, indicating they are not easily consumed by microorganisms. Meanwhile, Acetaminophen is the least cumulative OMP due to its highest degradation constant.

All of CRTs of the compounds are more than 10 times those of CSTRs. Longer CRTs result in better apparent removal. To explore the effect of reaction constant and adsorption coefficient, a figure is obtained as follows:

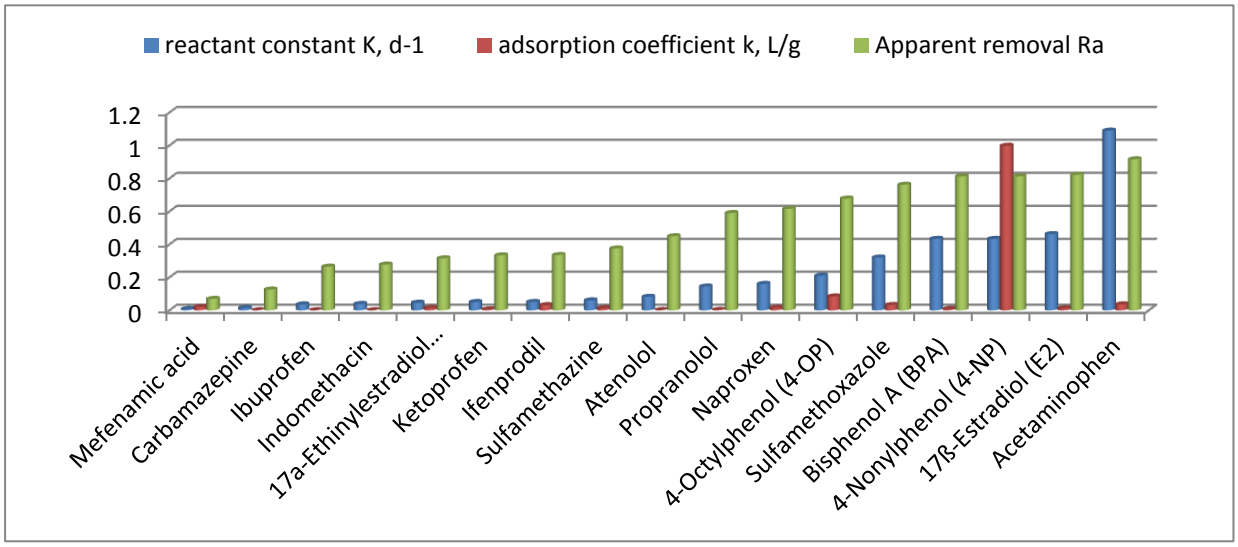


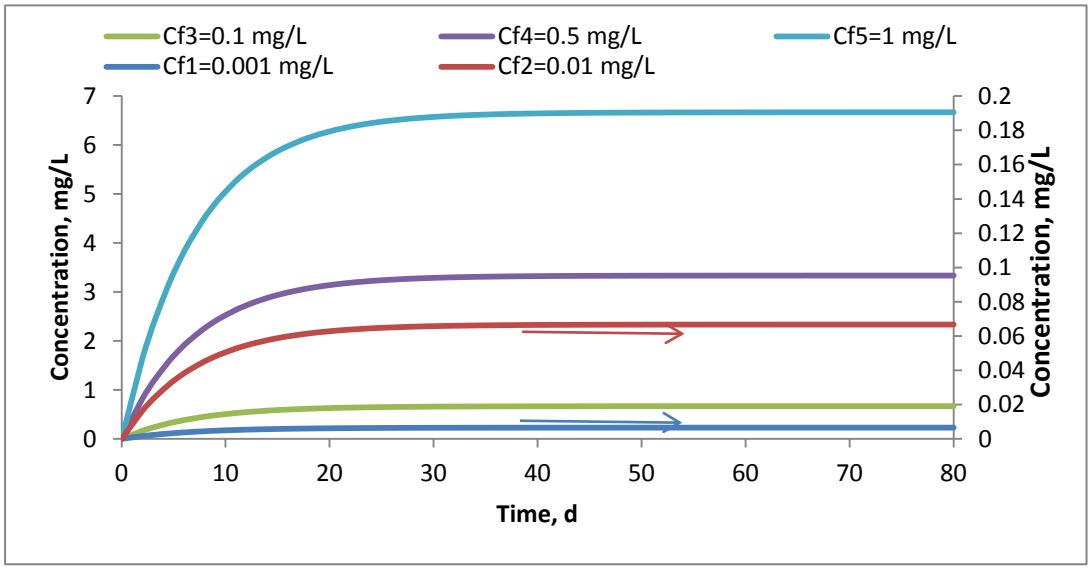
Figure 4-4 Effect of reaction and adsorption constant on apparent removal efficiency of OMPs

The removal efficiency is highly related with the reaction constant. Compared with CSTR, there are more OMPs can be removed. Half of OMPs can be removed more than 50%. Membrane can enhance the apparent removal of OMPs by adjusting CRT longer. In addition, adsorption constant have no obvious effect on the apparent removal.

In order to analyze the effect of feed concentration, HRT, SRT, etc, ketoprofen was chosen as the OMP for the further simulations because its reaction constant is in the middle of all and it has been used as one of the selected OMPs in the research.

4.2.3.2 Effect of feed concentration of OMPs

In order to explore the effect of feed concentration on the system, five feed concentrations 0.001, 0.01, 0.1, 0.5, 1 mg/L were chosen for ketoprofen. The the concentrations of OMPs in the reactor are as follows:



(C_{f1}=0.001 mg/L, C_{f2}=0.01 mg/L, C_{f3}=0.1 mg/L, C_{f4}=0.5 mg/L, C_{f5}=1 mg/L; for ketoprofen, MLSS=10 g/L, C_p=0.1C_l, HRT=1 d)

Figure 4-5 Effect of feed concentration on OMPs accumulation

It is clear that the higher the value of feed concentration of OMPs, the higher the stable concentration in the reactor and the longer the time for equilibrium. However, the ratio of stable liquid phase concentration of OMPs in the reactor to the feed

concentration remains about 6.7, and the ratio can also be calculated from the equations (4.31-33). Summary of the data below shows the feed concentration of OMPs does not affect the CRT and apparent removal.

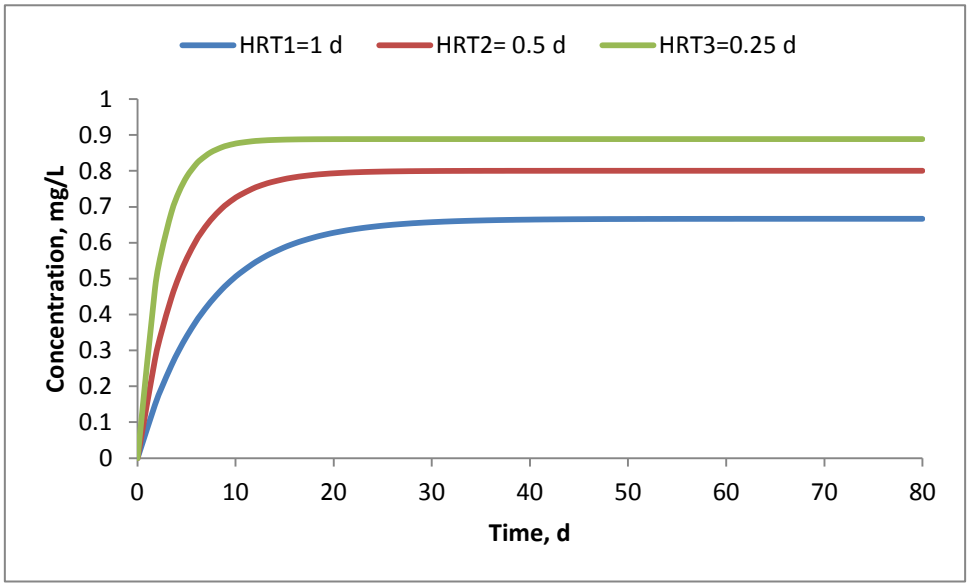
Table 4-4 effect of feed concentration

No	OMP	a	C_f, mg/L	C_p, mg/L	HRT, d	CRT=(1+k*MLSS)HRT/a, d	Apperant Removal Efficiency
1	Ketoprofen	0.1	0.001	0.0007	1	10.56	0.333
2	Ketoprofen	0.1	0.01	0.0067	1	10.56	0.333
3	Ketoprofen	0.1	0.1	0.0667	1	10.56	0.333
4	Ketoprofen	0.1	0.5	0.3333	1	10.56	0.333
5	Ketoprofen	0.1	1	0.6667	1	10.56	0.333

(The apparent removal can be calculated as:$R_a = 1 - \frac{C_p}{C_f}$ (4.21))

4.2.3.3 Effect of HRT

HRT may also have influence on the concentrations of OMPs in the reactor. Similar parameters were applied for the reactor analysis and 1, 0.5, 0.25 days were chosen for HRT for ketoprofen, as shown as follows:



(HRT1=1 d, HRT2=0.5d, HRT3=0.25 d; Cf=0.1 mg/L; for ketoprofen, MLSS=10 g/L, $C_p=0.1C_l$)

Figure 4-6 Effect of HRT on the OMPs accumulation

The different HRTs show different equilibrium times, and the longer the HRT, the longer it takes to reach equilibrium. The system with higher HRT has lower accumulation of OMPs. Lower HRT indicates more wastewater input every day and as a result there is more OMPs input based on the assumption that the feed concentration of OMPs remain the same. As a result, there are more OMPs accumulated in the reactor. Table below shows the CRT doubled with the half value of HRT, but the apparent removal efficiency increased a little with the doubled CRTs.

