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MEMBRANE BASED INTEGRATED ANAEROBIC-AEROBIC PROCESS FOR THE TREATMENT OF TEXTILE WASTEWATER

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DEDICATION

To the person from whom I learnt that success has to be deserved and not inherited,

"Sidi Khaled Bentounes"

To those who believed in me since my childhood, their love, their support, their education their sacrifice, made me understand what does family mean,

"My parents"

To the one whom without him I can never imagine my life, his fun, his love, his support in hard as in good times,

"My brother"

To my spiritual energy, my eternal love,

"Grandmothers and Grandfathers"

To my best friends for ever,

" Nesrine", " Zora"

To my spiritual family…

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SUMMARY

Chemical and allied process industries use water extensively, thus making them water intensive industries. These needs for water are satisfied using the following sources: Surface water groundwater, desalinated seawater, recycled water (industrial wastewater and urban sewage) (Ranade, Bhandari, 2014). This raises the question whether these sources are enough for the future generations? Is our water consumption reasonable? How can we improve sustainable treatment methods for the wastewater we produce? These questions were the starting point of this thesis, for which the main objective is to find a sustainable solution for the treatment and reuse of wastewater in the textile industry which is among the most serious problems in the wastewater sectors. Wastewater from dyeing and finishing processes in the manufacturing industry constitute a substantial source of pollution which exhibits intense colour, high COD, fluctuating pH and suspended particles (Merzouk et al., 2008).

The choice of this subject is based on the fact that, textile industry in Algeria constitutes one of the main activities in the manufacturing sector , what leads to a huge water consumption, and consequently a high loaded wastewater effluent that needs being treated either for reuse, or for discharge respecting the legal environmental regulations. For instance the industry in Béjaia (a coastal town in Algeria) is growing quickly and discharges around 80.000 m^3 every day with a large part contributed by the textile industry (Merzouk et al., 2008). This is an example that illustrates how pressing it is to study more efficient and economical water treatment process in this sector.

This thesis represents a scientific collaboration between the University of Mostaganem, Algeria and the Karlsruhe University of Applied Sciences, Germany. The whole experimental work has been conducted at the Karlsruhe University that offered the ground for profound research in the field of "Membrane Bioreactor (MBR) technology for textile wastewater treatment", which is regarded as a promising , efficient and sustainable process, providing a sufficient water quality for reuse (Judd et al., 2003). The MBR technology is a combination of the biological degradation process and membrane filtration technology (micro- and ultrafiltration, MF, UF) and it has proved to be very effective in a variety of cases especially for high strength and low-biodegradable wastewater as in the case of textile wastewater. However, up to now textile wastewater treated by aerobic MBR typically could not comply with the reuse standard due to its high colour concentration, and therefore combination of the MBR with a downstream nanofiltration (NF) or reverse osmosis (RO) process is proposed, in

order to enhance the water permeate quality (Huang et al., 2009). Besides non-compliance of reuse standards MBR technology faces membrane fouling, which adversely affects performance of the treatment process (Iversen et al., 2009). Therefore this PhD thesis basically aims to study a combined aerobic/anaerobic MBR process since it is known from previous studies that anaerobic treatment of textile wastewater can significantly contribute to decolourisation particularly in the case of azo dyes (Stolz, 2001). Beside the use of conventional commercially available membranes, this work studied novel antifouling membranes. For this purpose two categories of membranes have been tested in a side stream MBR unit mainly commercial membranes (UF,NF) and novel membranes developed through collaboration of the Institute on Membrane Technology (ITM), Cosenza, Italy and the Karlsruhe University of Applied Sciences. The active layer of the commercial membrane is based on polyethersulfone (PES) and is supplied by the company Microdyn-Nadir (Microdyn-Nadir, 2014). The novel membranes were developed by modifying the commercial UF PES with a nanostructured coating through polymerisable bicontinuous microemulsion (PBM) process, where the main goal is to achieve higher hydrophilicity and anti-microbial properties in order to increase its resistance to fouling (Galiano, 2014). All the membranes have been tested at first under aerobic conditions (first step), secondly under anaerobic conditions (second step); and finally, these membranes have been tested in a combined process, where the anaerobic effluent, has been used as influent for being treated under aerobic conditions (third step).

The experimental work, has been performed in a side stream MBR unit from the company Sartorius with a reactor volume of 20 L and an external flat sheet membrane module, with an area of 0,00856m^2. In order to keep the wastewater quality constant a model textile wastewater (MTWW) composed of two dyes: Acid Red 4 (Red) and Remazol Brilliant Blue R (Blue), as well as NaCl, $NaHCO_3$, Glucose, a detergent and NH_4Cl was used (Bouhadjar et al.,2015). The purpose of these experiments was to study membrane performance (e.g. flux, permeability) and the resulting quality of treated wastewater in terms of e.g. COD removal and colour removal efficiency. To deepen the study, all used membranes have been investigated through characterisation methods such as AFM and SEM image analyses. In parallel for conducting fouling tests with a model fouling (humic acid, HA) a lab scale cross flow unit has been used as well. Besides study of operational parameters of the MBR treatment processes this work intended to be a tool for preselecting suitable membranes which will subsequently be further studied in submerged MBR which is typically used for large-

scale applications. It is worth mentioning that in parallel a PhD work carried out in the same research group at the University of Applied Sciences Karlsruhe studied performance of the same commercial and novel anti fouling membranes on long-term (6 months) in a small submerged MBR (Deowan, 2014). A study comparing performance of both side-stream and submerged MBR has been published (Bouhadjar et al.,2015).

The experimental period of this work started by December 2012 and ended by the end of June 2015, where the operating conditions have been fixed according to each step; firstly for the aerobic step: Temperature 20±2 °C , TMP 0,3-0,5 bar , pH 7,5±0,5, permeate flux 5-15 L/(m^2 h), HRT145-200 h , MLSS 6-8 g/L , secondly for the anaerobic step Temperature 36±2 °C , TMP 0,1-0,3 bar, pH 7,5±0,5, permeate flux 2-20 L/(m^2 h), HRT 117-1400 h , MLSS 12-16 g/L, within these trials membrane performance and permeate water quality, have been analysed by online and offline measurement. For this purpose TOC, colour and COD removal efficiency, the total nitrogen balance (TN in permeate, NH_4^+, NO_3^-), MLSS (mixed liquor suspended solid), colour and COD measurements in the reactor have been the offline measurements; whereas the online parameters were pH, turbidity, dissolved oxygen, conductivity, temperature, air flow, feed, retentate and permeate pressure, cross flow, exhaust gas CO_2 and O_2, CH_4 (during the anaerobic trial). The data were saved by the software running the fermenter unit, and represented in graphics that allow controlling the process during the whole experimental time.

The present work has been divided as follows:

- First part: aerobic trials for 1 year
- Second part: anaerobic trials for 1 year
- Third part: combined (integrated anaerobic-aerobic) for trials 2,5 months

The purpose of the first aerobic step was to test the different membranes basically in terms of water permeability as well as COD and colour rejection. It is worth to mention that during this part a complete nitrification has been noticed, on the other hand we concluded that it is not an easy task to degrade azo dye (Red) under aerobic conditions, since the Red colour rejection showed 40% only for all the different membranes being tested during this part. Therefore during the second part the MTWW was treated under anaerobic conditions and the feed COD was increased from 2400 mg/L to 7000mg/L by adding more glucose as C-source since a higher COD level for anaerobic is preferred for anaerobic treatment. Regarding the anaerobic

treatment part, we had unexpectedly high permeability values in comparison to the one got within the aerobic trials, increasing from 25 L/(m^2 h bar) during the aerobic trials to 200 L/(m^2 h bar) during the anaerobic trials, this can be attributed to the high temperature for the anaerobic conditions, this fact was supported by the cross flow unit results, by the use of the model foulant HA. The elimination of the dyes was improved from 40% to almost 100% for the Red dye and from 50% to 85% for the Blue dye by moving from aerobic to anaerobic conditions respectively. Our target was not only having an improved elimination of the dyes but also producing biogas (CH_4), however, methane production was very low since the methanogenesis step has been inhibited. This inhibition has been indicted by occurrence of high amounts of short-chain fatty acid such as acetic acid and valeric acid. By the end of this step we realised that the acclimation time that has to be given for the biological population responsible on the degradation under anaerobic conditions, needs more time for being adapted with the operating conditions in order to produce considerable methane flow because of the dye inhibition, another reason that slowed down the methane production is that the experiments have been realised in a laboratory scale unit, which means the influent flux, may not be enough for a detectable methane flux by the methane sensor. Regarding the third part where the collected permeate from the anaerobic treatment was used as feed for aerobic treatment, called integrated anaerobic-aerobic process, a complete nitrification has been observed for all the membrane samples through the commercial as well as the novel membrane (for this step only one of the novel membrane has been tested for some technical reasons, being detailed in the PhD work): It is worth mentioning that no significant changes have been noticed in term of colour rejection during this part, since almost the whole dye amount in the MTWW has been rejected by upfront anaerobic treatment. But was remarkable is that a significant increase in term of COD rejection efficiency could be achieved from around 80% during the anaerobic trials to almost a complete rejection during the combined process.

To study fouling effect that occurred to all tested membranes, AFM and SEM images have been performed at Swansea University (England) and ITM University (Italy), these images were used to study potential fouling layers and showed consequently inline results in terms of roughness calculated based on AFM images. In general during the whole experimental work, novel membranes and NF performed better against fouling in comparison to the commercial UF.

For a clear report of this work, the thesis has been splitted into four main chapters.

Chapter 01: literature review that reported on textile wastewater industry as well as MBR technology, under the different operating systems mainly aerobic and anaerobic conditions.

Chapter 02: a detailed report regarding all the materials and methods being used for the experimental work trials during the three steps of this PhD.

Chapter 03: graphics, figures and tables that summarize all the results got within the three steps, in parallel a discussion in depth comparing our findings to those got through other scientific works close to our field of research.

Chapter 04: conclusion and outlook dealing with future work based on these PhD findings, and some points that still need to be elaborated and tested under different conditions other than the already performed. The results of this work should be compared in the future to a similar work that would be realised for the treatment of real textile wastewater at an industrial scale.

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ABSTRACT

We are surrounded by rich diversity colour in our daily life, we all like wearing colourful clothes, who can imagine among us our world in black and white? Clothes, flowers, rainbow, foods, animals, all remain in black and white; what kind of life would it be? Hence colours are very important in our life. This described beauty can hide harmful impacts in the background, where these colours are produced, if these issues wouldn't be immediately solved, this can lead definitively to a disaster and transform the world not only to black and white but to a polluted world where future generations would suffer from damages caused unintentionally with the pretext of replying to the high demand, which requires high production. In other words and as Saint Exupery said: "we do not inherit the earth from our ancestors, we merely borrow it from our children". It is a responsibility before being an issue to resolve, as explained above, colours are important in our life , but their production needs not only a huge amount of water , but produces at the same time incredibly a high level of pollution, it is a matter of water pollution or more specifically, the sector meant here is textile wastewater production. The main concern of this thesis is to deal with a Model Textile Dye Wastewater (MTDW) in a combined process anaerobic-aerobic treatment to membrane filtration technology (MBR) by testing and comparing the performance of commercial available membranes (nanofiltration NF and ultrafiltration UF) to the novel antifouling membranes prepared in the frame of BioNexGen EU Project (www.bionexgen.eu). The choice of this subject is based on several reasons, one of the most important is that Algeria is long regarded among MENA countries, as a land suffering from water scarcity, at the same time having great and active textile industry sectors that consume water and hamper the environment. On the other hand biological process proving being not only efficient but also economically cheap, but alone is not enough since this step is regarded as the first treatment stage, where COD and BOD levels are reduced, therefore the combination with the membrane filtration technology in order to discard the rest of the pollutant compounds.

ABBREVIATIONS

AEO alcohol ethoxylates

AFM Atomic Force Microscopy

AnMBR Anaerobic Membrane Bioreactor

APEOs alkylphenol ethoxylates

ASP Activated Sludge Process

AUTEAB Acryloyloxyundecyltriethyl Ammonium Bromide

BOD Biochemical Oxygen Demand

CAS Conventional Activated Sludge

COD Chemical Oxygen Demand

DO Dissolved Oxygen

EGDMA Ethylene Glycol Dimethacrylate

EPS Extra-cellular Polymeric Substances

F/M Food to Microorganism Ratio

FS Flat Sheet

HA Humic Acid

HEMA 2-Hydroxylethyl Methacrylate

HF Hollow Fibre

HRT Hydraulic Residence Time

H_2O_2 Hydrogen peroxide

KDa Kilo Dalton

LAS linear alkylbenzene sulphonates

MBR Membrane Bioreactor

MLSS Mixed Liquor Suspended Solids

MMA Methylmethacryate

MTDW Model Textile Dye Wastewater

MW Molecular Weight

MWCO Molecular Weight Cut Off

NF Nanofiltration

NH_4^+-N Nitrogen concentration in ammonia

NH_3^--N Nitrogen concentration in nitrate

NO_2^--N Nirogen concentration in nitrite

PBM Polymerisable Bicontinuous Microemulsion

PE Polyethylene

PES Polythersulfone

PET Polyethylene Terephthalate

PhACs Pharmaceutical Active Compounds

PVC Polyvinylchloride

PVDF Polyvinylidene Difluoride

PP Polypropylene

RO Reverse Osmosis

SEM Scan Electronic Microscopy

SRT Solid Retention Time

TC Total Carbon

TOC Total Organic Carbon

TMP Transmembrane Pressure

TMEDA Tetramethylethylene Diamine

TN Total Nitrogen

UF Ultrafiltration

UASB Conventional upflow anaerobic sludge blanket

WHO World Health Organization

WP Water Permeability

WWTPs Wastewater Treatment Plants

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Table 3.8. Characteristics of Model Textile Dye Wastewater (MTDW)

CHAPTER 01

LITERATURE REVIEW

1.1. Introduction

There is growing evidence of a global water crisis, of which the most obvious manifestation is that 1.2 billion people lack access to safe and affordable water for their domestic use (WHO, 2003). Of the total available water on earth, 97.5% is salty and is not usable for drinking purpose, of the remaining 2.5% of fresh water, only a marginal part, ~1%, is available for human consumption (V.Ranade and M.Bhandari, 2014). Since 1950, the world population has doubled, and water consumption has increased sixfold, this leads to a rapid industrial consumption growth. To a great extent, recently, parts of the world have already started feeling the ”water crunch”. It is believed that by 2030, India, China, and selected countries of Europe and Africa will face water scarcity (Figure 1.1). A recent UN report indicates that by 2025, two-thirds of the population of the world could face water stress (UNEP, 2007)

Since the distribution of water across the globe is not uniform, parts of the world are increasingly facing water scarcity. The reason can be of natural origin in some regions because of the reduced rainfall or climate changes; however, the human factor is most critical in aggravating this problem by wasting water, polluting water resources and inappropriately managing water.

Recent researches report that the total wastewater combining sewage, industrial and agricultural discharged globally is tens of millions of cubic meters per day (Corcan et al., 2010; UN Water, 2008).

Limited access to freshwater already impacts the lifestyle and development opportunities in water scarce areas (Qadir et al., 2007a). Freshwater resources and population densities are unevenly distributed worldwide. As a result, water demands already exceed supplies in regions with more than 40% of the world’s population (Bennett, 2000). By the year 2025, as much as 60% of the global population may suffer physical water scarcity (Pimentel et al., 1999; Rijsberman, 2006). Among them the Middle East and North African region is regarded as one of the most water scarce regions. In order to abate future water scarcity wastewater recycling and reuse is becoming increasingly important (Figure 1.2)

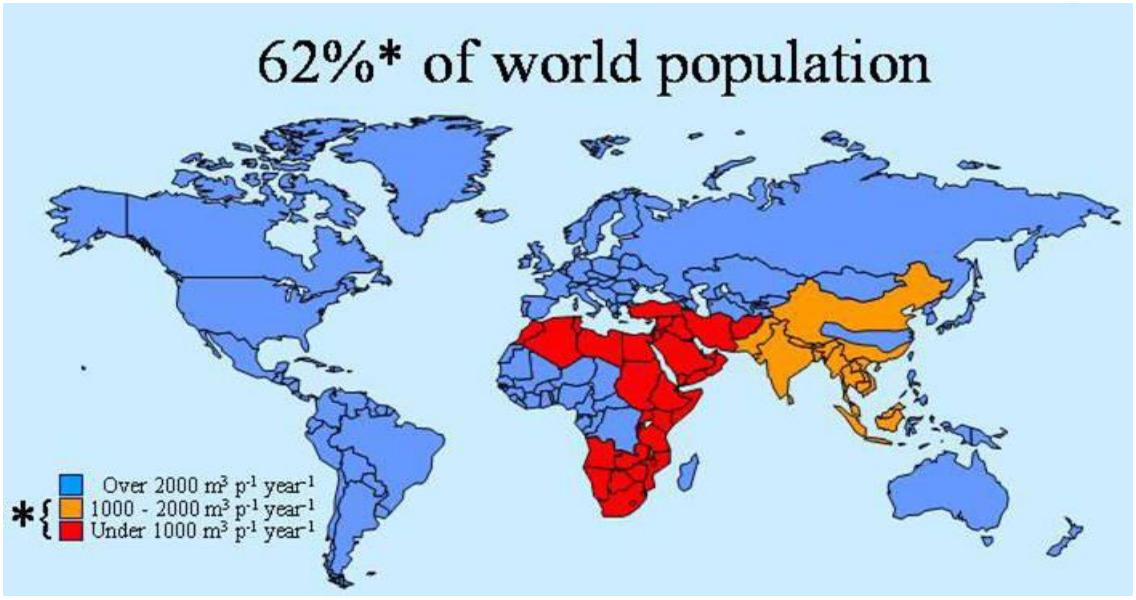


Figure 1.1.Water scarcity in 2030 based on the Falkenmark Indicator (Source: Wallace, 2000)

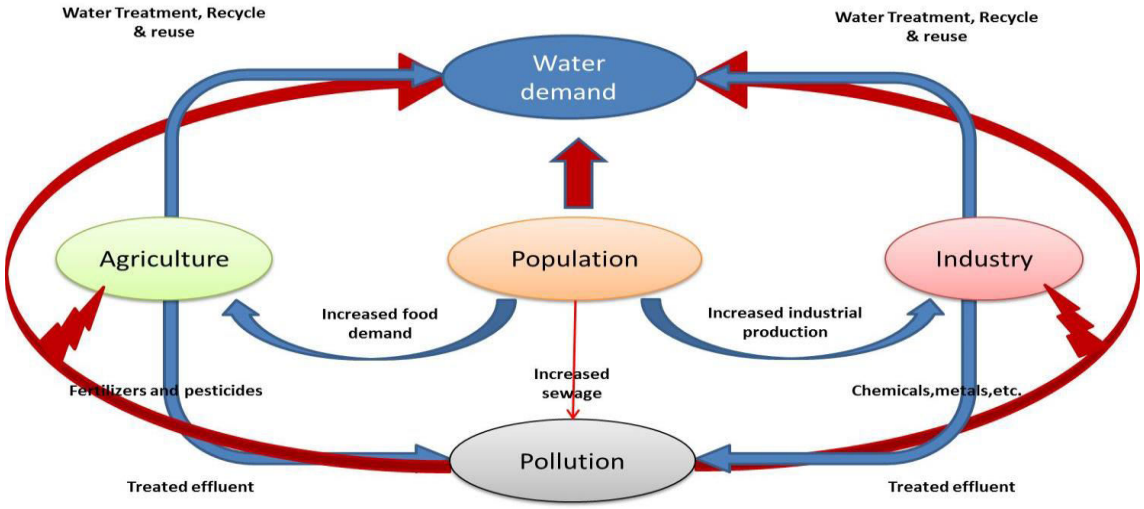


Figure1.2. Proper perspective for water sustainability (adapted from V.Ranade, M.Bhandari, 2014)

wastewater generated in the MENA region is 22.3 km^3/year, of which 51% (11.4 km^3/year) is treated (Table 1.1). The efficiency of wastewater treatment in the MENA region is highly variable and many treatment plants have design limitations to treat a mixture of domestic and industrial wastewater, which is usually the most prevalent form of wastewater reaching the treatment plants. In addition, the wastewater treatment plants do not have the capacity to accommodate the large volumes of wastewater resulting from increasing urban populations. In some treatment plants, the retention times for wastewater treatment have become too short to be effective (Qadir et al., 2010b).

Table.1.1. Wastewater generated, treated and used in Middle East and North Africa (MENA).

Country	Waste water Generated		Wastewater Treated		Treated waste water used	
	Reporting Year	Volume (km^3/year)	Reporting Year	Volume (km^3/year)	Reporting year	Volume (km^3/year)
Algeria	2010	0.730	2010	0.150	-	NA
Bahrain	2010	0.084	2005	0.062	2005	0.016
Egypt	2011	8.500	2011	4.800	2011	0.700
Iran	2010	3.548	2010	0.821	2010	0.328
Iraq	2012	0.580	2012	0.580	-	NA
Israel	2007	0.500	2007	0.450	2004	0.262
Jordan	2008	0.180	2011	0.115	2012	0.108
Kuwait	2008	0.254	2005	0.250	2002	0.078
Lebanon	2003	0.310	2006	0.004	2005	0.002
Libya	1999	0.546	1999	0.040	2000	0.040
Morocco	2010	0.700	2010	0.124	2008	0.070
Oman	2000	0.090	2006	0.037	2006	0.037
Palestenian Territories	2001	0.071	2001	0.030	1998	0.010
Qatar	2005	0.055	2006	0.058	2005	0.043
Saudi Arabia	2000	0.730	2002	0.548	2006	0.166
Syria	2002	1.364	2002	0.550	2003	0.550
Tunisia	2010	0.246	2010	0.226	2001	0.021
Turkey	2010	3.582	2010	2.719	2006	1.000
United Arab Emirates	1995	0.500	2006	0.289	2005	0.248
Yemen	2000	0.074	1999	0.046	2000	0.006
The data are from FAQ-AQUQSTAT(2012).NA refers to not available date						

Water is becoming a rare commodity in Algeria. Renewable natural water resources are estimated at approximately 15 bilion m^3 per year, that is approximately 404 m^3 per capita per year, near the threshold of 500 m^3 per capita per year, which is widely recognized as the scarcity threshold that indicates developing scarcity and underlying crises (Hamiche et al., 2014)

The Algerian water sector is facing several limitations and problems which could, if not properly handled, limit the dynamic of economic growth that Algeria is looking for by launching a huge range of water-related projects (Figure 1.3). These limitations and problems relate primarily to decreased water resources due to the impact of climate change which has become a reality in Algeria and whose effects on our environment are already visible.

The future development of water resources depends on solutions characterized by high energy consumption, for example sea water desalination. In contrast the reuse of wastewater and the introduction of drip irrigation are comparatively lower energy solutions.

In general development of the water sector will therefore be closely tied to the development of the energy sector.

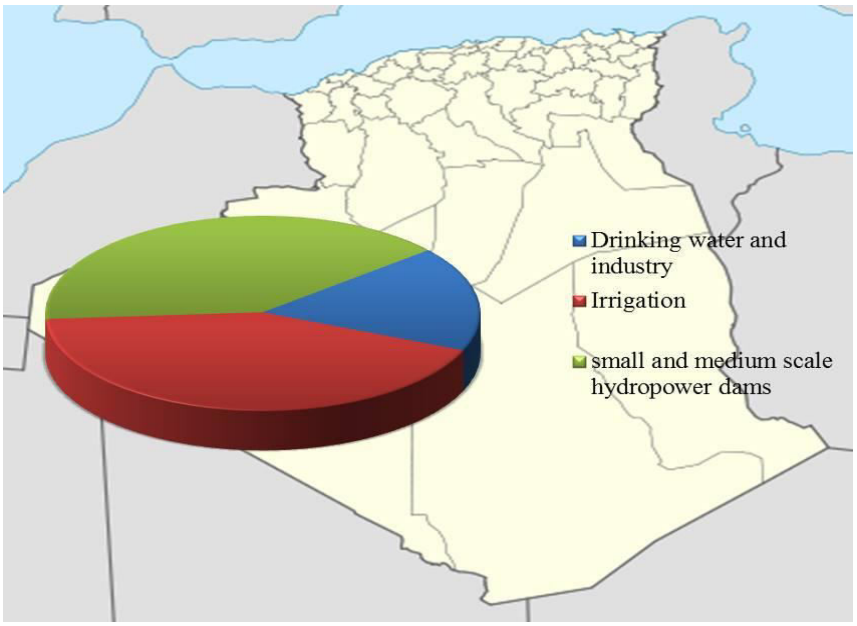


Figure.1.3. Future water demand in Algeria Hamiche et al,. 2014)

As it can be seen on the Figure1.3 above, the water demand for all use sectors is evaluated at approximately 20 billion m^3 in 2030.

After this brief report on the water demand, use as well as pollution, it is clear that MENA countries in general and Algeria in special are facing a severe current and future problem. For this reason and in order to find a viable development the water management in this area is directed toward economisation and rationalization of the water resources (Badani et al., 2005).

1.2. Textile wastewater

Textile industry is known to be a huge water consuming sector. In fact for the production of a ton of textile product, 200-350 m^3 of water are consumed (Judd et al., 2003; Schoeberl et al., 2005). Thus, the large quantity of aqueous waste generated by textile industries has become a significant environmental problem. Dye bath effluents in particular, are not only visible pollutants by the nature of their colour, but can hinder light penetration in the water of lakes, rivers or lagunas and therefore can disrupt biological processes in natural waters. Furthermore dye effluents can contain chemicals, which are toxic, carcinogenic, mutagenic, or teratogenic to various microbiological or animal species (Willcock et al.,1992).

Aoudj et al. (2010) mentioned that wastewater samples collected from the neighbourhood of textile industry located in Boufarik (Algeria) revealed a high contamination by synthetic dyes, most of them being toxic. In Algeria, the agricultural reutilization of treated wastewater, even industrial is more strongly in demand (Belkacem et al., 2007). It has been reported that the industry in Béjaia (coastal town in Algeria) is growing quickly and currently discharges about 80.000 m^3 of wastewater each day.

Wastewater from dyeing and finishing processes in the textile manufacturing industry constitute a substantial source of pollution which is characterized by intense colour, high Chemical Oxygen Demand (COD), fluctuating pH, and suspended particles. As illustrated in the Figure 1.4.

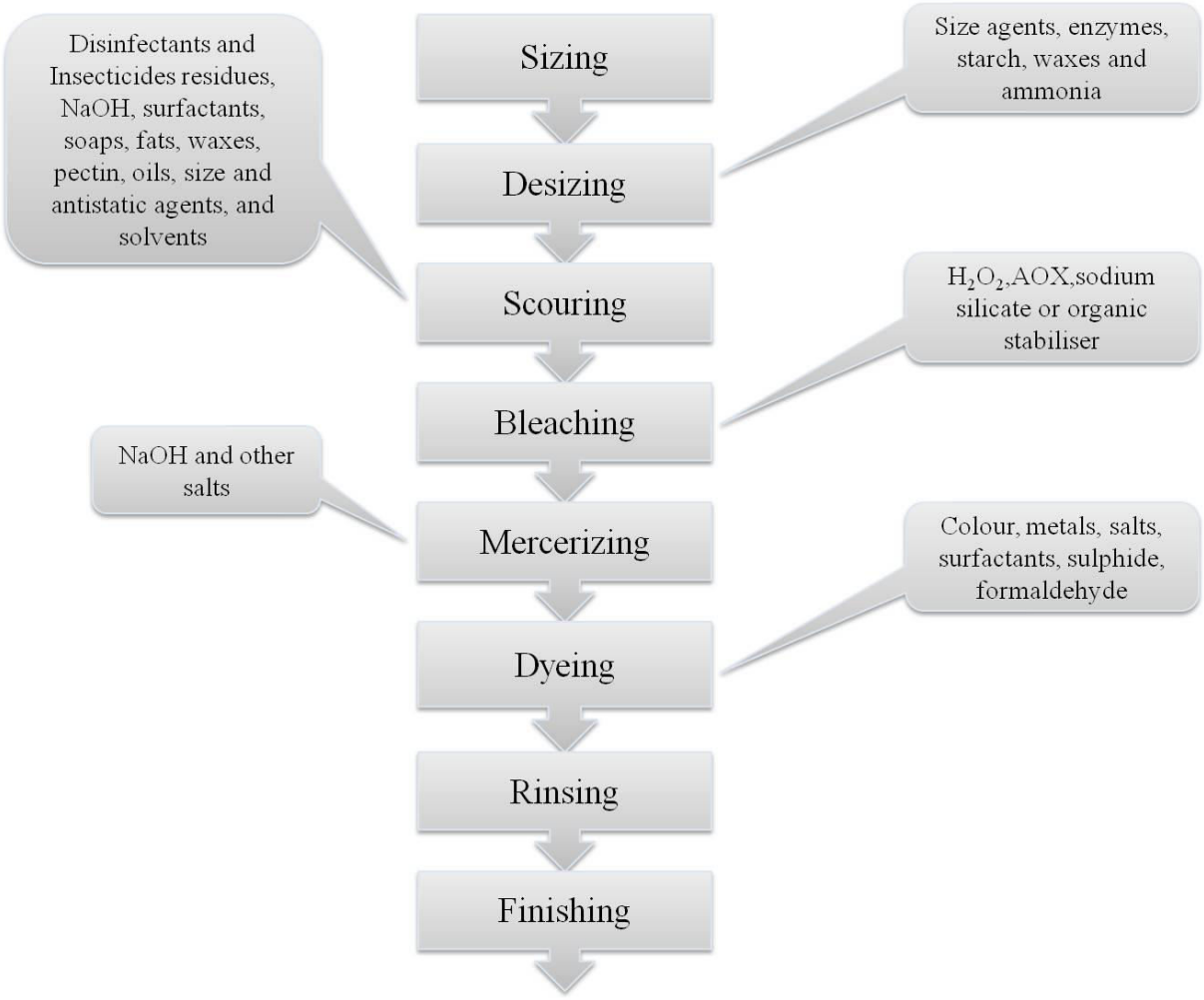


Figure.1.4. Schematic of operations involved in textile cotton industry and the main pollutants from each step (adapted from Dos Santos et al., 2007)

In order to illustrate in numbers the characteristics of the wastewater generated from each step among those mentioned on Figure.1. 4 above, the Table 1.2 shows a typical composition of cotton wet processing wastewaters.

Table. 1.2 Characterisation of the cotton wet processing (André B.dos Santos et al.,2007)

Process	COD (g/L)	BOD (g/L)	TS (g/L)	TDS (g/L)	pH	Colour (ADMI)	Water usage (L/kg)
Desizing	4.6-5.9	1.7-5.2	16-32.0	-	-	-	3-9
Scouring	8.0	0.1-2.9	7.6-17.4	-	10-13	694	26-43
Bleaching	6.7-13.5	0.1-1.7	2.3-14.4	4.8-19.5	8.5-9.6	153	3-124
Mercerising	1.6	0.05-0.1	0.6-1.9	4.3-4.6	5.5-9.5	-	232-308
Dyeing	1.1-4.6	0.01-1.8	0.5-14.1	0.05	5-10	1450-4750	8-300

ADMI: American Dye Manufacturer Institute

Indeed, the textile industry utilizes about 10,000 pigments or dyes, most of them are toxic substances to human and aquatic life and it has been reported that 15% of the used dyes are released into wastewaters (Daneshvar et al., 2006). Therefore they have be treated before finale discharge to achieve legal and aesthetic standards. EU Directive 91/271 imposes limits on colour, as it reduces light penetration in receiving water bodies (EU Directive, 2015). This is particularly a critical problem in Algeria where textile industry is highly developed. Conventional methods for removing dyes from textile waste water consist mainly of biological and physicochemical treatments and their various combinations (Belkacem et al., 2008).

Without adequate treatment these dyes are stable and can remain in the environment for an extended period of time. For instance, the half-life of hydrolysed Reactive Blue19 (RB19) is about 46 years at pH 7 and 25°C (Hao et., 2000)

Before moving to the several treatment methods, it is important to go further into details regarding dyes properties in general and azo and anthraquinone dyes in particular, since these two dyes were selected as model pollutants in this work.

Dyes are classified according to their application and chemical structure. They are composed of group of atoms responsible for the dye color, called chromophores, as well as an electron withdrawing or donating substituents that cause or intensify the color of the chromophores called auxochromes (André et al., 2006)

The most important chromophores are:

- Azo (-N=N-)
- Carbonyl (-C=O)
- Methine (-CH=)
- Nitro ($-NO_2$)

1.2.1. Azo dyes

It is estimated that almost 10^9 kg of dyes are produced annually in the world, of which azo dyes represent about 70% by weight (André et al., 2006). Azo dyes are one of the most important categories of synthetic dyes because they are easily synthesized and have a broad color spectrum (Geng et al., 2015). In general, they can be classified into monoazo dyes, disazo dyes, trisazo dyes and polyazo dyes, but the monoazo compounds account for the great majority of them. Azo dyes also have versatile applications in many fields such as optical data storage, non-linear optics, dye-sensitized solar cells, ink jet printers and metallochromic indicators. Even though some azo dyes have been reported poisonous, many additional dyes can be used in drugs and food (Kim et al., 2011). Azo dyes are generally recalcitrant due to their xenobiotic nature and exhibit considerable resistance to decolourization treatments (Novotny et al., 2006; Khalid et al., 2009; Hua et al., 2013).

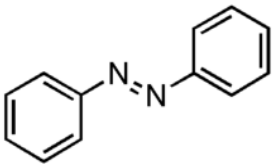


Figure.1.5. General chemical structure of azo compounds

Under anaerobic conditions the reductive cleavage of azo linkage, is the first stage in the complete anaerobic–aerobic degradation process, resulting in aromatic amine as metabolites. Aromatic amines, which are formed during anaerobic treatment, are generally colourless and hazardous. Though mineralization of the aromatic amines under aerobic conditions is more common, it was reported that some aromatic amines that are characterized by the presence of hydroxyl and carboxyl groups can be mineralized under only under anaerobic conditions. As a result, combined anaerobic and aerobic conditions are essential for the complete biodegradation of coloured wastewaters (Çinar and Demiröz, 2010). Figure 1.6 illustrate the pathway of azo dye degradation via anaerobic digestion and the degradation of the resulting aromatic amine via aerobic digestion.

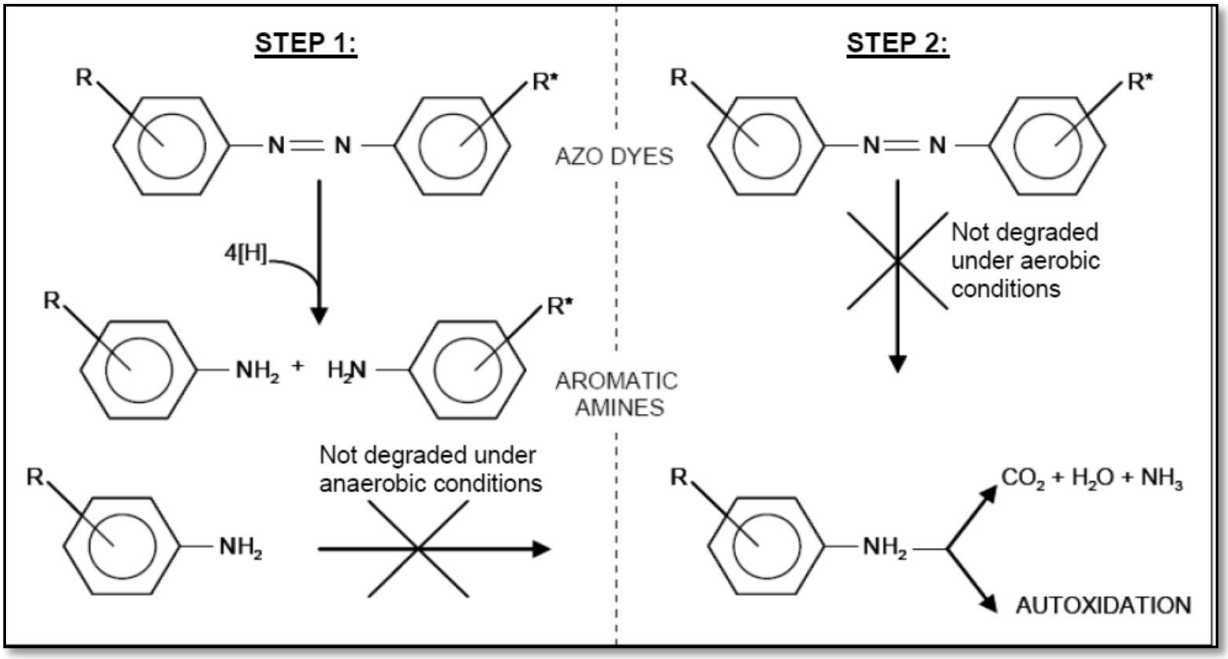


Figure.1.6.Anaerobic and aerobic degradation pathways of azo des and aromatic amines (De Jager et al., 2013)

1.2.2. Anthraquinone dye

This class of dyes is considered as the second most important class of textile dyes (Baughman and Weber, 1994). Anthraquinone dyes have a wide range of colors in almost the whole visible spectrum but they are commonly used for violet, blue and green colors.

They have chromophore groups, =C=O and =C=C=, and can be precipitated or adsorbed only in small amounts (Lixia et al., 2014)

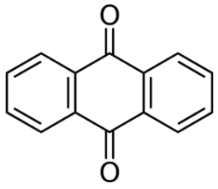


Figure.1.7.General chemical structure of anthraquinone compounds

1.3. Treatment methods for textile wastewater

Methods for dealing with textile wastewater consist of various biological, physical and chemical treatment processes that can be applied separately or be combined (Alinsafi et al., 2006). There are a variety of processes to remove dye from coloured effluents such as precipitation, adsorption, photodegradaion, biodegradation, chemical coagulation, electrocoagulation (Slokar et al., 1998).

Adsorption and precipitation have the inconvenience being very time consuming and costly with low efficiency (Daneshvar et al., 2006). Chemical degradation by oxidative agents such as chlorine is the most important and effective method, but it produces some very toxic products such as organochlorine compounds (Kim et al., 2002) . Photooxidation by UV/H_2O_2 or UV/TiO_2 needs additional chemicals, and therefore causes a secondary pollution.

In addition, it is known that a technical process must not only be efficient, but also economically feasible regarding the operating costs and its initial investments to reach the main target, solving the environmental problems. Thus it is primordial to find a compromise between the environmental issue and the economic cost of the treatment procedure, since this does not depend only on the choice of the treatment process, but also which kind of pollutant, that has to be eliminated and the cost involved. For example the costs of adsorption, ultrafiltration and ozonation usually exceed that of chemical coagulation. When chemical coagulation is used to treat dyed wastewaters, the pollution may be caused by chemical substances added at a high concentration (Belkacem et al., 2010). The ultimate goal is to find a compromise, where cost and efficiency are taken in consideration. Several papers have reported already regarding the cost of the wastewater treatment, whether for sewage wastewater or for industrial wastewater such as textile industry, where the cost includes the operating costs for conventional operations. But these reports are more specific in their presentations, and this can be limiting from generalization point of view. In times of increasing energy costs it is therefore preferable to classify the different separations methods according to their qualitative energy consumption, see Figure 1.8 (Ranade and Bhandari, 2014),.

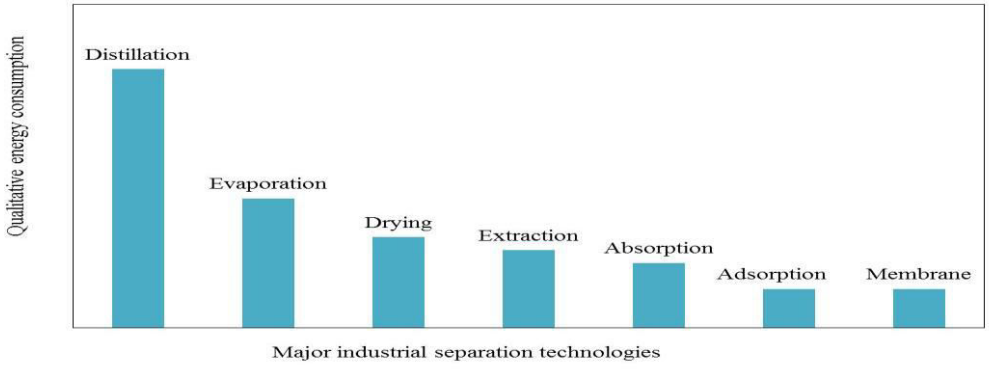


Figure.1.8. Energy consumption pattern in separation processes. (adapted from Ranade and Bhandari, 2014)

Most of the conventional treatment processes are summarised for illustration below:

Table 1.3. Conventional textile wastewater treatment processes[a]

Conventional treatment processes			
Physical methods	Chemical oxidation	Advanced oxidation processes	Biological methods
✓ **Coagulation** ✓ **Adsorption (Activated carbon)** ✓ **Ion exchange** ✓ **Membrane filtration** **(e.g. reverse osmosis, nanofiltration)**	✓ UV/O_3 ✓ UV/H_2O_2 ✓ Fenton reagent ✓ Ozonation	✓ Photocatalysis ✓ Electrochemical ✓ Sonolysis ✓ Ionising radiation	✓ Activated sludge (anaerobic, anoxic, aerobic) ✓ Sequencing batch reactor

[a] Summarised from Dafale et al., 2010 ; González-Zafrilla et al., 2008; Badani et al., 2005; Chakraborty et al., 2003; Kural et al.,2001; Ciardelli Ranieri, 2000; Gupta et al., 2000; Slokar and Le Marechal, 1998

1.3.1. Aerobic biological processes

In recent years, many studies focused on the ability of microorganisms and their capacity to biodegrade and biosorb dyes in wastewaters; bacteria, algae, and fungi are the most important microorganisms capable of decolourizing a wide range of dyes.

1.3.1.1. Bacterial processes

The biological decolourisation has been already investigated over the past decades (Libra et al., 2004). This treatment process can be realised either under aerobic conditions or under anaerobic conditions, both are able to degrade aromatic compounds. In the case of aerobic degradation, the enzymes mono-and di-oxygenase catalyse the incorporation of oxygen from O_2 into aromatic ring of organic compounds prior to ring fission (Dos Santos et al., 2007). Although azo dyes are aromatic compounds their substituents containing mainly nitro and sulfonic groups, make them quite recalcitrant to aerobic bacterial degradation (Claus et al., 2002). This can be explained either by the fact that the electron of the azo bond has a withdrawing nature, therefore being resistant to the to the oxygenases attack, or that the oxygen is a more effective electron acceptor, having tendency to more reducing equivalents than the azo dyes.

1.3.1.2. Fungi

In fungal decolourization of textile waste water, fungi can be classified into two kinds according to their life state:

- Living cells to biodegrade and biosorb dyes
- Dead cells (fungal biomass) to adsorb dyes.

Among enzymes, laccases and tyrosinases are two groups of phenoloxidases that catalyse the transformation of a large number of phenolic and non-phenolic aromatic compounds.

