Impacts of reverse osmosis concentrate recirculation on MBR performances in the field of wastewater reuse

Thi Thu Nga Vu

THÈSE

En vue de l'obtention du

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Titre :

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VU Thi Thu Nga

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Résumé :

Les eaux usées peuvent possiblement être traitées par un système membrane intégré et combinant les procédés de bioréacteur à membrane (BAM) et d'osmose inverse (OI) pour une élimination efficace des micropolluants en vue de la réutilisation des eaux. Cependant, le rejet des concentrats d'OI dans l'environnement pourraient représenter un danger en raison de la toxicité de certains de leurs composés (micropolluants, sels, matières organiques). Une des solutions possibles peut être de recycler le concentrat d'OI vers le BAM. Néanmoins, une étude approfondie s'impose pour une telle configuration car le recyclage mettrait en jeu la recirculation de matière organique non biodégradable, ou de fortes concentrations en sels ou micropolluants, qui pourraient finalement engendrer, directement ou indirectement, un colmatage de la membrane ainsi qu'une modification de l'activité bactérienne dans le BAM.

Les effets du recyclage de concentrat d'OI sur les performances de BAM ont été étudiés de deux différentes manières, en distinguant les effets à court-terme (ou court temps de contact) et les effets à long-terme (ou long temps de contact). Les résultats montrent qu'après un temps de contact de 3 heures entre le concentrat et les boues, les concentrations en protéines et polysaccharides dans le surnageant restent inchangées par rapport au début de l'opération. Une analyse HPLC-SEC a permis d'étudier les effets du concentrat d'OI sur la production de matières microbiennes solubles de types protéique. Un pic de concentration en substances protéiques ayant une masse moléculaire de 10 à 100 kDa a été observé dans le surnageant juste après l'addition du concentrat d'OI. Le pouvoir colmatant des boues n'a lui pas été modifié après l'injection du concentrat d'OI. Cette observation ouvre sur la possibilité de développer une opération d'OI comme traitement tertiaire en aval du BAM. La combinaison BAM-OI pourrait donc être une solution envisageable pour traiter le concentrat d'OI.

Pour les longs temps de contact, les résultats ont montré que l'impact de l'effluent toxique (concentrat d'OI) sur les boues dépendait du rendement de l'opération d'OI et des

caractéristiques du concentrat. Les mêmes tendances ont été observées quelle que soit la composition du concentrat en sels et en matière organique, puisqu'une augmentation de la concentration en protéine a été mise en évidence. L'effet du recyclage du concentrat d'OI a aussi été étudié à différents débits et avec différentes caractéristiques. Les effets sur les performances globales du BAM ainsi que sur son colmatage ont plus particulièrement été investigués. Le taux d'abattement en termes de Demande Chimique en Oxygène (DCO) est, dans tous les cas, supérieur à 93 %, quel que soit le débit de recyclage. Des résultats similaires ont été obtenus en termes de Carbone Organique Dissous. De plus, l'efficacité de la nitrification n'a pas été affectée en présence de concentrat d'OI dans le BAM. L'analyse HPLC-SEC a révélé un pic important de concentration en composés protéiques dans le surnageant, avec des masses moléculaires comprises entre 10 et 100 kDa et entre 100 et 1000 kDa. Par conséquent, une augmentation significative du pouvoir colmatant des boues a été observée et attribuée à la présence de protéines. Par ailleurs, le recyclage du concentrait d'OI n'a pas eu d'effet sur l'élimination de la carbamazépine et du diclofenac dans le BAM. Au contraire, l'élimination du ketoprofene a légèrement baissé, en passant de 94 à 72 %.

Enfin, l'effet du recyclage de concentrat d'OI sur la biodégradation a été révélé comme insignifiant, ce qui indique que le recyclage du concentrat d'OI pourrait être une bonne alternative pour réduire les concentrats d'OI et limiter leur rejet dans l'environnement.

Mots clés : Bioréacteurs à membrane, Réutilisation, Concentrat, micropolluant, colmatage membranaire, eaux usées

Abstract:

Wastewater effluents can be treated by an integrated membrane system combining membrane bioreactors (MBR) and reverse osmosis (RO) for effective removal of micropollutants in the field of high-quality water reuse. However, discharging the RO concentrate waste stream directly into the natural environment could lead to serious problems due to the toxic components contained in the concentrates (micropollutants, salts, organic matter). A possible solution could be the recirculation of RO concentrate waste to the MBR. However, such an operation should be studied in detail since the recirculation of non-biodegradable organic matter or high concentrations of salts and micropollutants could directly or indirectly contribute to MBR membrane fouling and modification of the biodegradation activity.

The effects of RO concentrate recirculation on the MBR performances were investigated in two different ways of contact, i.e. short term peak contact and long-term continuous contact at various operating conditions. The results demonstrated that after 3 hours of contact time between the sludge and concentrate, the same values of both protein and polysaccharide concentrations were found in the supernatant, compared to that at the beginning of the reactor. HPLC-SEC analysis was employed to study the effects of RO concentrate on the production of protein-like SMPs. A significant peak of protein-like substances with a molecular size of 10-100 kDa was observed immediately in the supernatant after the addition of RO concentrate. Besides, no significant change was found of the sludge fouling propensity after the injection of RO concentrate into the activated sludge. This finding proposes the opportunities to develop RO process as a tertiary treatment of the membrane bioreactor (MBR), hence, the integrated MBR - RO concept with the RO concentrate recirculation to the MBR might be a solution to treat the concentrate waste stream produced by RO.

During the long-term continuous contact, the results demonstrated that the impact of the toxic flow on activated sludge depends on the recovery of the RO step and the characteristics of the concentrate but the same trends were observed whatever the organic

matter and salt contents of the concentrates: the concentration of proteins increased. The effects of the reverse osmosis concentrate recirculation, at different flow rates and with different characteristics, to the MBR were investigated. Their impacts on MBR global performances, especially the MBR fouling were evaluated. The removal efficiencies of chemical oxygen demand (COD) at the different flow rates of concentrate were greater than 93%. Similar results for the dissolved organic carbon removal efficiency were found in the MBR. Additionally, the presence of RO concentrate in the MBR did not inhibit the nitrification process. HPLC-SEC analysis employed to study the effects of RO concentrate on the production of protein-like SMPs demonstrated a significant peak of protein-like substances corresponding to 10-100 kDa and 100-1000 kDa molecules in the supernatant. Thus a significant increase of sludge fouling propensity was observed, which could be attributed to the increased quantity of protein-like substances. Furthermore, the recirculation of RO concentrate to the MBR did not significantly affect the removal of carbamazepine and diclofenac in the MBR. Meanwhile, the removal rate of ketoprofen was impacted slightly by the RO concentrate recycling to the MBR (from 94 to 72%).

Finally, the effect of the concentrate on sludge activity was studied and no significant effect was observed on biodegradation, indicating that the return of the concentrate to the MBR could be a good alternative for the reduction of concentrate quantities before disposal to the environment.

Keywords: Membrane bioreactors, Reuse, Concentrate, micropollutants, membrane fouling, wastewater

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NOMENCLATURE

ABBREVIATIONS

AOPs	Advanced oxidation processes	-
DCF	Dimethylphenol	-
EDCs	Endocrine disrupting compounds	-
EPS	Extracellular polymeric substances	-
HPLC-SEC	Size- exclusion high performance liquid chromatography	-
MF	Microfiltration	-
MBR	Membrane bioreactor	-
NF	Nanofiltration	-
PPCPs	Personal care products	-
PES	Polyethersulfone	-
PS	Polysulphone	-
SMP	Soluble microbial products	-
RO	Reverse osmosis	-
TrOCs	Trace organic contaminants	-
UF	Ultrafiltration	-

LATIN LETTERS

A	Membrane area for filtration	m^2
C	Deposited mass on the membrane surface per filtered permeate volume	$kg.m^{-3}$
CBZ	Carbamazepine	$\mu g.L^{-1}$
COD	Chemical oxygen demand	$mg.L^{-1}$
DCF	Diclofenac	$\mu g.L^{-1}$
DOC	Dissolved organic carbon	$mg.L^{-1}$
dRf/dV	Fouling velocity	$m^{-1}.s^{-1}$

F/M	Food-microorganisms ratio	$gCOD.gMLSS^{-1}.day^{-1}$
HRT	Hydraulic retention time	h
J	Permeation flux	$L.m^{-2}.h^{-1}$ or $m.s^{-1}$
Lp_o	Permeability of the membrane	$L.m^{-2}.h^{-1}.bar^{-1}$
MLSS	Mixed liquor suspended solids	$g.L^{-1}$
SAD_m	Specific air demand based on membrane area	m^3 air.$m^{-2}.h^{-1}$
SAD_p	Specific air demand based on permeate volume	m^3 air.m^{-3} permeate
SRT	Solids retention time	day
SS	Suspended solids	$g.L^{-1}$
R_f	Fouling resistance	m^{-1}
R_m	Membrane resistance	m^{-1}
R_t	Total filtration resistance	m^{-1}
R_w	Recovery of membrane	%
TOC	Total organic carbon	$mg.L^{-1}$
TMP	Transmembrane pressure	bar
V	Cumulated permeate volume	m^3
V_r	Recirculation volume	L

GREEK LETTERS

μ (20°C)	Fluid viscosity at 20°C	Pa.s
α	The specific cake resistance	$m.kg^{-1}$
$\Delta\pi$	Osmotic pressure	Pa

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INTRODUCTION

Membrane bioreactors (MBR) and reverse osmosis (RO) process are both established technologies but their use together for advanced wastewater treatment with reusable water is relatively new. The MBR process is an improvement of the conventional activated sludge wastewater treatment process and is capable of producing excellent quality of treated water. This process allows the retention of the suspended particles, bacteria and soluble and colloidal compounds according to their sizes. Nevertheless, the MBR process also has some drawback; micropollutants present in municipal wastewater cannot be effectively removed by MBR process, even if their removal is improved in comparison with conventional treatment. Meanwhile, reverse osmosis process provides excellent removal of both inorganic and organic constituents, including trace constituents such as pharmaceuticals and personal care products (PPCPs) and endocrine disrupting compounds (EDCs). However, problems in RO applications include cost, fouling, and specially concentrate management.

The characteristics of the concentrate depend on the feed water characteristics, the pretreatment, the membrane process used, the recovery, and the additional chemicals used. Concentrates from microfiltration (MF) or ultrafiltration (UF) contain suspended solids and colloidal particles; whereas nano-filtration (NF) or reverse osmosis (RO) concentrates contain high concentrations of ions and small organic compounds. Their composition is of all the dissolved substances retained by the membrane (organic matter, micropollutants and salts). In addition, the concentrates are more difficult to treat because of the increased concentrations of salts and small organic compounds. Therefore, reuse of the concentrate waste stream is the feasibility option. The combination of MBR and RO process might be a solution to this problem.

The recirculation of RO concentrate could induce benefits like an increase of the residence time of the compounds, which may improve their biodegradation. An additional advantage is that the recirculation can improve the bio-flocculation process; the filterability of the sludge thereby can be also improved. Nevertheless, it could influence or changes of microbiological community in the MBR by increased RO concentrate concentrations. Besides, the

permeability of the MBR membrane could be decreased by the concentrate recycling and the MBR fouling can appear earlier.

In this context, the work is focused on the impacts of the reverse osmosis (RO) concentrate returned with real waste water to the MBR process. The RO performances are studied in another PhD thesis. The MBR global performances and MBR fouling are highlighted. Specially, the ability removal micropollutants in the MBR are also discussed. This study proposes the opportunities to develop RO process as a tertiary treatment of the membrane bioreactor (MBR), hence, the integrated MBR - RO concept with the RO concentrate recirculation to the MBR might be a solution to treat the concentrate waste stream produced by RO. To better understanding the effect of RO concentrate recirculation to the MBR, batch reactor and two sets of experiments were performed:

(i) Batch reactors were examined to characterize the effects of RO concentrate addition on the activated sludge taken from the wastewater treatment plants (WWTP). This study describes some of finding related to the impact of RO concentrate in peak injection on the fouling propensity and physico-chemical characteristics of the activated sludge.

(ii) Set 1: MBR was fed by the wastewater and the addition of RO concentrate, representing 15% of total MBR inflow. Our study focused on the MBR global performances with the characteristics of waste are different from the classical MBR, but stable during this experiment time.

(iii) Set 2: A combination of MBR and RO processes was investigated for municipal wastewater treatment with the RO concentrate recirculation continuously which was made up 20% of the total inflow of the MBR. The effects of RO concentrate recycling on the MBR performances, on fouling of the MBR membrane as well as the elimination of micropollutants in the MBR were examined.

In order to explain the effect of RO concentrate recirculation to the MBR, firstly, the compositions contained in the concentrate such as salt composition, organic matter and micropollutants are analyzed. The performances of the MBR concept is usually evaluated in

terms of conventional removal parameters (COD, DOC, ammonium, total nitrogen…), the difference in concentration of certain species between inflow and outflow and expressed as removal percentage. Filterability test is used to characterize the fouling propensity of MBR sludge and supernatant. Protein and polysaccharide concentrations are analyzed in the MBR supernatant and permeate to study the effects of RO concentrate on the change of SMP composition. HPLC-SEC-fluorescence is used to characterize the protein-like SMPs in the supernatant and permeate of the MBR.

Then, this thesis consists of five main parts:

The first part summarizes the background information for this thesis, including the synthesis of fouling mechanisms in the MBR process, the effects of high salinity and micropollutants, which are contained in the RO concentrate, on the MBR process. The combination of MBR-RO process is presented in this chapter. The following part will address the characteristics of the concentrate produced by RO in an integrated MBR-RO process and the methods for concentrate waste stream treatment. This part also highlights the opportunities and challenges regarding RO concentrate recirculation.

The second part gives the main details on the materiel and methods used in this study

The third part discusses the influences of RO concentrate injection on the activated sludge, especially, focusing on the change of the supernatant composition and the sludge fouling propensity, might due to the toxic components contained in the RO concentrate after a peak of concentrate in the sludge

The fourth part examines the effects of reverse osmosis concentrate recirculation, with its various characteristics, continuously to the MBR in an integrated MBR-RO process for the wastewater treatment and reuse. The impacts on the biodegradation in the MBR, the fouling propensity of the MBR membrane as well as the elimination of the micropollutants (such as carbamazepine, diclofenac, ketoprofen) in the MBR were studied and discussed.

Finally, the fifth part studies the effects of various operating parameters used in the combined MBR-RO process with the concentrate recirculation on the global performances and membrane fouling of the MBR.

CHAPTER I

BIBLIOGRAPHIC SYNTHESIS

1.1. Membrane bioreactor (MBR)

1.1.1 Membrane filtration

Membrane filtration, widely used in chemical and biotechnology processes, is already established as a valuable means of filtering and cleaning wastewater. Membrane filtration denotes the separation process in which a membrane acts as a barrier between two phases (Fig. 1.1). The membrane separates on the basis of particle size. It retains constituents bigger than the pore size. According to the pore size of the membrane, the filtration process can be classified as microfiltration (MF), ultrafiltration (UF), nano-filtration (NF) or reverse osmosis (RO). Figure 1.2 introduces the overview of existing membrane types for water treatment and their corresponding rejection behavior of common pollutants. As shown in Fig. 1.2 the microfiltration membrane can reject the bacteria, while the ultrafiltration membrane may also retain the viruses. In addition to the bacteria and viruses, the nano-filtration membrane can also reject the multivalent ions. Reverse osmosis membrane even reject both of the monovalent ions and multivalent ions.

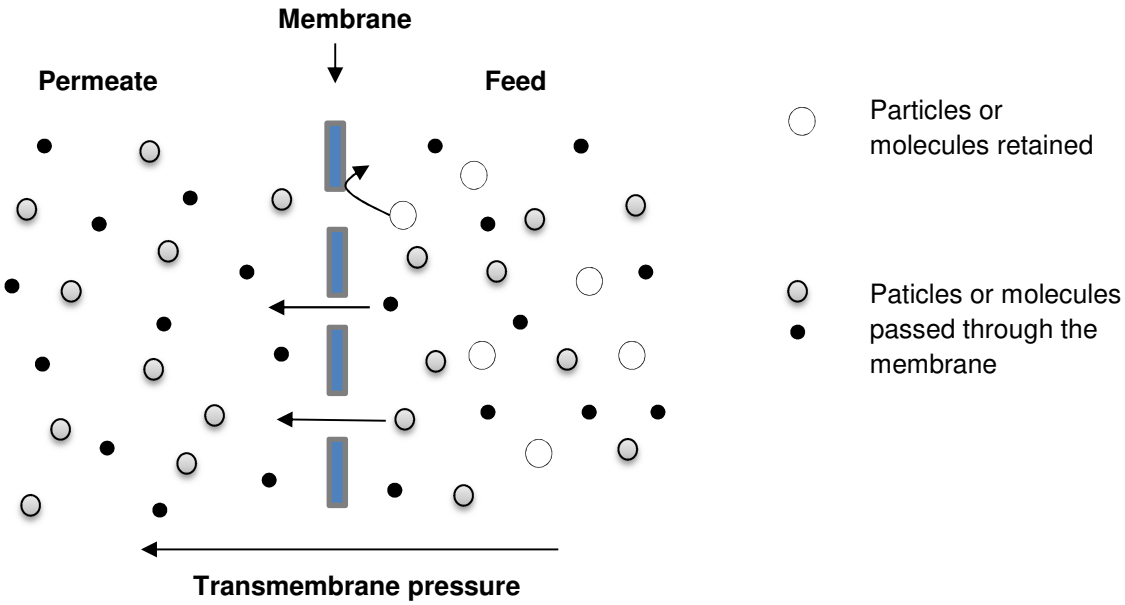


Figure 1.1 Schema of membrane filtration

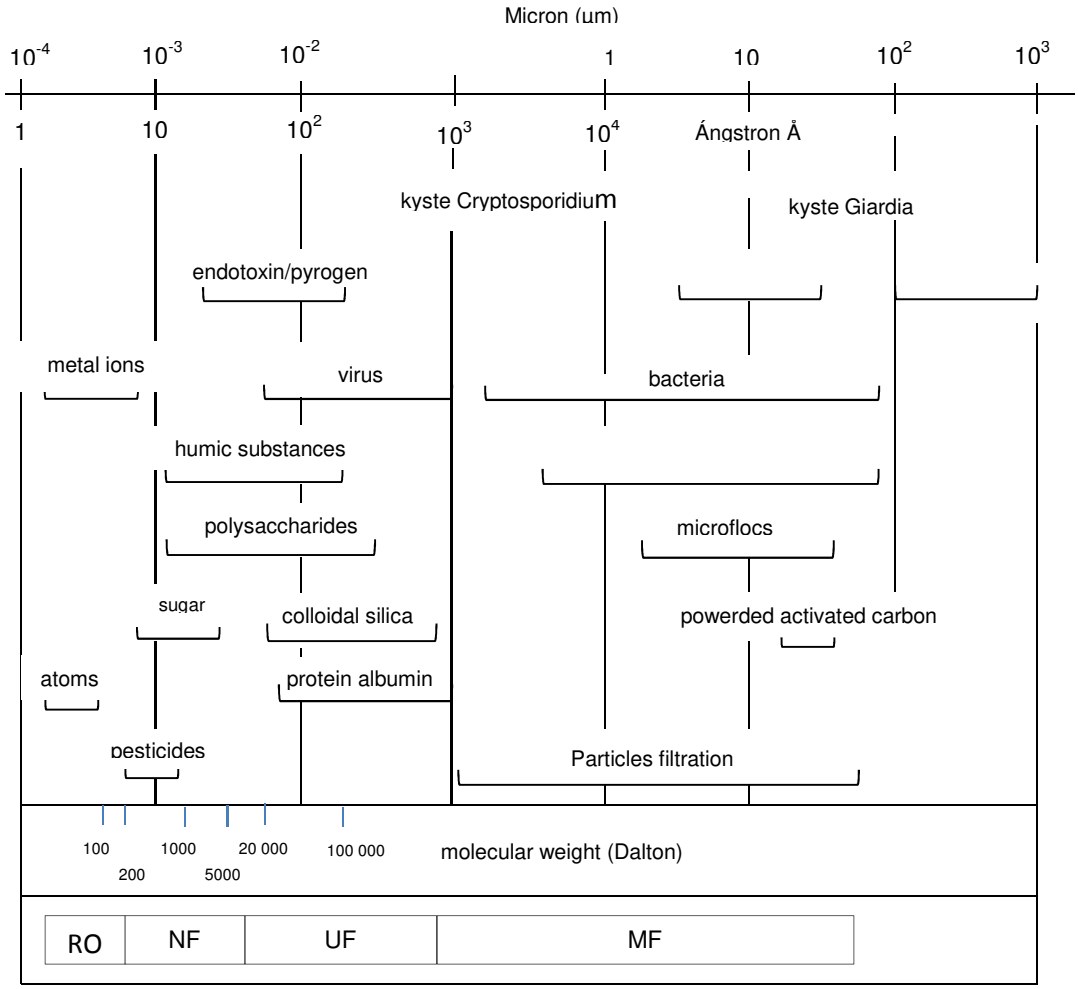


Figure 1.2 Different membrane type and ranges of compound rejections [102]

The MBR technology mostly employs microfiltration (MF) and ultrafiltration (UF). The membrane can be configured in membrane modules in different ways, such as hollow fiber membranes (outside-in), tubular membranes (inside-out) and flat-sheets (plate and frame membranes). The membrane configurations were commonly used hollow-fiber and plate and frame modules**.** The driving force for permeation is a transmembrane pressure (TMP) in most water treatment membrane filtration applications. The concentration polarization can decrease the membrane flux (increase resistance) for instance in ultrafiltration as it can lead to gel-layer formation causing additional resistance to filtration. In NF or RO concentration polarization can lead to decreased salt rejections or scaling at the membrane surface. In addition, concentration polarization causes increased osmotic pressures. The rate of permeate flux (J) may be described by Darcy's law as follows:

$$J = \frac{TMP}{\mu \times R_t} = \frac{TMP}{\mu \times (R_m - R_f)} \quad (1.1)$$

with

J: permeation flux [$L.m^{-2}.h^{-1}$] or [$m.s^{-1}$]

TMP: transmembrane pressure [Pa], or [bar]

μ: dynamic permeate viscosity at 20°C [Pa.s]

R_t: total filtration resistance [m^{-1}]

R_m: membrane resistance [m^{-1}]

R_f: fouling resistance [m^{-1}]

The permeability of the membrane (at T = 20°C) can be calculated as the ratio between the flux and the TMP, see eq. 1.2:

$$\text{Permeability, } L_P = \frac{J}{TMP} \ [L.m^{-2}.h^{-1}.bar^{-1}] \quad (1.2)$$

The rejection R (%) of a membrane for a specific compound can be calculated by:

$$R = \left[1 - \left(\frac{C_{per}}{C_{feed}}\right)\right] \times 100\% \quad (1.3)$$

with

C_{per}: permeate concentration ($mol.L^{-1}$)

C_{feed}: feed concentration ($mol.L^{-1}$)

All membranes retain the solids that are present in the reactor, so all MBR permeates are solid-free. In order to reuse easily the MBR permeate, tertiary treatment is still necessary to remove recalcitrant compounds like viruses, endotoxins, pesticides, micropollutants or heavy metals.

1.1.2. Membrane fouling in MBRs

Membrane fouling is a process whereby the solution or the particle is deposited on the membrane surface or in the membrane pores such as in the membrane bioreactor, so that the performance of the membrane is degraded. The increase rate of TMP or the decline in permeate flux is an important factor to evaluate the system performance in submerged MBR because it is directly related to the rate of membrane fouling.

1.1.2.1. Fouling mechanisms in the MBR

Normally, the different fouling mechanisms can be described: (i) pore blocking, the particles enter the pore and get stuck in its opening, reducing the number of pore channels available for permeation; (ii) pore narrowing by adsorption, the substances or particles enter the pore and are adsorbed to the pore wall, thus narrowing the pore channel, reducing the permeate flow; (iii) cake layer formation, the particles and macromolecules accumulate at the membrane surface, forming a more or less permeable layer; (iv) the biofilm formed on the membrane surface in MBR consists of both microorganisms growing and microbial flocs deposited on the membrane, the formation of a biofilm on the membrane surface was mainly responsible for the loss of filterability, therefore, it became necessary to further investigate the properties of biofilms which are closely associated with membrane filterability. In both cases the fouling mechanism will lead to an increase in total filtration.

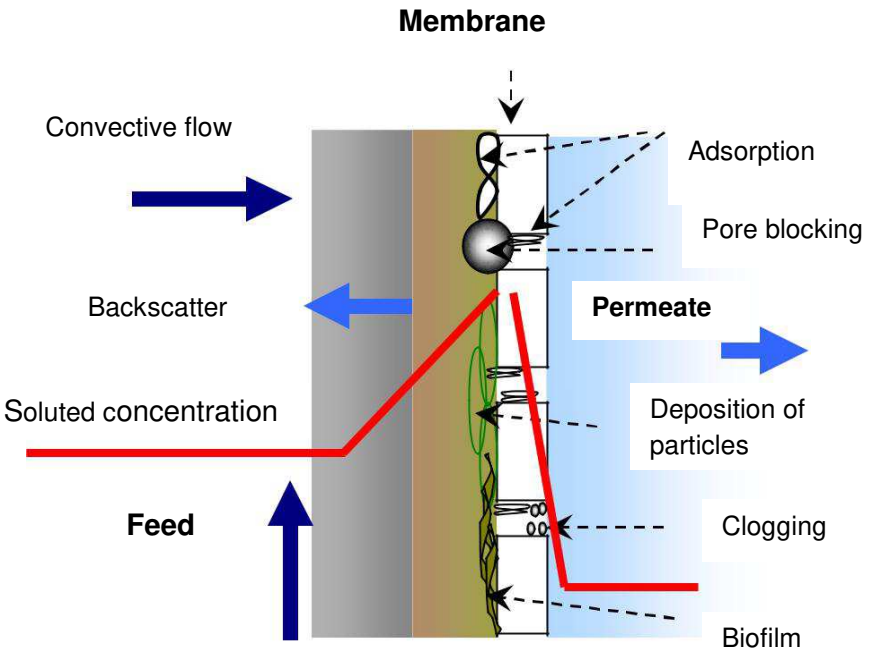


Figure 1.3 Schematic diagram of the various fouling mechanisms

The various factors affecting the membrane fouling in the MBR could include three categories: membrane characteristics, operating conditions and biomass characteristics (see Table 1.1).

Table 1.1 Factors affecting membrane fouling in membrane bioreactors (MBR)

Factor	Effect on membrane fouling
Membrane characteristics	
Membrane material	Membrane fouling occurs more readily on hydrophobic membrane than on hydrophilic ones because of hydrophobic interaction between foulants and membranes.
Hydrophobic character	The hydrophilicity or hydrophobicity property of the membrane material affects fouling in MBR. Membrane fouling is more severe in hydrophobic membranes compared to hydrophilic membrane

Membrane pore size	Increasing membrane pore size increases the tendency for pore blocking mechanism
Operating conditions	
Operating mode	Operating in cross-flow filtration mode reduces cake layer formation on the membrane surface
Aeration	Increasing aeration rates results in a reduction in membrane fouling
Solids retention time (SRT) (days)	Operating at high SRTs reduces the production of EPS, hence reduces fouling. However, extremely high SRTs rather increase membrane fouling due to the accumulation of MLSS and increased sludge viscosity
Hydraulic retention time (HRT) (hours)	Decreasing HRTs results in increasing rate membrane fouling. However, extremely high HRTs leads to an accumulation of foulants
Food-microorganisms (F/M) ratio	The rate of membrane fouling in MBRs increases with increasing F/M ratio due high food utilisation by biomass resulting in increased EPS production. Decreasing F/M ratios resulted in a reduction in the concentration of EPS.
Temperature	Low temperatures increase the propensity for membrane fouling as more EPS are released by bacteria and the number of filamentous bacteria increases. Sudden temperature changes also increase fouling rate due to spontaneous release of SMPs
Biomass characteristics	
Mixed liquor suspended solids	Increasing MLSS correlate with increased rate of

(MLSS)	membrane fouling. Other studies report no (or little) effect of MLSS on membrane fouling
Sludge apparent viscosity	Increasing the viscosity results in increased membrane fouling
Extracellular polymeric substances (EPS)	Increase in the concentration of EPS (bound EPS and SMPs) result in membrane fouling
Floc size	Decrease in floc size increases membrane fouling

1.1.2.2. Classification of MBR fouling

Fouling of membranes is characterized in general as a reduction of permeability or as an increase of transmembrane pressure (TMP) during the MBR operation. Different fouling mechanisms can occur during the filtration of the membrane, including three phenomena: *gel or cake layer formation* (particles and macromolecules accumulate at the membrane surface, forming a more or less permeable layer); *pore blocking* (particles enter the pore and get stuck in its opening, reducing the number of pore channels available for permeation); and *adsorption* (substances and/or particles enter the pores and are adsorbed to the pore wall thus narrowing the pore channels, reducing the permeate flow). Fouling can be classified into three major categories: *inorganic fouling* which refers to the deposit of inorganic material like salts, clay and metal oxides; *organic fouling* which includes all kind of deposit of organic material like grease, oil, surfactants, proteins, polysaccharides, humic substances and other organic biopolymers and *biofouling* which designates the formation of biofilms by compounds and microorganisms attached and growing at the membrane surface.

a) *Biofouling*

Biofouling is defined as undesirable accumulation of microorganisms, which may occur by deposition, growth and metabolism of bacteria cells or flocs on the membrane [36]. In addition, the microbial community structure and the characteristics of individual microbial

groups could play an important role in biofouling [69]. Biofouling mechanisms include (i) the adsorption of soluble and suspended extracellular polymers on membrane surfaces and in membrane pores; (ii) the clogging of membrane pore structure by fine colloidal particles and cell debris; (iii) the adhesion and deposition of sludge cake on membrane surfaces [64]. The biofouling layer formed on the membrane in an MBR mostly consists of microbial flocs deposited from the bulk phase. These microbial flocs are very heterogeneous, irregular structures consisting of microorganisms, organic and inorganic adsorbed particles, extra polymeric substances (EPS) and organic fibers [29,59,73]. Based on a few studies, biofouling can have several effects on the membrane systems. For examples, Yun et al. [126] reported in the aerobic MBR, the accumulation of biomass with the growth of biofilm was the main factor for the loss of permeability, so, the TMP rises up continuously with the growth of biofilm on the membrane surface. Miura et al. [80] demonstrated that the biofilm development on hollow-fiber MF membrane surfaces caused severe irreversible fouling during a long-term operation of pilot-scale MBRs treating municipal wastewater. As the bio-cake accumulates on the surface of the membrane, endogenous decay or cell-lysis at the bottom layer would be expected to occur due to poor oxygen and substrate transfer. It gave rise to the excretion of EPS (polysaccharides and proteins) which could reduce the permeability of the MBR membrane [59].

b) *Organic fouling by extracellular polymeric substances (EPSs) and soluble microbial products (SMPs)*

Many researchers indicates that soluble microbial products (SMP) and extracellular polymeric substances (EPSs) excreted by microorganisms, produced from cell lysis and adsorbed organic matter from wastewater also play important roles in the formation of biological foulants and cake layer on the membrane surface [30,76,98]. The key components of EPS have been believed to include carbohydrates, proteins and humic-acid [22,98]. Extracellular polymeric substances (EPSs) are key biological substances, which can block membrane pores, adhere to membrane surface, affect cake structure and induce osmotic effect, and therefore affect significantly membrane fouling in the MBR [70]. According to Gao

et al. [29], the protein concentrations of extracellular polymeric substances in conjunction with the carbohydrates of soluble microbial products were the main factors that accelerate the membrane fouling. Furthermore, Campo et al. [11] demonstrate that the fouling rate of the MBR membrane is closely related to the protein contents of the mixed liquor expressed by ratio proteins/polysaccharides. Due to their hydrophobic nature, proteins tend to adhere to the surface of the flocs, effectively constituting EPS_{bound}, and contributing to the irreversible cake deposition. Additionally, they also reported that an increase of EPSs in the MBR caused the de-flocculation of the sludge. Consequently, the specific cake layer resistance (α) is influenced by de-flocculation. In particular, the superficial cake deposition increased when the floc size decreased. Earlier study showed that EPS are recognized as the most direct and significant factor affecting biofouling in MBRs [105,112]. They indicated that the adsorption tests and atomic force microscopy observation confirmed that the EPS properties played an important role in membrane adsorption, eventually causing the different fouling behavior.

It is known that MBR fouling is related to the group of soluble microbial products (SMP), this group contains soluble and colloidal biopolymers, mostly polysaccharides or carbohydrates and proteins, the major organic constituents of sludge supernatant [65,76,97,102]. Generally, polysaccharides and proteins are assumed to be the major fractions [27,114] that may have a significant influence on the physicochemical properties of the fouling layer. The formation of SMPs is also dependent on several factors, e.g., the type of food source, diversity of microorganisms and adaptation time of MLSS to certain SRT [43, 56]. SMP could be divided into two categories: biomass associated products (BAP), which were formed by biomass decay and utilization associated products (UAP), which were produced directly substrate metabolism [44]. More recent studies indicated that SMP, especially polysaccharides, adsorbed on the membrane surface, blocked membrane pores and formed a cake layer, resulted in a hydraulic resistance to permeate flux [79,83,95]. Besides, Tian et al [113] demonstrated that the protein, polysaccharides of BAP (biomass-associated products)

concentrations increased throughout the experiment. The content of polysaccharides released by biomass was greater than that of proteins with the operation time increased. The polysaccharide concentrations were also effectively retained by the membrane, ranging from 26.6% to 46.8%. Therefore, the presences of polysaccharides and proteins in the supernatant would make serious contributions to membrane fouling. Recently, Dalmau et al. [17] demonstrate that the SMP concentration had an influence on the transmembrane pressure (TMP) in the MBR. The direct impact on TMP after an increase of SMP concentrations was observed in the MBR supernatant. Previous researches highlighted reported that the proteins concentration in SMP significant influenced on membrane fouling in terms of the specific resistances increase, when the value of proteins concentration in the supernatant changes from 30 to 100 $mg.L^{-1}$, the value of specific resistance increased by a factor of 10 [94]. Meanwhile, Chu and Li [13] and Yigit et al [124] showed that polysaccharide-like substances contributed to fouling more significantly than protein-like substances. Similarly result was found by Dvořák et al [28], they reported that carbohydrates were the majority component of SMP retained by the MBR membrane (about 60%). Therefore, it can be assumed that the concentration of carbohydrates in the MBR supernatant play an important role in membrane fouling.

On the other hand, the molecular weight (MW) distribution of SMP were measured in membrane bioreactor using membranes with nominal molecular weight cut-offs of 1, 10, 100 kDa (see Table 1.2) to investigate the impact of each of the fractions, i.e. >100, 10-100, 1-10, <1 kDa on fouling in MBRs . Arabi and Nakhla [4] showed that no correlation between fractions of >100 kDa and 10-10 kDa and fouling in MBRs was found. However, a strong correlation was observed between fouling and SMP concentration in the range of 10-100 kDa with higher fouling rate associated with higher concentration of 10-100 kDa fractions. The high molecular weight compounds play an important role in creating high resistance of the membrane, leading to a reduction of permeate flux. The fluorescence spectra of membrane

foulants also exhibited two peaks of protein-like substances, confirming that proteins played an important role in membrane fouling [108].

Tableau 1.2 Molecular weight distribution of SMP

Molecular weight	References
>100 kDa : 16% ; 30-100 kDa : 9% ; 3-30 kDa : 23% ; <3 kDa : 52%	[35] [(a)(c)]
>100 kDa : 31% ; 30-100 kDa : 8% ; 3-30 kDa : 32%; <3 kDa : 29%	[61] [(b)(d)]
>100 kDa : 20% ; 30-100 kDa : 37% ; 10-30 kDa : 12% ; 1-10 kDa : 18% ; <1 kDa : 13%	[99] [(a)(d)]
Most protein SMP in the supernatant >10 kDa	[42] [(e)]
>30 kDa: 25-37%; 3-30 kDa: 4-11%; <3 kDa: 52-59%	[26] [a,h]
>30 kDa: 56% 10-30 kDa: 24%; 5-10 kDa: 11%; <5 kDa: 9%	[85] [c,d,f]
Two groups of proteins-like molecules: 10-100 kDa and 100-1000 kDa	[65] [(g)]

[(a)]measurements by TOC; [(b)]measurements by COD; [(c)]centrifugation 10-15 minutes 4000rpm; [(d)]filtration 0,45µm; [(e)] measurements by centrifugal membrane devices; [(f)] soluble sample fractionated by molecular weight; [(g)]HPLC-SEC-fluorescence analysis of supernatants; [(h)]sludge retention time (SRT) from 10 days to 60 days

Pan et al [85] reported that membrane fouling is related to the reduction of SMP larger than 30 kDa in the effluent, which is due to the retention of large SMP by the formed cake layer. Hydrophilic fraction is the dominant species in SMP, which accumulates in the mixed liquor, so hydrophilic carbohydrates are most likely the major foulants in the MBR. In addition, Li et al [67] reported that the 100-1000 kDa SMPs could be completely retained by MF/UF membrane or MBR membrane during sludge filtration, leading to formation of biofilm in bio-cake, which contributes to higher sludge fouling propensity and steady increase of MBR

fouling. The 10-100 kDa protein-like SMPs could be partially retained by MF/UF membrane or MBR membrane during sludge filtration, leading to the reduction of the empty space of bio-cake and result in change of bio-cake structure, that could lead to higher sludge fouling propensity and higher fouling rate and TMP jump in MBR.

Furthermore, the composition and concentration of SMP is significantly affected by operating conditions. For example, the membrane fouling rate increased 20-fold (from 0.18 to 3.65 $LMH.bar^{-1}.day^{-1}$ as the organic loading rates (F/M) increased from 0.34 to 1.41 $gCOD.gVSS^{-1}.day^{-1}$ [115]. When the sludge retention time increased from 10 to 32-37 days, the protein and polysaccharide concentrations decreased in the supernatant of the MBR [85]. Stricot et al [102] reported that high shear stresses (72 Pa) induce a very high release of soluble microbial products, mainly as protein-like substances. This release could be induced by the breakage of internal high strength bonds (fragmentation and erosion). The concentrations of protein rose strongly from the second day (the sludge had passed through the pump 2000 times) and stabilized at around 600 mg L^{-1}.

Conclusion, the group of soluble microbial products (SMP) could be the major fractions which contribute to the membrane fouling. The accumulated SMP not only inhibited the metabolic activity of microorganisms, but also greatly decreased the membrane permeability as a result of organic fouling.

c) Inorganic fouling

In general, the membrane fouling in the MBR was the inorganic fouling can form through two ways (see Figure 1.4): chemical precipitation and biological precipitation [78]. Chemical precipitation occurs when the concentration of chemical species exceeds the saturation concentrations due to concentration polarization. Biological precipitation is another contribution to inorganic fouling. The biopolymers contain ionisable groups such as COO^-, CO_3^{2-}, SO_4^{2-}, PO_4^{3-}, OH^-. According to Guo et al [136] and Iorhemen et al [36], inorganic compound can cause fouling when the precipitation occurs on the membrane due to

hydrolysis and oxidation during filtration. Examples such substances include cations and anions such as Ca^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+}, SO_4^{2-}, PO_4^{3-}, CO_3^{2-}, OH^-, *etc*. Thus, high presentation of salt concentration in the feed water induces greater inorganic scaling propensity and more serious colloidal fouling. Early research has shown that the inorganic precipitation coupled the organic foulants enhanced the formation of gel layer and thus caused membrane fouling in the MBR [119].

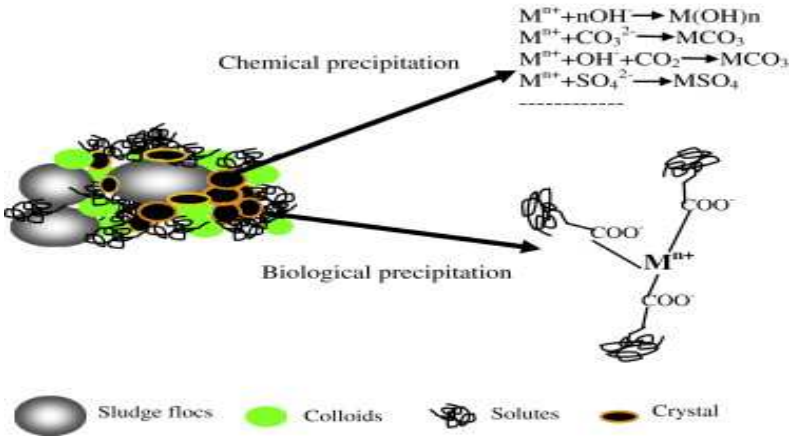


Figure 1.4 Schematic illustration of the formation of inorganic fouling in MBRs

Recent studies have shown that an increase in salt concentration (from 0 to 20 $g.L^{-1}$ NaCl) did not significantly change the dissolved organic carbon (DOC) removal efficiencies in the MBR (>95%) [40-41]. Besides, Luo et al [71-72] reported that the removal of total organic carbon (TOC) had decreased from 98% to 80% when the salinity was higher than 10 $g.L^{-1}$ NaCl. This phenomenon could due to the inhibitory effect of high salinity on the biomass, resulting in cell plasmolysis and /or loss of metabolic activity. Nevertheless, the removal efficiency recovered to approximately 99% when salt concentration was maintained at 10 $g.L^{-1}$ NaCl for two weeks. Small variations in TOC removal were also obtained (around 90 to 98%) during the increase of salinity loading from 10 to 16.5 $g.L^{-1}$. In contrast, Johir et al [46] reported that DOC removal efficiency decreased from 72% to 35% when salt concentration increased from 1 g $NaCl.L^{-1}$ to 10 g $NaCl.L^{-1}$. The lower removal of dissolved organic carbon with high salt concentration could be due to the adverse effect of salt on microbial activity.

According to Di Bella et al [19], after the addition of 10g $NaCl.L^{-1}$ in the inlet wastewater, it was observed a slight decrease of chemical oxygen demand (COD) removal efficiency (from 97% to 87%). The suggestion is that MBR can respond well to salt increase in term of organic matter removal in the MBR, as confirmed by previous study [40]. Similarly, Arabi and Nakhla [2] and also found that no impact of salinity was observed on the COD removal rate in the MBR. Besides, Yogalakshmi and Joseph [126] resulted under sodium chloride shock of 5- 30 $g.L^{-1}$, the COD removal efficiency dropped and was in the range of 83-87%.

On the other hand, salinity exhibited a significant negative impact on the nitrification process, ammonia removal efficiency decreased from 95 to 46% [41] and 87 to 46% [40]. Meanwhile, Hong et al [34] reported NH_4^+ removal efficiency decreased no significantly from 97 to 91% when the salinity increased from 0 to 35 $g.L^{-1}$; its removal rate was about 99% after one week of addition of 4 $g.L^{-1}$ NaCl [92]. It is of interest to note that the removal efficiency of total nitrogen decreased as the NaCl loading increased from 2 to 4 $g.L^{-1}$ and then its removal efficiency recovered to the normal condition (approximately 97%) despite the high NaCl loading of up to 12 $g.L^{-1}$, indicating that the microbial population has adapted to the hyper-saline condition [107].

In addition, the high salinity greatly affects the physical and biochemical properties of activated sludge, increasing proteins concentrations as well as decreasing membrane permeability. Sun et al [104] indicated that when the salt concentration increased from 5 to 15 $g.L^{-1}$, a larger impact was observed where protein concentration increased by 41% and carbohydrate concentration increased by 106%. This confirm that significant increase of salinity affected seriously the microorganisms, consequently more SMPs are released due to the stress and biomass detachment occurs, resulting in higher membrane fouling rate. Similarly, Tadkaew et al [107] reported that at NaCl concentration of 4 $g.L^{-1}$, the highest concentration of protein for SMP was observed. It then decreased gradually to a normal level as the salinity in the reactor to 12 $g.L^{-1}$, indicating that the microbial population has adapted to the hyper-saline condition; whereas, the concentration of carbohydrate fluctuated slightly

throughout their study. They also reported that a gentle increase in the transmembrane pressure (TMP) was observed as the salinity increased to 4 $g.L^{-1}$. This was followed by severe membrane fouling as the NaCl concentration increased to 8 and 12 $g.L^{-1}$. Previous study by Arabi and Nakhla [3] showed higher membrane permeability and lower fouling rate at the highest magnesium concentration of 96 $mg.L^{-1}$ (Mg : Ca ratio of 5 : 1), as compared to the other reactors at Mg:Ca of 1:5 and 1:1. This was due to magnesium bridging of negatively charged biopolymers thus enhancing bio-flocculation, and decreasing membrane fouling. Furthermore, an increased influent Mg concentration decreased the concentration of the fraction > 100 kDa and < 10 kDa for SMPs. Moreover, with increasing sodium chloride shock loads, an increase in soluble EPS was observed in the MBR. During higher sodium chloride shock loads (30-60 $g.L^{-1}$), the soluble EPS and its constituents (protein and carbohydrate) were almost doubled [125]. Recently, Zhang et al [127] demonstrate that the presence of 10 $g.L^{-1}$ NaCl, which was added into the MR feed, caused an obviously increase of polysaccharides in the supernatant (from 5.6 to 13.2 $mg.L^{-1}$ on average), whereas the proteins content had a slightly increase, suggesting the salt stress resulted in more polysaccharides than proteins in the supernatant, which was consistent with the previously report's Di Bella [19].

Conclusion, the presence of high salinity in the MBR could have no significant effects on the chemical oxygen demand (COD) removal rate. However, it could affect the increase of protein concentrations in the MBR supernatant, resulting in reduction membrane permeability.

1.1.3. Problematics of pharmaceutical micropollutants in the MBR

1.1.3.1. Removal of selected pharmaceutical micropollutants in the MBR

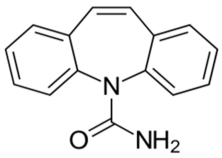
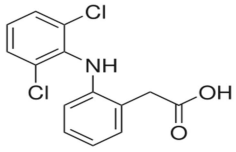
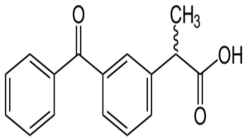
Although microfiltration (MF) and ultrafiltration (UF) are proved processes to efficiently eliminate turbidity, micropollutants are generally poorly removed during UF and MF, as the

membrane pore sizes are much larger than the molecular sizes of micropollutants. The removal of pharmaceuticals in activated sludge processes includes four mechanisms: biotransformation/biodegradation, sorption, air–stripping and photo-transformation [100]. According to Li et al [66], the main possible mechanisms for removal of pharmaceutical micropollutants in the MBR are biodegradation and sorption.

In this study, three pharmaceuticals, including carbamazepine (CBZ), diclofenac (DCF) and ketoprofen (KEP) are selected to examine their removal efficiencies in the MBR before and after the reverse osmosis concentrates recycled to the MBR. The results in Table 1.3 show that for carbamazepine and diclofenac the removal efficiencies can be negative. Carbamazepine is a special case because the concentrations in the effluent were frequently higher than those obtained in the influent. This phenomenon can be explained by the presence of input conjugated glucuronides of carbamazepine, which are not included in the original drug quantification. Thus, glucuronides are transformed into carbamazepine by means of microbial activity in the biological reactors [12,100]. On the other hand, carbamazepine has a value of sorption coefficient K_d (1.2 $L.kg_{SS}^{-1}$), defined as the partition of a molecule between the activated sludge and the water phase, far away from the critical value of 500 $L.kg_{SS}^{-1}$, indicating that it is not sorbed to activated sludge [66]. The explanation of the poor removal of diclofenac is similar to that of the carbamazepine, although the diclofenac has a K_d (16 $L.kg_{SS}^{-1}$) greater than that for CBZ [12]. Moreover, the poor removal observed with diclofenac could be probably attributed to the presence of chlorine in its structure, which made it difficult to degrade [55]. Therefore, these compounds could be classified into the poorly biodegraded group in the MBR.

In contrast, the removal efficiency of ketoprofen was from 44 to 97%, has been reported by many research (see Table 1.3). The elimination of this drug is enhanced in the MBR treatment, probably due to better adaptation of microorganisms to less degradable compounds [90].

Table 1.3. Structure and removal of the pharmaceuticals studied

Compound	Structure	MW[a] (g.mol^{-1})	K_d[b]	Removal efficiency (%)	References
Cabamazepine (CBZ) $C_{15}H_{12}N_2O$		236.3	1.2	-22-58	[8,10,12,14-15,54,86,91,93,100,106,121]
Diclofenac (DCF) $C_{14}H_{11}Cl_2NO_2$		296.15	16	-8-87	[8,10,12;14-15,49,55,86,91,93,100,106,116,121]
Ketoprofen (KEP) $C_{16}H_{14}O_3$		254.3	16	44-97	[8,55,86,91,100,106,116,121]

(a) Molecular weight, this data from Li et al [73]

(b) Sorption coefficient for activated sludge (L.kg$_{SS}^{-1}$)

1.1.3.2. Impacts of pharmaceutical micropollutants on the MBR process

The removal of many pharmaceutical compounds in MBR systems represent the main area of study today; however, little attention is paid to the potential effect of micropollutants on the performance of treatment plants, CAS or MBR systems [5]. They also reported that in the MBR, the continuous addition of CBZ at a concentration of 0.4 µg.L^{-1} did not perturb the global efficiency of the system, was just as effective in removing chemical oxygen demand (COD), with no change significantly in terms of sludge production.