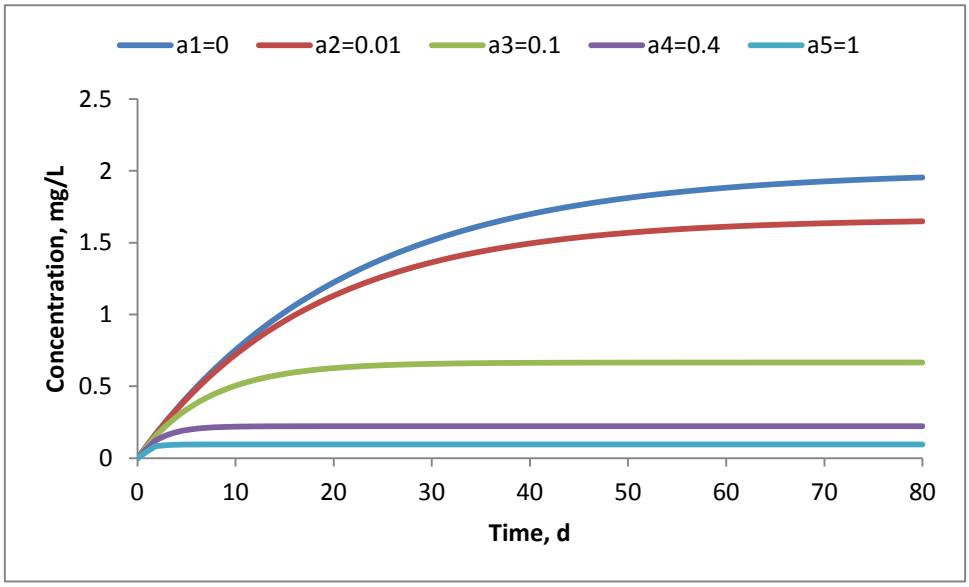
Table 4-5 effect of HRT

No	OMP	a	C_f, mg/L	C_p, mg/L	HRT, d	CRT=(1+k*MLSS)HRT/a, d	Apperant Removal Efficiency
1	Ketoprofen	0.1	0.1	0.0667	1	10.56	0.333
2	Ketoprofen	0.1	0.1	0.08	0.5	5.28	0.2
3	Ketoprofen	0.1	0.1	0.0889	0.25	2.64	0.111

(The apparent removal can be calculated as:$R_a = 1 - \frac{C_p}{C_f}$ (4.21))

4.2.3.4 Effect of membrane rejection for OMPs

The performance of the NF membrane has great impact on the retention time of compounds and different rejection ratios were chosen for the biodegradation of ketoprofen, results are as follows:



(C_{p1}=0, C_{p2}=0.01C_{l2}, C_{p3}=0.1C_{l3}, C_{p4}=0.4 C_{l4}, C_{p5}=C_{l5}; for ketoprofen, MLSS=10 g/L, HRT=1 d, C_f=0.1 mg/L)

Figure 4-7 Effect of membrane rejection on the OMPs accumulation

The performance of membrane determines the value of "a" (the rejection coefficient for membrane) in the equation (4.18). The greater the value of "a", the lower the concentration accumulated in the reactor, since much of OMPs flows out of the system with permeate. Table below also show that lower "a" resulted in longer CRTs.

Table 4-6 effect of membrane rejection

No	OMP	a	C_f, mg/L	C_p, mg/L	HRT, d	CRT=(1+k*MLSS)HRT/a, d	Apperant Removal Efficiency
1	Ketoprofen	0	0.1	0	1	-	1
2	Ketoprofen	0.01	0.1	0.0165	1	105.6	0.835
3	Ketoprofen	0.1	0.1	0.0667	1	10.56	0.333
4	Ketoprofen	0.4	0.1	0.0889	1	2.64	0.111
5	Ketoprofen	1	0.1	0.0952	1	1.056	0.048

(The apparent removal can be calculated as:$R_a = 1 - \frac{C_p}{C_f}$ (4.21))

4.2.3.5 Summary of general analysis

In MBR without sludge wastage, CRT is only related with HRT, sludge concentration (discussed later), adsorption constant and membrane performance. What is more, feed concentration does not affect CRT but affects the time to steady state. For the CRT based on membrane rejections, it is obvious that all of the compounds with different reaction and adsorption constants have a value of CRT of more than ten times the value of HRT, indicating CRT can be used for OMPs biodegradation in the reactor without sludge wastage and could enhance the biodegradation of OMPs. In addition, longer HRT and better OMPs rejection performance of the membrane result in longer CRT, even though long HRT is not practical in WWTP. And it is also clear that the longer the CRT, the greater the removal of OMPs.

4.3 Membrane reactor with sludge wastage (SRT≠+∞)

4.3.1 Description of reactor (SRT≠+∞)

An ideal membrane bioreactor for wastewater treatment with sludge wastage is shown

as below.

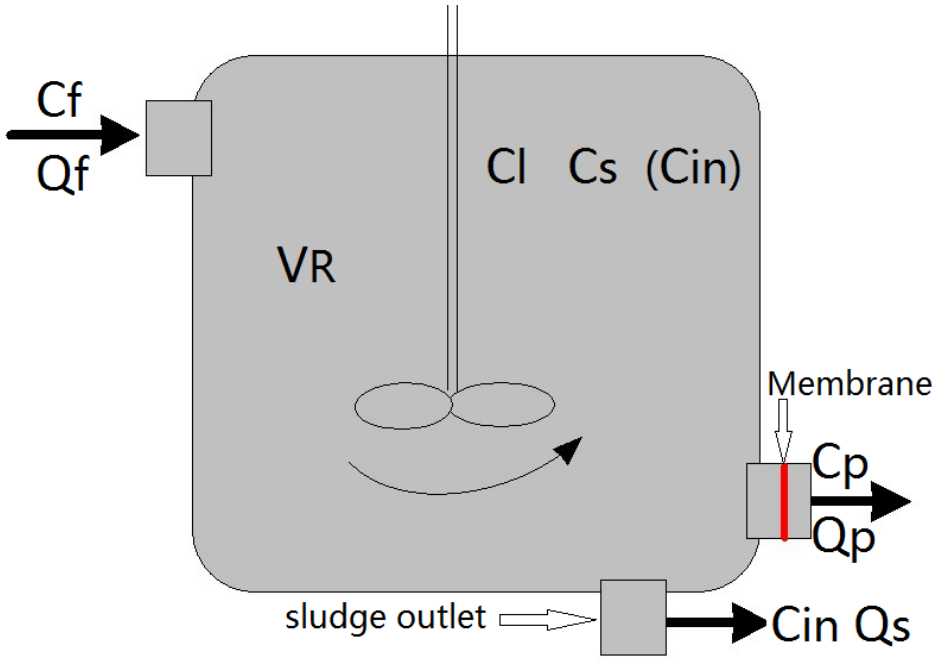


Figure 4-8 Set up of wastewater treatment reactor with sludge wastage

In this reactor, the liquid-solid mixture is homogenous anywhere within the reactor, with no dead zone. Ignoring the air in the tank, OMPs can distribute into liquid and solids in the reactor. Here are definitions of the abbreviations in the figure:

a—membrane rejection rate for OMPs (a = 0 – 1)

b*—equation (4.52)

C_f—concentration of OMPs in feed, mg/L

C_p—concentration of OMPs in permeate, mg/L

C_l—concentration of OMPs in liquid phase of the sludge water in the reactor, mg/L

C_s—concentration of OMPs in solid phase of the sludge water in the reactor, mg/g

C_{in}—mean concentration of OMPs in the reactor, mg/L

Q_f—flow rate of feed, L/day

Q_p—flow rate of permeate, L/day

Q_s—flow rate of sludge mixture, L/day

V_l—volume of liquid in the reactor, L

M_s—Mass of solid in the reactor, g

V_R—volume of the reactor (assume that the reactor is filled full and as a result, the volume of the mixture in the tank is VR), L

MLSS—solid concentration of the mixture in the reactor, g/L

k—linear partitioning coefficient of isotherm for adsorption of OMPs onto sludge, L/g