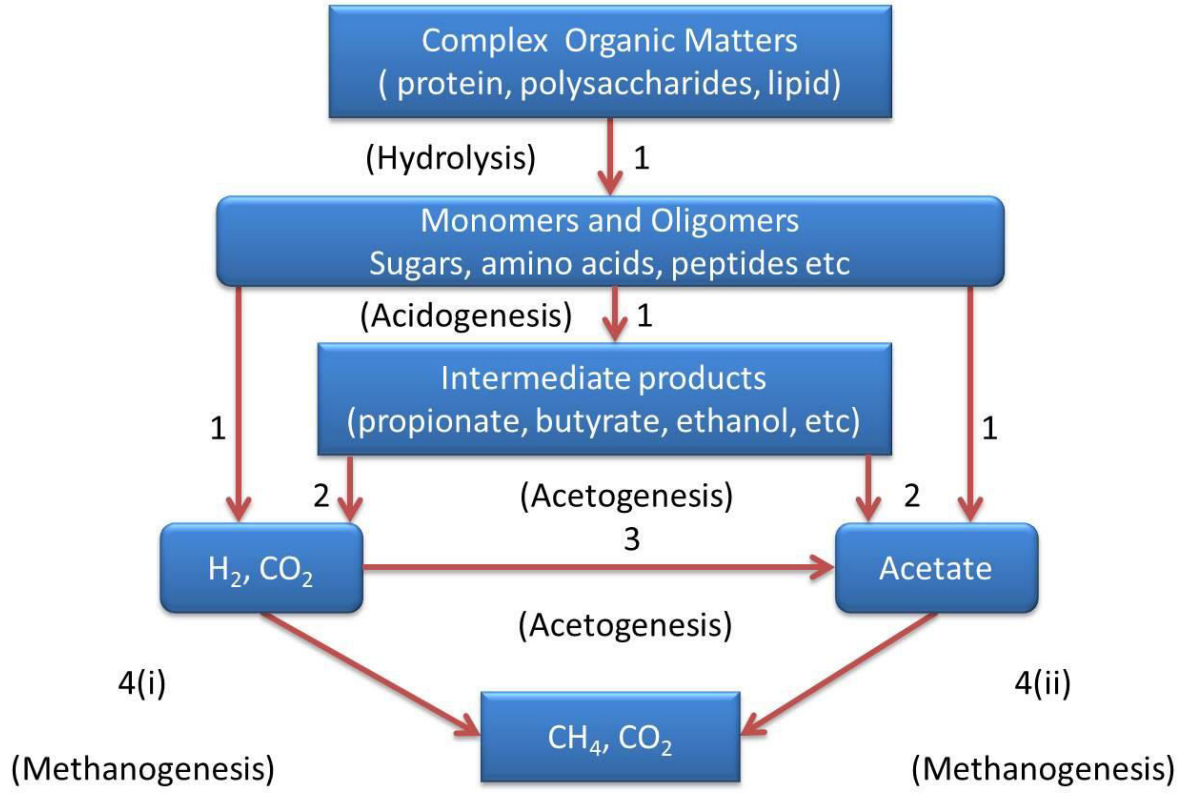
The capacity of fungi to reduce azo dyes is related to the formation of exoenzymes such as peroxidases and phenoloxidases. Peroxidases are hemoproteins that catalyse reactions in the presence of hydrogen peroxide (Duran et al., 2002). Lignin and manganese peroxidases have a similar reaction mechanism that starts with the enzyme oxidation by H_2O_2 to an oxidized state during their catalytic cycle. Afterwards, in a mechanism involving two successive electron transfers, substrates such as azo dyes reduce the enzyme to its original form (Stolz, 2001). The first report of aerobic degradation of azo dyes by lignolytic fungi appeared in 1990, when Cripps et al. (1990) demonstrated that nitrogen-limited cultures of Phanerochaete chrysosporium decolorized the azo dyes, Acid Orange 7 (Orange II), Acid Orange 6 (Tropaeolin O), or Direct Red 28 (Congo Red). Claus et al., (2002) mentioned that anthraquinone and indigoid-based dyes are better decolourised than the azo dyes and they represents poor substrates for laccases.. Chivukula et al. (1995) cited that azo dyes must be electron rich to be susceptible to oxidation by laccase. Miranda et al. (1997) reported that the highest color removal occured at a certain nutrient concentration, mainly: 1 g K_2HPO_4/L and 0,5 g $MgSO_4$. $7H_2O$/L. The optimum pH for decolourisation by an unidentified white-rot fungus was pH 4-5 (Zhang et al.,1999).

1.3.2. Anaerobic biological processes

Anaerobic biological treatment, generally has not prevalently been used in the past, for many reasons. Anaerobic reactors were supposed to be less stable under fluctuations, more expensive to install and a long start up time in comparison to the aerobic reactors. However, all these arguments were due to the weakness of the knowledge of the process and the reactor design. This remained the general opinion regarding this processes, till Young and McCarty started 1969 intense research in application of anaerobic process for the treatment of both industrial and municipal wastewaters (Younga and MCarty, 1969). In 1983 Gujer and Zehnder showed the sequence of the reactions that occur under anaerobic conditions in order

to transform the complex macromolecules of the organic matter present in the wastewater into biogas, thus several groups of microorganisms are required. Four different phases are distinguished in the overall conversion of the organic matter to biogas:

1) Hydrolysis ⟶ 2) Acidogenesis ⟶ 3) Acetogenesis ⟶ 4) Methanogenesis



1: Hydrolytic and non-hydrolytic fermentative bacteria. 2: Syntrophic acetogens.
3: Homoacetogens. 4: (i) Hydrogenetrophic methanogens (ii) Aceticlastic methanogens

Figure.1.9. Metabolic pathway of anaerobic degradation. (adapted from Khanal, 2008)

1) Hydrolysis

2) Acidogenesis

3) Acetogenesis

4) Methanogenic bacteria – methanogens: these are the microorganisms responsible for methane production. The doubling time of these bacteria is 2-10 days, and they are further divided into two groups:

a- Hydrogen utilizers (lithotrophs)

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$$

b- Acetic acid users (acetotrophs)

$$CH_3COOH \longrightarrow CH_4 + CO_2$$

It is important to mention that the methane producing bacteria are strict anaerobes and are extremely sensitive to pH and temperature changes: Anaerobic bacteria are active under two temperature zones, namely the mesophilic range where the temperature is in between 30°C-35°C and the thermophilic range (50°C-60°C). About 75% of methane production is from the decarboxylation of acetate and the rest is from CO_2 and H_2, as shown on Figure.1.9 (Visvanathan et al., 2011). The findings of Pavlostathis and Giraldo-Gomez (1991) demonstrated that the rate of hydrolyses is a function of pH, temperature, concentration of hydrolysing biomass and the type of particular organic matter, it has also been proven that the hydrolysis rate in anaerobic process is increased at elevated temperatures. This means in thermophilic range acetogens / acidogens need an optimum pH of 5.5-7.2 whereas methanogens need 6.8-7.8. The high rate of acetogen and the slow growth rate of methanogen make that the acetic acid accumulates in the anaerobic reactor. Thus the reactor pH drops and the methanogenesis is inhibited; therefore it is important to maintain the reactor pH close to neutral in order to keep the optimum methanogenic activity, either through a separated reactor operation or through alkalinity addition. Another reason that causes toxicity to the anaerobic microorganisms, is the presence of some of particular substances in the wastewater such as heavy metals, chlorinated hydrocarbons and cyanides as well as by-products of microorganisms such as ammonia, sulphide and volatile fatty acids. However, presence of inorganic nutrients such as calcium, and magnesium, trace elements such as cobalt and nickel can have a positive effect on the anaerobic metabolism. It has been found that there is 30 fold increase in CH_4 production rate when Ni and other trace elements are present (Speece et al., 2006) Since the purpose of this thesis is to study the treatment of azo as well as anthraquinone dyes their removal under anaerobic condition is of is of particular interest. The Table 1.4 illustrates the elimination rate of some of dyes treated by anaerobic granular sludge under mesophilic conditions.

Table.1.4. Colour removal by anaerobic granular sludge under mesophilic conditions

Type	Name	Decolouration (%)	Decolouration rates	Comments	Ref
Anthraquinone	Reactive Blue 19	70	-	About 50mg/l of dye	1
Anthraquinone	Acid Blue 80	7	-	About 50mg/l of dye	1
Anthraquinone	Acid Blue 25	67	-	About 50mg/l of dye	1
Anthraquinone	Basic Blue 22	62	-	About 50mg/l of dye	1
Anthraquinone	Reactive Blue 4	57	13.4 mg/l/h	About 50mg/l of dye	2
Anthraquinone	Reactive Blue 19	99	14.6 mg/l/h	About 50mg/l of dye	2
Anthraquinone	Reactive Blue 4	73	4.3 mg/l/h	About 50mg/l of dye	3
Anthraquinone	Reactive Blue 19	90	13.0 mg/l/h	About 50mg/l of dye	3
Anthraquinone	Reactive Blue 5	37	-		4
Anthraquinone	Reactive Blue 49	9	-		5
Anthraquinone	Acid Blue 25	68	-		6
Anthraquinone	Disperse Red 159	0	0		7
Anthraquinone	Disperse Blue 56	0	0		8
Anthraquinone	Reactive Blue 4	84	-	About 300mg/l of dye	9
Anthraquinone	Reactive Blue 19	84	-	About 300mg/l of dye	9
Anthraquinone	Reactive Blue 19	87	-	About 1032mg/l	10
Azo dye	Acid Orange 7	99	1.49 day^{-1}	About 0.3 mM of dye	11
Azo dye	Acid Red 266	95	0.20 day^{-1}	About 0.3 mM of dye	11
Azo dye	Acid Yellow 137	95	0.35 day^{-1}	About 0.3 mM of dye	11
Azo dye	Acid Yellow 159	97	0.72 day^{-1}	About 0.3 mM of dye	11
Azo dye	Basic Red 23	99	10.00 day^{-1}	About 0.3 mM of dye	11
Azo dye	Direct Black 19	99	3.00 day^{-1}	About 0.3 mM of dye	11
Azo dye	Direct Blue 53	99	0.24 day^{-1}	About 0.3 mM of dye	11
Azo dye	Direct Blue 71	100	0.61 day^{-1}	About 0.3 mM of dye	11
Azo dye	Direct Red 79	97	16.60 day^{-1}	About 0.3 mM of dye	11
Azo dye	Direct Red 81	99	7.80 day^{-1}	About 0.3 mM of dye	11
Azo dye	Direct Yellow 4	95	1.03 day^{-1}	About 0.3 mM of dye	11
Azo dye	Direct Yellow 12	86	1.17 day^{-1}	About 0.3 mM of dye	11
Azo dye	Direct Yellow 50	99	2.00 day^{-1}	About 0.3 mM of dye	11
Azo dye	Mordant Orange 1	97	1.74 day^{-1}	About 0.3 mM of dye	11
Azo dye	Reactive Black 5	99	5.00 day^{-1}	About 0.3 mM of dye	11
Azo dye	Reactive Red 2	100	0.31 day^{-1}	About 0.3 mM of dye	11
Azo dye	Reactive Red 4	99	0.45 day^{-1}	About 0.3 mM of dye	11
Azo dye	Reactive Yellow 2	73	0.01 day^{-1}	About 0.3 mM of dye	11
Azo dye	Reactive Red 235	100	4.42 day^{-1}	About 50 mg/l	12
Azo dye	Reactive Blue 235	100	23.5 day^{-1}	About 50 mg/l	12
Azo dye	Reactive Red 198	95	11.6 mg/l/h	About 300 mg/l of dye	13
Azo dye	Mordant Blue 13	83	-	About 50 mg/l of dye	1
Azo dye	Mordant Black 9	77	-	About 50 mg/l of dye	1
Azo dye	Basic Red 18	92	-	About 50 mg/l of dye	1
Azo dye	Acid Yellow 151	88	-	About 50 mg/l of dye	1
Azo dye	Direct Red 7	92	-	About 50 mg/l of dye	1
Azo dye	Acid Red 114	62	-	About 50 mg/l of dye	1
Azo dye	Direct Blue 15	83	-	About 50 mg/l of dye	1
Azo dye	Direct Yellow 12	75	-	About 50 mg/l of dye	1
Azo dye	Reactive Black 5	81	-	About 50 mg/l of dye	1
Azo dye	Acid Blue 113	94	-	About 50 mg/l of dye	1
Azo dye	Direct Black 19	51	-	About 50 mg/l of dye	1
Azo dye	Direct Black 22	61	-	About 50 mg/l of dye	1

[1]Brown and Laboureur (1983); [2] Fontenot et al. (2002); [3] Lee and Pavlostathis (2004);[4] Luangdilok and Paswad (2000); [5] Carliell et al. (1994); [6] Brown and Hamburger (1987);[7] Malpei et al. (1998); [8] Delée et al. (1998) ; [9] Lee et al. (2006); [10] Lee et al. (2005); [11] Van der Zee et al. (2001); [12] Willetts and Ashbolt (2000); [13] Fontenot et al. (2003).

As it can be seen in Table 1.4, azo dyes are generally better degradable under anaerobic conditions than the anthraquinone dyes. This has been confirmed also through the research work of this thesis, see Chapter 3 (Results and discussion).

1.3.3. Physical chemical processes

1.3.3.1. Chemical methods

The chemical processes comprise: reduction, ion exchange, neutralisation, chemical oxidation with UV/O_3, UV/H_2O_2 and Fenton reagent, advanced oxidation processes such as photocatalysis, electrochemical and ionising radiation.

Due to their simplicity of handling, oxidative processes are the most commonly used chemical decolouration processes. In most cases the oxidising agent is hydrogen peroxide, which due to its stability in pure form, needs to be activated, thus decolouration methods differ depending on the way which the hydrogen peroxide is activated.

- H_2O_2 – Fe(II) salts (Fenton's reagent) is an activated hydrogen peroxide by Fe(II) salts and is very suitable for the oxidation of wastewater that inhibit the biological treatment. This leads to some advantages mainly: COD and colour removal and toxicity reduction, nevertheless, since the process involves flocculation, impurities are transferred from the wastewater to the sludge, which is the major inconvenience. Therefore Peroxide-Chemie GmbH developed the so called FSR process (Fenton Sludge Recycling System), in which Fe(III)-sludge is eliminated. (Slokar et al., 1998). Fenton oxidation is recognised as a valuable method to remove colour and increase the biodegradability of dyeing wastewater, due to its high oxidative efficiency, non-selectivity and easy implementation (De Jager , 2013), but the high cost of this method makes it economically not suitable. Feng et al. (2010) found that by the combination of FOx based on the generation of highly reactive hydroxyl radicals with a submerged aerobic MBR composed of an activated sludge reactor with a hollow fibre membrane module reduced the total organic carbon (TOC) and the colour by 39.3% and 69.5% respectively. of a wastewater from dying industry under optimal operating conditions namely an initial pH of 5, hydrogen peroxide (H_2O_2) concentration of 17mmol/L, ferrous iron (Fe^{2+}) concentration of 1,7 mmol/L.
- Decolouration by means of H_2O_2/O_3 combination is applicable for direct metal-complex or blue disperse dyes (Strickland et al., 1995; Gregor et al., 1993). There are some problems with decolouration of acid and red (Strickland et al., 1995) disperse

dyes, though as well as with mixtures of direct, metal-complex, disperse and reactive dye (blue dye even more than red dyes) decolouration (Gregor et al.,1993).

Since BOD, COD and TOC removal efficiencies are the parameters indicating the effectiveness of a treatment process , several opinions have been discussed in different papers dealing with this subject, where (Gregor et al., 1993) claimed that COD remains unaffected by ozone treatment, while Ikehata et al. (1975) and Nebel et al.(1976) noticed a reduction in both COD and BOD values. On the other hand (Horning et al.,1992) indicated that these two parameters may increase following ozone treatment.

1.3.3.2. Physical methods

The physical processes comprise: coagulation, flocculation, sedimentation, adsorption on activated carbon and membrane processes (mainly nanofiltration and reverse osmosis).

Colour removal by adsorption method is based on the fact that many dyes have a high affinity to adsorbent materials, this process is influenced by some physical-chemical factors like dye-adsorbent interactions, adsorbent surface area, particle size, pH, contact time and temperature (Anjaneyulu et al., 2005). Activated carbon is the most common adsorbent and is very effective with many dyes. However, its efficiency is directly dependent upon the type of carbon material used and the textile wastewater characteristics, i.e. types of dyes being present in the wastewater (Robinson et al. 2001). In addition, activated carbon is expensive and requires regarding sustainability to be regenerated, which makes the material losing about 10% of its capacity. For these reasons and in order to decrease adsorbent losses during regeneration, new adsorbent materials have been tested for their ability for on-site regeneration. Among them were zeolites, polymeric resins, ion exchangers and granulated ferric hydroxide, however some of these adsorption materials showed either low sorption capacity like zeolites and microporous resins, others difficulties in regeneration like ion exchangers , and in the case where the cost is low like with peat, bentonite clay the removal efficiency of the material is too low and varies with the dye class. For example peat and bentonite have high affinity for basic dyes. (Anjaneyulu et al., 2005)

In case of membrane filtration the specific temperature and the chemical composition of the wastewater determine the type and the type of the membrane to be applied (Porter, 1997); mainly ultrafiltration, nanofiltration and reverse osmosis. The goal in many cases is not only water reuse but also chemicals recovery. In the field of textile industry these filtration methods can be used for both filtering and recycling not only pigment-rich streams, but also

mercerising and bleaching wastewaters. (Dos Santos et al., 2007). However the high cost and the fouling potential are the two main issues in the case of membrane filtration. Nevertheless (Porter, 1997) mentioned that the recovery of concentrates from membranes, e.g. recovery of the sodium hydroxide used in the mercerising step or sizing agents such as polyvinyl alcohol (PVA), can attenuate the treatment costs.

All the decolourisation methods described in this section have their pros and cons, and their selection depend on the characteristic of the textile wastewater being in the question of treatment solution (see Table 1.5)

Table.1.5. Advantages and disadvantages of some physical/chemical decolourisation processes applied to textile wastewaters (adapted from Robinson et al., 2001)

Physical/chemical methods	Method description	Advantages	Disadvantages
Fenton reagents	Oxidation reaction using mainly H_2O_2 – Fe(II)	Effective decolourisation of both soluble and insoluble dyes	Sludge generation
Ozonation	Oxidation reaction using ozone gas	Application in gaseous state: no alteration of volume	Short half-life (20 min)
Photochemical	Oxidation reaction using mainly H_2O_2 – UV	No sludge production	Formation of critical by-products
NaOCl	Oxidation reaction using OCl^- to attack the amino group	Initiation and acceleration of azo-bond cleavage	Release of aromatic amines
Electrochemical destruction	Oxidation reaction using electricity	Breakdown compounds are non-hazardous	High cost of electricity
Activated carbon	Dye removal by adsorption	Good removal of a wide variety of dyes	Very expensive
Membrane filtration	Physical separation	Removal of all dye types	Concentrated sludge production

However, there is no single economically and technically viable method to solve the colourisation issue, usually two or three methods have to be combined in order to achieve adequate level of colour removal (Robinson et al., 2001). During this PhD work our interest is to focus on the combination of biological treatment under aerobic as well as anaerobic conditions regarded as membrane technology filtration (MBR). Therefore, the following section reviews in-depth publications on MBR technology under both aerobic as well as anaerobic conditions.

1.4. Membrane bioreactor (MBR) technology and textile wastewater treatment

Membrane technology is a very promising technology that offers the possibility to improve the quality of the wastewater. In particular membrane bioreactor (MBR) has very good prospects for water reuse (Bouhadjar et al., 2015). It is a combination process of biological treatment (conventional activated sludge process) and membrane filtration technology and it is commonly regarded as one of the most innovative technologies for wastewater treatment and reclamation. In other words, membrane filtration in a MBR system replaces the solid-liquid separation that occurs conventionally in gravity-based clarifier. Hence the combination of the biological treatment and the membrane filtration efficiency lead to a complete solids removal, a significant physical disinfection capability. A very high degree of carbon, nitrogen compounds, and color removal are the main advantages of MBR processes, which result in very high quality of treated water for further reuse (Schoeberl et al., 2004, Stephenson et al.,2000). Therefore, MBR technology is particularly an attractive option for the treatment and reuse of industrial wastewaters from various industries including food processing, pulp and paper, chemical production, pharmaceuticals, mining and metal production and textile. The performance of MBR technology for treatment and reuse in textile industry has been studied in several research works.

The application of MBR technology in wastewater treatment in general and textile wastewater treatment in special, will be discussed in details in the following chapter where several case of studies are summarized based on what the literature review reported regarding the MBR systems under aerobic, anaerobic and combined conditions (see sections 1-2-5). Before looking into this part, different basic aspects concerning MBR technology such as e.g. membrane processes, MBR configurations are presented in the following.

1.4.1 Membrane processes

Membrane is simply a material that allows some physical or chemical components to pass more readily through it than others. It is thus perm-selective, since it is more permeable to those constituents passing through it (which then become permeate) than those which are rejected by it (which form the retentate); see Figure 1.10 below.

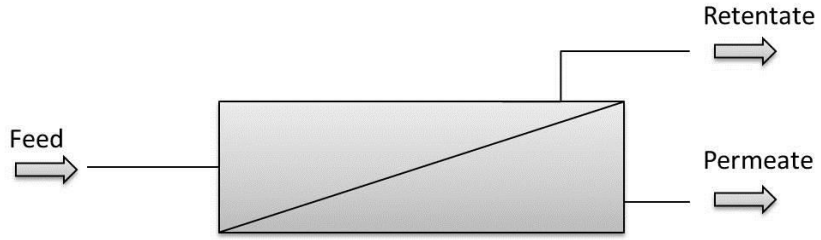


Figure1.10. Schematic of membrane (adapted from Judd, 2006)

Membrane separation systems where the permeate is formed of water, can be categorized into four groups based on the difference of the pore size of the membranes. These categories are sorted from the smallest to the largest pore size, as follows:

Reverse Osmosis (RO), Nanofiltration (NF), Ultrafiltration (UF) and Microfiltration (MF). (Judd, 2006). Figure 1.11 shows the wide variety of applications of membrane processes such as filtration, disinfection, organics removal, desalination, depending on the different pore size of the membrane.

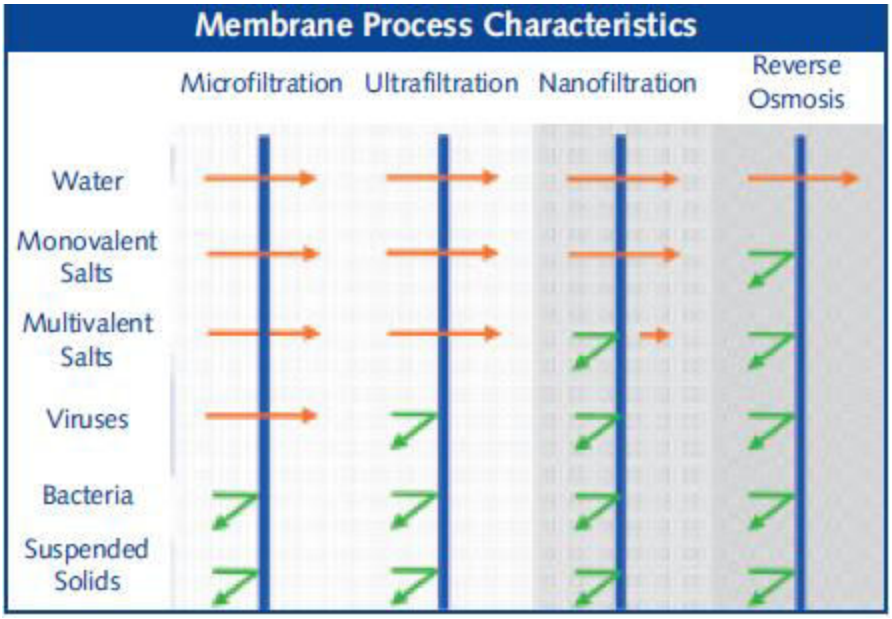


Figure1.11. Membrane processes characteristics (Biwater, 2015)

A slight difference can be noticed regarding the performance between MF and UF processes and RO and NF processes; as mentioned in (Pearce, 2007). The term membrane filtration refers to the removal of particles from a feed stream as performed by UF and MF processes, while NF and RO processes remove dissolved species from the stream.

Predominantly MF and UF membranes are used for MBR as these membranes achieve some sort of balance among effluent quality, energy requirement and membrane clogging for treatment of wastewater, whereas NF or RO membranes require much more transmembrane pressure and hence higher energy consumpton and will be subjected to frequent clogging. Therefore usually MBR using MF or NF membranes have been applied (Visvanathan,2011)

The membrane pore size can be defined either in terms of the effective equivalent pore diameter, normally in µm, or the equivalent mass of the smallest molecule in Daltons (Da) the membrane is capable of rejecting; where 1 Da represents the mass of a hydrogen atom (Judd, 2006). Thus membrane processes are classified depending on these parameters namely: pore size, molecular weight cut-off (MWCO) and the pressure under which the membrane operates. These categories are inter-related, because as the pore size is reduced or the MWCO decreases, the pressure applied to the membrane, to maintain the same flux, increases (De Jager et al., 2013).

Additional membrane processes functions, retaining contaminants and allowing water passing through are necessary to mention:

- Selectively extract constituents (extractive).
- Introduce a component in the molecular form (diffusive).

The membrane selectivity of MF and UF membranes basically depends on the pore size since they mainly reject particles whereas NF and RO also have the ability to retain dissolved compounds. Judd & Jefferson (2003) affirmed that NF selectively removes multivalent ions and certain charged or polar molecules, while RO removes monovalent ions, that is why membrane filtration processes using UF and MF are often used as pre-treatment for NF and RO processes (Pearce, 2007).

The fact of selectivity and the membrane pore size, make membrane processes ideal for meeting absolute filtration quality recommended by the regulation for the wastewater treatment.

1.4.2. Membrane Materials

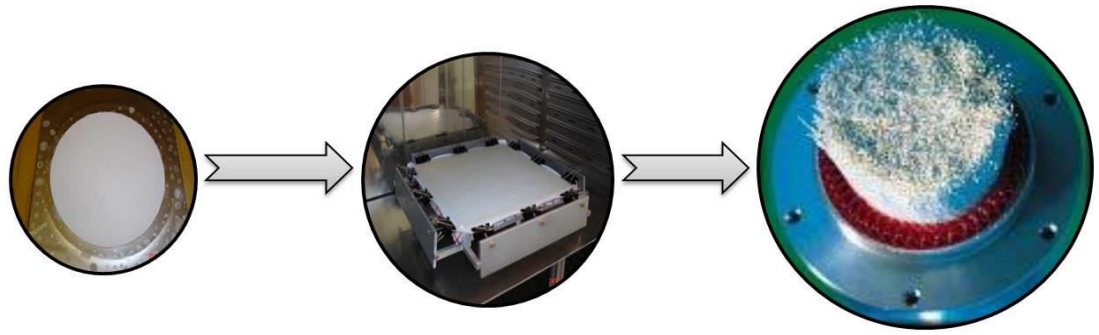
The membrane materials have to meet two principle criteria. Firstly being formed or configured in such a way to allow water passing through, and secondly being mechanically strong, since the membrane material must have resistance to thermal and chemical attack.

Generally there are two different types of membrane materials: polymeric and ceramic materials. Metallic membrane filters also exist, but these have specific applications which do not relate to membrane bioreactor (MBR) technology (Judd, 2006). Polymeric membranes are configured in such a way to have a high surface porosity and a narrow pore size distribution to provide a selective high degree of rejection.

The most common polymers being used to form MBR membrane materials are:

- Polyvinylidene difluoride (PVDF)
- Polyethylsulphone (PES)
- Polyethylene(PE)
- Polypropylene(PP)

The hydrophobic property of the polymer provides generally a hydrophobic character to the membrane. Hydrophobic materials are typically prone to fouling in MBRs since the mixed liquor contains besides flocculated bioactive suspended solids dissolved hydrophobic substanes such as humic acid, polysaccharides and proteins (Jamal et al., 2014) This is the reason why many research studies focused on the modification of the membrane surface in order to produce a more hydrophilic surface, either by chemical oxidation, organic chemical reaction, and plasma treatment (Galiano et al., 2015). The development of novel technical membranes typically starts at small scale in the lab and subsequently passes through pilot trials before being demonstrated on large industrial-scale (Figure 1.12)



1st step: Lab, diameter 5-7 cm

2 nd step: Small bench-pilot, Flat sheets,0.5 -2m^2

3rd step: Demonstration pilot with fibres, 5 -10m^2

Figure1.12. Membrane material, from lab-scale to industrial scale

1.4.3. Technical membrane modules

Membrane configuration is nothing else as its geometry and the manner in which the membrane is mounted and oriented in relation to the flow of water what determines the overall performance of the process. Individual membrane units are housed in "shells" to produce modules, the complete vessels through which the water flows (Judd, 2006).

In order to get the best process performance, the membrane should be configured as follows (Judd, 2006):

- A high membrane area to module bulk volume ratio,
- A high degree of turbulence for mass transfer promotion on the feed side,
- A low energy expenditure per unit product water volume,
- A low cost per unit membrane area,
- A design that facilitates cleaning,
- A design that permits modularisation

Currently, there are six principles configurations applied in membrane processes, in which a compromise has to be made regarding benefits and limitations (see Table 1.6). The configurations are based on either planar or cylindrical geometry:

1. Plate-and-frame/ flat sheet (FS)
2. Hollow fibre (HF)
3. (Multi)tubular (MT)
4. Capillary tube (CT)
5. Pleated filter cartridge (FC)
6. Spiral-wound (SW)

Table.1.6. Membrane configurations

Configuration	Cost	Turbulence Promotion	Backflush ability	Application
FC	Very low	Very poor	No	DEMF, low TSS Waters
FS	High	Fair	No	ED,UF,RO
SW	Low	Poor	No	RO/NF,UF
MT	Very high	Very good	No	CFMF/UF,high TSS waters,NF
CT	Low	Fair	Yes	UF
HF	Very low	Very poor	Yes	MF/UF,RO

DE: Dead-end, CF: crossflow

Since this thesis focuses on MBR technologies, it is necessary to mention that for MBR processes only the first three configurations (FS, HF, MT) are used, for the reason that these configurations promote a high degree of turbulence and are easy to clean.

As shown on the Figure 1.13 below; MT modules operate with the flow passing from inside to outside, while HF operates with the flow passing from outside to inside. For UF and MF the main products available for the purpose of wastewater treatment are dominated by HF and CM (Pearce et al., 2007).

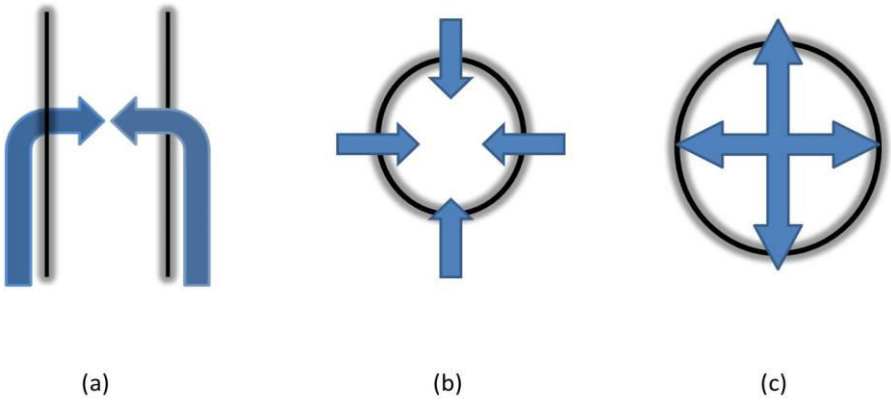


Figure1.13. Schematics showing flow through membrane configured as: (a) FS,(b) CT or (MT) and (c) HF(adapted from Judd, 2006)

1.4.4. Membrane system operations modes

There are two standard modes of operating in conventional pressure driven membrane processes, to talk about:

- Dead-end operation
- Crossflow operation

Dead-end operation

Many simple filtration processes use a dead-end technique; the flow of liquid to be filtered is directed perpendicular to the filter surface as presented on Figure1.14. This is effective whenever the concentration of particles to be removed is low or the packing tendency of the filtered material does not produce a large pressure drop across the filter medium.

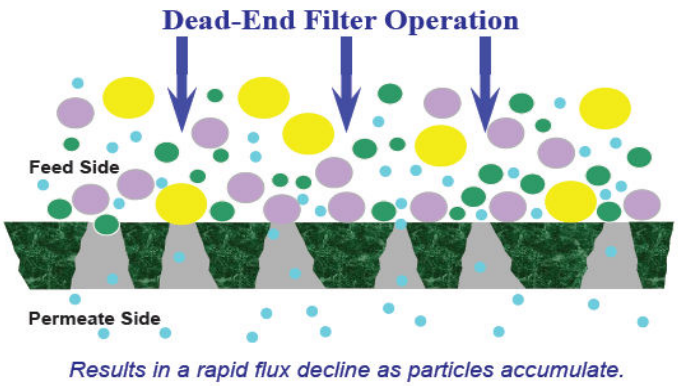


Figure1.14. Dead-end operating process

Usually processes streams have a high molecules and particles concentrations, such as proteins and precipitates that will rapidly compact on the filter surface (membrane) when operated in dead-end mode, which leads consequently to a significant drop in terms of filtration rate, therefore it is necessary to think about the next following mode, namely crossflow

Crossflow

This system provides the means to maintain stable filtration rates. Crossflow mode can operate with FS, SW, and HF, the crossflow is configured in such a way that it fits to the membrane geometry that suits the physical characteristics of the process fluid.

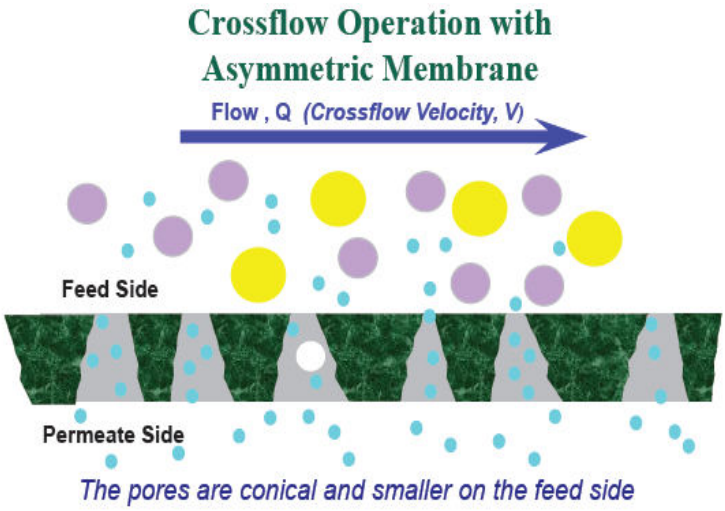


Figure 1.15. Crossflow operating process

1.4.5. MBR configurations

The MBR system has three significant parts that play an important role in the overall performance. The development of them has been moving fast since 1990 for its commercial usage (Frenkel, 2013).

Available MBR technologies employed for wastewater treatment can be classified according to membrane configuration: (FS); (HF) and (MT).

The FS based submerged MBR was piloted early in 1990 for wastewater application where the membrane material used was chlorinated polyethylene on a robust nonwoven support. The pore size of this membrane was 0,4 µm, which corresponds to MF size, but once a biofilm layer was formed over this surface, it worked in UF range and produced filtrate with good turbidity (Judd, 2011). The PES based flat membrane over PP support was reportedly used in sewage applications subsequently at a 150 kDa pore size, which falls into the UF range (Ranade,M.Bhandari, 2014).

The MBR configurations used in industrial applications are in general classified into two categories; namely submerged MBR (SMBR) and side-stream (SSMBR), as shown in Figure 1.16; where the main difference between the two configurations is the placement of the membrane module, either inside the reactor in the case of SMBR, or outside the bioreactor for SSMBR. Generally, the performance of both is based on the different operating parameters affecting the process , such as energy consumption, footprint, and type of water to handle.

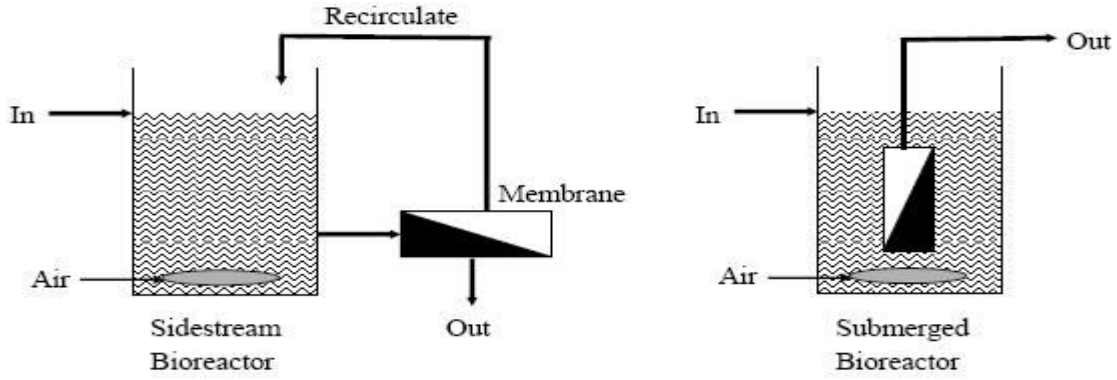


Figure1.16.Membrane Bioreactor (MBR) configurations

Table .1.7. Comparison between SSMBR and SMBR configurations (Visvanathan, 2011)

Comparaison Parameters	SMBR	SSMBR
Suitability	Low strength wastewater with good filterability	High strength wastewater with poor filterability
Membrane flux	Lower membrane flux or lower permeate per unit area of membrane	Higher membrane flux or higher permeate per unit area of membrane
Transmembrane pressure	Lower TMP is required	Higher TMP is required
Power requirement	Less power is required per m^3 of wastewater treated	More power is required per m^3 of wastewater treated
sensitivity	Less sensitive to variations in wastewater characteristics and flow fluctuations	More sensitive to variations in wastewater characteristics and flow fluctuations
Membrane area requirement	More area is required	Less are is required
economics	Generally less expensive at lower wastewater influent rate	Generally more expensive at lower wastewater influent rate
Membrane backwashing & cleaning	More frequent backwashing and cleaning required	Less frequent backwashing and cleaning is required
operation	Less operational flexibility	More operational flexibility with control parameters like, SRT, HRT, and MLSS
Extension of WWTP Capacity	Difficult to extend	Easier to extend

1.4.6. Factors affecting MBR technology

There are essentially five key elements of the MBR process which are crucial for its design and operation. These are:

- The membrane, its design and the durability of permeability,
- Feedwater, its characteristics and its pretreatment,
- Aeration of both membrane and the bulk biomass,
- Sludge withdrawal and residence time,
- Bioactivity and nature of the biomass.

These parameters are obviously related (see Figure 1.17). The rate at which sludge is withdrawn controls the residence time SRT which then determines the concentration of the biomass or the mixed liquor suspended solids (MLSS). The MLSS concentration then impacts both on the biological properties, that is the bioactivity and microbial speciation and also on the physical properties such as the viscosity and oxygen transfer. Whereas the feedwater chemistry has the greatest impact on MBR operation, in that the membrane fouling propensity of the mixed liquor is generally mainly dictated by the nature of the feedwater from which it is generated. Similarly, the rigour of the pretreatment of the feedwater by screening has a significant impact on the clogging propensity.

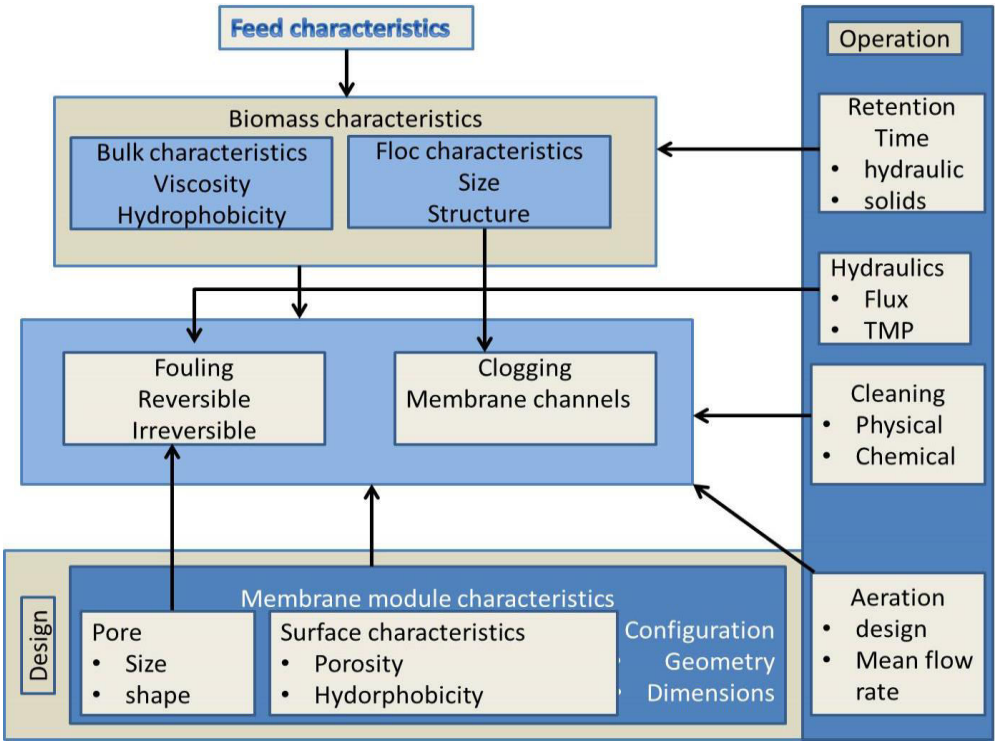


Figure 1.17.Inter-relationships between MBR parameters and fouling (adapted from Judd, 2006)

An understanding of the fundamentals MBR design, operation and maintenance can proceed through a comprehensive examination of the biological, chemical and physical phenomena occurring in MBR, since these interact to generate fouling through a number of mechanisms (Judd, 2006).

1.4.6.1. Membrane fouling

As mentioned above, it is well known that the major limitation that membrane processes face is "fouling". This phenomena result from the fact that the rejected constituents in the retentate tend to accumulate at the membrane surface, producing various phenomena which lead to a reduction in the flow of water through the membrane at a given transmembrane pressure (TMP). (Judd, 2006). Therefore several membrane research studies are conducted in the purpose of the characterisation and amelioration of the membrane material.

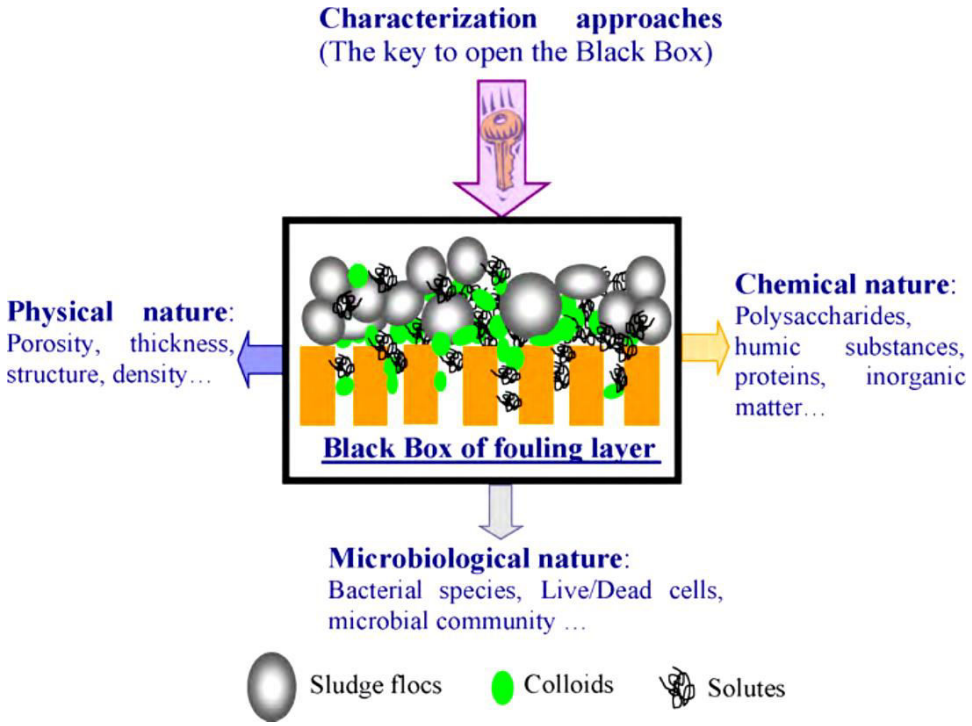


Figure1.18. Schematic illustration showing the role of characterization approaches in opening Black Box of membrane fouling (Fangang et al., 2010)

Fouling can be divided from the practical point of view in:

1. Reversible fouling that can be removed from the membrane by physical cleaning
2. Irreversible fouling removed by chemical cleaning
3. Irrecoverable fouling that cannot be removed by any cleaning

Physical cleaning in MBRs is normally achieved either by back-flushing or by relaxation (stopping the permeate flow and continuing to scour the membrane with air bubbles). Physical cleaning is a simple and short method (usually lasting less than 2 min) of fouling suppression which demands no chemicals and generally it is less likely that it will affect the membrane material. Chemical cleaning is a more effective method, which is able to remove more strongly the adsorbed deposits. Chemical cleaning is carried out mostly with sodium hypochlorite and sodium hydroxide for organic deposits removal, or with acidic solutions for removal of lime or other inorganic deposits (see Figure 1.19).