The earlier report on the activated sludge was published by Kraigher et al [57] , showing that the presence of selected pharmaceuticals, including ibuprofen, naproxen, ketoprofen, diclofenac, clofibric acid, in wastewater at a concentration of 50 µg.L^{-1} caused shifts in the structure of activated sludge bacterial communities and reduced bacterial diversity in the reactors, compared to the reactor without the selected pharmaceuticals. Navaratna and

Jegatheesan [81] presented that after 1 mg.L^{-1} of ametryn was added into the feed of the MBR, the concentrations of protein are less in SMP, compared to that before the ametryn injection. However, it can be seen that the concentrations of carbohydrate increased in SMP after introducing ametryn. Thus, concentration of carbohydrate in SMP is the main organic foulant that could be causing the fouling of membrane in the MBR.

Recently, Nguyen et al [84] and Hai et al [33], using the MBR process, showing that a stable TOC removal (97-99%) was observed after the trace organics (i.e. carbamazepine, diclofenac, ketoprofen…) were added in the feed of the MBR to achieve a constant concentration of approximately 5 µg.L^{-1} of each selected compound. Similar result from Alturki et al [1], they reported that after 40 trace organics contaminants were continuously introduced to the MBR feed at concentration of 2 µg.L^{-1} of each compound, no change of TOC removal was found in the MBR. However, total nitrogen removal decreased sharply from 97 to 66%. Besides, Li et al [67] also investigated that no signification was observed for chemical oxygen demand (COD) and total nitrogen (TN) removal before and after addition of 90 µg.L^{-1} CBZ in the MBR feed. Besides, a cocktail mix of pharmaceutical compounds containing carbamazepine, diclofenac, ibuprofen and naproxen were dosed into the feed of an osmotic membrane bioreactor (OMBR) at concentrations of 20–25 µg.L^{-1}, the DOC removal efficiency was above 99% [58], whereas, an increase significantly was observed in the protein: polysaccharides ratio of the supernatant, which could affect the membrane fouling in the OMBR. In addition, Avella et al [6] reported that the addition of 5 µg.L^{-1} cyclophosphamide in the MBR induced an increased concentration of macromolecular compounds (peak maximum corresponding to protein of about 18 kDa and polysaccharide of about 6 kDa).

Conclusion, the presence of micropollutants in MBR can affect microbial community structure of microorganisms in the activated sludge. Besides, the presence of micropollutants in MBR may also affect the removal rate of total nitrogen. In addition, the ratio of

protein/polysaccharide of the supernatant could increase, which may affect the membrane fouling in the MBR.

1.2. MBR-RO/NF process

1.2.1. The combination of MBR –RO process

The use of the membrane bioreactor (MBR) process for wastewater and reuse is increasing. Although, high solid–liquid separation efficiencies in the water treatment can be achieved with the use of microfiltration and ultrafiltration, which is usually in the MBR process, dissolved organic and inorganic impurities could not be effectively treated. This inadequacy could be overcome by the use of MBR–RO/NF hybrid systems. Moreover, the RO/NF membrane has a distinctively smaller pore size than microfiltration or ultrafiltration in the MBR, and so that an increased retention of smaller components by RO/NF. The combination of membrane bioreactor (MBR) coupled to reverse osmosis (RO) or nano-filtration (NF) for water treatment has been successfully applied for the treatment of municipal wastewater [20,24]. They showed that this integration provided a superb quality effluent (99.99% for suspended solids removal, 97.3% for removal of chemical oxygen demand (COD), with very low organic matter concentration (dissolved organic carbon level below 4 $mg.L^{-1}$), and devoid of heavy metals. Besides, Jacob et al [38] recorded that the average performance of total organic carbon (TOC) removal was about 93% by an integrated MBR-RO process at the different volume reduction factor (VRF). Additionally, MBR-RO process treatment indicated excellent overall removal of target emerging contaminants, with removal rate above 99% for some compounds (metronidazole, hydrocodone, codeine, ranitidine). Similar, Malamis et al [74] reported that COD removal efficiency achieved by the MBR-RO was very high (above 99%). More specifically, the adoption of the integrated MBR-RO system provided excellent water quality, with the complete removal of heavy metals (97% for Cu, 99% for Fe, 91% for Ni) and the monovalent cations Na and K were less effectively removed (95.7% and 94% respectively). Earlier study have also reported that treating wastewater with a microfiltration

membrane (MBR) using reverse osmosis is sufficient to effectively remove of various micropollutants, such as pharmaceuticals, personal care products (PPCPs) (above 95%) [54]. According to Cartagena et al [12], in order to study the possibility of producing better water quality from municipal wastewater, an MBR coupled with NF/RO was operated. The results showed that the high quality of water was observed with salinity removal efficiencies higher than 97%, 96% for total organic carbon (TOC), 91% for nitrates (NO_3^-) and 99% for total phosphorous (TP). This combined treatment process MBR-RO/NF can effectively remove emerging micropollutants, such as 78 - 93% for carbamazepine (CBZ), 87.5 – 98.1 % for diclofenac (DCF), 99.2- 99.9% for acetaminophen (ACE), and are in agreement with results obtained by Joss et al [48]. They indicated that most organic micropollutants are degraded and/or retained to below the detection limit (lower than 10 $ng.L^{-1}$) by MBR-RO. Jacob [37] reported that a high retention (>88%) of almost all micropollutants was observed by the RO membrane in the combination of MBR-RO process for wastewater treatment. For examples, the retentions of pentachlorophenol, atrazine and diuron were above 97%, > 95% for atrazine hydroxyl and 1,34 chlorophenylurea retention was about 88% by the MBR-RO process.

As for the reverse osmosis or nano-filtration process, the major disadvantage of this application include cost, fouling and specially concentrate management. The characteristics of the concentrate depend on the feed water characteristics, the pretreatment, the membrane process used, the recovery, and the additional chemicals used. This waste stream can be highly contaminated by for instance hardly biodegradable compounds (such as pharmaceutical, endocrine disrupting compounds), which limits the possibilities for discharge directly to the environment. In addition, concentrates from nano-filtration (NF) or reverse osmosis (RO) in the field of wastewater contain high concentrations of ions and small organic compounds, which make the concentrates more difficult to treat. Therefore, there is a need for technologies that can remove specific compounds from the concentrate before discharging to the environment. A possible solution to this issue may be to recirculate the

concentrated waste stream. This would not only minimize the environmental issues but would also enable a more sophisticated treatment to be investigated for the production of reusable water. Hence, the concept of integrated MBR - RO with RO concentrate recirculation to the MBR might provide a solution to this problem.

From this point of view, the detailed influences of RO or NF concentrate recirculation to the MBR need to be evaluated and discussed.

1.2.2. Retentions of RO/NF process in tertiary treatment

Even though the MBR system successfully removed suspended solids and most of the colloidal organic matter, it failed to remove the dissolved salts as well as micropollutants. Therefore, further treatment by employing a NF/ RO integrated system was investigated, and the performances of RO/NF process were resulted by some authors. Removal efficiency for RO membrane was high for the compounds: > 99.8 % for total organic carbon (TOC) (Vourch et al., 2008), > 90% for chemical oxygen demand (COD) [45], nitrogenous matter removal was around 96% and conductivity removal was about 97% [117]. Besides, high removal efficiency of the heavy metals could be achieved by RO process (98% and 99% for copper and cadmium, respectively). NF, however, was capable of removing more than 90% of the copper ions existing in the feed water [99]. High removal of ions also reported by Vourch et al [117], they showed that multivalent ions removal rate was above 95% and > 87% for monovalent ions in the RO process. Dolar's study [25] for treatment of wastewater from fertilizer factory indicated that the rejections of fluoride with RO membranes were higher than 80% (model waters) and higher than 96% (real wastewater), and with NF membranes higher than 40%. Rejections of phosphates were higher: > 95% (model waters) and > 97% (real wastewater).

Moreover, the elimination of micropollutants in the RO/NF process is supported by many researches. Comerton et al [16] demonstrated that RO membrane provided efficient

endocrine disrupting compounds (bisphenol A, oxybenzone) and pharmaceutically active compounds (acetaminophen, caffeine, carbamazepine) removal (>90%) According to Yangali-Quintanilla et al [123], average removal of neutral compounds (including 1,4-dioxane, acetaminophen, carbamazepine, bisphenol A) was about 82% and 85% for NF and RO, respectively, and average removal of ionic compounds (ketoprofen, sulfamethoxazole, naproxen) was about 97% and 99% for NF and RO, respectively, for water reuse. Jin et al [45] reported that higher than 87% for total cyanide (T-CN) removal by the nano-filtration process was found for coking wastewater treatment for industrial reuse purpose.

A previous study by Jacob et al [38] revealed the high retention of big molecules (molecular weight between 6 and 10 kDa) but very low retention of small molecules (molecular weight around 1kDa) is observed with the loose NF, and the tight NF has moderate retention of the two fractions of molecules; whereas, RO can retain almost all molecules.

1.3. Reverse osmosis concentrate

1.3.1. The characteristics of RO concentrate

The characteristics of the concentrate depend on the feed water, the membrane process employed, the recovery, the concentration factor and the additional chemicals used [37,88]. In addition, concentrates from nano-filtration (NF) or reverse osmosis (RO) contain high concentrations of ions and small organic compounds, which make the concentrates more difficult to treat. According to Zhao et al [128], the main constituents of reverse osmosis (RO) concentrate are dissolved inorganics salts and low molecular weight soluble refractory organics, which are closely related to the influent quality. The pollutant concentration in RO concentrate can be 2- 3 times higher than that in RO influent.

General characteristics of RO concentrate is summarized in Table 1.4 by some researches. The results indicated that the concentrations of total organic carbon (TOC) and chemical oxygen demand (COD) in the RO/NF concentrate were much lower than those in the MBR

influent. The reason for this is high biodegradable of these components in the MBR. In contrast, almost all cations and anions were higher in the concentrate, as compared to that in the MBR permeate, which was used as inflow to the RO/NF system. For examples, the concentrations of cations (Na^+, K^+, Mg^{2+}, Ca^{2+}) and anions (Cl^-, SO_4^{2-}, $P\text{-}PO_4^{3-}$) in the RO concentrate, were about 3 times higher than that in the RO influent (with the concentration factor =3, TMP = 6 bars, 5.5<pH<6.5) [37]. Similar, Joss et al [48] also showed that almost all ions concentrations were 2 times higher in the RO concentrate, compared to those in the RO influent.

Furthermore, micropollutants, such as pesticides, pharmaceuticals or endocrine disrupting compounds, present in the RO concentrate eventually find themselves in wastewater at concentrations in the range of $ng.L^{-1}$ to $\mu g.L^{-1}$. For example, wastewater was found to contain concentrations of about 0.5 $\mu g.L^{-1}$ of carbamazepine (CBZ), 1.2 $\mu g.L^{-1}$ of diclofenac, and 1.1 $\mu g.L^{-1}$ of ketoprofen [75]. The concentrations of some micropollutants in the raw wastewater are found in a few researchers. Carbamazepine concentration was about 0.2 - 0.3 $\mu g.L^{-1}$ [67], or 0.23 - 0.36 $\mu g.L^{-1}$ [13]. Jacob [41] reported that the wastewater contained about 0.5 $\mu g.L^{-1}$ of carbamazepine, 1.7 $\mu g.L^{-1}$ of ketoprofen and 0.7 $\mu g.L^{-1}$ of diclofenac concentrations.

Besides, Benner et al [9] showed the concentration of micropollutants in the effluent of wastewater treatment plant (WWTP) was lower than that in the RO concentrate. For examples, carbamazepine concentration in the WWTP effluent and RO concentrate was 1.2 $\mu g.L^{-1}$ and 3.4 $\mu g.L^{-1}$; 0.53 $\mu g.L^{-1}$ and 1.5 $\mu g.L^{-1}$ for diclofenac. These compounds dissolved in a ground-water matrix can be environmentally harmful and present serious risks to health.

Indeed, untreated or improperly managed concentrate, which produced by reverse osmosis or nano-filtration, can result in adverse environmental effects, due to high salinity, nutrients (phosphorus, nitrogen), organic contaminants including emerging contaminants, and trace amounts of inorganics [47].

Table 1.4 Characterization of RO/NF concentrates from the MBR-RO/NF process

Parameters	pH	Conductivity	COD	TOC	NH_4 -N	Na^+	K^+	Mg^{2+}	Ca^{2+}	Cl^-	$N\text{-}NO_3^-$	SO_4^{2-}	$P\text{-}PO_4^{3-}$
From study's Joss [48]													
MBR wastewater	7.7±0.4	1.3 ± 0.3	-	140 ± 40	-	125 ± 20	14.6± 1.4	20.4 ±1.6	118 ± 16	138 ± 25	<1	37 ± 7	2.3 ± 0.5
MBR wastewater + RO concentrate	8.1±0.1	-	-	-	-	365 ± 16	36 ± 1	66 ± 3	277 ± 7	472 ± 13	2.2 ± 0.2	133 ± 4	2.7 ± 0.1
MBR permeate	8.2 ± 0.1	3.2 ± 0.6	-	10 ± 5	-	352 ± 35	35.5 ±3.1	63 ± 6	148 ± 18	465 ± 34	2.6 ± 1.9	132 ± 11	1.7 ± 0.7
RO concentrate	6.8	6 ± 0.9	-	19 ± 9	-	693 ± 60	65 ± 7	127 ± 15	494 ± 52	930 ± 170	4.1 ± 1	263 ±35	3.1 ± 1.1
From study's Jacob [37]													
MBR permeate	6-8	0.6	18	5	-	63.6	16.4	7.7	73	50	24.9	61.7	5.2
RO concentrate	5.5-6.5	-	-	17	-	163	42	22	213	265	82	167	15
From study's Kappel [50]													
MBR influent	-	-	403 ±107	-	-	146 ± 24	24 ± 3	23 ± 4	81 ± 7	-	-	-	-
MBR permeate	-	-	39 ± 8	-	-	-	-	-	-	-	-	-	-
NF concentrate	-	-	80 ± 18	-	-	176 ± 16	31± 2	44 ± 7	131 ± 10	-	-	-	-

(-) not analyse

1.3.2. RO concentrate treatment

Recently, reverse osmosis has been also applied to further treat the secondary effluents of wastewater treatment plants. These RO concentrates present less salinity than RO concentrates from desalination plants although larger amounts of organic matter, including persistent micro- pollutants, are contained [88]. Regardless of the technology used, the treatment goal is to enhance the recovery of reusable water and to minimize quantities of contaminants disposed to the environment. Methods of treatment and the reduction of concentrate quality have to be based on the characteristics of the concentrate. Using advanced oxidation processes (AOPs), such as electro-oxidation, ozonation, fenton and UV or adsorption on activated carbon to treat concentrate was reported by many researches.

The application of the electro-oxidation technology provided with boron doped diamond (BDD), an electrode material which has shown outstanding properties in oxidation of organic and inorganic compounds, for the treatment of reverse osmosis (RO) concentrates generated in tertiary wastewater treatment plants (WWTP) was performed in Pérez's study [87]. They selected a group of 10 emerging pollutants (i.e. nicotine, caffeine, naproxen, ibuprofen…) with high concentration in order to test whether electro-oxidation can be also applied for their mitigation. The total time of this experiment was 60 mins, achieving after this time, removal percentages between 90 and 98.8%, except in the case of ibuprofen (about 55%). Feasibility test of ozonation for the removal of beta blockers (acebutolol, atenolol, bisoprolol, celiprolol, metoprolol, propranolol, timolol) from the RO concentrate was performed by Benner et al [9]. They reported that a moderate ozone doses (5-10 mg.L^{-}1) were found to be sufficient to remove beta blockers efficiently. Ozonation was demonstrated to be an effective method in increasing the biodegradability of RO brine obtained from a domestic wastewater treatment facility [60]. An ozone dosage ranging from 3 to 10 mg.L^{-1} was found to increase the biodegradability (BOD_5/TOC) of RO brine by 1.8-3.5 times.

Furthermore, in a combined ozone/H_2O_2 reactor system using a dosage of 0.7 mol H_2O_2 mol^{-1} O_3, dissolved organic carbon (DOC) removal was approximately 75% [120]. UV/TiO_2

treatment achieved up to 95% DOC removal at a UV dose of 10.4 $kWhm^{-1}$; this removal was nearly independent of titanium dioxide dose between 1 and 5 $g.L^{-1}$. Additionally, Bagastyo et al [7] reported that advanced oxidation (UV/H_2O_2) provided about 50-55% for removal of chemical oxygen demand in treating of RO concentrate obtained from water reclamation plants. Kappel [50] introduced an electrochemical system to recover phosphates. An electrochemical cell was divided into an anode and a cathode compartment separated by a cation exchange membrane. Precipitation of phosphates from nonofiltration concentrate was induced by locally increasing the pH at the cathode surface by water electrolysis. 80 to 95% recovery of total phosphate was observed at a pH of 8 to 10 near the cathode.

On the other hand, traditional treatments such as coagulation and activated carbon adsorption were used to treat RO concentrate. Dialynas et al [21] presented that adsorption with granular activated carbon achieved superior DOC removal up to 91.3% in the RO concentrate. Similarly, Zhou et al [129] indicated that activated carbon (AC) adsorption could achieve a high DOC removal efficiency in the RO concentrate. With the dosage of 5 g/L, 88% and 95% of DOC were removed by GAC (granular activated carbon) and PAC (powder activated carbon), respectively. However, coagulation at dosage of 1.0 mM $FeCl_3$, 26% of DOC present in the RO concentrate was removed. This efficiency was lower than that reported in other study [21], whereby 52% of DOC removal efficiency was obtained by coagulation with low molar dose $FeCl_3$ of 0.4 mM. When a simple integrated method, $FeCl_3$ coagulation + photo-catalysis (UVC/TiO_2), could finally achieve 95% of the organics removal from the RO concentrate within 6 h [129].

Besides, Jamil et al [39] used the forward osmosis (FO) with and without granular activated carbon (GAC) fixed-bed adsorption pretreatment for volume minimization of reverse osmosis concentrate, which was obtained from the Sydney Olympic Park Authority's (SOPA) MF/RO water filtration plant, and removal of organic micropollutants. The results showed that FO treatment without GAC pretreatment rejected 10 of the 18 organic micropollutants at >80%; whereas, GAC pretreatment followed by FO treatment removed 15 of the 18 organic

micropollutants (at > 80%) from reverse osmosis concentrates obtained from the MF/RO water filtration plant.

One approach to reduce the volume of the concentrate before disposal is the recirculation of RO/NF concentrate to the membrane bioreactors in an integrated MBR-RO/NF process and was reported in a few researches recently. For examples, Lew et al [63] and Kappel et al [51] examined an integrated membrane process (MBR-RO) with the recirculation of RO/NF concentrate to the MBR for wastewater treatment. Similarly, a pilot MBR-NF was used for treating antibiotic production wastewater with recycling NF concentrate to the aeration tank of the MBR [68,118]. Earlier study, Joss et al [48] proposed a combination of MBR-RO process with concentrate recycling and CO_2 addition for municipal wastewater treatment. Nevertheless, the impacts of RO/NF concentrate recirculation to the MBR, such as the MBR performances as well as the fouling propensity in the MBR, should be examined and discussed.

1.4. RO/NF concentrate recirculation to the MBR

The recirculation of RO/NF concentrate can add into the MBR all components, which contained in RO/NF concentrate. In literature, the recycling of RO/NF concentrate could deliver good performances in the MBR. For examples, Lew et al [63] reported that the integrated membrane process (MBR-RO) with concentrated recycling to the MBR could obtain a good efficiency of total organic carbon (TOC) removal (above 80%) in the MBR. They also indicated that both of the concentration of suspended solid (MLSS) and biomass in activated sludge (MLVSS) had increased slightly (from 10.12 ± 0.92 to 12.48 ± 2.19 $g.L^{-1}$ for MLSS, and from 8.2 ± 0.61 to 10 ± 1.81), after RO concentrate recirculation. Kappel [50] reported that high removal efficiency of chemical oxygen demand (> 90%) was found in the MBR after NF concentrate recycled to the MBR. An additional advantage is the removal efficiency of ammonium generally exceeded 95%, although in particular in the MBR without

concentrate recycled operational problems occasionally caused significantly lower efficiency (about 81%). The observation that similar high ammonium removal efficiencies could be accomplished in the MBR without and with NF concentrate recycling proved that the presence of NF concentrate did not inhibit the nitrification process in the MBR. This finding is in good agreement with Li's study [68]. They demonstrated the presence of NF/RO concentrate recirculation had a negative impact on the ammonium removal efficiency in the MBR; it was above 95% throughout the entire experiment.

Nevertheless, Kappel et al [51] observed an increase of the dissolved and colloidal chemical oxygen demand (COD) in the MBR supernatant after the recirculation of NF concentrate, which represented 15% of total MBR inflow and the wastewater the other 85%. To determine the colloidal and dissolved COD of the MBR sludge, samples were first filtered using a paper filtration to remove suspended matter. Syringe filters with 0.45 µm pore size were subsequently used to remove colloidal matter and to obtain dissolved COD. Colloidal COD was calculated by subtracting the value for dissolved COD from the COD value after paper filtration. The increase in dissolved COD was probably directly related to the NF concentrate recirculation, and that in the colloidal COD could be related to changes in the floc structure but may also have resulted from extracellular polymeric substances (EPS) or humics. This research also demonstrated that, in particular, dissolved and colloidal COD present in the supernatant of the MBR significantly influenced the MBR membrane performance. A faster increase of the TMP in the MBR was observed after NF concentrate recirculation, compared to that from the MBR without the concentrate. Additionally, Li et al [68] indicated that an increase of protein concentration was found in the MBR supernatant after the recycling of the NF concentrate to the MBR. Meanwhile, the polysaccharide concentration in the MBR supernatant did not change significantly. Therefore, the protein content in SMP, and SMP brought by NF concentrate were the main cause of the severe membrane fouling in the MBR.

One study performed by Wang et al [118] reported that a molecular biological technique, PCR-DGGE (polymerase chain reaction-denaturing gradient gel electrophoresis), and clone

library construction was used to analyze the difference in the activated sludge before and after the NF concentrate was recycled. The result showed that recycling the NF concentrate into the MBR did not change the microbial diversity of the activated sludge.

In order to better understand the opportunities and bottlenecks of a combined MBR-RO process with the recycling of RO concentrate to the MBR, with the main objective is not only the possibility of producing better water quality from municipal wastewater but also enable a reduction of concentrate waste stream. The recirculation of RO/NF concentrate to the MBR might provide an effective solution for the management of the concentrate generated from the RO/NF processes. However, it can return all components retained by the RO or NF (mainly high salinity, dissolved organic matters and micropollutants) to the MBR. To evaluate the real potential and remaining disadvantages of this membrane process combination with the concentrate recycling, more detailed studies and systematic researches regarding MBR performances in terms of biological degradation of the organic matters (such as chemical oxygen demand, dissolved organic carbon) and nitrification process, fouling propensity of MBR membrane as well as eliminative possibility of micropollutants in the MBR.

1.5. Conclusion

This chapter bibliographic provides the background information for the study of an integrated MBR-RO process with concentrate recirculation for wastewater and reuse. The MBR process alone could not assure the complete removal for all dissolved organic and inorganic impurities as well as micropollutants. This inadequacy could be overcome by the use of MBR–RO/NF hybrid systems for high water production. Nevertheless, the major drawback of RO/NF membranes is the production of a concentrate stream that cannot be discharged directly to the environment. The opportunities and challenges therefore regarding RO concentrate recirculation are the largest points that should be examined and discussed in this study.

The synthesis of fouling mechanisms in the MBR process, which is presented in the first part, shows that the soluble microbial products (SMPs) seems to play an important role in the fouling propensity of the membrane in the MBR. Besides, the effects of high salinity and micropollutants which are contained in the RO concentrate, on the MBR process are resulted from the literature. It can point out thereby the general overview of challenges of RO concentrate recirculation to the MBR.

The combination of MBR- RO process, with the main objective is the reusable water quality, is presented in the second part of this chapter. However, the concentrate waste stream produced by RO process is one of the disadvantages of this combination, which can cause the environmental problem if discharged untreated. So the characteristics of RO/NF concentrate are summarized in the third part; thereby, it can select the optimal method for waste stream treatment. Using advanced oxidation processes (AOPs) or adsorption on activated carbon to treat RO concentrate were performed and reported by many researches. Moreover, one approach to reduce the volume of the concentrate before disposal to the environment is the recirculation of RO/NF concentrate to the membrane bioreactors in an integrated MBR-RO/NF process was studied by some authors.

Indeed, a limited number of MBR-RO processes with the RO concentrate recirculation were presented in the literature. This combination with the RO concentrate recycled minimizes unwanted discharge of a concentrated waste stream. Following this introduction chapter the advantages and disadvantages of the RO concentrate recycling to the MBR more detailed need to be examined and discussed.

The recirculation of RO/NF concentrates whether or not affects the performances of the MBR? So, the main objective of this study is to examine the effects of RO concentrate recirculation on (i) the biodegradation in the bioreactors, (ii) the MBR supernatant and permeate composition and (iii) the membrane fouling in the MBR due to returning all toxic components (such as micropollutants) that rejected by RO membrane. Additionally, the elimination of micropollutants in an MBR for municipal wastewater treatment is investigated.

CHAPTER II

MATERIAL AND METHODS

This chapter aims to present the experimental device used of this study, the operating conditions and the analytical methods. The first part describes the lab-scale membrane bioreactor (MBR). Second part is dedicated to the presentation of the reverse osmosis (RO) pilot. The filterability test of sludge and supernatant is presented in the third part. The fourth part describes the batch reactors. The fifth part introduces the combination of MBR- RO process. Lastly, the presentation of all the analytical methods was performed in this study.

2.1. Membrane bioreactor set- up

Two reactors were contained in the lab-scale MBR: an anoxic reactor (5.4 L) and an aerobic reactor (12.6 L) (Figure 2.1). The aerobic reactor was equipped with one submerged flat sheet microfiltration membrane (Kubota, Japan) having an effective filtration area of 0.1 m^2 and a nominal pore size of 0.2 µm. The instantaneous permeate flux was fixed at 15 LMH (liter/m^2/hour) with relaxation steps of 4 min performed every 8 min, leading to a net permeate flux of 10 LMH. The MBR was fed with a municipal wastewater taken from a wastewater treatment plant close to Toulouse, France, after a primary physical treatment.

Aeration: the reactor was aerated with big air bubbles at a flow rate of 1.5 $L.min^{-1}$, i.e. SAD_m of 0.9 m^3 $air.h^{-1}.m^{-2}$. Another aeration system with fine air bubbles was also used to maintain the dissolved oxygen concentration in the sludge at about 2-3 $mg.L^{-1}$.

Recirculation: the sludge recirculation rate was fixed at 4 $L.h^{-1}$.

Sludge retention time (SRT): the MBR was operated with a 45 day SRT, which means that the sludge was discharged at flow rate of 0.4 $L.d^{-1}$.

Agitation: the mixture of mixed liquor in the anoxic tank was performed by a stirring of 180 $tr.min^{-1}$.

During the MBR operation, when the permeability of membrane reached to about 200 $L.h^{-1}.m^{-2}.bar^{-1}$, membrane was taken out from the aerobic tank, cleaned by water and then wiped

with a soft sponge. After physical cleaning, the membrane was soaked in 0.5 % sodium hypochlorite (NaClO) solution for 2 hours to check the effects of a chemical cleaning.

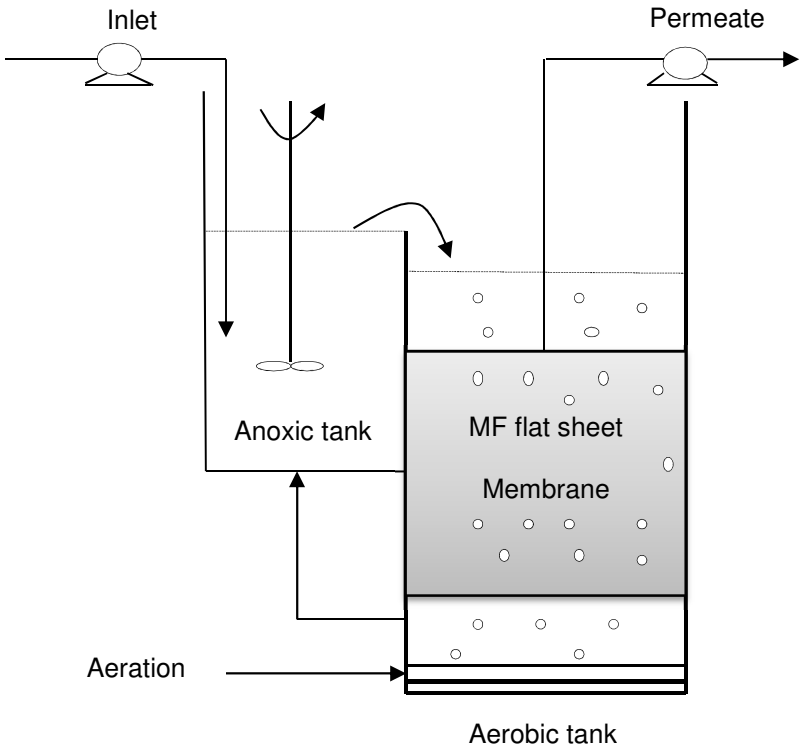


Figure 2.1. Flow diagram of the pilot-scale MBR

2.2. The reverse osmosis (RO) pilot

Reverse osmosis (RO) is a pressure driven membrane process. RO membrane (ESPA2, hydranautics) was operated in operated in crossflow mode, with a filtration surface of 0.051 m^2 and a concentration loop (see Fig. 2.2). The 0.8 L concentration loop enables to quickly reach high RO feed concentration, to set RO cell velocity inlet without any interferences with feed flowrate (Q_f) and to work at constant pressure. The pilot RO is fed by the permeate of MBR. The transmembrane pressure of RO membrane was 7 bars. With RO influent flow rate of 30 $L.h^{-1}$, the velocity is calculated by 0.18 $m.s^{-1}$.

The membrane flux J can be calculated according to Eq (2.1)

$$J = \frac{TMP - \Delta\pi}{\mu(R_m + R_f)} \quad (2.1)$$

with

TMP: transmembrane pressure [bar] or [Pa]

Δπ: osmotic pressure [bar] or [Pa]

μ: permeate dynamic viscosity [Pa.s]

R_m: the membrane resistance [m^{-1}]

R_f: the fouling resistance [m^{-1}]

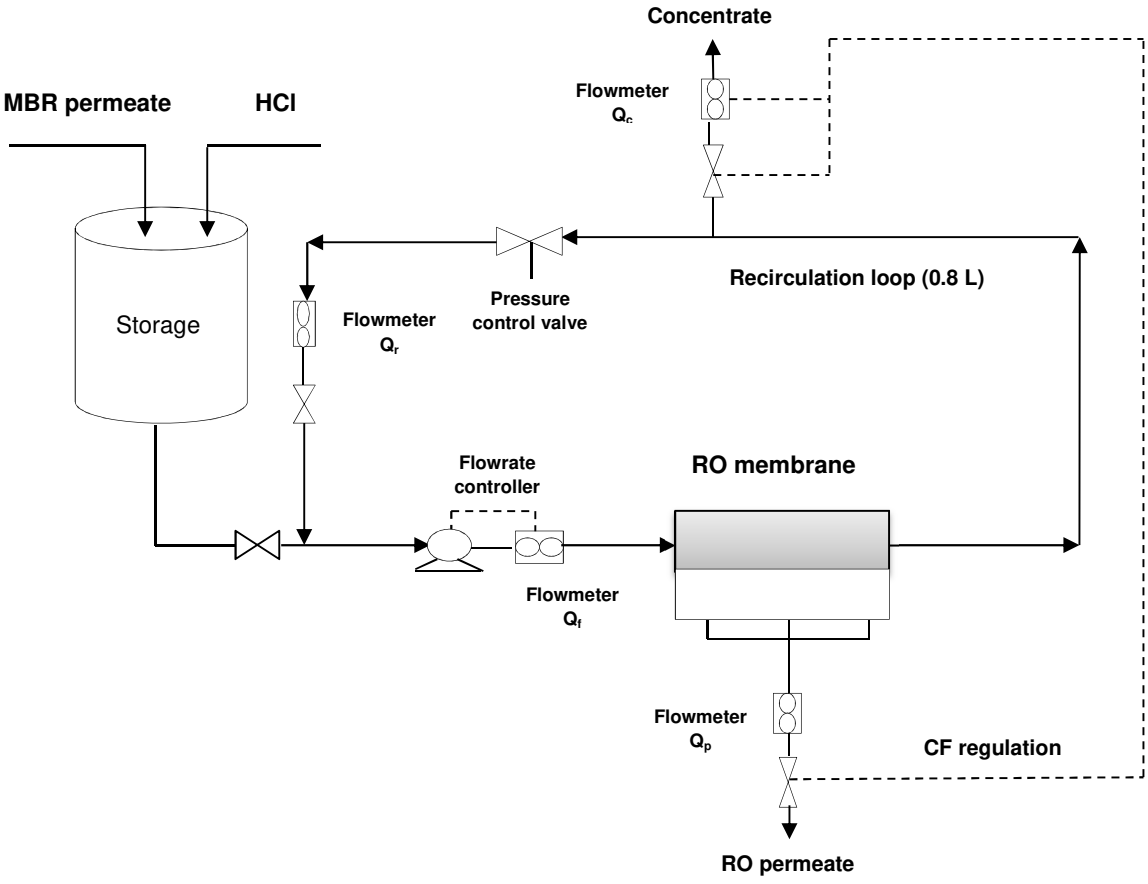


Figure 2.2. Schematic diagram of the reverse osmosis (RO)

The rejection R (%) of membrane for a specific compound can be calculated by Eq (2.2)

$$R = 1 - \left(\frac{C_p}{C_f} \right) \times 100\% \quad (2.2)$$

With C_p: RO permeate concentration ($mg.L^{-1}$)

C_f: RO influent concentration ($mg.L^{-1}$) (MBR permeate concentration)

Especially during filtration, a certain feed water volume is concentrated at the feed side. The volume reduction factor VRF, also known as the concentration factor CF (-), between the feed and the concentrate is calculated in Eq (2.3) (if the retention =1) [37]

$$CF = \frac{t.Q_f}{V_r} \quad (2.3)$$

With Q_f: feed flow rate ($L.h^{-1}$)

V_r: recirculation volume (0.8 L)

Regulation enables to set a ratio between concentrate flowrate (Q_c) and permeate flowrate (Q_p) in order to keep the concentration factor (CF) constant (equation 2.4).

$$CF = \frac{Q_p}{Q_c} + 1 \quad (2.4)$$

In this study, concentration factor (CF) is kept constant and defined as:

$$CF = \frac{Conductivity_{concentrate}}{Conductivity_{ROfeed}} \quad (2.5)$$

A certain amount of feed water is recovery as permeate that can be reused. The water recovery (%) is defined as:

$$R_w = \frac{Q_p}{Q_f} \times 100\% \quad (2.6)$$

with: R_w: recovery of a membrane (%)

Q_p: RO permeate volumetric flow rate ($L.h^{-1}$)

Q_f : RO feed volumetric flow rate ($L.h^{-1}$)

In some experiments, pH regulation ($\approx$ 6) was performed using acid HCl 37%.

2.3. Filterability tests

The filterability test was used with a stirred dead-end filtration cell (Amicon 8050, Millipore) to determine the fouling resistance and the permeate flux decline of the sludge and supernatant under transmembrane pressure 1bar.

The microfiltration membranes (from Alfa, Laval, FR), made of polysulphone (PS), with a pore size is 0.2 µm (L_{p0}= 250-320 $L.h^{-1}.m^{-2}.bar^{-1}$ at 20^0C) was used for the filterability test of sludge.

The ultrafiltration membranes (from Orelis, FR), made of polyethersulfone (PES), with a pore size of 0.01 µm (L_{p0}= 47-70 $L.h^{-1}.m^{-2}.bar^{-1}$ at 20^0C) was used for the filterability test of supernatants.

All membranes were soaked in ultra-pure water over night to maintain pores wetted. Then, they were rinsed with ultra-pure water at 1 bar during 15 minutes prior to filtration test. All filtration tests were carried out in an Amicon cell, with a membrane surface of about 13.4 cm^2. For supernatant, no stirring was performed, and for sludge filtration, the sludge was stirred at 200 rpm to prevent settling.

The permeability of the membrane is defined as (2.6):

$$J(20^oC)= \frac{TMP}{\mu(20^oC)\times R_m} = Lp_o \times TMP \qquad (2.7)$$

With: J (20^oC): the permeate flux at 20^oC ($L.h^{-1}.m^{-2}$),

R_m: the membrane resistance (m^{-1})

µ (20^oC): fluid viscosity at 20^oC (Pa.s)

Lp_o: the permeability of the membrane ($L.h^{-1}.m^{-2}.bar^{-1}$)

The membrane resistance was determined according to Eq (2.7)

$$J = \frac{TMP}{\mu(R_m + R_f)} \quad (2.8)$$

With R_f: the fouling resistance (m^{-1})

In the dead-end filtration cell, αC can be determined by cake deposit model as given by Eq (2.9)

$$R_f = \alpha C \frac{V}{A} \quad (2.9)$$

With α: the specific cake resistance ($m.kg^{-1}$),

C: the deposited mass per filtered permeate volume ($kg.m^{-3}$).

V: the cumulated permeate volume (m^3)

A: the membrane area for filtration (m^2).

For supernatants filtration, C could be calculated by retained dissolved organic carbon or protein ($kg.m^{-3}$); for sludge filtration, C was calculated from the MLSS value of sludge.

2.4. Batch reactors

Batch reactors were used to characterize the short-term effects of RO concentrate on the activated sludge taken from the wastewater treatment plant (WWTP) (see Fig. 2.3). Reverse osmosis (RO) concentrate samples were obtained from a RO-membrane that uses effluents of wastewater treatment plants as feed water.

The concentration factor of concentrate is kept constant (CF = 6).

The recovery of RO membrane is defined as:

$$R_w = (1 - \frac{1}{CF}) \times 100\% = 83\% \quad (2.10)$$

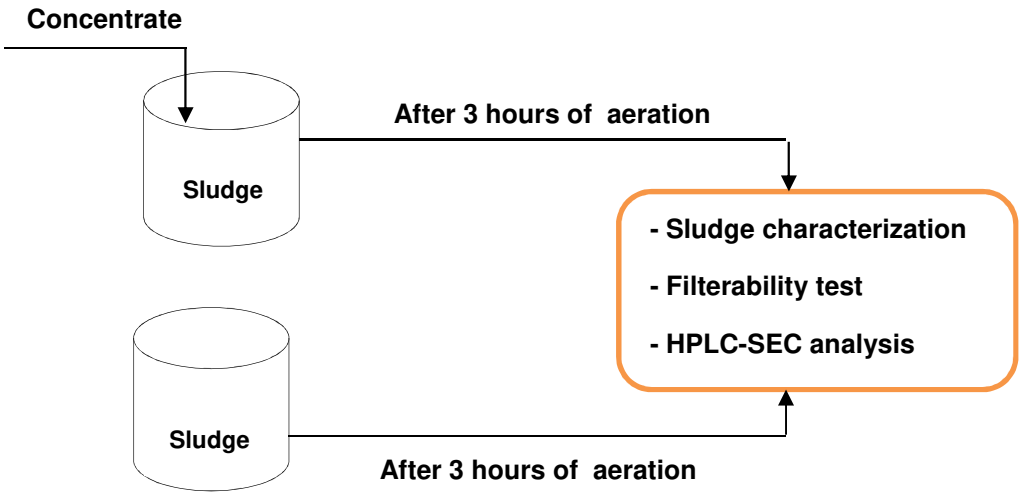


Figure 2.3. Schema of batch experiments

First, a same volume of sludge samples (1L) was injected to the two batch reactors operated in parallel. Then, 0.1L concentrate (about 9% of sludge volume) was added into one of the two batch reactors. Another batch reactor was operated without RO concentrate. The mixed liquids was stirred using the aeration in the bottom of each reactor during 3 hours. After that, the sludge samples in both reactors were sampled and the two corresponding supernatants were prepared by centrifugation of the sludge samples at 4000g during 10 minutes at room temperature at the same time.

In the second step, the volume of RO concentrate was modified to 0.2L concentrate (18%) /1L sludge. The increase of RO concentrate volume may induce the different effects. The impacts of RO concentrate on characteristics of the activated sludge and supernatant between two peaks injection (9% and 18%) of RO concentrate will be examined and discussed.

2.5. MBR-RO set up

Two sets of experiments were performed in this study. Before each Set, the MBR was operated during six weeks to stable performances.

In the *first set of experiments,* the MBR received 20.4 L.d^{-1} of wastewater (see Figure 2.4). The MBR permeate was collected over 3 weeks and used as inflow to the RO system. The concentrate produced by RO was taken and kept in the storage tank before being continuously recycled to the MBR at a flow rate of 3.6 L·d^{-1}. The concentration factor of RO concentrate in this case was 2.5 ± 0.2 so the RO water recovery was about 60% The RO concentrate made up 15% of the total inflow (wastewater + concentrate) and the wastewater 85%. The characteristics of concentrate were stable during the entire experiment (presented in Chapter 5).

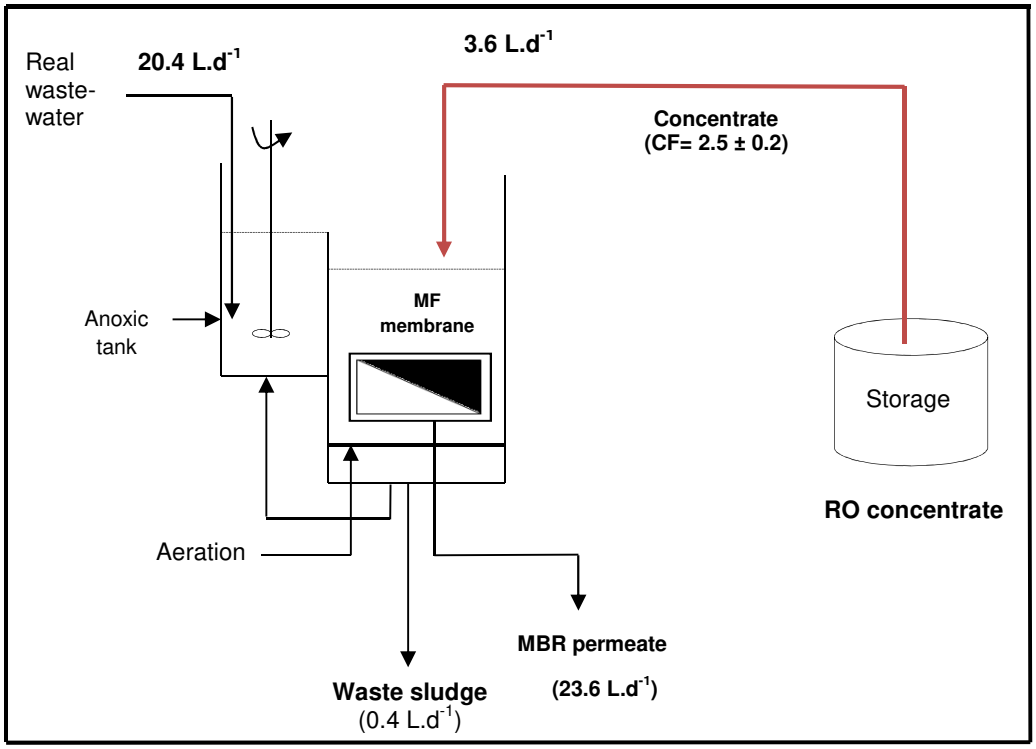


Figure 2.4. Schema of MBR-RO process (Set 1)

In the *second set of experiments,* the MBR was fed by the wastewater with addition of the RO concentrate produced by the subsequent RO process. In order to set up this recirculation loop, the MBR permeate was collected in a storage tank and used as inflow to the RO system. The MBR permeate fed the RO process continuously at a flow rate of 16.8 L.d^{-1}. The RO process produced 10.8 L.d^{-1} of permeate, so the RO water recovery was about 64%. The

RO concentrate was collected in a storage tank at a flow rate of 6 $L.d^{-1}$ to feed to the MBR (Fig. 2.5).

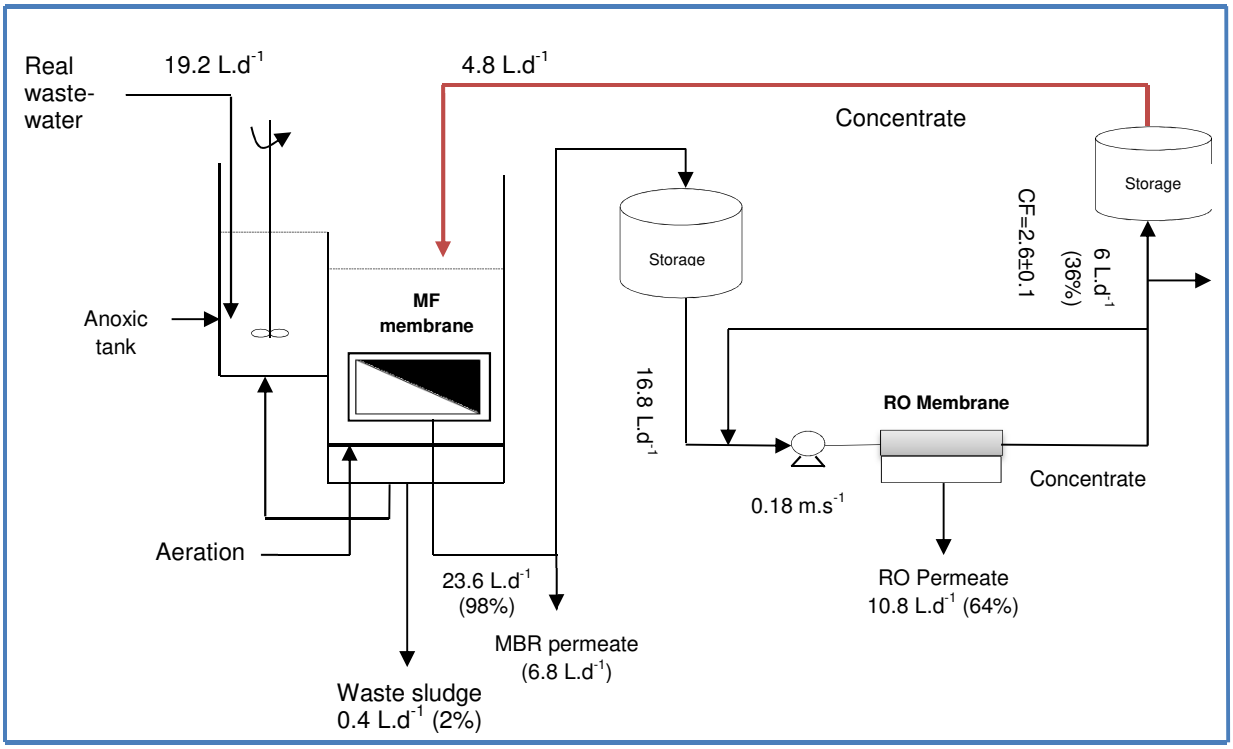


Figure 2.5. Schema of MBR-RO process (Set 2)

Table 2.1. Operating conditions of the reverse osmosis process

Parameters	Operating conditions
Transmembrane pressure (TMP)	7 bar
pH	6
Concentration factor (CF)	2.6 ± 0.1
Velocity	0.18 $m.s^{-1}$
Water recovery	64%

The recovery of global process is defined as:

$$R_w \text{ (global process)} = [\ \frac{(Q_{MBRpermeate} + Q_{ROpermeate})}{Q_{wastewater}}\ ] \times 100\% \quad (2.11)$$

R_w: recovery of global process (92%)

$Q_{MBR\ permeate}$: flowrate of MBR permeate ($L.d^{-1}$)

$Q_{RO\ permeate}$: flowrate of RO permeate ($L.d^{-1}$)

$Q_{wastewater}$: flowrate of wastewater ($L.d^{-1}$)

In this experiment, the continuous recirculation of RO concentrate to the MBR could lead to a change in the characteristics of the components rejected by the RO (presented in Chapter 4). The operating conditions of the reverse osmosis process are summarized in Table 2.1

As shown in Figure 2.5, the flow rate of the wastewater was 19.2 $L.d^{-1}$, which made up 80% of the total inflow in the MBR. Additionally, the concentrate from the RO system returned continuously to the MBR at a flow rate of 4.8 $L.d^{-1}$, making up 20% of the total MBR inflow (wastewater + concentrate).