K—reaction constant for the bio degradations of OMPs in the reactor, d^{-1}

R_a—apparent removal of compounds (R_a=1-C_p/C_f)

R_j—reaction rate, mg/L-d

HRT—Hydraulic Retention Time, day. HRT=V_R/Q

CRT—Compound Retention Time

Here are fundamental equations:

$$V_l = V_R \quad (4.1)$$

$$M_s = MLSS \times V_R \quad (4.2)$$

$$C_s = k \times C_l \quad (4.3)$$

$$\Rightarrow C_{in} = (1 + k \times MLSS) \times C_l \quad (4.4)$$

$$Q_f = Q_p + Q_s \quad (4.35)$$

$$SRT = \frac{V_R}{Q_s} \quad (4.36)$$

$$HRT = \frac{V_R}{Q_p + Q_s} = \frac{V_R}{Q_f} \quad (4.37)$$

Definition of CRT in the reactor with sludge wastage:

$$CRT = \frac{C_{in}V_R}{C_pQ_p + C_{in}Q_s} = \frac{C_{in}}{C_p\frac{Q_p}{V_R} + C_{in}\frac{1}{SRT}} \quad (4.38)$$

$$C_p\frac{Q_p}{V_R} + C_{in}\frac{1}{SRT} = \frac{C_{in}}{CRT} \quad (4.39)$$

Overall mass balance

$$Q_fC_f = Q_pC_p + C_{in}Q_s + \frac{dC_{in}}{dt}V_R - R_jV_R \quad (4.40)$$

$$C_p = f(C_l) = a\,C_l = \frac{aC_{in}}{1 + k \times MLSS} (4.22)$$

$$R_j = KC_l \quad (4.13)$$

4.3.2 CRT under steady state

For steady state

$$\frac{dC_{in}}{dt}V_R = 0 \quad (4.6)$$

$$Q_P + Q_s = Q_f = Q(\text{constant}) \quad (4.41)$$

$$Q_fC_f = Q_pC_p + C_{in}Q_s - R_jV_R \quad (4.42)$$

$$\frac{Q_fC_f}{V_R} = \frac{Q_pC_p}{V_R} + \frac{C_{in}Q_s}{V_R} - R_j \quad (4.43)$$

So

$$C_f\frac{1}{HRT} = C_p\frac{Q_p}{V_R} + C_{in}\frac{1}{SRT} - KC_l \quad (4.44)$$

$$C_p\frac{Q_p}{V_R} + C_{in}\frac{1}{SRT} = \frac{C_{in}}{CRT} \quad (4.45)$$

And thus:

$$\frac{C_f}{HRT} - \frac{C_{in}}{CRT} + KC_l = 0 \quad (4.46)$$

$$(\text{In} - \text{Out} + \text{Reaction} = 0)$$

Consider the first term in the left side as the feed concentration over the HRT (“In” term) and the second term as the concentration in the reactor over the CRT (“out” term). So the difference between the in term and out term is the reaction rate.

Based on equation (4.25), CRT can be calculated from the following equation:

$$CRT = \frac{C_{in}}{C_p \frac{Q_p}{V_R} + \frac{C_{in}}{SRT}} = \frac{1}{\frac{C_p Q_p}{C_{in} V_R} + \frac{1}{SRT}} \Rightarrow CRT = \frac{1}{\frac{a}{1 + k \times MLSS}\left(\frac{1}{HRT} - \frac{1}{SRT}\right) + \frac{1}{SRT}} \quad (4.47)$$

Equation (4.33) can also be used for CRT calculation resulting in the same value of CRT (note K<0 for consumption of OMPs).

When SRT=+∞, that is to say, Qs=0,

$$CRT = \frac{C_{in} V_R}{C_p Q_p + C_{in} Q_s} = \left(\frac{C_{in}}{C_p}\right) HRT \quad (4.48)$$

$$0 = \frac{C_f}{HRT} - \frac{C_{in}}{CRT} + KC_l = \frac{C_f}{HRT} - \frac{C_{in}}{HRT \frac{C_{in}}{C_p}} + KC_l = \frac{C_f - C_p}{HRT} + KC_l \quad (4.49)$$

This equation is the same with the previous one for membrane bioreactor without sludge wastage.

4.3.3 General analysis

To solve equation (4.6), the equation can be converted into the following form:

$$\frac{dC_{in}}{dt} + \left[\frac{Q_p \times a}{(1 + k \times MLSS)V_R} - \frac{K}{1 + k \times MLSS} + \frac{Q_s}{V_R}\right] C_{in} = \frac{Q_f \times C_f}{V_R} \quad (4.50)$$

And the result is:

$$C_{in} = \frac{c}{b^*}\left(1 - e^{-b^* t}\right) \quad (4.51)$$

$$b^* = \frac{Q_p \times a}{(1 + k \times MLSS)V_R} - \frac{K}{1 + k \times MLSS} + \frac{Q_s}{V_R} = \frac{(Q_f - Q_s) \times a}{(1 + k \times MLSS)V_R} - \frac{K}{1 + k \times MLSS} + \frac{1}{SRT} = \frac{a}{1 + k \times MLSS}\left(\frac{1}{HRT} - \frac{1}{SRT}\right) - \frac{K}{1 + k \times MLSS} + \frac{1}{SRT} \quad (K < 0 \; for \; consumption) \quad (4.52)$$

$$c = \frac{Q_f \times C_f}{V_R} = \frac{C_f}{HRT} \quad (4.18)$$

And the maximum value of C_{in} can be calculated according to the following equation:

$$C_{in,max} = \frac{c}{b^*} \quad (4.53)$$

According to equation (4.4), the maximum value of C_l can be calculated as follows:

$$C_{l,max} = \frac{C_{in,max}}{1 + k \times MLSS} = \frac{c}{b^*(1 + k \times MLSS)} \quad (4.54)$$

The apparent removal can be calculated as:

$$R_a = 1 - \frac{C_p}{C_f} \quad (4.21)$$

4.3.3.1 Effect of adsorption and biodegradation constants

The following parameters were set for the reactor: the initial concentrations of OMPs in the reactor are 0 mg/L, C_p = 0.1*C_l, MLSS=10 g/L, HRT=1 d, SRT=20 d, feed concentrations of OMPs are all 0.1 mg/L.

Table 4-7 effect of reaction and adsorption constant

No	Compound	K, d-1	k, L/g	b*	c	C_{inmax}, mg/L	C_{lmax}, mg/L	Ra	CRT
1	Mefenamic acid	0.00744	0.02	0.135367	0.1	0.739	0.062	0.384	7.74
2	Carbamazepine	0.0144	0.000085	0.159307	0.1	0.628	0.063	0.373	6.90
3	Ibuprofen	0.036	0.000093	0.180878	0.1	0.553	0.055	0.448	6.90
4	Indomethacin	0.0384	0.00012	0.18324	0.1	0.546	0.055	0.455	6.90
5	17a-Ethinylestradiol (EE2)	0.046	0.014	0.173684	0.1	0.576	0.051	0.495	7.50
6	Ketoprofen	0.05	0.0056	0.187311	0.1	0.534	0.051	0.494	7.14
7	Ifenprodil	0.0504	0.031	0.160992	0.1	0.621	0.047	0.526	8.16
8	Sulfamethazine	0.06	0.013	0.187168	0.1	0.534	0.047	0.527	7.46
9	Atenolol	0.0816	0.0013	0.224334	0.1	0.446	0.044	0.560	6.96

10	Propranolol	0.144	0.0022	0.283855	0.1	0.352	0.034	0.655	7.00
11	Naproxen	0.16	0.015	0.271739	0.1	0.368	0.032	0.680	7.54
12	4-Octylphenol (4-OP)	0.21	0.084	0.215761	0.1	0.463	0.025	0.748	9.84
13	Sulfamethoxazole	0.32	0.032	0.364394	0.1	0.274	0.021	0.792	8.20
14	Bisphenol A (BPA)	0.433	0.008	0.538889	0.1	0.186	0.017	0.828	7.25
15	4-Nonylphenol (4-NP)	0.433	0.998	0.098087	0.1	1.019	0.009	0.907	17.05
16	17ß-Estradiol (E2)	0.462	0.012	0.547321	0.1	0.183	0.016	0.837	7.42
17	Acetaminophen	1.09	0.036	0.921324	0.1	0.109	0.008	0.920	8.34

A plot of apparent removal efficiency vs OMPs is shown as follow:

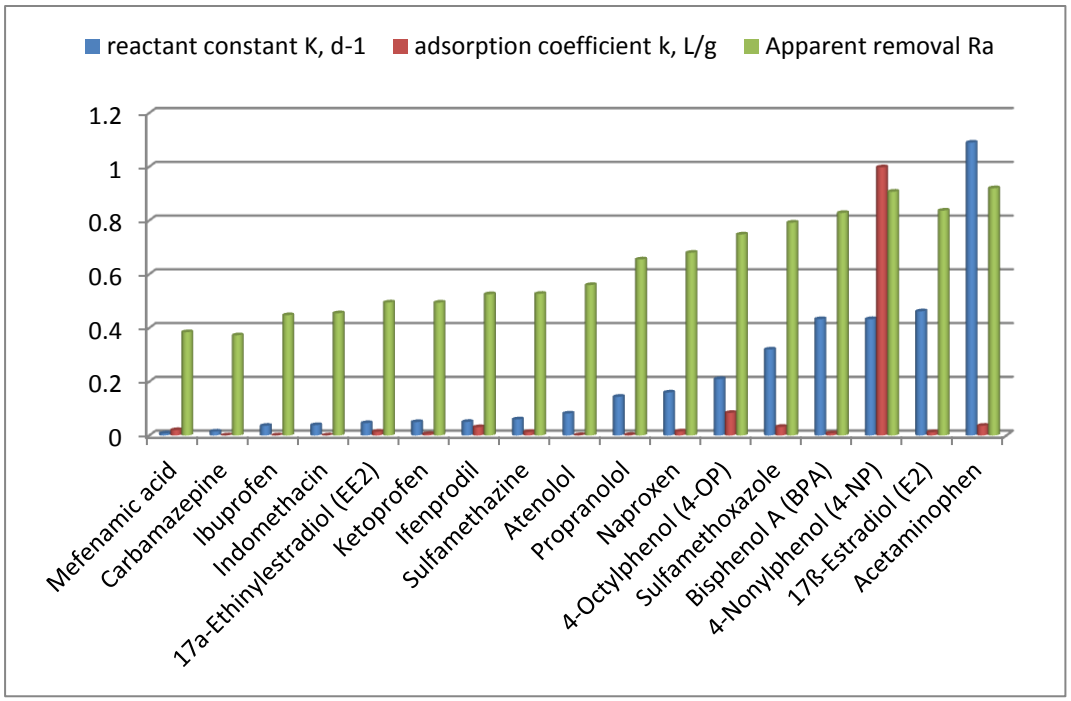


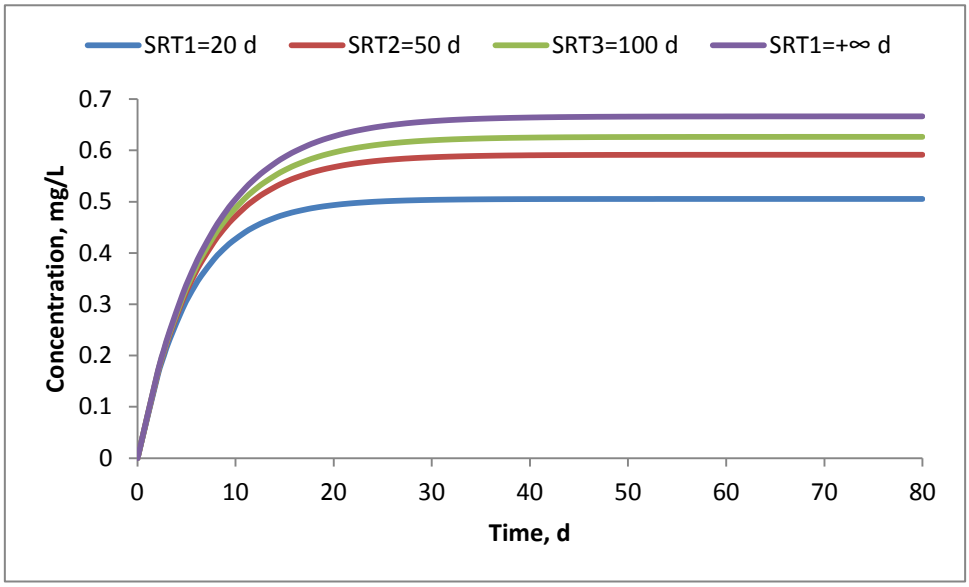
Figure 4-9 Effect of reaction and adsorption constant on apparent removal efficiency of OMPs

It is clear different adsorption constants and different reaction constants result in

different extents of accumulation of OMPs in the reactor. Similar to the results which are based on the system without sludge wastage, mefenamic acid and carbamazepine tend to be accumulated in the reactor with sludge easily. Most of the OMPs can be removed by more than 50%, indicating most OMPs in a MBR with a NF membrane can be eliminated to a great extent, especially for acetaminophen and E2. MBR with sludge wastage can still enhance the OMPs control, even though the OMPs in this reactor do not have the CRT as long as those in MBR without sludge discharge.

4.3.3.2 Effect of SRT

As is discussed that the reactor with sludge wastage has different extents of OMPs accumulation compared to that without sludge wastage, it can be concluded that SRT has an effect on the system, since the system without sludge wastage can be considered as a reactor with SRT=+∞. Four values of SRT for ketoprofen (keeping other parameters of the system the same) and a plot of liquid phase concentrations of OMPs in the reactor vs. time is shown below:



(SRT1=20 d, SRT2=50 d, SRT3=100 d, SRT4=+∞; for ketoprofen, MLSS=10 g/L, C_p = 0.1C_l, HRT = 1 d, C_f = 0.1 mg/L)

Figure 4-10 Effect of SRT on the OMPs accumulation

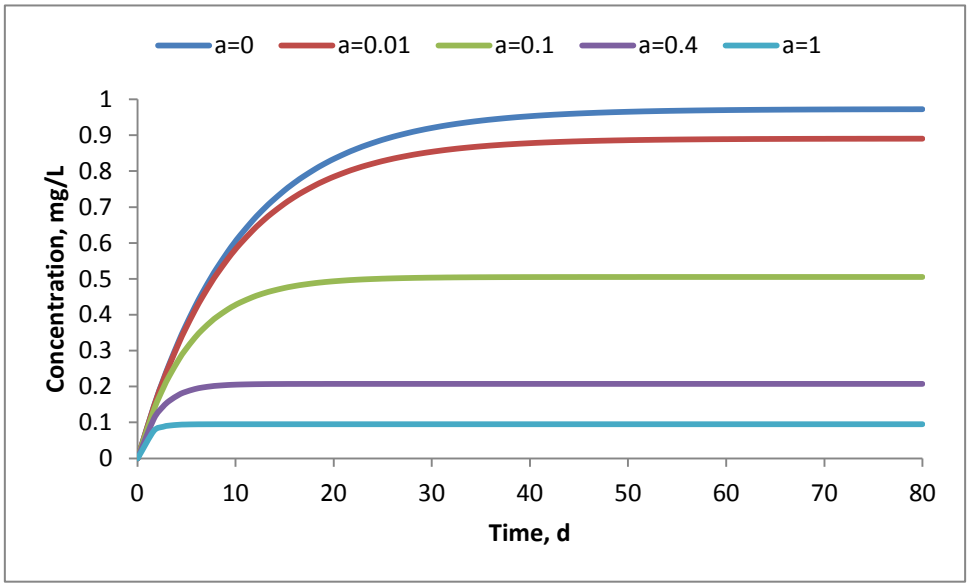
Obviously, the greater the value of SRT, the greater the extent of OMPs accumulated in the reactor and the longer time to steady state. The greater the value of SRT means less wastage of OMPs and thus there are more OMPs in the system. Of course, the biodegradation increases when increasing the SRT, but the microorganisms cannot consume all the amount of OMPs accumulated at beginning. As a result, the concentrations of OMPs still increases until a steady state. Based on the equations (4. 51-53), SRT determines the value of b* and the greater the HRT, the less the b*, and thus the greater the concentration in the reactor. Table below shows SRT have limited influence on CRT.

Table 4- 8 effect of SRT

No	OMP	a	C_f, mg/L	C_p, mg/L	C_{in}, mg/L	C_l, mg/L	HRT, d	SRT, d	CRT	Apperant removal efficiency
Section 4.2.3.2, different SRTs										
1	Ketoprofen	0.1	0.1	0.0506	0.5339	0.5056	1	20	7.14	0.494
2	Ketoprofen	0.1	0.1	0.0591	0.6244	0.5913	1	50	8.86	0.409
3	Ketoprofen	0.1	0.1	0.0627	0.6618	0.6267	1	100	9.64	0.373
4	Ketoprofen	0.1	0.1	0.0667	0.704	0.6667	1	+∞	10.56	0.333

(The apparent removal can be calculated as:$R_a = 1 - \frac{C_p}{C_f}$ (4.21))

4.3.3.3 Effect of membrane rejection for OMPs



("a" is the membrane rejection rate for OMPs; for for ketoprofen, MLSS=10 g/L, HRT=1 d, C_f=0.1 mg/L, SRT=20 d)

Figure 4-11 Effect of rejection performance of membrane on the OMPs accumulation

Similar with the reactor without wastage, the better the performance of membrane, the more concentrated OMPs in the reactor and longer time to steady state. Following table is the summary for the simulation.