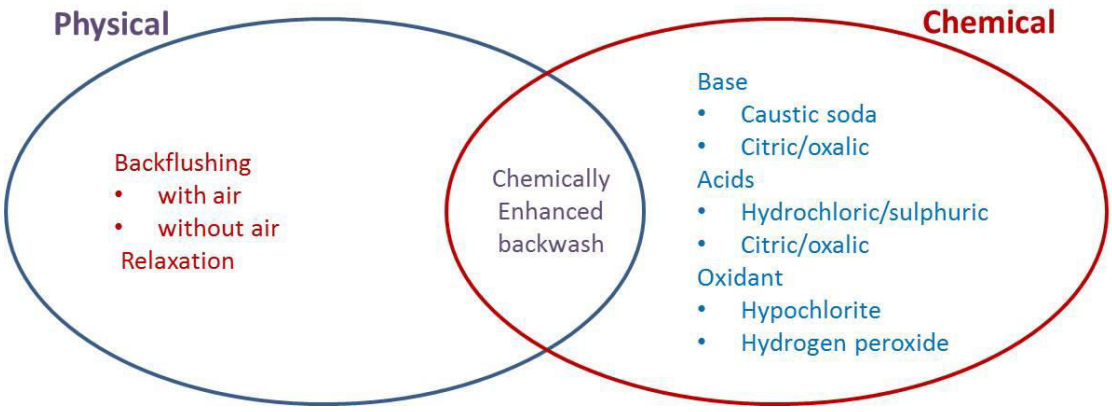


Figure1.19. Membrane cleaning methods

1.4.7. Applications of MBR

The application of MBR technology varies for the treatment of wastewater with a low organic loading rate such as the municipal wastewater, to the more or less intermediate to high loaded wastewater from industrial processes such as textile industry. This doesn't exclude the use of MBR technology for the treatment of other effluents; these could be: e.g. agricultural, fisheries, food processing industries.

1.4.7.1. MBR Technology in wastewater treatment

Since the 1990s numerous medium to large-scale MBR plants have proved their high treatment performance and superiority over the conventional treatment system in a variety of domestic and industrial applications (Judd, 2006). In 1990 Governor Dummer Academy (GDA), which is the oldest private day and boarding school in the United States, founded in 1763, and located on a 350 acre campus in Byfield, Massachusetts, was upgrade by use of conventional technologies. However, despite the upgrade, the wastewater treatment plant

could not achieve the required effluent quality by the permit under which it operates. Schwartz et al. (2005); have proved that MBR system was the best alternative for this application. In August 2000, the installation of a 380m^3/day MBR system used to treat domestic wastewater was completed, where steady state operations were achieved during September of 2000, and it showed a successful function since, thus MBR system in this case of study has successfully increased the wastewater treatment plant capacity, enabling the academy to meet permit discharge limitations for BOD and TSS; (< 10mg/L).

According to (Hunter, 2007) the first MBRs were introduced over 30 years ago in the 1970s by Dorr-Oliver; where the main application is the treatment of industrial wastewater. However, it has been quickly taken up by the Japanese in the 1980s. According to Martin Hind´s statement (Farrer Consulting Limited, Lancashire) regarding new wastewater treatment systems, MBR combined with downstream low pressure reverse osmosis is a relative cheap option and today this combined process is so advanced that the treated wastewater is of a superior quality to enable it to be used over and over again. One of the most famous MBR operations has been established in Singapore where the plant, in combination with Reverse Osmosis (RO) produces exceptionally high quality water from sewage, which is reused for watering municipal gardens but it may also be blended with raw water for potable supply". (Hunter, 2007).

Within a research project which was was carried out through cooperation of the Karlsruhe University of Applied Sciences and a commercial laundry in Germany water treatment and reuse was studied (Hoinkis and Panten, 2008). The designed process has been up-scaled as full-scale unit for the entire laundry (wastewater capacity: 200 m^3/d). The flux was around 12 L/ (m^2 h) at an average permeability of 150 – 300 L/(m^2 h bar). The feed COD (around) 1000 mg/L was reduced to less than 100 mg/L and the elimination rate was higher than 90%. Part of the MBR effluent was treated by reverse osmosis and subsequently blended with the MBR effluent. The water quality was well suited for all washing and rinsing processes. In total 80% of the wastewater could be reused.

The next paragraph 1.4.7.2 highlights published findings on application of MBR technology in textile industry which is the general topic of this research work. This paragraph will look into MBRs under aerobic and anaerobic condition.

1.4.7.2. MBR Technology in textile wastewater treatment

MBR technology has demonstrated sustained performance over several years with reliable product quality, providing a clear cost benefit (Judd, 2006). For instance Sheldon et al., 2012; Judd, 2011; Monclús et al., 2010 ; Dialynas & Diamadopoulos, 2009 ; Henkel et al., 2009 ; Yigit et al., 2009 ; Lesjean & Huisjes, 2008 ; Melin et al., 2006; You et al., 2006 , are a number of examples that proved a successful implementation of MBR in wastewater treatment across a range of applications, including both municipal as well as industrial wastewater treatment (Judd, 2006). Nevertheless the main drawback of this technology is the high cost associated to the MBR system. (Judd, 2011; Kraume & Drews, 2010) mentioned that the commercialisation of the immersed MBR in 1990, lead to a decrease in the cost. The main focus now days regarding the cost of the MBR, concerns the energy demand associated to preventing and removing membrane fouling (Kraume & Drews, 2010). Based on what Helble and Möbius (2009) reported; the total operating cost for a SMBR with aerated tubular crossflow membranes amounted to 0.22€/m^3 treated water, while the cost of a an MBR with a classic tubular crossflow membranes amounted to 0.33€/m^3. This difference is related to the higher energy requirements.

With respect to the present PhD subject, the upcoming section is a summary of some of the MBR application for wastewater treatment in general including municipal as well as industrial wastewater, these under aerobic and anaerobic conditions.

The full-scale commercial aerobic MBR, first appeared in North America in the late 1970s and then in the Japan in the early 1980s. At around the same time, anaerobic MBR processes were introduced to the industrial wastewater market in South Africa. The aerobic MBR was introduced into Europe in mid-1990 (Stephenson, 2000).

MBRs are favoured when treating high-strength wastewater since the membrane area is determined on the hydraulic throughput and not the biological load. Therefore, when the strength of the wastewater increases the membrane area remains constant. Which differs to conventional wastewater treatment plants, as the strength of the wastewater increases, so does the required aeration volume and power (Hunter, 2007).

MBR technology has been also considered for treatment of saline wastewater as the presence of the membrane can potentially counteract the negative impact of salinity on the treatment of biological treatment processes containing activated sludge (Jang et al., 2013). In this application (Sharghi et al., 2013) studied the organic removal in a MBR using halophilic bacterial consortium for the treatment of a hypersaline produced water from oil industry at

varying organic loading rates from 0.3 to 2.6 kg COD $m^{-3}.d^{-1}$ which achieved a COD removal efficiency of 83-93%.

Once Pharmaceutical Active Compounds (PhACs) enter the WWTP, pharmaceutical residues are usually not completely degraded or retained by adsorption to sludge. Hence they pass through wastewater treatment and end up in the receiving waters in certain percentage. Their removal depends on the properties of the substance and the process parameters as SRT, HRT, and temperature (Radjenovic et al., 2008).

MBR process is expected to enhance trace organic removal to a greater extent than the conventional treatment (see Figure.1.20). This is related to the higher sludge age, higher biomass concentration, as well as complete retention of solids and microorganisms.

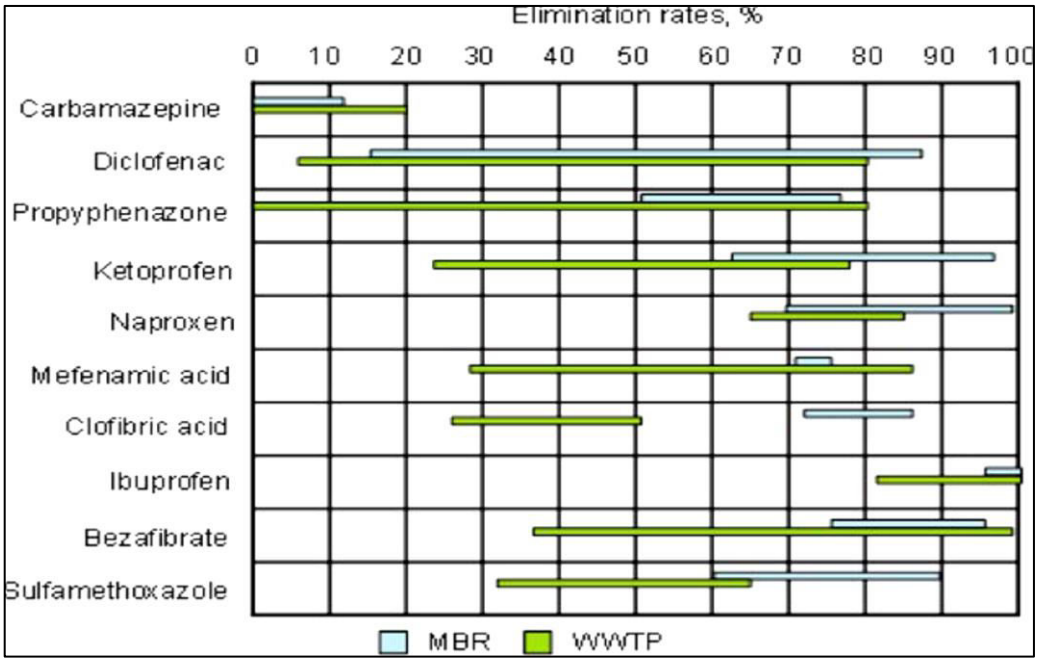


Figure.1.20. Elimination rate of PhACs in MBR and CAS treatment (Radjenovic et al., 2007a)

(Radjenovic et al., 2007) found significantly improved removal of lipid regulators and cholesterol lowering statin drugs (gemfibrizol, bezafibrate, clofibric acid and pravastatin), ß-blockers (atenolol and metoprolol), antibiotics (ofloxacin and erythromycin), anti-ulcer agent (ranitidine) and some analgesics and anti-inflammatory drugs as well (propyphenazone, mefenamic acid, and diclofenac).

It is important to mention that although the higher elimination rate of the PhACs through MBR process as reported in some papers, still the understanding of the biotransformation of these and their biodegradation pathways and mechanisms responsible about is still incomplete.

Radjenovic et al. (2007b) noted a significant removal of diclofenac and clofibric compounds when using MBR unit. The elimination rate in MBR of diclofenac and clofibric acid were 87% and 72%, compared to 50% and 28% found by conventional activated sludge process (CAS), respectively.

(Joss et al., 2006) established three different classes of compounds according to their susceptibility to biological degradation as follows:

1. Compounds with $K_{biol} < 0.1$ kg_{ss}^{-1} d^{-1}, that have no removal (e.g., carbamazepine,diclofenac, diazepam),

2. Partially removed compounds, $0.1 < k_{biol} < 10$ kg_{SS}^{-1} d^{-1}, (e.g. roxythromycin,fenoprofen, acetylsalicilic acid, naproxen, bezafibrate, clofibricacid, fenofibric acid, gemfibrozil, piracetam, and some iodinated contrast agents),

3. Compounds removed with more than 90% efficiency, $k_{biol} > 10$, (e.g.,ibuprofen and acetaminophen).

Surface active substances are an extensively used group of chemicals, e.g.,domestic detergents, pesticide formulations, industrial products, etc. Several main classes of surfactants (e.g., linear alkylbenzene sulphonates (LAS), alkylphenol ethoxylates (APEOs) and alcohol ethoxylates (AEO)) have shown very high ubiquity in the environment, thus presenting a serious environmental problem. LAS elimination in MBR unit has been reported to be very similar to a conventional treatment by several authors. However, Bernhard et al. (2006) studied elimination of persistent polar pollutants (P^3) pollutants in MBR and CAS, whereas MBR showed a significant improvement when removal of LAS is considered.

Besides aerobic MBR AnMBRs proved their reliability for the treatment of industrial wastewater. Table 1. gives a summary of some papers that studied the application of AnMBRs to a variety of industrial wastewaters.

Starting from the early 2000's the growth of journal publications on AnMBR has been mounting. Figure 1 illustrates the number of articles published in journals on AnMBR with regard to those on Upflow Anaerobic Sludge Blanket (UASB).

High rate anaerobic treatment on industrial wastewater is a proven technology that offers many advantages such as higher organic matter removal efficiency, recovery of energy, and excess sludge reduction. This depends on the retention of slow growing methanogenic bacteria in the reactor. (R. Dereli et al., 2012)

The first AnMBR installation in North America, known as the largest AnMBR installation in the world, was built at Ken's Foods in Massachusetts, USA. This system has a design influent rate of 475 m^3/d with 39,000 mg/L COD, 18,000 mg/L BOD, and 12,000 mg/L TSS. The system produces a high quality effluent with non-detectable TSS concentrations and average COD and BOD concentrations of 210 and 20 mg/L with removals of 99.4 and 99.9 % respectively. Fouling in this case is reduced by scouring the produced biogas across the membrane surface (Scott et al., 2011).

Table.1.8. Treatment performance of lab-scale AnMBRs used for the treatment of various industrial wastewaters.

Ref	Specific CH_4 Production (m^3/ $kgCOD_{removed}$)	COD Rem. (%)	TSS (g/L)	HRT (d)	OLR (KgCOD/ m^3.d)	T° (°C)	Reactor volume (L)	Wastewater type
1	0.25-0.57	96-99	11.8-20.8	6.8-600	1-11	-	50	**Palm oil mill**
2	0.21	76-83	10.9±0.5	-	2.59±0.53	37-45-55	10	**Thermo-mechanical pulping pressate**
3	-	>97	25	-	1-12	30	4.5	**Brewery with surplus yeast**
4	0.35±0.05	97-99	9	-	3.1±0.8	55	10	**Kraft evaporator condensate**
5	-	97	30-36	0.71	<25	37	23	**Simulated petrochemical**
6	0.3	98.5	6.4-10	4	5-20	37	15	**Acidified cheese whey**
7	0.136	81-94	6-8	2.5	0.88-4.52	37	400	**Food processing**
8	-	93-97	2	1	3-3.5	55	5	**Alcohol fermentation**
9	-	-	1-3.2	-	1.5	53-55	4	**Alcohol distillery**

(1)Abdurrahman et al., 2011 (2) Gao et al., 2011(3) Torres et al., 2011 (4)Lin et al., 2009 (5)Van Zyl et al., 2008(6) Saddoud et al., 2007(7) He et al., 2005(8) Kang et al., 2002(9) Choo and Lee (1998)

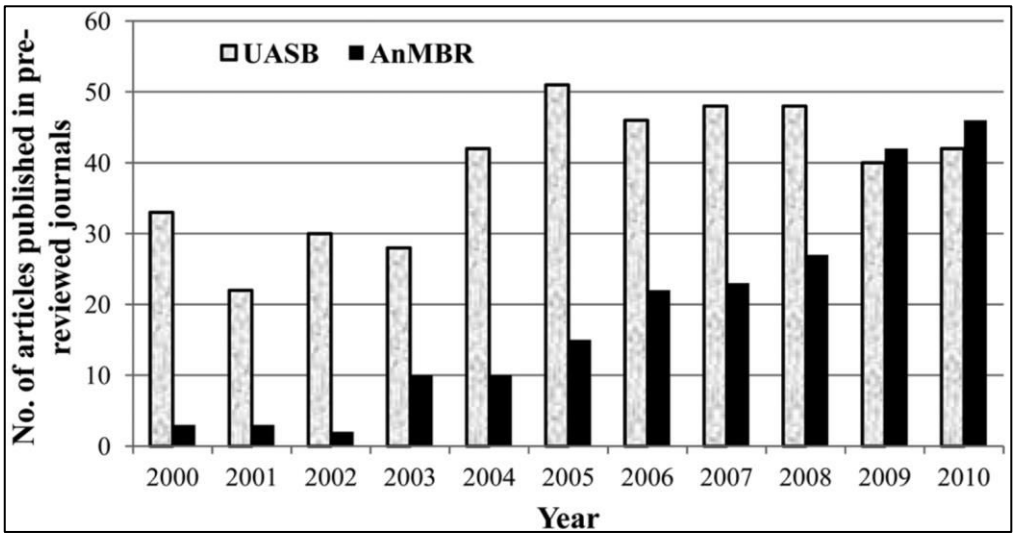


Figure.1. 21.Number of articles published in journals on AnMBR and UASB (Scopus 2011)

Meabe et al. (2013) studied the treatment of sewage sludge under mesophilic and thermophilic conditions in an AnMBR. Coupling the membrane filtration to the digestion process allows the digestion being operated with longer SRT, thus increases the volumetric load considerably. Values of 50 and 30 days were obtained for 55 and 35°C with organic loads of 6.4 and 4.6 g COD/(L.d) respectively. This study showed also better filtration performances for the system operating under thermophilic conditions, where a larger flow could be attained and the lower viscosity enabled operation with higher SRT.

MBR application for industrial wastewater treatment is a vast field and the number of papers available is huge, this concerns the wastewater resulting from PhACs, hormones, surfactants, sulfunated organic compounds, pesticides, musk fragrances and other micropollutants and so on. Since this thesis is dealing with the treatment of textile wastewater, the following section will focus on case studies in this field, namely MBR technology for textile wastewater treatment. A summary of the literature review is listed in Table 1.9 and 1.10.

The first part of this section concerns MBR application in textile wastewater treatment under aerobic conditions (AeMBR).

Badani et al.,(2005) observed an average of around 96% in COD rejection and an elimination rate of 70% in ammonium nitrogen with a decrease in colour of 72% for the treatment of waste of textile industry in a pilot scale in a reactor of 500 L. The purpose of this study was to determine the operating conditions for a membrane bioreactor with external membrane for three different feed flows. The sludge concentration was kept at 15g/L and the

operating pressure ranged between 0.5 to 1.5 bar. In addition the dissolved oxygen was maintained at 1-3 mg/L and an HRT of 1.2 days.

Schoeberl et al. (2004) studied treatment of industrial textile wastewater from a polyester finishing company. The activated sludge reactor with a working volume of 20 L was coupled with a external tubular cross flow UF unit. The tubular PVDF membrane had a filter area of 0.28 m^2, and 15 kDa cutoff. The COD and dye removal efficencies were 75-91% and 46-99%, respectively. Additionally the collected MBR effluent was treated downstream by CA-based NF (DESAL CK2540F) showning 91.8% COD and 97.8% dye removal efficiency.

Schoeberl et al. (2005) investigated the optimization of operational parameters for a submerged membrane bioreactor treating wastewater of a textile mill producing knitted polyester fabrics. The experimental study has been performed using an array of tubular PES MF membrane module (total surface area 2 m^2, pore size 0,4 μm)submerged in a 60 L aerated activated sludge tank. They optimized parameters such as suction pressure and back flush time, as well as aeration intensity in order to minimize fouling propensity. COD removal efficiency was between 89 and 94%, and the colour removal was between 65 and 91% at a COD loading rate of 0.52 g COD/(L d) and HRT of 2.9 – 5 d.

Brik et al. (2006) investigated its capability to achieve a water quality meeting reuse criteria with a laboratory scale MBR which was fed with textile wastewater originating from a polyester finishing mill. At the beginning the trials were performed at a TMP of 0.4 bar and a flux of 30 l/(m^2 h). Due to cake layer formation and fouling phenomena, flux gradually decreased to 18 l/(m^2 h) at the end of MBR operation. As a consequence of declining flux rates, permeate pressure decreased, which led to an increase of TMP from 0.4 to 0.6 at the end of MBR operation. COD removal efficiency was found to vary between 60 and 95%. Colour removal was above 87% for all wavelengths examined. However, in order to reuse MBR treated wastewater additional polishing steps have to be considered since the MBR permeate did not comply with the required water reuse standards. In this regard, an NF membrane was suggested in order to further upgrade water quality.

Zheng and Liu (2006) tested a laboratory laboratory-scale MBR with a gravity drain for dyeing and printing wastewater treatment from a wool mill. The MBR was operated with continuous permeate flow by gravity and without chemical cleaning at a HRT of 6-12 h for 135 d. The initial membrane flux in this study was set at a low value of 6 L/(m^2 h) at 0.127 bar in the first 35 days. The flux was stepped in increments to about 12 L/(m^2 h) from a low value at the same pressure before the 64th day. Along with a pressure-head increase, the

membrane flux increased to 15 L/(m^2 h) at 0.174 bar from the 65th to the 114th day. However, membrane flux did not increase correspondingly with increasing the pressure-head from 0.174 bar to 0.203 bar after 114 days. The findings showed that excellent effluent quality could meet the reuse water standard in China. The average removal rates of COD, BOD_5, turbidity, and colour were 80.3, 95.0, 99.3, and 58.7%, respectively.

You et al. (2006) compared the performance of a submerged MBR and a sequencing batch reactor (SBR) without membrane for treating real textile wastewater from an industrial park in Taiwan which produces around 15,000 m^3/d of highly coloured textile dyeing wastewater. The experiments were conducted in a tank of 25 L working volume with an submerged PE hollow-fiber module supplied by Mitsubishi Rayon Co. Ltd. (0.2 m^2 membrane area, 0.4 μm pore size). Thereby the MBR showed better results regarding COD and colour removal efficiency (79%, 54%) over the SBR (70%, 51%). For the MBR colour, COD, BOD and SS meet the Taiwan EPA standards, while for the SBR only the colour and COD meet these standards. Yigit et al. (2009) investigated the performance of a pilot scale MBR with submerged hollow-fiber membranes for the treatment of a highly concentrated mixed wastewater from wet processes (dyeing, finishing, and sizing) of a denim producing textile industry. The findings indicate that complex and highly polluted denim textile wastewaters could be treated very effectively by MBR systems at a target HRT of 12 h. The system was operated at two different operation stages: (1) no sludge wastage with a typical permeate flux of 20 L/(m^2 h) and (2) a solids retention time (SRT) of 25 days with the same flux. F/M and OLR values were in the range of 0.03-0.07 kg BOD_5/kg MLSS day and 0.37-1.01 kg BOD_5/m3 day, respectively, for both of the MBR operation stages. Irrespective of the high variations in F/M and OLR values, almost complete and continuous oxidation of organic compounds was achieved in both of the operation stages. COD removal efficiency was >95% and colour values from as high as 8,100 Pt Co levels were significantly reduced to about 50 Pt Co levels indicating that MBR effluent could be reused in the production processes. This study showed that MBR processes are more effective than the conventional activated sludge systems.

Huang et al. (2009) used a submerged hollow-fiber MBR with a capacity up to 400 L/d for treatment of dyeing wastewater from a printing and dyeing factory in Changzhou, China. The pilot-scale MBR was operated continuously for 100 d The respective permeate flux was between 2 and 8 L/(m^2 h) at a transmembrane pressure of 0.05−0.1 bar. The removal ratio of COD achieved was around 90% irrespective of HRT which was adjusted between 6

and 22.5 h. The removal efficiencies for NH_3-N and colour were 90–95 and 60–75%, respectively. However, the colour removal efficiency was not enough in order to directly reuse the MBR permeate, and hence, further treatment is necessary.

Some work used fungi-based acitvated sludge since unlike bacteria in conventional activated sludge system, it can degrade wide varieties of textile dyes.

In a study by Kim et al. (2004) a membrane bioreactor (MBR) with a MF membrane and white-rot fungi was employed for the decolorization of dye solutions. The decolorization of dye solutions by *Trametes versicolor* KCTC 16781 and membrane filtration were combined, and the applicability of this process was investigated using reactive dye solutions. The feasibility of MBR using fungal biodegradation was studied with nanofiltration and reverse osmosis (RO) membranes to improve permeate flux and separation efficiencies. The effects of dye types on fungal biodegradation and membrane filtration (permeate flux and rejection) were also investigated. The fungal MBR combined with RO was found effective for decolorization and organic removal of dye wastewater.

In a work conducted by Hai et al. (2009) removal of an azo dye (Acid Orange II, 100 mg L^{-1}) a fungal (white rot fungi) MBR (11.8 L, 1.07 m^2 membrane area) with submerged hollow fiber membranes (pores size 0,4 μm) achieved 93% removal during long-term non-sterile operation at a hydraulic retention time (HRT) of 1 d. However, as compared to the activity of pure fungus culture, the bacteria-contaminated disintegrated MBR-sludge demonstrated low decoloration and undetectable enzymatic activity, indicating detrimental effect of bacterial contamination.

The hitherto research findings lead to the conclusion that aerobic MBR has only limited ability to for dye degradation in particularly for azo and anthraquinone dyes. This has also been concluded by Simonic (2013) in a review on MBR-based textile wastewater treatment. Therefore the effort of recent researches is directed towards sustainable hybrid MBR technologies for textile wastewater treatment in order to achieve reuse standards (Simonic, 2013).

Consequently researcher recently looked into combined aerobic MBR processes.

You et al. (2008) compared the performance of a submerged MBR with a a combined anaerobic-oxic membrane bioreactor (AOMBR) and a AOMBR/RO process treating a synthetic textile dyeing wastewater (Reactive Black 5). The experiments were conducted in tanks of 25 L working volume with an submerged PE hollow-fiber module supplied by Mitsubishi Rayon Co. Ltd. (0.2 m^2 membrane area, 0.4 μm pore size). Regarding COD

removal AOMBR and AOMBR/RO performed significantly better (88% removal efficiency) than the single stage MBR (78% removal efficiency). As far as colour removal is concerned the improved treatment efficiency of AOMBR and AOMBR/RO over the single stage MBR is even more pronounced (81%, 97% and 43%, respectively). It was found that all membrane-based processes meet the Taiwan EPA effluent criteria but only the AOMBR/RO process meets the water reclamation criteria for toilet flushing, landscaping, irrigation, sprinkling and cooling water usage (You et al., 2008).

Hai et al. (2011) studied long-term performance of a bioaugmented membrane bioreactor (MBR) with a working volume of 0.85 L containing a GAC-packed anaerobic zone for treatment of textile wastewater containing structurally different azo dyes. Dye was introduced through the GAC-zone while the rest of the colorless media was simultaneously fed through the aerobic zone. A PE-based hollow fiber module from Misubishi Rayon (0.4 μm) with a surface area of 0,256 cm^2 was submerged in the aerobic zone. Stable decoloration along with significant TOC removal during a period of over 7 months under HRT of 1 day and under extremely high dye-loadings demonstrated the superiority of the proposed hybrid process. Whereas the GAC-packed anaerobic zone played the key role in decoloration, while the aerobic zone was vital for TOC removal (Hai, 2011).

De Jager et al. (2014) used a pilot-scale dual-stage dsMBR incorporating two ultrafiltration (UF) sidestream membrane modules which was designed, constructed, operated for 250 days and evaluated on-site for treating high strength textile wastewater. The MBR system consisted of a 1m^3 anaerobic tank, a 2.5 m^3 anoxic tank and a 2.5 m^3 aerobic tank followed by two Norit X-flow Airlift UF-membrane modules (5.1 m^2 surface each). The residual colour and remaining salts were treated with reverse osmosis (XUS-SW30XHR-2540). The wastewater stream was characterised by a colour range of 195–2070 ADMI units (standard of American Dye Manufacturer´s Institute) and a chemical oxygen demand (COD) of between 728 and 1033 mg/L. A consistent reduction in the colour of the incoming wastewater was evident observed. The colour in the wastewater was reduced from an average of 660 ADMI units (effluent of MBR) to ~12 ADMI units in the RO permeate, a lower ADMI compared to the potable water (~17 ADMI units) used on-site by this textile company.

Feng et al. (2010) studied the performance of combined Fenton oxidation and membrane bioreactor (MBR) process for the advanced treatment of an effluent from an integrated dyeing wastewater treatment plant. They used a reactor volume of 6 L with a submerged hollow fiber PVDF membrane of 0.04 m^2.and pores size of 0.2 μm. The COD of

the influent was 1100-1300 containing 10-20 mg Reactive Blue 4. The findings showed that under the optimum Fenton oxidation conditions (initial pH 5, H_2O_2 dosage 17 mmol/L, and Fe^{2+} 1.7 mmol/L) the average total organic carbon (TOC) and color removal ratios were 39.3% and 69.5% after 35 min of reaction, respectively (Feng et al., 2010). Regarding further purification of MBR process, TOC removal capacity was studied at different hydraulic retention times (HRT) of 10, 18 and 25 hr. Under the optimum HRT of 18 hr, the average TOC concentration and color of the final MBR effluent were 16.8 mg/L and 2 dilution time, respectively. The sludge yield coefficient was 0.13 g MLSS/g TOC and TOC degradation rate was 0.078 kg TOC/(m^3·day).

The following part concerns MBR application in textile wastewater treatment under anaerobic conditions (AnMBR).

The limited use of AnMBR compared to aerobic ones is generally due to more intense fouling potential of AnMBR (Lin et al., 2013). Lin et al. (2013) noted in their review study that the treatment of textile wastewater using anaerobic MBR (AnMBR) has been reported only once by Baeta et al. (2013) They studied the degradation of a model azo dye (Remazol Yellow Gold RNL) in a submerged AnMBR with powdered activated carbon. They reported that one disadvantage of anaerobic treatment of textile wastewater is the formation of toxic by-products such as aromatic amines, what can hamper the degradation of volatile fatty acids (VFA) and methanogenesis. Consequently VFA accumulation may lead to process failure in terms of COD removal and biomass loss (Baeta et al., 2013). In order to minimize biomass loss caused by the presence of toxic compounds they added powdered activated carbon (PAC) to the biomass of the MBR. Their study was conducted in a reactor with working volume of 3.25 L in which polyimide hollow fiber membranes manucfatured by Membranas Seletivas were immersed (0.8 m^2 area, 0.4 μm pore size). For control another AnMBR was operated without addition of PAC. The experiments were carried out at 35°C and at HRT of 24 h. The results showed that COD removal efficiencies were higher for the AnMBR with PAC (4 g/L) than the one without (90-94% vs. 73-94%). Furthermore the PAC increased the reactor stability and thereby leading to a lower accumulation of VFA.

Considering generally higher biological decolorization efficiency under anaerobic conditions (compared to aerobic conditions) and generally higher temperature of textile industry effluent (Kurt et al., 2012), it is evident that more studies are needed on AnMBR treatment of textile wastewater.

A. Spagni et al. (2012) evaluated the applicability of submerged anaerobic bioreactors for the decolouration of dyeing wastewater containing an azo dye. In this case, Orange 16 was used as a model of an azo dye, which demonstrated a very high decolourisation rate of 99% at an azo dye concentration up to 3.2g/L. Methane production was inhibited up to 80-85%, due to the accumulation of volatile fatty acids, which increased in parallel with the increase of the azo dye concentration which could be attributed to the occurrence of toxic by-products in the degradation process as reported by Baeta et al. (2013). Hence methanogenes seems to be the most sensitive microbial populations of the anaerobic biocenosis. This study was carried out in reactor with total volume of 21.6 L and operated under 35±1°C, using a flat sheet membrane MF module from Kubota (pore size 0.4 μm, filtration area of 0.12 m^2). A low membrane flux was applied (approximately 2 L/(m^2 h)) resulting in a HRT of 2.5 d. The TMP values were always below 0,4 bar (limiting TMP recommended by membrane supplier). Consequently the membrane permeability was always greater than 5 L/(m^2 h bar). The COD removal efficiency dropped from 95% to 10% due to hampered methanogenesis and consequently led to accumulation of VFAs and only after filtration was switched off the COD removal efficiency regained. The colour removal was always > 90%. The sludge TSS remained rather stable (20.3+/-1.9 g/L) with a downward trend during the experimental campaign what might be attributed to inhibited methanogenesis due to occurrence of toxic by-products.

The study of Yurtsever et al. (2015 aimed at comparatively evaluating anaerobic and aerobic MBRs for the treatment of azo-dye (Remazol Brilliant Violet 5R) containing synthetic wastewater. The study not only aims at comparing their removal performances but also their filtration performances during long term operation under similar operational conditions (T=32-34°C). Both MBRs (4.5 L working volume) were fitted with with flat sheet PES MF membranes (0,45 μm pore size, 0.01 m^2 area) and were operated in parallel with the same wastewater. In both MBRs, high COD removal efficiencies were observed. Although almost complete colour removal was observed in AnMBR, only partial (30–50%) colour removal was achieved in AeMBR. AnMBR was successfully operated up to 9 L/(m^2 h) (LMH) and no chemical cleaning was required at 4.5 L/(m^2 h) for around 50 days. AeMBR was operated successfully up to 20 L/(m h^2).. The filtration resistance of AnMBR was generally higher compared to AeMBR although reversible fouling rates were comparable. Only during the first experimental phase (until day 80 of 160 days in total) the AeMBR showed rather high fouling

tendency which was mainly attributed to the low MLSS concentration of 6 g/L.(Yurtsever et al., 2015).

In summary it can be stated that aerobic MBRs generally have limitations in treating textile wastewater due to limited colour reduction under aerobic conditions (Simonic, 2013). Therefore a variety of research work study combined processes either combined biological or chemical processes. Anaerobic MBRs in general perform very well in colour removal, however, show drawbacks regarding process stability in particular in the methanogenesis process which can be hampered by toxic by-products. Additional membrane fouling generally plays more dominant role than in the aerobic MBR process (Lin et al., 2013). Due to its high ability to decolourize textile wastewater anaerobic treatment is a very interesting option. However, up to now there is only limited research work done in the field of textile wastewater. In particular combined processes applying AnMBR with downstream AeMBR have not been studied so far.

It is therefore the objective of this PhD work to study such combined process using different commercial membranes as well novel self-made anti-fouling membranes by using a membrane preparation process which has been developed at the Institute on Membrane Technology, Cosenza, Italy (reference Francesco).

Table. 1.9 Literature summary of aerobic MBR processes for the treatment of textile wastewater

MBR configure-ation	MBR membrane (geometry, material, average pore size/MWCO, surface area)	Synthetic or industrial textile waste-water	Plant size	Average COD removal	Average colour removal	Refere-nces
Tangential flow side-stream MBR preceded by an equalisation tank (2-stage process)	Tubular PVDF, 0.025 μm	Industrial mixed textile wastewater	300-500 L (bioreactor)	96%	72%	Badani et al., 2005
Side-stream MBR	Tubular, PVDF, 15kDa, 0.28 m^2	Industrial, polyester finishing	20 L	75-91%	46-99%	Schoeberl et al., 2004
Submerged MBR	Tubular, PES, 0.4 μm, 2 m^2	Industrial, polyester knitting fabrics	60 L	89-94%	65-91%	Schoeberl et al., 2005
MF followed by a) NF and b) RO (2-stage process)	N/A	Synthetic textile wastewater (3 reactive dyes)	2.5 L (bioreactor)	N/A	97%	Kim et al., 2004
Side-stream MBR	Tubular, PVDF, 15kDa, 0.28 m^2	Industrial, polyester finishing	20 L	60-95%	>87%	Brik et al., 2006
Airlift reactor with side-stream membrane with gravity drain, upfront anaerobic reactor	Hollow fiber, PVDF, 0.22 μm, 0.18 m^2	Industrial dyeing and printing wastewater from a wool mill	16 l aerobic bioreactor with upfront 12 L anaerobic reactor	80.3%	58.7%	Zheng and Liu, 2006
Submerged MBR	Mitsubishi Rayon, PE, hollow fiber, 0.4 μm, 0.2 m^2	Mixed wastewater of an industrial park	25 L	79%	54%	You et al. 2006

Submerged MBR, upfront anaerobic reactor (AOMBR), downstream RO (AOMBR/RO)	Mitsubishi Rayon, PE, hollow fiber, 0.4 μm, 0.2 m^2	Synthetic, Reactive Black B	25 L	Single MBR: 78% AOMBR, AOMBR/RO: 88%	Single MBR: 43%, AOMBR: 81%, AOMBR/RO: 97%	You et al., 2008
Submerged MBR	Zenon PVDF hollow fiber, 0.04 μm, 0.93 m^2	Industrial, denim producing textile industry	230 L	>95%	>95%	Yigit et al., 2009
Submerged MBR,	Motian Membrane Co. Ltd., PVDF hollow fiber, 0.2 μm, two modules of 1 m^2	Industrial, printing and dying factory, upfront treated by hydrolysis and acidification	90 L	90%	60-75%	Huang et al., 2009
Submerged MBR	Hollow fiber, PE, 0.4 μm, 1.07 m^2	Synthetic (Acid Orange II)	11.8 L	>98% (TOC)	93%	Hai et al., 2009
Submerged MBR combined with GAC-packed anaerobic zone	Mitsubishi Rayon, PE, hollow fiber, 0.4 μm, 0.256 cm^2	Synthetic wastewater with different with azo dyes	0.85 L	>94% (TOC)	>90%	Hai et al., 2011
MBR with external membranes combined with upfront anaerobic + anoxic tank	Norit X-Flow Airlift UF membranes, 0.03 μm, 2 modules with 5.1 m^2 each	Industrial high strength wastewater	2,500 L aerobic tank with upfront 2,500 L anoxic and 1000 L anaerobic tank	75-94%	28.6%	De Jager et al., 2014
Submerged MBR combined with upfront Fenton oxidation	Hollow fiber, PVDF, 0.2 μm, 0.04 m^2	Industrial from integrated dyeing wastewater treatment plant	6 L	Total: 88.2% (TOC) Fenton oxidation: 39.3% MBR: 48.9%	Total: 91.3% Fenton oxidation: 69.6% MBR: 21.7%	Feng et al., 2010

Table. 1.10. Literature summary of anaerobic MBR processes for the treatment of textile wastewater

MBR configuration	**MBR membrane (geometry, material, average pore size/MWCO, surface area)**	**Synthetic or industrial textile wastewater**	**Plant size**	**Average COD removal**	**Average colour removal**	**References**
Submerged MBR with PAC	Membranas Seletivas,,hollow fiber polyimide, 0.4 μm, 0.8 m^2	Synthetic, Remazol Yellow Gold RNL	3.25 L	90-94%	89.6-94.3%	Baeta et al., 2013
Submerged MBR	Kubota, PE, 0.4 μm, 0.12 m^2	Synthetic, Orange 16	21.6 L	10-95%	>90%	Spagni et al., 2012
Submerged AnMBR parallel with AeMBR	Flat sheet, PES, 0,45 μm, 0.01 m^2)	Synthetic, Remazol Brilliant Violet 5R	AnMBR and AeMBR 4 L	AnMBR: 94% AeMBR: 97%	AnMBR: >99% AeMBR. 30-50%	Yurtsever et al., 2015

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This PhD work is basically divided in three parts:

- ✓ Model textile dye wastewater treatment under aerobic conditions followed by permeate characterization
- ✓ Model textile dye wastewater treatment under anaerobic conditions followed by permeate characterization
- ✓ Treatment of the permeate from the anaerobic treatment subsequently under aerobic conditions

As illustrated on the diagram below:

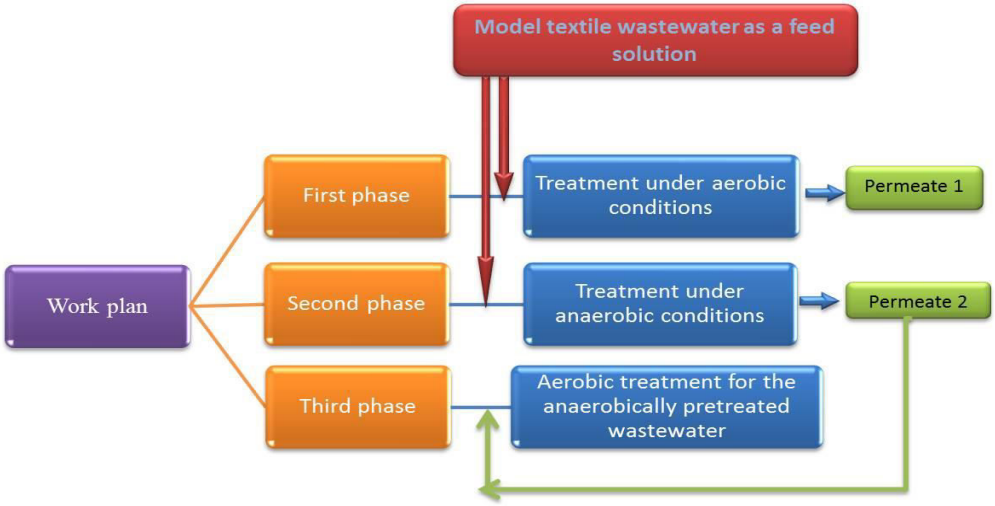

Figure 2.1. Simplified diagram for the PhD work

This chapter reports about the equipment setup in which the experiments were carried out as well as all materials and methods which have been used, starting from membrane preparation, till all feed and permeate analyses. In parallel to this PhD work, another PhD thesis has been realised by (Deowan, 2014) using the same membrane material and treating the same model textile waster. Therefore some of the analyses and characterisations reported in this chapter have been already performed within this work.

2.1 Experimental set-up: Side Stream Membrane Bioreactor unit (SSMBR)

Before moving further into details regarding the realization of the different steps of this Thesis, a description of the laboratory scale side stream membrane bioreactor (SSMBR), in which the experiments were performed is given below.

Two types of commercial membranes (UF and NF) from the company Microdyn-Nadir, Germany (see Table 2.7 technical data of UF and NF) and two types of novel membranes coated in our laboratory (see Table 2.8) have been tested in a SSMBR named "BIOSTAT® C-DCU" provided by the company Sartorius AG as shown in Figure.2.2.

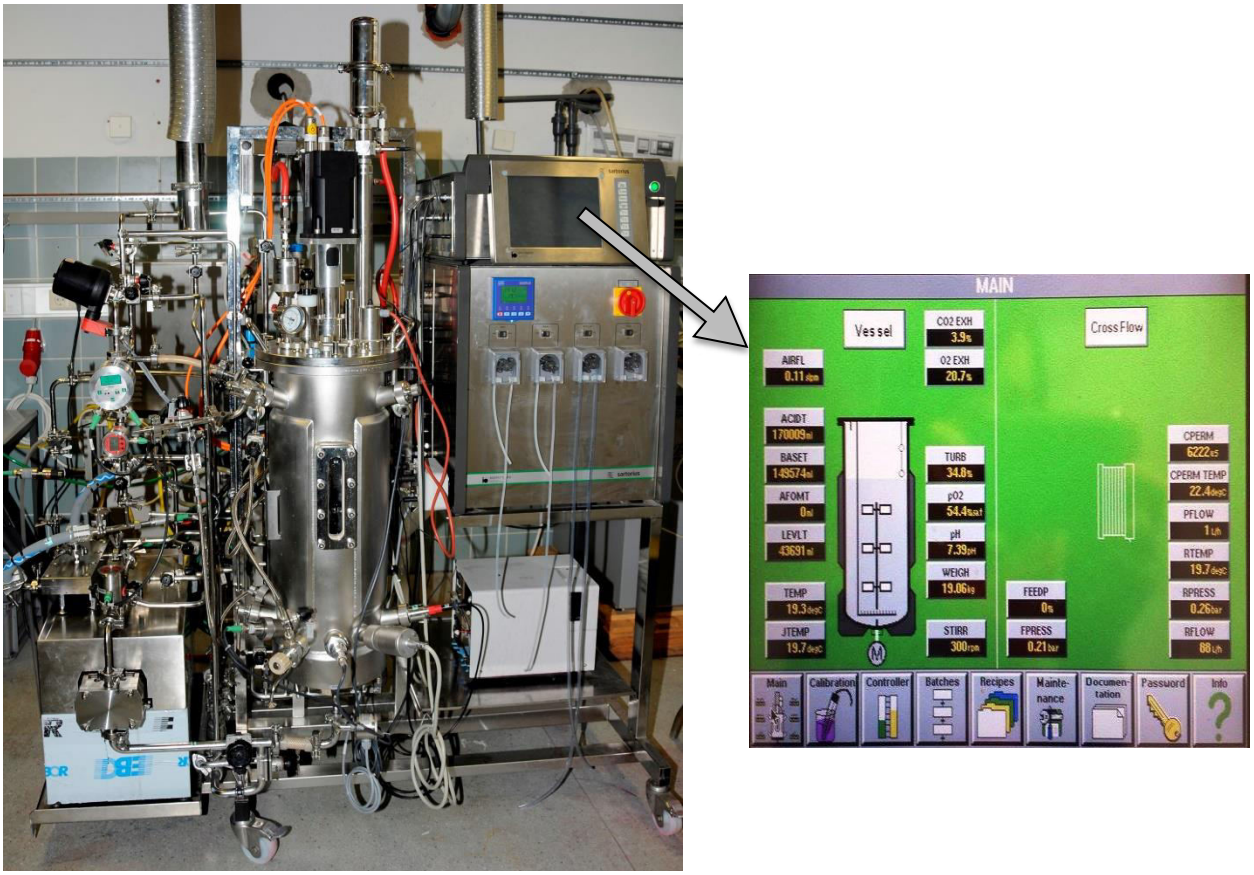

Figure.2.2. Experimental setup of the side stream MBR unit and main screen of the DCU system showing all sensor data (see Figure 2.3)

Figure.2.3 shows a simplified diagram of the SSMBR BIOSTAT ® C-DCU, with its most important parts:

- A Digital Control Unit (DCU) which includes process measurements, calibration routines and a standard set of control loops. The DCU is operated using a graphical interface on a flat panel touch-screen.
- A jacketed stainless steel tank (1) (working volume up to 30 L) with mass flow controlled aeration (3) and an air inlet filter (4) on top to ensure that the air is free of dust and oil, an impeller for homogenous mixing of the sludge, a feed pump (2) which is controlled by weight sensor. Air mass flow is controlled by a dissolved oxygen sensor (pO_2) and temperature is controlled by a thermostat (5) while, a turbidity sensor determines the sludge concentration. Temperature (T), pH and electrical conductivity (Cond) are measured as well. O_2 , CH_4 and CO_2 are measured in the gas phase.