The characteristics of two sets of experiments are summarized in Table 2.2

The process efficiencies in the MBR can be characterized:

$$\text{Global removal efficiency (\%)} = \left(\frac{(C_{wastewater} - C_{MBRpermeate})}{C_{wastewater}}\right) \times 100\% \quad (2.12)$$

$$\text{MBR removal efficiency (\%)} = \left(\frac{(C_{MBRmixed\,influent} - C_{MBRpermeate})}{C_{MBRmixed\,influent}}\right) \times 100\% \quad (2.13)$$

$$\text{Biodegradable removal efficiency (\%)} = \left(\frac{(C_{MBRmixed\,influent} - C_{MBR\,supernatant})}{C_{MBRmixed\,influent}}\right) \times 100\% \quad (2.14)$$

$$\text{Membrane retention (\%)} = \left(\frac{(C_{MBR\,supernatant} - C_{MBRpermeate})}{C_{MBR\,supernatant}}\right) \times 100\% \quad (2.15)$$

With:

$C_{wastewater}$: wastewater concentration ($mg.L^{-1}$) (COD, DOC, TN….)

$C_{MBRpermeate}$: MBR permeate concentration ($mg.L^{-1}$) (COD, DOC, TN…)

$C_{MBRsupernatant}$: MBR supernatant concentration ($mg.L^{-1}$) (COD, DOC, TN…)

$$C_{MBRmixed\ influent} = \frac{[(C_{wastewater} \times Q_{wastewater}) + (C_{concentrate} \times Q_{concentrate})]}{(Q_{wastewater} + Q_{concentrate})}\ (mg.L^{-1}) \qquad (2.16)$$

$C_{MBRmixed\ influent}$: MBR mixed influent concentration ($mg.L^{-1}$) (COD, DOC, TN…)

$C_{concentrate}$: concentrate concentration ($mg.L^{-1}$) (COD, DOC, TN…)

$Q_{wastewater}$: flow rate of wastewater ($L.d^{-1}$)

$Q_{concentrate}$: flow rate of concentrate ($L.d^{-1}$)

Table 2.2. Characteristics of the wastewater ($mg.L^{-1}$)

Parameters	Set 1	Set 2
Suspended solids (SS)	420 ±42	300 ± 30
Chemical oxygen demand (COD)	799 ± 10	830 ± 10
Dissolved organic carbon (DOC)	155 ± 3	231 ± 5
Total nitrogen (TN)	35 ± 1.8	52 ± 2.6
Nitrogen-ammonia ($N\text{-}NH_3$)	21 ± 1	22 ± 1
Proteins	41.4 ± 4	33.4 ± 3.3
Polysaccharides	-	7.4 ± 0.7
Cations		
Na^+	160 ± 16	174 ± 17
K^+	8.4 ± 0.8	7.7 ± 0.8
Mg^{2+}	4.1 ± 0.4	8.4 ± 0.8
Ca^{2+}	44 ± 0.4	124 ± 12
Anions		
Cl^-	71 ± 7	64 ± 6
$N\text{-}NO_3^-$	1.1 ± 0.1	0.2 ± 0.02
SO_4^{2-}	18.5 ± 1.9	42 ± 4
$P\text{-}PO_4^{3-}$	0.2 ± 0.02	3 ± 0.3

2.6. Analytical methods

2.6.1. Mixed liquor suspended solids (MLSS)

The concentration of mixed liquor suspended solids (MLSS) was measured according to the standard method AFNOR NFT 90-105. It was filtered on a 0.47 µm membrane (WHATMAN glass fiber - GF6).The residue left on the filter is dried to a constant weight at a temperature 105^0C. The increase in weight of the filter represents the total suspended solids of the sample. The analytical deviation for the method is about 10%.

2.6.2. Particle size analysis

Laser diffraction is used for determination of particle size distribution. The laser diffraction instrument applied by particle analytical (Malvern Mastersizer 2000). It is possible to measure particles sizes between 0.02 and 2000 µm. The sample is dispersed in either air or a suitable liquid media. The laser passes through the dispersion media and is diffracted by the particles. The diffraction light pattern (He-Ne laser) is dependent on the particle size.

The sludge sample diluted with deionized water is injected into a measuring cell by a peristaltic pump located downstream of the cell. The sludge is therefore not subjected to the shearing caused by the pump before the measurement.

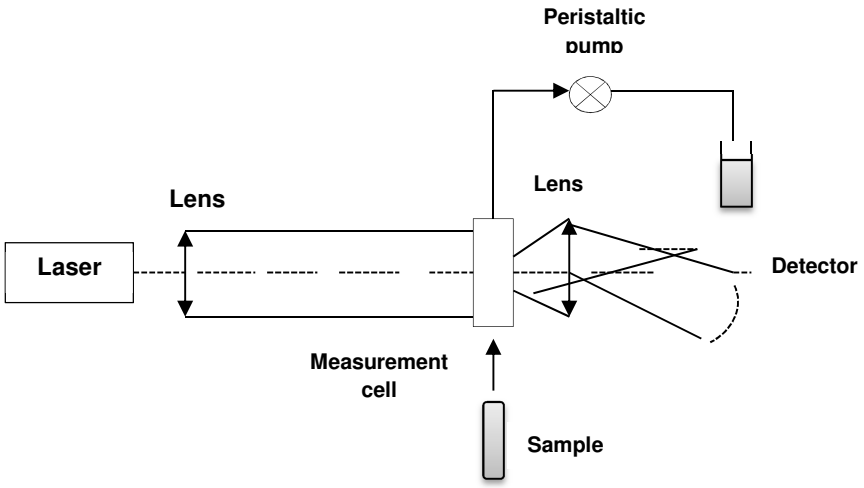


Figure 2.6. Schema of laser diffraction [102]

2.6.3. Dissolved organic carbon (DOC)

DOC measurements were performed with a total organic carbon analysis. The device used is a TOC-V Series (Shimadzu, France). The analyzed samples are heated to 680°C in the presence of a catalyst. The combustion and degradation compounds are in the form of CO_2. This CO_2 is then analyzed by an infrared NDIR detector and quantified by comparison with a calibration curve. Two types of measurements can be defined:

- The total organic carbon representing the amount of carbon contained in the colloidal and soluble compounds.
- The dissolved organic carbon representing the amount of carbon contained in the soluble compounds. Before the analyses, each sample was pre-filtered at 0.45 µm, in order to remove particles. All pre-filters used were rinsed with ultra-pure water (three times) to remove any organic contamination.

The analytical deviation for this method is about 2% [110].

2.6.4. Total nitrogen and ammonia analysis

Total nitrogen (TN) was measured by persulfate digestion method (10072). The formation of total nitrogen (TN) includes ammonia (NH_3), organic- nitrogen (org-N), nitrite (NO_2) and nitrate (NO_3). An alkaline persulfate digestion converts all forms of nitrogen to nitrate. Sodium metabisulfite is added after the digestion to eliminate halogen oxide interferences. Nitrate then reacts with chromotropic acid under strongly acidic conditions to form a yellow complex. The measurement wavelength is 410 nm for spectrophotometers.

The salicylate method (10031) was used for nitrogen-ammonia ($N\text{-}NH_3$) detection. Ammonia compounds combine with chlorine to form mono-chloramine. Mono-chloramine reacts with salicylate to form 5-aminosalicylate. The 5-aminosalicylate is oxidized in the presence of a sodium nitroprusside catalyst to form a blue colored compound. The blue color is masked by the yellow color from the excess reagent present to give a green-colored solution. The measurement wavelength is 655 nm for spectrophotometers.

The analytical deviation for both methods is about 5%.

2.6.5. Chemical oxygen demand (COD)

The COD value indicates the amount of oxygen which is needed for the oxidation of all organic substances in the water. It is representative of the majority of organic compounds as well as oxidizable mineral salts. For this study, a reagent kit (HACH) is used for a COD range of 0 to 150 $mg.L^{-1}$ or 0 to 1500 $mg.L^{-1}$, depending on the organic matter content of the sample. 2mL of sample was added to COD digestion reagent vial then to be heated with 150^0C for two hours. The potassium dichromate is used as an oxidizer. Test results for the 0 to 150$mg.L^{-1}$ range and 0 to 1500$mg.L^{-1}$ were measured at 420nm and 620nm respectively. The analytical deviation for this method is about ± 2 $mg.L^{-1}$ for the low range and ±10 $mg.L^{-1}$ for the high range.

2.6.6. Centrifugation

As seen in Figure 2.7, the sludge samples taken from MBR aerobic tank were sampled and the corresponding supernatants were prepared by centrifugation of the sludge samples at 4000rpm during 10 minutes at room temperature at the same time.

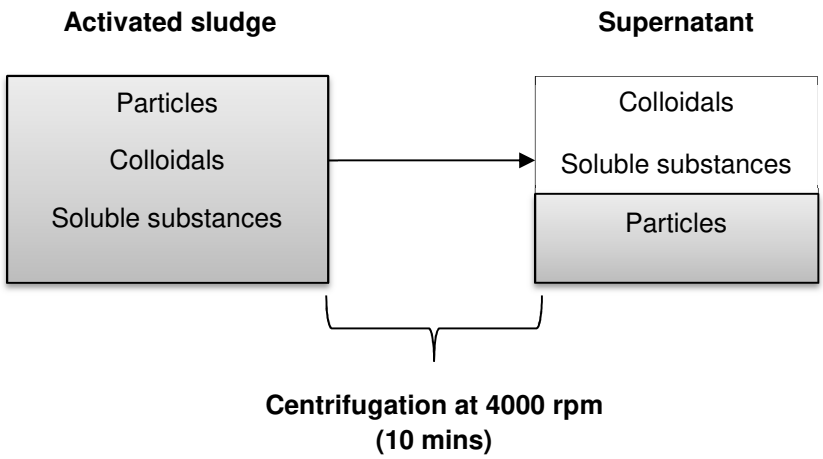
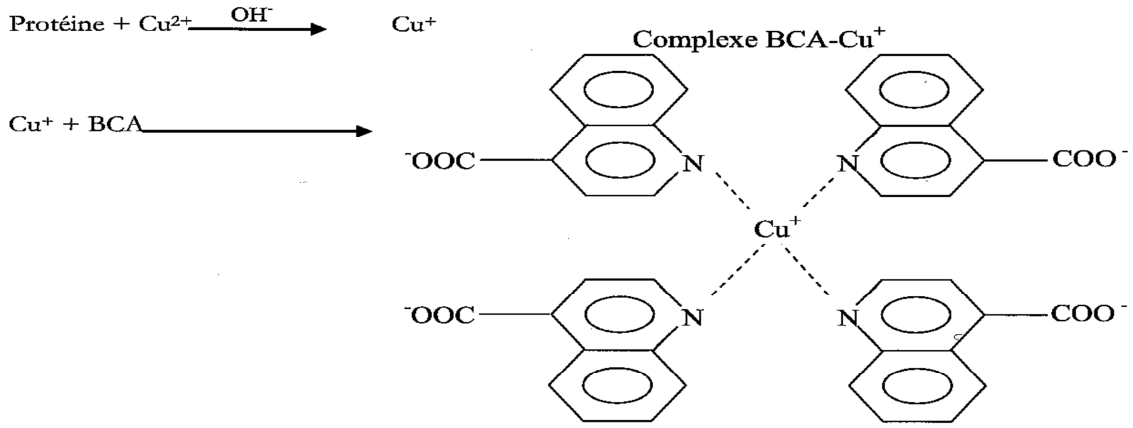


Figure 2.7. Protocol of fractionation by centrifugation of particles, colloidal and soluble compounds of activated sludge [110]

2.6.7. Dosage of proteins: BCA method

Protein content in supernatant, expressed in mg equivalent of bovine serum albumin per liter, was measured by the acid bicinchoninic method (BCA). Proteins reduce alkaline Cu (II) to Cu (I) in a concentration dependent manner. Bicinchoninic Acid is a highly specific chromagenic reagent for Cu (I) forming a complex with an absorbance maximum at 570 nm. Because of this property, the resultant absorbance at 570 nm is directly proportional to the protein concentration. Bovine serum albumin (BSA) is used as a protein standard. The mixture of the two solutions (solution of BCA and copper sulfate 4%) is used as a sample solution [102].



The operational protocol of protein dosage is described (Table 2.3)

Table 2.3. Protocol of protein dosage

Protein
50µL sample + 1mL sample solution
Mixing with the vortex
Put in the bath thermostated at 60°C during 15 minutes
Cool to room temperature, 30 minutes
Absorbance at 570 nm
Calibration
Range standard of BSA

The analytical deviation for this method is about 20% for the protein concentration ≤ 25 $mg.L^{-1}$ and 10% for the protein concentration ≥ 25 $mg.L^{-1}$.

2.6.8. Dosage of polysaccharide

The polysaccharide concentration in supernatant is established from a range standard carried out with glucose and is expressed in mg equivalent of glucose per liter. The sample is heated in the presence of sulfuric acid and anthrone (0.2 g anthrone in 100 mL sulfuric acid 98% → anthrone solution). Polysaccharides are hydrolyzed during the heating by the sulfuric acid, and then monosaccharides are dehydrated by anthrone (green color). The analytical deviation for this method is about 10% [102].

The operational protocol of polysaccharide dosage is described (Table 2.4)

Table 2.4. Protocol of polysaccharide dosage

Polysaccharide
500 µL sample + 1mL anthrone solution
Mixing with the vortex
Put in the drying oven at 105°C during 15 minutes
Cool to room temperature, 30 minutes
Absorbance at 620 nm
Calibration
Range standard of glucose

2.6.9. Cations and anions concentration

Cations (Mg^{2+}, Ca^{2+}, Na^{+}, K^{+}) and anions (Cl^{-}, $N\text{-}NO_2^{-}$, $N\text{-}NO_3^{-}$, SO_4^{2-}, $P\text{-}PO_4^{3-}$) concentrations were performed by Dionex ion chromatography method. This is a method of chromatography in liquid phase (chromatographs LC30 and IC25 of DIONEX), using a column with exchanging resins of ions (IONPAC® CS12A for the cations and AS16 for the anions of analytical column). The ions having the greatest affinity with the column take the longest time

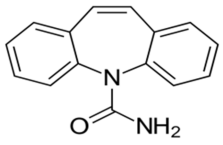
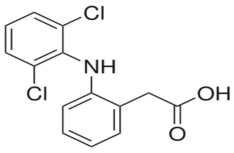
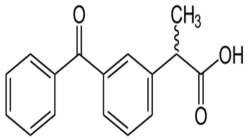
out of the column. A conductivity detector makes it possible to detect at the column outlet the peaks corresponding to each ion. A calibration curve allows the transition from the peak area to the concentration of the ion in the sample. The analytical deviation for this method is about 10% [37].

2.6.10. Micropollutants

Three pharmaceuticals, including carbamazepine (CBZ), diclofenac (DCF) and ketoprofen (KEP) are selected to examine their removal efficiencies in the MBR before and after the recirculation of reverse osmosis concentrate. The results from Table 2.5 showed that a high retention of these selected pharmaceuticals by the RO membrane was observed for wastewater treatment. The effect of these toxic compounds recirculation to the MBR on their biodegradation in the MBR will be studied and discussed in Chapter 4.

These compounds are analyzed using MOA26 HPLC-MS/MS method by the Departmental Water Laboratory in Toulouse, France.

Table 2.5. Structure and retention of selected pharmaceuticals by RO process

Compound	Structure	MW[a] ($g.mol^{-1}$)	K_d[b]	Retention by RO (%)	References
Cabamazepine (CBZ) $C_{15}H_{12}N_2O$		236.3	1.2	> 85	[16, 123]
Diclofenac (DCF) $C_{14}H_{11}Cl_2NO_2$		296.15	16	> 99	[37]
Ketoprofen (KEP) $C_{16}H_{14}O_3$		254.3	16	> 99	[37, 123]

(a) Molecular weight, this data from Li et al [73]

(b) Sorption coefficient for activated sludge ($L.kg_{SS}^{-1}$)

2.6.11. Size-exclusion high performance liquid chromatography (HPLC-SEC) analysis

The protein–like substances, thence different spectrophotometers were used (UV and fluorescence) associated to the HPLC-SEC line to determine the presence of protein-like substance. The UV wavelength 254 nm was chosen in order to characterize double bonds (carbon sp^2). The UV detection was used a s global indicator of organic matter (with double bonds) in each fluid. A fluorescence detector was added (Varian, USA) at the end of the HPLC-SEC line. Excitation /emission wavelengths were set at 280/350 nm, which were conformed as the required values by EEM fluorescence results, to detect protein-like substances [111]. HPLC-SEC apparatus was an Akta Purifer (GE Healthcare, USA). The column Protein Kw804 (Shodex, Japan), was a silica-based column (particle size 7 µm, 8.0×300 mm) with an exclusion limit of 1000 kDa. The column was calibrated using standard proteins: thyroglobulin (669 kDa), ferritin (440 kDa), aldolase (158 kDa), conalbumin (75 kDa), ovalbumin (43 kDa), carbonic anhydrase (29 kDa), ribonuclease A (13.7 kDa) and aprotinin (6.5 kDa) from GE Healthcare. The buffer solution for the mobile phase was prepared with 25 mM Na_2SO_4 and a phosphate buffer (2.4 mM NaH_2PO_4 and 1.6 mM Na_2HPO_4 at pH 6.8). The flow rate of effluent passing through the column was 1.0 mL/min, prior to analysis of HPLC-SEC-fluorescence, each sample was prefiltered on a 0.45 µm membrane.

CHAPTER III

SHORT-TERM EFFECTS OF REVERSE OSMOSIS CONCENTRATES IN PEAK INJECTION ON THE ACTIVATED SLUDGE

Abstract

Batch reactors were performed to characterize the effects of reverse osmosis (RO) concentrate injection on the activated sludge taken from the wastewater treatment plants (WWTP). The results demonstrated that the presence of RO concentrate affected no significantly the supernatant compositions. HPLC-SEC analysis was employed to study the effects of RO concentrate on the production of protein-like SMPs. A significant peak of protein-like substances with a molecular size of 10-100 kDa was observed immediately in the supernatant after the addition of RO concentrate. The increase of both small and large protein-like substances in the supernatant after three hours of reactor may be caused by the microorganisms mainly release protein-like SMPs when facing the stress of toxic component that contained in the RO concentrate. In addition, no significant change of permeate flux decline was occurred in comparison between two case of without and with concentrate.

Key-words

Reverse osmosis, concentrate, membrane bioreactor, organic matter, and fouling propensity

3.1. Introduction

The reverse osmosis (RO) process has been widely applied for water reclamation of effluents from wastewater treatment plant (WWTP) [129]. Several advantages of the reverse osmosis process that make it attractive for wastewater treatment, were reported by Garud et al [31], including: (1) reverse osmosis system are simple to design and operate; (2) both inorganic and organic pollutants can be removed simultaneously by RO membrane process; (3) require less energy as compared to other technology (microfiltration ultrafiltration); and (4) can considerably reduce the volume of waste streams so that these can be treated more efficiently and cost effectively by other processes such as incineration. In addition, RO system can be used in conjunction with the others treatment processes such as oxidation, adsorption or biological treatment to produce a high quality product water that can be reused or discharged directly to the natural environment. Nevertheless, one of the main disadvantages of using RO is the volume of concentrate produced during the process. The characteristics of the concentrate depend on the secondary effluent characteristics, the pretreatment, and the membrane process used. The concentrate is composed of all the dissolved substances retained by the membrane (organic matter, micropollutants and salts). Concentrates from microfiltration and ultrafiltration contain suspended solids and colloidal particles; whereas nano-filtration and reverse osmosis concentrates contain high concentrations of ions and small organic compounds. If the reverse osmosis concentrate is discharged directly to the natural environment, serious environmental impacts may occur due to the toxic components contained in the concentrate (e.g. micropollutants, salts and organic matter). So, the treatment of the concentrate is a major problem for implementation of the membrane processes. The concentrates from nano-filtration or reverse osmosis process are more difficult to treat because of the increased concentrations of salts and small organic compounds. Therefore, reuse of the concentrate waste stream seems to be the feasibility option.

Research on the reuse of reverse osmosis concentrates has been extended recently. The recirculation of non-biodegradable organic matter could contribute, directly or indirectly, to membrane fouling of the MBR. Nevertheless, recirculating multivalent cations such as calcium, magnesium and iron may facilitate bio-flocculation, which may reduce fouling of the MBR membranes by reducing the cake layer resistance through a decrease in the filamentous bacteria and better flocculation caused by cation bridges [2, 53]. Whilst some studies recently, high salinity greatly affects the physical and biochemical properties of activated sludge, both protein and carbohydrate levels in SMP rise as well as decreasing membrane permeability [92,122]. Some studies reported that an increase of salt concentration in the sludge resulted in a decrease in dissolved organic carbon removal. For example, Johir et al [46] found that DOC removal efficiency decreased from 72% to 35% when salt concentration in the MBR increased from 1 g $NaCl.L^{-1}$ to 10 g $NaCl.L^{-1}$, more specially, the removal efficiency of DOC concentration in the MBR considerably decreased to 10% at 25 $g.L^{-1}$ NaCl. The lower removal of dissolved organic carbon with high salt concentration could be due to the unfavorable effect of salt on microbial activity. In contrast, some other studies investigated that an increase in salt concentration did negligible change the removal efficiency of dissolved organic carbon in the MBR, its value was maintained above 95% at 20 g $NaCl.L^{-1}$ [40], it was in the range of 83-87% under sodium chloride shock of 5–30 $g.L^{-1}$ [125]. The removal efficiency of ammonia decreased as salt concentration increased, for example, sodium chloride shock loads of 5-30 $g.L^{-1}$ showed ammonia removal efficiency between 84-64% [125], removal rate of ammonia decreased from 87% to 46% as salt concentration increased from 0 to 20 $g.L^{-1}$ NaCl [44]; and its removal was gradually decreased from 98% to 70% with increasing salinity from 0-35 $g.L^{-1}$ NaCl [122]. Additionally, multivalent cations have been known to be important components of activated sludge floc structure due to their bridging ability of the negatively charged sites on the biopolymer network. According to Kara et al [52], the floc structure is significantly weakened with the monovalent cations (potassium and sodium). The particle size decreased obviously along with increasing salinity. It dropped from 70 µm to 56 µm, while the salinity increased from 0 to

35 $g.L^{-1}$ (referring to NaCl) [122]. From this point of view, the influences of RO or NF concentrate addition to the characteristics of activated sludge need to be examined and discussed.

The presence of micropollutants, such as pesticides, pharmaceuticals or endocrine disrupting compounds in the RO concentrate and eventually find themselves in wastewater at concentrations in the range of ng L^{-1} to µg L^{-1}, they can be environmentally harmful, and present serious risks to health. They are highly water soluble and are not properly removed by conventional treatment processes [101]. According to Delgado et al [18] after addition of 5 $\mu g.L^{-1}$ cyclophosphamide (CPs) to the MBR, the biomass production rate decreased, however, average total nitrogen removal was steady over 93%. The excellent performance in terms of soluble COD and ammonia removal in the MBR were observed, with elimination rates up to 95% and 99%, respectively, after the pharmaceutical and personal care products (PPCPs) were spiked into the MBR influent [93]. Whereas, the TMP significantly increased after the addition of PPCPs. Navaratna et al [82] also found that biomass production after 1 $mg.L^{-1}$ ametryn ($C_9H_{17}N_5S$) was added to the MBR feed, was significantly low. A slight decrease in COD removal was recorded immediately after addition of ametryn, however, it was improved and stabilized within 2 weeks; whereas, protein and carbohydrate increased significantly. Additionally, Avella et al [6] also indicated that the presence of CPs in the MBR induced an increase in EPS concentration in the biological sludge, especially of soluble substances, mainly proteins and polysaccharides. Another author showed that after the chloroform and chromium were injected into the MBR, no change in SMP composition was found. Li et al [67] reported that, before the addition of CBZ (carbamazepine) to the MBR, the MBR membrane retained almost all the 100-1000 kDa protein–like substances. In contrast, after CBZ addition, almost all the 10-100 kDa protein-like substances passed through the MBR membrane. Since a significant increase of the 10-100 kDa protein-like substances and a significant decrease of 100-1000 kDa was observed in the MBR supernatant, after addition of CBZ to the MBR, the small biopolymer appears to play an important role in the sludge

fouling propensity. Lesage et al [62] found that the toxic effect of 2.4 dimethylphenol (DMP) at a peak concentration of 78 ± 10 mg.L-1 could cause 50% inhibition of respiration on the activated sludge.

Kappel et al [51] reported that the recirculation of NF concentrates did not have a negative impact on the nitrification performance. The average MLSS and MLVSS concentrations are higher when the RO concentrate is sent back to the MBR [63]. Besides, the recirculation of RO concentrate caused slightly increase of total solids concentration in the aerated rotating membrane bioreactor system (ARMS) effluent [109]. Kappel et al [51] examined the impacts of NF concentrate recirculation on membrane performance in an integrated MBR and NF membrane process for wastewater treatment, and observed that dissolved and colloidal COD were always higher in the MBR supernatant. The increased dissolved COD was probably directly related to the NF concentrate recirculation and the colloidal COD could be related to changes in the floc structure. These may have been the cause of a continuous increase in transmembrane pressure.

This study describes some of findings related to the impact of reverse osmosis concentrate addition on the biomass physico-chemical characteristics and the soluble microbial product (SMP) production of activated sludge taken from WWTP. For this purpose, batch reactors were used with the directly injection of RO concentrate into the activated sludge. The particle size of the sludge was analyzed to investigate the effect of RO concentrate on the biomass characteristics. The impacts of RO concentrate on salts composition in the sludge supernatant was also carried out by the measurement of dissolved ion concentrations (cations and anions) in the supernatant before and after the concentrate injection. Additionally, the change of supernatant composition after the addition of RO concentrate was identified by protein and polysaccharide concentration analysis. Finally, this study also presents the observations of a batch reactor that was carried out to examine the effect of RO concentrate on the fouling propensity of the activated sludge.

3.2. Characteristics of the sludge supernatant and RO concentrate

The composition of the sludge supernatant and RO concentrate sample used in this study are given in the Table 3.1. The results shows that the concentrations of dissolved organic carbon in the RO concentrate were 6 times higher than that in the sludge supernatant. Besides, the concentrations of protein and polysaccharide in the RO concentrate were also 5 times higher than that in the activated sludge.

Table 3.1 Characteristics of sludge and RO concentrate

Parameters	Unit	Sludge[a]	Sludge[b]	Concentrate
MLSS[(c)]	$g.L^{-1}$	3.4 ± 0.3	2.7 ± 0.3	-
Conductivity	$mS.cm^{-1}$	-	-	5.6 ± 0.01
DOC[(d)]	$mg.L^{-1}$	6.4 ± 0.1	5.9 ± 0.1	38 ± 0.8
Proteins	$mg.L^{-1}$	11 ± 2	10.3 ± 2	49.6 ± 5
Polysaccharides	$mg.L^{-1}$	3 ± 0.3	2.2 ± 0.2	10.3 ± 1
Cations				
Na+	$mg.L^{-1}$	51 ± 5	49 ± 5	324 ± 32
NH_4^+	$mg.L^{-1}$	-	0.1 ± 0.01	3.6 ± 0.4
K^+	$mg.L^{-1}$	17 ± 2	15 ± 2	135.1 ± 14
Mg^{2+}	$mg.L^{-1}$	14 ± 1	15 ± 2	63 ± 6
Ca^{2+}	$mg.L^{-1}$	123 ± 12	125 ± 13	354 ± 35
Anions				
Cl^-	$mg.L^{-1}$	119 ± 12	113 ± 11	870 ± 87
$N\text{-}NO_3^-$	$mg.L^{-1}$	0.4 ± 0.04	0.8 ± 0.08	9.1 ± 1
$N\text{-}NO_2^-$	$mg.L^{-1}$	-	-	5 ± 0.5
SO_4^{2-}	$mg.L^{-1}$	48 ± 5	45 ± 5	290 ± 29
$P\text{-}PO_4^{3-}$	$mg.L^{-1}$	16.5 ± 2	10.2 ± 1	0.4 ± 0.04

(a) at the beginning of the reactor without 9% RO concentrate
(b) at the beginning of the reactor without 18% RO concentrate
(c) mixed liquor suspended solid
(d) dissolved organic carbon

Furthermore, almost all cations and anions concentration in RO concentrate were higher significantly than those in the sludge. For examples, dominant monovalent ions such as Na^+ and K^+ cation concentrations were 324±32 and 135±14 $mg.L^{-1}$, respectively, in the RO

concentrate; whereas, its value in the sludge was 6 times lower for Na^+ ion and 8 times lower for K^+ ion. In addition, the concentration of Cl^- anion in the concentrate was also 7 times higher than that in the sludge. The exception was a lower of $P\text{-}PO_4^{3-}$ anion concentration in the concentrate than in the sludge. The much higher concentrations of almost cations and anions in the RO concentrate, compared to those in the activated sludge, could relate to these ions concentrations in the WWTP effluent, which was used as feed water of RO system (the data is not shown in this study).

On the other hand, only one peak in protein-like substances corresponding to 10-100 kDa molecules was found in the RO concentrate from the HPLC-SEC results (see Figure 3.1); whereas, two peaks of 10-100 kDa and 100-1000 kDa protein-like SMPs were observed in the sludge supernatant (see Fig. 3.2). However, the amount of 10-100 kDa protein-like substances obtained in the sludge supernatant was much lower than that in the RO concentrate.

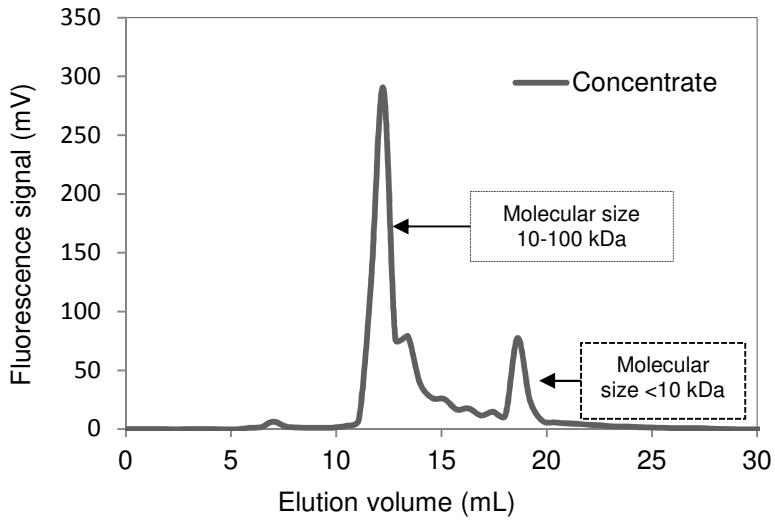


Figure 3.1 HPLC-SEC analysis of reverse osmosis concentrate

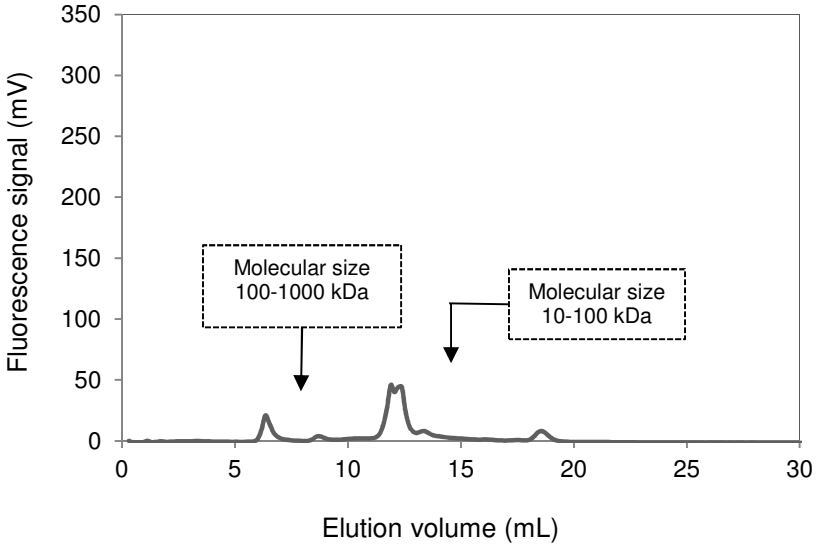


Figure 3.2 HPLC-SEC analysis of the sludge supernatant

Therefore, after the RO concentrate was added into the activated sludge, the characteristics of the sludge supernatant may be changed. Hence, the effects of RO concentrate injection on the activated sludge will be examined and discussed in the following sections.

3.3. Results and discussion

3.3.1. Effect of RO concentrate on salt composition in the supernatant of batch reactor

Table 3.2 gives measured dissolved concentrations of dominant monovalent ions (Na^+, K^+ and NH_4^+) and multivalent ions (Ca^{2+} and Mg^{2+}), as well as anions in the supernatant before and after the addition of RO concentrate (at beginning of the reactor).

The results shows that after 9% RO concentrate was injected into the reactor, the concentrations of almost all cations and anions significant increased immediately. For example, sodium and potassium ions increased by 41% and 59%; Cl^- and SO_4^{2-} anions also increased by 56% and 52%, respectively; whereas, no change was found in the concentration of $P\text{-}PO_4^{3-}$ anion in the supernatant at the beginning of the reactor. This finding could relate to the much lower of $P\text{-}PO_4^{3-}$ ion concentration in the RO concentrate (only 0.4± 0.04 $mg.L^{-1}$), compared to that in the sludge supernatant (above 10 $mg.L^{-1}$). This result may

show that the presence of RO concentrate in the activated sludge could lead to increasing of the concentrations of cations and anions in the supernatant.

Table 3.2 Effect of RO concentrate on salt composition in the sludge supernatant at the beginning of the reactor (T=0h)

Parameters	Reactor with 9% RO concentrate		Reactor with 18% RO concentrate	
	Sludge	Sludge + concentrate	Sludge	Sludge + concentrate
Cations ($mg.L^{-1}$)				
Na^+	51 ± 5	72 ± 7	49 ± 5	87 ± 9
$N\text{-}NH_4^+$	-	-	0.1 ± 0.01	0.3 ± 0.03
K^+	17 ± 2	27 ± 3	15 ± 2	31 ± 3
Mg^{2+}	14 ± 1	18 ± 2	15 ± 2	19 ± 2
Ca^{2+}	123 ± 12	145 ± 15	125 ± 13	156 ± 16
Anions ($mg.L^{-1}$)				
Cl^-	119 ± 12	186 ± 19	113 ± 11	224 ± 22
$N\text{-}NO_3^-$	0.4 ± 0.04	1.4 ± 0.14	0.8 ± 0.1	1.3 ± 0.1
SO_4^{2-}	48 ± 5	73 ± 7	45 ± 5	91 ± 9
$P\text{-}PO_4^{3-}$	16.5 ± 2	16 ± 2	10.2 ± 1	8.8 ± 1

Like results from the reactor with 9% RO concentrate, the concentrations of ions increased significantly after the addition of 18% RO concentrate to the activated sludge. The concentration of dominant monovalent ions such as Na^+ and K^+ had increased considerably, about 78% and 100%, respectively, after the concentrate adding. An increase was found in the concentration of Mg^{2+} and Ca^{2+} ions after the addition of RO concentrate. Besides, the anions such as Cl^-, SO_4^{2-} increased by 110% and 98%, respectively (see Table 3.2). This result could explain why the addition of RO concentrate to the activated sludge induced an increase significantly in the concentration of cations and anions in the supernatant.

Furthermore, after the short-term contact in the reactor (3 hours), no difference of almost all cations and anions concentrations in the supernatant was observed, as compared to those from the reactor at the beginning of the RO concentrate injected into the activated sludge (see Table 3.3).

Excepting, an increase was found in the concentration of nitrate ion, from 1.4±0.14 to 3.5±0.4 $mg.L^{-1}$ (in the reactor with 9% RO concentrate) and from 1.3±0.1 to 2.3±0.2 $mg.L^{-1}$ (in the reactor with 18% RO concentrate). This observation may relate to the nitrification process in the activated sludge.

Table 3.3 Comparison of the effects of RO concentrate injection on salt composition in the sludge supernatant between T=0 h and T=3 h

Parameters	Reactor with 9% RO concentrate		Reactor with 18% RO concentrate	
	T=0 h[a]	T= 3 h[b]	T=0 h	T= 3 h
Cations ($mg.L^{-1}$)				
Na^+	72 ± 7	75 ± 8	87 ± 9	87 ± 9
$N\text{-}NH_4^+$	-	-	0.3 ± 0.03	0.3 ± 0.03
K^+	27 ± 3	27 ± 3	31 ± 3	30 ± 3
Mg^{2+}	18 ± 2	16 ± 2	19 ± 2	17 ± 2
Ca^{2+}	145 ± 15	135 ± 14	156 ± 16	147 ± 15
Anions ($mg.L^{-1}$)				
Cl^-	186 ± 19	194 ± 19	224 ± 22	235 ± 24
$N\text{-}NO_3^-$	1.4 ± 0.14	3.5 ± 0.4	1.3 ± 0.1	2.3 ± 0.2
SO_4^{2-}	73 ± 7	79 ± 8	91 ± 9	95 ± 10
$P\text{-}PO_4^{3-}$	16 ± 2	7 ± 0.7	8.8 ± 1	5.6 ± 0.6

(a) T=0 h: at the beginning of the reactor

(b) T=3 h: 3 hours after the addition of RO concentrate

Whereas, a significant decrease was found in the concentration of $P\text{-}PO_4^{3-}$ anion after the contact time of 3 hours (including both cases of 9% and 18% RO concentrate injected into the activated sludge). This removal could relate to the accumulation of phosphorus in bacterial cells in the form of polyphosphate granules in excess of the levels normally required to satisfy the metabolic demand for growth [96].

On the other hand, as the volume of RO concentrate, which was added into the sludge, was increased from 9% to 18%, the concentrations of almost all ions in the salt compositions were higher than those from the reactor with 9% RO concentrate. For instant, after the addition of 9% RO concentrate, ion Na^+ increased from 51±5 to 72±7 $mg.L^{-1}$; whereas, after 18% RO concentrate added, its value increased from 49±5 to 87±9 $mg.L^{-1}$.

3.3.2. Effect of RO concentrate on the biomass characteristics

Floc size distribution was analyzed to investigate the effect of RO concentrate on the biomass characteristics. Figure 3.3a, b indicated that, after the injection of 9% and 18% RO concentrate, no change of particle size of the activated sludge sampled from the batch reactors were found, its value was stable at 109 µm. Moreover, the mixed liquor suspended solid (MLSS) concentration remained almost constant after 3 h of RO concentrate injection. For examples, MLSS concentrations was about 3.4 ± 0.3 $g.L^{-1}$ before and after 3h of the addition of 9% RO concentrate and it was also stable at 2.7 ± 0.3 $g.L^{-1}$ for the reactor before and after 3h of 18% RO concentrate adding. These results demonstrate that the presence of RO concentrate had not influence on the floc size distribution of the activated sludge during the short contact time.

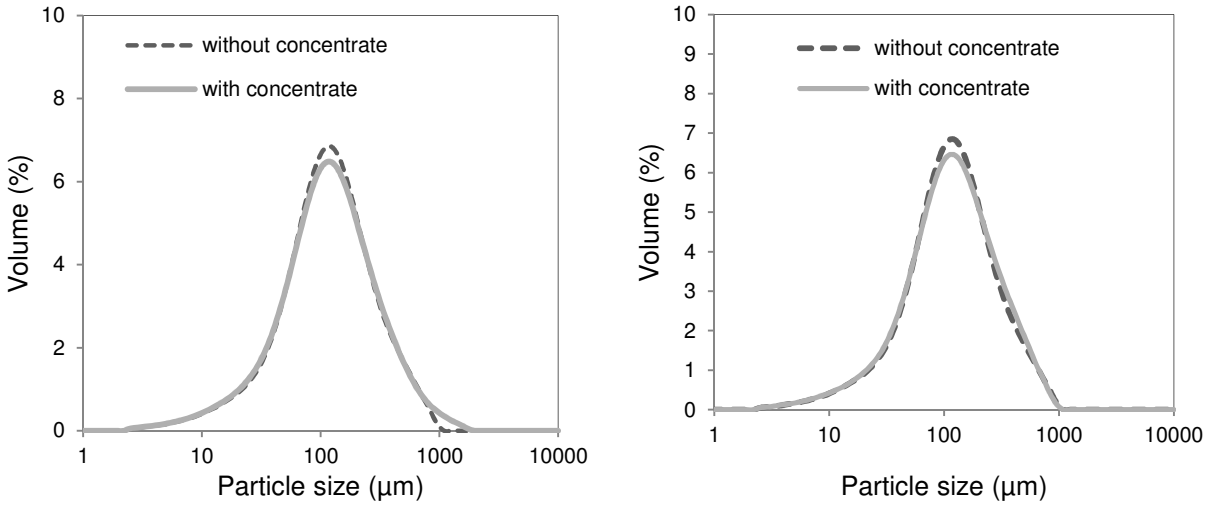


Figure 3.3 Effect of RO concentrate on sludge floc size distribution:
(a) 9% RO concentrate; (b) 18% RO concentrate

3.3.3. Effect of RO concentrate on supernatant composition

Figure 3.4 shows the result of dissolved organic carbon concentration in the supernatant of sludge sample prepared from the batch reactor. After the addition of 9% RO concentrate into the activated sludge, DOC concentration in the supernatant increased immediately from 6.4±0.1 $mg.L^{-1}$ to 9.1±0.2 $mg.L^{-1}$, about 39% (Fig. 3.4a). When 18% of RO concentrate was injected into the activated sludge, at the beginning of the reactor, DOC concentration in the sludge supernatant had increased from 5.9±0.1 $mg.L^{-1}$ to 10.8±0.2 $mg.L^{-1}$, about of 83% (see Fig. 3.4b). Therefore, the presence of RO concentrate in the activated sludge could lead to an increase of DOC concentration in the sludge supernatant.

After 3 hours of contact time between the sludge and RO concentrate, no change of the concentration of DOC in the sludge supernatant was observed in both of the two reactors (with 9% and 18% RO concentrate). This result shows that the presence of RO concentrate may not affect the cell lysis in the activated sludge.

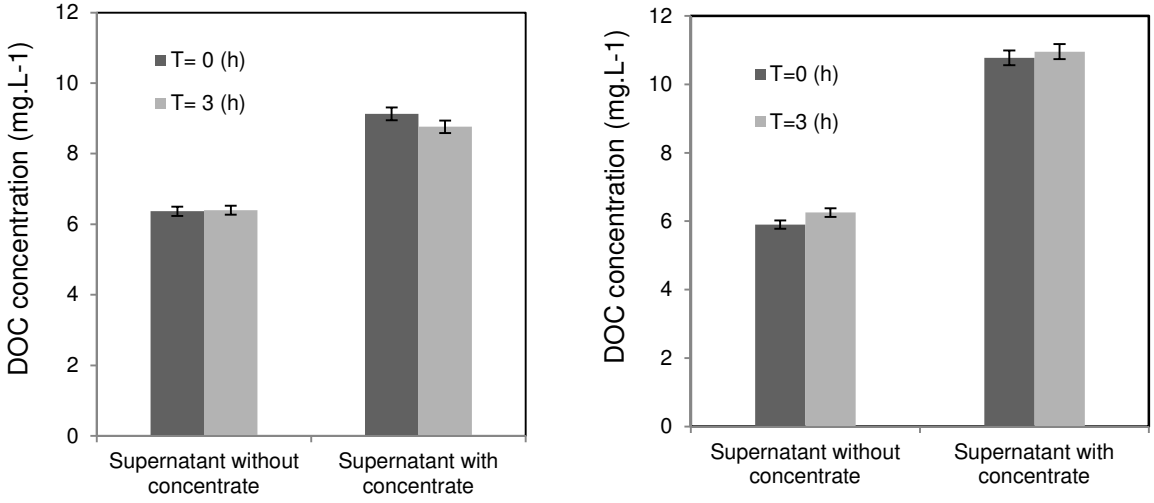


Figure 3.4 Effect of RO concentrate on dissolved organic carbon (DOC): 9% RO concentrate injected; (b) 18% RO concentrate injected

Figure 3.5 shows the results for the concentrations of protein in the supernatant of sludge sampled before and after the addition of RO concentrate (at the beginning T= 0 and after 3 hours of reactor T= 3 h). The results indicated that, protein concentrations increased immediately after the injection of RO concentrate (at T=0 h), about 30% in the reactor with 9% concentrate and 60% in the reactor with 18% RO concentrate (see Fig. 3.5a). These results could relate to the higher concentration of protein contained in the RO concentrate, compared to that in the activated sludge (see Table 3.1).

Similarly results in the polysaccharide contents were also observed after the RO concentrate addition to the activated sludge. The results from Figure 3.6a showed that a slight increase was found of the polysaccharide concentration in the supernatant after the RO concentrate added (T= 0 h), from 3 to 3.7 $mg.L^{-1}$ for reactor with 9% concentrate and from 2.2 to 3.7 $mg.L^{-1}$ for reactor with 18% concentrate.

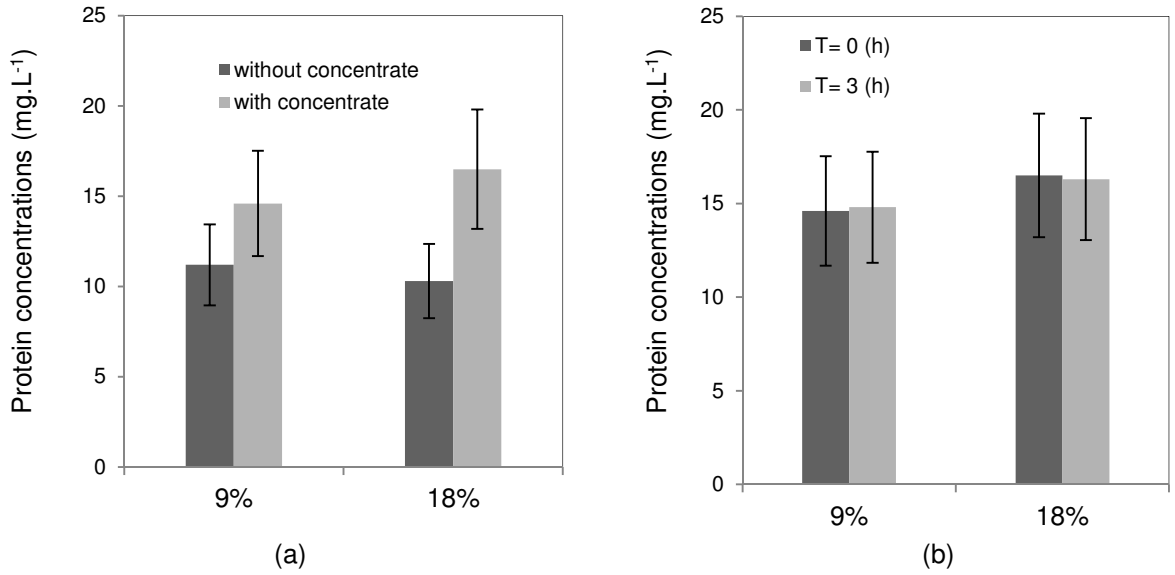


Figure 3.5 Effect of RO concentrate on protein concentrations in the supernatant: a) before and at the beginning of RO concentrate injection; b) at the beginning and after 3 hour of RO concentrate addition

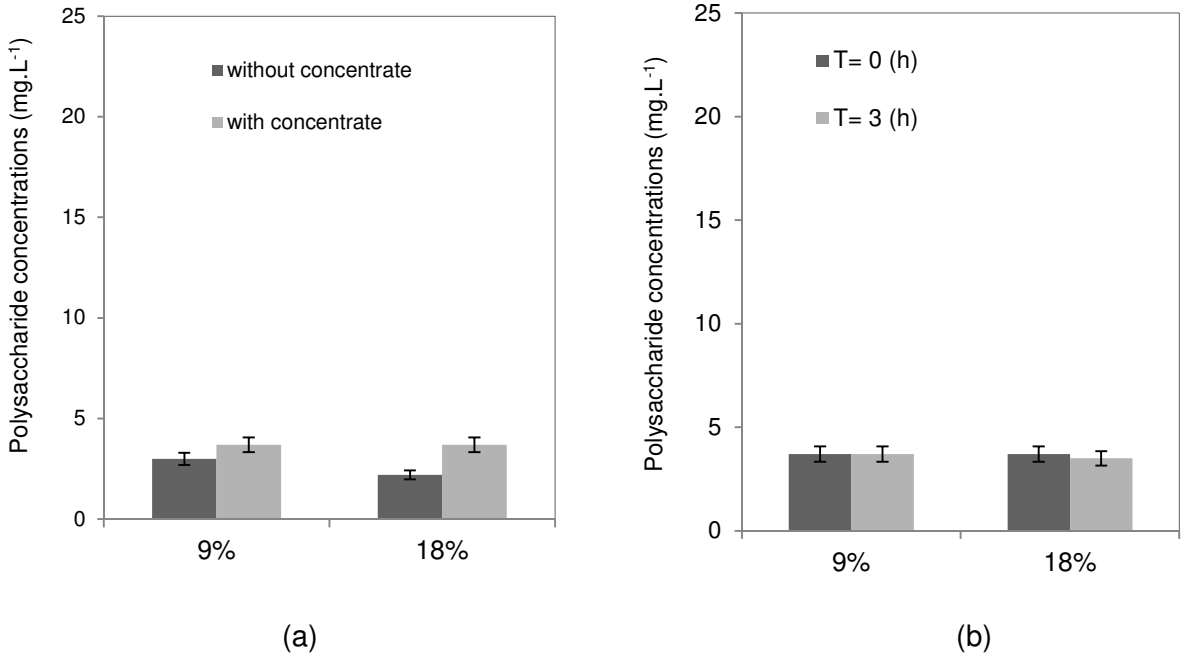


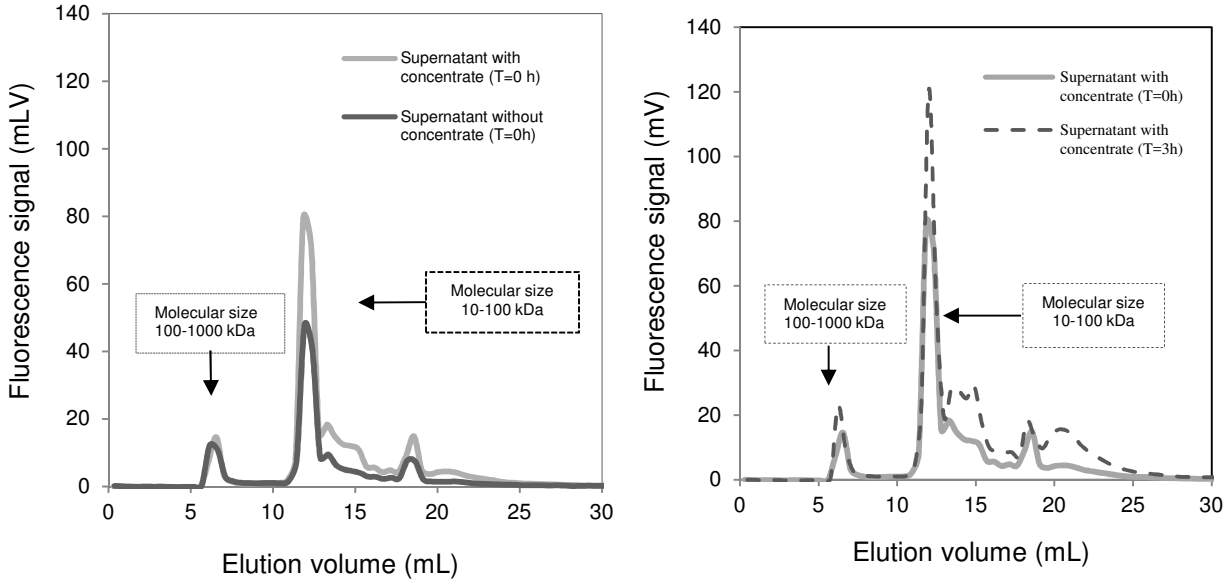
Figure 3.6 Effect of RO concentrate on polysaccharide concentrations in the supernatant: a) before and at the beginning of RO concentrate injection; b) at the beginning and after 3 hour of RO concentrate addition

After 3 hours of RO concentrate injected into the activated sludge, no change was recorded of protein contents (see Fig. 3.5b) and polysaccharide content (see Fig. 3.6b) in the

supernatant of both two reactors (with 9% and 18% concentrate), as compared to that at the beginning of RO concentrate addition.