Table 4-9 effect of membrane rejection

No	OMP	a	C_f, mg/L	C_p, mg/L	C_{in}, mg/L	C_l, mg/L	HRT, d	SRT, d	CRT	Apperant removal efficiency
1	Ketoprofen	0	0.1	0	1.0268	0.9724	1	20	19.98	1
2	Ketoprofen	0.01	0.1	0.0089	0.9401	0.8903	1	20	16.94	0.911
3	Ketoprofen	0.1	0.1	0.0506	0.5339	0.5056	1	20	7.14	0.494
4	Ketoprofen	0.4	0.1	0.0829	0.2187	0.2071	1	20	2.44	0.172
5	Ketoprofen	1	0.1	0.095	0.1003	0.095	1	20	1.05	0.05

(The apparent removal can be calculated as:$R_a = 1 - \frac{C_p}{C_f}$ (4.21))

4.3.3.4 Effect of sludge concentration

As we know, the concentration of sludge also results in different removal efficiencies of OMPs. A plot of the effect of sludge concentration (MLSS) on the removal of OMPs is shown below (all HRTs are 1 day).

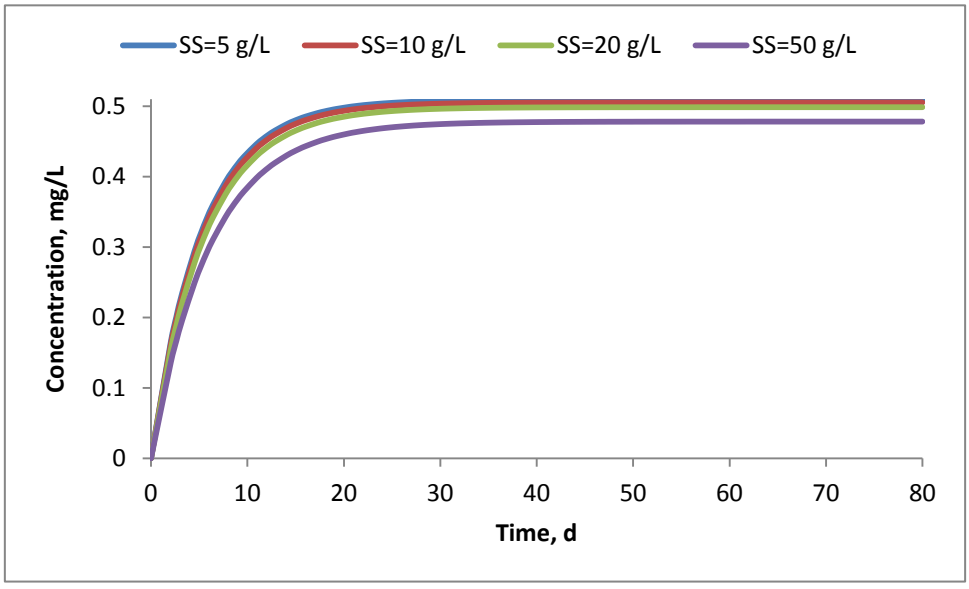


Figure 4-12 Effect of sludge concentration on biodegradation of OMPs with sludge wastage

It is obvious that a higher sludge concentration can lead to a lower liquid phase concentration of OMPs. However, summary table below shows the sludge concentration had limited influence on CRT and thus has limited impact on the apparent removal efficiency.

Table 4-10 effect of sludge concentration

No	OMP	a	C_f, mg/L	C_p, mg/L	C_{in}, mg/L	C_l, mg/L	MLSS, g/L	SRT, d	CRT	Apperant removal efficiency
1	Ketoprofen	0.1	0.1	0.0509	0.5234	0.5092	5	20	7.02	0.491
2	Ketoprofen	0.1	0.1	0.0506	0.5339	0.5056	10	20	7.14	0.494
3	Ketoprofen	0.1	0.1	0.0499	0.5543	0.4985	20	20	7.38	0.501
4	Ketoprofen	0.1	0.1	0.0478	0.6124	0.4785	50	20	8.05	0.522

(The apparent removal can be calculated as:$R_a = 1 - \frac{C_p}{C_f}$ (4.21))

4.3.3.5 Summary of general analysis

Different from the CRTs of the reactor without sludge wastage, the values for the reactor with sludge wastage are less, but seven or eight times that of HRT for different biodegradation and adsorption constants, indicating that the biodegradations of OMPs in the reactor are still enhanced. OMPs tend to have a longer CRT when there is a higher membrane rejection, or longer SRT, but CRT can only be increased to a limited value, as can be seen from the table. As indicated by the last two columns, longer CRT results in better removal efficiency for the same SRT value. However, the shorter the SRT, the better apparent removal efficiency due to the fact that the wastage sludge help remove OMPs by flowing out of the reactor directly, even though they have not

been biodegraded.

4.4 Simulation of anaerobic membrane bioreactor with NF membrane

4.4.1 Anaerobic adsorption and degradation of ketoprofen and naproxen

4.4.1.1 Adsorption of selected OMPs onto anaerobic sludge

(1) Determination of adsorption equilibrium time

The adsorption test was described in 2.6. A plot of concentration of OMPs vs. time is as shown below:

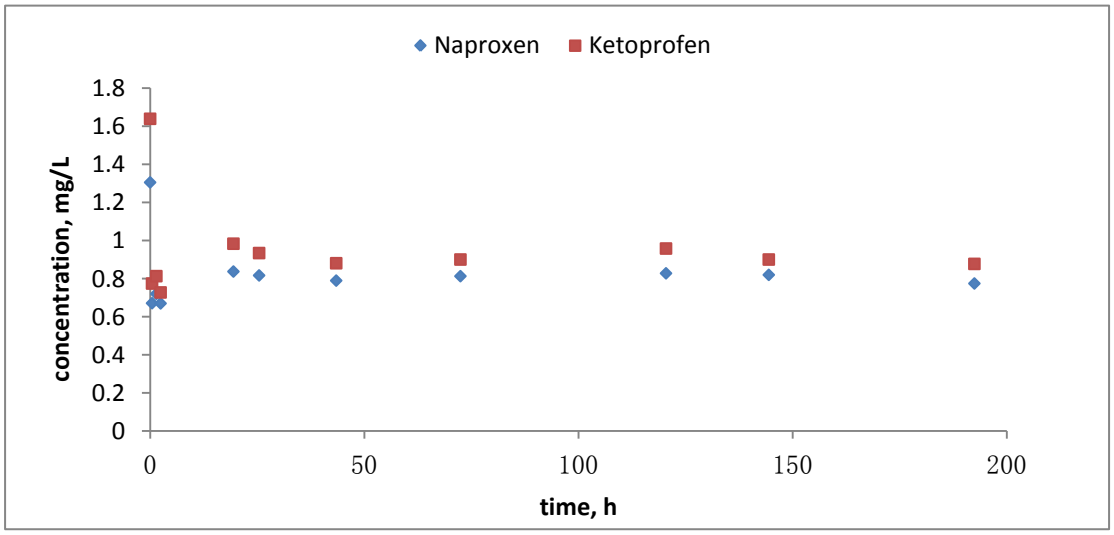


Figure 4-13 Adsorption of ketoprofen and naproxen onto sludge

The adsorption process happened soon after mixing OMPs solution with sludge together, and about half of the amount of OMPs (both ketoprofen and naproxen) was absorbed by sludge within one hour, and desorption process occurred after that. The equilibrium state reached at about 20 hours, with the concentrations of ketoprofen and

naproxen 0.9 and 0.8 mg/L, respectively for the later 180 hours. The adsorption capacities for ketoprofen and naproxen are 56 and 40 mg/kg sludge, which are comparable with the adsorption capacity by immobilized process [65] and agricultural soil [66].