- The cross flow flat sheet filtration unit (membrane area 0.00856 m^2) is fed by a frequency controlled recirculation pump; which has been replaced during anaerobic and combined process for technical reasons by a peristaltic pump. The permeate is drained and the concentrate is returned into the tank from which flow rate can be adjusted. Due to failure of the permeate flow sensor all permeate flow data were measured manually with a stop watch and measuring cylinder. The transmembrane pressure (TMP) was calculated from feed (P1), concentrate (P2) and permeate pressure (P3):

$$TMP = (P_1+P_2)/2-P_3 \qquad \ldots(2.1)$$

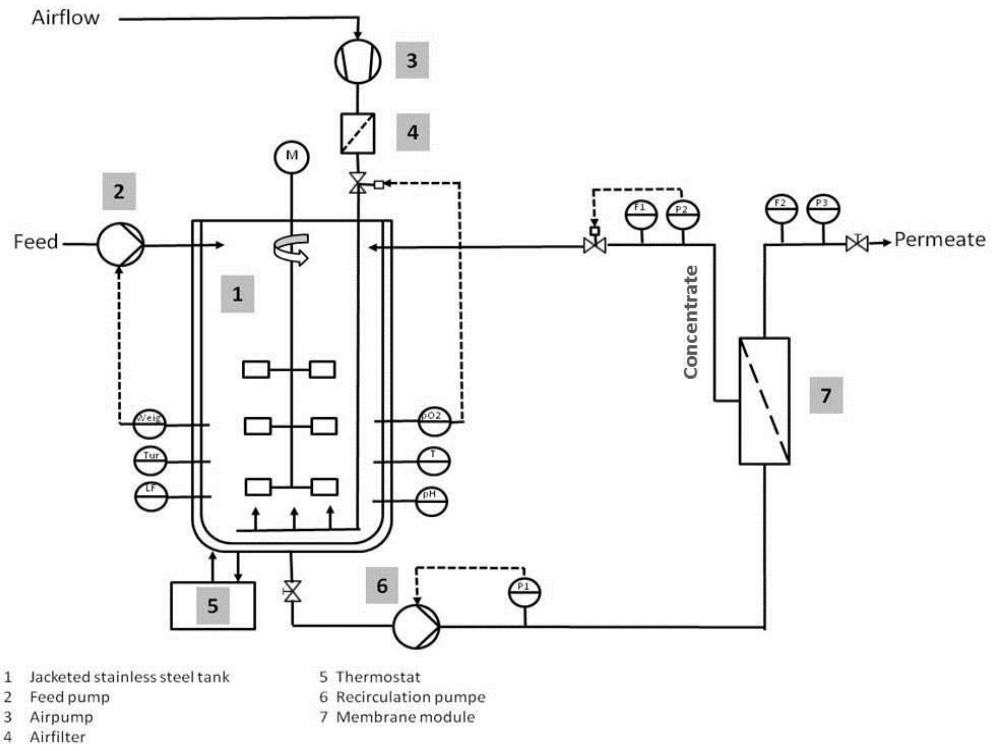

Figure.2.3.Schematic representation of the side stream MBR unit

2.2 Model Textile Dye Wastewater (MTDW)

In order to keep the feed wastewater quality constant, a Model Textile Dye Wastewater (MTDW) was developed as test media because the composition of real textile dye wastewater typically changes over the time and season of the year. The MTDW was developed by (Deowan,2014) for aerobic treatment and modified in this thesis for the anaerobic trials based on collected information from different publications. It is mainly based on a blue anthraquinone reactive dye (Remazol Brilliant Blue R) and on a red azo dye (Acid Red 4); (named in this Thesis blue and red dye respectively) which represent typical industrial dyes widely applied in textile industry (Figure. 2.4 and Figure.2.5). Besides, glucose was added as carbon-source, a typical industrial detergent (Albatex DBC) was used along with the following salts: NaCl, $NaHCO_3$ and NH_4Cl (N-source). The Chemical Oxygen Demand (COD) is one of the key parameters since it determines the wastewater strength. In this work the chemical components were selected in such a way that the COD value during the first

aerobic phase remains close to 2450 mg/L which is typical for end of pipe effluents in textile factories (Deowan et al. 2013, Bouhadjar et al. 2015).

As far anaerobic treatment during phase 2 is concerned the COD level has been increase by adding more glucose since anaerobic treatment usually needs to be higher in strength. Hence the MTDW for anaerobic treatment represents a typical in-process wastewater stream.

Table 2.1 and Table 2.2 summarize the composition and the characteristics of the applied MTDW.

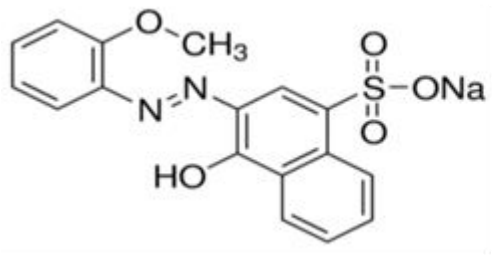

Figure.2.4. Structure of Acid Red4

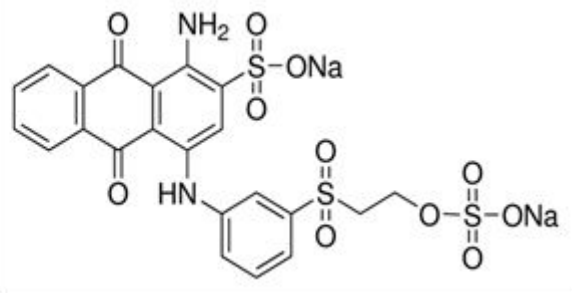

Figure. 2.5. Structure of Remazol BlueR

Based on the chemical structure shown on Figure 2.4 and Figure 2.5 ; the red is considered as azo dye whereas the blue is an anthraquinone dye. For elucidating a brief description regarding these two dyes categories is given in (CHAPTER 1 section 1.2 Textile Wastewater).

Table 2.1. Composition of the Model Textile Dye Wastewater (MTDW)

No.	Dyestuff & chemicals	Concentration (mg/L)	References
1	Remazol Brilliant Blue R[a]	50	
2	Acid Red 4[b]	50	
3	NaCl[c]	2500	Idil et.al.,2002
4	$NaHCO_3$[c]	1000	Mustafa et. al.,2008
5	Glucose[c]	2000*/6000**	Mustafa et. al.,2008 /A.Spagni et al.,2012
6	Albatex DBC (Detergent)[d]	50	Bahadur et. al.,2009
7	NH_4Cl[c]	300	

[a] BOC Sciences, [b] Chemos GmbH, [c] Merck, analytical grade, [d] Huntsman
* Aerobic trials, 1st phase , ** Anaerobic trials, 2nd phase

Table 2.2. Characteristics of Model Textile Dye Wastewater (MTDW)

Parameters	Unit	Measured values for aerobic trials	Measured values for anaerobic trials	
pH		7.5 ± 0.5	7.5 ± 0.5	7.5 ± 0.5**
COD	mg/L	2450 ± 25	6732±80	7364**
BOD_5	mg/L	750 ± 90	2387±298	2577**
Total - N	mg/L	85 ± 3.5	78±8	82**
Conductivity	mS/cm	6.6 ±0.15	5.8±0.15	6.2±0.15**

** data correspond to the measured values for the 2nd phase used during the anaerobic trials, where the COD value has been increased.

Since the red dye is sparingly soluble in water, it has been dissolved at first separately in an amount of 2 L of DI water under a higher temperature of 80°C for ½ hour, the rest of the components have been added and dissolved subsequently forming a homogenous solution after filling to 20 L.

Different characteristics of the two dyes used in this MTDW namely red and blue are listed in Table 2.3. It is important to highlight that besides different chemical composition the choice of these two dyes depend on the difference of their maximum absorbance wavelength in order to facilitate analysis by spectrophotometer, as shown in Table 2.3 below:

Table 2.3. Characteristics of red and blue dyes

Characteristic	Unit	Acid red 4	Remazol Blue R
Maximum absorption wavelength	nm	505	595
Molecular weight	g/mol	380.4	626.5
Empirical formula		$C_{17}H_{13}N_2NaO_5S$	$C_{22}H_{16}N_2Na_2O_{11}S_3$

2.3 Spectrophotometer method (UV-VIS)

The concentration of the red and the blue dyes, in the feed and in the permeate solutions were determined by the use of spectrophotometer (Model: UV-1800) from Shimadzu (Japan). The wavelength of maximum absorbance for the red and the blue dyes were found at 505 and 595 nm, respectively (see Table 2.3). A calibration routine based on Beer´s Law was used to calculate concentration from absorbance. (Bouhadjar et al.,2015) .This involved the following steps:

- Firstly, absorbance spectrum were recorded for each dye solution separately, and measured by the spectrophotometer in a range of 200-700nm. (see Figure 2.6 and Figure 2.7).
- Secondly, since the model textile wastewater is a mixture of both dyes, the spectrum of the mixed dye solution is necessary to present the influence of the light absorbance once the dyes are mixed as shows Figure .2.8.

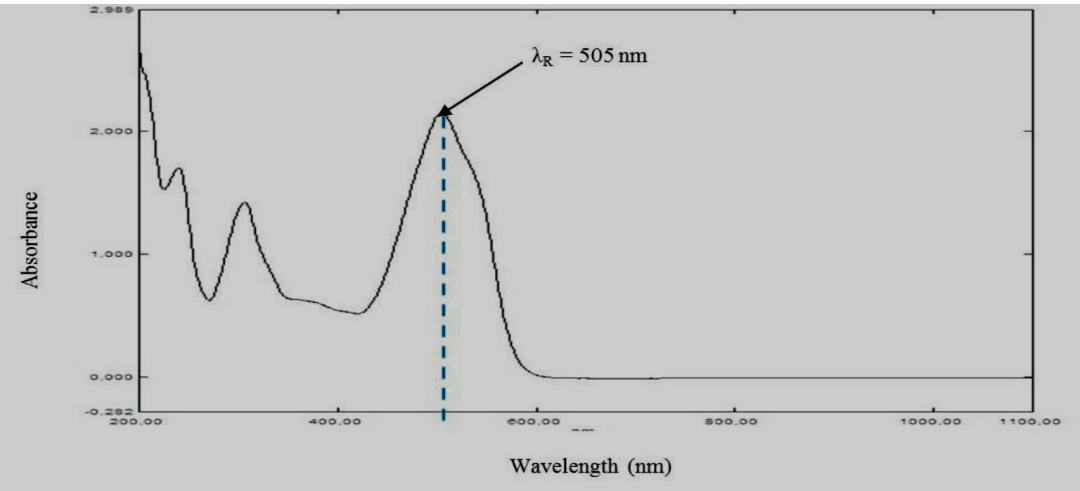

Figure 2.6. Absorption spectrum of the red dye solution (50mg/L)

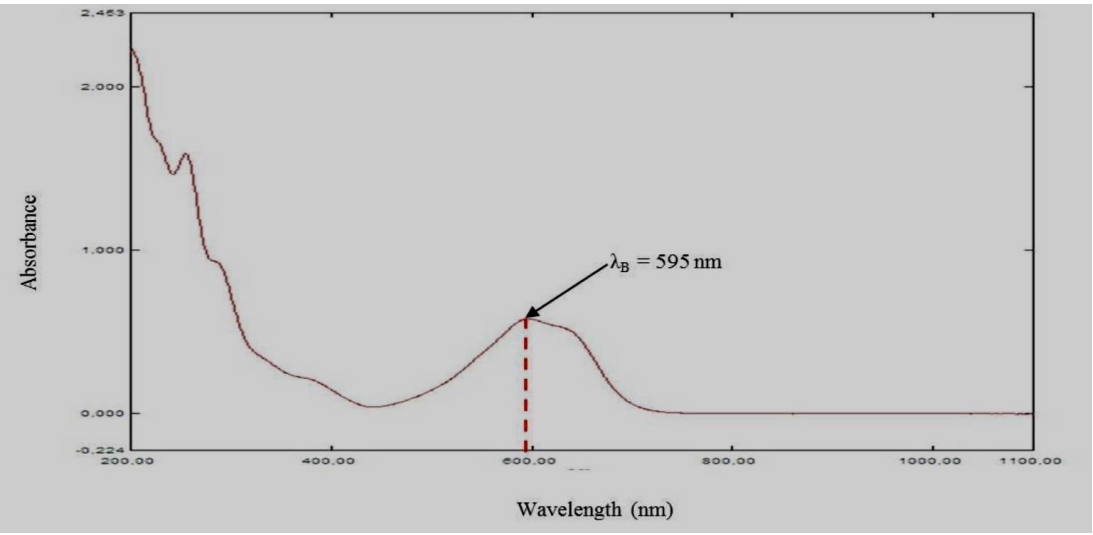

Figure 2.7. Absorption spectrum of the blue dye solution (50mg/L)

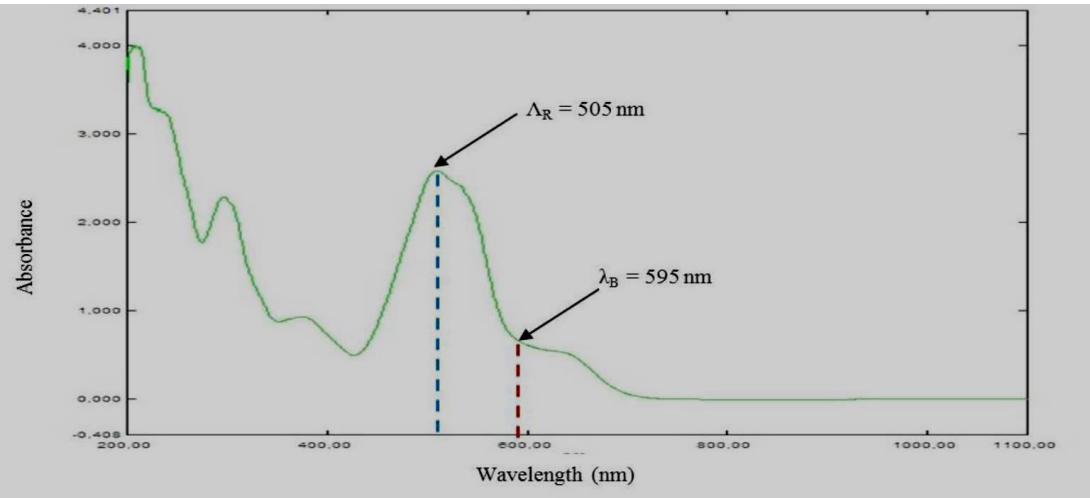

Figure 2.8. Absorption spectrum of the mixed solution of the red and blue dye (50% of each dye)

By the use of mathematical procedure the concentration of the single dye components can be calculated (Deowan 2014).

2.4 COD measurement

All COD values were determined using COD cell tests (Method 1.14541) from Merck KGaA (Germany), where the range of measurement is 25-1500 mg/L of COD. According to the COD product brochure the coefficient of variation (% standard deviation) is supposed to be ±0.68% (Merck 2014); whereas the standard deviation got within experimental measurements was ±2.08%, this gap of accuracy could be explained by the fact that different COD measuring levels have been applied.

2.5 BOD_5

BOD_5 analyses have been realized through BOD_5 measuring device (Model: OxiTop®IS6) from WTW GmbH, (Germany); with an accuracy of ±1% (WTW GmbH, 2015) and a standard deviation of the analysed samples within this work of ±13%.

2.6 TOC

All the TOC analyses for the feed as well as for the permeate solution have been performed in a Total Organic Carbon analyzer (Model: TOC-L CPH/CPN) from Shimadzu (Japan) with within a calibration range of 5-100 mg/L, and an accuracy of the measurement of ±1.27%.

One of the most important features of TOC-L is the capacity to efficiently oxidize hard-to-decompose organic compounds, including insoluble and macromolecular organic compounds. The 720°C combustion catalytic oxidation method achieves

total combustion of samples by heating them to 680°C in an oxygen-rich environment inside TC combustion tubes filled with a platinum catalyst. The carbon dioxide generated by oxidation is detected using an infrared gas analyzer (NDIR). By adopting a newly-designed, high-sensitivity NDIR, the TOC-L series achieves high detection sensitivity. (Shimadzu.com, 2015). Figure.2.9 below shows the analyzing process for TC (total carbon) as well as for IC (inorganic carbon), hence the TOC value can be calculated based on the following formula:

$$TOC=TC-IC\ldots..(2.2)$$

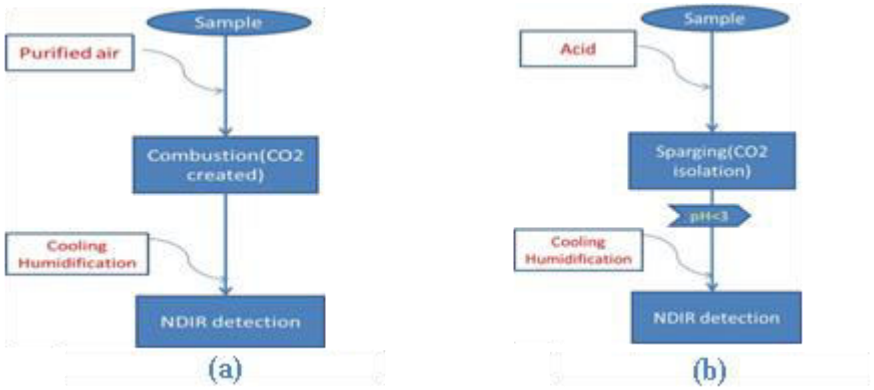

Figure 2.9. Schematic diagram for TOC measurement process (a) TC measurement, (b)TIC measurement.(adapted from Shimadzu, 2015)

2.7 Sonicated reactor sample

In order to analyze the performance of the biological process in the reactor, COD and color analyses were performed by collecting samples from the reacto.r These samples are sonicated for 10 min, then filtered through a microfiltration type (PES, 150kDa) membrane from (Microdyn-Nadir, Germany) applying vacuum pressure similar to the one TMP applied in the MBR unit in order to keep more or less the same filtration conditions. Subsequently the collected permeate was analysed similarly like the permeate sample got within the MBR trails for COD and color measurements.

2.8 Nitrogen (N-) compounds

For all the samples collected the N-compounds measurements have been realized as described below:

2.8.1 Total-N

The total-N has been determined by TOC-L CHP/CPN analyser (Shimadzu, Japan).

2.8.2 Ammonium NH_4^+-N

All NH_4-N analyses have been conducted by photospectrometric cell tests (Method: 1.14558) from Merck KGaA (Germany). The measuring range of this method is 0.2 – 8 mg/L. The product brochure indicates a standard deviation of ± 1.0%; experimentally it was found within this work ±6.85%. The difference could be related to the higher number of samples used to get the accuracy, 39 samples used in the case of the brochure compared to maximum 5 samples that have been used for the this work.

2.8.3 Nitrate NO_3^--N

Similar to NH_4^+-N analyses, all NO_3-N analyses have been conducted by photospectrometric cell tests (Method: 1.14542) from Merck KGaA (Germany). The measuring range of this method was 0.5 –18 mg/L, with a standard deviation of ± 1.5% indicated in the product brochure; whereas the one got within this work was found at ±7.9.

2.9 Mixed Liquor Suspended Solids (MLSS)

Mixed Liquor Suspended Solid (MLSS) is a parameter that allows the measure of the suspended solid mass in the reactor tank during the activated sludge processsince the adjustment of the MLSS concentration in the bioreactor is very important fora good effluent quality and smooth process operation . MLSS concentration is given in g/L. The process used for all the MLSS measurements for the experimental work was conducted at a temperature of 105±2°C.

The MLSS measurement procedure was determined as follows:

- Four ceramic crucibles (a, b, 1, 2) were dried at105±2°C.
- 40 mL of sludge and permeate sample were refilled in each crucible and after that the weight of each empty crucible has been noted down (m_a, m_b, m_1, m_2) respectively.
- All crucibles have been kept in the oven for 24 hours under 105°C.
- After 24 hours the weight of the dried crucibles have been noted down (m_a^*, m_b^*, m_1^*, m_2^*)

MLSS was calculated following the equation mentioned below:

$$\mathrm{MLSS} = \left(\frac{(ma*-ma)+(mb*-mb)-(m1*-m1)+(m2*-m2)}{2}\right) * \frac{1000g}{40mL} \quad \ldots\ldots(2.3)$$

With:

m_a* : weight of the dried crucible with sludge sample 1. m_b* : weight of the dried crucible with sludge sample 2. m_1* : weight of the dried crucible with permeate sample 1.m_2* : weight of the

dried crucible with permeate sample 2. m_a, m_b,m_1,m_2 are the weight of the dried empty crucibles.

2.10 pH sensor

In order to measure the pH values in the feed solution as well as in the permeate samples, pH glass electrode " pH 325" from the company " WTW Wissenschaftlich-Technische Werkstätten GmbH" was used, with an accuracy of 0.01±1 digit. The standard deviation within this work based on a great number of measurements was ±0.5.

2.11 Conductivity sensor

Conductivity values in the feed solution and the permeate sample were measured by a conductivity sensor "Cond315i" from WTW company where the accuracy is ±0.5% with a range of measurement of 0.00- 19.99 mS/cm.

2.12 Dissolved oxygen sensor

To determine the dissolved oxygen concentrations in sludge samples from the aerobic trials, an oxygen sensor "Oxi340i" from WTW GmbH Germany has been used, with an accuracy of ±0.5 %.

2.13 Theoretical calculation of the MTDW

2.13.1 Chemical Oxygen Demand (COD)

The calculation of the amount of oxygen needed to oxidise the different main organic components of the MTDW (glucose, red dye, blue dye) is given in detail below.

Table 2.4. Oxidation reactions for the carbon containing components in the MTDW

Component	**Chemical reaction**
Glucose	$C_6H_{12}O_6 + 6\ O_2 \longrightarrow 6\ CO_2 + 6\ H_2O$
Red dye	$C_{17}H_{13}N_2NaO_5S + (35.5/2)\ O_2 \longrightarrow 17\ CO_2 + 8\ H_2O$
Blue dye	$C_{22}H_{16}N_2Na_2O_{11}S_3 + (41/2)\ O_2 \longrightarrow 22\ CO_2 + (13/2)\ H_2O$

It is known that the textile wastewater treated under anaerobic condition, is characterised by higher organic load, in comparison to treatment under aerobic conditions (see 2.2) Therefore the MTDW prepared in this work which was treated under aerobic conditions is characterised by a lower COD than the MTDW prepared for anaerobic treatment. For this reason the MTDW used for the anaerobic trials, the glucose concentration has been increased in order to

achieve a COD of >6000 mg/L(see Table 2.1) whereas all other components were kept constant. The COD level of this work was in-line with the synthetic wastewater prepared by Spagni (2012) showing a COD of 6750 mg/L for the study of decolourisation of an azo dye under anaerobic conditions in a submerged MBR unit.

The calculation of COD was carried out by using the following equation:

$$\mathrm{COD} = \left(\frac{([C_6H_{12}O_6] * 6 * M_{O2})}{M_{C_6H_{12}O_6}}\right) + \left(\frac{([Red] * 35.5 * M_{O2})}{2 * M_{Red}}\right) + \left(\frac{([Blue] * 41 * M_{O2})}{2 * M_{Blue}}\right)$$

Where:

$[C_6H_{12}O_6]$; [Red];[Blue] are the concentrations of glucose, red and blue dye respectively.

M_{O2};$M_{C6H12O6}$;M_{Red} ;M_{Blue} are the molecular weight of oxygen, glucose, red and blue dye respectively.

Thus theoretical COD values as well as the measured ones are given in Table 2.5 for the MTDW used for aerobic and anaerobic trials as well.

Table 2.5. Theoretical and measured COD values

	Theoretical COD values	**Measured COD values**
Aerobic MTDW	2260	2450 ± 25
Anaerobic MTDW 1	6527	6732± 319
Anaerobic MTDW 2	6804	7364

2.13.2 Total Nitrogen (TN)

As shown on Table 2.1, the source of nitrogen in the MTDW is represented by NH_4Cl, red and blue dyes. This leads to the following calculation for the TN in the feed solution:

$$N\%_{(NH4Cl)} = \frac{atomic\ weight\ of\ N}{Molecular\ weight\ of\ NH_4Cl} = \frac{14}{53.5} * 100 = 26.17\%$$

$$N\%_{(Red)} = \frac{2 * atomic\ weight\ of\ N}{Molecular\ weight\ of\ Red\ dye} = \frac{28}{380.4} * 100 = 7.36\%$$

$$N\%_{(Blue)} = \frac{2 * atomic\ weight\ of\ N}{Molecular\ weight\ of Blue\ dye} = \frac{28}{626.5} * 100 = 4.47\%$$

Where:

$N\%_{(NH4Cl)}$, $N\%_{(Red)}$, $N\%_{(Blue)}$ are the nitrogen fraction from ammonium chloride, red and blue dyes respectively.

It follows that :

$TN = N\%_{(NH4Cl)} * 300\ mg/L + N\%_{(Red)} * 50mg/L + N\%_{(Blue)} * 50mg/L$

$TN = 84.5mg/L$

The TN measured value was 85 ± 3.5mg/L.

2.13.3 Total Organic Carbon (TOC)

Similarly to the calculation of TN in the feed solution, the TOC concentration is calculated based on the carbon ratio of total molar mass in the MTDW as follows:

$$C\%_{(C6H12O6)} = \frac{6 * atomic\ weight\ of\ C}{Molecular\ weight\ of\ C_6H_{12}O_6} = \frac{72}{180} * 100 = 40\%$$

$$C\%_{(Red)} = \frac{17 * atomic\ weight\ of\ C}{Molecular\ weight\ of\ Red\ dye} = \frac{204}{380.4} * 100 = 53.63\%$$

$$C\%_{(Blue)} = \frac{22 * atomic\ weight\ of\ C}{Molecular\ weight\ of Blue\ dye} = \frac{264}{626.5} * 100 = 42.14\%$$

Where:

$M\%_{(C6H12O6)}, M\%_{(Red)}, M\%_{(Blue)}$ are the carbon fraction from glucose, red and blue dyes respectively.

It follows that:

$TOC = M\%_{(C6H12O6)} * [C_6H_{12}O_6] + M\%_{(Red)} * [Red] + M\%_{(Blue)} * [Blue]$

Where :

$[C_6H_{12}O_6]$;[Red];[Blue] are the concentrations of glucose , red and blue dye respectively see table2.1.

$M\%_{(C6H12O6)}$;$M\%_{(Red)}$;$M\%_{(Blue)}$ are the carbon proportion of glucose, red and blue dye respectively.

Since the glucose concentration has been changed for the MTDW used for anaerobic trials as mentioned above, all different TOC values of the anaerobic and aerobic trails are calculated and compared to the measured values in the Table 2.6.

Table2.6:Theoretical and measured TOC values

	Theoretical TOC values	**Measured TOC values**
MTDW aerobic	848	903 ± 101
MTDW anaerobic 1	2448	2568±117
MTDW anaerobic 2	2496	2752

2.13.4 Total Inorganic Carbon (TIC)

The only component contibuting to inorganic carbon TIC in the MTDW is sodium hydrogen carbonate, as shown on Table 2.1, therefore it follows:

$$C\%_{(NaHCO3)} = \frac{atomic\ weight\ of\ HCO_3}{Molecular\ weight\ of\ NaHCO_3} = \frac{61}{84} * 100 = 72.62\%$$

$TIC = C\%_{(NaHCO3)} * 1000\ mg/L = 726.2\ mg/L$

2.14 Membrane Materials

Within this work two types of membranes namely commercially available from MICRODYN-NADIR GmbH (Microdyn-Nadir, 2014) and novel ones prepared by polymerizable bicontinuous microemulsion method (PBM)were used. The technical data of the commercial membranes ar shown in Table 2.7. The ultrafiltration (UF) membrane is typically used for MBR application, whereas the nanofiltration (NF) membranes has not yet been tested for MBRs. Novel membranes based on PBM method have been developed by the Institute of Membrane Technology (ITM-CNR), Italy within the frame of an EU funded project named "Development of the next generation membrane bioreactor system (BioNexGen) 2011".

Table 2.7. Technical data of UF and NF membranes from the company MICRODYN-NADIR (Microdyn-Nadir, 2014)

Technical data	**UF membrane**	**NF membrane**
Active layer	PES	PES
Support layer	PET	PES
MWCO (kDa)	150 kDa	1 kDa
Pore size (µm)	0,04	-
Water permeability ($L/(m^2\ h\ bar)$)	> 280	> 5

In the present work the novel PBM membranes were produced by casting an additional layer onto the MICRODYN-NADIR UF-PES membrane following the protocol which was developed within the BioNexGen project. (see Table 2.7). More details of this PBM based procedure can be found in the publication of Galiano et al. (2015). PBM membranes, due to their characteristics were considered as ideal candidates for wastewater treatment processes such as MBRs since they have higher hydrophilic character and show antimicrobial effects (Deowan, 2014; Galiano, 2014).

The applied novel PBM membranes were produced under different conditions namely varied temperature and use of two different cationic surfactants, 1 acryloyloxyundecyltriethylammonium bromide (AUTEAB) and dodecyltrimethylammonium bromide (DTAB) (see Figure 2.10 and Figure 2.11). AUTEAB has been synthesized at the University of Calabria, Italy within the BioNexGen project. All other chemicals used for PBM polymerization are commercially available. The composition of the microemulsion was (Galiano et al., 2015):

1) Methyl methacrylate (MMA), used as monomer constituting the oil phase of the microemulsion.

2) Water, used as the aqueous phase of the microemulsion.

3) Surfactant AUTEAB or DTAB used to lower the surface tension of the microemulsion facilitating the formation of a single phase and they eventually give an antimicrobial effect to the coating;

4) 2-Hydroxylethyl methacrylate (HEMA), used to enhance the dispersion of the oil and water phase.

5) Ethylene glycol dimethacrylate (EGDMA), added as cross-linker in order to consolidate the final membrane structure.

6) Ammonium persulfate (APS) and N,N,N´,N´, -tetramethyl ethylenediamine (TMEDA), added as redox initiators in order to promote the polymerization.

The conditions of preparation of the novel PBM membranes are summarized in Table 2.8. Figure 2.12 shows the different steps needed for preparing the coating on the surface of the commercial UF PES membrane by PBM.

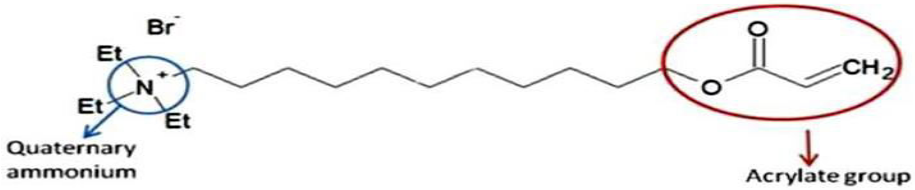

Figure 2.10 AUTEAB Molecular structure of AUTEAB (Galiano, 2014)

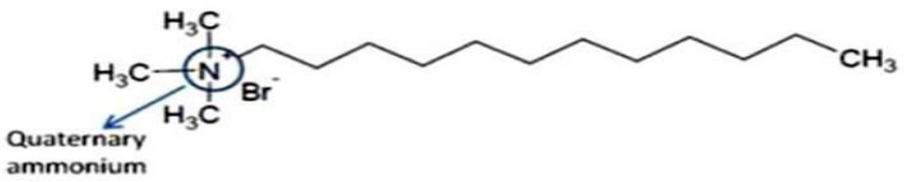

Figure2.11 DTAB Molecular structure of DTAB (Galiano, 2014)

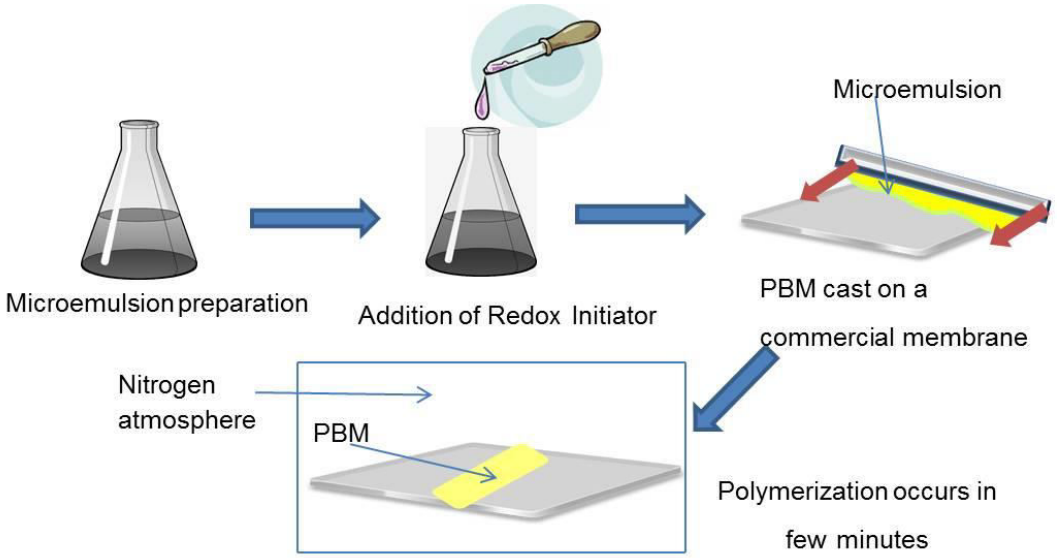

Figure 2.12 Coating of a commercial UF PES membrane by Polymerisation of Bicontinuous Microemulsions (PBM) (adapted from Galiano, 2014)

The reason for using AUTEAB and DTAB is besides lowering the surface tension of the microemulsion their ability give an antimicrobial effect to the PBM coating. Whereas AUTEAB due to its double bond (Figure 2.10) is polymerizable and consequently can be chemically linked to the polymer, however DTAB is only physically distributed in the PBM polymer and hence can be washed out when being applied in the MBR.

Table 2.8 Preparation conditions of novel membranes

Membrane	MMA %	HEMA %	H_2O %	Surfactant %	EGDMA %	Initiator %	Conditions
N1	21	10	41	AUTEAB 25	3	APS 0,3% on the weight of 'H_2O + 4 drops of TMEDA	T = 20°C , Polymerization time: 4,5 min. Casting knife: 200 µm
N2	10	40	40	DTAB 10	4 on the weight of MMA+HEMA	APS 0,3% on the weight of 'H_2O + 4 drops of TMEDA	T = 20°C , flat heating plate, Polymerization time: 4,5min., Casting knife..
N3	10	40	40	DTAB 10	4 on the weight of MMA+HEMA	APS 0,3% on the weight of 'H_2O + 4 drops of TMEDA	T = 22,5°C , flat heating plate, Polymerization time: 4,5 min. Casting knife ??
N4	12	35	42	DTAB 11	4 on the weight of MMA+HEMA	APS 0,3% on the weight of 'H_2O + 4 dropes TMEDA	Varied HEMA concentration. T= 20°C Casting knife: 250 µm.
N5	10	40	40	DTAB 10	4 on the weight of MMA+HEMA	APS 0,3% on the weight of 'H_2O + 4 drops of TMEDA	T = 20°C , flat heating plate, Polymerization time: 4,5 min., Casting knife: 200 µm

2.15 Characterization of membranes

The following section deals with equipment for characterization of the membranes which were used in this thesis, namely the novel membranes as well as the commercial ones.

2.15.1 Scan Electron Microscopy (SEM)

The SEM analyses were carried out at Swansea University (England) by Dr. Daniel Johnson and at the University of Calabria, ITM (Italy) by Dr. Francesco Galiano..

The SEM used at Swansea University is an Hitachi Field Emission SEM(model S-4800). The resolution is:

- Accelerating voltage 15kV ,Working distance: 4mm-1.0nm
- Accelerating voltage 1kV , Working distance: 1.5mm-2.0nm

The SEM used at Calabria University is a ZEISS EVO/MA10, with same resolution options used for the SEM device used at Swansea University.

2.15.2 Atomic Force Microscopy (AFM)

All the AFM measurements were performed at Swansea University by Dr. Daniel Johnson by using a multimode AFM with Nano-scope controller (Veeco, USA) using manufacturer supplied software. Tapping mode measurements in air were performed using TESP (nominal spring constant 20-80 N/m) cantilevers (Bruker AXS). All other measurements were performed using NP-S probes (long thick lever, nominal spring constant 0.12 N/m). Roughness values were obtained from topography scans using the instrument software. The resolution of the most of the images created by AFM instrument was in the form of 512× 512 pixels.

2.15.3 Cross flow membrane testing cell

The auto-controlled ultrafiltration (UF) cross-flow testing cell (Figure.2.13 and Figure. 2.14) was purchased from company SIMA-tec GmbH (Germany), in order to test different types of membranes. This testing unit was equipped with heat-exchanger/temperature controller (2) and LabVIEW program based computerised data acquisition system. To abate the vibration of the unit, it was equipped with damping system (9) by filling vibration controller with N_2 gas at 16 bar pressure. The experiments with this unit were carried out continuously for longer time.

Figure.2.13.Experimental setup of the auto-controlled UF cross-flow testing cell.
(1 pressure controller,2 temperature controller, 3 feed tank,4 membrane module, 5 permeate valve,6 concentrate valve,7 feed valve, 8 drain valve, 9 damping system)

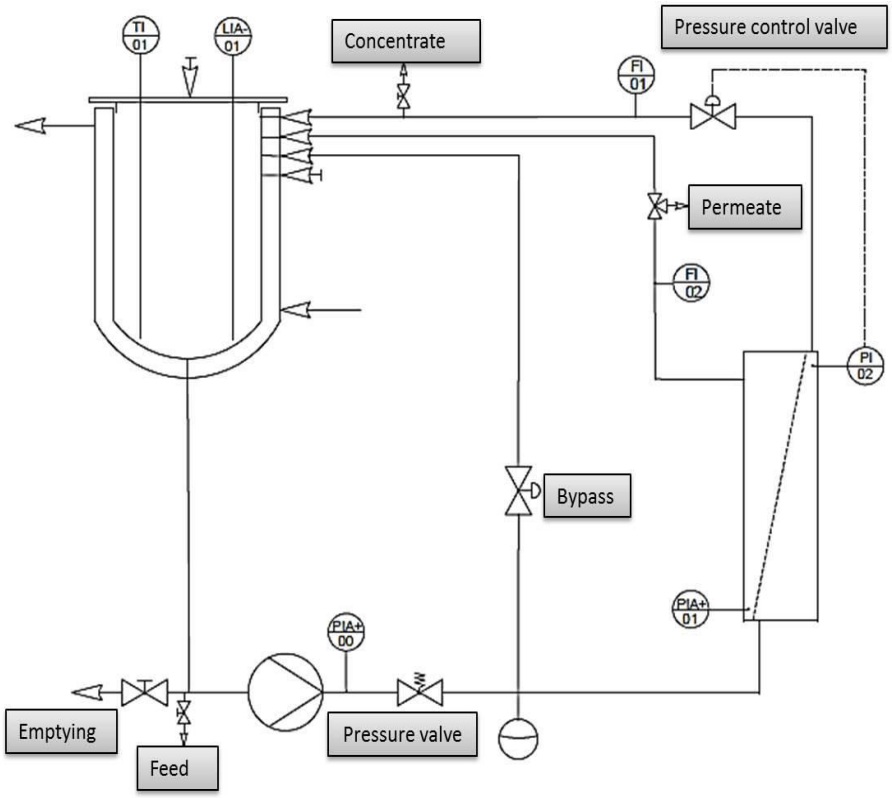

Figure.2.14 Schematic diagram of the auto-controlled UF cross-flow cell (modified from SIMA-tec GmbH)

The UF cross-flow cell has been used to compare the performance of all the membranes of this work regarding DI water flux as well as a model water based on humic acid as model foulant. In this case it is important to perfectly keep the same operating conditions in terms of temperature and pressure over a longer period (>24 h). The pressure was set by the pressure controller (1). The pressures 0.5 bar, 1 bar and 2 bar were selected as operating pressures to test the membranes. The temperature was set by the temperature controller (2). The temperature of 20°C ± 2°C and 36°C ± 2°C were set as the working temperature for the experiments carried out. For the experiments, the feed solution was fed into the feed tank (3) which has a capacity of 5 L. The membrane was placed in the membrane module (4) with an active membrane surface area of 85.6 cm^2. The feed solution from the feed tank was pumped into the membrane module and through the membrane at defined pressure. Permeate and concentrate were recirculated back to the feed tank. The flux of the solution was measured and recorded by integrated LabVIEW program. During the experiment, it was also possible to collect the permeate , concentration and the feed samples by opening the valves (5), (6) and (7) respectively. After the experiment was finished the solution in the feed tank was emptied by opening the drain valve (8). The applied pressure indicator showed ± 2% and temperature indicator had ±1 % accuracy. The error of the flux recorded by LabVIEW program has been assumed as ± 2% since it varied with applied pressure. For fouling test humic acid (HA) was applied since many fundamental studies of the fouling phenomena have been done by using humic acid as a model foulant (Sutzkover-Gutman et al., 2010). In addition humic acid represents the dominant foulant in biological sludge systems. HA ($C_9H_9NO_6$, MW 227) was supplied by Alfa Aesar GmbH, Germany.

2.15.4 Porosoty

The porosity of the membranes was measured by PMI capillary flow porometer which provided fully automated through-pore analysis including bubble point, poresize distribution and mean flow pore size with accuracy of 0.15% of reading (PMI, Porous materials, Inc., USA).

2.15.5 Molecular weight cut-off (MWCO)

The MWCO values are resumed on the Table 2.9. And provided from Mycrodyn-Nadir, GmbH, Germany, and from ITM-CNR, Calabria, Italy.(Galiano, 2014).

2.15.6 Contact angle

Contact angle measurements were performed by Francesco Galiano (ITM-CNR) using ultrapure water by the method of the sessile drop using a CAM200 instrument (KSV Instrument LTD, Finland). The resolution of the instrument was 800600 pixel. For each sample, at least 10 measurements were taken; the average value and the corresponding standard deviation were then calculated. Water CAM was performed for the active side of PES membranes and for the coating side of coated membranes.

Table.2.9. characterisation of commercial and PBM novel membranes.

	UF	**NF**	**PBM AUTEAB**	**PBM DTAB**
Roughness RMS (nm)	15,35±4,52	4,8±1,91	7±3	5±1
Pore diameter (nm)	0,1±0,08	-	0,075±0,06	0,039±0,04
MWCO kDa	150*/270**		100**	-
Contact Angle (°)	68	57±1	47	58

(*) From Mycrodyn-Nadir, GmbH, Germany. (**) based on ITM-CNR, Calabria, Italy.