This finding shows that the presence of RO concentrate in the activated sludge could lead to an increase in both protein and polysaccharide concentrations. However, there is no effect of the concentrate on the SMP production.

One more experiment was employed to study the effect of RO concentrate on production of protein-like SMPs. Figure 3.7a, b showed the result of HPLC-SEC analysis of supernatant from the batch reactors without and with 9% RO concentrate, two peaks were observed in the HPLC-SEC results that represent two groups of protein-like molecules, i.e. molecular size of 100-1000 kDa and 10-100 kDa. The results shows that at the beginning in the reactor, a significant peak of protein-like substances corresponding to 10-100 kDa molecules in the supernatant prepared from the batch reactor was found (see Fig. 3.7a), whereas, no change was observed for 100-1000 kDa protein-like SMPs. This explanation could be that the composition of RO concentrate contains only small molecules (see Fig. 3.1)



(a) (b)

Figure 3.7 HPLC-SEC analysis of sludge supernatant taken:

(a) reactor without and with 9% concentrate injected at the beginning, (b) with 9% concentrate injected at the beginning and after 3 h

In addition, three hours after the addition of RO concentrate, a slight increase peak of protein-like substances corresponding to 100-1000 kDa was observed. More specifically, an increase significantly was found in the small molecules (about 50%), as compared with that at the beginning of the concentrate injected (see Fig. 3.7b). Possible explanation for the increase of both small and large protein molecules in the supernatant may be caused by the microorganisms mainly release protein-like SMPs when facing the stress of toxic component that contained in the RO concentrate.

Figure 3.8 presented the results of HPLC-SEC analysis of the sludge supernatant taken from batch reactors without and with 18% RO concentrate. As shown in Figure 3.8a, at the beginning of RO concentrate addition, no difference of peak heights of protein-like substances with a molecular size of 100-1000 kDa was observed; whereas, a significant peak in protein-like substances corresponding to 10-100 kDa molecules in the sludge supernatant was found.

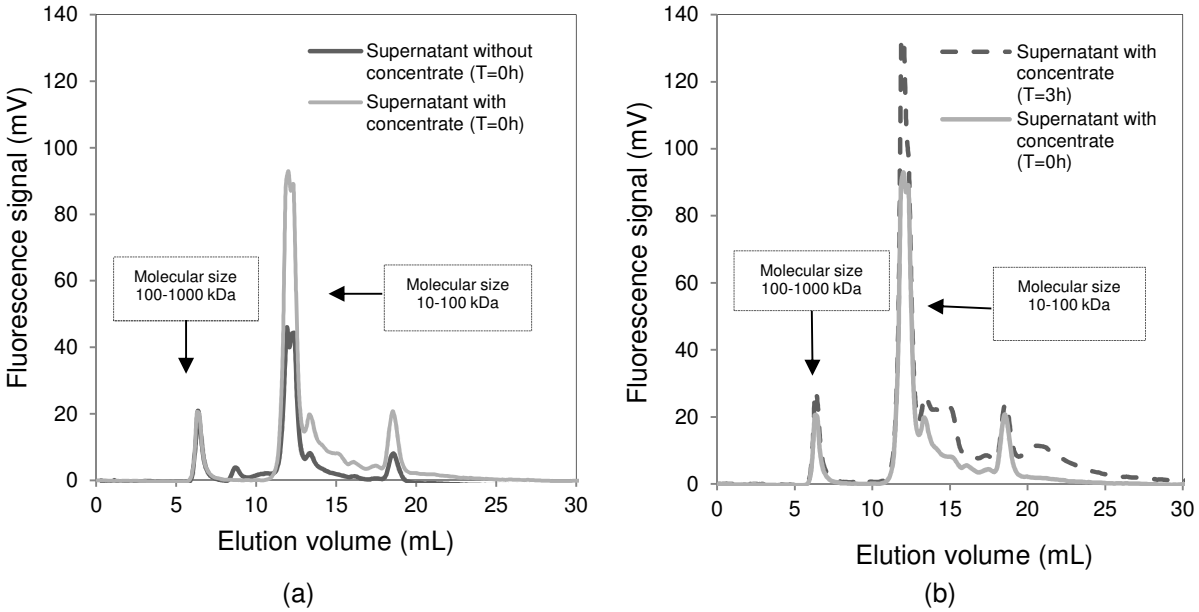


Figure 3.8 HPLC-SEC analysis of sludge supernatant: (a) reactor without and with 18% RO concentrate injected at the beginning, (b) reactor with 18% RO concentrate injected after 3h

After 3 hours of RO concentrate addition, like the result from the reactor with 9% concentrate, an increase both of small molecules and macro molecules were observed in the

supernatant, as compared to that at the beginning in the reactor (see Fig. 3.8b). This result indicates that only 3 hours contact of the activated sludge with RO concentrate could lead to the lysis of some bacteria and release of some protein-like SMPs inside the bacterial cells. Similarly, Li et al [67] found that only 3 hours contact of 100 µg.L^{-1} CBZ with activated sludge caused an increase of macro molecules protein-like substances in the supernatant.

3.3.4. Effect of RO concentrate on permeate flux decline

The filterability tests using the dead-end filtration cell were examined on the sludge sampled from the batch reactors, using sludge taken from the WWTP at 1 bar to investigate the effect of RO concentrate on the permeate flux decline in the microfiltration membrane (Figure 3.9)

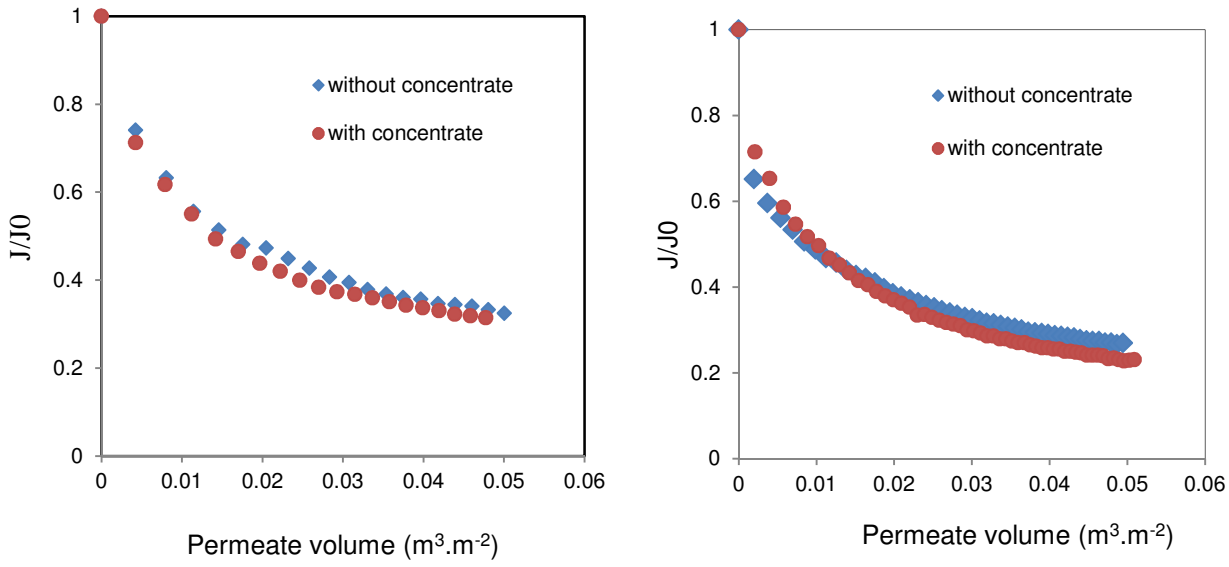


Figure 3.9 Effect of RO concentrate on the permeate flux decline in the sludge filterability test as a function of the permeate volume ($m^3.m^{-2}$)
a) 9% RO concentrate added, b) 18% RO concentrate added

The result from Fig. 3.9a indicated that, after 3 hours of RO concentrate addition, no significant change of the permeate flux decline was occurred in both of the reactors without and with 9% RO concentrate. Like the results from the reactors without and with 9% RO

concentrate, the permeate flux decline was not impacted by the addition of 18% RO concentrate (see Fig. 3.9b).

To further investigate the effects of RO concentrate on the permeate flux decline, HPLC-SEC analysis of the supernatant prepared from the reactors without and with RO concentrate (at T=3 h) and the corresponding permeate obtained in sludge filterability test (using the 0.2 µm PS membrane). As shown in Figure 3.10, the 10-100 kDa protein-like substances passed throughout this membrane; whereas, the membrane could retain almost all 100-1000 kDa protein-like SMPs, both of two reactors without and with concentrate. However, the 100-1000 kDa protein-like SMPs produced by RO concentrate recirculation to the MBR had no significant effect on filterability of the sludge.

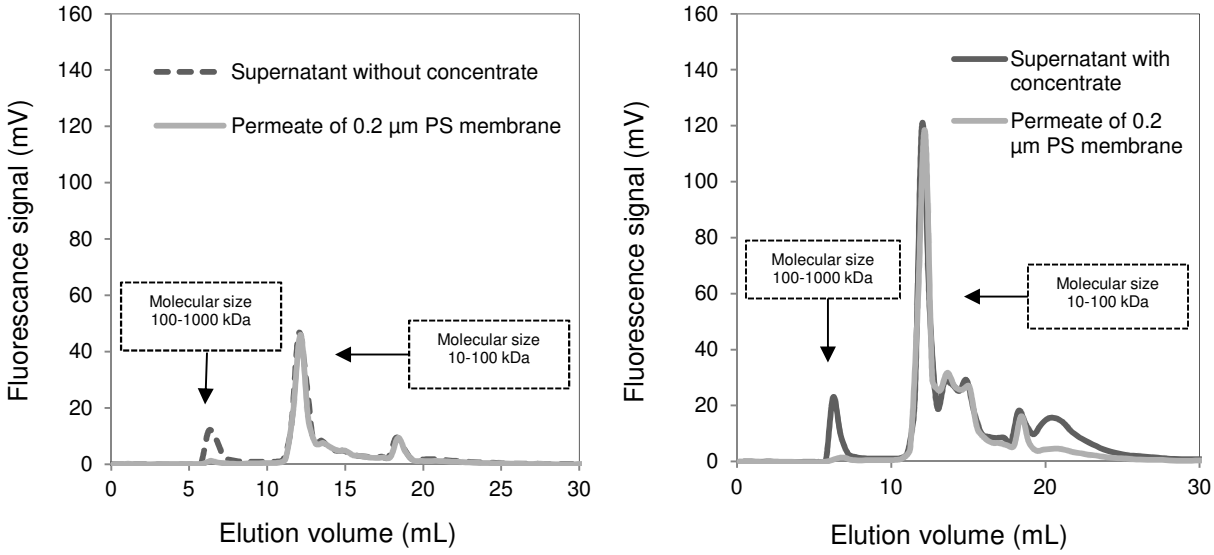


Figure 3.10 HPLC-SEC analyses of sludge supernatant taken from reactors without and with 9% concentrate and permeate obtained in sludge filterability test

Like the results from the batch reactor with 9% RO concentrate, almost all the 10-100 kDa protein-like substances had passed through the membrane and the 100-1000 kDa protein-like SMPs was rejected completely by the membrane in the reactor without and with 18% RO

concentrate (see Fig. 3.11). This result could explain why the injection of RO concentrate did not affect the permeate flux decline.

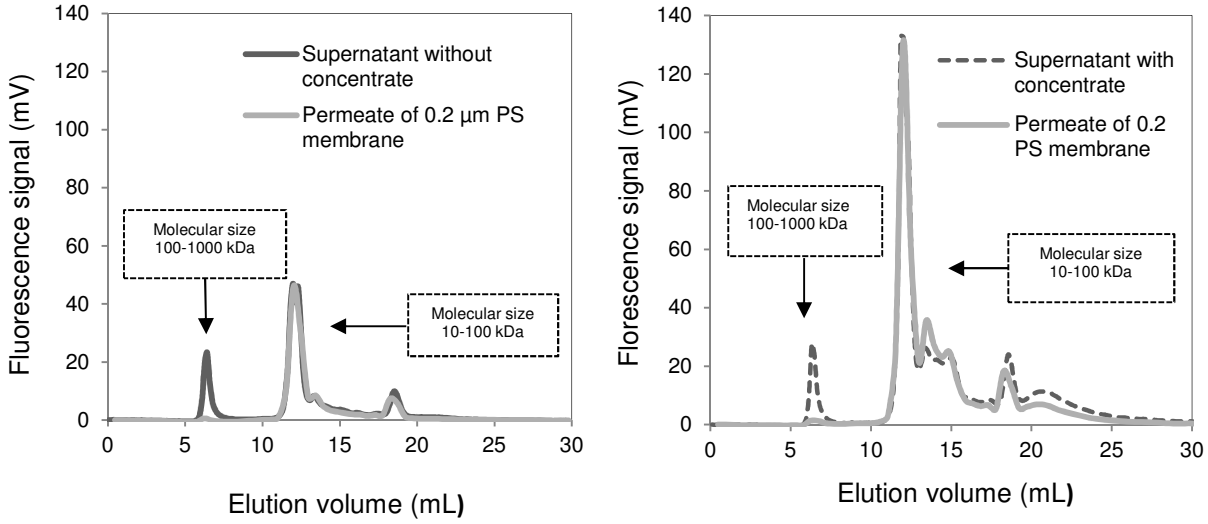


Figure 3.11 HPLC-SEC analysis of sludge supernatant taken from the reactors without and with 18% concentrate (at T= 3 h) and permeate obtained in sludge filterability test

Figure 3.12a display the effect of RO concentrate on the permeate flux decline from the supernatant filterability test (using the 0.01 *µm* PES membrane). The filterability test using the dead-end filtration cell was examined on the supernatant sampled from the batch reactors with 9% RO concentrate (at 1 bar). This result indicate that no significant change of permeate flux decline was occurred in comparison between two case of without and with concentrate for 9% addition. However, a slight effect on the permeate flux decline was found, compared between two reactors without and with 18% RO concentrate injection (see Fig.3.12b).

To better understand the change on the permeate flux decline of the 0.01 µm PES membrane, HPLC-SEC analysis of the supernatant and the corresponding permeate was performed on the membrane. The result of Figure 3.13 demonstrates that the membrane retained almost all of the 100-1000 kDa protein-like substances in two cases without and with 9% RO concentrate. Although the 10-100 kDa protein-like SMPs had increased significantly

in the supernatant after the concentrate adding, but these small protein molecules passed through the membrane during the filtration time. This observation indicated that the formation of a fouling layer on the membrane surface could due to the 100-1000 kDa protein like-substances.

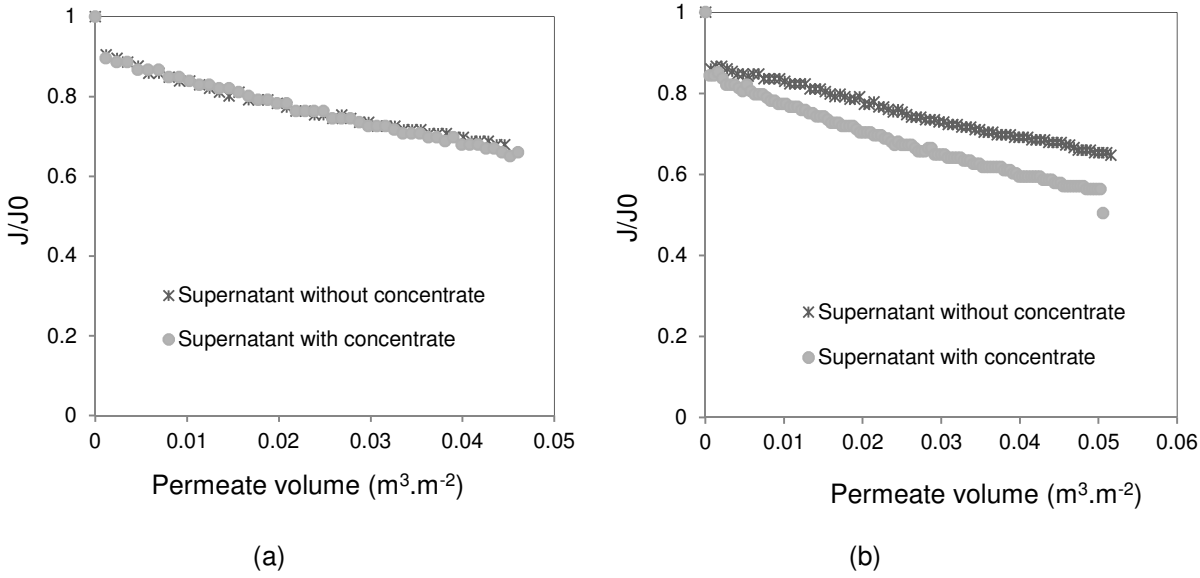


Figure 3.12. Effect of RO concentrate on the permeate flux decline from supernatant filterability test as a function of the permeate volume: (a) 9% RO concentrate added; b) 18% RO concentrate added

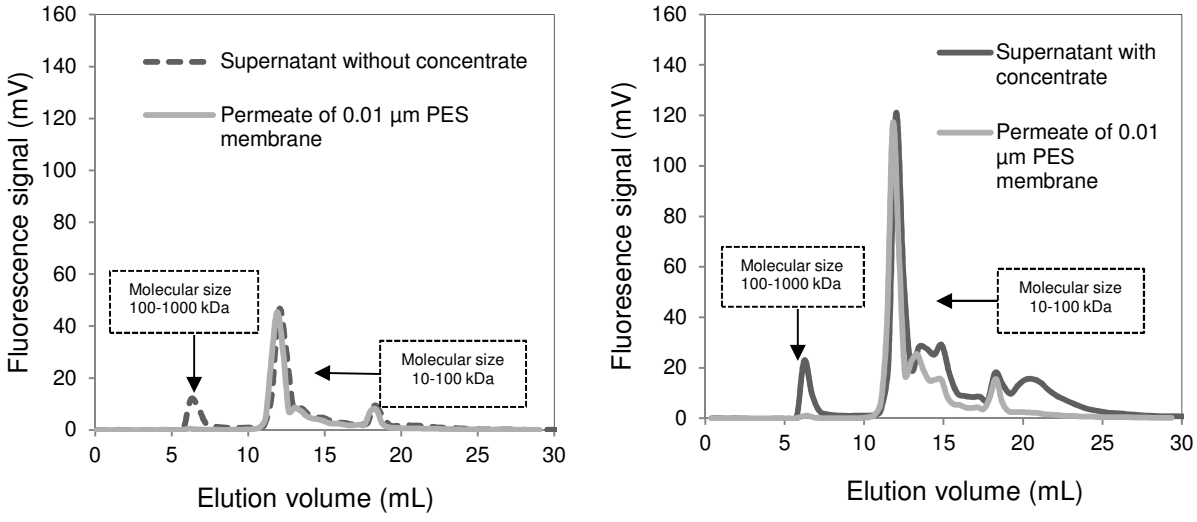


Figure 3.13. HPLC-SEC analyses of sludge supernatant taken from reactors without and with 9% concentrate and permeate obtained in supernatant filterability test

Similarly, the 100-1000 kDa protein-like SMPs was retained completely by the 0.01 *µm* PES membrane, as the volume of concentrate injection increased to 18% (both of the reactors without and with concentrate) (see Fig.3.14). From the reactor without 18% concentrate, almost all the small molecules passed through the membrane. While, some small protein molecules could be retained by this membrane from the reactor with concentrate, thus reducing the pore size and the decline of permeate flux could occur.

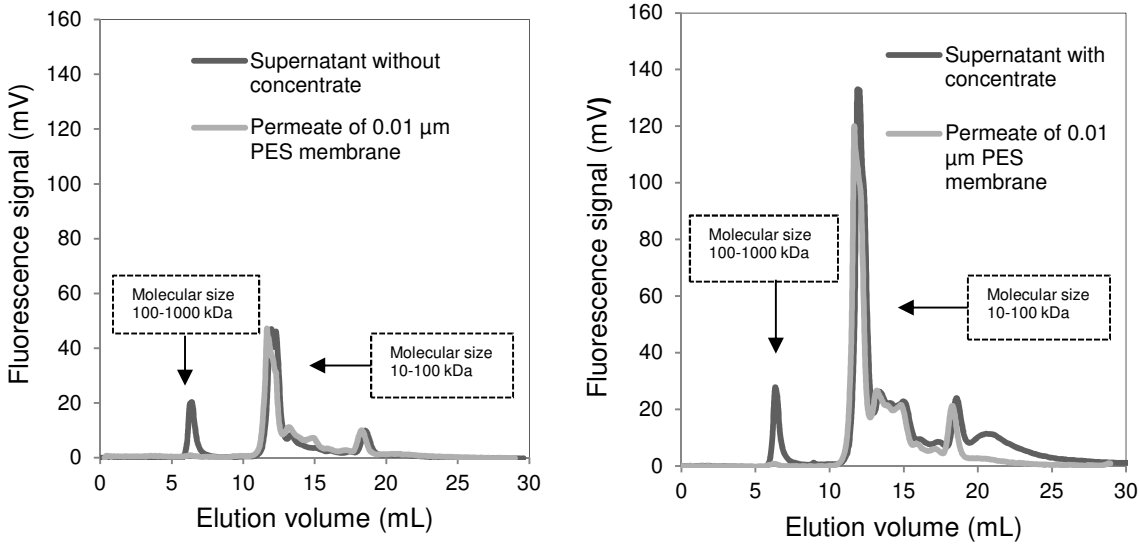


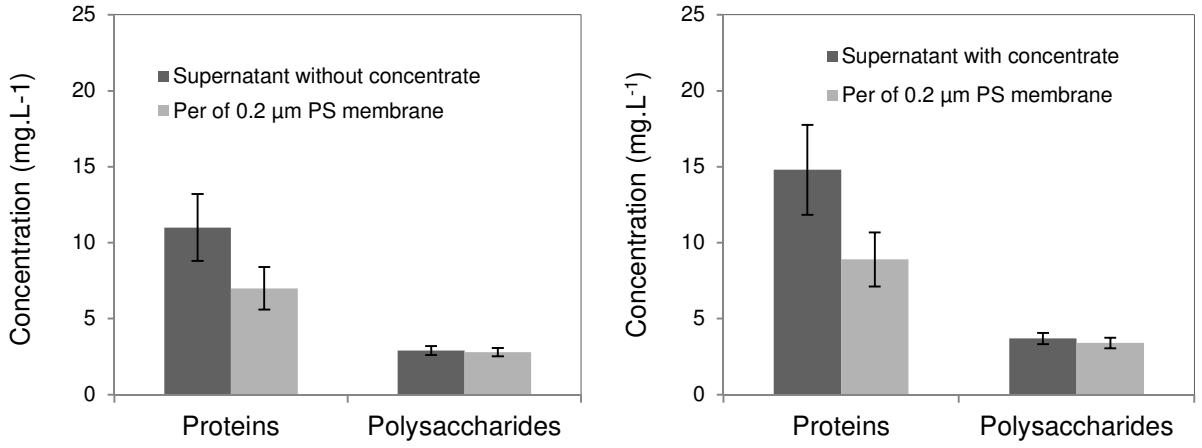
Figure 3.14 HPLC-SEC analyses of sludge supernatant taken from reactors without and with 18% concentrate and permeate obtained in supernatant filterability test

3.3.5. Effect of RO concentrate on fouling layer characteristics of sludge

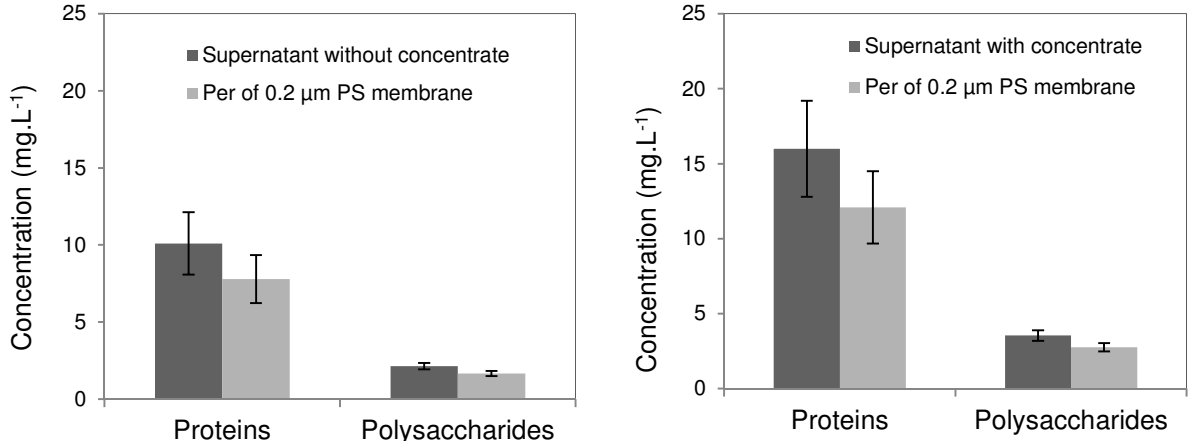
The fouling layer of the membrane during sludge filtration test (using the 0.2 *µm* PS membrane) is related the retained components in the sludge. The result of Figure 3.15a shows that, when the 9% RO concentrate was added into the activated sludge, no difference was observed in the retention of the protein concentration by the membrane, in comparison between two reactors (without and with concentrate), about 37 ± 0.8% for the reactor without concentrate and 40 ± 0.8% for the reactor with concentrate. When the volume of RO

concentrate was modified to 18%, the retention of protein concentration by the membrane was recorded, about 24 ± 5 % for the reactor with concentrate added, and about 22 ± 4% for the reactor without concentrate (see Fig. 3.15b).

Although the retention of protein concentrations on this membrane surface is quite similar in both of the reactors without and with concentrate addition, a slight difference was observed in the protein concentrations retained on the membrane surface, between the reactor without and with concentrate adding. After the 9% of RO concentrate injection, protein concentration retained on the membrane surface had increased from 4 to 5.9 mg.L^{-1}. For the reactor with 18% RO concentrate addition, the concentration of protein increased from 2.3 to 3.9 mg.L^{-1}.



(a)



(b)

Figure 3.15 Effect of RO concentrate on SMP concentration in the supernatant and the permeate observed from sludge filterability test (after 3h reactor): a) 9% RO concentrate, b) 18% RO concentrate

Moreover, the retention of almost all 100-1000 kDa protein-like SMPs by the 0.2 *µm* PS membrane, which has been discussed in the previous section (see Fig. 3.10 and 3.11), indicating that a fouling layer could be formed on the membrane surface. The results also point out the important role of large protein-like SMPs in the fouling propensity of the sludge.

In addition, the fouling layer was characterized by specific resistance (α value) obtained from the filterability test. The results of Table 3.4 shows α value calculated in filterability test of sludge sampled from batch reactors using sludge taken from WWTP. No significant difference was found of α value between two reactors without and with 9% RO concentrate addition, about (18 ± 1.6) × 10^{-12} m.kg^{-1} and (21 ± 2) × 10^{-12} m.kg^{-1}, respectively. The results seem to be related to the retention of mass liquor suspended solid (MLSS) by the 0.2 µm PS membrane surface. As seen in Fig. 3.16, the MLSS value, which was deposited on the membrane surface, did not change in both case of without and with RO concentrate injection.

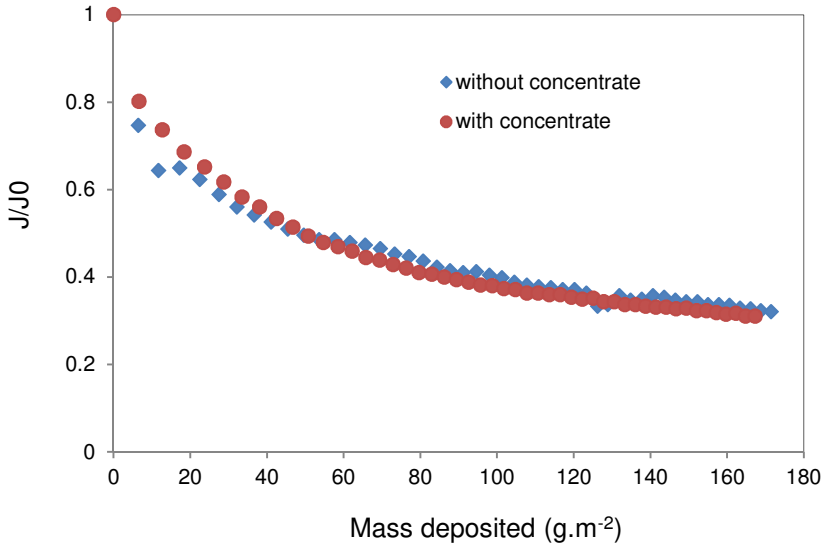


Figure 3.16. Effect of RO concentrate on the permeate flux decline as function of mass deposited on the membrane surface in the sludge filterability test: 9% concentrate addition into the sludge (Mass deposited is calculated by MLSS value of sludge)

It was found that after 18 % RO concentrate injected into the sludge, a slight increase of MLSS deposition on the membrane surface was observed, as compared to that from the

reactor without 18% concentrate adding (see Fig. 3.17). This observation could explain why the difference slightly of α value (see Table 3.4), between two reactors without and with concentrate injection, was recorded. The α value of reactor without concentrate was about $(22.2 \pm 2) \times 10^{-12}$ m.kg^{-1}, and $(29.6 \pm 3) \times 10^{-12}$ m.kg^{-1}

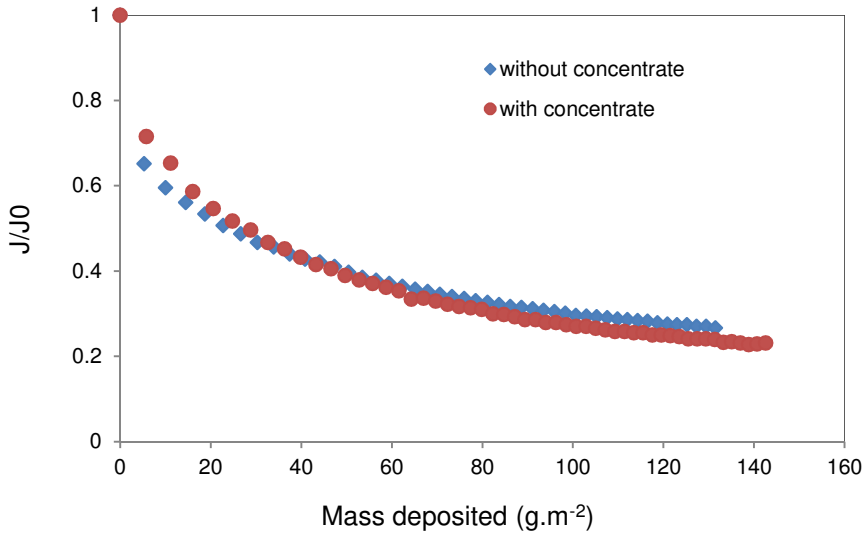


Figure 3.17. Effect of RO concentrate on the permeate flux decline as function of mass deposited on the membrane surface in the sludge filterability test: 18% concentrate addition (Mass deposited is calculated by MLSS value of sludge)

Table 3.4. Effect of RO concentrate on fouling propensity of sludge
(C is assumed to be MLSS value of sludge)

	ΔP (bar)	αC×10^{-13} (m^{-2})	α×10^{-12} (m.kg^{-1})
9% RO concentrate *(C= 3.4 g.L^{-1})*			
Sludge without concentrate	1	6.1 ± 0.5	18 ± 1.6
Sludge with concentrate	1	7.2 ± 0.6	21 ± 2
18% RO concentrate *(C = 2.7 g.L^{-1})*			
Sludge without concentrate	1	6 ± 0.5	22.2 ± 2
Sludge with concentrate	1	8 ± 0.7	29.6 ± 3

3.4. Conclusion

This study investigated the impacts of the RO concentrate addition on the fouling propensity and physico-chemical characteristics of the activated sludge.

Although an increase of almost all cations and anions concentration in the supernatant at the beginning of the concentrate addition, however, no significant change of these component concentrations was found after the short-term contact in the reactor (3 hours).

Similarly, after 3 hours of contact time between the sludge and RO concentrate, no difference of the dissolved organic carbon (DOC) concentration in the sludge supernatant was observed in both of the two reactors (with 9% and 18% RO concentrate), as compared to that at the beginning of RO concentrate injected.

The presence of RO concentrate in the activated sludge caused an increase of both protein and polysaccharide concentrations, at the beginning of the injection of RO concentrate (T=0h). However, after 3 hours of contact time between the sludge and concentrate, the same values of both protein and polysaccharide concentrations were found in the supernatant, compared to that at the T= 0 h.

The results of HPLC-SEC analysis showed that at the beginning of the reactor with 9% RO concentrate, a significant peak of protein-like substances corresponding to 10-100 kDa in the supernatant was recorded; whereas, no change was obtained for 100-1000 kDa protein-like SMPs. Similar results were found for the reactor of 18% RO concentrate addition. More specifically, the amount of both small and large protein-like SMPs had increased slightly in the supernatant after 3 hours of concentrate adding.

In addition, the presence of RO concentrate in the activated sludge did not affect the permeate flux decline in the filterability test of sludge. For the supernatant filterability test, the permeate flux decline was effected slightly by 18% RO concentrate addition; whereas, no impact of RO concentrate on the permeate flux decline was found from the reactor with 9% concentrate adding.

Finally, to better understand the possibility of using RO process as a tertiary treatment of the membrane bioreactor (MBR), with the RO concentrate recirculation to the MBR, the study concerning effects of RO concentrate on the MBR process, specifically on the MBR performances and fouling propensity in the MBR, should to be carried out.

CHAPTER IV

REVERSE OSMOSIS CONCENTRATE CONTINUOUS RECIRCULATION TO THE MBR-RO PROCESS FOR WASTEWATER TREATMENT

Abstract

A pilot-scale double membrane of MBR-RO was found to be effective for wastewater treatment with recirculation of the reverse osmosis (RO) concentrate to the MBR. The continuous presence of RO concentrate in the MBR caused quite a significant increase of both protein and polysaccharide contents in the MBR supernatant. This finding could relate to the recirculation of highly salt loaded stream, which contained in the RO concentrate, back to the MBR. HPLC-SEC analysis was employed to study the effects of RO concentrate on protein-like substances in the supernatant of the MBR. Both the 10-100 kDa and 100-1000 kDa protein-like substances had increased markedly in the MBR supernatant. An important effect of large protein-like SMPs was observed in the fouling propensity of sludge. A continuous introduction of RO concentrate into the MBR induced a significant increase of the transmembrane pressure (TMP). This indicated that the recirculation of RO concentrate could cause enhanced membrane fouling.

In addition, a decrease from 94 to 72% of the ketoprofen removal efficiency was observed in the MBR after 14 days of concentrate addition. Poor removal rates of carbamazepine and diclofenac in the MBR were found both before and after the addition of the RO concentrate. This means that the recirculation of RO concentrate to the MBR had no significant impact on the removal of the selected pharmaceutical micropollutants in the MBR.

Finally, the effectiveness of the integrated MBR-RO process was also evaluated in terms of the MBR performance and nitrification in the MBR. The experimental results revealed no significant effect on the removal efficiencies of chemical oxygen demand, dissolved organic carbon when RO concentrate were recirculated to the MBR. The recirculation of RO concentrate did not affect the nitrification process in the MBR.

Keywords: Membrane bioreactor, reverse osmosis concentrate, fouling propensity, soluble microbial product, micropollutants

4.1. Introduction

Although membrane bioreactors (MBR) and the reverse osmosis (RO) process are both established technologies, their use together for advanced wastewater treatment is relatively new. The MBR process is an improvement on the conventional activated sludge wastewater treatment process and is capable of producing treated water of excellent quality. Reverse osmosis is a process that has traditionally been used for seawater and industrial desalination processes. RO provides excellent removal of both inorganic and organic constituents, including trace constituents such as pharmaceuticals, personal care products (PPCPs) and endocrine disrupting compounds (EDCs). However, problems in RO applications include cost, fouling and, particularly, concentrate management. The characteristics of the concentrate depend on the feed water characteristics, the pretreatment, the membrane process employed, the recovery, and the additional chemicals used [98]. In addition, concentrates from nano-filtration (NF) or reverse osmosis (RO) contain high concentrations of ions and small organic compounds [101], which make the concentrates more difficult to treat. A possible solution to this issue may be to recirculate the concentrated waste stream. This would not only minimize the environmental issues but would also enable a more sophisticated treatment to be investigated for the production of reusable water. Hence, the concept of integrated MBR - RO with RO concentrate recirculation to the MBR might provide a solution to this problem.

Research on reverse osmosis concentrates and their impacts on membrane bioreactors have been extended recently. According to Kim and Jang [53] and Arabi and Nakhla [2], recirculating multivalent cations, such as calcium, magnesium and iron, to the MBR may facilitate bio-flocculation. This, in turn, may reduce fouling of the MBR membranes by reducing the cake layer resistance through a decrease in the amount of filamentous bacteria and through better flocculation caused by cation bridges. Some recent studies have shown that high salinity greatly affects the physical and biochemical properties of activated sludge: both protein and carbohydrate levels in the soluble microbial product (SMP) rise and

membrane permeability decreases [92,122]. In addition, Joss et al [48] and Kappel et al [51] reported that the high salinity of NF concentrate returned to the MBR caused an increase in salinity in the long term, which could affect the characteristics of the sludge and the membrane fouling. Some studies have reported that an increase of salt concentration results in a decrease in dissolved organic carbon removal. For example, Johir et al [46] found that DOC removal efficiency decreased from 72% to 35% when salt (NaCl) concentration increased from 1 $g.L^{-1}$ to 10 $g.L^{-1}$. The lower removal of dissolved organic carbon with high salt concentration could be due to the unfavorable effect of salt on microbial activity. In contrast, some other studies have shown that an increase in salt concentration has a negligible effect on the removal efficiency of dissolved organic carbon in the MBR, its value being maintained above 95% at 20 $g.L^{-1}$ NaCl [44]. However, the efficiency of ammonia removal decreases as salt concentration increases. For example, when the salinity was increased from 0 to 20 $g.L^{-1}$ NaCl [40], and from 15 to 35 $g.L^{-1}$ NaCl [122], the NH_4^+ (ammonium) removal efficiency fell, from 87 to 46% and from 99% to 70%, respectively. Additionally, multivalent cations have been shown to be important components of activated sludge floc structure due to their ability to bridge the negatively charged sites on the biopolymer network. According to Kara et al [52], the floc structure is significantly weakened with monovalent cations (potassium and sodium). In presence of NaCl, the particle size clearly decreases as salinity increases, dropping from 70 µm to 56 µm when the salinity increases from 0 to 35 $g.L^{-1}$ [122].

Furthermore, micropollutants, such as pesticides, pharmaceuticals or endocrine disrupting compounds, present in the RO concentrate at concentrations in the range of $ng.L^{-1}$ to $\mu g.L^{-1}$. For example, the concentrate produced by RO was found to contain concentrations of about 3.4 $\mu g.L^{-1}$ of carbamazepine (CBZ) and 1.5 $\mu g.L^{-1}$ for diclofenac [9], 1.4 $\mu g.L^{-1}$ for CBZ and 0.2 $\mu g.L^{-1}$ for ketoprofen [39]. These compounds dissolved in a water matrix can be environmentally harmful and present serious risks to health. In general, a bioreactor membrane using micro- and ultra-filtration membranes cannot remove micropollutants

directly by sieving (the molecules are at least 100 times smaller than the pore size of the membrane) [49]. In activated sludge, the mechanisms for the removal of pharmaceutical micropollutants include biotransformation, sorption, air-stripping and photo-transformation [66,100]. The last two mechanisms are generally considered to be insignificant in the MBR. The elimination of micropollutants in the MBR is supported by other studies. The poor removal of carbamazepine and diclofenac (DCF) in an MBR has been reported by many researchers: 10-30% for CBZ and about 17% for DCF [116], about 4% for CBZ [12], 20% for DCF [55] and no removal of CBZ in MBR [67]. Notably, the removal of CBZ can be negative. For example, the removal of CBZ has been found to be -22 to 23% [100] and -12.7 to 12.5% [15]. These authors demonstrated that the elevated effluent concentration of CBZ was most likely due to enzymatic cleavage of the glucuronic conjugate of CBZ and release of the parent compound in the treatment plant. These data also indicate that carbamazepine is poorly biodegraded in the MBR. In contrast, high removal efficiencies were found for the compounds that are easily biodegraded in the MBR, with average removal rates higher than 90% for acetaminophen, ibuprofen, caffeine, nicotine and ketoprofen [12,55,93,121]. With regard to the effect of micropollutants on activated sludge, Dionisi et al [23] reported that 10 organic xenobiotics (such as 1.8 $mg.L^{-1}$ benzene, 1 $mg.L^{-1}$ 1,3,5-trichlorobenzene, etc.) and two heavy metals (Cd and Pb) induced a significant reduction in overall nitrogen removal (considering the sum of ammonia and nitrate nitrogen), from 65% to 36%, with ammonium removal efficiency also decreasing from 82% to 37%. This result could due to the presence of micropollutants in the feed significantly inhibiting nitrification. A previous study by Wijekoon et al [121] revealed that the presence of a set of 29 TrOCs (trace organic contaminants), approximately 5 $\mu g.L^{-1}$ of each compound, in the feed of an MBR did not affect the efficiency of total organic carbon (TOC) removal in the MBR process, which was stable at 90±1%. Li et al [67] reported that the introduction of 90 $\mu g.L^{-1}$ CBZ into the MBR via the feed induced a significant decrease of 100-1000 kDa protein-like SMPs and a more significant increase of the 10-100 kDa protein-like substances in the MBR supernatant. They showed that the small biopolymer appeared to play an important role in the sludge fouling

propensity. Lesage et al [69] found that the toxic effect of 2.4 dimethylphenol (DMP) at a peak concentration of 78 ± 10 $mg.L^{-1}$ could cause 50% inhibition of respiration in the activated sludge.

In recent years, a few studies have focused on the impacts of RO/NF concentrate recirculation to the MBR in an integrated MBR-RO/NF process for wastewater treatment. Lew et al [63] reported that an increase of the average MLSS and MLVSS concentrations was observed when the RO concentrate made up about 17% of the total MBR inflow and that MBR TOC mass removal rate increased from 5.72 to 6.44 $g.d^{-1}$. This finding indicated that concentrate recycling resulted in a higher TOC mass removal rate which, in turn, suggested that, in addition to the residual readily degradable organic compounds, a fraction of the slow and hard to degrade organic compounds present in the recycle stream could be biodegraded in the MBR. Kappel et al [51] observed an increase of the dissolved (after 0.45 µm filter) and colloidal chemical oxygen demand (COD) in the MBR supernatant after the addition of NF concentrate. The increase in dissolved COD was probably directly related to the NF concentrate recirculation, and that in the colloidal COD could be related to changes in the floc structure but may also have resulted from extracellular polymeric substances (EPS) or humics. This research also demonstrated that, in particular, dissolved and colloidal COD present in the supernatant of the MBR significantly influenced the MBR membrane performance. A faster increase of the TMP in the MBR was observed after NF concentrate recirculation, compared to that from the MBR without the concentrate. The NF concentrate recirculation could also have a negative impact on the nitrification in the MBR when treating wastewater from antibiotic production. For instance, the NH_4^+ removal rate was steadily higher than 95% throughout the entire experiment [68].

In addition, Wang et al [118] reported that the total organic carbon concentration in the MBR permeate after the addition of concentrate was higher than before and, consequently, the concentration of organic compounds in the MBR permeates could also be higher. Moreover, the main organics, such as proteins, polysaccharides, and humic-like substances increased

in the MBR effluent after the NF concentrate was added into the MBR. In their study, a molecular biological technique, PCR-DGGE (polymerase chain reaction-denaturing gradient gel electrophoresis), and clone library construction was used to analyze the difference in the activated sludge before and after the NF concentrate addition. The result showed that recycling the NF concentrate into the MBR did not change the microbial diversity of the activated sludge. Additionally, Li et al [68] showed that the protein content increased in the MBR supernatant with the recycling of the NF concentrate to the MBR. They reported that, when the volume of NF concentrate returned to the MBR (R_{cb}) made up 90% of the total volume of the NF concentrate produced, the protein contents in the MBR supernatant were 2.5 times higher than with an R_{cb} of 40% and 3.3 times higher than that before the concentrate recycling. Meanwhile, the polysaccharide content in the MBR supernatant did not change significantly. Therefore, the protein content in SMP, and SMP brought by NF concentrate were the main cause of the severe membrane fouling in the MBR.

The main objective of this study was to examine the effects of recirculation of concentrate produced by RO on the global performance, the MBR membrane fouling propensity and the elimination of micropollutants in an MBR for municipal wastewater treatment. For this purpose, a combination of MBR and RO processes was run with RO concentrate recirculation, which made up 20% of the total inflow of the MBR. The removal efficiencies of chemical oxygen demand (COD) and dissolved organic carbon (DOC) were identified before and after the concentrate recirculation. The impact of RO concentrate on the nitrification process was evaluated by the analysis of ammonia and total nitrogen removal in the MBR. Changes in MBR supernatant compositions after the concentrate recycling were also identified by protein and polysaccharide concentration analysis. The fouling propensity of the membrane was assessed by testing the filtration of MBR sludge and supernatant. In addition, HPLC-SEC analysis was performed to investigate the mechanism of fouling by small molecules or macro molecules in the MBR.