(2) Sorption isotherms

The sorption isotherms for ketoprofen and naproxen are as follows:

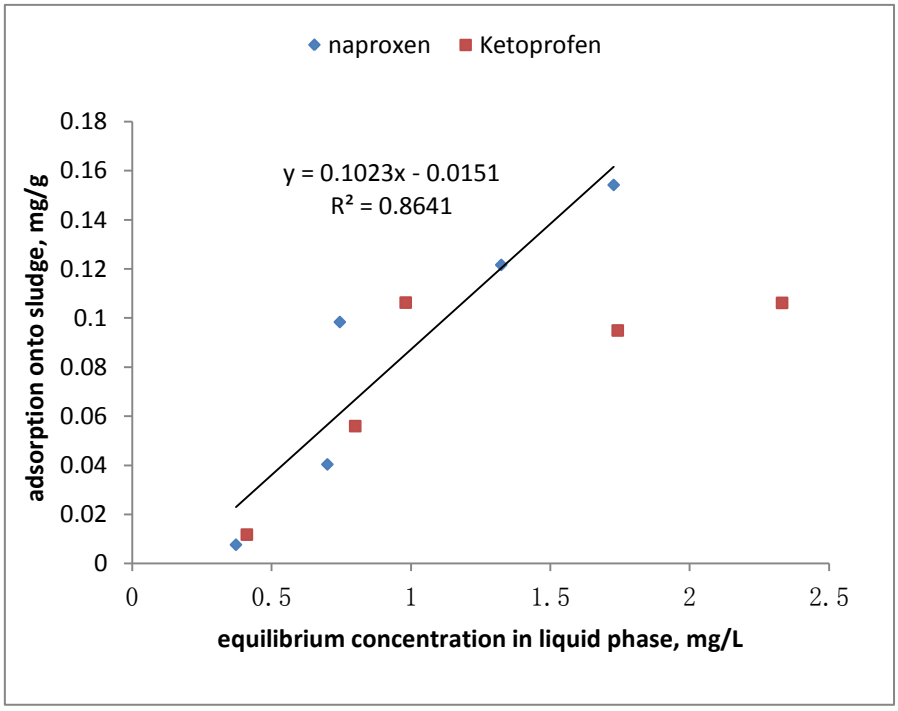


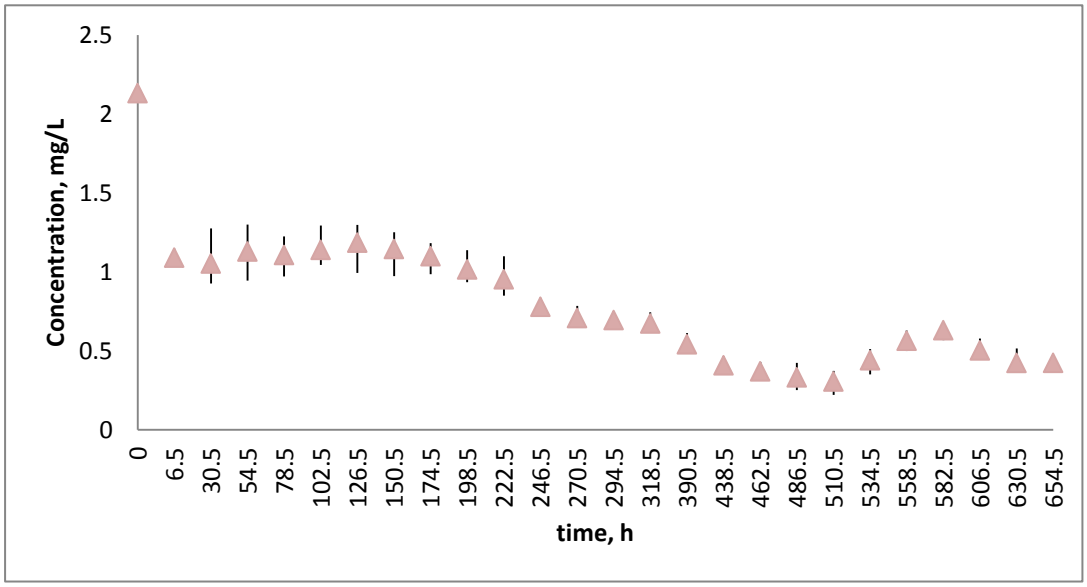
Figure 4-14 Isotherms for adsorption of ketoprofen and naproxen onto sludge (the line is for naproxen)

The adsorption isotherm for naproxen is linear and no maximum capacity was observed during our tests. However, the adsorption isotherm for ketoprofen is different. The adsorption capacity of ketoprofen was increasing from about 0.01 mg/g to about 0.1 mg/g when the equilibrium concentration of ketoprofen in liquid phase increased from 0.4 mg/L to 1 mg/L, and the capacity remained almost unchanged at

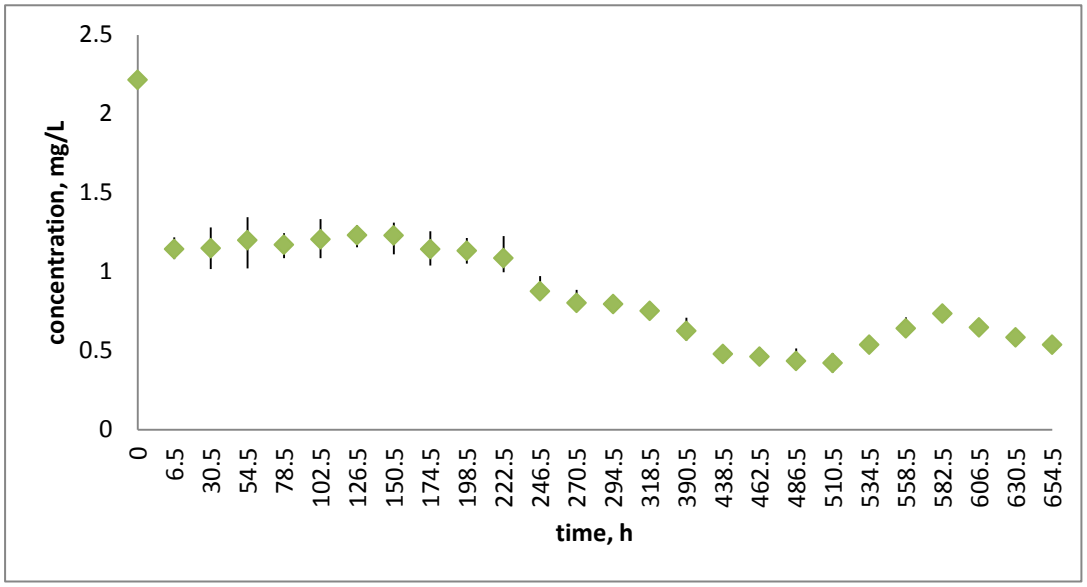
the maximum capacity of 0.1 mg/g (based on the three points from C_l 1 – 2.5 mg/L) sludge when the equilibrium concentration was greater than 1 mg/L.

4.4.1.2 Anaerobic biodegradation of selected OMPs

The anaerobic biodegradation test was described in Chapter *2*. The system is completely anaerobic and microorganisms grow well in the reactor. The following figure shows the concentrations of OMPs in the reactor.



(1) Ketoprofen



(2) Naproxen

Figure 4-15 Concentration of OMPs in the liquid phase of the anaerobic bioreactor

Results show a trend of the concentration decreasing. It required about 100 hours for the microorganisms starting to consume OMPs because it needs time to reach the adsorption equilibrium and to adapt to the OMPs, which is longer than that of sorption tests (within 20 hours). After reaching equilibrium, there is a continuous decrease of concentrations of OMPs, which can be considered as the biodegradation and dilution of OMPs (substrate and acid were added into the reactor to maintain a suitable environment for the growth of microorganisms).

First order reaction:

$$\frac{dC}{dt} = KC \Rightarrow C = C_0 e^{Kt} \quad (4.55)$$

Linear equation:

$$\ln C = \ln C_0 + Kt \quad (4.56)$$

By adjusting concentration values based on the volume and biodegradation kinetics,

the figure based on a first order reaction was obtained as below.

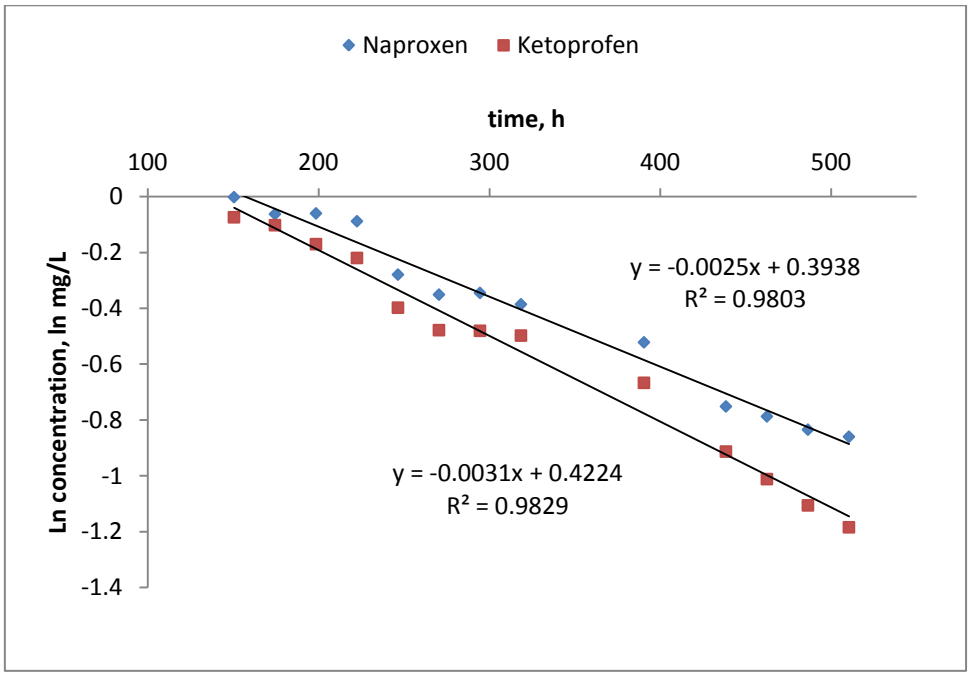


Figure 4-16 Kinetics of biodegradation of ketoprofen and naproxen

Both of the biodegradation data sets fit well with first order reaction model, with R^2>0.98. The first order reaction constants were 0.0025 h^{-1} (0.060 d^{-1}) and 0.0031 h^{-1} (0.074 d^{-1}) for naproxen and ketoprofen, respectively. These constants will be discussed in the next section.