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CHAPTER 03

EXPERIMENTAL RESULTS

3.1. Water permeability and fouling test

All water permeability and fouling tests were performed in a cross-flow flat sheet testing unit (see chapter 2.15.3). The water permeability was done with DI water and the fouling tests were conducted with humic acid (HA) solution as model foulant. The same model foulant has been also used in previous work in order to study performance of novel low-fouling membranes prepared by polymerizable bicontinuous microemulsion technique (Galiano, 2015). The purpose of these experiments is to study the percentage drop of water flux by humic acid treatment at the two temperatures (20°C and 36°C) which have been applied for the experiments under aerobic and anaerobic conditions. These temperatures represent conditions in typical technical wastewater treatment units.

3.1.1. Commercial membranes

3.1.1.1. UF

Figure 3.1 shows the water flux vs. the transmembrane pressure (Δp= TMP) for the commercial UF membrane. The water permeability WP was calculated by simple linear regression:

$$J = WP\,\Delta p$$

As can been seen water flux increases with higher temperature what is in line with theoretical expectation. The water permeability at 20°C is in line with the information of manufacturer Microdyn-Nadir (see Table..) which is given as >250 L/(m^2 h bar). However, it is significantly higher than previous results (Deowan, 2014) what could be explained by the fact that this is a technical membrane which may differ in its properties. The water flux *J* through UF membranes can be described by a model based on the Hagen-Poiseuille flow through capillaries (Mulder, 1996)

$$J = \frac{\varepsilon_s d^2 \, p}{32 \, \tau \, x} \qquad (3.1)$$

(ε_s= surface poprosity, d= pore diameter, Δp= TMP, η= viscosity, τ= tortuosity, Δx= membrane thickness)

Based on this equation flux depends only on the temperature dependency of water viscosity η. Considering η of water at 20° and 35°C which is 1002 10^{-6} kg/(m s) and 719,6 10^{-6} kg/(m s) the theoretically expected flux increase should be 1002/719.6 = 1.39. This is close to the measured flux increase 1478.4/ 953.45 = 1.55. Figure 3.2 gives the decrease of the water permeability after treatment with humic acid. Thereby the flux under HA treatment has been measured only at one TMP (0,5bar).

It is noticeable that the percentage decrease at 36°C is lower than at 20°C what basically shows a lower effect of fouling at higher temperature. This could be explained with the lower adsorption effects of the fouling layer at higher temperature. However, Figure 3.3 shows by visual impression stronger fouling (darker colour). But this visual impression does not give information about the layer density which could be different. Therefore SEM images of the layer were taken[1]. The SEM images, show a more compact layer at 20°C in comparison to the rather fluffy structure under 36°C (see Figure 3.4).

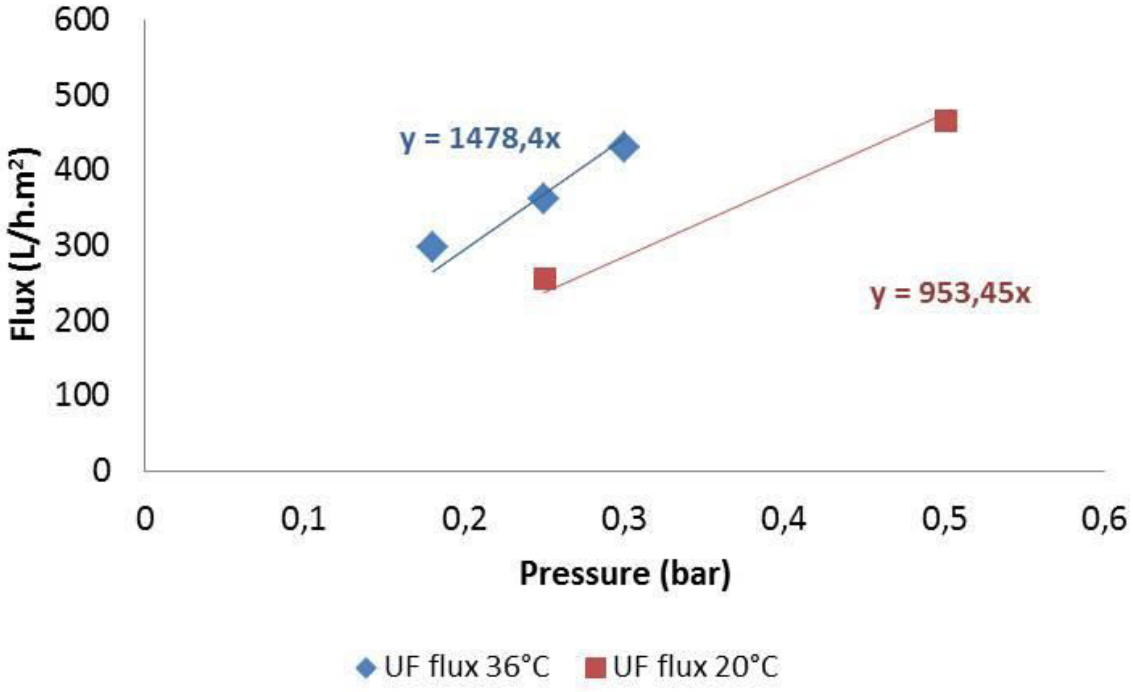


Figure 3.1 Water flux vs. TMP of the commercial UF membrane

[1] SEMs taken by Dr. D. Johnson at Swansea University, UK

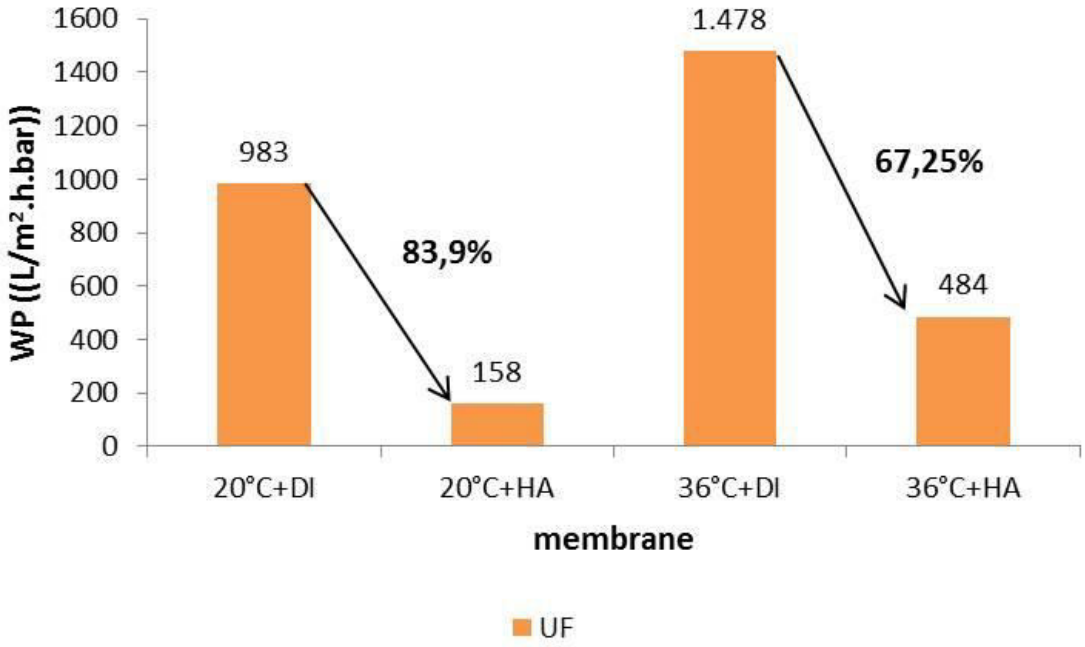


Figure 3.2 Reduction of water permeability for the UF membrane after treatment with HA

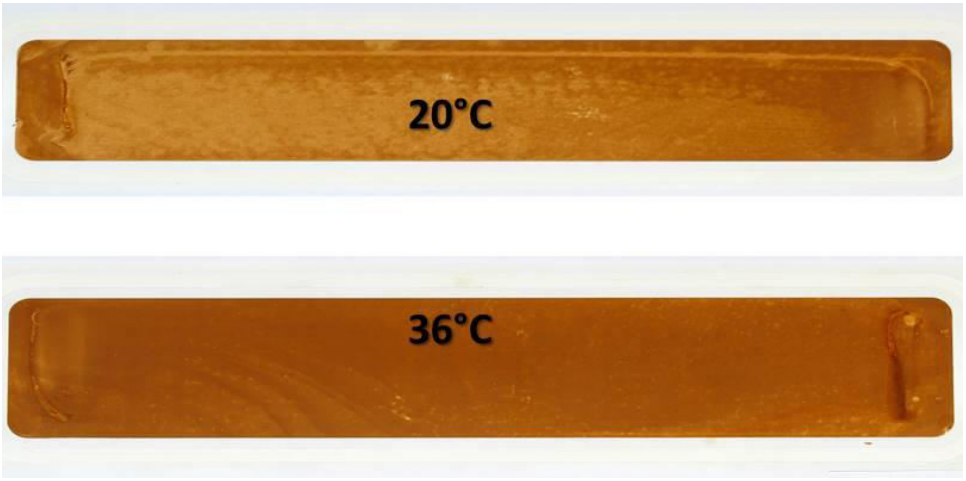


Figure 3.3 Visual impression of the UF membrane samples after HA treatment

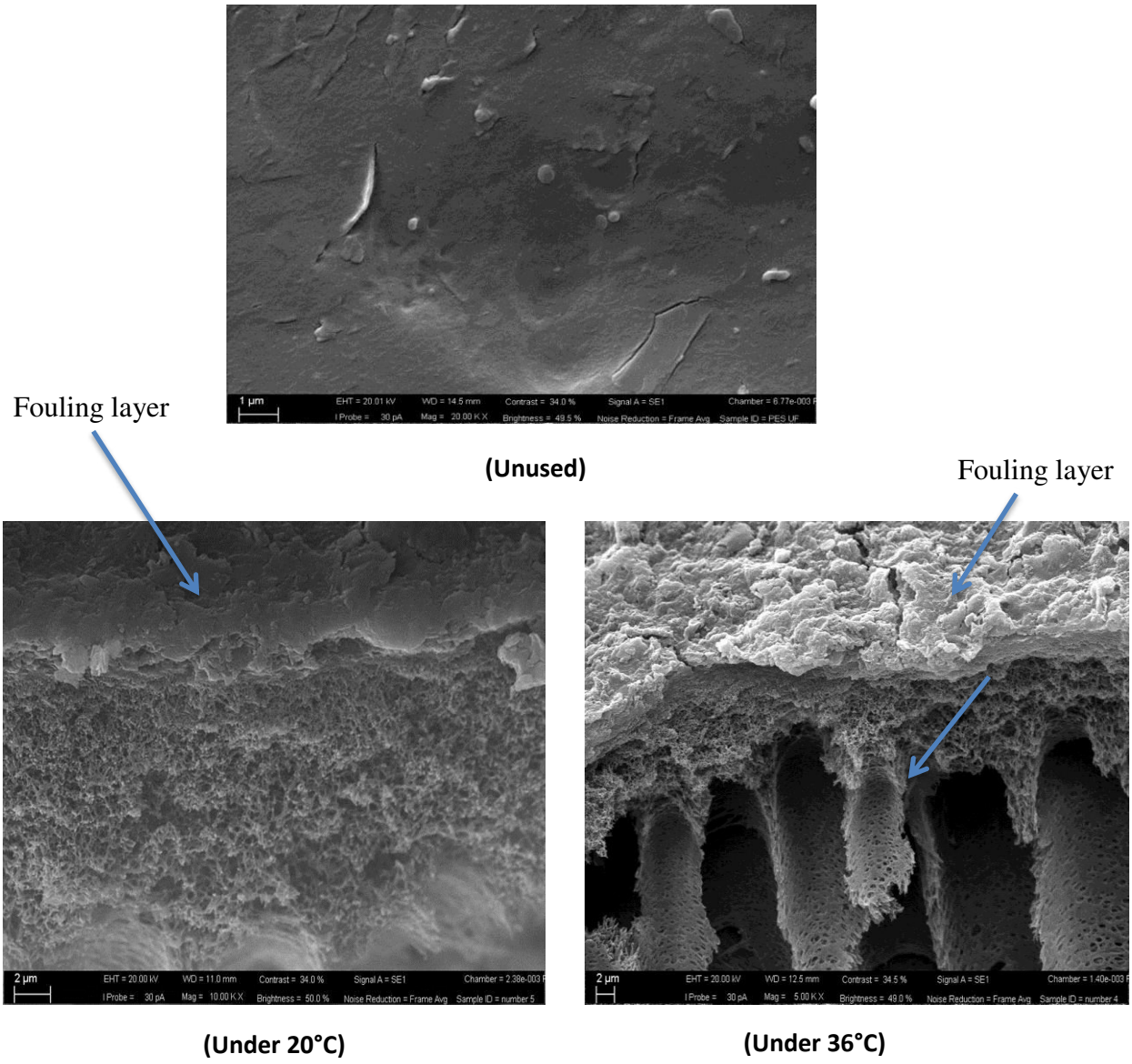


Figure 3.4 SEM images of the UF membrane, unused and after HA treatment

3.1.1.2. NF

As expected the water flux through the NF membrane is significantly lower than for the UF membrane since NF membranes are typically a much denser than UF membrane. The water permeability calculated by linear regression is 25.1 L/(m^2 h bar) and 45.1 L/(m^2 h bar) at 25° and 36°C, respectively. The water permeability coefficient based on the solution-diffusion model which applies for dense membranes such as NF is given as (Mulder, 1996):

$$A = \frac{D_w c_w V_w}{RT \; x} \qquad (3.2)$$

(D_w= Diffusion coefficient of water in the membrane, c_w= concentration of water in the membrane, V_w= molar water volume, R= universal gas constant, T= temperature)

According to (3.2) the temperature dependency of A relies mainly on the diffusion coefficient of water in the membrane which increases with higher temperature. The percentage drop of water permeability is similar at 20°C and 36°C (Figure 3.6). However, the visual impression of the membrane samples after HA treatment shows significantly greater fouling at 36°C (Figure 3.7). But the fouling layer looks rather loosely attached. The SEM of the particular samples indicates that the fouling layer under 20°C for the NF membrane is less important than the one under 36°C. It shows for the UF membrane a fluffy structure that is loosely attached.

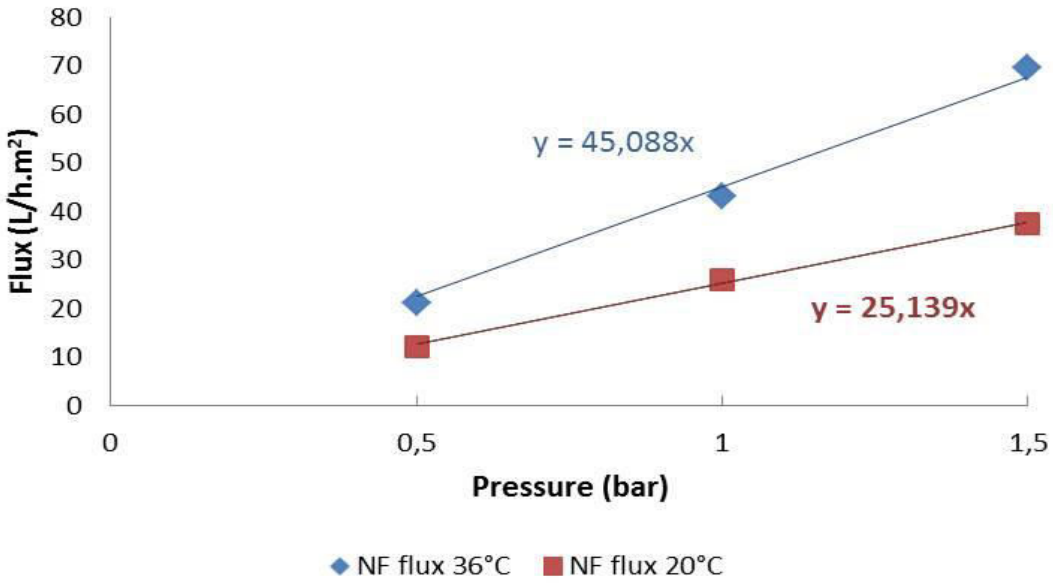


Figure 3.5 Water flux vs. TMP of the commercial NF membrane

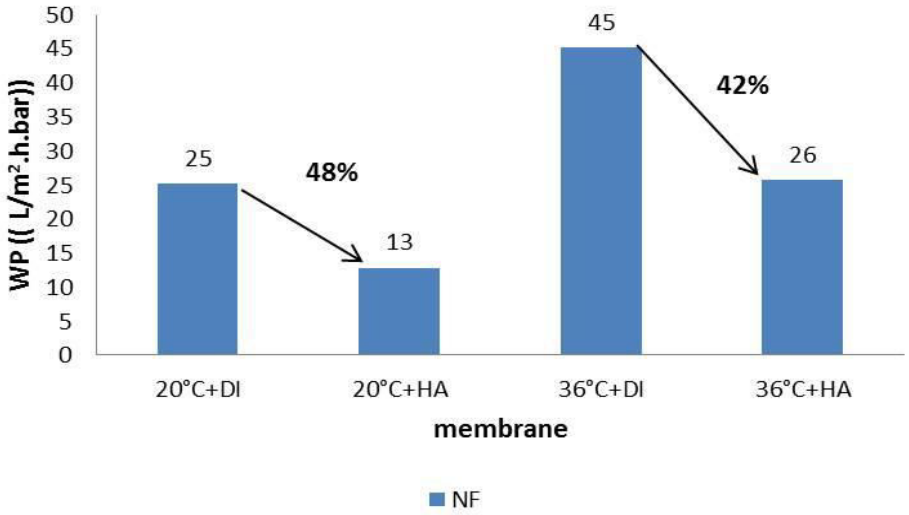


Figure 3.6 Reduction of water permeability for the NF membrane after treatment with HA

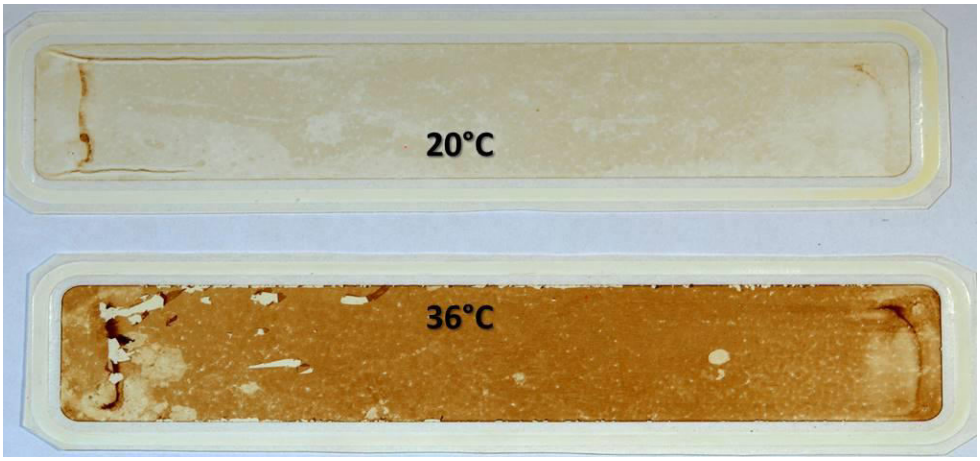


Figure .3.7. Visual impression of the NF membrane samples after HA treatment

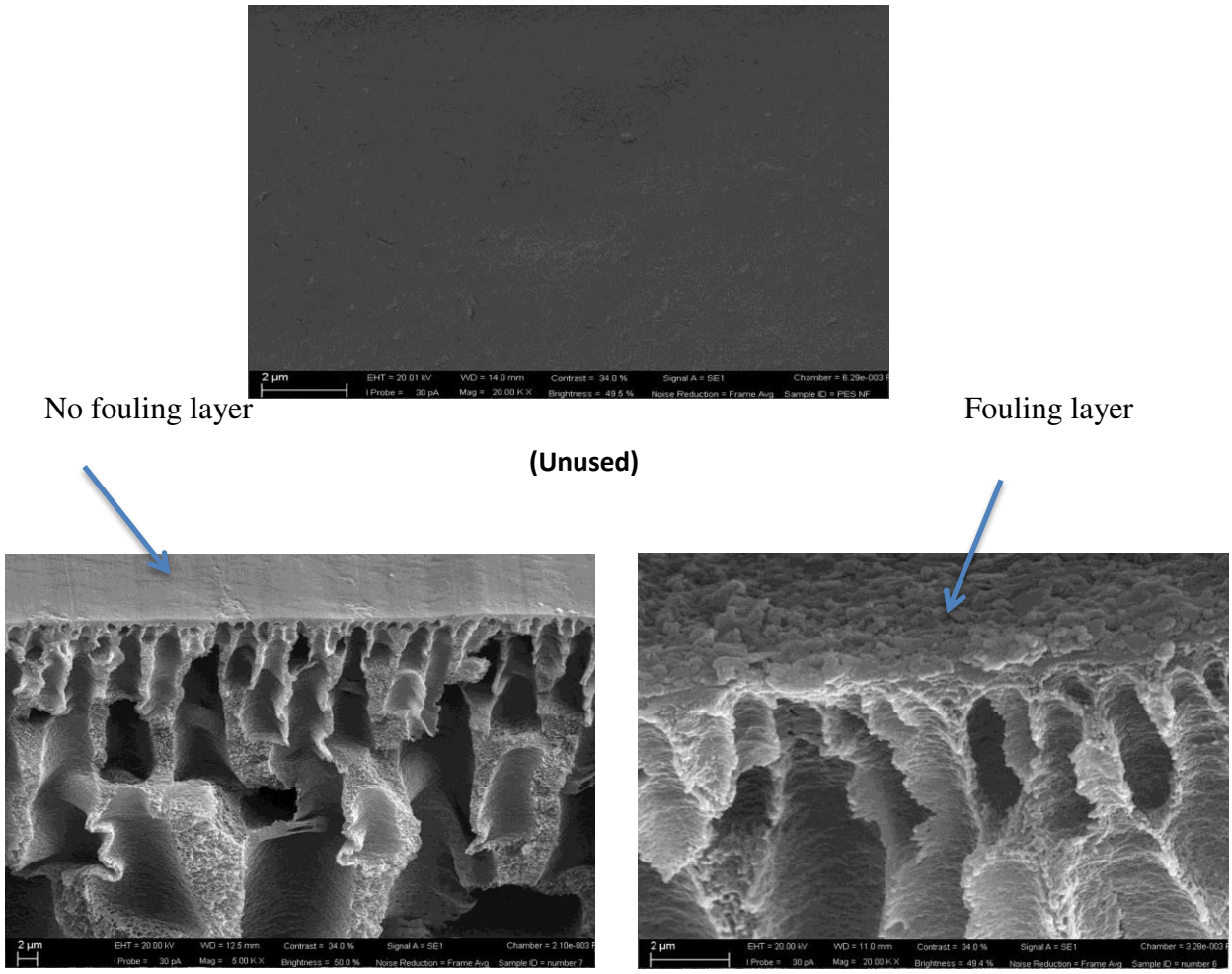


Figure .3.8. SEM images of the NF membrane, unused and after HA treatment

3.1.2. Novel membranes

3.1.2.1. Novel PBM membrane based on DTAB

The water permeability of the novel PBM based membrane using DTAB as surfactant (named N2 in Table 2.8) is shown in Figure 3.9. As can been seen water permeability is higher than for the commercial UF membrane 1646,6 vs. 1478.4 L/(h m^2 bar) at 25°C and 1005.1 vs. 953.5 L/(h m^2 bar) at 36°C. The ratio of water permeability is slightly greater than for the commercial UF membrane (1.64 vs. 1.55). However, it should be noted that the slope of flux at 20°C looks rather low and the flux at 0.25 bar should be further studied. The generally higher water permeability of the PBM coated membrane is not in line with the fact that the coating should add an additional resistance and hence water permeability is expected to be lower. Furthermore as can be seen with Figure 3.10 the percentage drop after HA treatment is

significantly higher than for the commercial UF membrane (Figure 3.2). Additionally Figure 3.11 gives the visual impression of no anti-fouling property of the novel membrane. This is confirmed by the SEM which looks similar as the commercial UF membrane (Figure 3.4). It might be that the PBM coating was not attached mechanically stable onto the UF membrane support what might be attributed to slow polymerisation. In further later study it was noticed that a more stable PBM layer is formed when increasing the concentration of the redox initiator. This should be studied by follow up experiments.

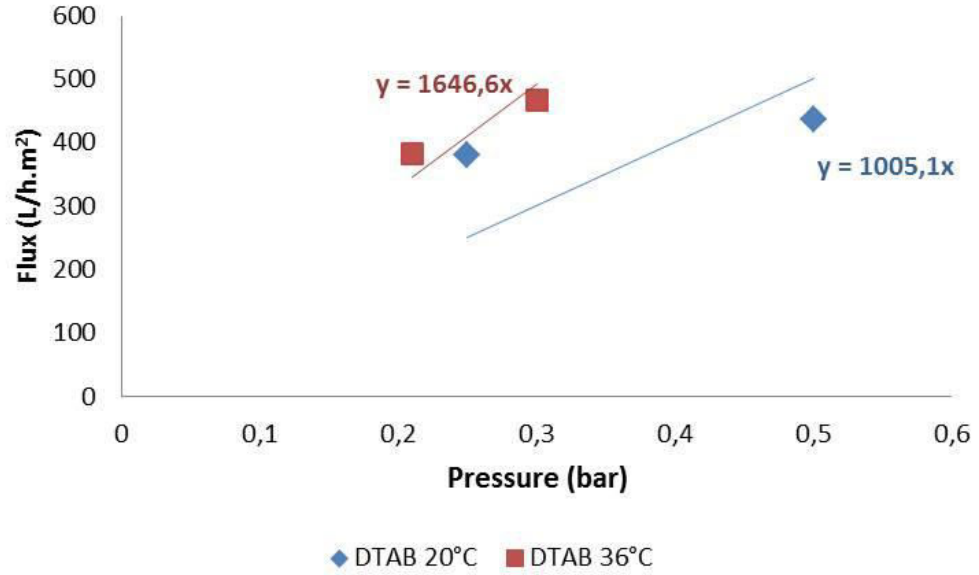


Figure 3.9 Water flux vs. TMP of the novel PBM membrane (DTAB based)

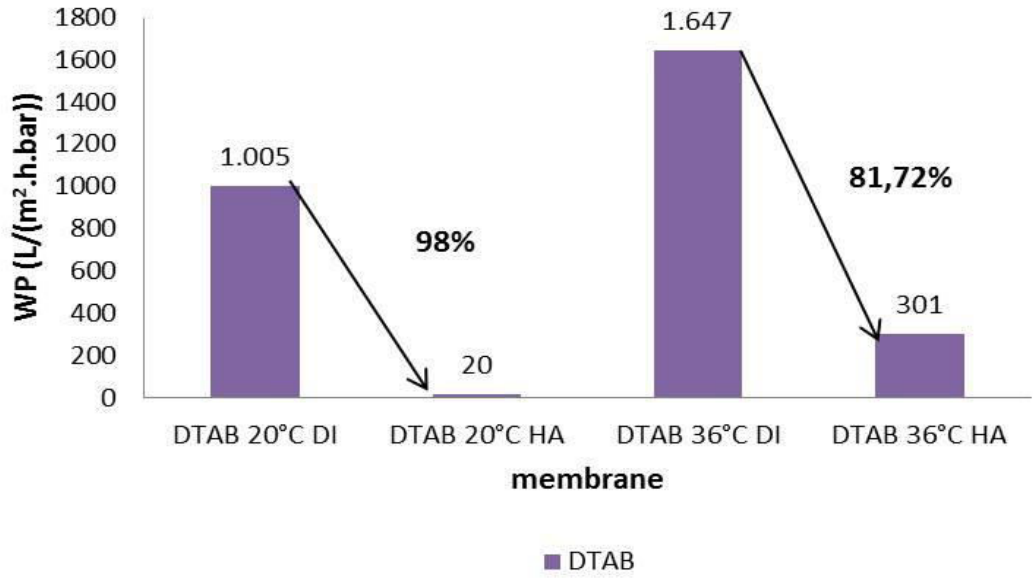


Figure 3.10 Reduction of water permeability for the novel PBM membrane (DTAB based) after treatment with HA

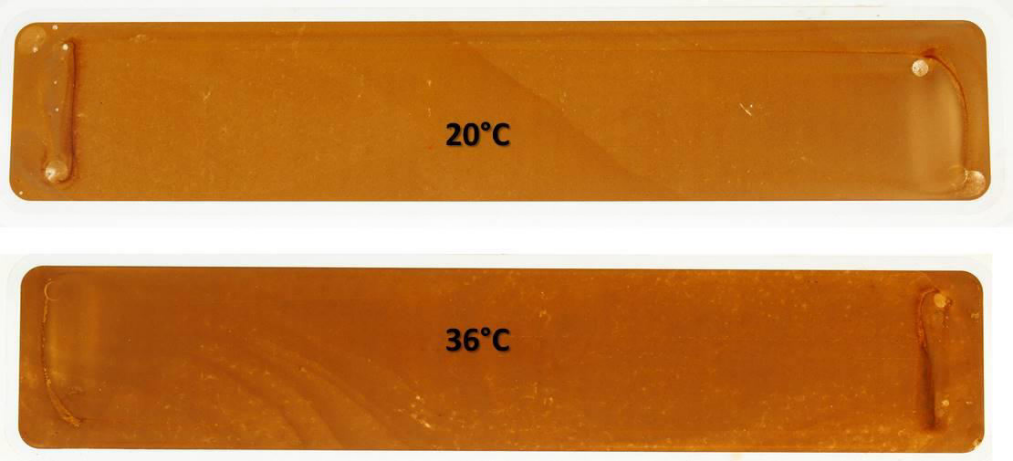
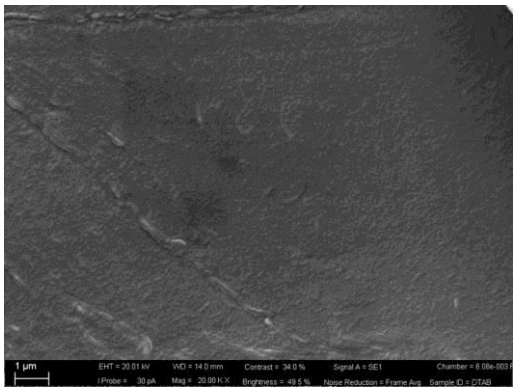


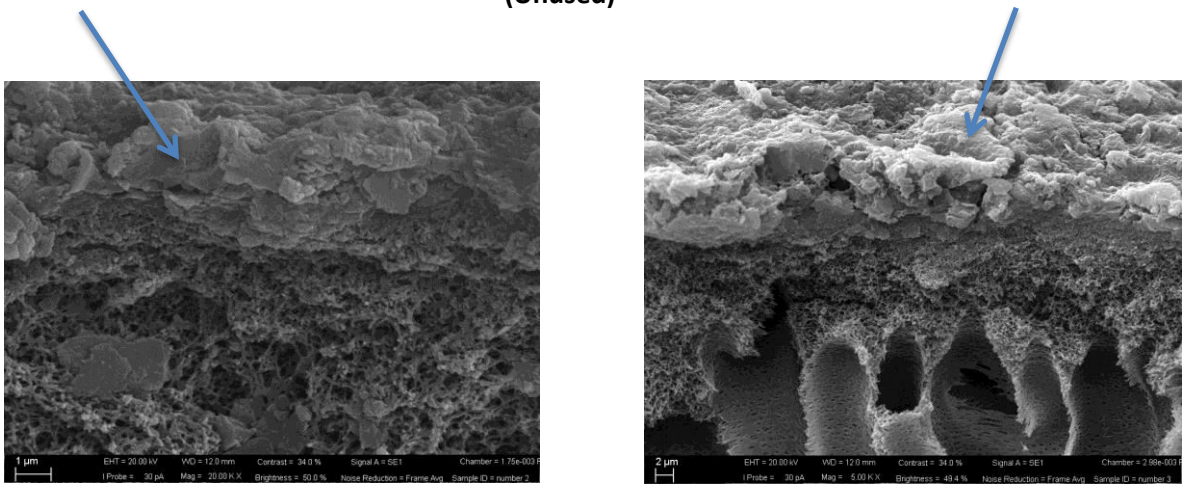
Figure 3.11 Visual impression of the novel PBM membrane (DTAB based) after HA treatment



Fouling layer

Fouling layer

(Unused)



(Under 20°C)

(Under 36°C)

Figure 3.12 SEM images of the novel PBM membrane (DTAB based), unused and after HA treatment

3.1.2.2. Novel PBM membrane based on AUTEAB

The water permeability of the novel PBM based membrane using AUTEAB as surfactant, (named N1 see Table 2.8) is lower than the permeability of the commercial UF and the DTAB based novel membrane. This basically shows that there is an additional resistance due to the layer (Figure 3.13). However, the flux points at 0.2 and 0.3 bar are not well correlated. Moreover the water permeability ratio at 36°C and 25°C significantly greater than for the commercial UF and the DTAB based novel membrane (1.8 vs. 1.55 and 1.64, respectively). The percentage drop of the water permeability after HA treatment is higher than for the commercial UF membrane what indicates low antifouling properties which is not in line with previous findings of the research group at ITM and HsKA (Figure 3.14). This is confirmed by the visual impression of the membrane samples after HA treatment (Figure 3.15). As already mentioned for the DTAB based PBM coating a more stable PBM layer could be formed when increasing the concentration of the redox initiator. The SEM image for the novel untreated membrane shows a nonuniform surface (Figure 3.16) which is not in line with previous findings from Galiano et al. (2015). The fouling layer of the HA treated membrane at 36°C looks thinner than for the commercial UF (Figure 3.4), however, the image gives the impression that the layer is more compact. As mentioned for the DTAB based novel PBM membrane the membrane preparation and characterisation needs to be further studied.

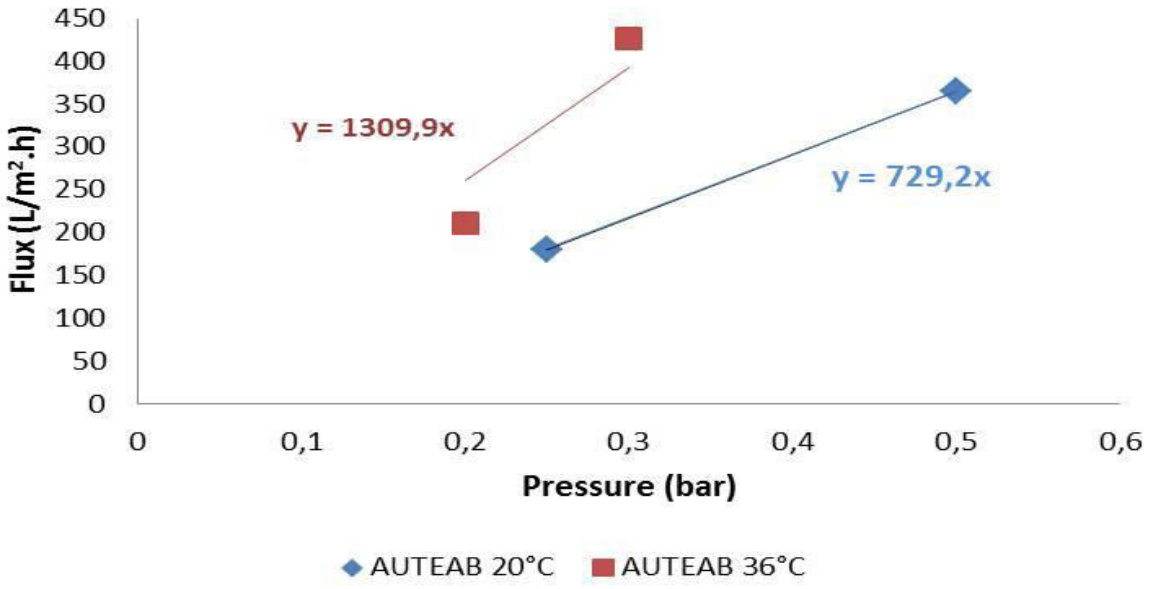


Figure 3.13 Water flux vs. TMP of the novel PBM membrane (AUTEAB based)

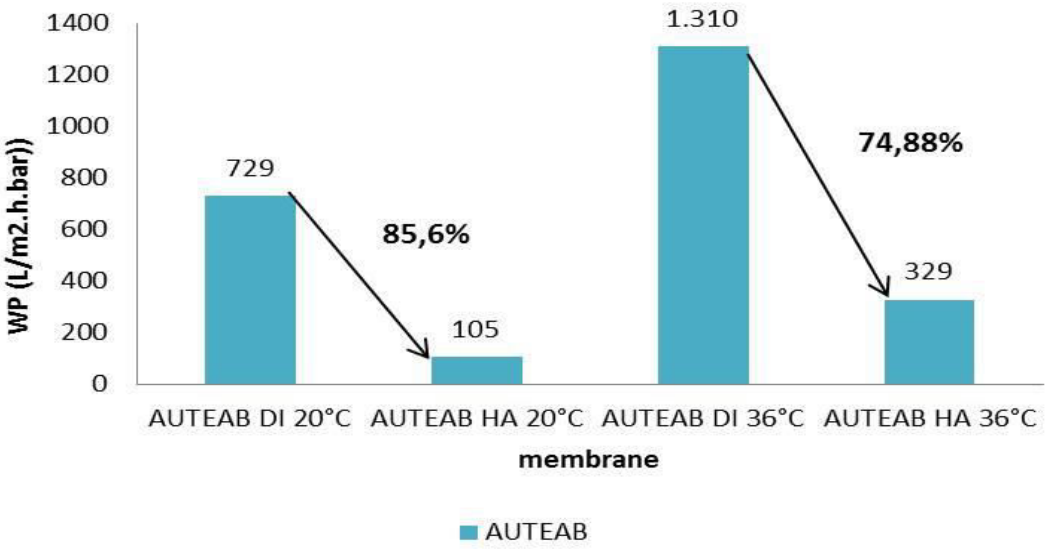


Figure 3.14 Reduction of water permeability for the novel PBM membrane (AUTEAB based) after treatment with HA

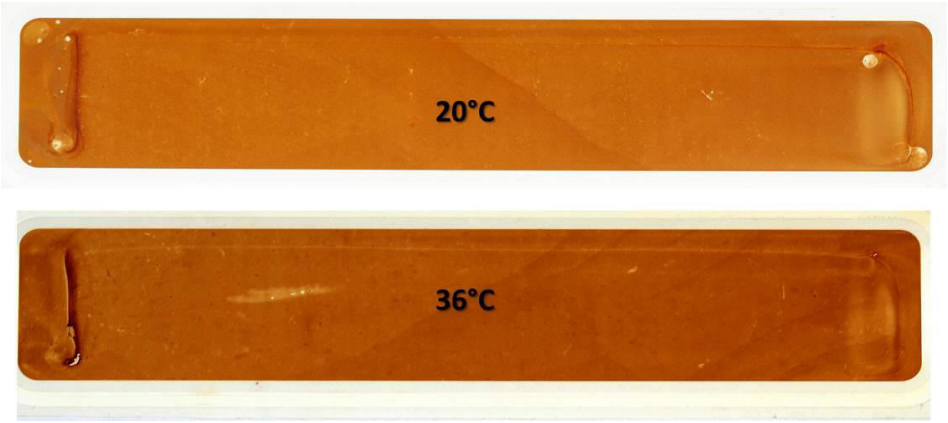
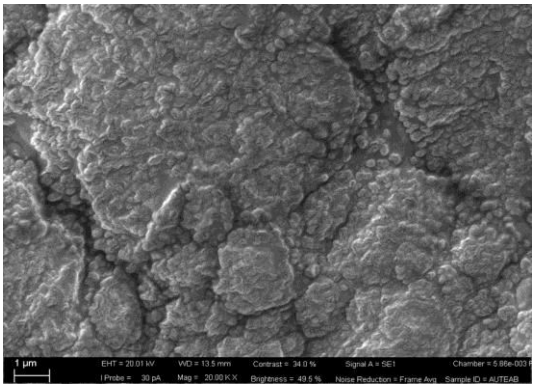


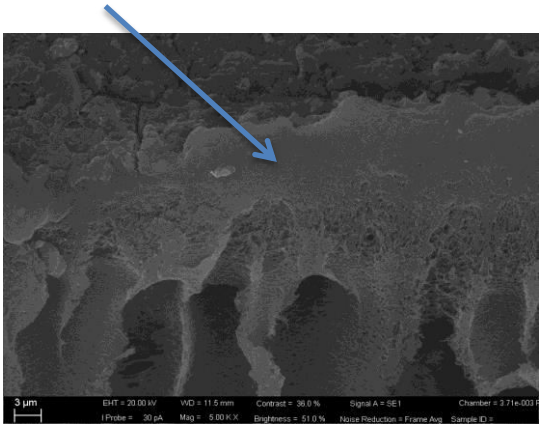
Figure 3.15 Visual impression of the novel PBM membrane (AUTAB based) after HA treatment

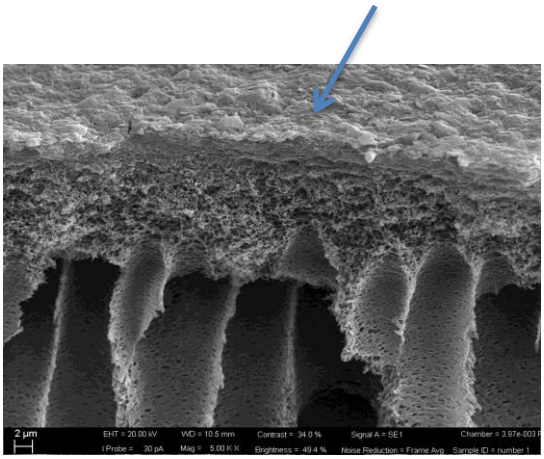


Fouling layer

Fouling layer

(Unused)





(Under 20°C)

(Under 36°C)

Figure 3.16 SEM images of the AUTEAB based membrane, unused and after HA treatment

3.2. Treatment under aerobic conditions

The Table 3.1 shows all membranes used during the first part of this work as well as the abbreviation and the operating time.

Table 3.1. Commercial and novel membranes used under aerobic conditions

Membrane	Abbreviation	Operation Time (d)
Ultrafiltration 1	UF1	1-34
Novel based AUTEAB	N1	35-52
Ultrafiltration 2	UF2	55-67
Novel based DTAB 1	N2	70-85
Novel based DTAB 2	N3	86-92
Ultrafiltration 3	UF3	93-114
Novel based DTAB 3	N4	115-143
Novel based DTAB 4	N5	144-172
Ultrafiltration 4	UF4	175-217
Ultrafiltration 5	UF5	218-231
Ultrafiltration 6	UF6	232-238
Nanofiltration	NF	239-260
Ultrafiltration 7	UF7	261-274

The membrane test experiments were started only after acclimation period for the micro-organisms to the feed conditions (1 month). Subsequently tests were carried out continuously investigating a variety of parameters mainly COD, TOC, pH, TMP, MLSS, HRT, flux, color rejection, conductivity, dissolved oxygen, N-balance. The operating conditions are summarized in Table 3.2.

The test duration for each membrane was in average of 15-30 days, which can be considered a short period with respect to usual test periods in MBRs. However, the reason is that the main objective of this thesis is to select the best membrane in terms of permeability and color rejection, in order to subsequently test them in long term with a laboratory scale submerged MBR unit. As shown in Table 3.2 the Hydraulic Retention Time (HRT) for all experiments is high compared to values in practical application. This was due to the small membrane area of filtration in relation to the fermenter tank volume, however, the main objective of this work was to keep comparable conditions in order to select the best membranes, so that they subsequently can be studied under more practical conditions with a submerged MBR system.

Table. 3.2. Operating conditions of MBR under aerobic conditions

Parameter	Unit	Values
Temperature	°C	20±2
TMP	bar	0.3-0.5
pH Feed pH Effluent	---	7.5 ± 0.5 8 ± 0.5
Permeate flux	L/(m^2 h)	5-15
HRT	h	100-500
OLR	(g COD((L d)	0.5-3.0
F/M ratio	(g COD)/(g MLSS d)	0.02-0.11
MLSS	g/L	7-11
Dissolved oxygen	mg/L	2-8

3.2.1. Water permeability

All experiments were run at a permeate flux of 5-15 L/(m^2 h) and TMP of 0.3-0.5 bar. Under these operating conditions (Table 3.2) the water permeability of the commercial UF membranes was in the range of ca. 20-35 (L/ (m^2 h bar) whereas it was lower around 18 (L/ (m^2 h bar) for the NF membrane, due to higher density of the active layer of NF membrane in comparison to the UF one (see Figure 3.17). As can be seen in Figure 3.17 the UF membranes typically show a transient phase in which the permeability is reduced and subsequently achieving constant values. This reduction might be explained by pore swelling of the UF membrane.