4.2. MBR-RO set up

Two reactors were contained in the lab-scale MBR: an anoxic reactor (5.4 L) and an aerobic reactor (12.6 L). The aerobic reactor was equipped with one submerged flat sheet microfiltration membrane (Kubota, Japan) having an effective filtration area of 0.1 m^2 and a nominal pore size of 0.2 µm. The instantaneous permeate flux was fixed at 15 LMH (liter/m^2/hour) with relaxation steps of 4 min performed every 8 min, leading to a net permeate flux of 10 LMH. The reactor was aerated with big air bubbles at a flow rate of 1.5 $L.min^{-1}$, i.e. SAD_m of 0.9 m^3 $air.h^{-1}.m^{-2}$. Another aeration system with fine air bubbles was also used to maintain the dissolved oxygen concentration in the sludge at about 2-3 $mg.L^{-1}$. The sludge recirculation rate was fixed at 4 $L.h^{-1}$. The MBR was operated with a 45 day SRT (sludge retention time), which means that the sludge was discharged at flow rate of 0.4 $L.d^{-1}$.

The MBR was fed by the wastewater with addition of the RO concentrate produced by the subsequent RO process. In order to set up this recirculation loop, the MBR permeate was collected in a storage tank and used as inflow to the RO system. The MBR permeate fed the RO process continuously at a flow rate of 16.8 $L.d^{-1}$. The RO process produced 10.8 $L.d^{-1}$ of permeate, so the RO water recovery was about 64%. The RO concentrate was collected in a storage tank at a flow rate of 6 $L.d^{-1}$ to feed to the MBR. The operating conditions of the reverse osmosis process are summarized in Table 4.1

Table 4.1. Operating conditions of the reverse osmosis process

Parameters	Operating conditions
Transmembrane pressure (TMP)	7 bar
pH	6
Concentration factor (CF)	2.6 ± 0.1
Velocity	0.18 $m.s^{-1}$
Water recovery	64%

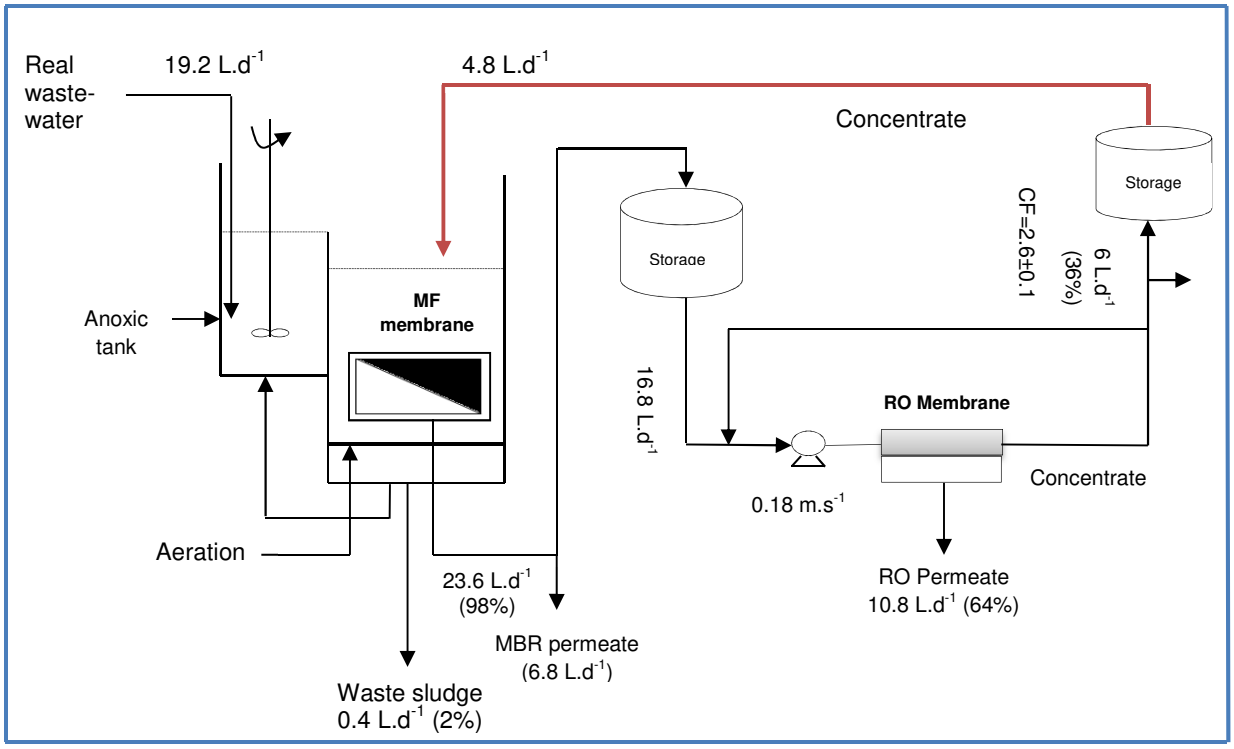


Figure 4.1. MBR-RO process

The MBR feed was taken from a wastewater treatment plant close to Toulouse, France, after a primary physical treatment. As shown in Figure 4.1, the flow rate of the wastewater was 19.2 L.d^{-1}, which made up 80% of the total inflow in the MBR. Additionally, the concentrate from the RO system returned continuously to the MBR at a flow rate of 4.8 L.d^{-1}, making up 20% of the total MBR inflow (wastewater + concentrate).

The recovery of global process is around 92%

4.3. Characterization of reverse osmosis concentrate

A comparison of the characteristics of the wastewater and the concentrate produced by the RO step before recirculation to the MBR is presented in Table 4.2. It may be important to point out the main components contained in the RO concentrate, which could increase the membrane fouling propensity in the MBR. Overall, the literature shows that the biological performance is generally high in the MBR process. Simply because of the large number of

microorganisms in the MBR, the uptake rates of pollutants can be increased. For example, the chemical oxygen demand (COD) removal rate was about 75-98% [37,50,65,76]; removal of nutrients, such as NH_4^+, was above 80% [50], higher 95% [68]. So, the concentrations of these components decrease significantly in the MBR permeate. Therefore, the component concentrations can be much lower in the concentrate produced by the RO process than in the wastewater (see Table 4.2). Thus the concentration of the MBR mixed influent could be reduced when the RO concentrate was recycled to the MBR.

In addition, all cations and anions passed through the MBR membrane. The concentration factor of RO concentrate was about 2.6 ± 0.1 in term of conductivity, so the concentrations of these ions in the RO concentrate were about 3 times higher than those in the original wastewater. More specifically, the concentration of Cl^- anion in the RO concentrate was almost 15 times higher than that in the wastewater. The reason for this issue may be related to the decrease of the pH in the RO process (from 8 to 6). These results clearly show the possibility that the concentration of these ions increase in the MBR mixed influent after the concentrate recirculation to the MBR.

In this study, the continuous recirculation of RO concentrate to the MBR could lead to a change in the characteristics of the components rejected by the RO. It was thus necessary to also obtain some information on the characteristics of RO concentrate during the experiment time, which could affect the MBR sludge and supernatant compositions. The results in Table 4.3 show that the concentration of most of parameters in RO concentrate increased continuously throughout this experiment.

Table 4.2 Characteristics of wastewater and RO concentrate before recirculation to the MBR

Parameters	Unit	Wastewater	RO concentrate before recirculation
pH	-	-	6
UV	-	-	0.59
Conductivity	$mS.cm^{-1}$	-	4.5
SS[a]	$g.L^{-1}$	0.3 ± 0.03	-[d]
COD[b]	$mg.L^{-1}$	830 ± 10	64 ± 2
DOC[c]	$mg.L^{-1}$	231 ± 5	19 ± 0.4
$N\text{-}NH_3$	$mg.L^{-1}$	22 ± 1	1.1 ± 0.05
Total nitrogen	$mg.L^{-1}$	52 ± 2.6	20 ± 1
Protein	$mg.L^{-1}$	33.4 ± 3.3	24 ± 5
Polysaccharide	$mg.L^{-1}$	7.4 ± 0.7	3.5 ± 0.4
Cations			
Na^+	$mg.L^{-1}$	174 ± 17	653 ± 65
K^+	$mg.L^{-1}$	14 ± 1.4	40 ± 4
Mg^{2+}	$mg.L^{-1}$	8.4 ± 0.8	21 ± 2
Ca^{2+}	$mg.L^{-1}$	124 ± 12	285 ± 29
Anions			
Cl^-	$mg.L^{-1}$	64 ± 6	989 ± 99
$N\text{-}NO_3^-$	$mg.L^{-1}$	0.2 ± 0.02	15 ± 1.5
SO_4^{2-}	$mg.L^{-1}$	42 ± 4	181 ± 18
$P\text{-}PO_4^{3-}$	$mg.L^{-1}$	3 ± 0.3	0.8 ± 0.08

(a) suspended solids; (b) chemical oxygen demand; (c) dissolved organic carbon; (d) no analysis

Higher concentrations in the RO concentrate were recorded after 11 days of recycling the concentrate to the MBR. For example, the concentrations of organic matters increased from 64 ± 2 to 92 ± 2 $mg.L^{-1}$ of chemical oxygen demand (COD) and from 19 ± 0.4 to 31 ± 0.6 $mg.L^{-1}$ of dissolved organic carbon (DOC). The concentrations of all ions varied greatly, especially Na^+ cation and Cl^- anion, which increased from 653 to 983 $mg.L^{-1}$ and from 989 to

1690 mg.L^{-1}, respectively. These results show why the MBR mixed influent characteristics can be changed after RO concentrate recirculation

Table 4.3 Characteristics of the concentrate produced by RO

Parameters	Unit	RO concentrate				
		Before recycling	1 d after recycling	3 d after recycling	8 d after recycling	11 d after recycling
pH	-	6	6	6	6	6
UV	-	0.59	0.58	0.6	0.7	0.7
Conductivity	$mS.cm^{-1}$	4.5	4.5	4.8	5.5	5.3
MLSS[a]	$g.L^{-1}$	-	-	-	-	-[d]
COD[b]	$mg.L^{-1}$	64 ± 2	66 ± 2	64 ± 2	80 ± 2	92 ± 2
DOC[c]	$mg.L^{-1}$	19 ± 0.4	22 ± 0.4	22 ± 0.4	30 ± 0.6	31 ± 0.6
$N\text{-}NH_3$	$mg.L^{-1}$	1.1 ± 0.05	1.1 ± 0.05	1.2 ± 0.05	1.1 ±0.05	1.1 ± 0.05
Total nitrogen	$mg.L^{-1}$	20 ± 1	20 ± 1	24 ± 1.2	23 ± 1.2	23 ± 1.2
Protein	$mg.L^{-1}$	24 ± 5	17 ± 3.4	23 ± 5	32 ± 3	35 ± 4
Polysaccharide	$mg.L^{-1}$	3.5 ± 0.4	3.5 ± 0.4	4.2 ± 0.4	5.4 ± 0.5	6.1 ± 0.6
Cations						
Na^+	$mg.L^{-1}$	653 ± 65	667 ± 67	693 ± 69	857 ± 86	983 ± 98
K^+	$mg.L^{-1}$	40 ± 4	41 ± 4	45 ± 5	59 ± 6	63 ± 6
Mg^{2+}	$mg.L^{-1}$	21 ±2	22 ± 2	24 ± 2.4	31 ± 3	33 ± 3
Ca^{2+}	$mg.L^{-1}$	285 ± 29	284 ± 28	299 ± 30	330 ± 33	335 ± 34
Anions						
Cl^-	$mg.L^{-1}$	989 ± 99	969 ± 97	1155±116	1489±149	1690±170
$N\text{-}NO_3^-$	$mg.L^{-1}$	15 ± 1.5	15 ± 1.5	16 ± 1.6	17 ± 1.7	18 ± 2
SO_4^{2-}	$mg.L^{-1}$	181 ± 18	181 ± 18	186 ± 19	228 ± 23	244 ± 24
$P\text{-}PO_4^{3-}$	$mg.L^{-1}$	0.8 ± 0.08	0.8 ± 0.08	2 ± 0.2	3.2 ± 0.3	4.6 ± 0.5

(a) mixed liquor suspended solids, (b) chemical oxygen demand, (c) dissolved organic carbon

Table 4.4 Characteristics of the MBR mixed influent before and after RO concentrate recirculation

Parameters	Wastewater ($mg.L^{-1}$)	MBR mixed influent ($mg.L^{-1}$)				
		after 1 d of recycling	after 3 d of recycling	after 8 d of recycling	after 11 d of recycling	after 14 d of recycling
COD	830 ± 10	677 ± 10	677 ± 10	679 ± 10	680 ± 10	682 ± 10
DOC	231 ± 5	189 ± 4	189 ± 4	190 ± 4	191 ± 4	191 ± 4
TN	52 ± 2.6	46 ± 2.3	46 ± 2.3	46 ± 2.3	46 ± 2.3	46 ± 2.3
$N\text{-}NH_3$	22 ± 1	17.8 ± 1	17.8 ± 1	17.8 ± 1	17.8 ± 1	17.8 ± 1
Protein	33.4 ± 3.3	31.5 ± 3.2	30 ± 3	31.3 ± 3	33 ± 3.3	34 ± 4
Polysaccharide	7.4 ± 0.7	6.6 ± 0.7	6.6 ± 0.7	6.8 ± 0.7	7 ± 0.7	7.1 ± 0.7
Cations						
Na^+	174 ± 17	270 ± 27	273 ± 27	278 ± 28	311 ± 31	336 ± 34
K^+	14 ± 1.4	19 ± 2	19 ± 2	20 ± 2	23 ± 2.3	23.7 ± 2.4
Mg^{2+}	8.4 ± 0.8	11 ± 1	11 ± 1	11.5 ± 1	13 ± 1.3	13 ± 1.3
Ca^{2+}	124 ± 12	156 ± 16	156 ± 16	159 ± 16	165 ± 17	166 ± 17
Anions						
Cl^-	64 ± 6	249 ± 25	245 ± 25	282 ± 28	349 ± 35	389 ± 39
$N\text{-}NO_3^-$	0.2 ± 0.02	3.2 ± 0.3	3.2 ± 0.3	3.4 ± 0.3	3.6 ± 0.4	3.8 ± 0.4
SO_4^{2-}	42 ± 4	70 ± 7	70 ± 7	71 ± 7	79 ± 8	82 ± 8
$P\text{-}PO_4^{3-}$	3 ± 0.3	2.6 ± 0.3	2.6 ± 0.3	2.8 ± 0.3	3 ± 0.3	3.3 ± 0.3

As shown in Table 4.4, an immediate reduction of the chemical oxygen demand (COD), from 830±10 to 677±10 $mg.L^{-1}$ was observed in the MBR mixed influent just 1 day after the start of

concentrate recirculation. This concentration then remained almost constant throughout the experiment. Similarly, the concentrations of dissolved organic carbon (DOC), total nitrogen and N-NH_3 in the MBR mixed influent also dropped after the RO concentrate was recycled to the MBR. This could be the cause of the change in the MBR global performance. Meanwhile, neither protein nor polysaccharide contents in the MBR mixed influent were impacted by the recirculation of RO concentrate. More detailed observation showed that a large increase was recorded in the concentrations of Na^+ cation and Cl^- anion. For example, after 14 days of RO concentrate recirculation, the amount of Na^+ ion was two times higher and Cl^- anion was six times higher than before recirculation of the RO concentrate. From these results, it can be hypothesized that the change of the protein or polysaccharide concentration in the MBR supernatant may be affected by the increase of the concentration of these ions. This impact will be discussed in more detail in the following sections.

To better understand the fouling mechanism in the MBR, the wastewater and RO concentrate were examined by HPLC-SEC analysis. Figure 4.2 indicates that only one peak in protein-like substances, corresponding to 10-100 kDa molecules, was found in the HPLC-SEC results for RO concentrate before it was added into the activated sludge (see Fig. 4.2a). Probably only small molecules were present in the composition of the RO concentrate. Similar results were observed in the RO concentrate composition during the time of the experiment (see Fig. 4.2b). This result confirms that the RO concentrate component contained one peak of 10-100 kDa protein-like substance. Meanwhile, two peaks were observed in the HPLC-SEC results for the wastewater (see Fig. 4.3), representing two groups of protein-like molecules, with molecular sizes of 100-1000 kDa and 10-100 kDa.

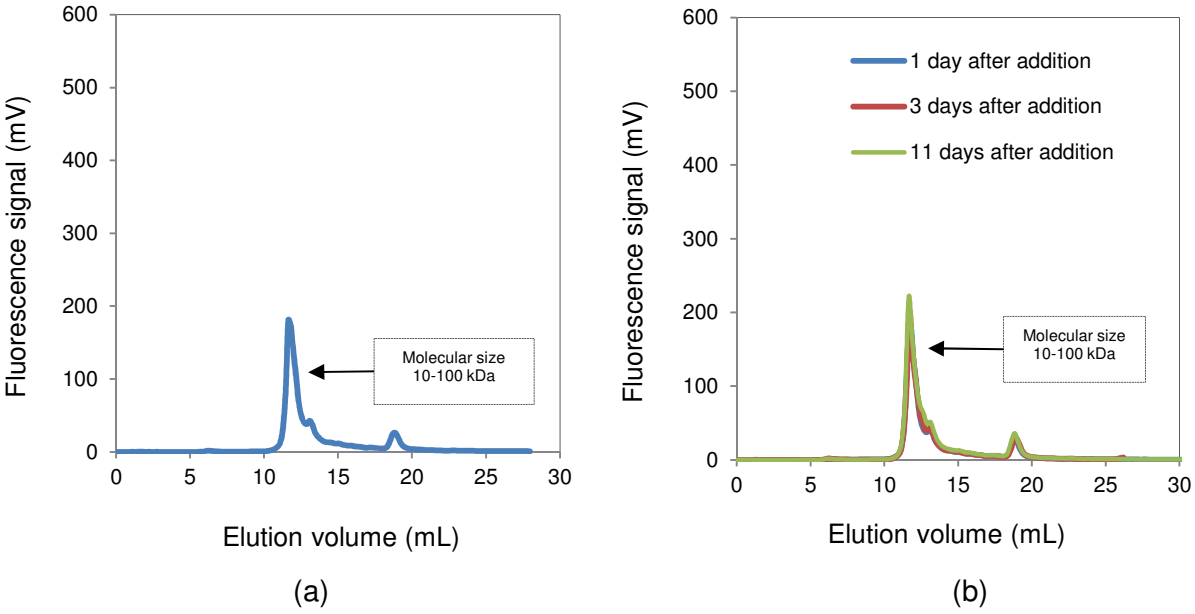


Figure 4.2. HPLC-SEC analysis of RO concentrates: (a) before concentrate recirculation; (b) after concentrate recirculation

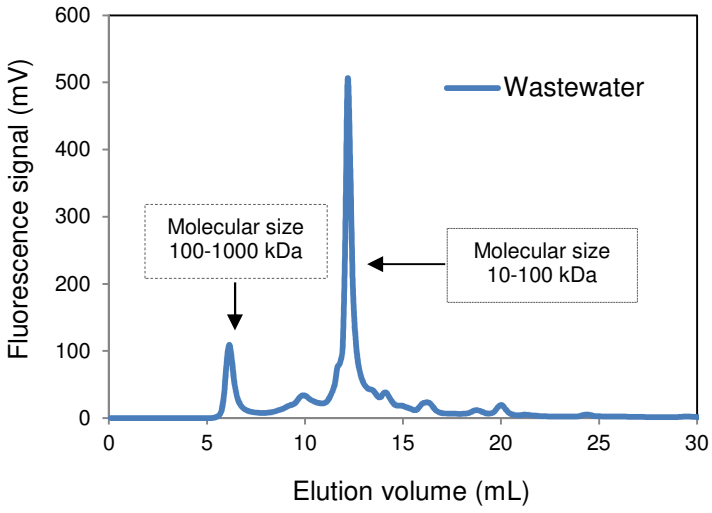


Figure 4.3. HPLC-SEC analysis of wastewater

4.4. Results and discussion

4.4.1. Effect of concentrate on the biomass characteristics

One of the important factors that affect membrane fouling in an MBR is the particle size distribution of biomass. So, the effect of RO concentrate on the biomass characteristics was

examined and discussed in our study. The floc size distribution was analyzed on the activated sludge taken from the MBR before and after the recirculation. As shown in Figure 4.4, no change was found for the particle size of the activated sludge after 1 day of recycling the concentrate to the MBR; it was about 96 µm. Similarly, after 3 days and 8 days of RO concentrate recirculation, it remained almost constant. However, the floc size had decreased slightly, from 100 to 80 µm, after 11 days of RO concentrate recycling (see Fig. 4.4). This data proves that the presence of concentrate in the MBR had a slight influence on the floc size distribution. As the MLSS concentration of the sludge in the MBR was quite stable during the experiment time (about 7.7±0.8 g.L^{-1}), it can be concluded that decay of sludge did not occur.

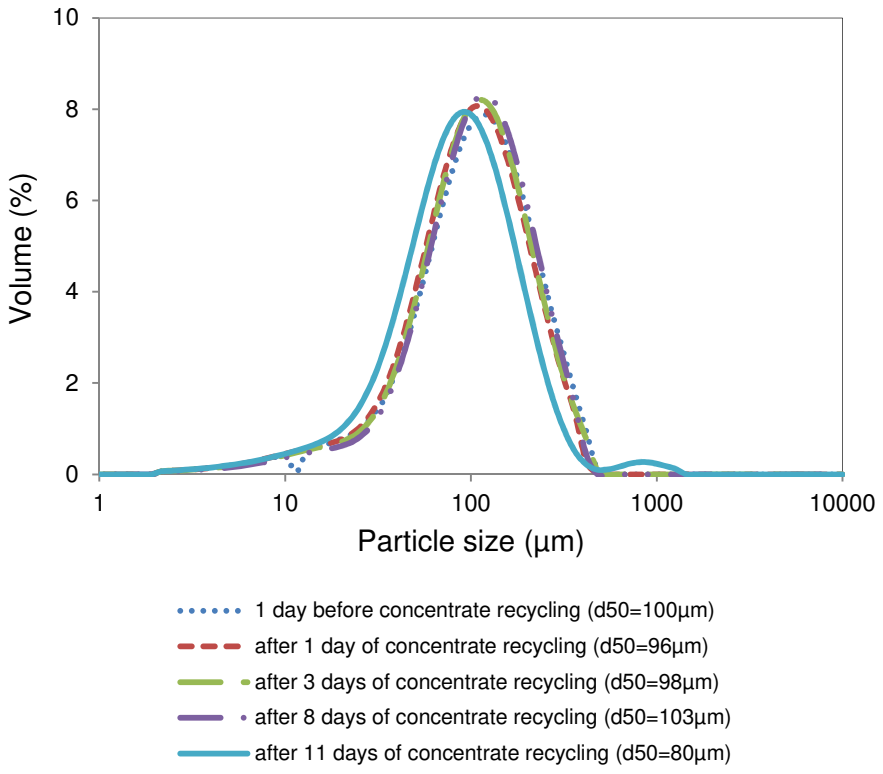


Figure 4.4 Effect of RO concentrate recirculation on sludge floc size distribution

4.4.2. Effect of RO concentrate on the MBR performances

In the literature, the performance of the MBR is usually evaluated by the conventional removal parameters (COD, N, P…). COD or TOC removal, nitrification (ammonium removal)

and total nitrogen removal are frequently reported. The detailed characteristics of the MBR mixed influent after the continuous recirculation of RO concentrate are given in Table 4.4.

The calculation of chemical oxygen demand (COD) process removal efficiency in the MBR was based on the COD concentration measured in the MBR influent before concentrate recirculation (wastewater) and the permeate produced by the MBR before and after RO concentrate recycling. In the wastewater, COD concentration was about 830±10 $mg.L^{-1}$ and 19±2 $mg.L^{-1}$ for the MBR permeate before the recirculation of RO concentrate. So high process efficiency, about 98%, of COD removal was observed in the MBR (see Fig. 4.5). One day after the start of RO concentrate recycling to the MBR, an increase of COD concentration was observed in the MBR permeate, from 19±2 $mg.L^{-1}$ to 28±2 $mg.L^{-1}$. However, no change was observed in the process removal efficiency of COD in the MBR. The COD concentration increased to 55±2 $mg.L^{-1}$ in the MBR permeate after 14 days of RO concentrate recirculation. Thus, a slight decrease was recorded in the process efficiency of COD removal in the MBR but it remained above 93%.

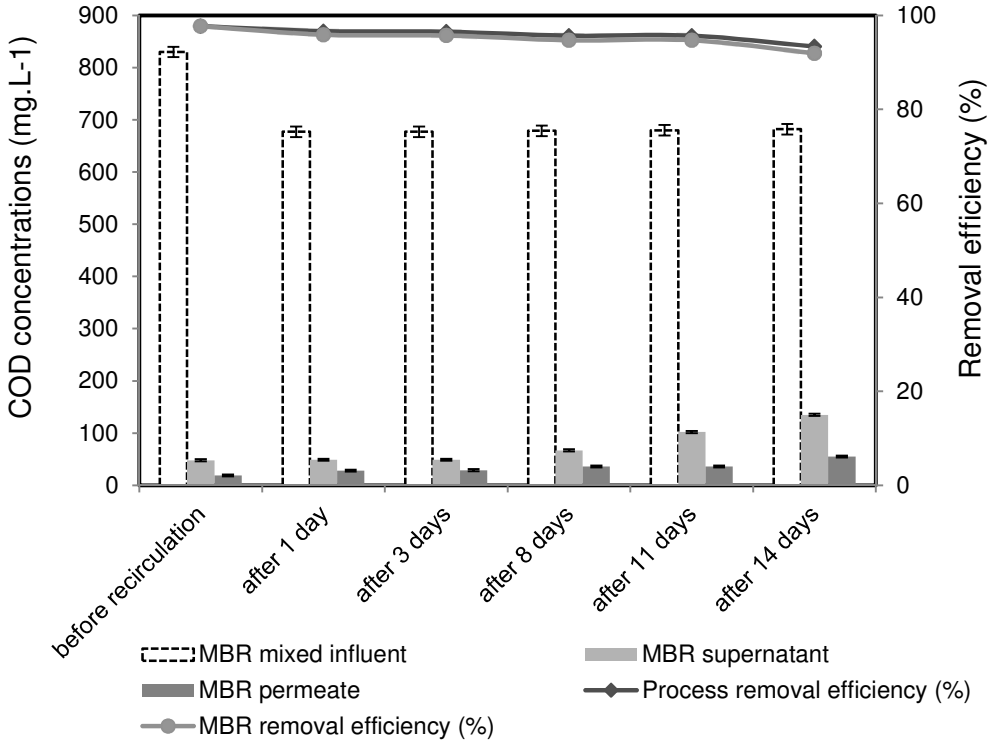


Figure 4.5. Effect of RO concentrate recirculation on chemical oxygen demand removal efficiency in the MBR

The effect of RO concentrate on the MBR removal efficiency of COD is also presented in Figure 4.5. The calculation of COD removal rate is based on the MBR mixed influent (wastewater + concentrate) and MBR permeate after the recirculation of RO concentrate. The results show a decrease of COD concentration in the MBR mixed influent after the RO concentrate had been recycled to the MBR, from 830 ± 10 to 677 ± 10 $mg.L^{-1}$ (see Table 4.4). After 1 day of RO concentrate recirculation, no significant change was found in the removal rate of COD concentration in the MBR (from 98% to 96%) and it remained almost constant in the next 10 days. After 14 days of RO concentrate recycling, a slight decrease of COD removal, to 92%, was recorded in the MBR.

These data demonstrate that the recirculation of RO concentrate could be a good solution for the management of RO concentrate.

Moreover, a decrease of biodegradable removal of chemical oxygen demand was observed in the MBR after 14 days of RO concentrate recirculation (from 94% to 80%). Whereas, the MBR membrane retention had increased after the recirculation of concentrate. These observations could demonstrate that RO concentrate recirculation did not significant affect the global performance in the MBR process.

The process efficiency of dissolved organic carbon (DOC) removal is also an important parameter for evaluating the filtering performance of the MBR membrane. Figures 4.6 shows the DOC concentration in the MBR supernatant and permeate before and after the recirculation of RO concentrate. Only 1 day after the recirculation of RO concentrate, a significant increase of DOC concentration was found, from 8.5±0.2 to 12±0.3 $mg.L^{-1}$ for the MBR supernatant and from 5.9±0.1 to 8.5±0.2 $mg.L^{-1}$ for the MBR permeate. The DOC concentrations remained constant for the next 3 days in both of the supernatant and the permeate in the MBR. After 11 days of RO concentrate recirculation, DOC concentration had increased to 11.7±0.2 $mg.L^{-1}$ for the MBR permeate and 22.2±0.5 $mg.L^{-1}$ for the MBR supernatant. A more significant increase, to 16.5±00.3 $mg.L^{-1}$ for the permeate and 29.5±0.6 $mg.L^{-1}$ for the supernatant of the MBR was observed after 14 days of RO concentrate

recycling. The increased dissolved organic carbon concentration in the MBR supernatant was probably related to the organic matter contained in the RO concentrate component, which was added directly into the MBR, or concerned biomass growth and cell lysis in the MBR.

Although the concentrations of DOC in both the permeate and supernatant of the MBR had increased, its calculated process removal efficiency, which is based on the DOC concentration measured in the MBR influent (wastewater) and the permeate produced by the MBR before and after the RO concentrate recycling, remained almost constant during the entire experiment. As can be seen in Fig. 4.6, before the concentrate was recycled to the MBR, the process efficiency of DOC removal was about 97% and its value did not change after 1 day of concentrate recirculation. In the next 10 days, its removal efficiency was almost constant. After 14 days of recycling of concentrate, a negligible drop in DOC process removal efficiency, to 93%, was found in the MBR.

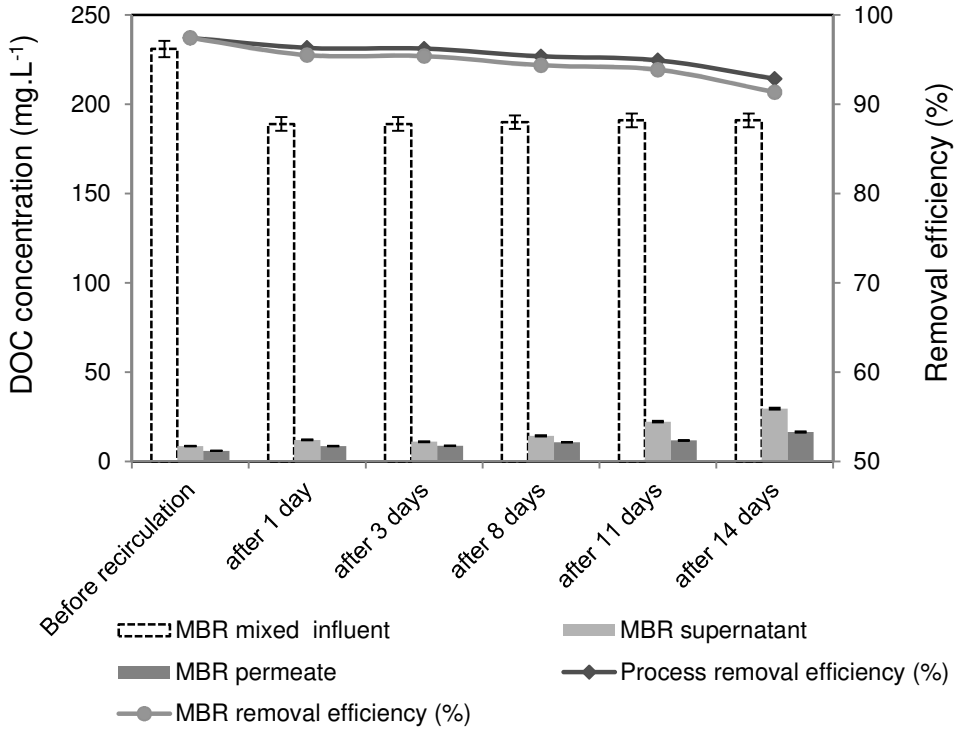


Figure 4.6. Effect of RO concentrate recirculation on dissolved organic carbon (DOC) removal efficiency in the MBR

The effect of RO concentrate on the MBR removal efficiency of dissolved organic carbon (DOC) is also shown in Figure 4.6. The calculated DOC removal rate is based on the DOC concentration in the MBR mixed influent and MBR permeate after the recirculation of RO concentrate. Although a decrease of DOC concentration occurred in the MBR mixed influent after concentrate recycling (from 231 to 189 $mg.L^{-1}$), no significant effect of concentrate was observed on the MBR removal efficiency of DOC : after 1 day of concentrate recycling, the removal rate of DOC was found to be similar to its value before the recirculation of concentrate (about 96%). After 14 days of RO concentrate recirculation, a slight decrease of its removal rate was recorded in the MBR. These results confirm that the recirculation of RO concentrate did not affect the DOC removal efficiency in the MBR.

In the MBR, the process efficiency of total nitrogen (TN) removal exceeded 85% (calculated as the percentage removed from the wastewater by the MBR membrane) before the RO concentrate recirculation (see Figure 4.7). After 1 day of RO concentrate recycling, a slight increase was observed in TN concentrations in the MBR permeate (from 7 to 9.5 $mg.L^{-1}$) and supernatant (from 13 to 16 $mg.L^{-1}$), so the process efficiency of TN removal in the MBR decreased slightly, to 80%. This efficiency was steady for the next three days. It decreased slightly to 75% after 8 days of concentrate recirculation to the MBR. A more important observation, after 14 days of recirculation of RO concentrate, was that the process efficiency of total nitrogen removal decreased significantly to 62%, the concentration of TN increasing to 20 $mg.L^{-1}$ in the MBR permeate and 25 $mg.L^{-1}$ in the MBR supernatant. This observation demonstrates that the recirculation of RO concentrate affected the process removal efficiency of total nitrogen in the MBR.

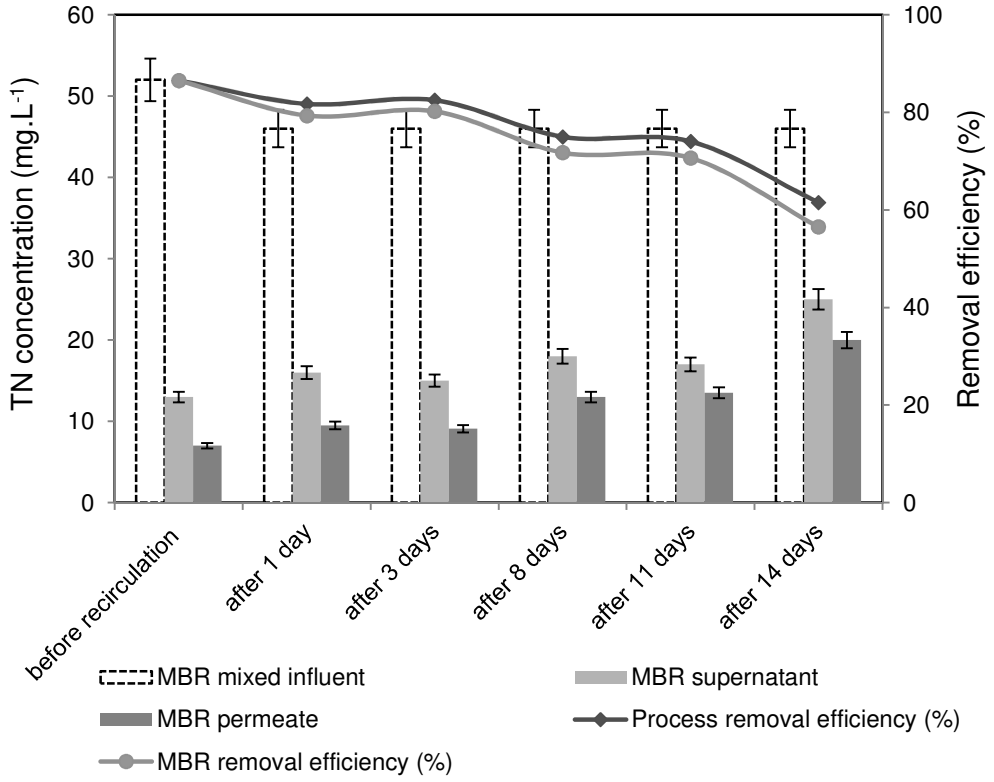


Figure 4.7. Effect of RO concentrate recirculation on total nitrogen removal efficiency in the MBR

The effect of RO concentrate on the MBR removal efficiency of total nitrogen (TN) is also presented in Figure 4.7. The calculated TN removal rate is based on the TN concentration measured in the MBR mixed influent and the permeate produced by the MBR after the RO concentrate recycling. Because a reduction of TN concentration in the MBR mixed influent (from 52 to 46 $mg.L^{-1}$) and its increase in the MBR permeate (from 7 to 9.5 $mg.L^{-1}$) occurred after 1 day of concentrate recirculation, so a slight effect of concentrate was observed on the MBR removal efficiency of total nitrogen. The removal rate of total nitrogen remained constant for the next three days, and then, it had decreased to 72% after 8 days of concentrate recycling. After 14 days of RO concentrate recirculation, an important decrease of its removal rate was recorded (about 57%) in the MBR. The results demonstrate that the recirculation of RO concentrate could have an important effect on global process efficiency of total nitrogen in the MBR.

In addition, the biodegradable removal of total nitrogen had decreased in the MBR after 14 days of RO concentrate recirculation (from 75% to 46%). Similarly, a decrease of total nitrogen retention by the membrane was observed in the MBR after RO concentrate recirculation.

In order to better understand the effect of RO concentrate on total nitrogen removal efficiency in the MBR, a few parameters, such as ammonia, nitrate and organic nitrogen also need to be examined as the formation of total nitrogen (TN) includes ammonia (NH_3), organic-nitrogen (org-N), nitrite (NO_2) and nitrate (NO_3). Nitrification is the biological transformation of ammonia to nitrate by oxidation, while denitrification is the conversion of nitrate to nitrogen gas, using the nitrate of heterotrophic bacteria as the oxygen source to break down organics under anoxic conditions.

The process removal efficiency of nitrogen-ammonia, which calculated as the percentage removed from the wastewater by the MBR membrane, generally exceeded 90% in the MBR process. Figure 4.8 shows that the concentration of nitrogen-ammonia ($N\text{-}NH_3$) in the MBR influent (wastewater) was around 21±1 $mg.L^{-1}$, before the RO concentrate was recycled to the MBR and it was much lower, reaching 1.2±0.06 $mg.L^{-1}$, in the MBR permeate. So, the process efficiency of nitrogen-ammonia removal was about 94%. The observation of a similarly high nitrogen-ammonia process removal efficiency during the entire experiment demonstrates that the recycling of RO concentrate to the MBR did not inhibit the nitrification process.

Although a decrease of nitrogen-ammonia concentration occurred in the MBR mixed influent after concentrate recycling (from 21 to 17.8 $mg.L^{-1}$), no significant effect of concentrate was observed on the MBR removal efficiency of nitrogen- ammonia: after 1 day of concentrate recirculation, the MBR removal efficiency of $N\text{-}NH_3$ was found to be similar to its value before concentrate recycling, about 93% (Fig. 4.8). The MBR removal efficiency of nitrogen ammonia, which is based on the $N\text{-}NH_3$ concentration measured in the MBR mixed influent and the permeate produced by the MBR after the recirculation of RO concentrate, was

steady in the MBR during the entire experiment. This finding again demonstrates that RO concentrate recirculation did not affect the nitrification process in the MBR.

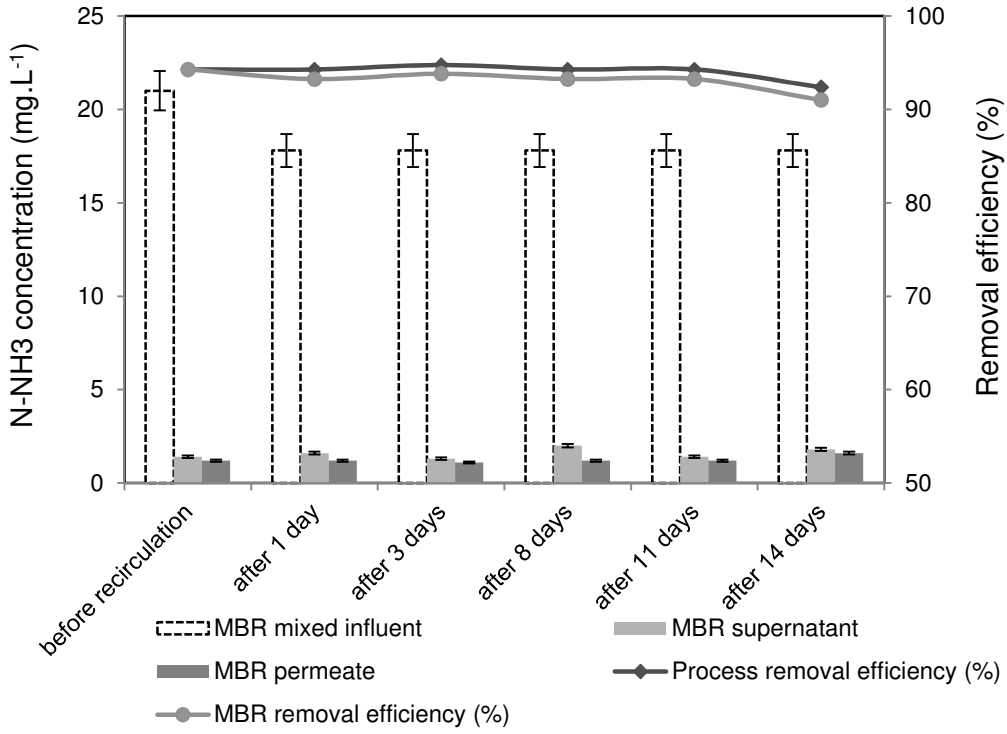


Figure 4.8. Effect of RO concentrate recirculation on nitrogen-ammonia ($N\text{-}NH_3$) removal efficiency in the MBR

In this study, the MBR process was designed to accommodate denitrification. However, the concentrations of nitrate ion in the MBR permeate and supernatant were higher than that in the MBR mixed influent both before and after the recirculation of RO concentrate (see Fig. 4.9). This finding demonstrated that the denitrification process was not completely in the MBR.

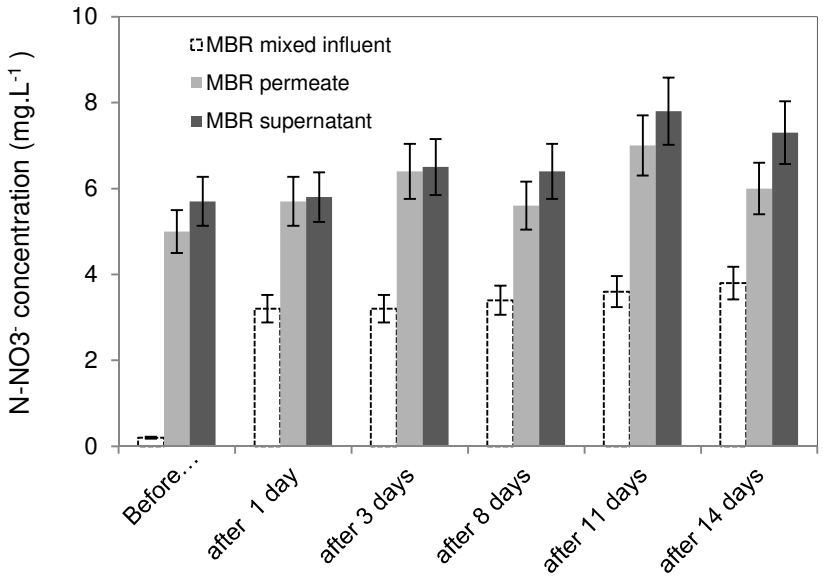


Figure 4.9. Effect of RO concentrate recirculation on the nitrate ion concentration ($N\text{-}NO_3^-$) in the MBR

In addition, the effect of RO concentrate recirculation on organic-nitrogen removal efficiency in the MBR is shown in Figure 4.10. In the MBR, a high process efficiency of organic-nitrogen removal was found, about 98% (calculated as the percentage removed from the wastewater by the MBR membrane) before the RO concentrate recirculation. After 1 day of RO concentrate recycling, a slight decrease of process removal efficiency of organic-nitrogen was observed in the MBR (from 98 to 90%). This efficiency decreased importantly to 52% after 14 days of concentrate recirculation to the MBR. This observation demonstrates that the recirculation of RO concentrate affected the process removal efficiency of organic- nitrogen in the MBR

Similarly, MBR efficiency of organic-nitrogen removal had decreased slightly after 1 day of RO concentrate recirculation, from 98 to 89% (see Fig. 4.10). The calculated organic-nitrogen removal efficiency is based on the organic-nitrogen concentration measured in the MBR mixed influent and the permeate produced by the MBR after the RO concentrate recycling. More importantly, after 14 days of the recirculation of RO concentrate, this

efficiency decreased to 38%. These finding again demonstrates that RO concentrate recirculation affected the organic-nitrogen removal efficiency in the MBR.

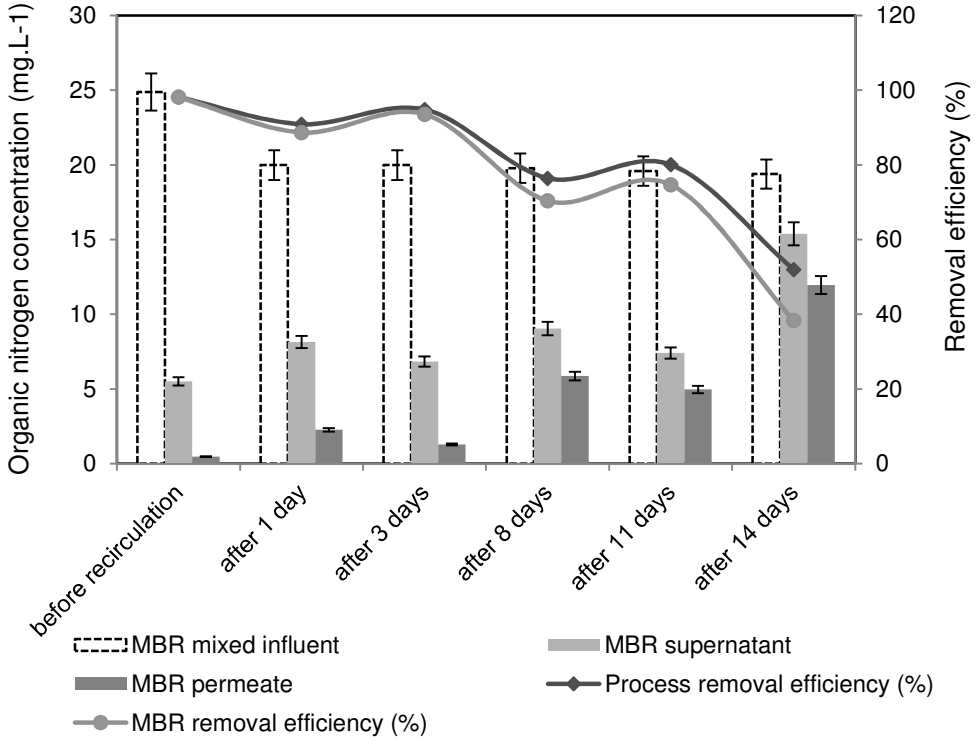


Figure 4.10. Effect of RO concentrate recirculation on organic- nitrogen removal efficiency in the MBR

These results could explain why the RO concentrate recirculation had a significant effect on the removal efficiency of total nitrogen in the MBR.

4.4.3. Effect of RO concentrate on salt composition of MBR supernatant

Table 4.5 gives an overview of the effect of the recirculation of RO concentrate on the salt composition of MBR supernatant. Generally, before the RO concentrate was recycled to the MBR, the concentrations of ions in the MBR supernatant were observed to be similar to their values in the wastewater. The exceptions were the increase of nitrate anion and the

decrease of $P\text{-}PO_4^{3-}$ anion found in the supernatant of the MBR as compared to their values in the wastewater.