4.4.2 Simulations of AnMBR-NF

Consider an example as follows: HRT = 24 h, MLSS = 15 g/L, initial concentrations of OMPs in the reactor = 0 mg/L. OMPs are ketoprofen, naproxen. It takes several days for the system to adapt to the new microorganism. That is to say, it takes several days for microorganism to reach the maximum degradation rate.

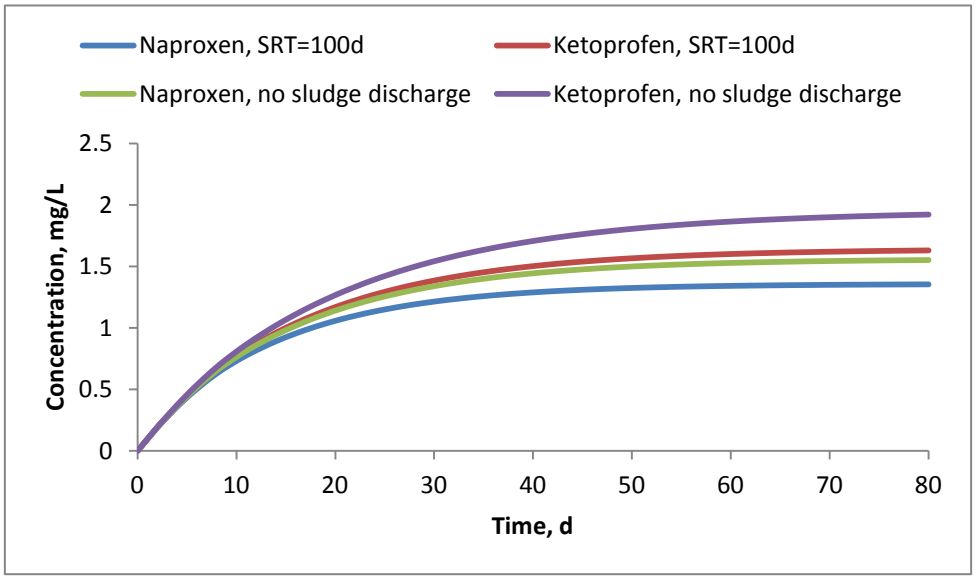
Assume in the first 10 days, the reaction rate constants are increasing linearly. The data for reaction constant and adsorption constant are from biodegradation experiments, which have been discussed in the previous section. Here are the data:

Table 4-11 Details of OMPs for simulation of AnMBR-NF

chemical	First order reaction constant K, d^{-1}	half life, d	Adsorption constant k, L/g	Initial concentration
Naproxen	0.060	11.6	0.10	0.1mg/L
Ketoprofen	0.074	9.4	0.16	0.1mg/L

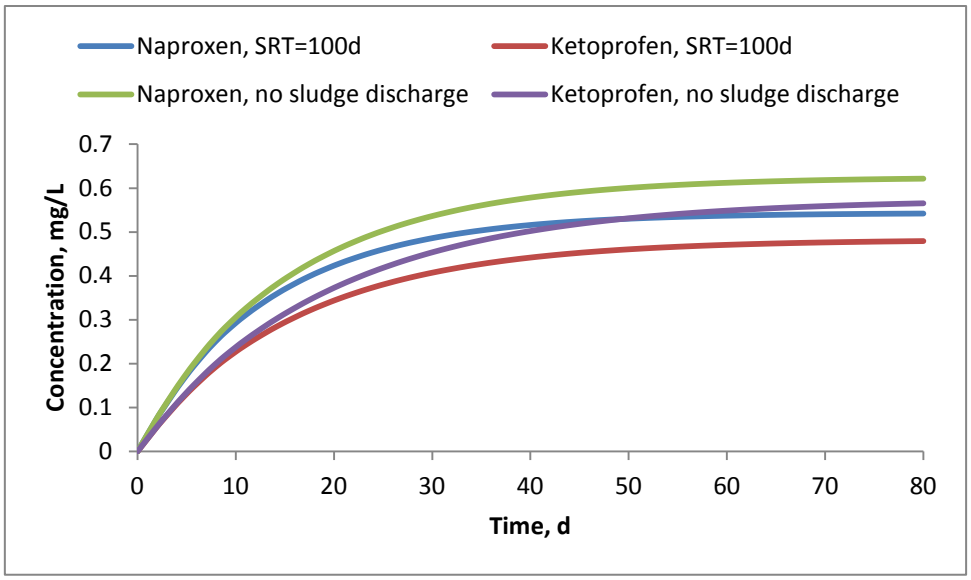
4.4.2.1 Effect of sludge wastage

As is discussed before, MLSS has effect on the biodegradation of OMPs. In the AnMBR-NF, given the factor of OMPs rejection (a) of 0.1 with and without sludge wastage, the plot of effect of sludge wastage on OMPs removal is as follows:



(HRT=24h, Cf=0.1 mg/L, MLSS=15 g/L, a=0.1)

Figure 4-17 Simulation of mean concentration (C_{in}) of OMPs (all phases) in AnMBR-NF



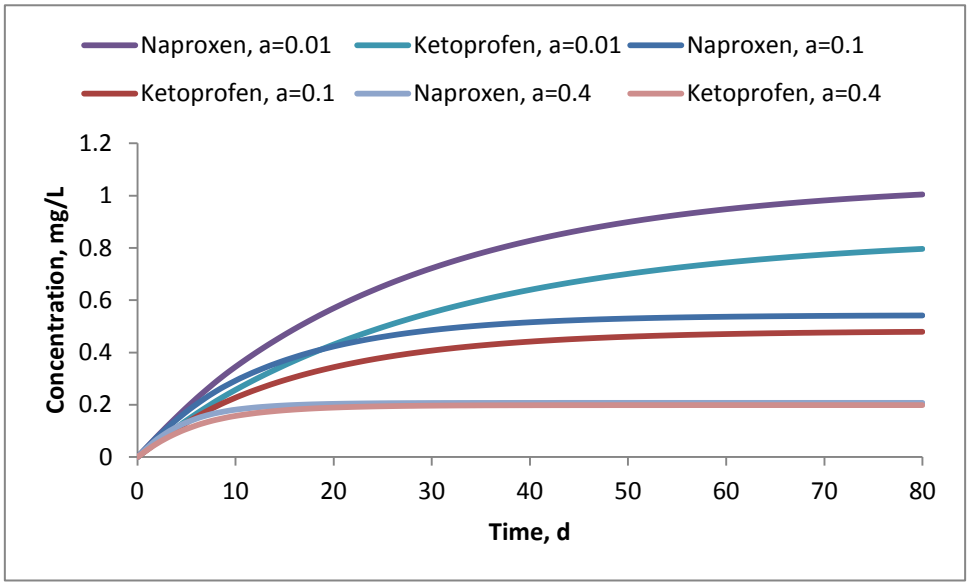
(HRT=24h, Cf=0.1 mg/L, MLSS=15 g/L, a=0.1)

Figure 4-18 Simulation of liquid phase concentration (Cl) of OMPs in AnMBR-NF

The figure is similar with previous ones even though the biodegradation has an adaption period. However, the apparent removal efficiencies ($1-C_p/C_f$) for OMPs are only 52% and 46% for ketoprofen and naproxen, respectively. This is mainly due to the strong adsorption of OMPs onto the sludge, and thus there is a high total accumulated concentration of OMPs but low liquid OMPs concentration. That is to say, the compound with high adsorption constant and high biodegradation constant may have high removal efficiency (including both biodegradation and adsorption).

4.4.2.2 Effect of membrane performance

Different membrane rejection performances are also chosen for simulation.