Regarding the novel membranes developed in our laboratory (see Figure 3.18), the highest permeability value was obtained for the N1 membrane which was prepared based on the AUTEAB surfactant. It is worth to note that for this membrane permeability 30-35 L/(m^2 h bar) is even higher than for the commercial ones. This is not in line with the findings using HA as model foulant. After having treated the AUTEAB based novel membrane with HA it shows a lower water permeability than the commercial UF being treated under same condition (see 3.1.1.1 and 3.1.2.2). This could be explained by variation of the properties of the PBM coating which is manually prepared at lab-scale. The preparation process is currently studied and further optimized in a parallel PhD thesis (S.Schmidt). The DTAB based PBM coated membranes show lower permeability about 10-15 (L/ (m^2.h.bar). This is follows the logic that the PBM coating adds an additional resistance to the pristine commercial membrane and is inconsistent to the findings of the flat sheet testing unit which shows already higher water permeability for the PBM coated membrane compared to the commercial one (see 3.1.2.1).

This should be further studied in a follow up work. The water permeability remains constant and shows no decline which could be attributed to fouling.

The PBM coated N3 (DTAB based) shows significantly lower permeability 1,5 L/(m^2.h.bar) since the PBM coating was polymerized at higher temperature and resulted in higher density of the layer (Table 2.8). Due to the very low permeability the experiment with N3 was stopped after short time. Due to significant lower materials cost of DTAB (which is commercially available) compared to AUTEAB this study was more focused on DTAB based PBM coating.

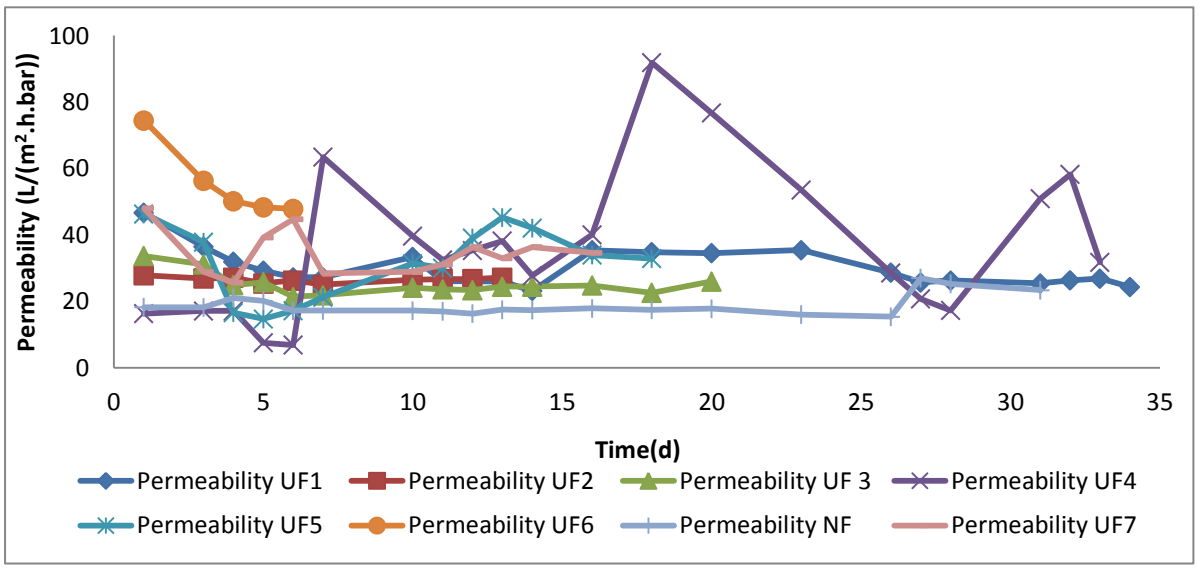


Figure.3.17. Water permeability for the commercial membranes

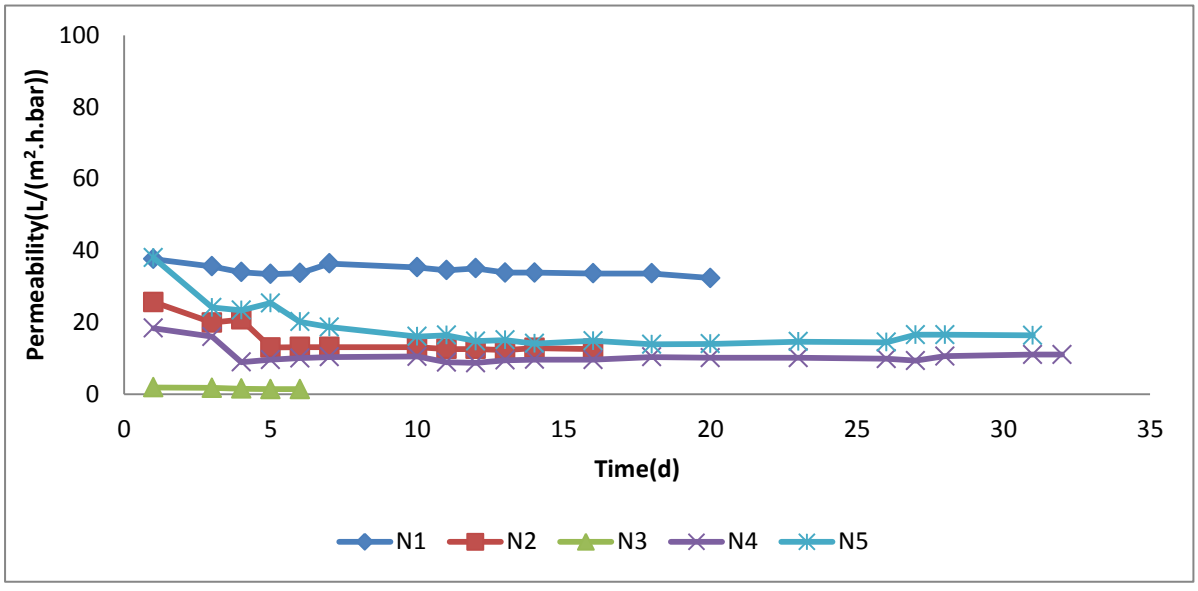


Figure.3.18. Water permeability for the novel membranes

3.2.2. COD removal efficiency

Regarding COD removal efficiency generally no significant difference could be noticed between the commercial UF and the novel membranes (see Figure 3.19 and Figure 3.20). After an initial period COD removal efficiency fluctuates between 93 to 95%. However, the NF membrane shows the highest removal efficiency up to 97% what can be explained by the denser structure of this membrane compared to UF membranes. For the dense PBM membrane N3 the COD removal efficiency significantly drops to 84%. This might be attributed to the very dense structure of the membrane and consequently the biological degradation process facing stress due to high rejection of low biodegradable compounds (e.g. dyes).

It is known that MBR reactor actually is always an interplay between rejection of the membrane and biodegradation by the activated sludge system.

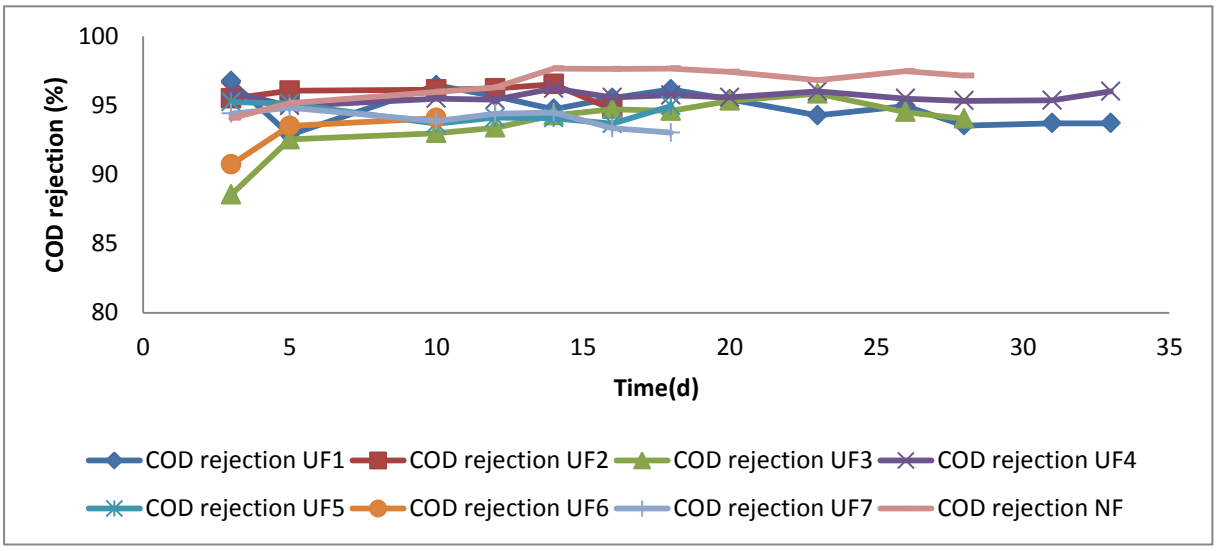


Figure.3.19. COD removal efficiency for commercial membranes.

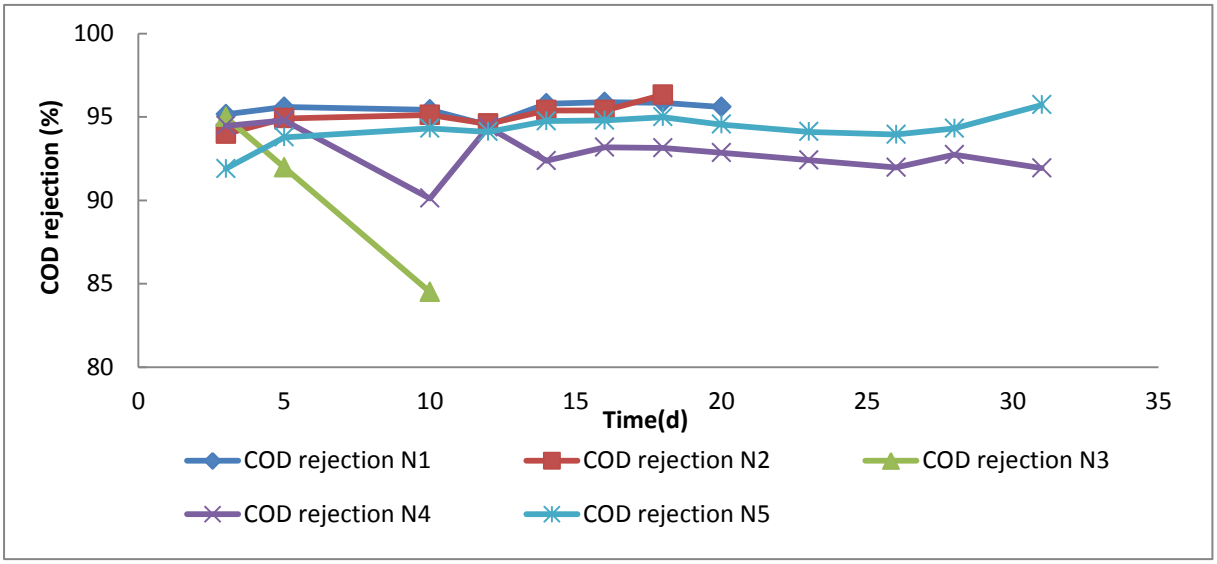


Figure.3.20. COD removal efficiency for novel membranes.

3.2.3. COD in feed and COD in reactor

Figure 3.21 shows the COD values in the permeate compared to the filtered mixed liquor reactor samples. As can be seen the COD level of the permeate samples is typically lower than for the filtered reactor samples (using the same UF membrane). This fact has ben also noticed by Yurtsever et al. (2015) who studied performance of anaerobic and aerobic MBRs for the treatment of synthetic wastewater. They explained this fact due to cake or gel layer formation on the membrane submerged in the mixed liquor which increases COD either by increased physical rejection or degradation of organic matter by the biofilm on the membrane surface. The basically greater difference between permeate and reactor COD for the commercial UF compared to the novel membranes (particularly UF2, UF6, UF7) might be attributed to more pronounced gel layer formation due to fouling.

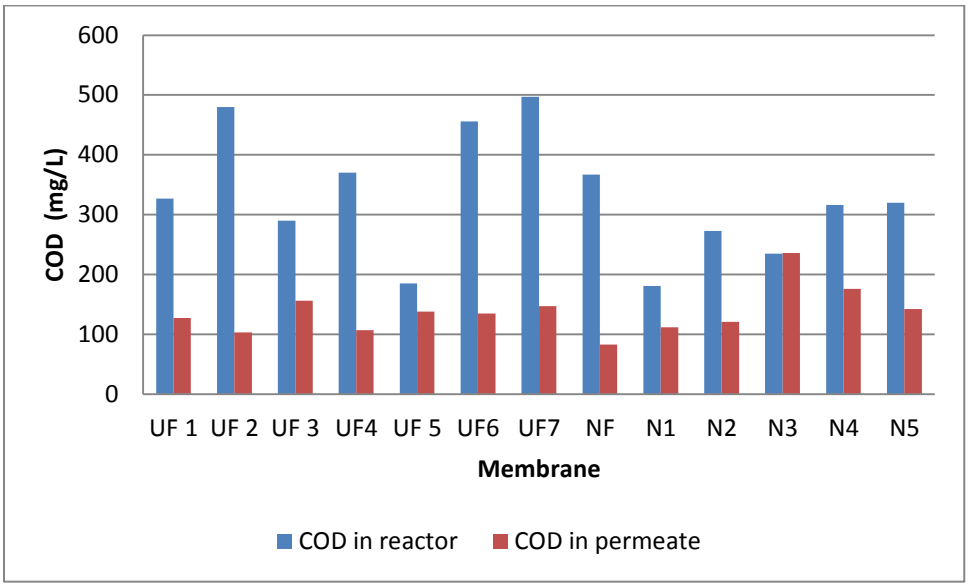


Figure.3.21. COD values in the reactor vs COD in permeate for commercial and novel membranes

3.2.4. COD to TOC removal efficiency (ratio)

COD as well as TOC are parameters that can be calculated theoretically as shown in (chapter 2 section theoretical calculations). COD and TOC are related to the organic load and should be correlated to each other. It is well known that COD is used in order to determine the pollution strength of a wastewater, but this is alone is not enough, since this parameter shows generally the amount of oxygen consumption needed for the oxidation of the wastewater. In addition the TOC gives the total amount only of the organic carbon load in the wastewater, which represents the exact strength of the organic pollution in the wastewater. Generally, TOC is considered as 1/4 to 1/3 of COD values based on theoretical calculation. Based on theoretical calculation, the TOC and COD values of the MTDW are 848 mg/L and 2367 mg/L respectively. This indicates that the TOC value is 1/3 of COD value which is in line with expected values. As shown in Figure 3.22 the TOC/COD ratio is basically between 0.2 and 0.3 with some greater spikes at the beginning (day 1-60). It can be also seen that the TOC in permeate fluctuates less compared to the COD values.

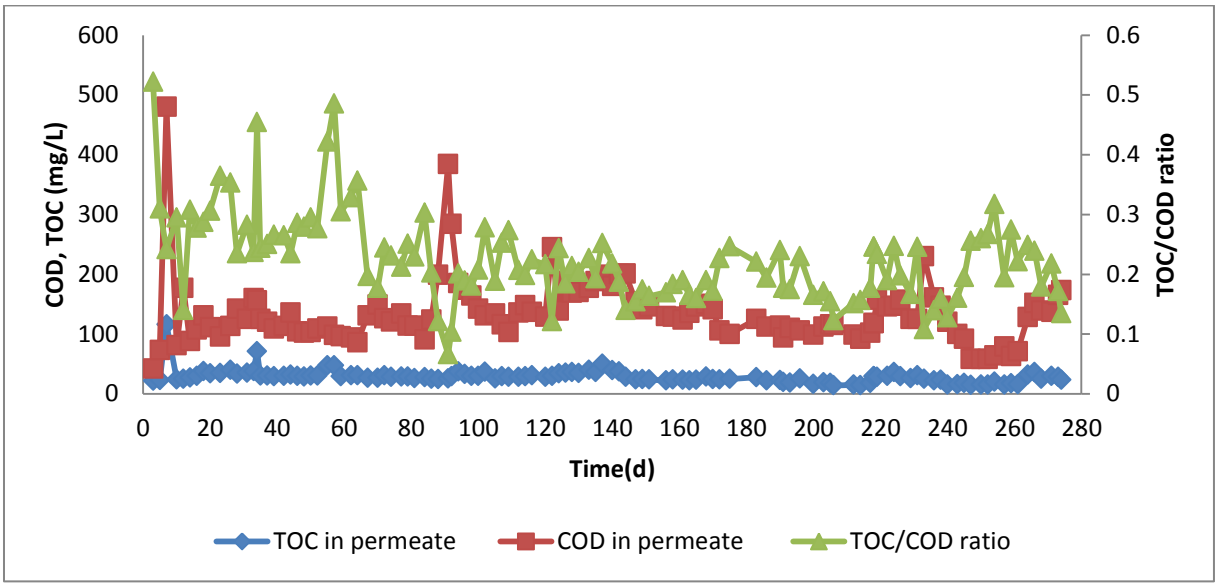


Figure 3.22. TOC correlation to COD for the whole experimental period.

3.2.5. COD and TOC removal efficiency

In Figure 3.23 it can be seen that the TOC rejection is generally higher than the COD rejection. This could be explained by the particular composition of the MTDW. As already mentioned the COD generally represents oxidation of all chemical compounds, however, the TOC concerns only carbon containing compounds.

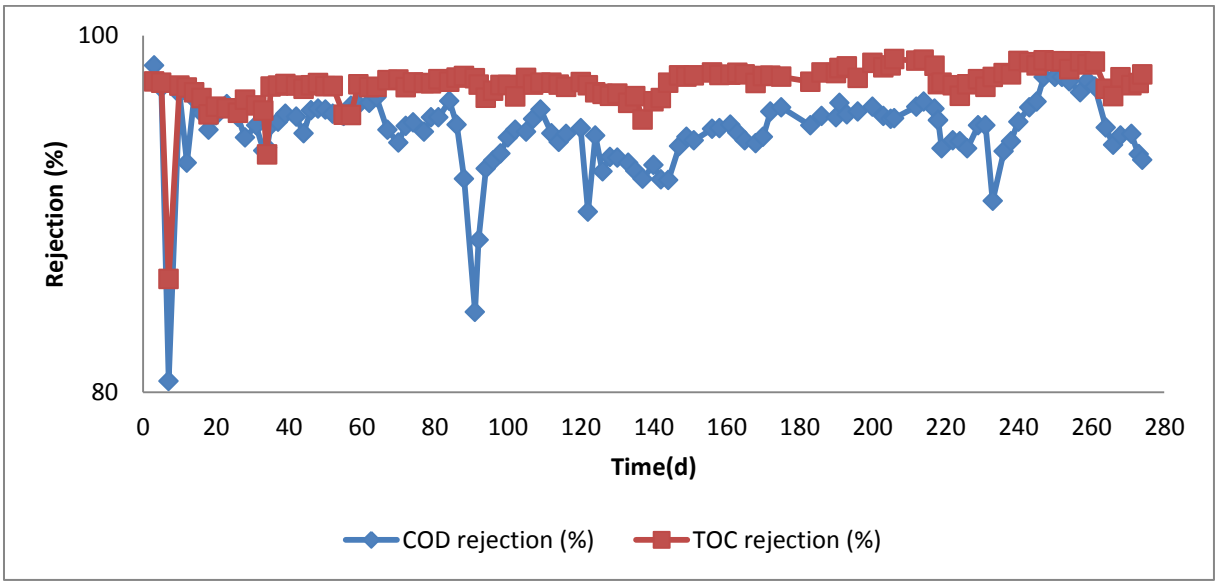


Figure.3.23. Comparison of COD to TOC removal efficiency

3.2.6. Nitrogen balance

A complete nitrification has been noticed during the entire experimental period independently from the different membranes being tested (Figure 3.24). This shows that the bacterial strains such as *nitrosomonas* and *nitrobacter* which are responsible for the nitrification process find suitable conditions in the biocenosis of the activated sludge and they are not hampered by toxic by-products which may occur in the degradation process chain. Figure 3.24 shows that generally all N in the permeate occurs as nitrate (NO_3^-) and ammonia (NH_4^+) which has been added with the MTDW is always below detection limit It is remarkable that after day 20 the Total N goes across the Total N in feed what could be explained by biological release process of N due to stress of the biocenosis. From day 40 the Total N remains significantly below the Total N of the feed what could be attributed to either accumulation of in in the mixed liquor or partial denitrification in anoxic zones of the MBR reactor.

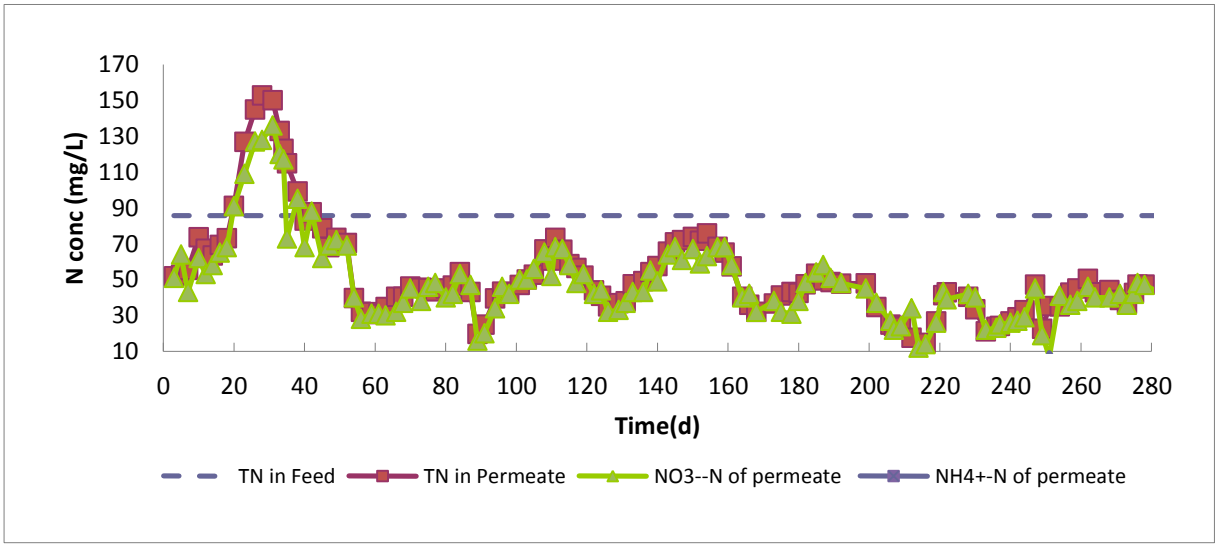


Figure 3.24 N-compounds in the SSMBR unit during the whole experimental period

3.2.7. Hydraulic Retention Time (HRT)

The HRT was generally kept between 100 and 500 h (Figure 3.25) with an average of 250 hours. The applied HRT is typically much higher than the one in typical aerobic MBRs what can be attributed to the small membrane area in the cross-flow cell (ca. 80 cm^2) compared to the working volume in the reactor (ca. 20 L). However, it is the purpose of this thesis to only compare performance of different membrane samples under same conditions and subsequently testing the best performing ones in a submerged MBR under more realistic conditions. Since the TMP has been kept around 0.3-0.5 bar the HRT was mainly governed by

the water flux through the membrane. Only during the period when the novel membrane N3 was tested (which showed extremely low permeability), the HRT spiked up to 3500 hours.

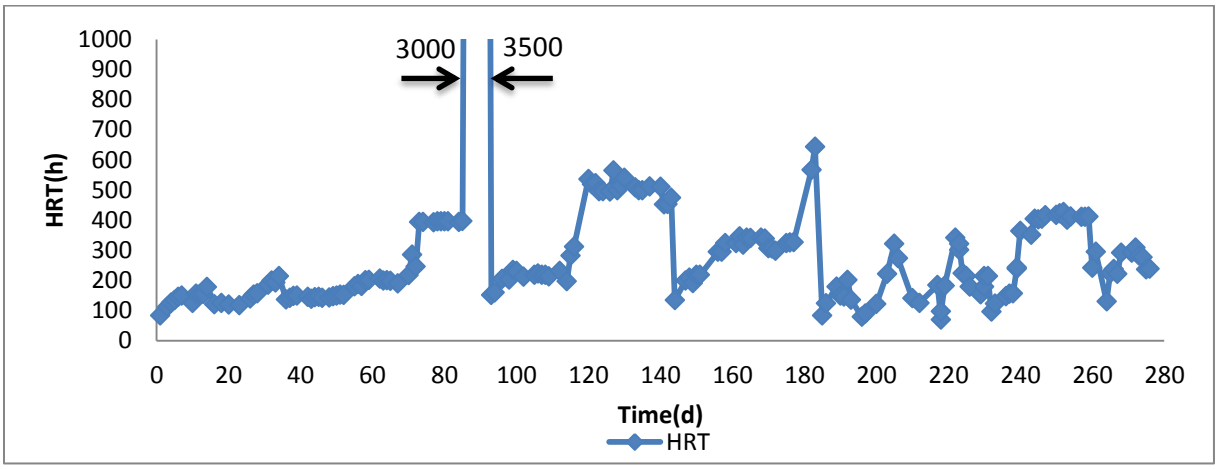


Figure 3.25 HRT for commercial and novel membranes during the entire experimental period

3.2.8. Organic Loading Rate (OLR)

The OLR is an important design and controlling parameter in biological wastewater treatment process. It is measured by the amount of food provided to a unit amount of biomass (or reactor volume) for a unit period of time. The organic loading rate is also an important parameter which indicates how many kilograms of organic dry solids are loaded per m^3 of digester volume and unit of time. The organic loading rate is important for the plant components (especially mixer/agitator) and for the biocenosis. If the organic loading rate is too high (over 4.0 g COD/L d) technical components like mixers or pumps could be damaged due to the overload that stresses the bacteria, by too much feed load. Consequently the digestion process stops completely.

For the entire experimental period the OLR was kept between 0.5 and 3 gCOD/(L d), see Figure 3.26 which is in the typical range for MBRs (Table 3.3). Only for the extremely dense novel N3 the OLR moved up to 18 . gCOD/(L d). For all other membranes the OLR was kept in a reasonable range since the COD removal efficiency was generally greater than 90%.

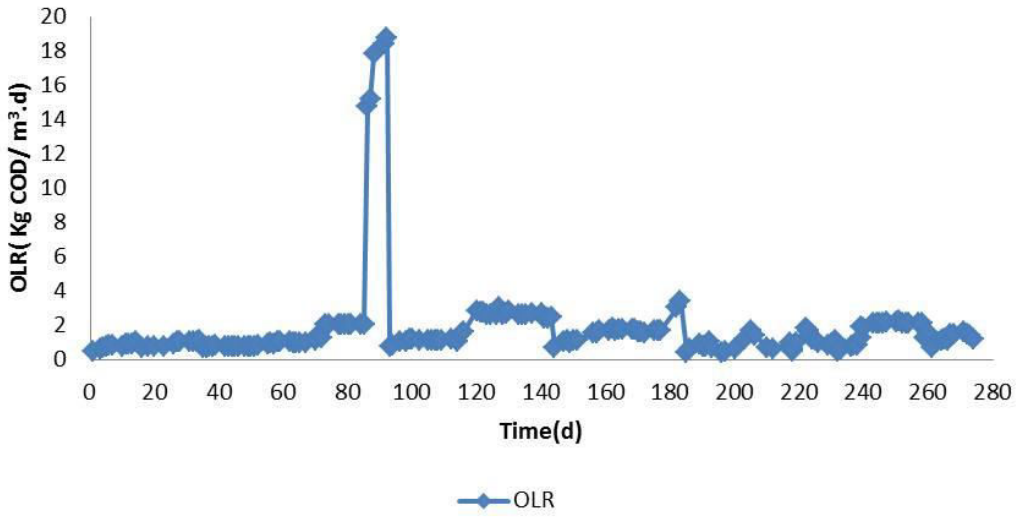


Figure 3.26 OLR for commercial and novel membranes during the entire experimental period.

3.2.9. F/M Ratio

Food to microorganism (F/M) ratio is one of the most fundamental control parameters for the activated sludge process. This is the relationship between load of COD fed into the tank, and the bacterial population in the tank, and is given in (g COD/g MLSS d), Typically MBR runs at lower F/M ratio than conventional activated sludge (CAS) process in order to mitigate membrane fouling and maintain high oxygen transfer efficiency. The preferred COD F/M ratio range in MBR is approximately a third to a half of that in CAS (see Table 3.3).

Table 3.3 Preferred ranges of operating parameters in MBR and CAS (Yoon, S.H., 2015)

Parameter	Unit	MBR	CAS
OLR	g COD/(L d)	1.0-3.0	1.2-1.8
F/M ratio	g COD/(g MLSS d)	0.08-0.24	0.32-0.48
MLSS	g/L	8-12	2-4

As shown in Figure 3.27 the F/M ratio for the entire experimental period ranges approximately between 0.02 and 0.11 (g COD/g MLSS.d) with some fluctuations within UF1 attributed to the acclimation period. However, it can be seen clearly that the UF2 and UF3 had the same F/M ratio since the conditions were more or less stable and the bacterial population got acclimated to the system. The F/M ratio during test of the NF membrane (day 239-260) is lower than for the F/M ratio of the UF membranes due to higher the COD rejection and lower water flux. The F/M ratio during test of the very dense novel N3 was close to zero due to very

low water flux. Furthermore the F/M ratio applied in this work 0.02 -0.11 g COD/(g MLSS d) is close to an experimental study of Wu et al. (2013) which was conducted at an average F/M ratio of 0.08 (g COD/g MLSS.d) in a full scale submerged MBR plant treating TFT-LCD (Thin-film transistor liquid crystal display) wastewater.

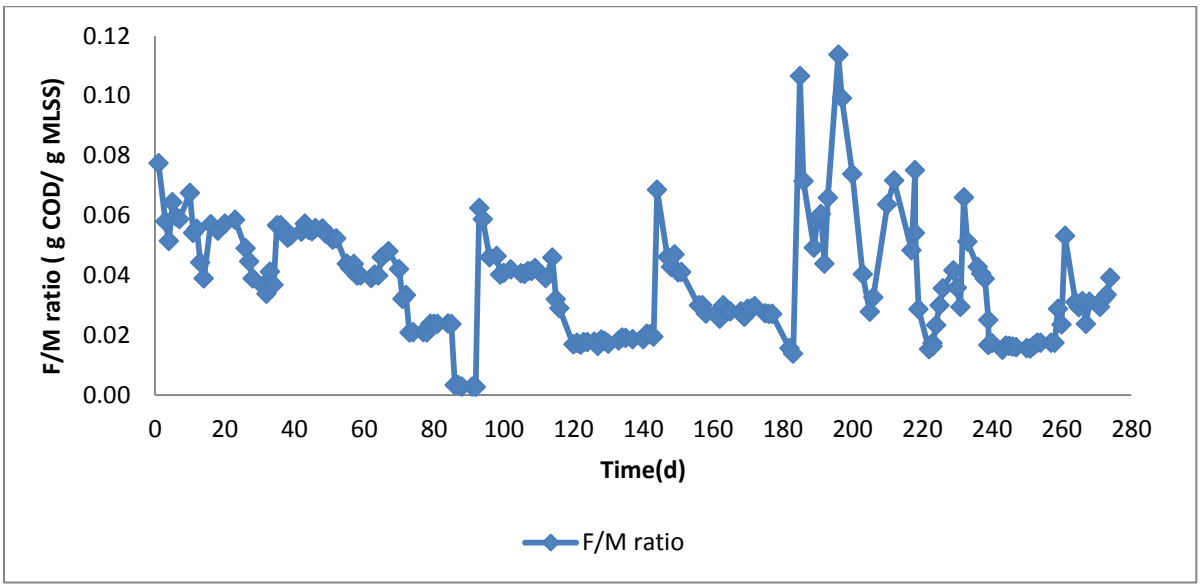


Figure.3.27. F/M ratio for commercial and novel membranes during the whole process.

3.2.10. Mixed Liquor Suspended Solids (MLSS)and Turbidity

The MLSS value during the whole experimental period under the aerobic conditions was kept smoothly between 7 and 11 g/L except for some sudden changes due to adding of sludge or loss due to some technical problems (Figure 3.28). This is basically in line with the recommended MLSS of 8-12 g/L in MBRs (Table 3.3) In addition to measurement of MLSS the activated sludge concentration was monitored with an inline optical sensor in the reactor However, as it can be seen with Figure 3.28 the basic trend of percentage turbidity does not follow the general trend of the MLSS. This could be explained with variation of the sludge structure what may have affected the optical measurement of the sensor.

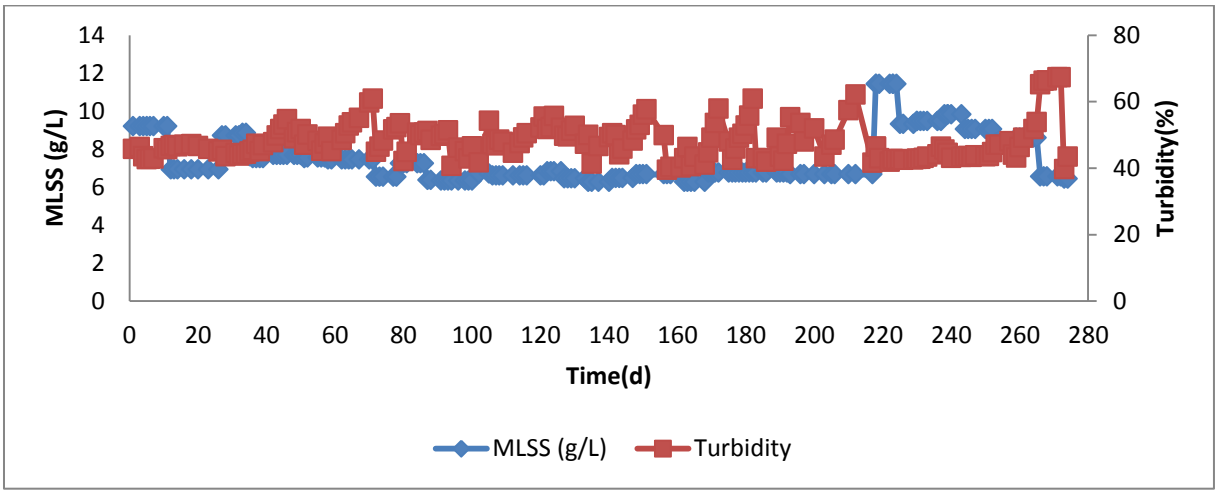


Figure.3.28. MLSS vs turbidity during the entire experimental period.

3.2.11. pH value

pH values for the MTDW feed solution was kept constant in the range of 7.5±0,5 for the entire experimental period (Table 3.2). The resulting pH of permeate remained constant slightly higher at 8.0±0,5 over the entire period independent for all tested membranes.

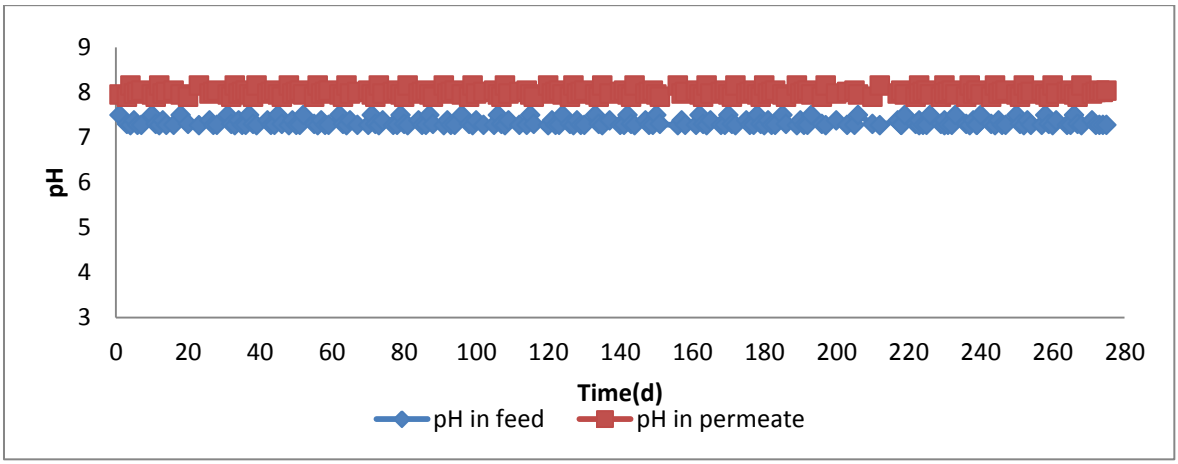


Figure.3.29. pH in feed and in permeate during the whole process

3.2.12. Conductivity

The electrical conductivity in the MTDW feed and permeate was basically same during all experiments in the range of 5000-6000 µS/cm. This is understandable since the conductivity is mainly governed by the salts (NaCl, $NaHCO_3$, NH_4Cl) added to the MTDW and salts typically can pass UF membranes.

3.2.13. CO_2 and O_2 in exhaust air

Figure 3.30 shows CO_2 as well as O_2 in the exhaust air of the bioreactor detected by the sensor during the biological activity of the bacteria during the entire process period. The O_2 concentration remained stable slightly below 21 Vol(%) unitl day 220. Around day 220 a technical problem with the oxygen sensor as noticed and after having fixed the sensor the signal returned back to approximately 21 Vol(%) from day 260. In contrast CO_2 concentration shows a high fluctuation between almost zero and 0.2Vol(%) which is lower and higher than the natural CO_2 level of 0.04Vol(%). The fluctuations can be attributed to changes in the biological degradation processes (basically converting dissolved organic compounds into CO_2 and H_2O). However, these changes can not be reflected in the COD or TOC removal efficiency (Figure 3.22).

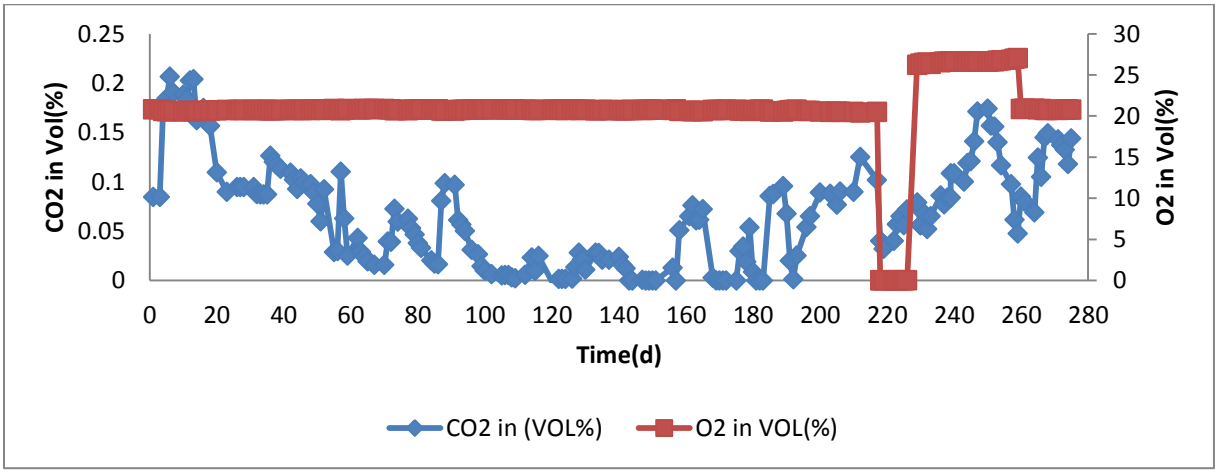


Figure 3.30. Concentration of CO_2 and O_2 in exhaust air during the entire experimental period

3.2.14. Temperature

During the entire experimental period temperature in the bioreactor and side-stream cross-flow membrane cell of was fixed at 20±2°C which is the typical temperature for activated sludge working under aerobic conditions in common sewage treatment plants. As it can be seen with the Figure 3.31 below, this was kept constant during the whole experimental period, except for the period between day 220 till day 240 due to technical problem with the thermostat of the reactor. This could explain the higher permeability of the UF6 membrane which was operated from day 232-238 (Table 3.1, Figure 3.17).

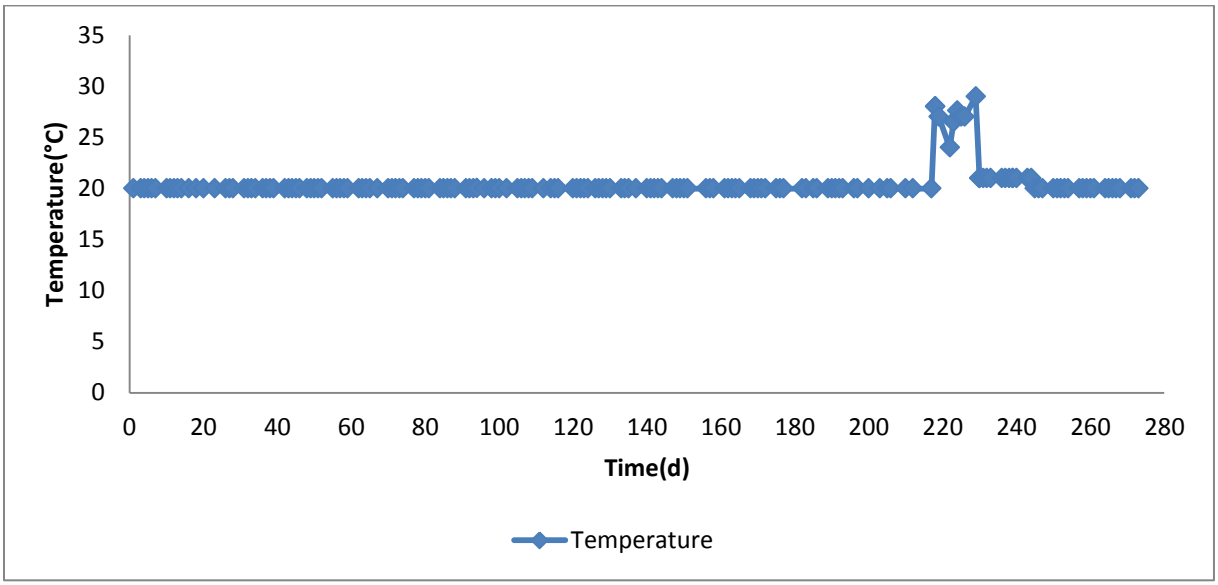


Figure.3.31. Temperature during the whole process.

3.2.15. Colour removal efficiency

The color concentration was measured via spectrophotometer, and calculated based on Beer´s law by calibration curves (see chapter 2.3). As shown in Figures 3.32.a, b the average percentage reduction rate of the red dye was between 10 and 90% whereas the very high rejection rate of the UF1 and UF4 look like an outliers considering the fact that azo dyes such as the red dye show usually rather low permeability under aerobic condition. The red rejection obtained from the UF1 is more or less fluctuating and should not be considered, since UF1 is the 1st membrane used during acclimation period, where the sludge concentration was still lower than the one in the feed. Since the molecular weight of the red dye is only 380 g/mol, it is not expected to be rejected neither by the UF nor by the NF membrane (MWCO: 1 kDa, see Table 2.7). However, previous experimental studies with the same MTDW which have been done in a flat sheet cross flow cell showed a red dye rejection using the commercial UF membrane of about 25%. This might be attributed to a charge exclusion effect since the PES membrane surface is positively charged and the red dye also has positive charge. However, with the exception of UF1 and UF4 the NF basically exhibits the highest rejection of the red dye what shows the denser structure of the active membrane layer.

For the blue dye rejection rate was generally higher than for the red dye. Rejection averaged 40-60% for the UF. Among the commercial membranes rejection for the NF is outstandingly high achieving almost 90%. This can be attributed to the dense nature of the membrane (MWCO: 1 kDa) compared to the UF membranes and the molecular weight of the blue dye (627 g/mol) being significantly higher than for the red dye. Experiments carried out

in a flat sheet cross flow cell with MTDW showed blue dye rejection of approximately 45%. As for the red dye this could be also attributed to the size exclusion effect since the blue dye molecule is also negatively charged.