Table 4.5. Effect of RO concentrate on salt composition of MBR supernatant

Parameters	MBR supernatant ($mg.L^{-1}$)					
	Before the recirculation	1 d after the recirculation	3 d after the recirculation	8 d after the recirculation	11 d after the recirculation	14 d after the recirculation
Cations						
Na^+	189 ± 19	261 ± 26	298 ± 30	293 ± 29	416 ± 42	421 ± 42
K^+	13 ± 1	17 ± 2	20 ± 2	21 ± 2	26 ± 3	27 ± 3
Mg^{2+}	6 ± 0.6	8.6 ± 0.9	10 ± 1	10.2 ± 1	13 ± 1	13 ± 1
Ca^{2+}	73 ± 7	106 ± 11	115 ± 12	114 ± 11	121 ± 12	120 ± 12
Anions						
Cl^-	60 ± 6	202 ± 20	257 ± 26	323 ± 32	354 ± 35	397 ± 40
$N\text{-}NO_2^-$	-	-	-	-	-	5±0.5
$N\text{-}NO_3^-$	5.7 ± 0.6	5.8 ± 0.6	6.5 ± 0.7	6.4 ± 0.6	7.8 ± 0.8	7.3 ± 0.7
SO_4^{2-}	47 ± 5	67 ± 7	75 ± 8	81 ± 8	86 ± 9	97 ± 10
$P\text{-}PO_4^{3-}$	0.8 ± 0.1	1.9 ± 0.2	0.9 ± 0.1	0.9 ± 0.1	1.8 ± 0.2	6.2 ± 0.6

(-) not detected

Just one day after the RO concentrate was recycled to the aerobic tank, the concentrations of almost all cations and anions significantly increased in the MBR supernatant. For instance, monovalent sodium ion increased from 189±19 to 261±26 $mg.L^{-1}$, and divalent Ca^{2+} ion from 73±7 to 106±11 $mg.L^{-1}$. In particular, there was 3.4 times more Cl^- anion than before the concentrate recirculation (increase from 60±6 to 202±20 $mg.L^{-1}$). The results can be related

the salt composition of the RO concentrate (see Table 4.3), where concentrations were much higher than in the wastewater. More importantly, the amounts of these ions had increased significantly in the MBR supernatant after 11 days of RO concentrate recirculation, and there was six times more Cl^- ion than before the concentrate recycling. The reason for this may be a continuous increase in ion concentrations in the concentrate produced by the reverse osmosis. The recirculation of this highly salt loaded stream back to the MBR would then change the salt composition in the MBR supernatant.

4.4.4. Effect of RO concentrate on the change in supernatant characteristics

The effects of RO concentrate on protein and polysaccharide concentrations in the MBR supernatant were attributable to their potential fouling capacity. Figure 4.11 shows that the recirculation of RO concentrate caused a slight rise (from 9.6±2 to 12±2.4 $mg.L^{-1}$) in the protein concentration in the MBR supernatant after only 1 day of recirculation of concentrate. After 3 days of RO concentrate recycling, the protein concentration had returned to a value similar the one it had before the RO concentrate recycling. A continuous increase was found in the protein concentration of the MBR supernatant during the experiment time: 14.4±3 $mg.L^{-1}$ after 8 days, 19±4 $mg.L^{-1}$ after 11 days, and 21±4 $mg.L^{-1}$ after 14 days of RO concentrate recirculation to the MBR.

In addition, a change was observed for the polysaccharide concentration in the MBR supernatant. Fig. 4.11 also shows that, 1 day after the concentrate was added to the MBR, the concentration of polysaccharide in the MBR supernatant had increased from 4±0.4 to 5.6±0.6 $mg.L^{-1}$. It increased continuously, reaching 9.7±1 $mg.L^{-1}$ after 11 days and 14.4±1.4 $mg.L^{-1}$ after 14 days of the addition of concentrate. As shown in Table 4.4, after the concentrate was recycled to the MBR, the changes in concentrations of protein and polysaccharide in the MBR mixed influent were negligible. Therefore, this increase of both protein and polysaccharide contents in the MBR supernatant seems unrelated to those in the RO concentrate and is probably related to the recycling back to the MBR of the stream highly

loaded with salt. Although only 1- 1.5 $g.L^{-1}$ of the chloride ion concentration was recycled to the MBR, its concentration in the MBR supernatant after the concentrate recirculation was from 3.4 to 6 times higher than before the concentrate recycling. This hypothesis is supported by results found in the literature: Reid et al [92] reported that a salt shock (from 0-1 $g.L^{-1}$ NaCl) resulted in increased protein content in the soluble microbial product (SMP) in the activated sludge for the MBR. Yogalakshmi and Joseph [125] demonstrated that, after a sodium chloride shock load of 5 $g.L^{-1}$, the protein concentration of SMP increased from 15 to 22 mg.gVSS. A possible explanation could be that an increase in salinity increases the solubility of proteins and carbohydrates, leading to the higher SMP concentrations observed. The increase in solubility due to the presence of a significant NaCl concentration can be attributed to electrostatic binding of salt ions to the protein and carbohydrate molecules. Another hypothesis for the increase of protein contents in the supernatant could be the release of protein-like SMPs by the microorganisms when facing the stress of toxic components contained in the RO concentrate.

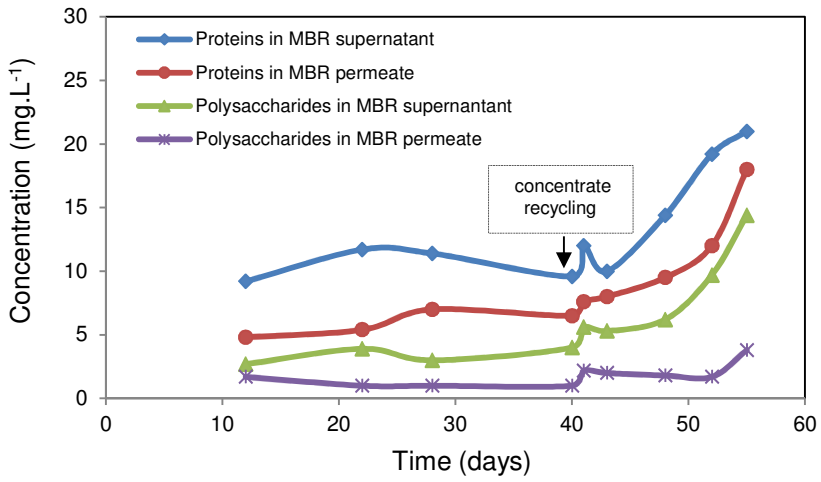


Figure 4.11. Effect of RO concentrate on supernatant composition in the MBR

To further investigate the effects of RO concentrate on the release of protein-like SMPs, MBR supernatants before and after addition of RO concentrate were analyzed by HPLC-SEC. Figure 4.12 shows the results of HPLC-SEC analysis of MBR supernatant before and 1 day after the RO concentrate addition. A significant increase, of about 25%, was observed in

protein-like substances corresponding to 10-100 kDa molecules in the MBR supernatant after only 1 day of RO concentrate addition but no change was found for 100-1000 kDa protein-like SMPs. Therefore, it seems that only small molecules were contained in the RO concentrate that was injected into the MBR (see Fig. 4.2a).

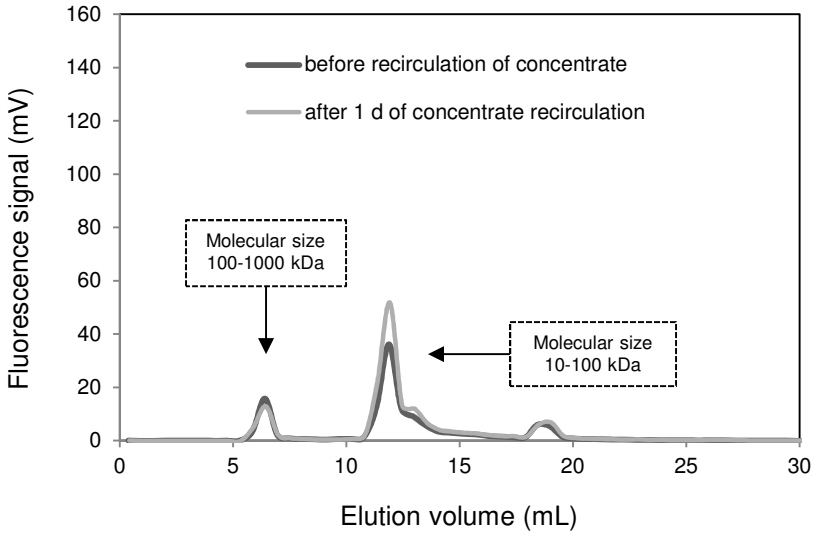


Figure 4.12. HPLC-SEC analysis of MBR supernatant before and 1 day after recirculation of concentrate: $[Na^{+}]$: 189±19 $mg.L^{-1}$ (before recirculation) and 261±26 $mg.L^{-1}$ (after 1 day of recirculation); $[Ca^{2+}]$: 73±7 $mg.L^{-1}$ (before recirculation) and 106±11 $mg.L^{-1}$ (after 1 day of recirculation), in MBR supernatant

The results in Figure 4.13 show that the continuous presence of RO concentrates could have effects on the protein-like SMPs between 1 day and 11 days of concentrate recirculation. A significant peak (about 48% higher than for the MBR supernatant 1 day after the addition of concentrate) was found in protein-like substances with a molecular size of 10-100 kDa. After between 8 days and 11 days of concentrate recycling to the MBR, a more significant increase for the peak heights of 100-1000 kDa protein-like SMPs was observed in the MBR supernatant.

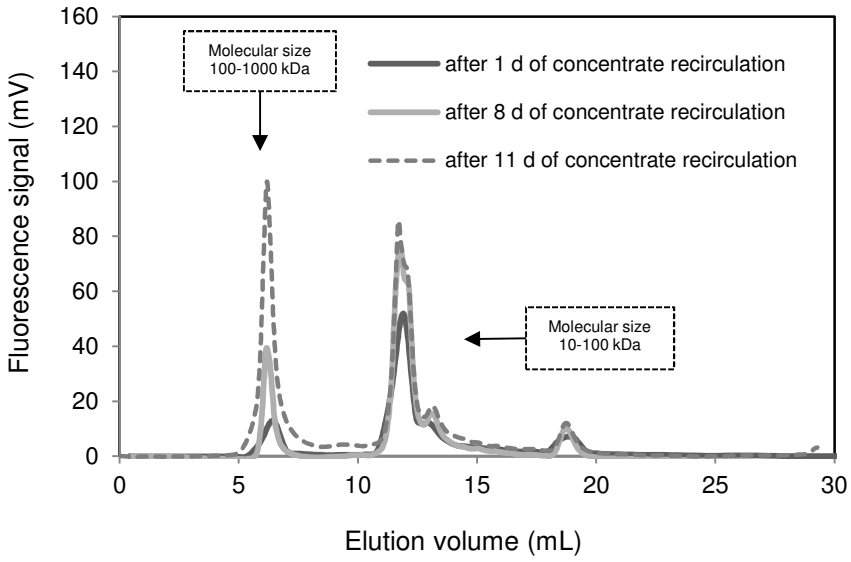


Figure 4.13. HPLC-SEC analysis of MBR supernatant after 1 day, 8 days and 11 days of concentrate recirculation: [Na^+]: 293±29 mg.L^{-1} (after 8 days of recirculation) and 416±42 mg.L^{-1} (after 11 days of recirculation); [Ca^{2+}]: 114±11 mg.L^{-1} (after 8 days of recirculation) and 121±12 mg.L^{-1} (after 11 days of recirculation), in MBR supernatant.

As shown in Figure 4.2b, there was only one peak of 10-100 kDa protein-like SMPs in the RO concentrate component. This suggests that the increase of small molecule proteins in the MBR supernatant could be directly related to the recirculation of RO concentrate. A possible explanation for the significant increase in 100-1000 kDa protein-like substances in the MBR supernatant may be that the microorganisms mainly released protein-like SMPs when facing the stress of toxic components, such as carbamazepine micropollutants that were contained in the RO concentrate.

4.4.5. Effect of RO concentrate on sludge and supernatant filterability test

To further investigate the fouling potential of the sludge and supernatant fractions, filterability tests were performed with samples taken from the MBR. Figure 4.14 shows that the fouling resistance in the sludge filterability test (using the 0.2 μm PS membrane) increased 1 day after the recirculation of concentrate. This result could concern the increased protein and

polysaccharide levels in the SMP. The fouling resistance of this membrane increased quite significantly after 8 days and 11 days of recirculation of RO concentrate.

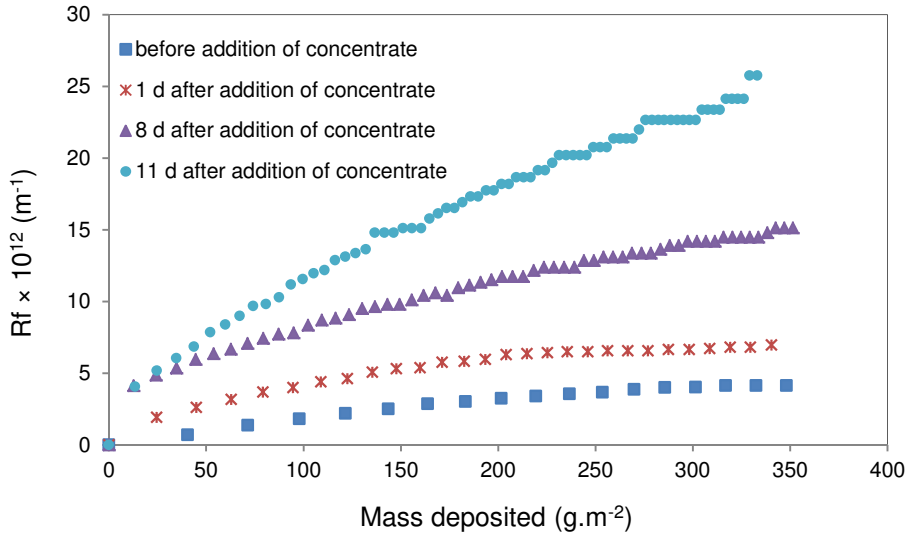
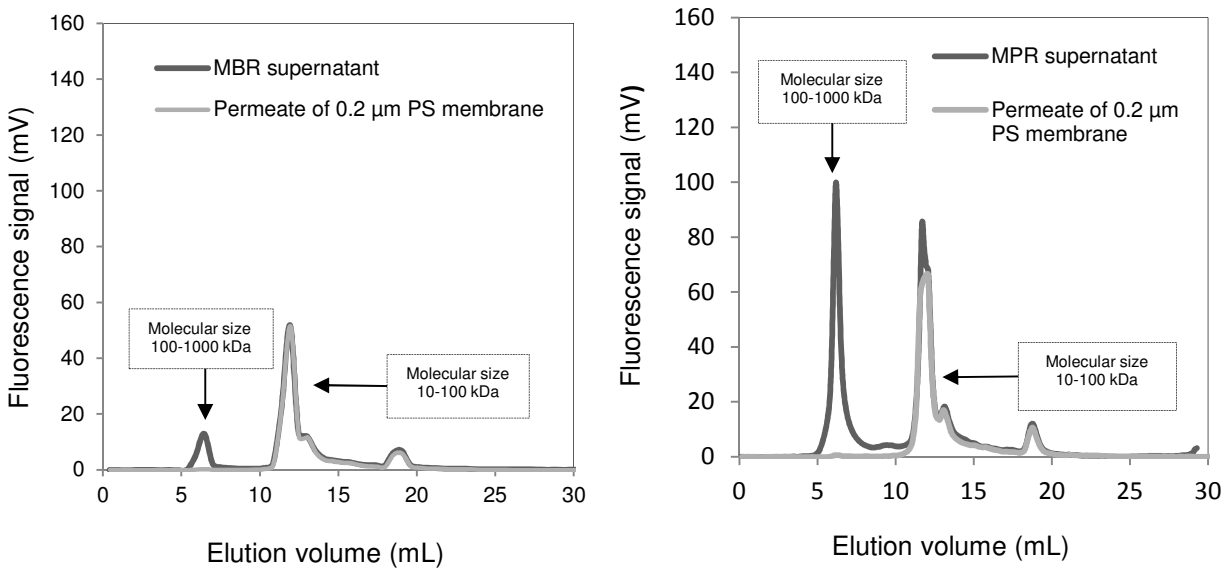


Figure 4.14. Effect of RO concentrate on sludge filterability test
(Mass deposited was calculated from the MLSS value of sludge)



(a) (b)

Figure 4.15. HPLC-SEC analysis of MBR supernatant and permeate observed in sludge filterability test at (a) 1 day; (b) 11 days after recirculation of RO concentrate

For a clearer explanation, an HPLC-SEC analysis of the MBR supernatant and permeate obtained on a 0.2 µm PS membrane was performed. As shown in Figure 4.15 a, b, the 0.2 µm PS membrane could reject almost all 100-1000 kDa protein-like SMPs, which could thus form a gel layer on the membrane surface. After 11 days of RO concentrate recycling, the membrane could partially retain the small protein-like SMPs, about 24% (see Fig. 4.15b) during sludge filtration. These results also point out the important role of large protein-like SMPs in the fouling propensity of the sludge

Table 4.6 Effect of RO concentrate on fouling propensity of sludge

Sludge filterability test	$\alpha C^{a} \times 10^{-13}$ (m^{-2})	$\alpha \times 10^{-12}$ ($m.kg^{-1}$)
Before recirculation of concentrate	9.7 ± 0.7	12 ± 0.9
After 1 day of recirculation of concentrate	15 ± 1.3	19 ± 2
After 8 days of recirculation of concentrate	25 ± 2	35 ± 3
After 11 days of recirculation of concentrate	49 ± 4	67 ± 5.6

(a) C is assumed to be MLSS value of sludge

The fouling layer was characterized by its specific resistance (α value) obtained from the filterability test. Table 4.6 shows the α value calculated in the filterability test of the sludge sample taken from the MBR. It can be seen that the α value had increased slightly 1 day after the RO concentrate started to be injected into the activated sludge and had increased significantly after 8 days of recirculation of concentrate. The specific resistance (α value) was very high after 11 days of the concentrate recycling. This result could stem from the increase of both small and macro molecules in the MBR supernatant after the recirculation of concentrate (see Fig. 4.13). This could modify the structure of the fouling layer formed during the sludge filtration. For a clearer explanation, an HPLC-SEC analysis of MBR supernatant and permeate obtained on a 0.2 µm PS membrane was also performed. As shown in Figure 15 b, after 11 days of concentrate recycling, the 0.2 µm PS membrane rejected almost all 100-1000 kDa protein-like SMPs. They could form a gel layer on the membrane surface. The membrane could partially retain the small protein molecules (only 24%) during the sludge

filtration. This observation demonstrates that the macro molecules could affect importantly the fouling resistance of the membrane.

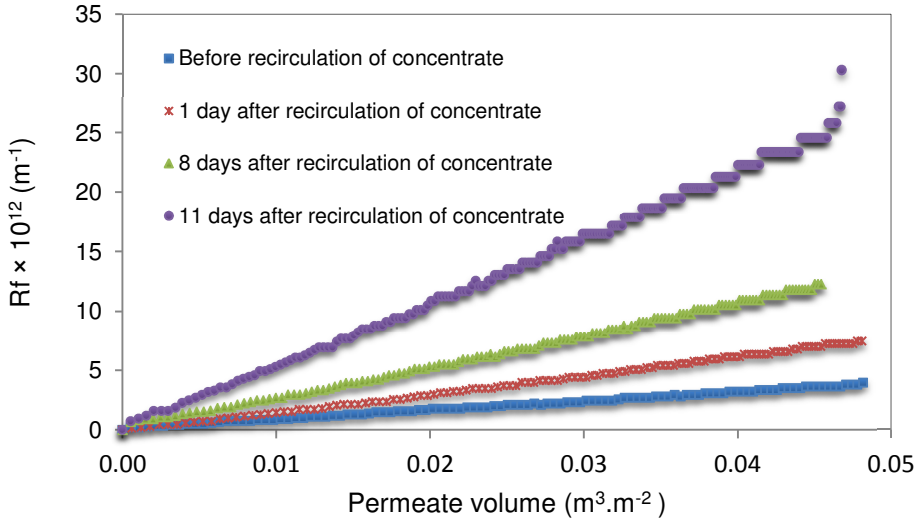


Figure 4.16 Fouling resistance of the 0.01 μm PES membrane as a function of the permeate volume ($m^3.m^{-2}$) in the supernatant filterability test

As in the filterability test of the sludge, the fouling resistance of the 0.01 μm PES membrane of the supernatant filterability test increased slightly after 1 day of recirculation of concentrate (see Fig.4.16) and after 11 days of RO concentrate recycling to the MBR; quite a significant increase was observed in the fouling resistance of this membrane. The results seem to be related to a change of fouling velocity of the 0.01 µm PES membrane after the concentrate was recycled to the MBR.

As shown in Figure 4.17, before the recirculation of the concentrate, the fouling velocity, which is based on the permeate volume produced by the filtration of this membrane (dRf/dV), as a function of peak-height in 100-1000 kDa range (mV) of the MBR supernatant, was 0.54×10^{14} ($m^{-1}.L^{-1}$), it increased to 0.83×10^{14} ($m^{-1}.L^{-1}$) after 1 day of concentrate recirculation. After 11 days of recycling of the concentrate, the fouling velocity increased to

3.3×10^{14} ($m^{-1}.L^{-1}$). These results could demonstrate that the large protein-like SMPs affected importantly the fouling velocity of this membrane.

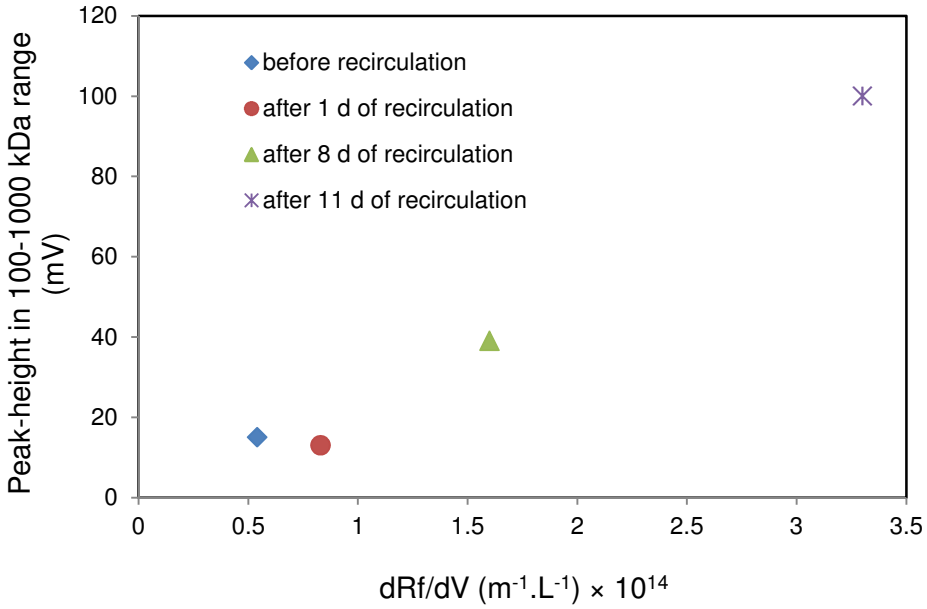


Figure 4.17. Fouling velocity *(based on the permeate volume of the filtration)* as a function of peak-height in 100-1000 kDa range (mV) of the MBR supernatant

To better understand the rise in supernatant fouling propensity, HPLC-SEC analysis of the supernatant and the corresponding permeate was performed on a 0.01 µm PES membrane. The result in Figure 4.18b demonstrates that, after 11 days of concentrate recirculation, only 10% of the 10-100 kDa protein-like SMPs could not pass through the 0.01 µm PES membrane The fouling mainly originated therefore from the almost complete rejection of 100-1000 kDa protein-like SMPs in the MBR supernatant by the 0.01 µm PES membrane, indicating that a gel layer could be formed on the surface of this membrane (see Figure 4.18a, b).

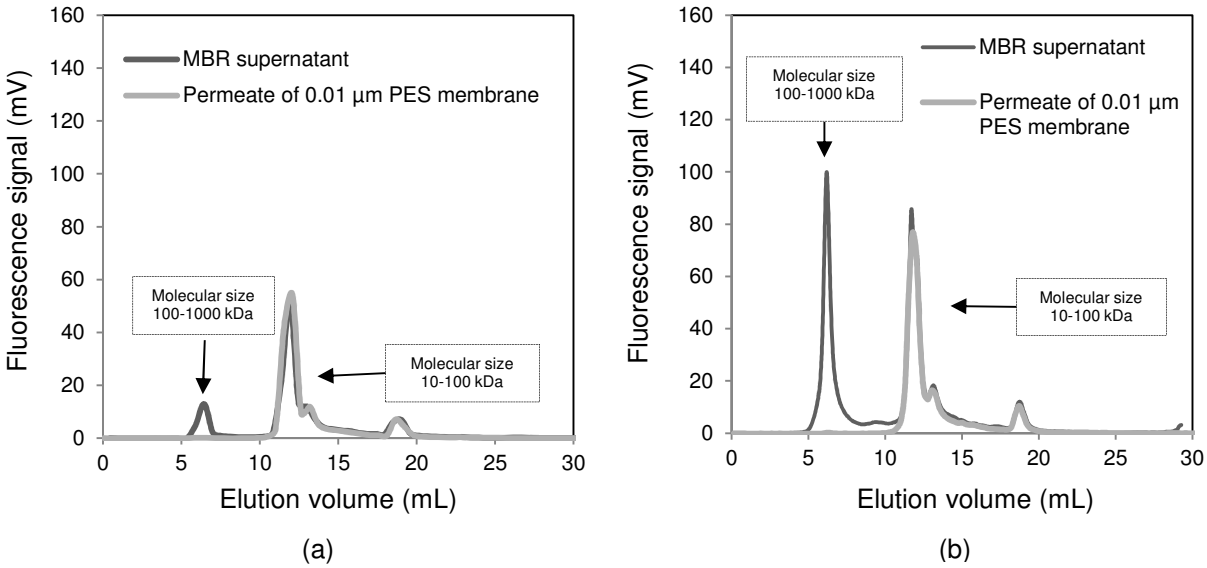


Figure 4.18. HPLC-SEC analysis of supernatant and permeate observed in supernatant filterability test at (a) 1 day; (b) 11 days of recirculation of concentrate

In addition, the fouling layer of a membrane formed during the filtration of the sludge supernatant may be related to the components retained in the supernatant. Table 4.7 shows the results of α value calculated from the retained protein concentration in the supernatant filterability test. After 1 day of the concentrate addition, an increase of the specific resistance was observed, from 1.7×10^{-16} to 4.7×10^{-16} ($m.kg^{-1}$). It increased to 6.9×10^{-16} ($m.kg^{-1}$) after 8 days and, after 11 days of the continuous recirculation of the concentrate, its value was 8×10^{-16} ($m.kg^{-1}$). This result seems not to originate from the rise of 10-100 kDa protein-like SMPs in the supernatant after the addition of RO concentrate, because all of them had passed through the 0.01 µm PES membrane during the filtration of the supernatant (see Fig. 4.18a, b). Thus, the fouling mainly originated from the almost complete retention of the 100-1000 kDa protein-like SMPs by the 0.01 µm PES membrane and the formation of the gel layer on the membrane surface. This result also points out the important role of macro molecules in the supernatant fouling propensity.

Table 4.7 Effect of RO concentrate on fouling propensity of supernatant

Supernatant filterability test	$\alpha C^a \times 10^{-13}$ (m^{-2})	$\alpha \times 10^{-16}$ ($m.kg^{-1}$)
Before recirculation of concentrate	7.3 ± 0.7	1.7 ± 0.2
After 1 day of recirculation of concentrate	15 ± 1	4.7 ± 0.5
After 8 days of recirculation of concentrate	25 ± 2	6.9 ± 0.7
After 11 days of recirculation of concentrate	52 ± 5	8 ± 0.8

(a) C was calculated from retained protein concentration

4.4.6. Effect of RO concentrate on MBR fouling

Membrane fouling in an MBR was examined by the variation of transmembrane pressure (TMP) during the filtration in the MBR. The changes of the TMP during operation of the MBR before and after the recirculation of RO concentrate in the MBR is presented in Figure 4.19.

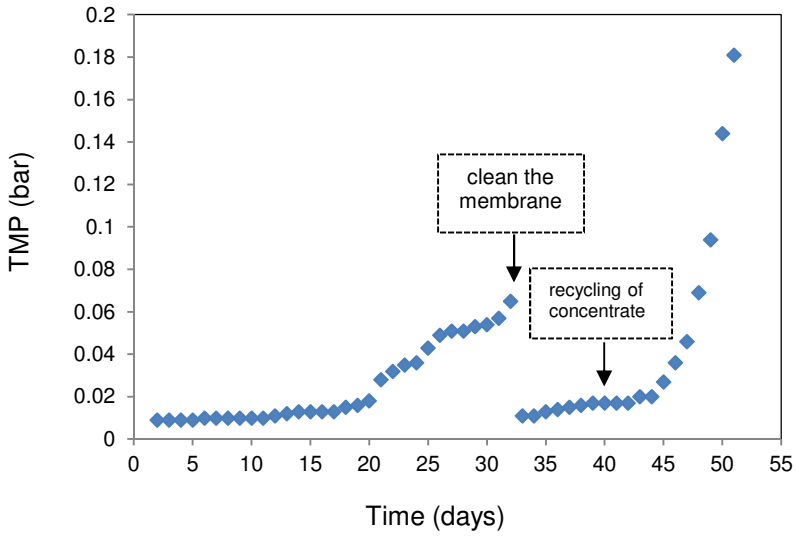


Figure 4.19. Effect of RO concentrate on MBR fouling

Before concentrate recycling to the MBR, continuously increasing TMP values were found in the MBR. On the 32nd day of the filtration time in the MBR, the membrane needed cleaning, because the TMP value had increased by 0.065 bar. Thus, the permeability of the MBR membrane decreased to 230 $L.h^{-1}.m^{-2}.bar^{-1}$. As shown in the literature, the MBR filtration

performance inevitably decreases with filtration time. This is due to the deposition of soluble and particulate materials on and in the membrane, attributed to the interactions between activated sludge components and the membrane. Moreover, the data in Figure 4.20a indicate that almost all the 100-1000 kDa protein-like SMPs could be retained by the membrane, whereas all the 10-100 kDa protein-like substances passed through. So, the increase of TMP during the filtration could be ascribed to the rejection of the large protein molecules by the MBR membrane. Consequently, these macromolecules could form a gel layer on the membrane surface.

The RO concentrate was recycled directly to the activated sludge on the 40th day of the experiment. As can be seen in Fig. 4.19, one day after the recirculation of RO concentrate, no change of the TMP was recorded in the MBR. On the 43rd day, after 3 days of concentrate recirculation, a slight rise of TMP occurred and the increase continued in the following days. Starting from 8 days after addition of concentrate (48th day), a quite significant increase of the TMP was observed in the MBR; its value was similar to that on the 32nd day of the filtration time in the MBR, about 0.069 bar. A more important observation was recorded in the MBR: after 11 days of concentrate recirculation, the TMP threshold value of 0.18 bar was too high for the MBR process. The faster TMP increase may have been caused by higher concentrations of dissolved and colloidal organic matter such as SMPs, as discussed in the previous section, indicating that the recirculation of RO concentrate elevated the fouling potential in the MBR.

Furthermore, HPLC-SEC analysis of MBR supernatant and permeate was performed after 11 days of recycling of concentrate. The results showed that the MBR membrane retained all the 100-1000 kDa protein-like substances, indicating that a fouling layer could be formed on the membrane surface. Additionally, a small amount of the 10-100 kDa substances were rejected by the membrane of the MBR (see Fig. 4.20b). These data point out the important role of large protein-like substances in fouling behavior in the MBR.

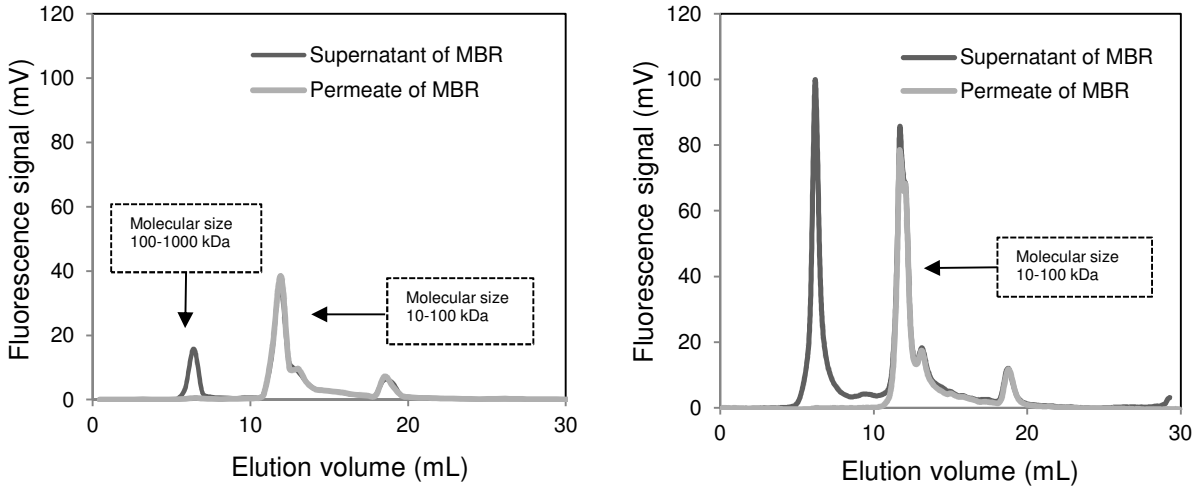


Figure 4.20. HPLC-SEC analysis: (a) supernatant and permeate of MBR before recirculation of concentrate; (b) supernatant and permeate of MBR after 11 days' recirculation of concentrate

4.4.7. Removal of selected pharmaceutical micropollutants in the MBR

4.4.7.1. Removal of selected pharmaceutical micropollutants in the MBR before the recirculation of concentrate

A large number of trace organic contaminants (TrOCs) may be present in the raw wastewater. These include steroid hormones, pharmaceuticals, personal care products, surfactants, pesticides, and disinfection by-products. Biodegradation and/or adsorption can be responsible for the removal of TrOCs by MBR treatment. Carbamazepine, diclofenac and ketoprofen were selected as the pharmaceutical micropollutants used in the examination of the elimination of micropollutants in the MBR before and after the RO concentrate recirculation.

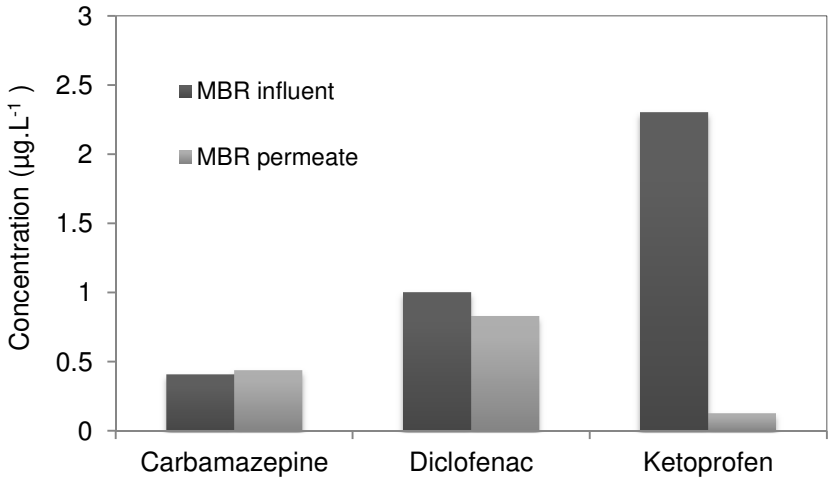


Figure 4.21. The removal rate of selected micropollutants in the MBR before concentrate recirculation

The results in Figure 4.21 further show that the removal rate of carbamazepine (CBZ) could be negative, indicating that the concentration of MBR permeate was higher than the influent concentration; its removal rate was about -7%. Several studies even reported higher CBZ concentration after the wastewater treatment by the MBR. This behavior can be explained by the cleavage of the glucuronide conjugates of carbamazepine leading to increasing CBZ concentration being obtained in the MBR permeate [12,100]. The low removal rate of CBZ in the MBR could be attributed to its low sorption and biodegradation capacities. Carbamazepine is not easily adsorbed onto sludge because it has a value of distribution coefficient (1.2 L kg_{SS}^{-1}) between water and sludge (K_d) far from the value required to produce significant sorption onto sludge (500 L kg_{SS}^{-1}) [66].

The low removal rate of diclofenac, about 17%, was also observed in the MBR. The explanation for the poor removal of diclofenac is similar to that for carbamazepine, although the diclofenac has a K_d (16 L kg_{SS}^{-1}) larger than that of carbamazepine. Furthermore, the resistance to biodegradation of diclofenac is lower than that of carbamazepine although both are classified in the same biodegradability group of below 0.1 L kg_{SS}^{-1} d^{-1} [12]

In contrast, a high removal rate of ketoprofen was obtained in the MBR. Figures 4.21 also present the concentrations of ketoprofen determined for the influent and permeate of the

MBR. The results show that ketoprofen was easily removed by the biological treatment. This compound was contained in the wastewater at a concentration of 2.3 $\mu g.L^{-1}$ (see Table 4.8). Its concentration was decreased to 0.13 $\mu g.L^{-1}$ after the filtration in the MBR. This indicated that ketoprofen is readily biodegradable in the MBR. Thus, the removal efficiency of ketoprofen was high, about 94%.

4.4.7.2. Characteristics of selected pharmaceutical micropollutants in the RO concentrate and the MBR mixed influent

In this study, three pharmaceutical micropollutants were selected to examine the capacity of the MBR to remove them. The results in Table 4.8 indicate that, before the concentrate was recycled to the MBR, carbamazepine concentration in the wastewater was 4 times lower than in the RO concentrate. In addition, the concentration of diclofenac was about 1 $\mu g.L^{-1}$, 3 times lower than in the RO concentrate. Thus, an increase in the concentration of these pharmaceuticals in the MBR mixed influent could occur after the concentrate was continuously recycled to the MBR.

After 1 day of concentrate recirculation, no significant change of either carbamazepine or diclofenac concentration was found in the RO concentrate (see Table 4.8). The concentration of carbamazepine increased from 1.6 to 2 $\mu g.L^{-1}$ and the increase was from 2.9 to 3.7 $\mu g.L^{-1}$ for diclofenac concentration, in the concentrate produced by RO. These data show why the increased concentration of both carbamazepine and diclofenac could be obtained in the MBR mixed influent with concentrate recycling. For example, after 11 days of concentrate recirculation, carbamazepine concentration in the MBR mixed influent increased from 0.41 to 0.7 $\mu g.L^{-1}$ and diclofenac concentration from 1 to 1.5 $\mu g.L^{-1}$, compared to values in the MBR before the recycling of RO concentrate.

In contrast, the ketoprofen concentration in the wastewater was 5 times higher than that in the RO concentrate. Moreover, no significant difference of ketoprofen concentration was found in the concentrate produced by RO throughout the experiment time. Therefore, a slight

decrease of the ketoprofen concentration was found in the MBR mixed influent, after the recycling of RO concentrate (see Table 4.8).

Table 4.8. Characteristics of selected pharmaceutical micropollutants in the RO concentrate and MBR mixed influent

RO concentrate ($\mu g.L^{-1}$)[a]						
Compounds	Before recirculation	After 1 day of recirculation	After 3 days of recirculation	After 8 days of recirculation	After 11 days of recirculation	After 14 days of recirculation
Carbamazepine	1.6	1.7	1.6	1.9	2.0	-[b]
Diclofenac	2.9	3.0	2.8	3.3	3.7	-
Ketoprofen	0.43	0.45	0.37	0.35	0.46	-
MBR mixed influent ($\mu g.L^{-1}$)						
Compounds	Wastewater	After 1 day of recirculation	After 3 days of recirculation	After 8 days of recirculation	After 11 days of recirculation	After 14 days of recirculation
Carbamazepine	0.41	0.65	0.67	0.65	0.7	0.73
Diclofenac	1.0	1.4	1.4	1.4	1.5	1.5
Ketoprofen	2.3	1.9	1.9	1.9	1.9	1.9

(a) analyzed by the Departmental Water Lab
(b) no analysis

The effect of RO concentrate recirculation on the elimination of selected micropollutants in the MBR will be presented in more detail and discussed in the following section.

4.4.7.3. *Effect of RO concentrate on the MBR removal efficiency of selected pharmaceutical micropollutants*

The impact of RO concentrate recirculation on the MBR removal efficiency of carbamazepine, which is based on the carbamazepine concentration measured in the MBR

mixed influent and MBR permeate after the recirculation of RO concentrate, is presented in Figure 4.22. The results show that, after 1 day of concentrate recycling, no change of the carbamazepine removal rate was observed. Compared to that in the MBR before the concentrate recirculation, its value remained negative, about -9%. However, after 3 days of concentrate recirculation, a higher removal of the CBZ was obtained in the MBR, about of 24%. It decreased by 8% after 14 days of the concentrate recycling to the MBR. This result suggested that carbamazepine removal efficiency in the MBR was not significantly affected by the recirculation of the RO concentrate.

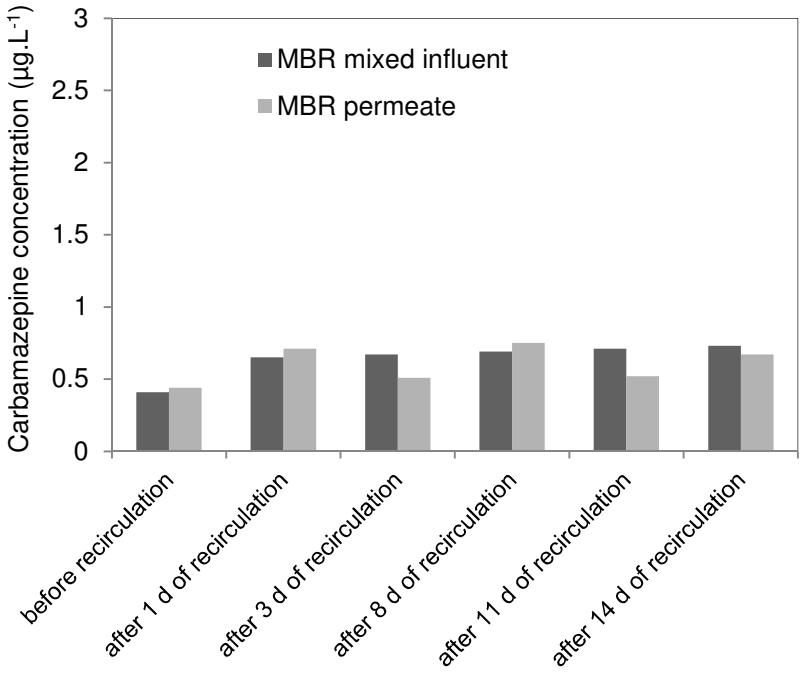


Figure 4.22. Carbamazepine concentrations in the MBR mixed influent and permeate before and after recirculation of RO concentrate

The MBR removal efficiency of diclofenac after the recirculation of reverse osmosis concentrate is shown in Figure 4.23. The results indicate that one day after the recycling of RO concentrate, diclofenac removal rate increased slightly, from 17 to 28%, in the MBR However, it decreased by 8% after 8 days of the concentrate recycling to the MBR. After 11 days of concentrate recirculation, an increase was found in the removal of diclofenac in the MBR, of about 33%, and it remained constant for the next 3 days. These results could be

related to the diclofenac concentration in the RO concentrate, which was presented and discussed in the section above.

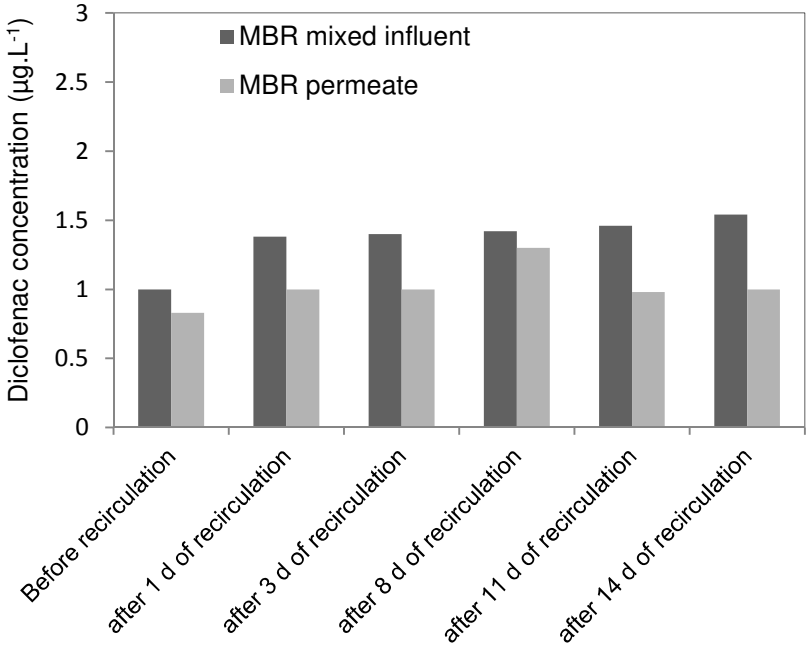


Figure 4.23. Diclofenac concentrations in the MBR mixed influent and permeate before and after recirculation of RO concentrate

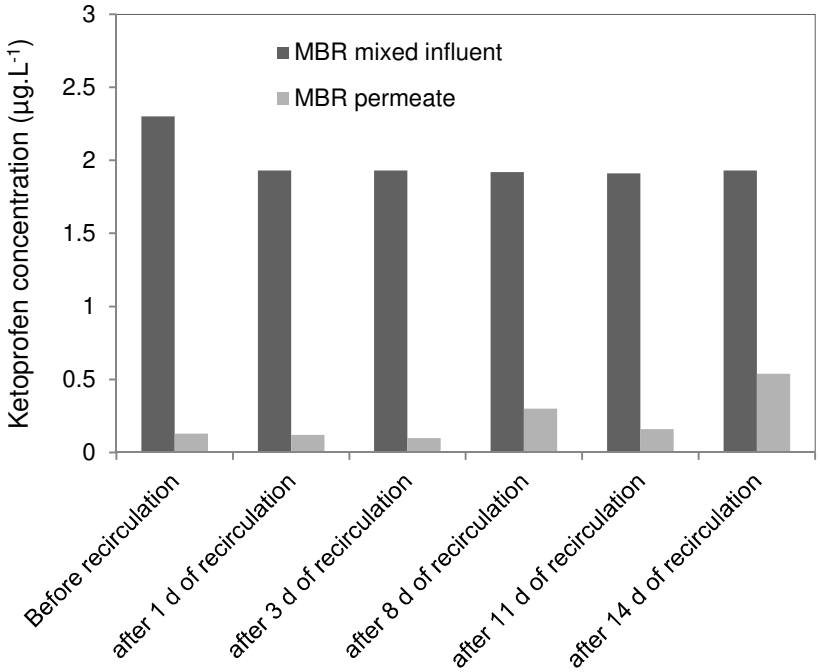


Figure 4.24. Ketoprofen concentrations in the MBR mixed influent and permeate before and after recirculation of RO concentrate

In contrast, high MBR efficiency of ketoprofen removal was obtained. The concentration of ketoprofen was decreased to 0.13 $\mu g.L^{-1}$ by the MBR before the concentrate was recycled (see Figure 4.24). The results show that ketoprofen was easily removed by the biological treatment. This compound was contained in the wastewater at a concentration of 2.3 $\mu g.L^{-1}$ (see Table 4.8). Thus, the MBR removal efficiency of ketoprofen was high, about 94%. Similar results were found after 1 day and 3 days of RO concentrate recycling to the aerobic tank. After 8 days, the removal rate of ketoprofen had dropped slightly to 82% and it continued to decrease, reaching 72% after 14 days of concentrate recirculation. This means that the presence of RO concentrate in the MBR had a slight influence on the elimination of ketoprofen.

4.5. Conclusion

A pilot-scale double membrane of MBR-RO was studied for wastewater treatment with recirculation of the RO concentrate to the MBR. In this study, the RO concentrate was continuously recycled directly into the aerobic reactor of the MBR. The experimental results revealed no significant effect on the removal efficiencies of chemical oxygen demand, dissolved organic carbon in the MBR when RO concentrate were recirculated to the MBR. Additionally, the recirculation of RO concentrate did not affect the nitrification process but affected the total nitrogen removal efficiency in the MBR.

The recirculation of highly salt loaded stream, which contained in the RO concentrate, back to the MBR would then the change the salt composition in the MBR supernatant. This observation could cause quite a significant increase in both protein and polysaccharide contents in the supernatant of the MBR. A slight increase was recorded in the MBR supernatant, from 9.6±2 to 12±2.4 $mg.L^{-1}$ for protein concentration and from 4±0.4 to 5.6±0.6 for polysaccharide concentration after 1 day of RO concentrates recycling. After 14 days of the recirculation of RO concentrate, these concentrations had increased significantly to 21±4 $mg.L^{-1}$ for protein and 14.4±1.4 for polysaccharide.

The results of HPLC-SEC analysis showed that, after only 1 day of RO concentrate recycling, a significant increase (about 25%) was found in 10-100 kDa protein concentration but no change was found for 100-1000 kDa protein-like SMPs. The continous presence of RO concentrates could have effects on the protein-like SMPs between 1 day and 11 days of concentrate recirculation. A significant peak (about 48% higher than for the MBR supernatant 1 day after the recirculation of concentrate) was found in protein-like substances with a molecular size of 10-100 kDa. After between 8 days and 11 days of concentrate recyling to the MBR, a more significant increase for the peak heights of 100-1000 kDa protein-like SMPs was obtained in the MBR supernatant.

The effects of concentrate produced by RO on the MBR fouling were examined. The TMP increase in the MBR was faster and higher after the recirculation of RO concentrate than before it. This result indicated that the recirculation of RO concentrate to the MBR induced enhanced membrane fouling.