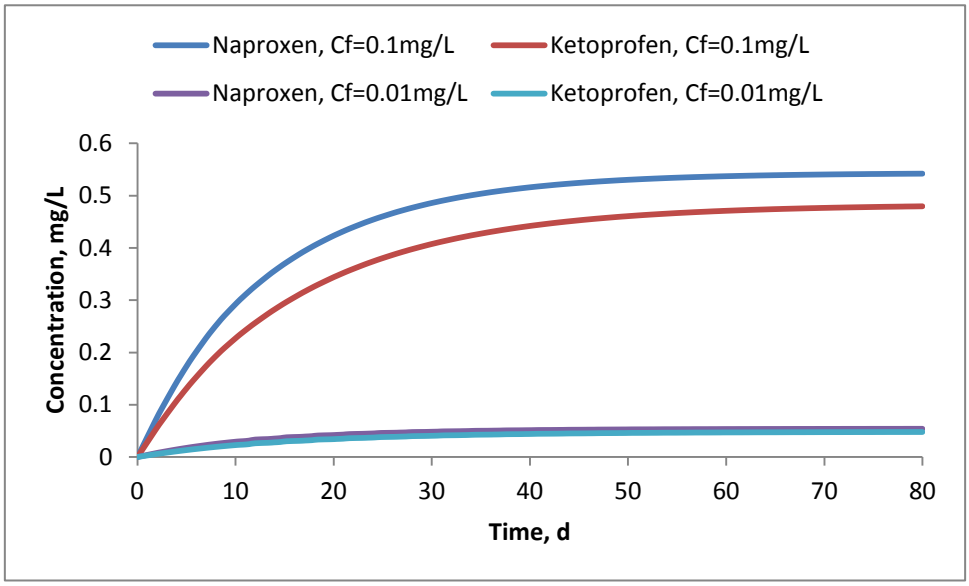
(HRT=24h, Cf=0.1 mg/L, MLSS=15 g/L)

Figure 4-19 Simulation of liquid phase concentration of OMPs in AnMBR-NF with different membrane rejection performances

It is clear that better membrane rejection performance results in higher liquid concentrations of OMPs, which is similar with the simulations performed in the previous two sections. This demonstrates that membrane rejection performance is a very important factor for the system.

4.4.2.3 Effect of feed concentration of OMPs

Generally, OMPs may have various concentrations in a wastewater system, two concentrations were chosen for the simulations here, see figure below.



(HRT=24h, MLSS=15 g/L, a=0.1)

Figure 4-20 Simulation of liquid phase concentration of OMPs in the AnMBR-NF with different feed concentrations

Reasonable high feed concentration results in high liquid phase concentration of OMPs, and a low feed concentration can reach equilibrium within a shorter time.

4.4.2.4 Summary for simulations

Following is the CRT calculations for naproxen and ketoprofen.

Table 4-12 Summary of ketoprofen and naproxen in AnMBR-NF

No	OMP	a	C_f, mg/L	C_p, mg/L	C_{in}, mg/L	C_l, mg/L	HRT, d	SRT, d	CRT	Apperant removal efficiency
Section 4.3.2.1 with or without sludge wastage										
1	Naproxen	0.1	0.1	0.054	1.359	0.544	1	100	20.2	0.457
2	Ketoprofen	0.1	0.1	0.048	1.643	0.483	1	100	25.6	0.517
3	Naproxen	0.1	0.1	0.063	1.563	0.625	1	+∞	25.0	0.375
4	Ketoprofen	0.1	0.1	0.058	1.954	0.575	1	+∞	34.0	0.425
Section 4.3.2.2 different membrane rejections										
1	Naproxen	0.01	0.1	0.010	2.510	1.004	1	100	63.1	0.900
2	Ketoprofen	0.01	0.1	0.008	2.706	0.796	1	100	65.9	0.920
3	Naproxen	0.1	0.1	0.054	1.359	0.544	1	100	20.2	0.457
4	Ketoprofen	0.1	0.1	0.048	1.643	0.483	1	100	25.6	0.517
5	Naproxen	0.4	0.1	0.083	0.520	0.208	1	100	5.9	0.168
6	Ketoprofen	0.4	0.1	0.079	0.675	0.198	1	100	7.9	0.206
Section 4.3.2.3 different feed concentration of OMPs										
1	Naproxen	0.1	0.01	0.005	0.136	0.054	1	100	20.2	0.457
2	Ketoprofen	0.1	0.01	0.005	0.163	0.048	1	100	25.6	0.517
3	Naproxen	0.1	0.1	0.054	1.359	0.544	1	100	20.2	0.457
4	Ketoprofen	0.1	0.1	0.048	1.643	0.483	1	100	25.6	0.517

(The apparent removal can be calculated as: $R_a = 1 - \frac{C_p}{C_f}$ (4.21))

Results show, a value of CRT that is more than 20 times that of HRT (much greater than the value of half life) when the membrane performance is $C_p = 0.1\ C_l$, leading to more biodegradation of OMPs. The better membrane performance results in a longer CRT, while feed concentration does not affect the CRT.

It is worthy to mention that high adsorption may result in high biodegradation since most of the biodegradation happens after the adsorption and in this case adsorption is important for degradation. However, the biodegradation analysis here is based on the concentration in the liquid phase of the wastewater. This is a limitation. Tato Urase

and Tomoya Kikuta [67] developed a two-phase fate model for the adsorption and degradation for OMPs in the activated sludge process which is much more precise and accurate for estimation of the removal of OMPs. However, this model needs more details on adsorption and degradation mechanisms, which are not available here in our experiments. The two-phase fate model can be applied after the mechanisms of degradation have been explored.

In addition, salt rejection of membranes should be also taken into consideration for the simulation since accumulated salts in the reactor influence the activity of microorganisms and organic matter rejection. Andrea [68] reported that the removal efficiencies of aluminum were always above 98 % by NF membranes, indicating MBRs will have concentrated salts, which should be paid attention for the design and simulation of OMPs biodegradation.

Chapter V Conclusions and suggestions

5.1 Conclusions

5.1.1 OMP rejection by KOCH NF 200

(1) OMPs can be almost completely removed from MQ in the short-term filtration tests. Results show the removal efficiencies for both of the selected OMPs (ketoprofen and naproxen) were above 90%. However, the removal efficiencies decreased with filtration continuing. The main mechanism for the removal was adsorption of OMPs on/in the membrane.

(2) The KOCH NF200 can reject about 40% OMP (Ketoprofen and Naproxen) molecules in a MQ matrix and more than 90% OMPs in a secondary effluent (wastewater) matrix under steady state in long term filtration tests. The mechanism for the removal is initially adsorption, followed by size exclusion and electric interaction under MQ matrix conditions. Wastewater matrix can enhance OMPs rejection due to enhanced size exclusion and electric charge interaction through blocking membrane pores and forming a gel layer as well as binding some OMPs through partitioning followed by retention by NF. Processes of filtration of OMPs can modify the surface of the membrane, increasing the contact angle and decreasing the zeta potential of the membrane surface, which may enhance the rejection of OMPs. The mechanism of OMPs rejection by NF can be summarized in the following table.

Table 5-1 Mechanisms of OMPs rejection by NF membranes

Mechanisms	Filtration in MQ		Filtration in WW		MQ+fouling membrane	
Filtration process	initial	steady	Initial	steady	Initial	steady
Adsorption	+++	+	++	+		+
Size exclusion		+++		+++	+++	++
Charge interaction		+	+	+++	+	+
Partitioning of OMPs between water and organic matters in wastewater matrix			++	+++		+

5.1.2 Simulation of removal of OMPs based on CRT

(1) An ideal model for OMPs biodegradation in the reactor was investigated. The effects of SRT, HRT, sludge concentration, feed concentration, membrane performance, adsorption and degradation constants on the biodegradation were assessed and the mathematical analysis was also discussed.

(2) The concept of compound retention time (CRT) was created, which is suitable for aerobic and anaerobic biodegradation. A membrane can increase CRT and thus increase the contact time between OMPs and microorganism in the reactor, resulting in more biodegradation of OMPs. The mathematical expressions for CRT with or without sludge wastage were also discussed.

(3) For the adsorption test of selected OMPs in the anaerobic bioreactor, it is found that the OMPs can be adsorbed onto sludge rapidly, and it takes about 1 day to reach

equilibrium. The isotherm for adsorption of OMPs is linear for naproxen but there is a maximum value for ketoprofen in the experimental range.

(4) OMPs can be biodegraded by anaerobic microorganisms at 35 ℃ with a carbon source. The first order reaction constants were 0.0025 h^{-1} (0.060 d^{-1}) and 0.0031 h^{-1} (0.074 d^{-1}) for naproxen and ketoprofen, respectively.

5.2 Suggestions

Different kind of membranes can be applied in the long term filtration and detailed mechanism of membrane separation can be further explored by studying thepore size of the membrane & the size of the OMP molecule, and the functional groups on the surface of the membrane. A model can be created to simulate or predict the rejection performance of OMPs by different membranes.

More time is needed for the anaerobic reactor to degrade OMPs. Different carbon sources and concentration levels can be applied to investigate the optimum conditions for biodegradation. And the specific microorganisms in the anaerobic bioreactor system need also to be studied.

In the future, an AnMBR-NF can be set up, combining the anaerobic bioreactor with UF/MF and NF membranes, and the continuous OMPs feed with low concentration could be applied to check the applicability of the model for CRT and OMPs removal performance.

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