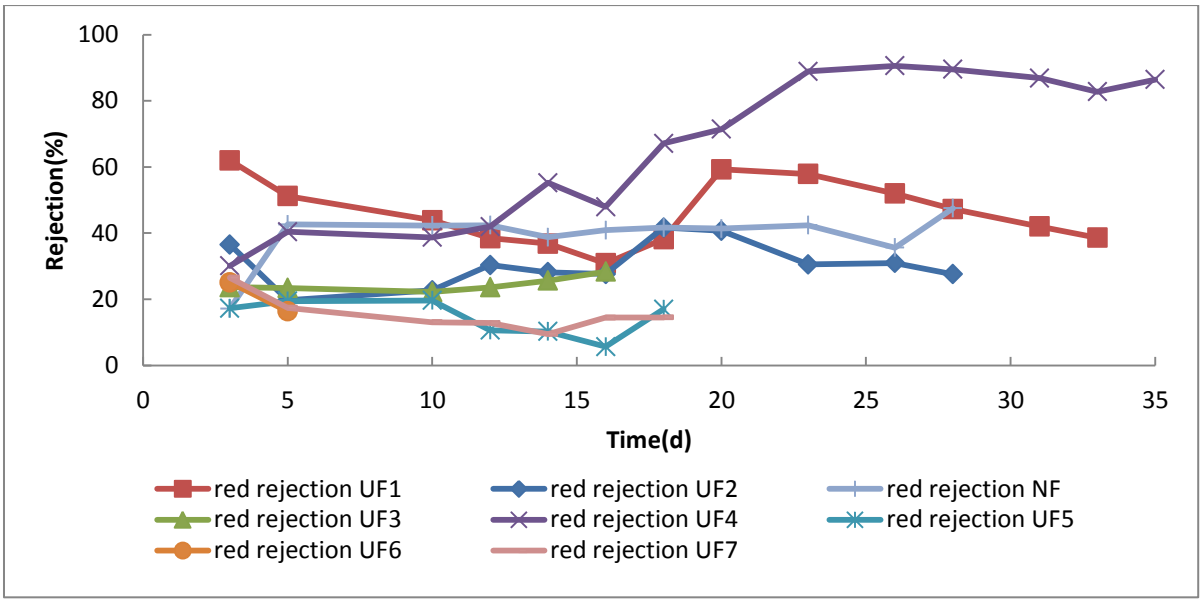


Figure 3.32.a Red dye removal efficiency for the commercial membranes.

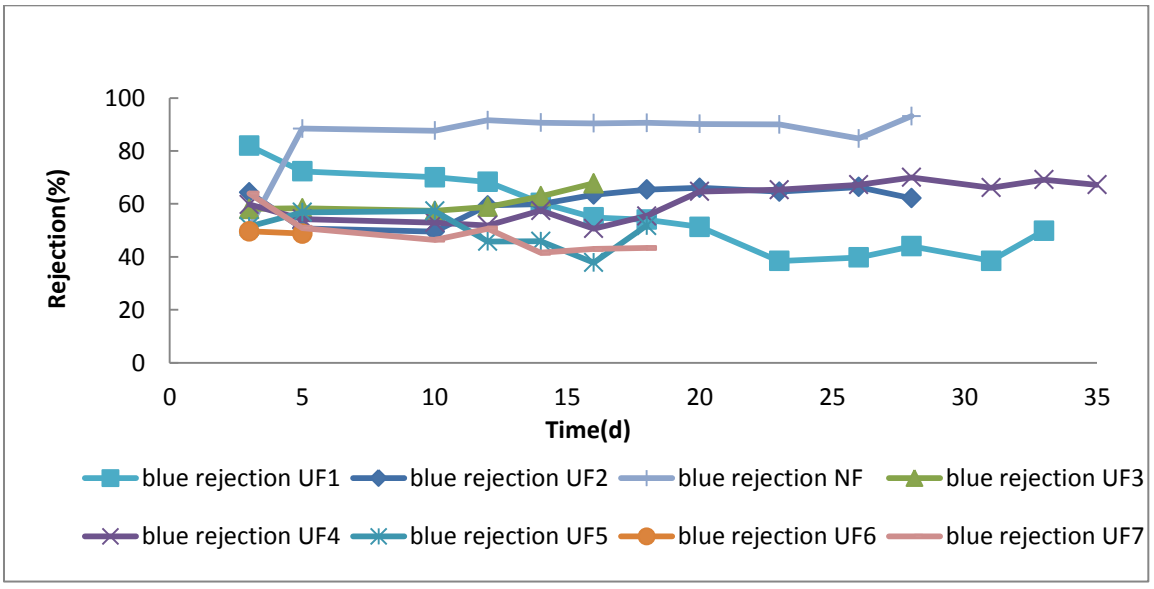


Figure 3.32.b Blue dye removal efficiency for the commercial membranes.

The Figure 3.33a and b give the red dye and blue dye removal efficiency for the novel membranes. All novel membranes show basically a very stable rejection over the test period. Regarding red dye removal efficiency ranges between 20 and 40% which is similar to the results for the commercial membranes. Also blue dye rejection is similar to the findings of the commercial membranes (rejection efficiency 50-70%). Rejection of the very dense novel N3 is the highest for both dyes, however, water permeability is extremely low (Figure 3.18).

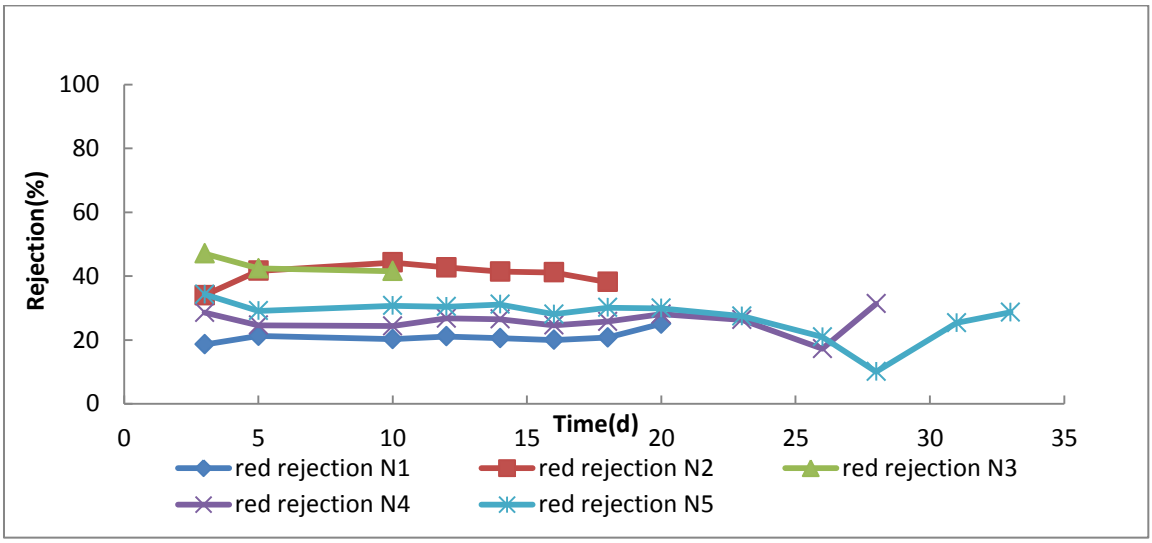


Figure.3.33. a. Red removal efficiency for novel membranes.

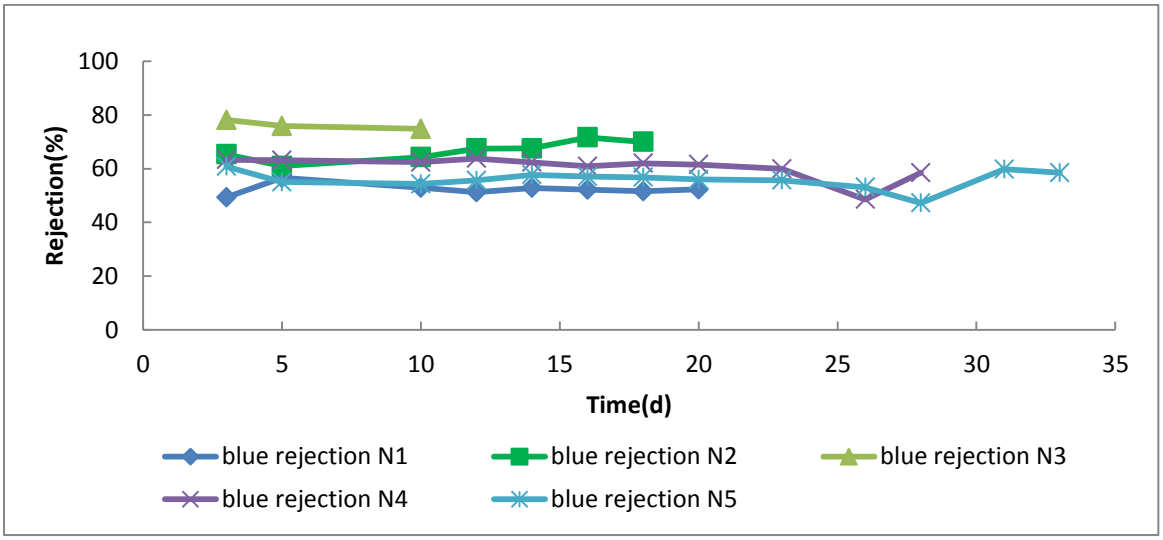


Figure.3.33. b. Blue removal efficiency for novel membranes.

3.3. Treatment under anaerobic conditions

This chapter reports about performance (under anaerobic condition) of the same commercial and novel membranes which were used for the trials under aerobic treatment (chapter 3.2) The respective operation times of all studied membranes are summarized in Table 3.4. The sludge used in this part, was taken from an anaerobic sludge fermenter in a sewage treatment plant where the MLSS concentration was approximately 26 g/L. The sludge was diluted in the reactor in order to avoid clogging in the side-stream membrane module. For this purpose a MLSS of 15-16 g/L was regarded as optimum value. After the acclimation period, samples were collected and measured as described in chapter 2. For the final set of results, the membrane was replaced with a coated novel membrane (PBM). There was a break in feeding the system on day 79 until day 86 and that was done in order to improve the methanogenesis reaction which forms CH_4 and which is known to be the most critical step of anaerobic degradation (see chapter 1) . A commercial UF membrane was used throughout this idle period.

Table 3.4. Commercial and novel membranes used under anaerobic conditions

Membrane	Abbreviation	Operation Time (d)
Ultrafiltration 1	UF1	1-103
Ultrafiltration 2	UF2	103-134
Nanofiltration	NF	134-146
Ultrafiltration 3	UF3	150-203
Novel based DTAB	DTAB	207-228
Novel based AUTEAB	AUTEAB	230-256
Ultrafiltration 4	UF4	256-279

3.3.1. Water Permeability

Figure 3.34.a illustrates the average permeability of all tested membrane. It can be seen that the UF1 has the highest average permeability achieving almost 180 L/(h m^2 bar). When compared to the aerobic results (see 3.2, Figure 3.17) it can be noticed that the permeability in the anaerobic system is much higher and mostly more fluctuating. The generally higher permeability under anaerobic conditions compared to the aerobic conditions is unexpected since fouling rates are typically higher under anaerobic conditions (Deowan et al., 2015 MBR book). This might be attributed to the generally higher flux at higher temperature which has been shown for the experiments using HA (see 3.1.1.1).

The permeability fluctuates and the sudden increase on day 38 of the UF1 (see Figure 3.34.b) can be explained by the addition of some fresh sludge to the reactor. After an acclimation period until day 60 the permeability went back to more stable conditions . The permeability for the UF2 started at a very high pressure because this membrane was used after a technical failure and therefore a fresh batch of sludge was added. There was again an acclimation period and the reactor needed a few days to get back to a stable conditions. As can be seen in Figure 3.34.a the average permeability is higher for the UF1 than for the UF2 and this can be attributed to the new sludge added for the UF2 which may represented different biological conditions.

The NF membrane has the lowest permeability ranging from 7-10 L/(m^2 h bar) which was expected as it is a dense membrane and therefore has a much lower flux. This is in line with the findings under aerobic conditions. The novel membranes, DTAB and AUTEB had a slightly lower average permeability than the UF membranes. This was expected since the PBM coating generally gives slightly denser membranes (Galiano, 2015).

In general it can be said that the average permeability is typically higher compared than under aerobic conditions and shows greater fluctuations.

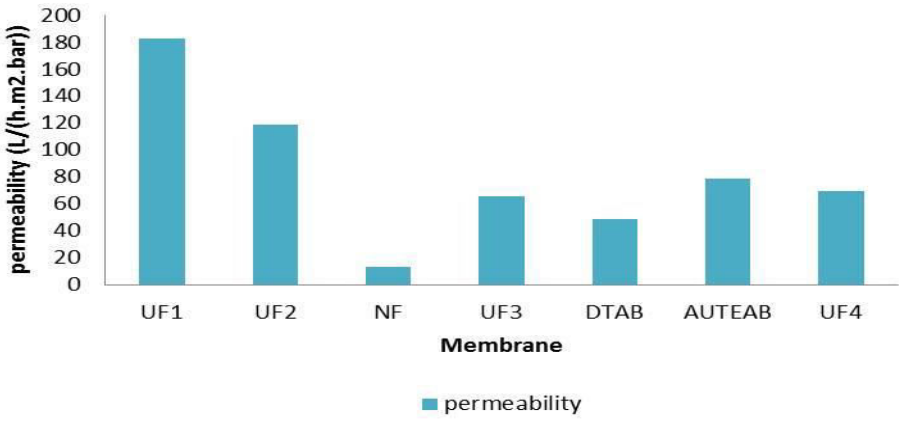


Figure.3.34.a. Reactor permeability for each membrane

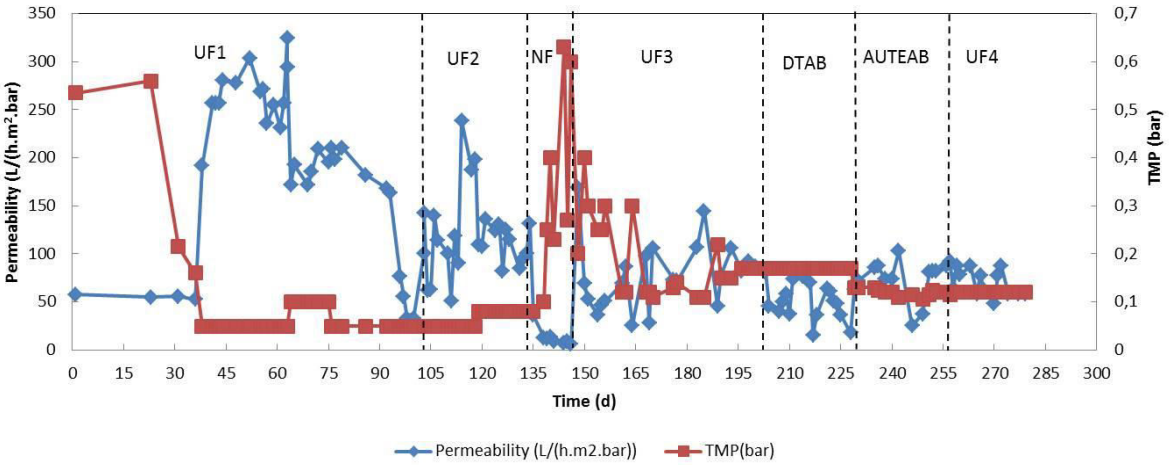


Figure.3.34.b. Reactor permeability for the whole experimental period

3.3.2. COD removal efficiency

Figure 3.35 displays the comparison of the COD rejection and the COD in the permeate throughout the whole anaerobic experimental period. The COD in the feed is kept constant throughout each phase of this trials at a value of 6732 mg/L. This value is significantly higher than in an aerobic system (see Table 2.5) due to the higher glucose concentration in the feed, which is required for a potentially better methane production. Sudden drop in the rejection between day 65 and day 86, can be explained by the already mentioned break to improve the methanogenesis reaction. While the drop from day 146 till 165 was due to a technical failure in the reactor. Compared to degradation under aerobic conditions anaerobic digestion runs much more unstable and responds very sensitive to the conditions of the sludge. It is known from literature that the methanogenesis step is the most sensible step in the course of the digestion process (see chapter 1).

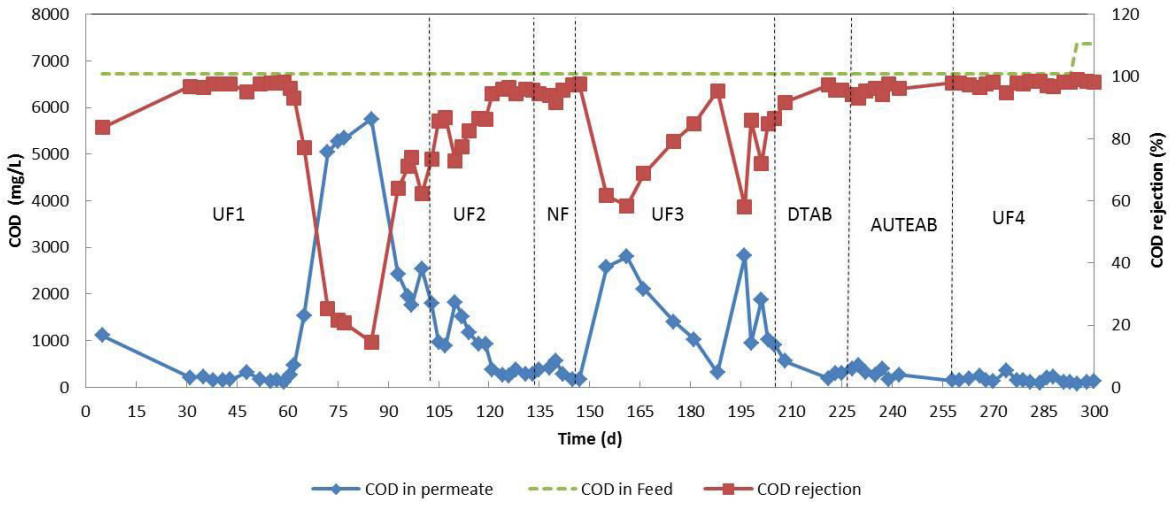


Figure .3.35. Comparison of COD in permeate and COD rejection

Figure 3.36 displays the average COD rejection of each tested membrane. During the first half of the anaerobic trials, the NF shows highest COD rejection, in the range of 94-97%, which was expected as it is the densest membrane and displays high physical rejection. The NF also has a higher HRT which generally results in higher biochemical degradation. Whereas, UF2 showed fluctuations at the beginning but gradually achieved a high removal efficiency similar as for the NF. This indicates that under anaerobic conditions even by use of looser membranes a high COD removal can be achieved if the conditions arte favorable for the biocenosis. This is particularly true for methanogenesis step which can be hampered after an initial period due to toxic byproducts. Hampering of the methanogenesis is typically indicated by increase of VFAs which will be accumulated due to slow conversion rate into methane. VFA production is studied in chapter 3.3.10. Spagni and Casu (2012) achieved the highest COD removal efficiency at the beginning of their anaerobic trials with textile wastewater and noticed a drop due to impairment by toxic byproducts.

Throughout the course of the UF1, the COD degradation rate increases steadily from 72-95% over the 31 days. This is related to a steady decrease in VFA during this period (refer to Figure 3.49). The VFA increase is caused by the presence of azo dyes which appear to inhibit the methanogenic biomass (Spagni and Casu, 2012). The significant difference in values between the UF1 and UF2 can be attributed to the fresh batch of sludge for the UF2 which may represent different biological conditions. The experiments using novel membranes (DTAB and AUTEAB based) started from day 200 and performed relatively stable with the COD rejection fluctuating between 80-95%. From day 200 all membranes performed better than the previous ones which could be attributed to more stable conditions in the sludge since another commercial UF which was run right after the novel membranes showed also high and stable COD degradation. As already mentioned the findings indicate that under anaerobic conditions performance is more governed by favorable biological conditions than by the membrane properties.

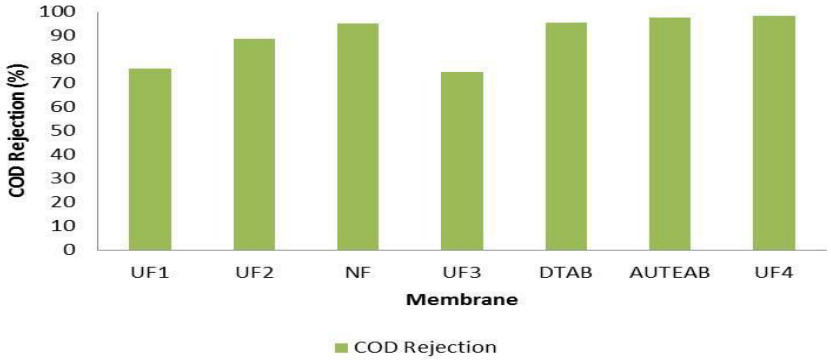


Figure .3.36. COD rejection for each membrane

3.3.2.1.COD in reactor

Figure 3.37 displays the COD in the reactor (sonicated and filtered) and permeate throughout the whole anaerobic experimental period. With the exception of the period until day 120 the results are very similar throughout, with the COD in the reactor being marginally higher. This can be interpreted as low gel layer formation on the membrane in the side-stream unit. This eventually results in similar filter efficiency. In the previous aerobic trial period, the higher COD in the reactor tank samples were interpreted as significant gel layer formation which does improve removal efficiency (see chapter 3.2.3). This higher gel layer formation can be explained by the lower temperature.

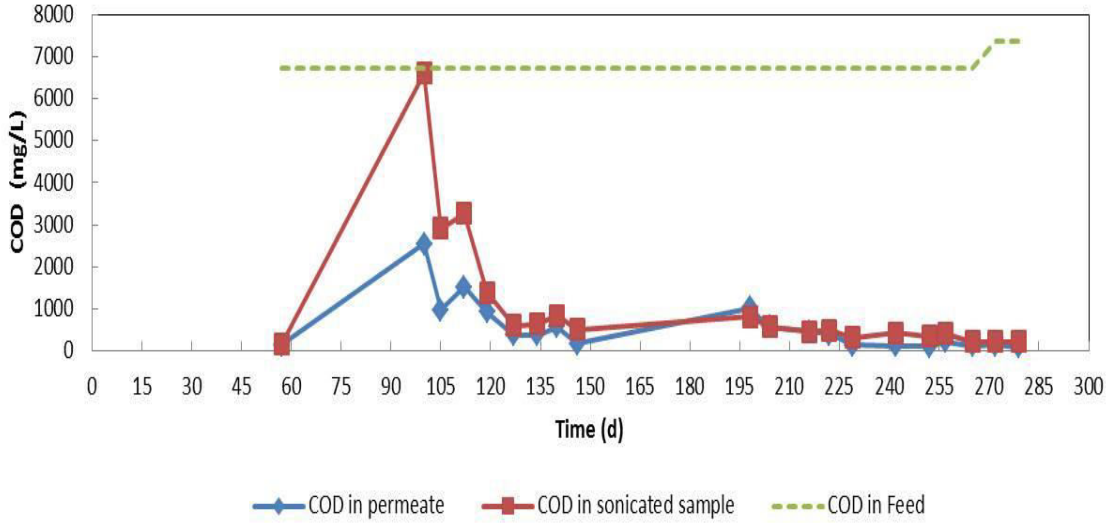


Figure .3.37. COD in reactor and permeate

3.3.2.2.COD Rejection and CH_4 Production

Figure 3.38 displays the COD rejection and CH_4 production of the system throughout the whole anaerobic experimental period. Generally one could expect that high COD rejection should be accompanied by high CH_4 production indicating high degradation efficiency. As can be seen in Figure 3.38 methane production generally does not follow COD degradation rate.. This can be explained with the fluctuation of efficiency in the methanogenesis step which forms methane. A inhabitation of methanogenesis an hence lower formation of methane is typically indicated by higher concentration of VFAs (see Figure 3.49). It needs to be emphasized that during the entire experimental period no measureable flow of methane gas production could be noticed at the flow sensor of the fermenter.

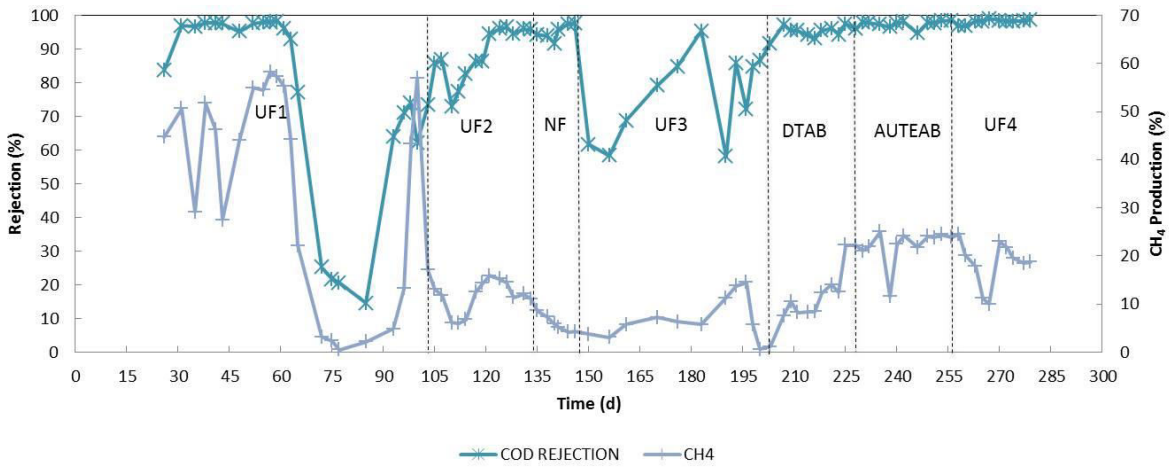


Figure .3.38. COD rejection and CH_4 production during the experimental period

3.3.3.TOC Rejection

Figure 3.39 displays the comparison of the TOC rejection and the TOC in the permeate throughout the whole anaerobic experimental period. The TOC in the feed is maintained at approximately 2568 mg/L. The sudden drop in rejection on day 147 can again be seen due to a technical failure in the reactor. The TOC rejection efficiency follows the trend of the COD degradation rate which is shown in Figure 3.41.

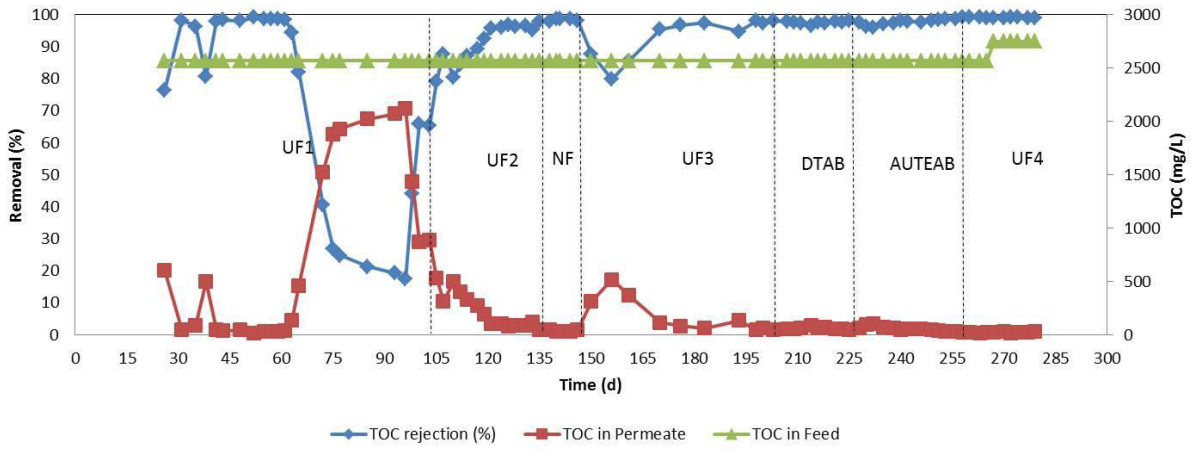


Figure.3.39. Comparison of TOC in permeate and TOC rejection

Figure 3.40 displays the average TOC rejection for each of the tested membranes. In general, the TOC rejection is slightly higher than the COD rejection (see Figure 3.41). The UF1 has the lowest rejection rate, whereas the UF2 and UF3 were show similar rejection rate. NF and UF4 had the highest rejection. As already mentioned this can be attributed on the one hand to the density of the NF and the favorable and to stable biological conditions during the test of the UF4. The novel membranes stay in the range of 90-95%.

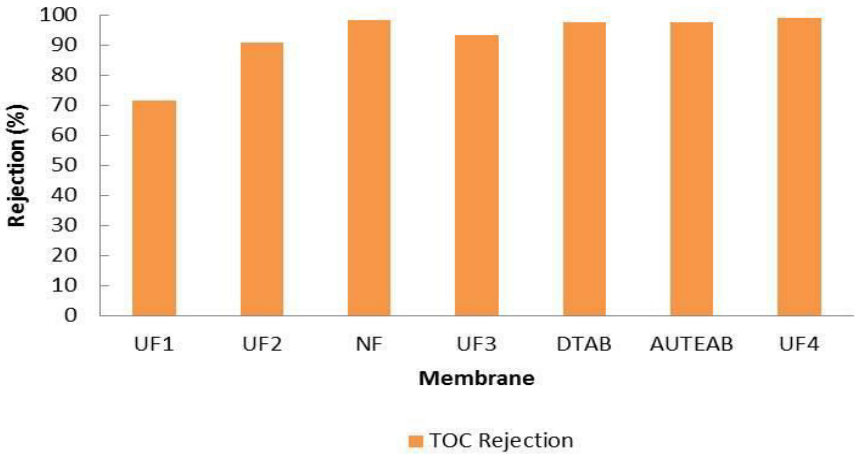


Figure .3.40. TOC rejection for the tested membranes

3.3.3.1.TOC vs COD removal efficiency

Figure 3.41 shows a comparison of the TOC and the COD rejection throughout the whole anaerobic experimental period. It can be seen that COD and TOC removal efficiency has the same trend.. It is worth mentioning that in general, the TOC rejection is approximately 10% higher than for the COD. The reason for this fact might be the chemical composition of the MTDW. From the experimental period, the highest TOC rejection was recorded at 99% during UF1, AUTEAB and UF4. While the lowest rejection was 63% on day 150.

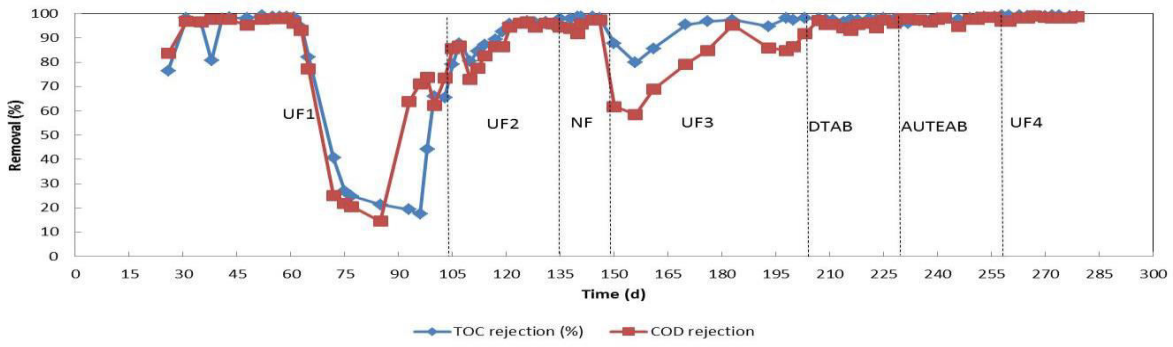


Figure .3.41. Comparison of COD and TOC rejection

3.3.4. Nitrogen (N) balance

Figure 3.42 displays the total nitrogen in the reactor throughout the whole anaerobic experimental period. The Total N in the system is dependent on the compounds used in the MTDW and the used anaerobic sludge. For this experiment, the main sources of N in the MTDW are the red dye, blue dye and NH_4Cl (see chapter 2). The calculated theoretical value of N is 84.5 mg/L, while the average measured value was 79.3±0.48 mg/L. It can be seen that during the experimental period that several TN peaks being significantly higher than the average Total N of the MTDW (see Figure 3.42). This can be explained by the high TN (> 1000 mg/L) of the sludge which has been taken from a sludge fermenter of a common sewage treatment plant.. So whenever new sludge was added to the reactor the TN spiked up and dropped in the course of the trials due to washing-off. Therefore the trials started with high TN during the UF1. The next small peak occurred on day 90 when some sludge was added to the system.and the TN it jumped up to 296 mg/L. The further major spikes on day 110 and 154 can also be explained by sludge addition to the system from the same source. The small spike on 221 can be explained by an accumulation of sludge and therefore a sudden increase in the TN of the permeate. Since the system is completely anaerobic basically $N\text{-}NH_4^+$ contributes to TN and follows the general trend of TN. Subsequent to the DTAB based novel membrane (from day 200) the TN in permeate dropped smoothly to values below TN of the MTDW which indicates of complete washing-off of the initial TN of the anaerobic fermenter sludge. This period from day 200 is characterized by stable COD rejection rate (see Figure 3.35) and hence it can be concluded that only after complete washing-off of the elevated TN originating from the fermenter sludge the system could be run smoothly and stable.

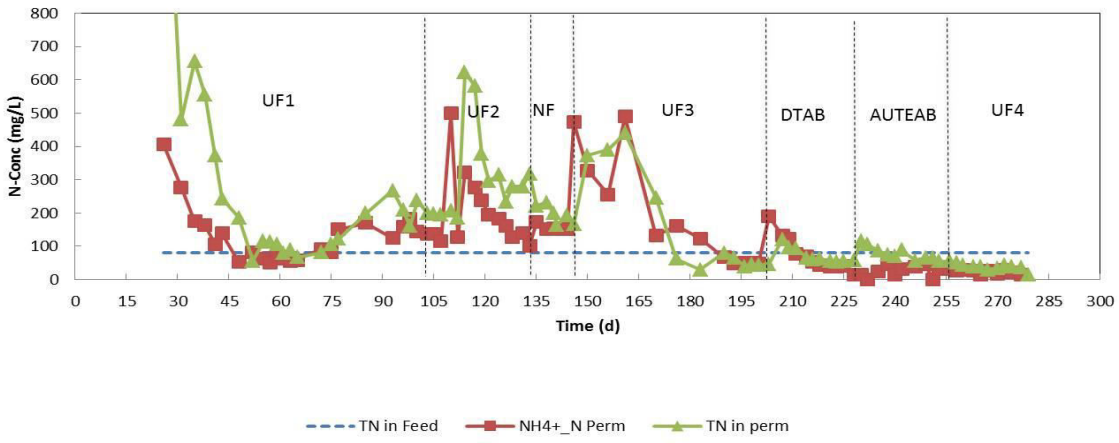


Figure .3.42. TN in permeate for the entire experimental period

3.3.5. Hydraulic Retention Time (HRT)

Figure 3.43 illustrates the HRT throughout the entire anaerobic experimental period. It can be seen that from day 100 to day 147 there are significant fluctuations in the HRT value which can be explained by changing flux values. From day 135 to 146 the highest fluctuations were experienced and this can be attributed to the NF membrane. This denser membrane resulted in a slower flux and therefore a higher HRT. The HRT then remains relatively stable until day 215. From around day 221, which is when the second novel membrane (AUTEAB based) was used, the HRT dropped back to the initial values and remained relatively stable until the end of the experimental period.

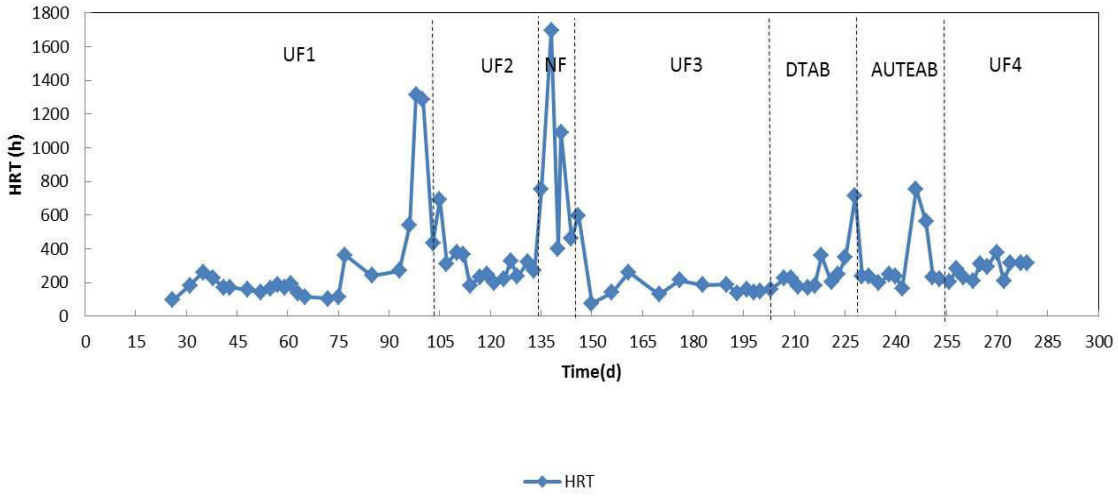


Figure .3.43. HRT for the entire experimental period

3.3.6. OLR

Figure 3.44 shows the OLR of the system throughout the whole anaerobic experimental period. The OLR fluctuates between 2.5 and more than 20 kg COD/(m^3 d). It can be seen that the highest OLR was achieved during the period of the NF. Here the OLR goes up to 25 kg COD/(m^3 d). A typical anaerobic OLR is 2.7 kg COD/m^3 d (Spagni and Casu, 2012) and it can be seen that the average OLR of this system is in line with this reference (with the exemption of some higher peaks). which is not ideal because with an AnMBR the idea is to maintain a high OLR along with a high HRT but in this instance the HRT is equally high at this point (Hoinkis, Deowan et al, 2014). In this kind of system, the OLR typically stays between 2 and 5 kg COD/m^3 d. The drop to 0 can be explained by an unexpected technical failure in the system. After this drop the OLR remains relatively stable until the end of the second novel membrane where it spiked up again to 10.4 kg COD/(m^3 d) this could be explained by a weight decrease in the reactor.

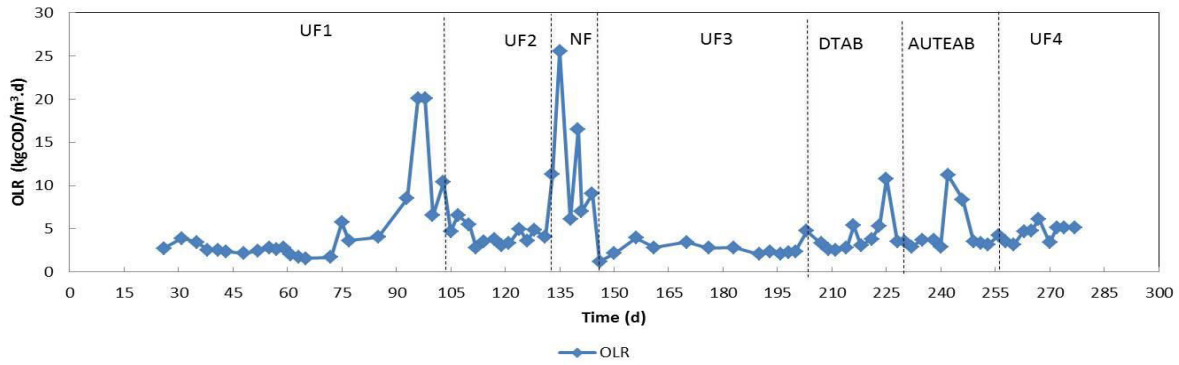


Figure .3.44. OLR for the entire experimental period

Figure 3.45 compares the COD rejection rate and OLR throughout the whole experimental period. The plot shows that there is no clear correlation between OLR and COD rejection. On day 70 COD rejection drops significantly despite only slight increase of OLR. From day day 90 COD degradation rate steadily increases despite high fluctuation of OLR. Only from day 200 COD removal efficiency and OLR were running smoothly with the exeption of two OLR peaks at ady 225 and 245.

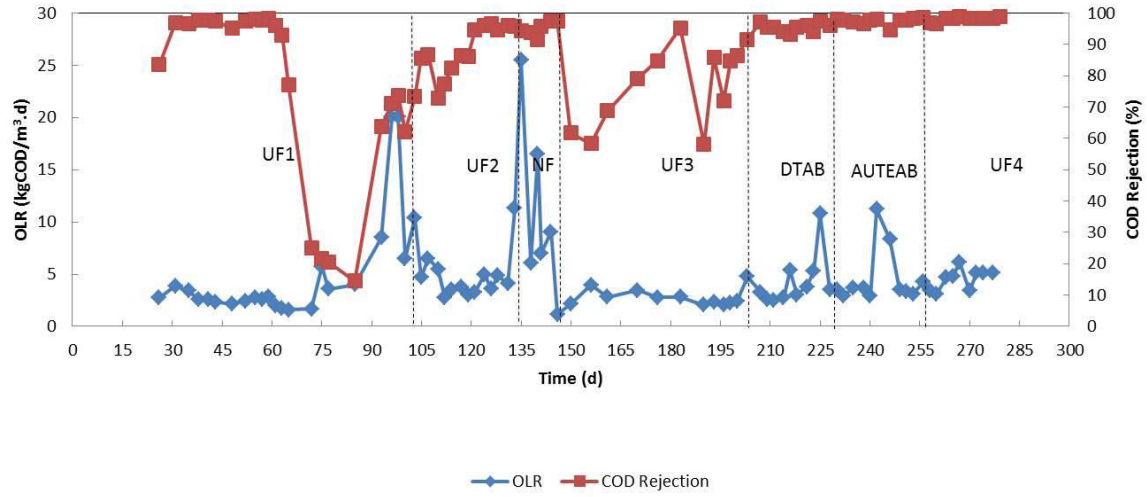


Figure .3.45. Comparison of OLR and COD rejection for the entire experimental period

3.3.7. F/M Ratio

Figure 3.46 displays the F/M ratio of the system throughout the whole anaerobic experimental period. It can be seen that the F/M ratio fluctuates throughout the experimental period, ranging from 0.01 up to 0.12 kg COD/(kg MLSS). It drops down to 0 on 147 days which was when there was the technical failure in the system.

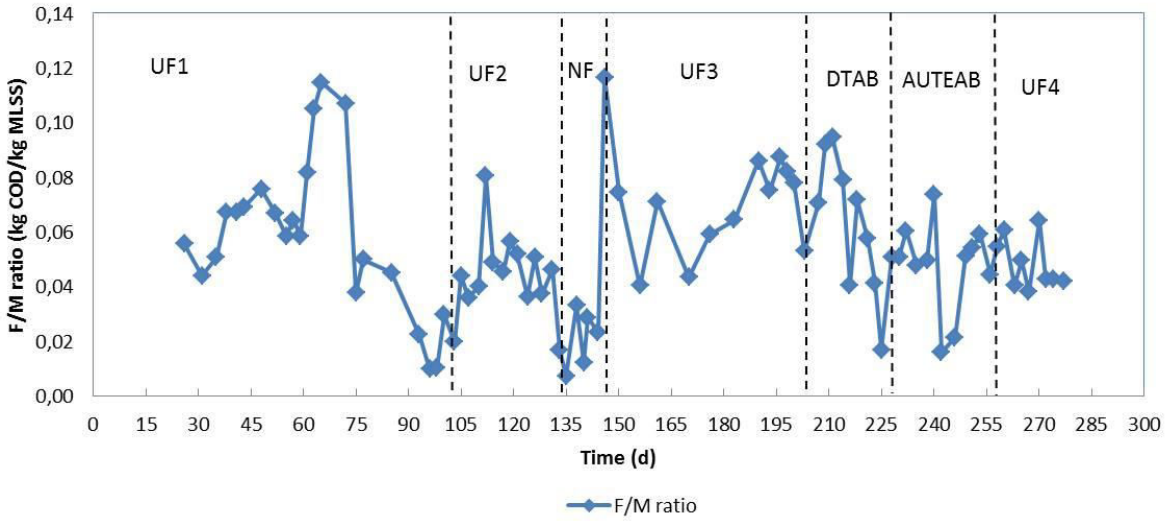


Figure.3.46. F/M ratio for the entire experimental period

3.3.8. MLSS

Figure 3.47 shows the MLSS of the system throughout the whole anaerobic experimental period. The MLSS value basically shows a steady decrease and the values fluctuate in general between 12 and 17 g/L. This downward trend was expected and relates to the results in Spagni and Casu, 2012, which also experienced a decrease in MLSS during the experimental campaign and which can be explained by inhabitation due to toxic by-products The increase of MLSS is always due to adding of new sludge to the fermenter in order to keep the MLSS level stable. So the MLSS increased from on day 110, 153, 170 and 200 due to adding of sludge. There is a steady decline until day 146 on which a technical failure in the reactor took place. The significant MLSS increase up to 17.8 g/L on day 153 is a direct consequence of an entire batch of fresh sludge being added to the system. The spike on day 174 was unexpected and cannot explained. The drop on day 223 can be explained by a recorded u weight decrease in the reactor tank due to failure of level sensor in the fermenter. After starting the second novel membrane (AUTEAB based) it can be seen that the MLSS remains relatively stable at

around 11 g/L. This was the most stable period regarding COD removal efficiency of the entire experimental period.