In addition, an elimination of at least 94% was seen for ketoprofen before RO concentrate was recycled to the MBR. However, a decrease of 72% in the removal efficiency of ketoprofen was observed in the MBR after 14 days of the concentrate addition. Poor removal rates were found for carbamazepine and diclofenac in the MBR both before and after the recirculation of the RO concentrate. This means that the recirculation of RO concentrate to the MBR did not significantly affect the removal of selected pharmaceutical micropollutants efficiency in the MBR.

Finally, this combined process of MBR-RO with the RO concentrate recycled minimized unwanted discharge of a concentrated waste stream. However, to avoid the fast, large increase in TMP induced by the toxic components contained in the RO concentrate, more studies should be carried out with the objective of improving the RO concentrate treatment, e.g. by using oxidation by ozone and UV or adsorption on activated carbon before returning it to the MBR.

CHAPTER V

EFFECT OF OPERATING PARAMETERS ON PROCESS EFFICIENCY

Abstract

The combination of a membrane bioreactor (MBR) and reverse osmosis (RO) with recirculation of RO concentrate to the MBR was developed in the field of high-quality water reuse. The work reported here focuses on the recirculation of such concentrates in an MBR, paying specific attention to MBR fouling. The characteristics of RO concentrate (COD, DOC, TN, proteins, polysaccharides, cations, and anions) are analyzed and compared between two sets of experiments.

The results demonstrate that the removal efficiencies of chemical oxygen demand (COD) at the difference flow rates of concentrate were greater than 93%. Similar results for the dissolved organic carbon removal efficiency were observed in the MBR. The recirculation of RO concentrate with stable characteristics did not inhibit the nitrification process.

Besides, the effects of RO concentrate on the supernatant compositions in the MBR depend on the characteristics of RO concentrate recirculation to the MBR. Additionally, a variation of the fouling mechanisms in the MBR operated under different concentrate flow rate and characteristics was also observed.

In order to obtain sustainable operation of the integrated MBR-RO process with the RO concentrate recirculation, it is therefore very important to select the most appropriate operating parameters and effective solutions for the mitigation of membrane fouling in the MBR.

Key words: Reverse osmosis, concentrate characteristics, membrane filtration performance, membrane fouling,

5.1. Introduction

So far, few studies have focused on the impacts of reverse osmosis (RO) or nano-filtration (NF) concentrate recirculation to the MBR in an integrated MBR-RO/NF process for wastewater treatment and reuse [51,63,68,109,118]. Although recycling concentrated constituents could impose an inhibitory effect on the biomass and suppress microbial respiratory activities, results obtained suggested that operating the MBR (in the MBR-RO process) at an F/M ratio below 0.03 g TOC/g VSS.day could yield an effluent quality comparable to that achievable without concentrate [63]. They found that, when the RO concentrate is sent back to the MBR, the average MLSS and MLVSS concentrations are higher than those before the addition of RO concentrate. The total organic carbon (TOC) mass removal rate in the MBR increased from 5.72 to 6.44 $g.d^{-1}$ and a slight increase of total solids concentration was found in the aerated rotating membrane bioreactor system (ARMS) effluent after the recirculation of RO concentrate [109]. According to Kappel et al [51], a faster increase of the TMP in the MBR was observed after the NF concentrate recirculation, compared to that without the concentrate. They also indicated that an increase of the dissolved and colloidal chemical oxygen demand (COD) was observed in the MBR supernatant after the addition of NF concentrate. Li et al [68] reported that the NF/RO concentrate recirculation had a negative impact on the nitrification removal efficiency in the MBR: the NH_4^+ removal rate was steadily higher than 95% throughout the entire experiment.

Nevertheless, little attention has been paid to the effect of RO/NF concentrate at different flow rates and characteristics and concentrate backflow ratios recycled to the MBR. Li et al [68] investigated the optimization of the nano-filtration concentrate backflow ratio and the influence of NF concentrate on the MBR. They reported that the backflow ratio was optimized at 60% based on the removal rates of chemical oxygen demand (COD) and NH_4^+ by the MBR.

Therefore, in the present study, the combined MBR-RO process was operated at different flow rates of both MBR feed and RO concentrate recirculation and with various

characteristics of the RO concentrate recycled to the MBR. To compare the effects on filtration performance and membrane fouling between the two sets of experiments, which will be presented in the next sections, the characteristics of RO concentrate were analyzed and a simultaneous comparison was made of their effects on the efficiency of chemical oxygen demand, dissolved organic carbon removal and nitrification process. In addition, the change in the supernatant composition in the MBR after the recirculation of RO concentrate was examined and compared between the two sets of experiments. More specifically, the impacts of RO concentrate recirculation, with its various characteristics, on the fouling propensity in the MBR were evaluated in the present work.

5.2. Lab scale MBR-RO set up

Two reactors were contained in the lab-scale MBR: an anoxic reactor (5.4 L) and an aerobic reactor (12.6 L). The aerobic reactor was equipped with one submerged, flat-sheet, microfiltration membrane (Kubota, Japan) having an effective filtration area of 0.1 m^2 and a nominal pore size of 0.2 µm. The instantaneous permeate flux was fixed at 15 LMH (liter/m^2/hour) with relaxation steps of 4 min performed every 8 min, leading to a net permeate flux of 10 LMH. The reactor was aerated with big air bubbles at a flow rate of 1.5 $L.min^{-1}$, i.e. SAD_m of 0.9 m^3 $air.h^{-1}.m^{-2}$. Another aeration system with fine air bubbles was also used to maintain the dissolved oxygen concentration in the sludge at about 2-3 $mg.L^{-1}$. The sludge recirculation was fixed at 4 $L.h^{-1}$. The MBR was operated with a 45 day SRT (sludge retention time); this means that the sludge was discharged at flow rate of 0.4 $L.d^{-1}$.

The MBR-RO process combining a membrane bioreactor (MBR) with a reverse osmosis (RO) membrane, where the MBR can be considered as the secondary treatment with the MBR permeate serving as feed for the tertiary treatment membrane (RO). The MBR was fed with the wastewater taken from a wastewater treatment plant close to Toulouse, France, after a primary physical treatment, to which RO concentrate was added.

The variation of the characteristics of RO concentrate that was recycled to the MBR was examined to evaluate its effects on the global performance as well as the fouling behavior in the MBR. For this purpose, two sets of experiments were performed in our study (see Figure 5.1)

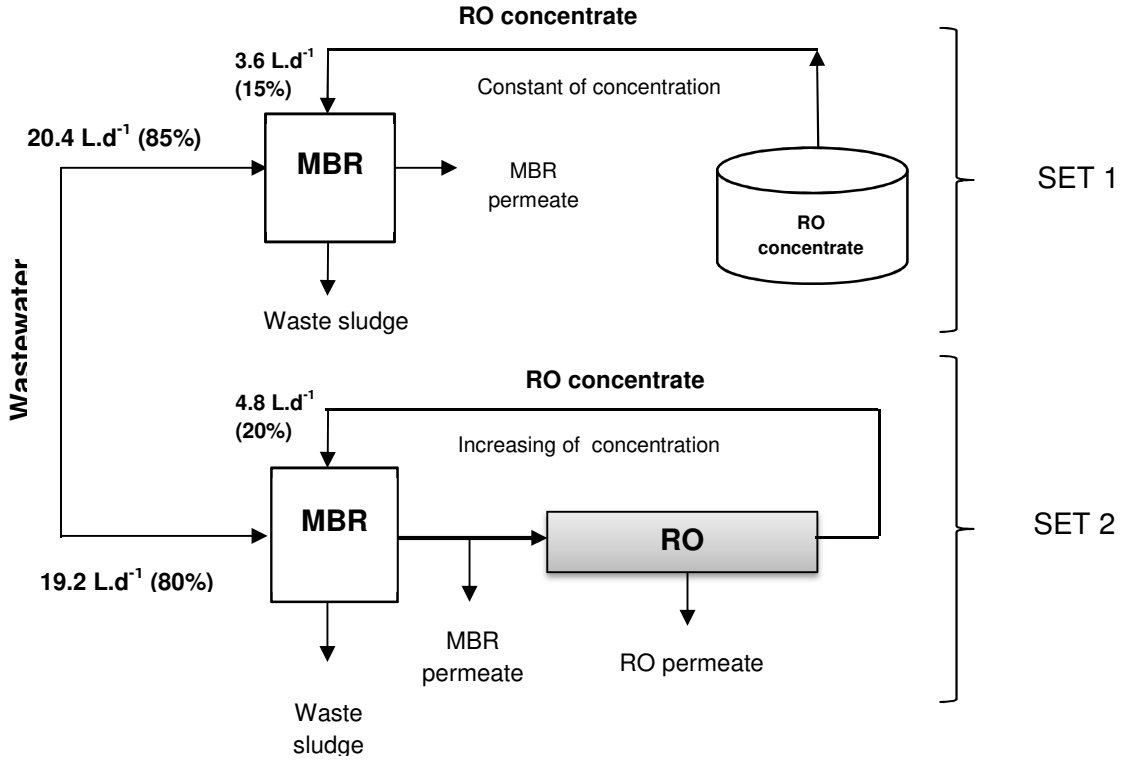


Figure 5.1 Process scheme of the MBR systems with the recirculation of RO concentrate at different flow rates and characteristics

In the *first set of experiments,* the MBR received 20.4 $L.d^{-1}$ of wastewater. The MBR permeate was collected over 3 weeks and used as inflow to the RO system. The concentrate produced by RO was taken and kept in the storage tank before being continuously recycled to the MBR at a flow rate of 3.6 $L \cdot d^{-1}$. The concentration factor of RO concentrate in this case was 2.5±0.2. The RO concentrate made up 15% of the total inflow (wastewater + concentrate) and the wastewater 85%. The characteristics of RO concentrate were stable during the entire experiment (see Table 5.2)

In the *second set of experiments,* the RO concentrate was fed continuously to the MBR at a flow rate of 4.8 $L.d^{-1}$ in addition to the wastewater. The concentrate made up 20% of the total MBR inflow. The concentration factor of RO concentrate was around 2.6 ± 0.1. In this experiment, the continuous recirculation of RO concentrate to the MBR could lead to a change in the characteristics of the components rejected by the RO. The variation between the two experimental sets of characteristics of the RO concentrate recycled to the MBR could lead to different impacts of concentrate on the MBR performance. It is necessary to evaluate and discuss the concentrate characteristics so that we can choose the optimal operating parameters for the integrated MBR-RO process.

The detailed characteristics of the wastewater from the two sets of experiments are given in Table 5.1. The results show that the concentrations of chemical oxygen demand (COD), nitrogen-ammonia ($N\text{-}NH_3$) and protein were similar in the wastewater of both sets of experiments. The dissolved organic carbon (DOC) concentration in the wastewater of Set 1 was lower than in Set 2. The concentrations of monovalent cations Na^+ and K^+ and of anion Cl^- were found in both sets of experiments. However, divalent cation Mg^{2+} concentration in the second set was twice that in the first set of experiments; and Ca^{2+} concentration in Set 1 was one third of that in Set 2.

Table 5.1 Characteristics of the wastewater ($mg.L^{-1}$)

Parameters	Set 1	Set 2
Suspended solids (SS)	420 ±42	300 ± 30
Chemical oxygen demand (COD)	799 ± 10	830 ± 10
Dissolved organic carbon (DOC)	155 ± 3	231 ± 5
Total nitrogen (TN)	35 ± 1.8	52 ± 2.6
Nitrogen-ammonia ($N\text{-}NH_3$)	21 ± 1	22 ± 1
Proteins	41.4 ± 4	33.4 ± 3.3
Polysaccharides	-	7.4 ± 0.7
Cations		
Na^+	160 ± 16	174 ± 17
K^+	8.4 ± 0.8	7.7 ± 0.8
Mg^{2+}	4.1 ± 0.4	8.4 ± 0.8
Ca^{2+}	44 ± 0.4	124 ± 12
Anions		
Cl^-	71 ± 7	64 ± 6
$N\text{-}NO_3^-$	1.1 ± 0.1	0.2 ± 0.02
SO_4^{2-}	18.5 ± 1.9	42 ± 4
$P\text{-}PO_4^{3-}$	0.2 ± 0.02	3 ± 0.3

5.3. Characteristics of the reverse osmosis concentrate and the MBR mixed influent after recirculation of concentrate

The characteristics of the concentrate produced by the RO step between the first and second sets of experiments before recirculation to the MBR are compared in Table 5.2. Overall, the literature shows that the biological performance is generally high in the MBR process. Simply because of the large number of microorganisms in the MBR, the uptake rates of pollutants can be increased. For example, the chemical oxygen demand (COD) removal rate was about

75-98%. Therefore, the concentrations of these components were much lower in the concentrate produced by the RO process than in the wastewater. Thus the concentration of the MBR influent could be reduced when the RO concentrate was recycled to the MBR.

Table 5.2 Characteristics of RO concentrate from two sets of experiments

Parameters	Set 1 ($mg.L^{-1}$)	Set 2 ($mg.L^{-1}$)				
		Before recirculation	After 1 day of recirculation	After 3 days of recirculation	After 8 days of recirculation	After 11 days of recirculation
COD	42±2	64±2	66±2	64±2	80±2	92±2
DOC	16±0.3	19±0.4	22±0.4	22±0.4	30±0.6	31±0.6
$N\text{-}NH_3$	0.95±0.05	1.1±0.05	1.1±0.05	1.2±0.05	1.1±0.05	1.1±0.05
TN	30±1.5	20±1	20±1	24±1.2	23±1.2	23±1.2
Protein	20±4	24±5	17±3.4	23±5	32±3	35±4
Polysaccharide	2.7±0.3	3.5±0.4	3.5±0.4	4.2±0.4	5.4±0.5	6.1±0.6
Cations						
Na^+	560±56	653±65	667±67	693±69	857±86	983±98
K+	36±3.6	40±4	41±4	45±5	59±6	63±6
Mg^{2+}	17±1.7	21±2	22±2	24±2.4	31±3	33±3
Ca^{2+}	25±2.5	285±29	284±28	299±30	330±33	335±34
Anions						
Cl^-	338±34	989±99	969±97	1155±116	1489±149	1690±169
$N\text{-}NO_3^-$	11±1	15±1.5	15±1.5	16±1.6	17±1.7	18±2
SO_4^{2-}	108±11	181±18	181±18	186±19	228±23	244±24
$P\text{-}PO_4^{3-}$	0.04±0.004	0.8±0.08	0.8±0.08	2±0.2	3.2±0.3	4.6±0.5

The results in Table 5.2 show no significant difference between Set 1 and Set 2 in the concentrations of chemical oxygen demand (COD), dissolved organic carbon (DOC), nitrogen-ammonia, protein or polysaccharide before the concentrate was recycled to the MBR. The only exception was a lower total nitrogen (TN) concentration in Set 2 than in Set 1.

In addition, almost all cations and anions passed through the MBR membrane. The concentration factor of RO concentrate was around 3 for both of the experimental sets, so the concentrations of these ions in the RO concentrate were 3-4 times higher than those in the original wastewater. A closer look at the concentration of Cl^- anion in the RO concentrate revealed that it was 3 times higher in Set 2 than in Set 1. The reason for this may be related to the regulation of pH value in the RO process (from 8 to 6) of Set 2, whereas no change of pH value was performed in Set 1.

Additionally, the continuous recirculation of reverse osmosis concentrate to the MBR could lead to a change of the concentrate concentration in an integrated MBR-RO process. This was discussed in detail in the previous chapter. At the end of the second set of experiments, the concentrations of almost all parameters were higher, than those in the first set. For instance, COD and DOC concentrations in Set 2 were double those in Set 1. More specifically, Cl^- anion concentration in RO concentrate of Set 2 after 11 days of concentrate recirculation was 5 times higher than that in Set 1.

These results show why the MBR mixed influent characteristics may differ after RO concentrate recirculation.

In order to better understand the fouling mechanism in the MBR, the RO concentrate was examined by HPLC-SEC analysis. Figure 5.2 indicates that no 100-1000 kDa protein-like SMPs were observed in either of the sets of experiments but the peak height of 10-100 kDa protein-like substance obtained in the second set was higher than that in the first set. Furthermore, during the all experiments of set 2, only small molecules of protein-like SMPs were recorded (see Fig. 5.3). This result confirms that the RO concentrate component of both sets of experiments contained one peak of 10-100 kDa protein-like substance.

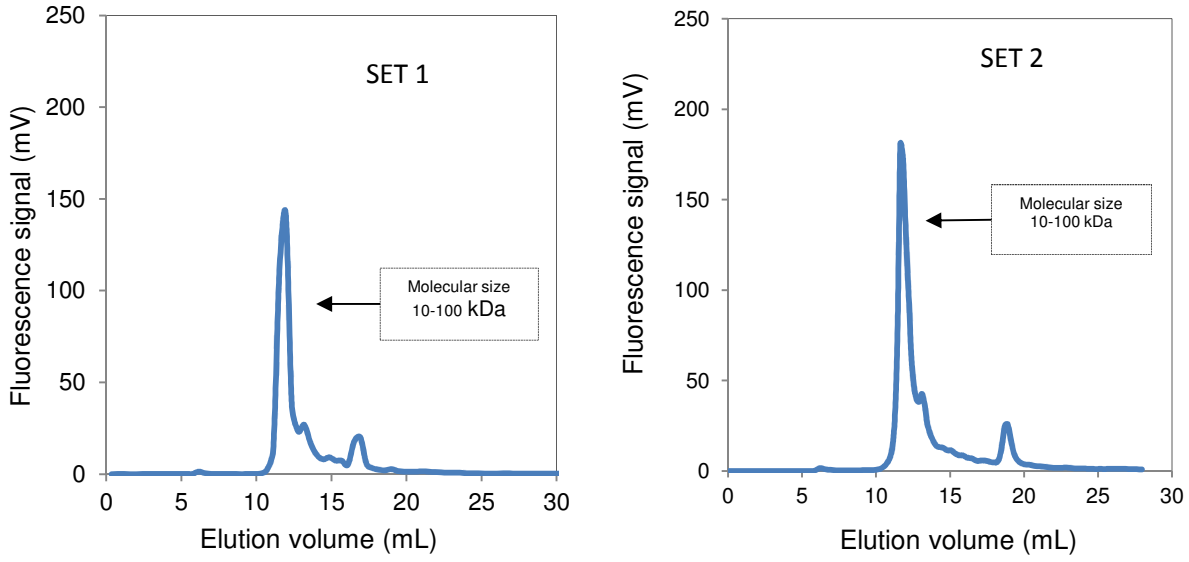


Figure 5.2 HPLC-SEC analysis of RO concentrates before returning to the MBR from 2 sets of experiments

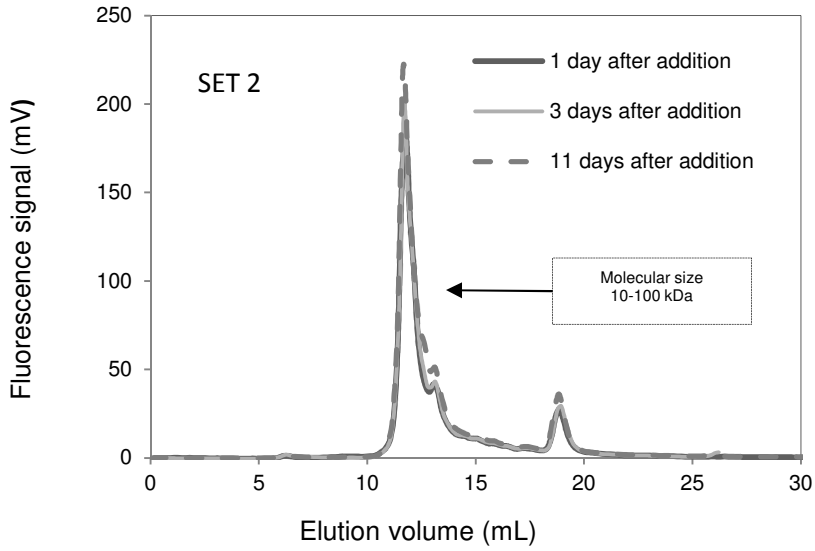


Figure 5.3 HPLC-SEC analysis of RO concentrate during the experimental time of Set 2

Table 5.3 Characteristics of MBR mixed influent

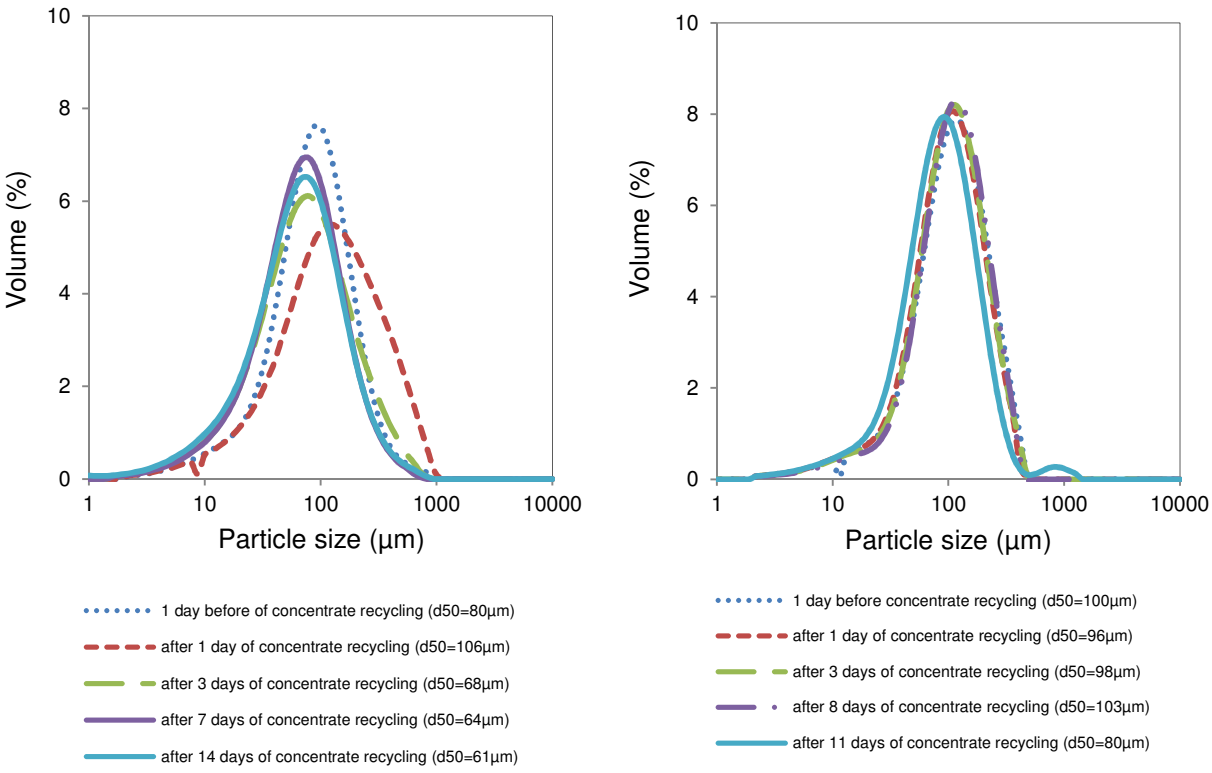
Parameters	Set 1 ($mg.L^{-1}$)	Set 2 ($mg.L^{-1}$)				
		After 1 day of recirculation	After 3 days of recirculation	After 8 days of recirculation	After 11 days of recirculation	After 14 days of recirculation
COD	685±10	677±10	677±10	679±10	680±10	682±10
DOC	134±3	189±4	189±4	190±4	191±4	191±4
$N\text{-}NH_3$	18±1	17.8±1	17.8±1	17.8±1	17.8±1	17.8±1
TN	34±2	46±2.3	46±2.3	46±2.3	46±2.3	46±2.3
Proteins	38±4	31.5±3.2	30±3	31.3±3	33±3.3	34±4
Polysaccharides	-	6.6±0.7	6.6±0.7	6.8±0.7	7±0.7	7.1±0.7
Na^+	220±22	270±27	273±27	278±28	311±31	336±34
K^+	12.5±1.3	14.2±1.4	14.4±1.4	15.2±1.5	18±1.8	19±1.9
Mg^{2+}	6±0.6	11±1	11±1	11.5±1	13±1.3	13±1.3
Ca^{2+}	41±4	156±16	156±16	159±16	165±17	166±17
Cl^-	111±11	249±25	245±25	282±28	349±35	389±39
NO_3^-	2.6±0.3	3.2±0.3	3.2±0.3	3.4±0.3	3.6±0.4	3.8±0.4
SO_4^{2-}	32±3	70±7	70±7	71±7	79±8	82±8
$P\text{-}PO_4^{3-}$	0.2±0.02	2.6±0.3	2.6±0.3	2.8±0.3	3±0.3	3.3±0.3

As shown in Table 5.3, an immediate reduction of the chemical oxygen demand (COD), from 799±10 to 685±10 for Set 1 and from 830±10 to 677±10 $mg.L^{-1}$ for Set 2, was observed in the MBR mixed influent just 1 day after the start of concentrate recirculation. Similarly, the concentrations of dissolved organic carbon (DOC), and ammonia nitrogen in the MBR mixed

influent also dropped after the RO concentrate was recycled to the MBR, for both of the sets. A slight decrease was obtained in the concentration of total nitrogen from Set 2, whereas no change was found for TN concentration in Set 1. This may have been the cause of the change in the MBR global performance. Meanwhile, neither protein nor polysaccharide contents in the MBR mixed influent from either set of experiments were impacted by the recirculation of RO concentrate. In addition, almost all monovalent and divalent cations and anions in the MBR mixed influent of the second set of experiments were significantly higher than those obtained from the first set. In particular, a continuous increase of Cl^- anion in the MBR mixed influent during the all experiments of Set 2 could lead to the higher SMP concentration in the MBR.

5.4. Comparison of the effects of RO concentrate recirculation on the biomass characteristics between the two sets of experiments

In order to compare the effects of RO concentrate on the biomass characteristics, the floc size distribution from each experiment set was analyzed on the activated sludge taken from the MBR. As shown in Figure 5.4a, after 1 day of RO concentrate recycling to the MBR, the floc size increased slightly, from 80 to 106 µm. In contrast, no change was found of the floc size distribution from the second set, after 1 day of concentrate recirculation (see Fig. 5.4b). After 3 days of concentrate recirculation, the floc size of MBR sludge from set 1 had dropped by 68 µm and remained almost constant for the next 11 days. Meanwhile, a slight decrease was found in the sludge floc size distribution after 11 days of concentrate recirculation in Set 2. These data prove that the variation of RO concentrate flow rates and characteristics in the MBR had a slight influence on the floc size distribution. As the MLSS concentration of the MBR sludge was quite stable during the experiment time of both sets (about 7.7 ± 1 $g.L^{-1}$), it can be concluded that decay of sludge did not occur.



(a) (b)

Figure 5.4 Effect of reverse osmosis concentrate on sludge floc size distribution from two sets of experiments: a) Set 1, b) Set 2

5.5. Comparison of MBR global performances between two experimental sets

In the literature, the performance of the MBR is usually evaluated by the conventional removal parameters (COD, N, P…). COD or TOC removal, nitrification (ammonium removal) and total nitrogen removal are frequently reported.

Figure 5.5 presents the process efficiency of chemical oxygen demand (COD) removal in the MBR between the two sets of experiments. The calculation of chemical oxygen demand (COD) process removal efficiency in the MBR was based on the COD concentration measured in the MBR influent (wastewater) and the permeate produced by the MBR before and after RO concentrate recirculation. The results indicated that the COD removal rate in the first set of experiments was steady at above 96% throughout the entire experiment. A

slight change of process removal efficiency in the second set of experiments was recorded after 14 days of concentrate recycling to the MBR; it decreased from 98% to 93%.

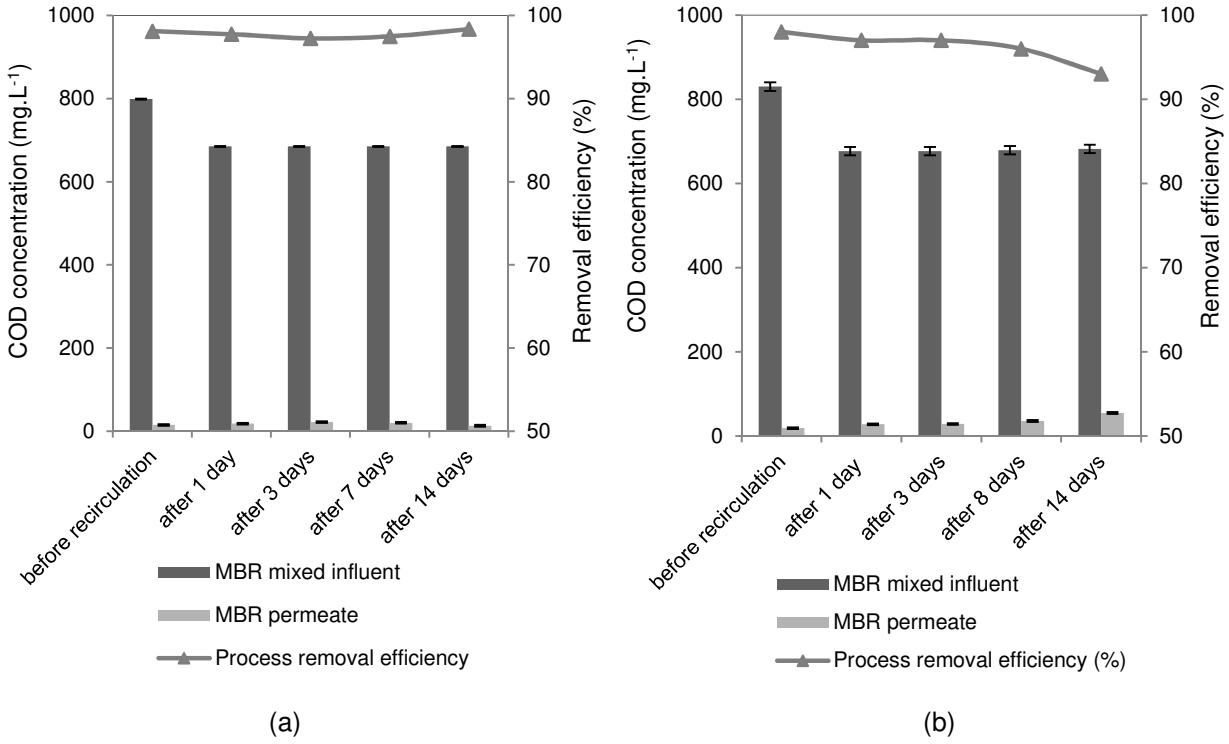
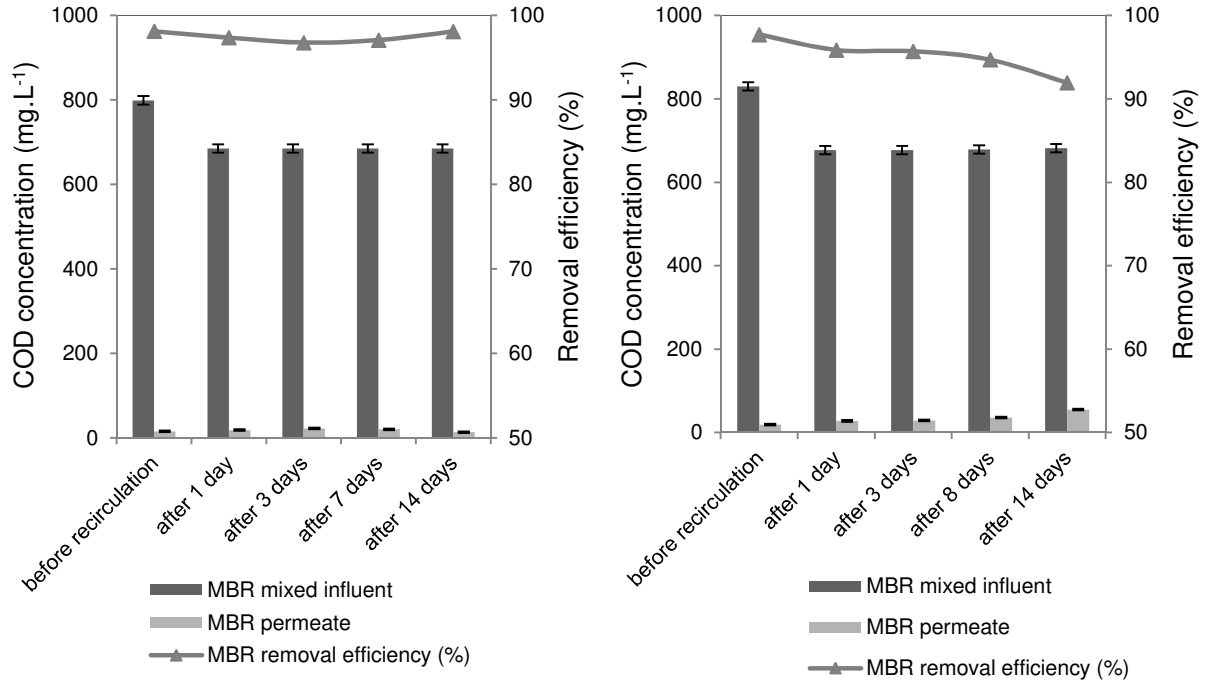


Figure 5.5 Process removal efficiency of chemical oxygen demand (COD): a) Set 1, b) Set 2

Although the characteristics of RO concentrate were different between the two experimental sets, its recirculation to the MBR did not affect the MBR removal efficiency of COD. The results in Figure 5.6 show a decrease of COD concentration in the MBR mixed influent after the RO concentrate had been recycled to the MBR, from 799±10 to 685±10 $mg.L^{-1}$ in Set 1 and from 830±10 to 677±10 $mg.L^{-1}$ in Set 2 (see Tables 5.1 and 5.3). For the first set of experiments, no significant change was found in the MBR removal efficiency of COD concentration in the MBR during the entire experiment (above 96%). While, from the second set, after 1 day of RO concentrate recirculation, a non-significant change was found in the MBR removal efficiency of COD concentration (from 98% to 96%) and it remained almost constant over the next 10 days. After 14 days of RO concentrate recycling, a slight decrease of COD removal, to 92%, was recorded in the MBR.



(a) (b)

Figure 5.6. MBR removal efficiency of chemical oxygen demand (COD): a) Set 1, b) Set 2

These observations demonstrate that the recirculation of RO concentrate did not significantly affect the COD removal efficiency in the MBR process.

In addition, no change was recorded in the COD concentration of the MBR permeate either before or after the recirculation of RO concentrate, from the first set of experiments. Although its value increased continuously and significantly during the filtration time of the second set of experiments, it remained below detection limits for the natural environment (see Table 5.4).

Table 5.4 Characteristics of the MBR permeate before and after RO concentrate recirculation from the two sets of experiments

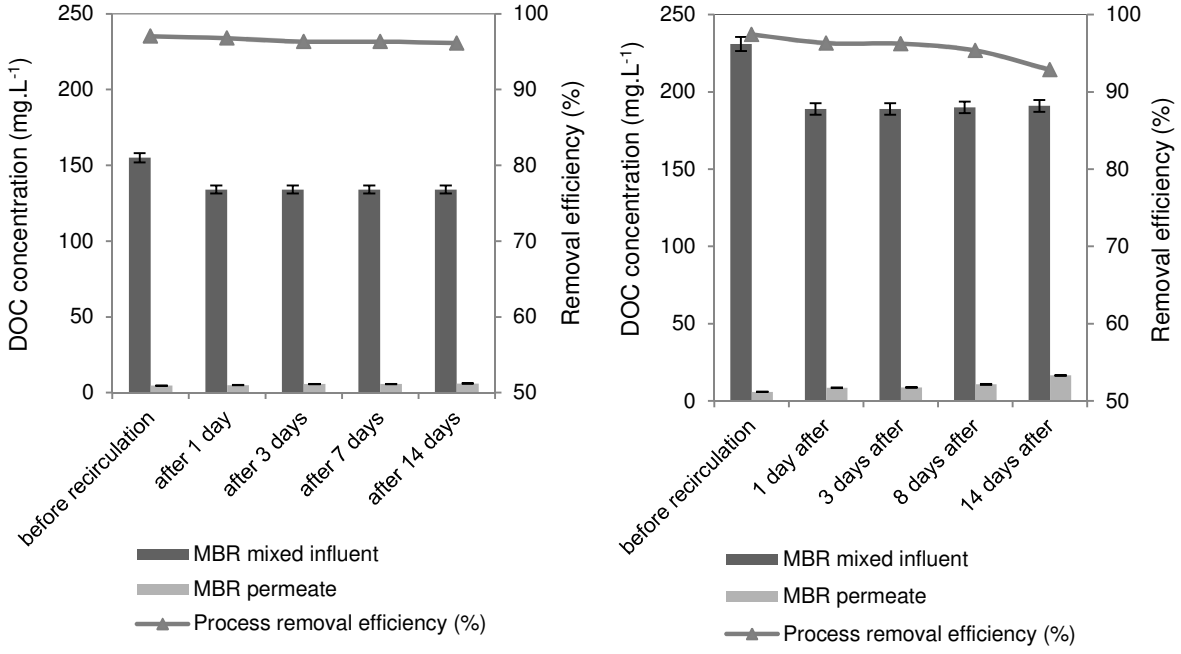
Parameters	Set 1 ($mg.L^{-1}$)			Set 2 ($mg.L^{-1}$)			Minimum performance
	Before	after 1 d	after 14 d	Before	after 1 d	after 14 d	
COD	15±2	18±2	14±2	19±2	28±2	55±2	75%
DOC	4.6±0.1	5±0.1	6±0.1	5.9±0.1	8.5±0.2	16.5±0.3	-
TN	9±0.5	8.5±0.5	9±0.5	13±0.7	16±0.8	25±1.3	-
$N\text{-}NH_3$	1.2±0.06	1.1±0.06	1.1±0.06	1.2±0.06	1.2±0.06	1.6±0.08	-

(*) data taken from regulations of 22 June 2007

The process efficiency of dissolved organic carbon (DOC) removal, which is based on the DOC concentration measured in the MBR influent (wastewater) and the permeate produced by the MBR before and after the RO concentrate recycling, is also an important parameter for evaluating the filtering performance of the MBR membrane. High efficiency of DOC removal, about 96%, was observed in an MBR with stable characteristics of RO concentrate recirculation (in Set 1) and remained almost constant throughout the filtration time (see Figure 5.7a). Although the DOC concentration in the MBR supernatant had increased by 24 % (from 5.2 to 6.5 $mg.L^{-1}$), leading to a slight change in the organic compounds in the sludge, the presence of RO concentrate in the MBR of Set 1 did not affect its removal efficiency.

When the concentrate was recycled to the MBR at the flow rate of 4.8 $L.d^{-1}$ and with varied characteristics (Set 2 of experiments), an increase of DOC concentration was recorded (from 8.5 to 12 $mg.L^{-1}$) in the MBR supernatant, after just 1 day of concentrate recirculation. However, no change was observed in the process efficiency of DOC removal in the MBR; it

was about 96%. A slight decrease was found in the process efficiency of DOC removal, from 96% to 91%, in the MBR, after 14 days of recycling of RO concentrate (see Fig. 5.7b). These results proved the steady efficiency of DOC removal by the MBR process with the recirculation of RO concentrates.

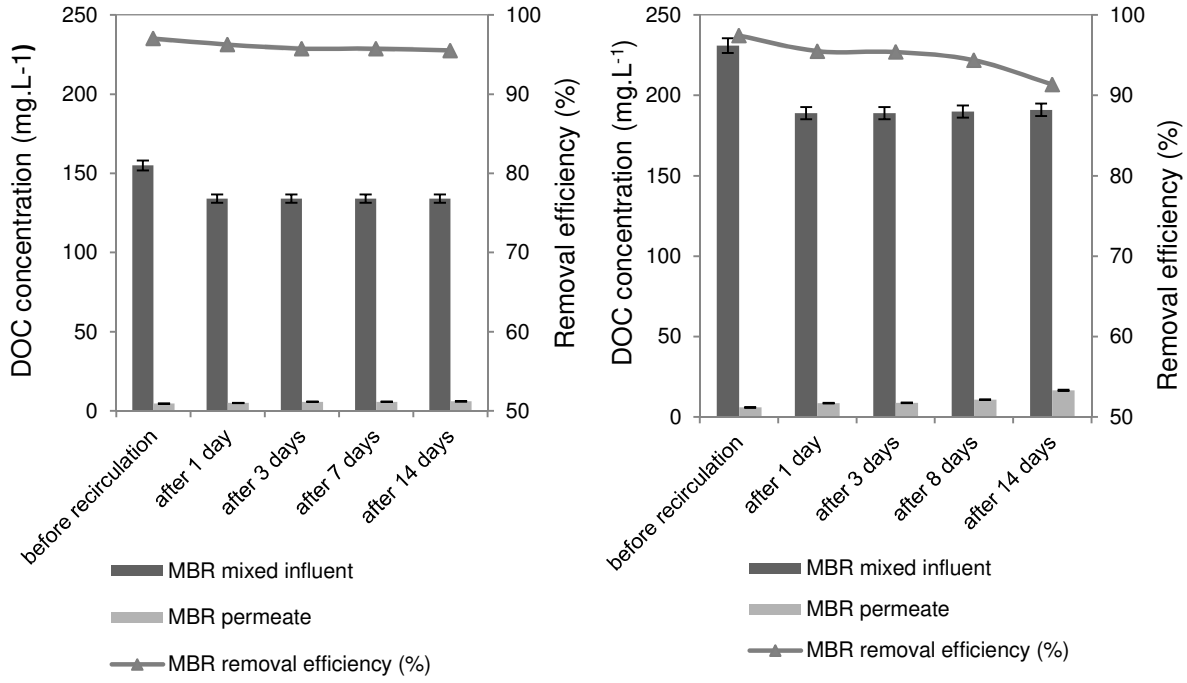


(a) (b)

Figure 5.7. Process efficiency of dissolved organic carbon (DOC) removal in the MBR: a) Set 1, b) Set 2

The effect of RO concentrate on the MBR removal efficiency of dissolved organic carbon for the two sets of experiments is shown in Figure 5.8. Although a decrease of DOC concentration occurred in the MBR mixed influent after concentrate recycling (from 155 ± 3 to 134 ± 3 $mg.L^{-1}$ in Set 1 and from 231 ± 5 to 189 ± 4 $mg.L^{-1}$ in Set 2), no significant effect of concentrate was observed on the MBR removal efficiency of DOC: after 1 day of concentrate recycling, the removal rate of DOC was found to be similar to its value before the recirculation of concentrate (about 96%), and it remained constant during the experiment time in Set 1. A slight effect of RO concentrate on MBR removal efficiency of DOC was found in the experiments of Set 2: after 14 days of RO concentrate recirculation, a slight decrease

of DOC removal rate was recorded in the MBR (from 97% to 91%).



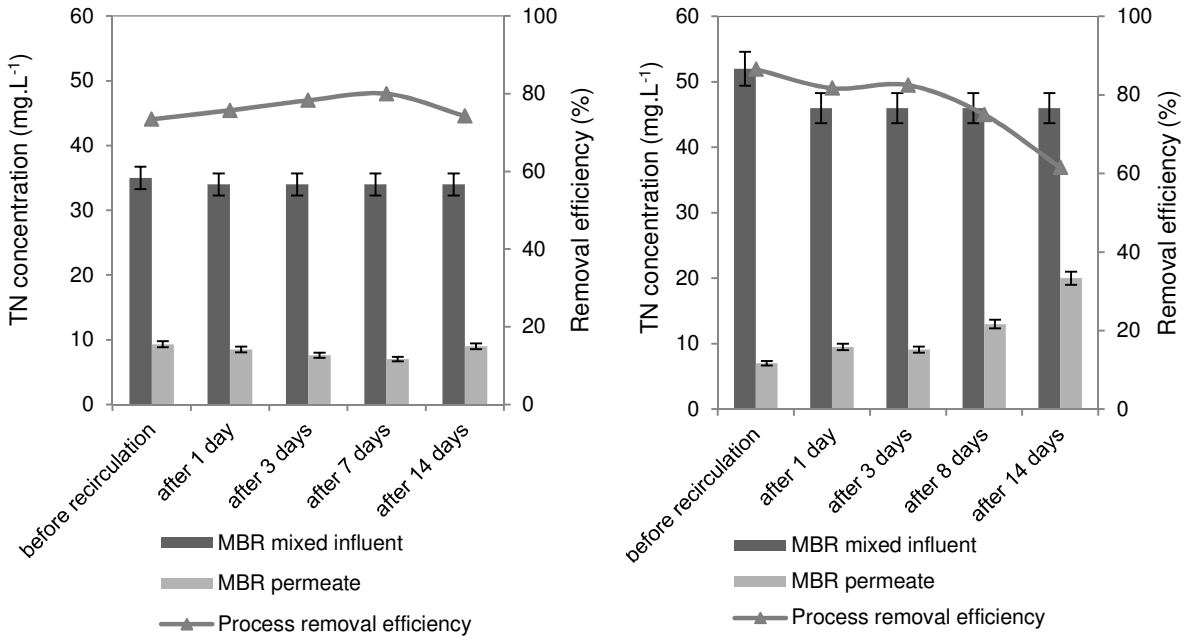
(a) (b)

Figure 5.8. MBR removal efficiency of dissolved organic carbon (DOC): a) Set 1, b) Set 2

In the MBR, the process efficiency of total nitrogen (TN) removal exceeded 74% in Set 1 and 85% in Set 2 (calculated as the percentage removed from the wastewater by the MBR membrane) before the RO concentrate recirculation (see Figure 5.9). With RO concentrate recycled to the MBR at the flow rate of 3.6 $L.d^{-1}$, the process removal efficiency of total nitrogen was steady for 2 weeks after the start of RO concentrate recirculation (see Fig. 5.9 a). The phenomena mentioned could explain why the recirculation of RO concentrate did not affect the inhibition of the nitrification process.

In contrast, from the experiments of Set 2, after 1 day of RO concentrate recycling, the process efficiency of TN removal in the MBR decreased slightly, to 80%. This efficiency was steady for the next three days. It again decreased slightly, to 75%, after 8 days of concentrate recirculation to the MBR. A more important observation, after 14 days of

recirculation of RO concentrate, was that the process efficiency of total nitrogen removal decreased significantly, to 62%. This observation demonstrates that the recirculation of RO concentrate affected the removal efficiency of total nitrogen in the MBR. This finding is different from the result for Set 1 and is supported by the data in this case.



(a) (b)

Figure 5.9. Process efficiency of total nitrogen (TN) removal in the MBR: a) Set 1, b) Set 2

On the other hand, no significant changes of total nitrogen (TN) concentration were recorded in the MBR mixed influent or permeate of Set 1 after the recirculation of concentrate, so the MBR removal efficiency of TN was not affected by the presence of concentrate in the MBR. The removal rate of total nitrogen was steady, above 74%, during the entire experiment of Set 1 (see Fig. 5.10a). Meanwhile, the total nitrogen concentration decreased in the MBR mixed influent of Set 2 (from 52 to 46 $mg.L^{-1}$) and increased in the MBR permeate (from 7 to 9.5 $mg.L^{-1}$) after 1 day of concentrate recirculation, so a slight effect of concentrate was observed on the MBR removal efficiency of total nitrogen: the removal rate of TN decreased from 86% to 79% (see Fig. 5.10b). This removal rate was steady in the next three days and then decreased to 72% after 8 days of concentrate recycling. After 14 days of RO

concentrate recirculation, a large decrease of its removal rate was recorded (about 57%) in the MBR. These results demonstrate that the recirculation of RO concentrate significantly affected the MBR removal efficiency of total nitrogen.

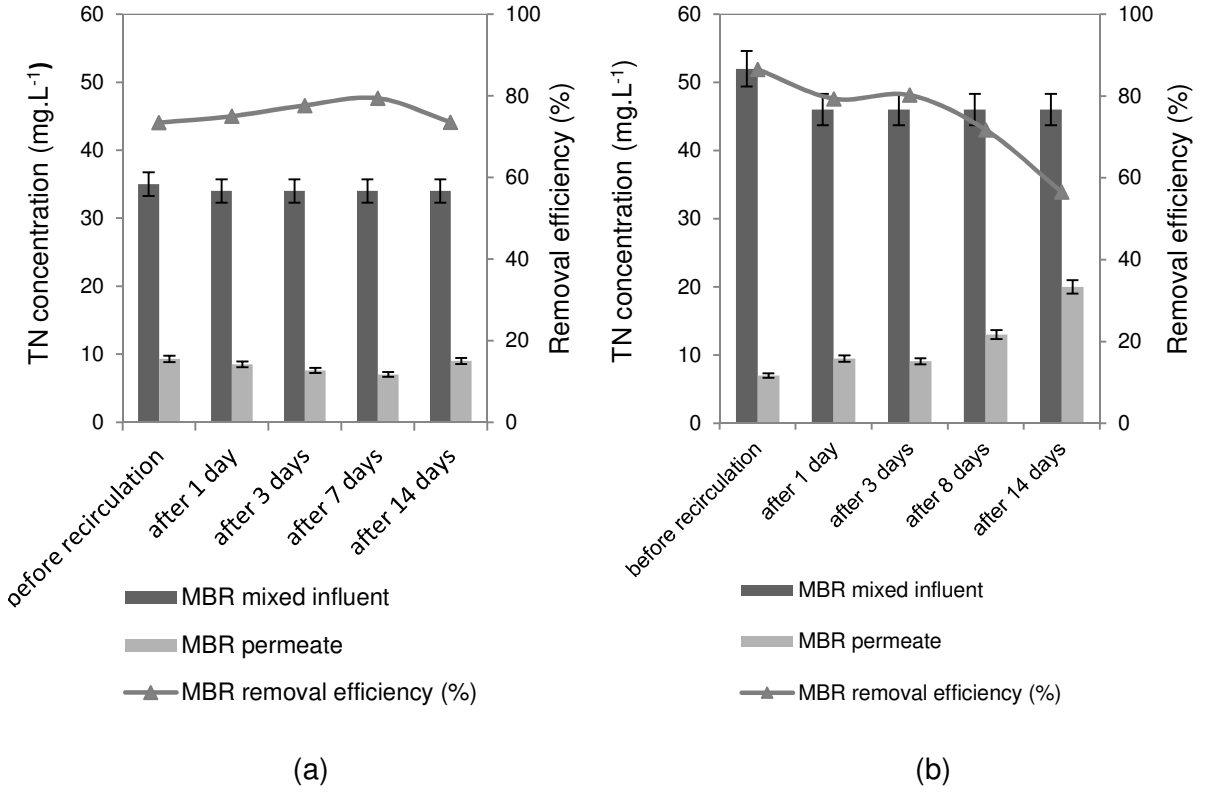


Figure 5.10. MBR removal efficiency of total nitrogen (TN): a) Set 1, b) Set 2

Furthermore, the nitrogen-ammonia removal efficiency of generally exceeded 92% in the MBR process of both sets of experiments. The results in Figure 5.11a, b show that the concentration of nitrogen-ammonia in the MBR influent (wastewater) both of the sets was around 21±1 $mg.L^{-1}$, before the RO concentrate was recycled to the MBR. After filtration by the MBR membrane, its concentration was lower, at 1.2±0.06 $mg.L^{-1}$. Throughout the experiments of both sets, before and after the concentrate recirculation, a negligible change of nitrogen-ammonia concentration was recorded in the MBR permeate, which remained around 1.2 ± 0.06 to 1.6 ± 0.08 $mg.L^{-1}$. The observation of high nitrogen-ammonia removal rate in the MBR demonstrates that the recycling of RO concentrate did not inhibit the

nitrification process.

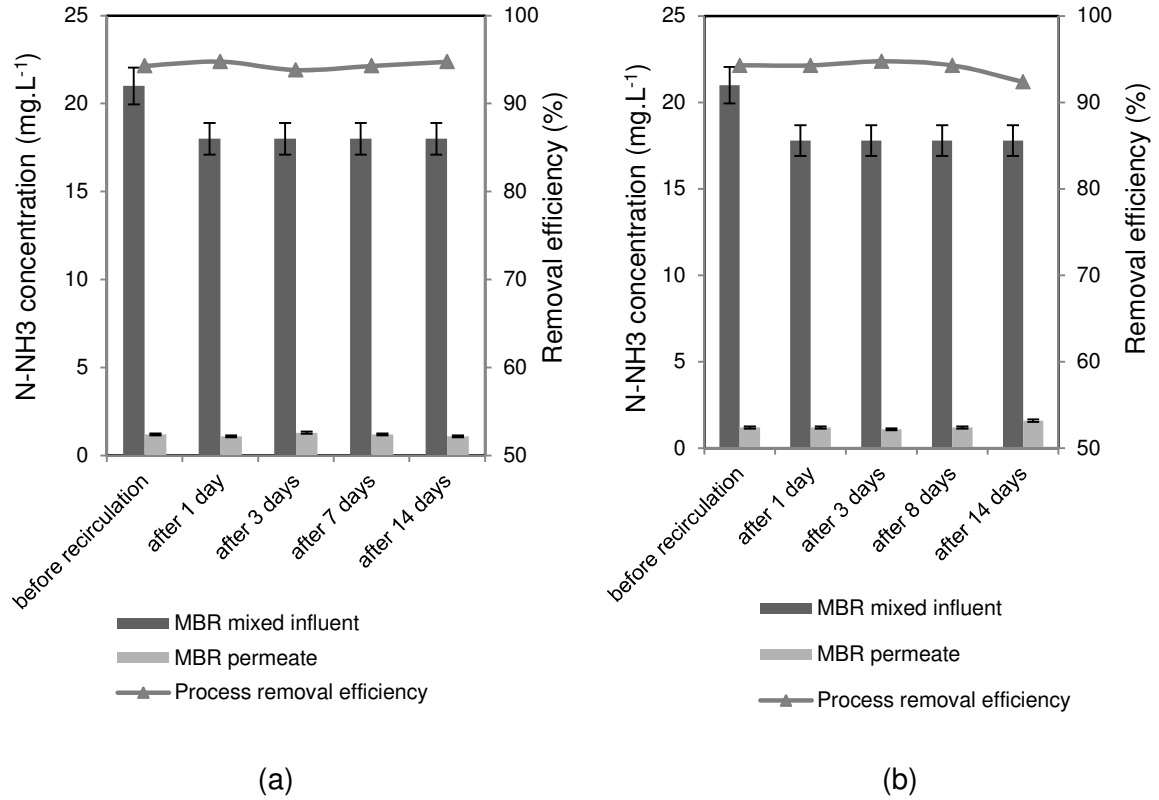
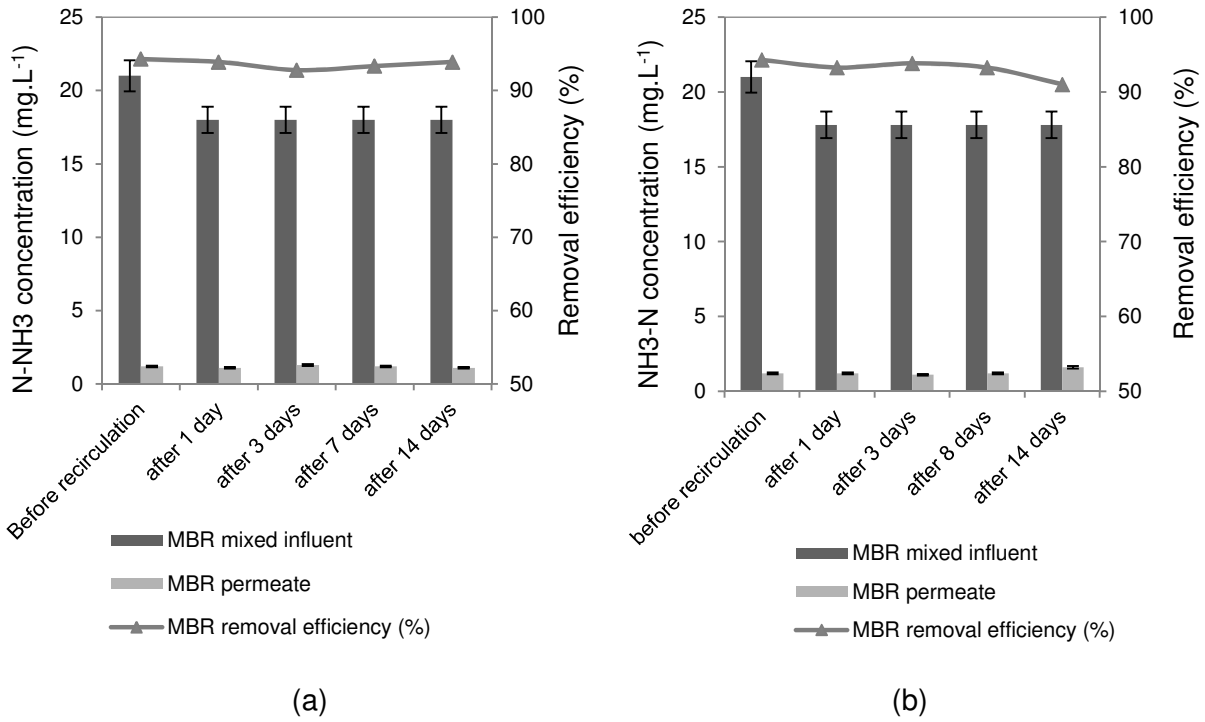


Figure 5.11. Process efficiency of nitrogen-ammonia ($N\text{-}NH_3$) removal in the MBR: a) Set 1, b) Set 2

Although a decrease in nitrogen-ammonia concentration occurred in the MBR mixed influent after concentrate recycling, from 21±1 to 18±1 $mg.L^{-1}$ in both of the sets, no significant effect of concentrate was observed on the MBR removal efficiency of $N\text{-}NH_3$: after 1 day of concentrate recirculation, the removal rate of $N\text{-}NH_3$ was found to be similar to its value before concentrate recycling (about 93%) (Fig. 5.12). The removal rate of nitrogen-ammonia was steady in the MBR during the entire experiment for both sets of experiments. This finding again demonstrates that RO concentrate recirculation did not affect the nitrification process in the MBR.



(a) (b)

Figure 5.12. MBR removal efficiency of nitrogen-ammonia (N-NH_3): a) Set 1, b) Set 2

In conclusion, the performance of the MBR depends on the characteristics of the concentrate produced by RO, which is recycled to the MBR in an integrated MBR-RO process. When the composition of the RO concentrate entering the MBR was stable (Set 1), it did not affect the MBR global performance of the organic matter (COD, DOC, TN, NH_3-N) in the MBR. When the characteristics of the RO concentrate changed during the experiment time (Set 2), an impact was observed on the global removal efficiency of total nitrogen in the MBR but the nitrogen-ammonia removal rate was not affected. The fact that no variation was observed in the nitrogen-ammonia removal efficiency demonstrates that the presence of RO concentrate did not inhibit the nitrification process in the MBR

5.6. Composition of supernatant in the MBR

The data reported in Figure 5.13 show that the concentrations of protein and polysaccharide in the MBR supernatant varied considerably between the two sets of experiments. On the

35th day of filtration of Set 1 and on the 40th day of filtration of Set 2, RO concentrate was recycled to the MBR. The concentrations of protein were about 10.9±2.2 mg.L^{-1} in Set 1 and 9.6±2 mg.L^{-1} in Set 2. After 1 day of RO concentrate recirculation, the values had increased to 14.4±3 mg.L^{-1} in the first set and 12±2.4 mg.L^{-1} in the second. Similar results were recorded after 3 days of recirculation of RO concentrate in both of the experimental sets; protein concentrations had dropped to a value similar to their values before the RO concentrate recirculation. The largest effects of RO concentrate on the composition of MBR supernatant were recorded for Set 2. For example, a significant increase of the protein concentration was obtained from the second set, to 21±4 mg.L^{-1}, after 14 days of RO concentrate recycling. In contrast, in the first set of experiments, after two weeks of concentrate recirculation, the protein concentration in the MBR supernatant was similar to its value after 1 day of recycling of RO concentrate, at 14.4±3 mg.L^{-1}.

Additionally, a significant change was found for the polysaccharide concentrations in the MBR supernatant of the experiments of Set 2. The results in Fig 5.13 show that the polysaccharide concentrations had increased from 4±0.4 to 9.7±1 mg.L^{-1} after 11 days and up to 14.4±1.4 mg.L^{-1} after 14 days of concentrate recirculation. Meanwhile, for Set 1, the polysaccharide concentrations were below 3 mg.L^{-1} and quite stable during the entire experiment.

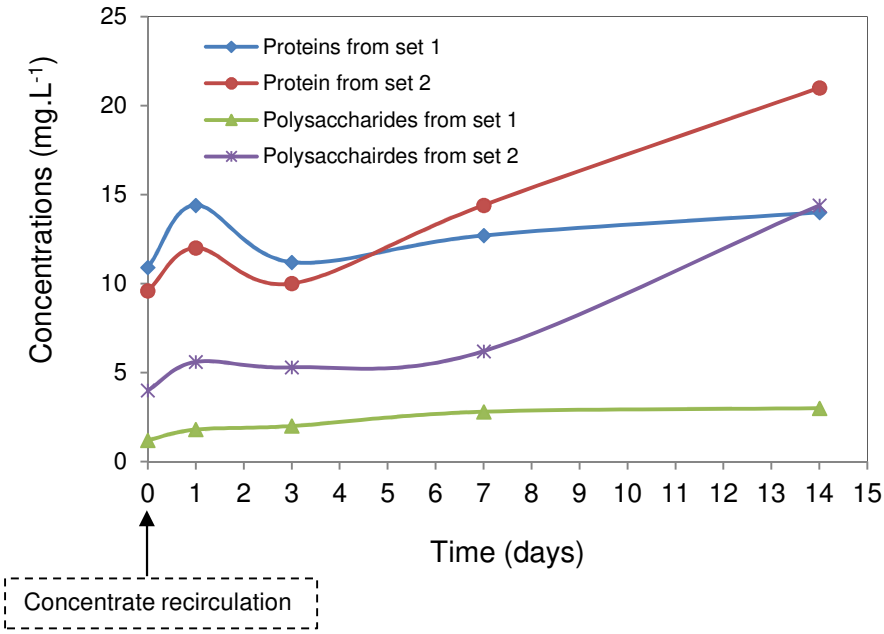


Figure 5.13. Comparison of protein and polysaccharide concentrations in the MBR supernatant of 2 experimental sets

To better understand the effect of RO concentrate on the release of protein-like SMPs, MBR supernatant was analyzed by HPLC-SEC before and after the recirculation of RO concentrate. As shown in Figure 5.14a, an increase of 10-100 kDa protein-like substances (about 25%) from the MBR was recorded after only 1 day of RO concentrate recirculation, whereas no change was found for 100-1000 kDa protein-like SMPs. After 14 days of concentrate recirculation, an increase of the 100-1000 kDa protein-like SMPs was observed in the MBR supernatant.

Like the results for Set 1, no change was observed for 100-1000 kDa protein-like substances after 1 day of concentrate recirculation for Set 2. Meanwhile, the small protein molecules increased significantly, by 67%, in the MBR supernatant (see Fig. 5.14b). More specifically, after 14 days of recirculation of RO concentrate, a more significant increase was found for both the 10-100 kDa and the 100-1000 kDa protein-like substances.

Moreover, as shown in Figures 5.2 and 5.3, there was only one peak of 10-100 kDa protein-like SMPs in the RO concentrate component. This suggests that the increase of small protein

molecules in the MBR supernatant of both experimental sets could be related directly to the recirculation of RO concentrate. A possible explanation for the significant increase of 100-1000 kDa protein-like substances in the MBR supernatant may be that the microorganisms mainly released protein-like SMPs when facing the stress of toxic components, such as the carbamazepine micropollutants contained in the RO concentrate.

A more interesting finding relating to the increase of both protein and polysaccharide contents in the MBR supernatant, it may be the main factor affecting the increase of SMP concentrations of Set 2. In addition, the results of Fig. 5.14b also indicate that both the 10-100 kDa and the 100-1000 kDa protein-like substances increased significantly in the supernatant of the MBR and their concentrations became much higher than those for Set 1 experiments.

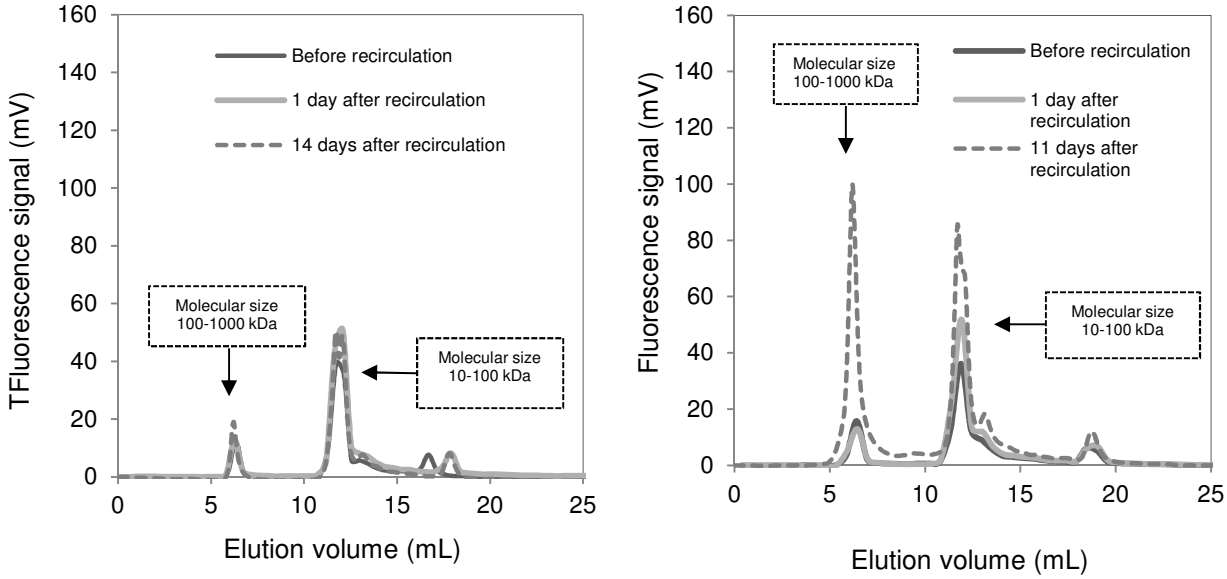


Figure 5.14. HPLC-SEC analysis of MBR supernatant: a) Set 1, b) Set 2

5.7. Fouling propensity in the sludge and supernatant filterability test

The variation of the fouling potential of the sludge between two sets of experiments is shown in Figure 5.15. Figure 5.15a indicates that, after 1 day of recirculation of RO concentrate, a decrease of the fouling resistance was recorded in the sludge filterability test (using 0.2 µm

PS membrane). This result could concern an increase of particle size (d_{50}) in the MBR sludge, from 80 µm to 106 µm (see Fig. 5.4a), leading to an increased filterability of the activated sludge. In contrast, an unexpected rapid increase of the fouling resistance of the 0.2 µm PS membrane was recorded just 1 day after the addition of RO concentrate from Set 2 of experiments (see Fig. 5.15b). This result could concern the increased protein and polysaccharide levels in the SMP.

After 14 days of RO concentrate recirculation to the MBR in Set 1, the fouling resistance increased to 4×10^{12} (m^{-1}) (see Fig. 5.15a). While a quite significant increase of the fouling resistance was observed from the second set of experiments, the value was up to 25.8×10^{12} (m^{-1}) after 11 days of RO concentrate recirculation (see Fig. 5.15b), 6 times higher than that in the first set. The different effects of RO concentrate on sludge fouling propensity between two sets of experiments could be related to the concentrations of protein and polysaccharides in the MBR supernatant (see section 5.6).

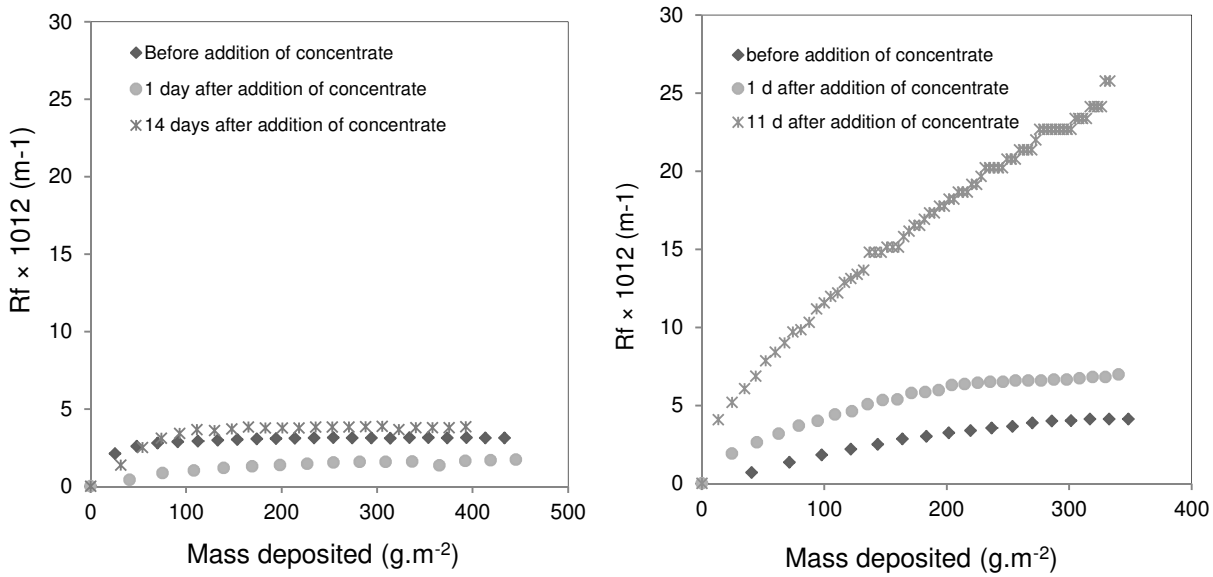


Figure 5.15 Fouling resistance of the 0.2 μm PS membrane as a function of the mass deposited in the sludge filterability test: (a) Set 1 (b) Set 2

(Mass deposited was calculated from the MLSS value of sludge)

This observation demonstrates that the reverse osmosis concentrate with stable characteristics returned to the MBR could have no important effect on filterability of the activated sludge

For a clearer explanation, an HPLC-SEC analysis of the MBR supernatant and permeate obtained on a 0.2 µm PS membrane was performed. The results of Fig. 5.16a indicate that, after 14 days of concentrate recycling, almost all 10-100 kDa protein-like SMPs passed through the membrane, whereas the membrane retained almost all the protein macro molecules, which could thus form a gel layer on the membrane surface, during the sludge filtration. Therefore, the fouling behavior of the membrane may be mainly related to the almost total rejection of the large protein molecules by the 0.2 *µm* PS membrane. However, the production of large protein-like SMPs due to the concentrate had no significant impact to the filterability of this membrane

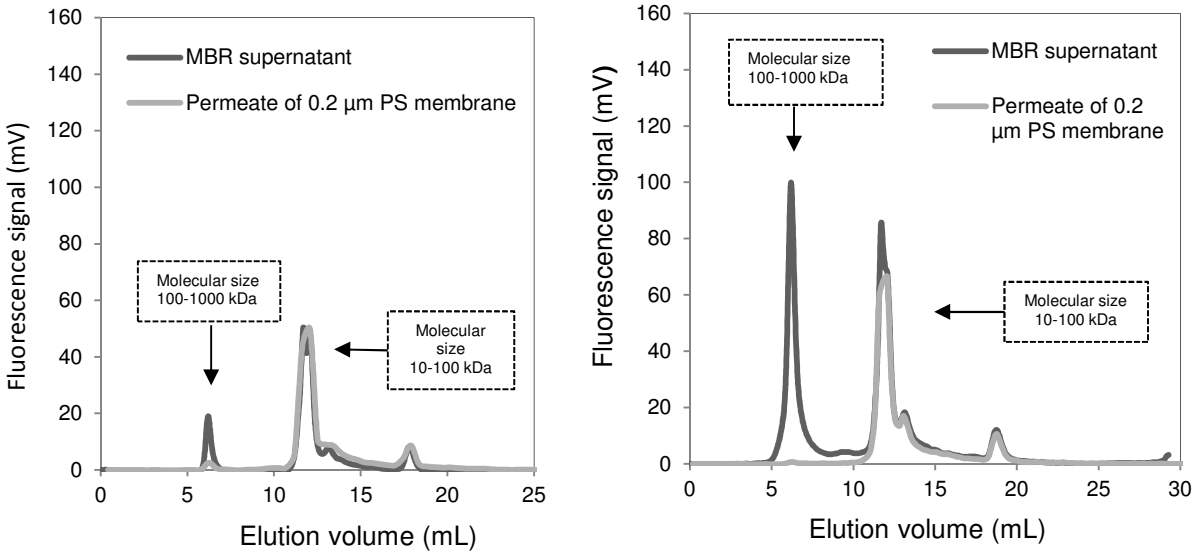


Figure 5.16. HPLC-SEC analysis of MBR supernatant and permeate observed in sludge filterability test: a) 14 days after concentrate recirculation (Set 1), b) 11 days after recycling of concentrate (Set 2)

On the other hand, the significantly higher fouling resistance in Set 2 could be due not only to the rejection of almost all 100-1000 kDa protein-like substances but also to the partial retention of 10-100 kDa protein-like substances by the membrane in the sludge filterability test after 11 days of RO concentrate recirculation (see Figure 5.16b). This phenomenon indicated that a fouling layer could be formed on the 0.2 μm PS membrane surface and the fouling inside the membrane pores could be modified by adsorption of small molecules, or pore blocking by colloids. As in the sludge filterability test, the fouling resistance of the 0.01 μm PES membrane of the supernatant filterability test decreased in the first set and increased slightly in the second set, after 1 day of recirculation of concentrate (see Figure 5.17a, b). More importantly, after 11 days of concentrate recycling, the fouling resistance of the 0.01 µm PES membrane had increased significantly, up to 30×10^{12} (m^{-1}), in the second set (see Fig. 5.17b). From the first set of experiments, a slight increase of the fouling resistance was found in the supernatant filterability test (see Fig. 5.17a).

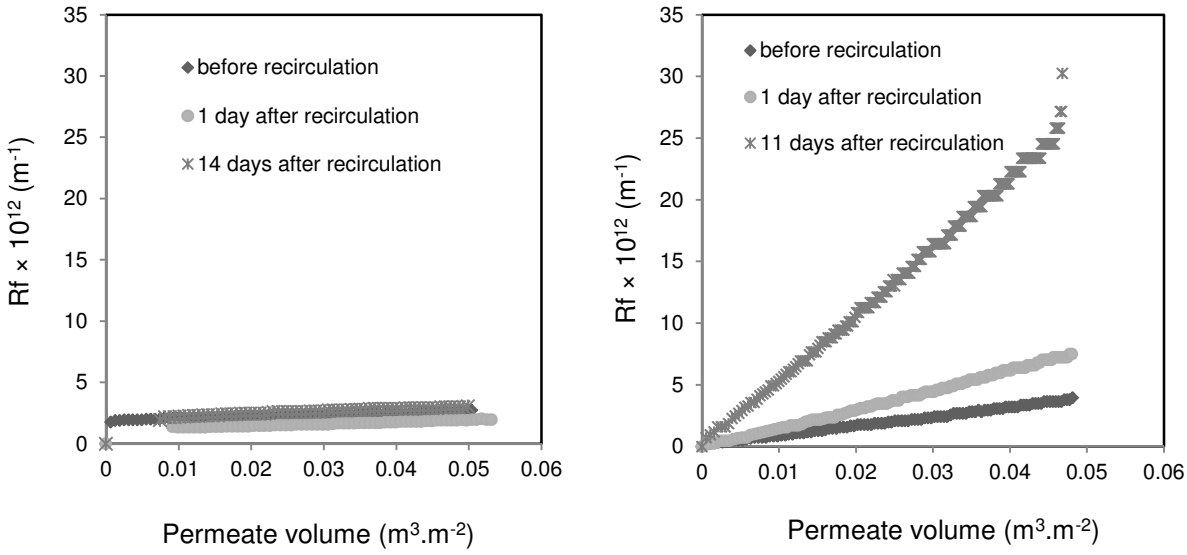


Figure 5.17. Fouling resistance of the 0.01 μm PES membrane as a function of the permeate volume ($m^3.m^{-2}$) in the supernatant filterability test: a) Set 1,(b) Set 2

To better understand the rise in the supernatant fouling propensity in the two sets, HPLC-SEC analysis of the supernatant and the corresponding permeate was performed on a 0.01 µm PES (polyethersulfone) membrane. The results of Figure 5.18a demonstrate that the small protein-like SMPs could pass through the 0.01 µm PES membrane. So, in Set 1, the fouling may be mainly related to the almost complete rejection of large protein-like SMPs in the supernatant by the 0.01 µm PES membrane. Additionally, only 10% of the 10-100 kDa protein-like SMPs could not pass through the 0.01 µm PES membrane (in Set 2). So it is possible that the fouling mainly originated from the almost complete rejection of 100-1000 kDa protein-like SMPs in the MBR supernatant by the 0.01 µm PES membrane, indicating that a gel layer could have formed on the surface of this membrane (see Figure 5.18b). Moreover, the amounts of both the 10-100 kDa and 100-1000 kDa protein-like SMPs in the MBR supernatant of Set 2 were much higher than those of Set 1, after the concentrate had been recycled to the MBR. These results could also explain why the fouling resistance of the 0.01 µm PES membrane was significantly higher in Set 2 than Set 1. These data also point out the important role of large protein-like substances in the fouling propensity of supernatant.

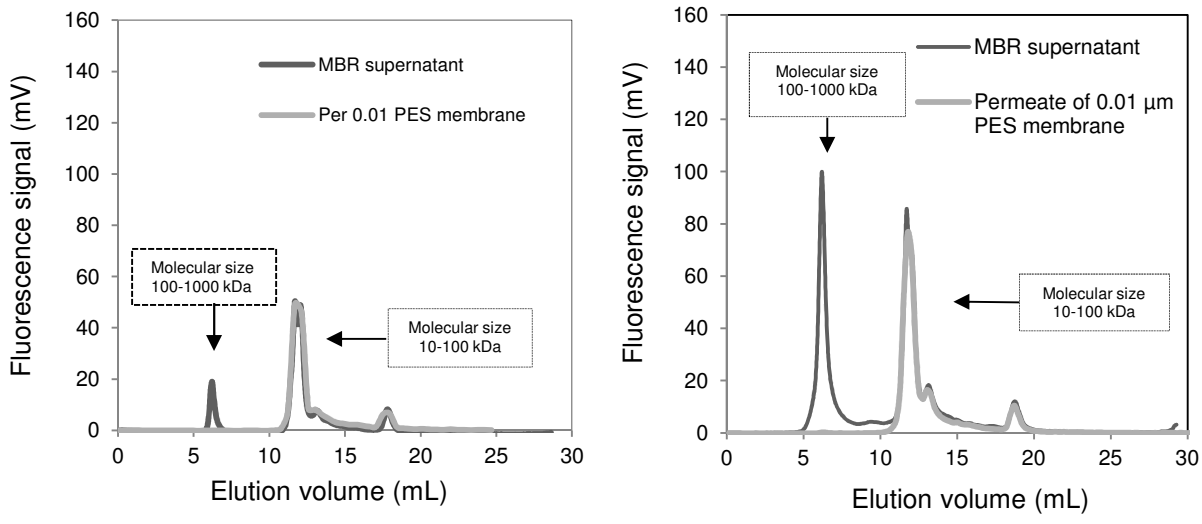


Figure 5.18 HPLC-SEC analysis of MBR supernatant and permeate observed in the supernatant filterability test: a) 14 days after recirculation of concentrate started (Set 1), b) 11 days after the beginning of concentrate recirculation (Set 2).

5.8. Comparison of the effects of RO concentrate on the MBR fouling between two experimental sets.

The transmembrane pressure (TMP) or the membrane permeability is an important parameter for the evaluation of the fouling propensity of the membrane in an MBR.

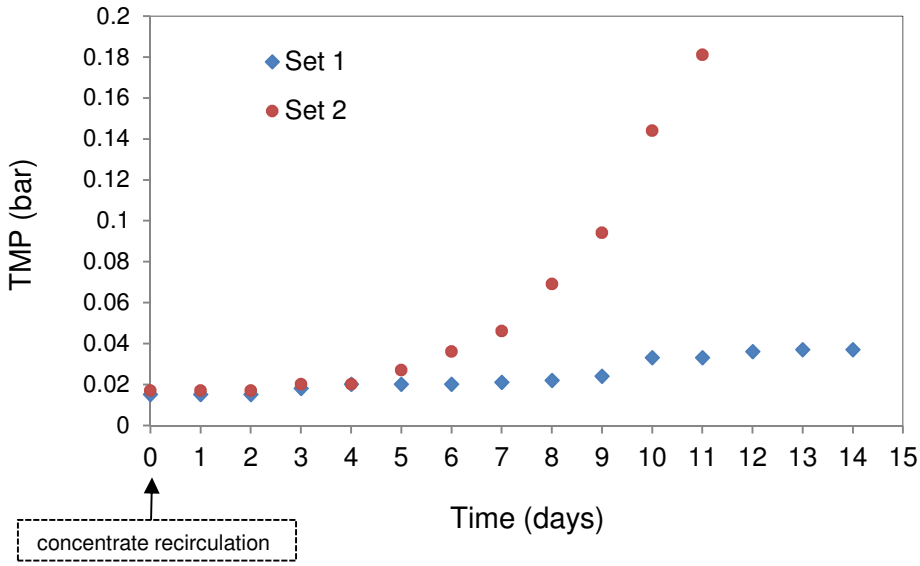


Figure 5.19 Comparison of transmembrane pressure of the MBR membrane operated under two different operating conditions of experiments

Figure 5.19 illustrates the transmembrane pressure profile of the MBR membrane throughout the two sets of experiments. For the first set, the reverse osmosis concentrate with stable characteristics was returned to the MBR at the membrane permeability of 1000 $L.h^{-1}.m^{-2}.bar^{-1}$ ($LMH.bar^{-1}$). For the second set of experiments, the flow rate of the concentrate recirculation to the MBR was increased from 3.6 to 4.8 $L.d^{-1}$ and its characteristics changed during the filtration time. The recycling of RO concentrate was performed at the membrane permeability of 882 $L.h^{-1}.m^{-2}.bar^{-1}$. Similar results were observed for both sets of experiments: after 1 day of the concentrate recirculation, no change of the TMP was found in the MBR. An increase of the TMP was observed in the MBR, from 0.015 to 0.018 bar for Set 1 and from 0.017 to 0.022 bar for Set 2, after 3 days of the concentrate being returned to the MBR. As a result, an increase of the transmembrane pressure of 0.069 was recorded in Set 2 after 8 days of concentrate addition, compared to that in Set 1 of about 0.022 bar. At the end of the

experiment for Set 1 (14 days after the recycling of concentrate began) the TMP in the MBR was around 0.037 bar. A more important observation was recorded in the MBR of Set 2: the TMP threshold value of 0.18 bar was too high for the MBR process, after 11 days of concentrate recirculation. The faster TMP increase in the MBR of the second set may have been caused by higher concentrations of dissolved and colloidal organic matter such as SMPs, as discussed in the previous section, indicating that the recirculation of RO concentrate elevated the fouling potential in the MBR.

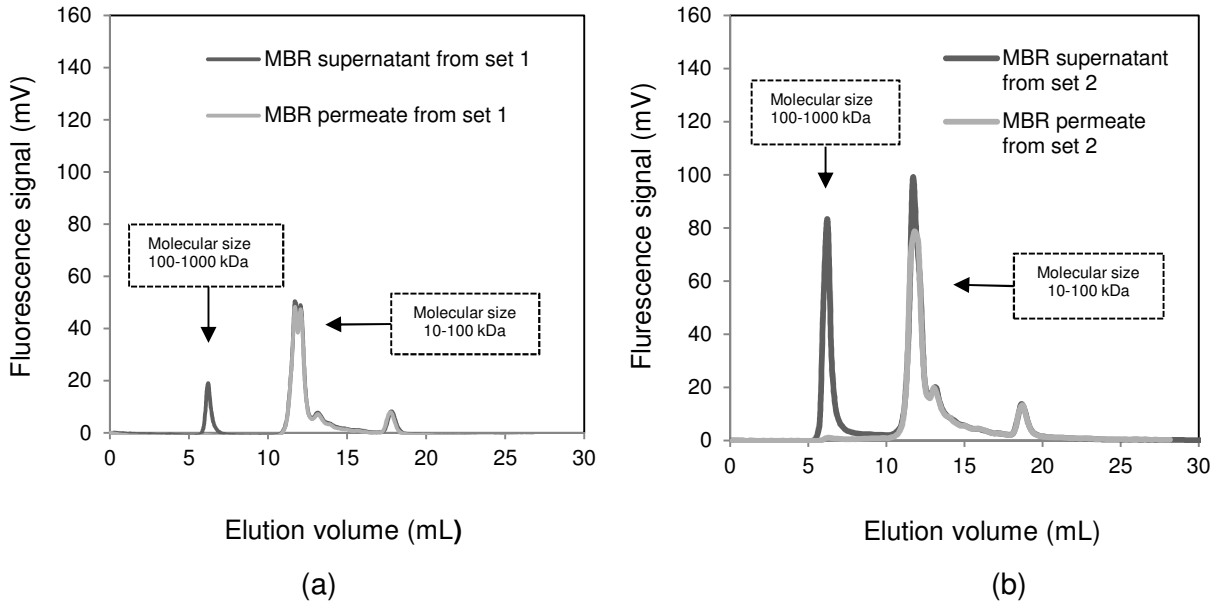


Figure 5.20 HPLC-SEC analysis of MBR supernatant and permeate: a) 14 days after concentrate recirculation (Set 1), b) 11 days after recycling of concentrate (Set 2)

Furthermore, HPLC-SEC analysis of the MBR supernatant and permeate was performed after 14 days (for Set 1) and after 11 days (for Set 2) of the recirculation of the concentrate. The results showed that almost complete retention of the 100-1000 kDa protein-like SMPs by the MBR membrane was recorded from both sets, indicating that a fouling layer could be formed on the MBR membrane surface (see Fig.5.20). In contrast, almost all 10-100 kDa protein-like substances passed through the MBR membrane in Set 1 of experiments (see

Fig. 5.20a). However, small amount of the 10-100 kDa substances were rejected by the membrane of the MBR in Set 2.

These data point out the important role of large protein-like SMPs in fouling behavior in the MBR.

5.9. Conclusion

The effects of the reverse osmosis concentrate recirculation, at different flow rates and with different characteristics, to the MBR were investigated. Their impacts on MBR global performances, especially the MBR fouling were evaluated. Satisfactory MBR permeate quality was obtained in the MBR operated under varied operating parameters. The removal efficiencies of chemical oxygen demand (COD) at the different flow rates of concentrate were greater than 93%. Similar results for the dissolved organic carbon removal efficiency were found in the MBR. These results were consistent with the literature [50]. Although the recirculation of RO concentrate with varied characteristics affected the removal rate of total nitrogen in the MBR, its presence did not inhibit the nitrification process, as observed in Li's study [68] of MBR-NF for treating wastewater from antibiotic production.

Furthermore, the effects of RO concentrate on activated sludge of MBR as well as MBR supernatant compositions depend on the characteristics of the RO concentrate recycled to the MBR. The recirculation of RO concentrate with stable characteristics to the MBR affected no significantly on MBR supernatant composition. .

An increase slightly of both small and large protein-like SMPs in the MBR supernatant was observed after the RO concentrate with stable characteristics recirculated to the MBR.

In addition, the stable characteristics of RO concentrate recirculation did not affect significantly on membrane fouling in the MBR.

The integrated MBR-RO process with RO concentrate recirculation minimizes unwanted discharge of a concentrated waste stream. In order to avoid a higher TMP being induced rapidly by the toxic components contained in the RO concentrate, suitable operating parameters for the MBR need to be selected. The characteristics of the RO concentrate recycled to the MBR should be stable during the filtration time with the MBR membrane. The first set of experiments might provide a suitable choice for the return of the concentrate to the MBR (Figure 5.21).

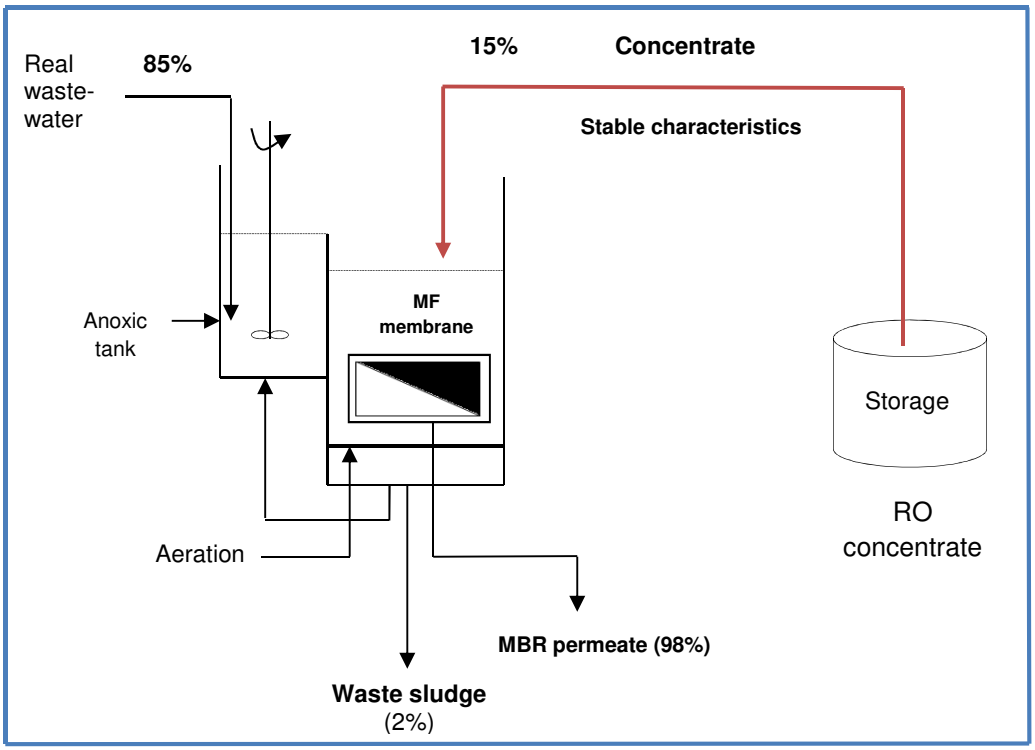


Figure 5.21 Scheme of the process using MBR systems with recirculation of RO concentrate

CONCLUSIONS AND PERSPECTIVES

CONCLUSIONS

Wastewater effluents can be treated by an integrated membrane system combining membrane bioreactors (MBR) and reverse osmosis (RO) for effective removal of micropollutants in the field of high-quality water reuse. However, discharging the RO concentrate waste stream directly into the natural environment could lead to serious problems due to the toxic components contained in the concentrates (micropollutants, salts, organic matter). A possible solution could be the recirculation of RO concentrate waste to the MBR. However, such an operation should be studied in detail since the recirculation of non-biodegradable organic matter or high concentrations of salts and micropollutants could directly or indirectly contribute to MBR membrane fouling and modification of the biodegradation activity.

This research gives more detailed into the advantages and challenges of the presence of reverse osmosis concentrate in the MBR. The effects of RO concentrate recirculation on the MBR performances were investigated in two different ways of contact, i.e. short- term peak contact and long-term continuous contact at various operating conditions.

The impacts of RO concentrate recirculation on global process efficiency in the MBR?

The removal efficiencies of chemical oxygen demand (COD) were greater than 93% after RO concentrate recirculation. Similar results for the dissolved organic carbon removal efficiency were found in the MBR. Additionally, the presence of RO concentrate in the MBR did not inhibit the nitrification process. The recirculation of RO concentrate to the MBR therefore could maintain good performances of carbon and nitrogen in the MBR.

The recirculation of RO concentrate affected on biodegradation in the MBR?

Reverse osmosis concentrate recirculated to the MBR had no significant modification of selected pharmaceutical micropollutants (carbamazepine, diclofenac, ketoprofen) removal efficiency in the MBR. So, the presence of RO concentrate did not improve the biodegradation in the MBR.

The effects of RO concentrate recirculation on the MBR supernatant?

The impact of the toxic flow on activated sludge of MBR as well as MBR supernatant compositions depends on the flow rate and the characteristics of RO concentrate recycled to the MBR. The concentration of protein and polysaccharide had increased significantly after the recirculation of RO concentrate with increasing of characteristics. In contrast, after two weeks of concentrate recirculation with stable characteristics, the protein concentration in the MBR supernatant increased slightly and the polysaccharide concentration was below 3 $mg.L^{-1}$ and quite stable during the entire experiment.

The results of HPLC-SEC analysis showed that both the 10-100 kDa and 100-1000 kDa protein-like substances increased significantly in the MBR supernatant after the recirculation of RO concentrate with increasing of characteristics. Thus a significant increase of sludge fouling propensity was observed, which could be attributed to the increased quantity of large protein-like substances. This observation demonstrated that an important effect of large protein-like SMPs on fouling propensity in the MBR

Finally, in order to obtain sustainable operation of the integrated MBR-RO process with the RO concentrate recirculation, it is therefore very important to select the most appropriate operating parameters and effective solutions for the mitigation of membrane fouling in the MBR

PERSPECTIVES

The impacts of small protein-like SMPs are not discussed in well detail in this work, so studies concerning the irreversibility of fouling in the filterability test should be investigated.

More studies concerning the effects of salt compositions on the change of the soluble microbial products (SMPs) such as proteins and polysaccharides content should be carried out.

More experiments and simulations relating to the operating conditions in an integrated MBR-RO process with RO concentrate recirculation should be performed to evaluate the acceptable range of operating parameters.

More research should be carried out with the objective of the RO concentrate treatment before returning to the MBR to obtain a sustainable operation of the integrated MBR-RO process. For examples, the process like MBR-RO-ozonation or capacitive deionization process (CDI) should be examined, which uses ozonation or CDI process for RO concentrate treatment before recycling to the MBR. The capacitive deionization process could be able to achieve high removal of ions. The ozonation could reduce the toxic effects and improve biodegradability of persistent substances in the RO concentrate.

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APPENDIX

1. Appendix N°1 : Calculation of ion Cl^- concentration added into the RO feed tank (Chapter 4)

Prepare the HCl 37% solution: 83 mL HCl 37% is diluted with 917 mL H_2O → HCl 37% solution with C_M = 1 $mol.L^{-1}$

In order to regulate pH value in the RO process (from 8 to 6), 500 mL HCl 37% (C_M = 1 $mol.L^{-1}$) was added into the 50 L of RO feed tank.

n (HCl) = n (Cl^-) = 1 $mol.L^{-1}$

m (HCl) = m (Cl^-) = 1 × 35.5 = 35.5 g

The concentration of ion Cl^- added into the RO feed tank is calculated by Eq:

$$\frac{0.5\times 35.5g}{50L} = 0.355\ g.L^{-1} = 355\ mg.L^{-1}$$

So, the concentration of Cl^- ion in the RO feed was 419 $mg.L^{-1}$

→ Cl^- concentration in RO concentrate could be 1089 ± 42 $mg.L^{-1}$ (with concentration factor CF = 2.6 ± 0.1)

2. Appendix N°2: Calculation NH_4^+ concentration in the wastewater (Table 3- Chapter 4)

The concentration of $N\text{-}NH_3$ = 22 $mg.L^{-1}$ (see Table 4.3- Chapter 4)

C ($N\text{-}NH_3$) = C (NH_3) = 1.57×10^{-3} $mol.L^{-1}$

→ $[NH_3] + [NH_4^+] = 1.57\times10^{-3}$ $mol.L^{-1}$ (1)

Considering this equilibrium reaction: $NH_4^+ \rightleftharpoons NH_3 + H^+$

$$k_{NH_4^+} = \frac{[NH_3][H^+]}{[NH_4^+]} \rightarrow \frac{[NH\ ]}{[NH_4^+]} = \frac{k_{NH^+_4}}{[H^+]} = \frac{10^{-9.25}}{10^{-8}} = 10^{-1.25}$$

→ $[NH_3] = 10^{-1.25}\,[NH_4^+]$ (2)

From (1) and (2) → $[NH_4^+] = 26.7\ mg.L^{-1}$

3. Appendix N°3: Calculation of the concentration of hydrogen phosphate (HPO_4^{2-} and dihydrogen phosphate ($H_2PO_4^-$) in the wastewater (Table 4.3- Chapter 4)

With: the concentration of ion $P\text{-}PO_4^{3-} = 3\ mg.L^{-1}$ (see Table 4.3- Chapter 4)

pH = 8 ; $M_{PO_4^{3-}} = 95\ g.mol^{-1}$

→ the concentration of $PO_4^{3-} = 3.16 \times 10^{-5}\ mol.L^{-1}$

Considering these three equilibrium reactions:

$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$

$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$

$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$

The corresponding constants at 25 °C (in $mol.L^{-1}$) are:

$$K_{a1} = \frac{[H^+][H_2PO_4^-]}{[H_3PO_4]} \approx 7.5 \times 10^{-3} \quad (3)$$

$$K_{a2} = \frac{[H^+][HPO_4^{2-}]}{[H_2PO_4^-]} \approx 6.2 \times 10^{-8} \quad (4)$$

$$K_{a3} = \frac{[H^+][PO_4^{3-}]}{[HPO_4^{2-}]} \approx 2.14 \times 10^{-13} \quad (5)$$

From (5) → $[HPO_4^{2-}] = 1.48\ mol.L^{-1} = 142\ g.L^{-1}$ (6)

From (6) and (4) → $[H_2PO_4^-] = 0.24\ mol.L^{-1} = 23.2\ g.L^{-1}$