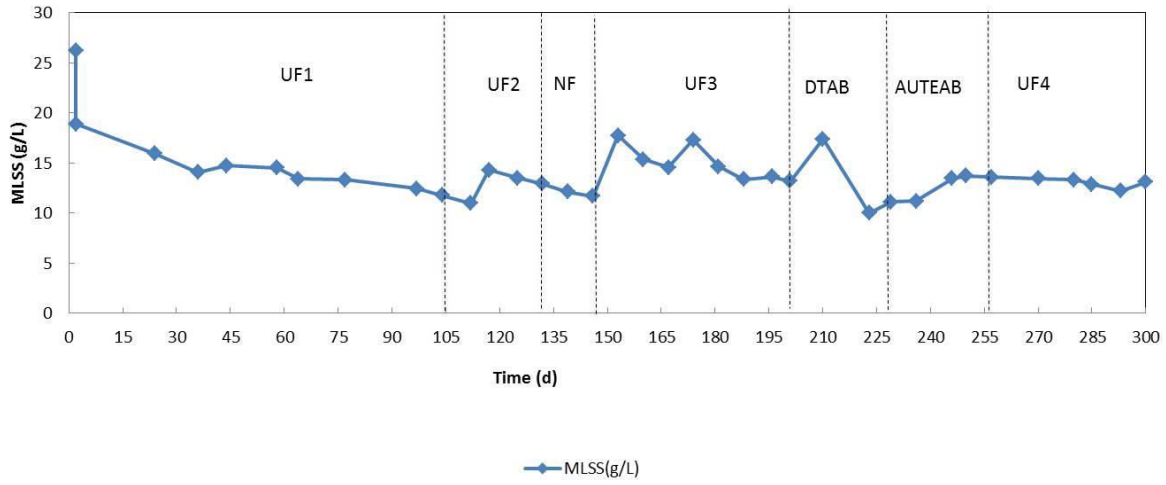


Figure.3.47. MLSS for the entire experimental period

3.3.9. pH

The pH throughout the experiment remained relatively stable around 7 with the some occasional fluctuations since it was automatically controlled by adding caustic (NaOH 10 weight%) The slight fluctuations can be explained by minor problems with pH sensor and control unit of the fermenter. A pH around 7 is particularly needed for running a smooth methanogenesis reaction.

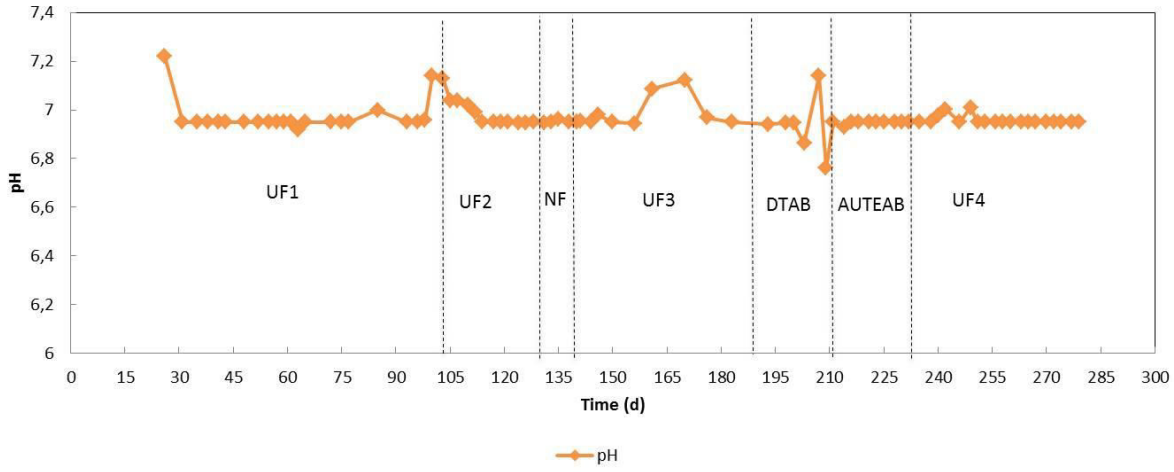


Figure .3.48. pH for the entire experimental period

3.3.10.CH_4 in Exhaust Gas and Volatile Fatty Acid (VFA) Comparison

Figure 3.49 displays the CH_4 concentration in exhaust gas and VFA production of the system throughout the whole anaerobic experimental period. As can be seen an increase in VFA production generally results in a decrease in the production of CH_4.what can be explained by inhabitation of methanogenesis and consequently accumulation of of VFAs. After start-up with relatively high CH_4 concentration it dropped and the butyric acid increases a sharply. In the following the methane production was much lower and fluctuated. Only after day 200 a steady increase of methane concentration can be noticed and no VFA could be detected. This is with stable high COD removal and hence is another indication factor showing relatively stable biological conditions. Table 3.5 shows the chemical formulae of each of all VFA which were analysed Additionally Figure 3.49 shows the same data but with the sum of all VFAs compared to the CH_4 production.

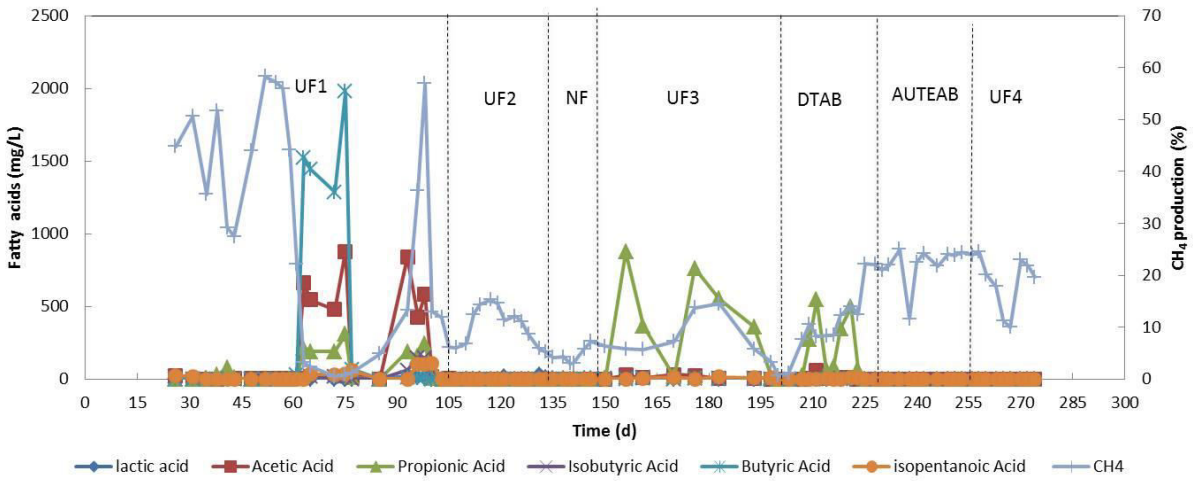


Figure .3.49. CH_4 concentration and VFAs for the entire experimental period

Table .3.5. VFA chemical formulae

Short Chain Fatty Acid	Chemical Formula
Acetic Acid	$C_2H_4O_2$
Propanoic Acid	$C_3H_6O_2$
Lactic Acid	$C_3H_6O_3$
Butyric Acid	$C_4H_8O_2$
Isobutyric Acid	$C_4H_8O_2$
Isopentanoic Acid	$C_5H_{10}O_2$

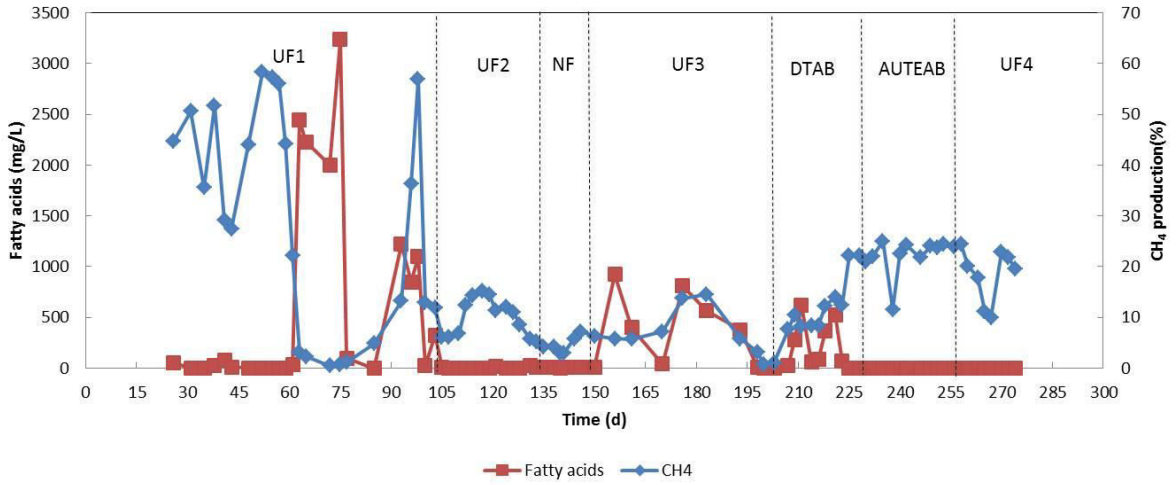


Figure .3.50. CH_4 and Total VFA comparison for the entire experimental period

3.3.11.CH_4 in Exhaust Gas and NaOH Dosing

Figure 3.51 displays the CH_4 production and volume of NaOH dosing throughout the whole anaerobic experimental period. It can be seen in general that as the NaOH consumption is increased, the CH_4 production decreased. This can be explained by more NaOH being consumed to neutralize VFAs which inhibit the production of CH_4.

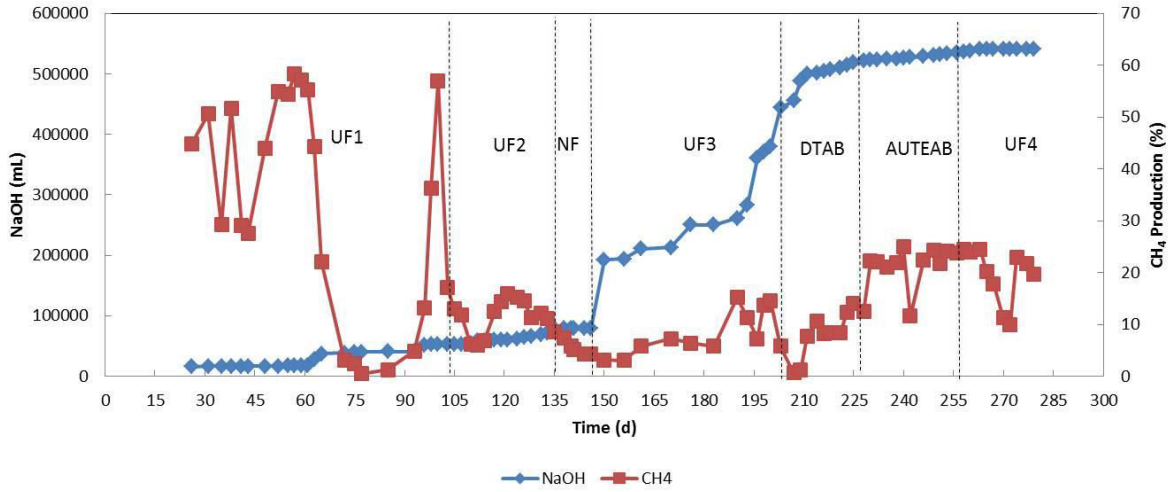


Figure .3.51. CH_4 concentration and amount of NaOH dosing for the entire experimental period

3.3.12. CO_2/CH_4 concentration in Exhaust Gas

Figure 3.52 shows the CH_4 and CO_2 in the exhaust gas of the system throughout the whole anaerobic experimental period. It can be seen throughout that the CH_4 concentration is always higher than the CO_2 level which was expected. The expected ratio was 70% CH_4 production and 30% CO_2 production and the Figure 3.52 shows that the findings generally confirm this ratio (see chapter 1). Only between day 150 and 200 the concentration of CH_4 and CO_2 are almost the same what can be explained by significantly hampered methanogenesis.

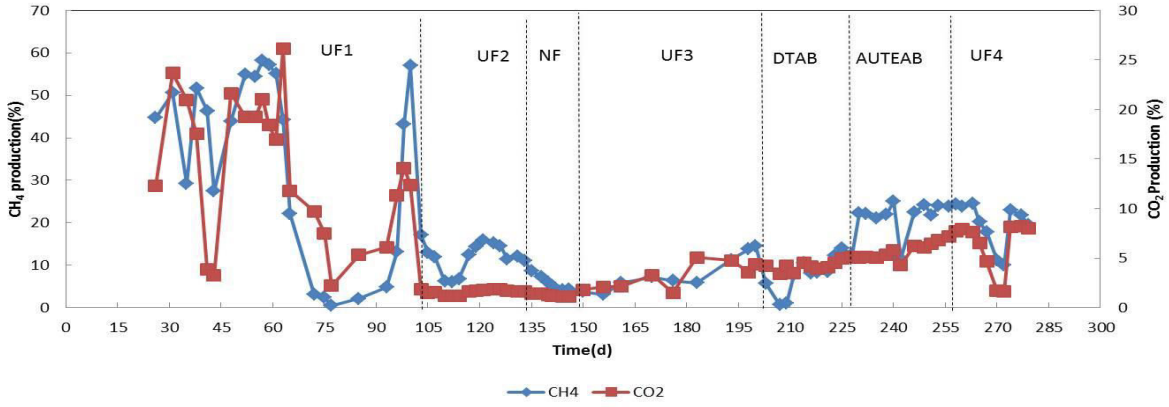


Figure .3.52. CH_4 and CO_2 concentration for the entire experimental period

3.3.13. Colour removal efficiency

Figure 3.54 illustrates the red and blue dye rejection for all tested membranes. Figure 3.55 and 3.56 shows the respective average reduction rate. These results are almost entirely due to the biological degradation process of the dyes and the degradadtion rate is significantly higher than for the aerobic treatment. This cannot be explained by physical membrane rejection since the MW of the dyes is much lower than the MWCO. This finding is in line with results of literature (Spagni and Casu, 2012). Even the MWCO of the NF (1 kDa) is greter than the MW of the applied dyes. The MW of the red and blue dyes are 380.4 g/mol and 626.5 g/mol, respectively. Spagni and Casu (2012) also showed that particularly azo dyes can be very well degraded under anaerobic conditions. For all of the tested membranes it can be seen that the red rejection was very high, rarely dropping below 90%. The lowest drop was day 1 of the UF1 to around 85% and this can be explained by a decline in the HRT at this time. These results correlate to those from (Spagni and Casu, 2012), where the red rejection was constantly in the region of 90-95% which was due to azo dye removal. A slight drop in rejection on day 120 of the UF2 can be explained by the slight increase in VFA which could have inhibited the anaerobic process (Figure 3.49).

As far as the blue dye is concerned the removal efficiency is lower than for the red dye (80-95%). This can be explained by the chemical structure which is anthraquinone based and these compounds basically cannot be degraded as good as the azo dyes (Spagni and Casu, 2012).

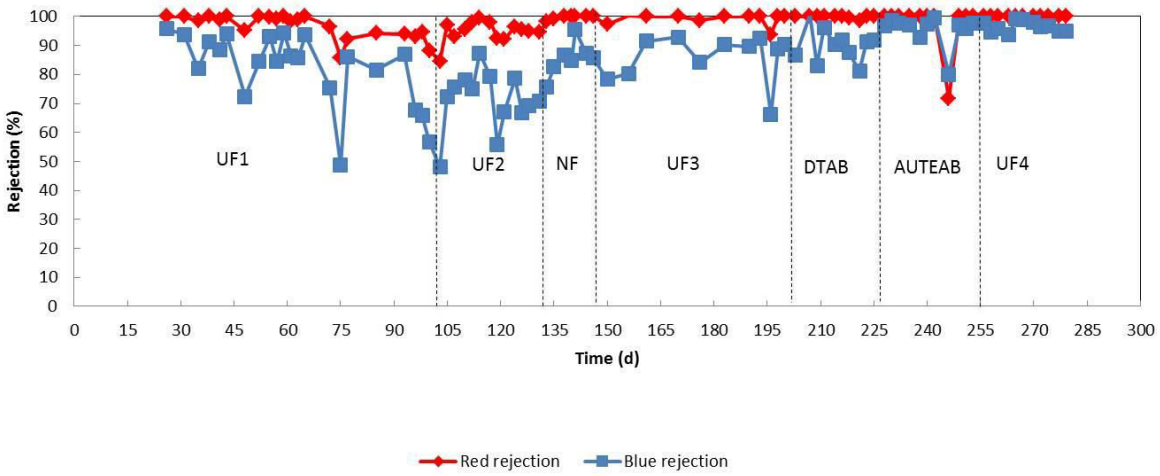


Figure .3.53. Red and blue colour rejection for the whole experimental period

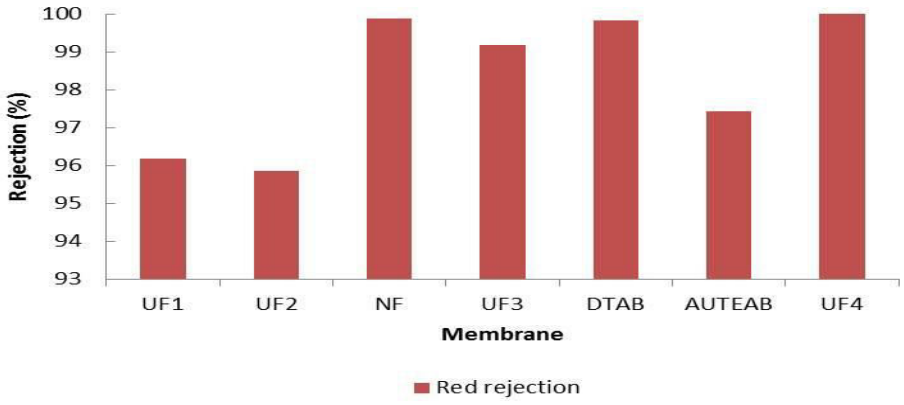


Figure .3.54. Red colour rejection in each membrane

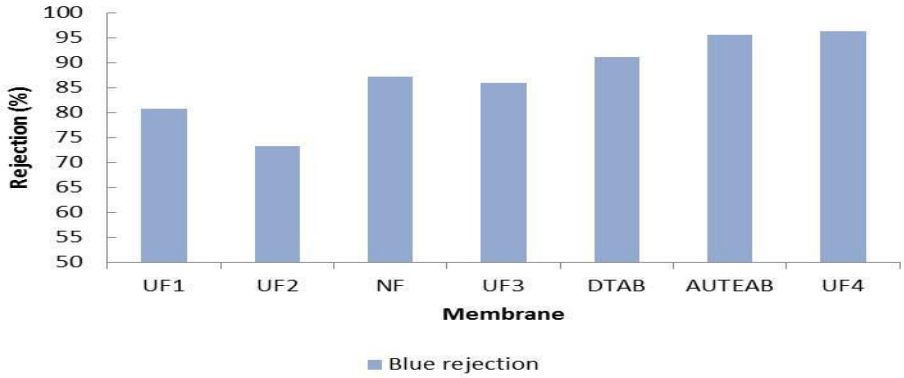


Figure .3.55. Blue colour rejection in each membrane

3.4. Aerobic MBR as part of an integrated anaerobic/aerobic MBR process

The treated wastewater of the AnMBR process (chapter 3.3) was kept in cool box and subsequently used as feed for aerobic MBR. The purpose of this study is to analyse the performance of a combined AnMBR and AeMBR process which is not published so far in literature since most of the research on AeMBR for treatment of textile wastewater only made use of upfront conventional anaerobic treatment (see Table 3.7). This study was carried out with the commercial UF, NF and the novel AUTEAB based PBM coated membrane (Table 3.6).

Table. 3.6. Operating conditions of MBR under aerobic conditions

Parameter	Unit	Values
Temperature	°C	20±2
TMP	bar	0.17-0.25
pH Feed pH Effluent	---	7.0 ± 0.5 8 ± 0.5
Permeate flux	L/(m^2 h)	2-19
HRT OLR	h (Kg COD/(m^3 d))	100-1215 0.5-3.0
F/M ratio	(g COD)/(g MLSS d)	0.009-0.8
MLSS DO	g/L mg/L	~6 3,5-6

Table 3.7. Commercial and novel membranes used under aerobic conditions.

Membrane	Abbreviation	Operation Time (d)
Ultrafiltration	UF	1-49
Nanofiltration	NF	49-62
Novel (AUTEAB based)	Novel	62-75

Table 3.8. Characteristics of Model Textile Dye Wastewater (MTDW)

Parameters	Unit	Measured values for aerobic trials
pH		7.5 ± 0.5
COD	mg/L	700 ± 25*
Total - N	mg/L	84,05 ± 3.5
Conductivity	mS/cm	7.68±0.15

* COD in feed during this phase, has been decreasing already in the feed tank, bevor being in the reactor. See Figure 3.56.

3.4.1. Water permeability

The conditions were kept similar to the operating conditions for the first part of the experimental part of this work (see 3.2.1). The first part of the trials (commercial UF) from day 1 until day 30 can be regarded as acclimation period showing significant fluctuations in the permeability values. From day 30 until day 50 water permeability was relatively stable at approximately 45-60 L/(m^2 h bar). This is significantly higher than for the trials under aerobic conditions using the untreated MTDW as feed (ca. 20-35 L/(m^2 h bar)) and could be explained with the generally lower organic strength of the feed due to anaerobic pre-treatment (see 3.4.2). The decrease of permeability down to 8 – 20 L/(m^2 h bar) is due to change to NF membrane sample. Unlike the permeability for the first aerobic trials which was operated stable around 18 L(m^2 h bar) a drop to 8 L/(m^2 h bar) is noticeable. From day 62 trials using a novel PBM coated membrane started and permeability went up to 40 -60 L/(m^2 h bar) which is significantly higher than for the first aerobic trial using MTDW.

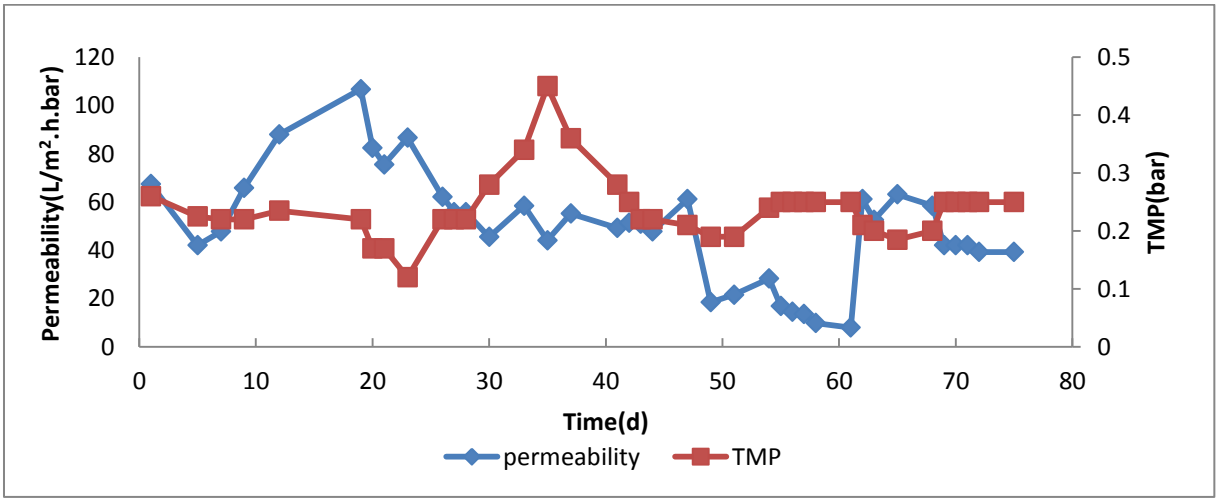


Figure .3.56. Water permeability for the anaerobically pretreated wastewater

3.4.2. COD removal efficiency

COD removal efficiency ranged between 65-85% for the UF, almost 100% for the NF and 70-99% for the novel membrane. It is important to mention that the COD in feed continuously dropped from approximately 700 mg/L to 200 mg/L during the experimental period since due to biological degradation in the feed tank, before being in contact with the biological population in the fermenter. See Figure 3.57 below.

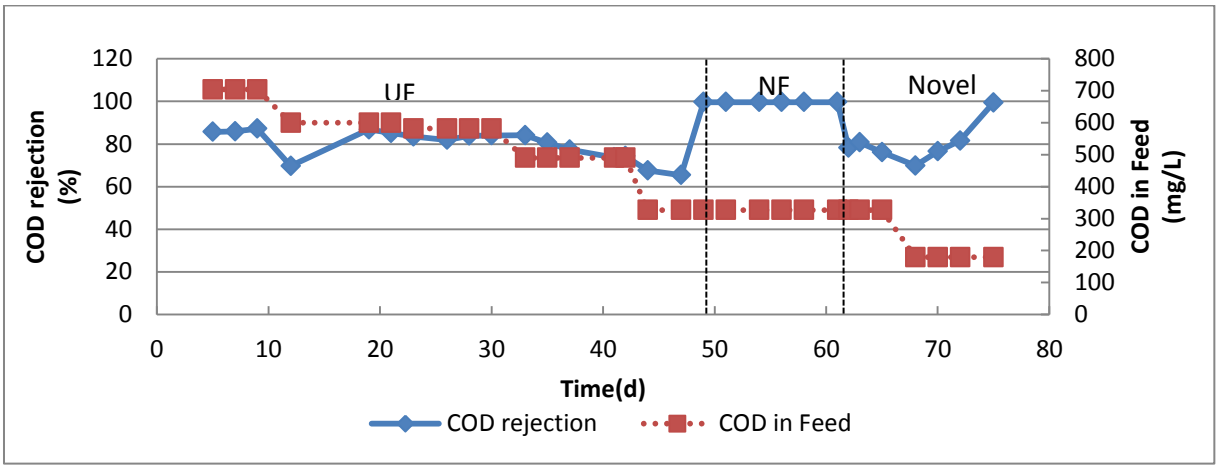


Figure 3.57 COD removal efficiency for the anaerobically pretreated wastewater

3.4.3. TOC in feed and removal efficiency

TOC removal efficiency for the UF membrane (60%-85%) was similar to COD removal efficiency (65%-85%), see also 3.4.4. However, TOC rejection of the NF membrane showed basically lower values as the COD removal efficiency (75-85% vs. almost 100%). As far as the novel membrane is concerned TOC removal (65%- 80%) shows similar range as COD removal efficiency (70%-80%, with a final outlier at 99%). As in the case of COD values TOC in feed dropped during the experimental period due to the degradation of wastewater in the feed tank (450 – 100 mg/L) .

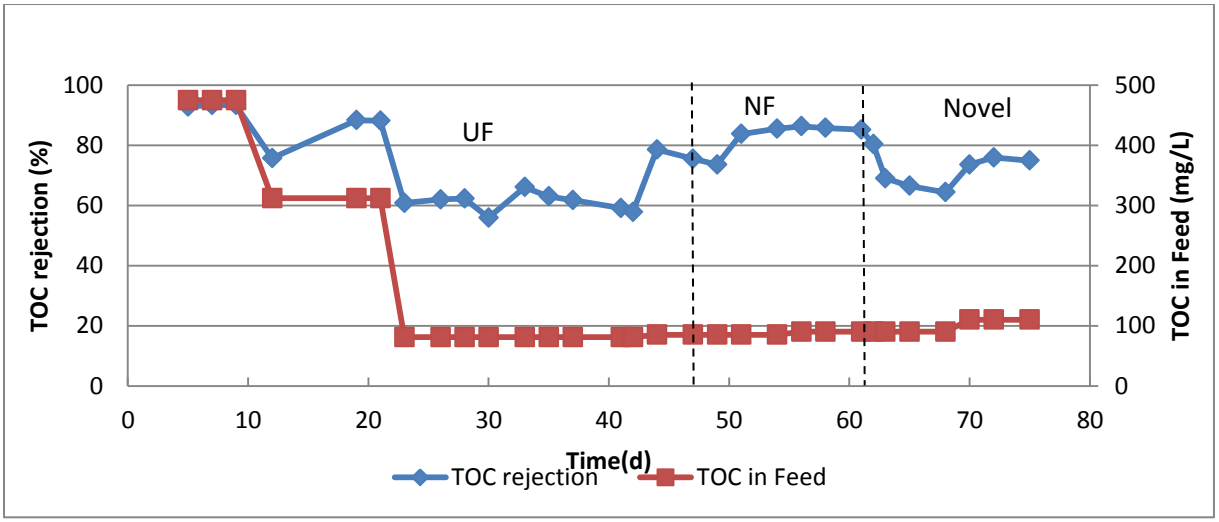


Figure .3.58. TOC removal efficiency and TOC in feed for the anaerobically pretreated wastewater

3.4.4 COD and TOC removal efficiency

As can be seen with Figure 3.59 during the entire experimental period TOC and COD removal efficiency basically shows the same trend.

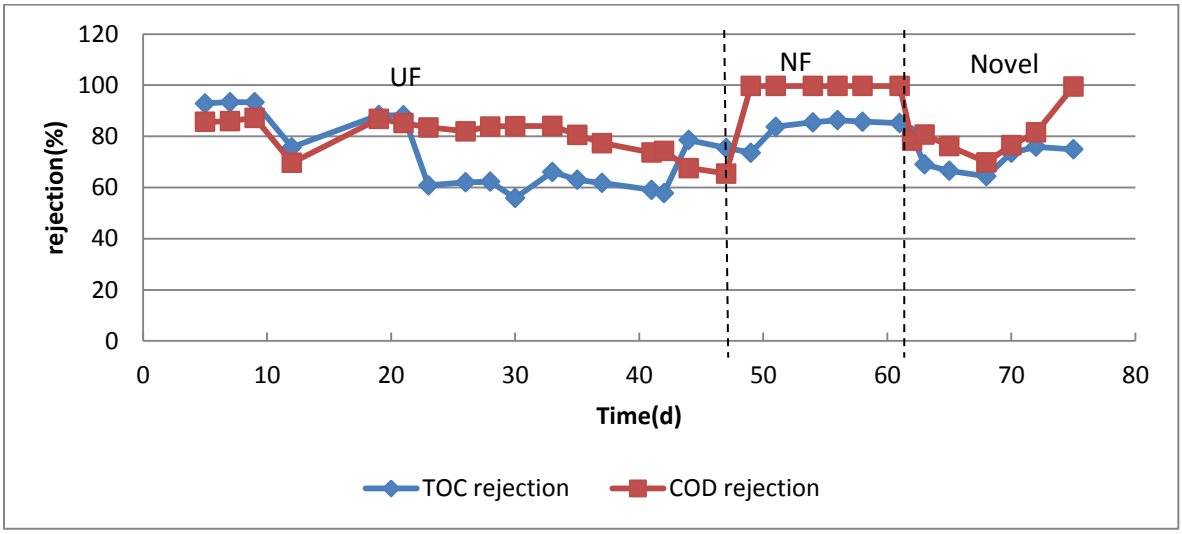


Figure 3.59. Correlation between COD and TOC removal efficiency for the anaerobically pretreated water

3.4.5. TN balance

To obtain the nitrogen (N) balance, the nitrogen content in permeate in terms of Total-N, NH_4^+-N, NO_3^--N were analysed. The main sources of Total-N were mainly NH_4Cl as well as the red and blue dyes used in the MTDW. It dropped from approximately 90 to 44 mg/L due to biodegradation processes in the feed tank. A complete nitrification has been noticed during the whole experimental period for all tested membranes (NH_4^+-N below detection limit), see Figure 3.60. From day 45 TN in permeate is significantly higher than TN in feed what might be explained be N release processes from the activated sludge. The fact that NO_3^--N got greater than TN in feed from day 20 (with two speaks at day 23 and day 30) cannot be explained and might be due to measurement error. From day 48 (NF membrane) NO_3^--N in permeate decreased below TN.

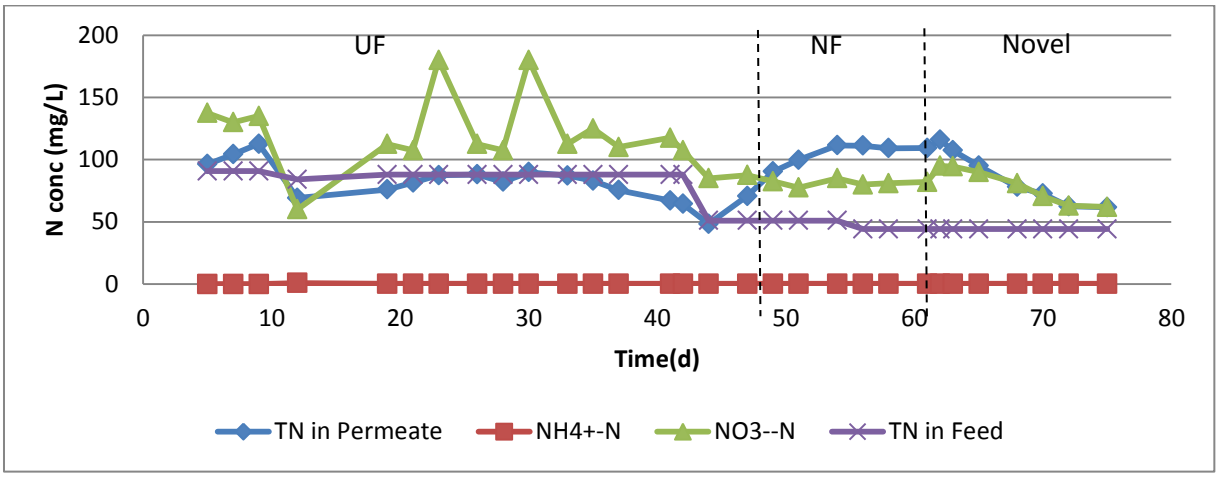


Figure .3.60. The TN- balance for the anaerobically pretreated water

3.4.6. Hydraulic Retention Time (HRT)

HRT average was around 100-230 hours, except for the NF due to the low flux HRT increased to around 1200 hours.

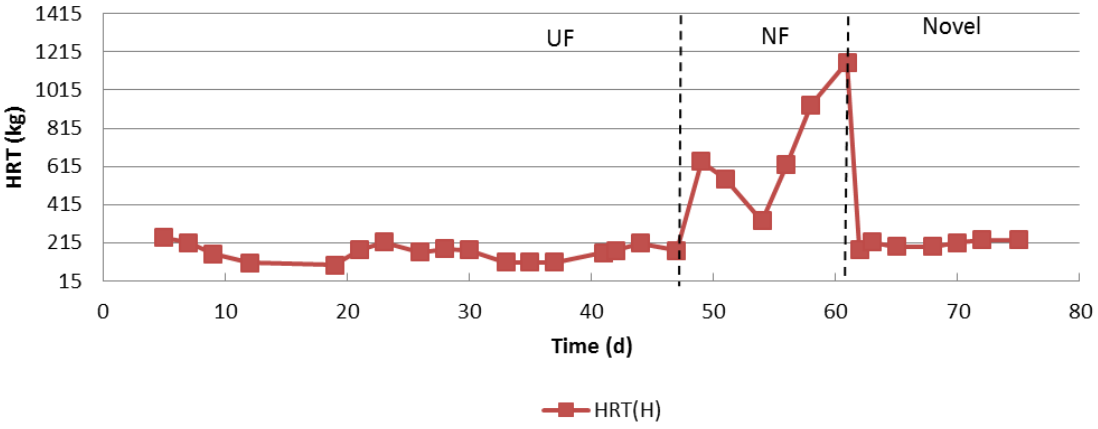


Figure .3.61. HRT results for the anaerobically pretreated water

3.4.7. OLR

OLR showed an average between 0,1 to 0,4 (kg COD/m^3.d) for the UF as well as for the novel membrane. As far as the the NF membrane is concerned the OLR went up to 0.8 (kg COD/m^3.d) due to the low flux Generally the OLR of the anaerobically pretreated wastewater is significantly lower than for the first phase of aerobic treatment which ranged between 0.5-3.0 (kg COD/m^3.d). This can be explained with the lower COD load of the pretreated wastewater.

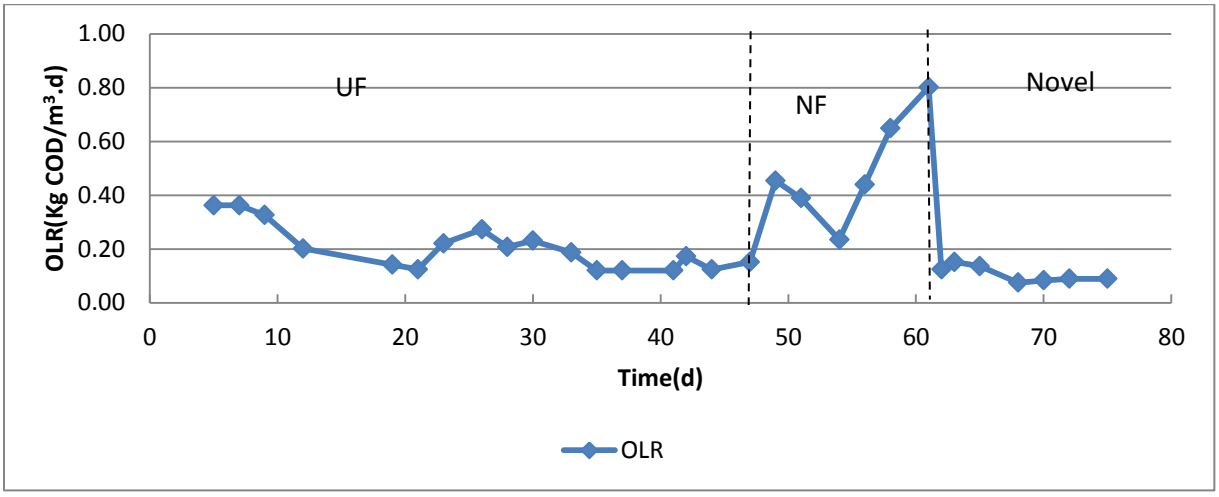


Figure .3.62. OLR for the anaerobically pretreated water

3.4.8. F/M Ratio

F/M ratio showed an average of 0,005 to 0,03 (g COD/g MLSS) for the UF as well as for the novel membrane, only for the NF F/M ratio decreased to lower than 0,001 (g COD/g MLSS). The F/M ratio is significantly lower than for the first aerobic treatment phase what can be expalined with the much lower COD loading.

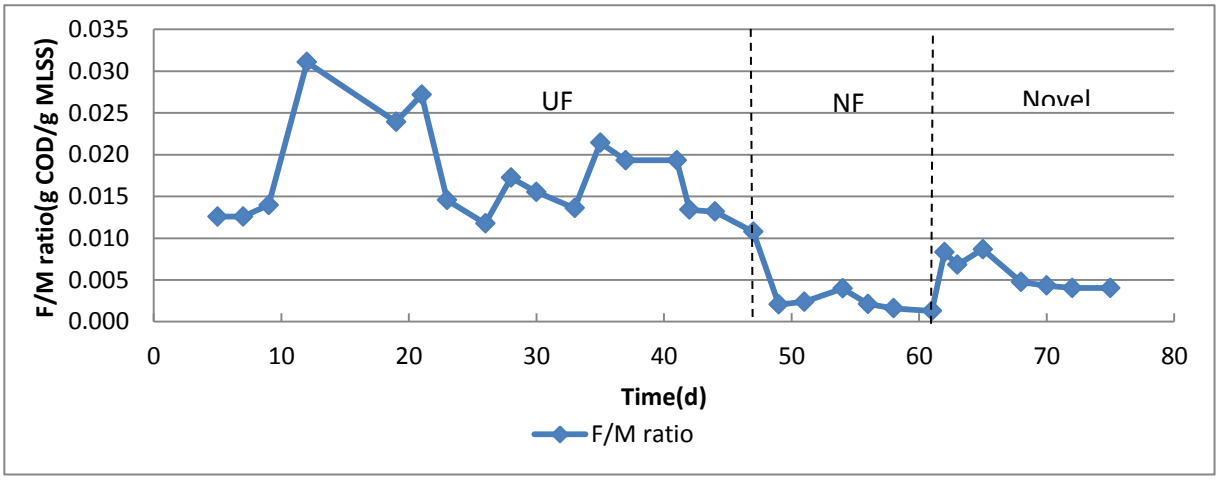


Figure .3.63. F/M ratio for the anaerobically pretreated water

3.4.9. Mixed Liquor Suspended Solids (MLSS)

The MLSS ranged beteen 3 and 5 g/L which is rather low for MBR systems (preferred range 8-12 g/L, see Table 3.7). However since the anaerobically pretreated wastewater represents a low very low strength wastewater lower MLSS can be justified. Interestingly the online turbidity of the activated sludge basically followed the same trend during the entire experimental period with the exemption of drop at day 43.

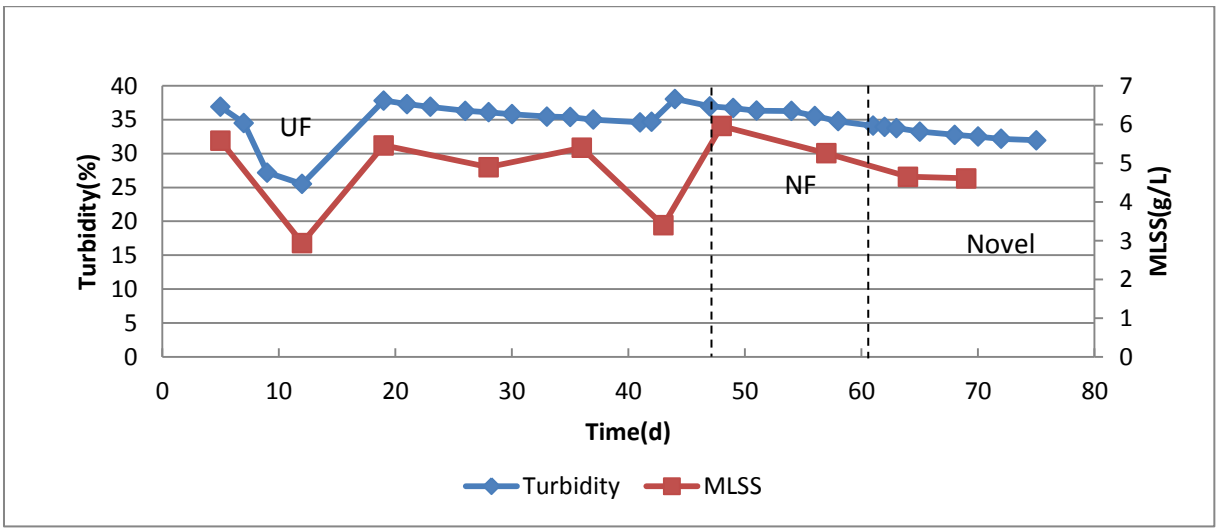


Figure .3.64. MLSS and turbidity for the anaerobically pretreated water

3.4.10. pH

The pH was fluctuating between 7 to 7,5 for the UF, NF and the novel membrane, what is similar to the results during the first aerobic part of this work.

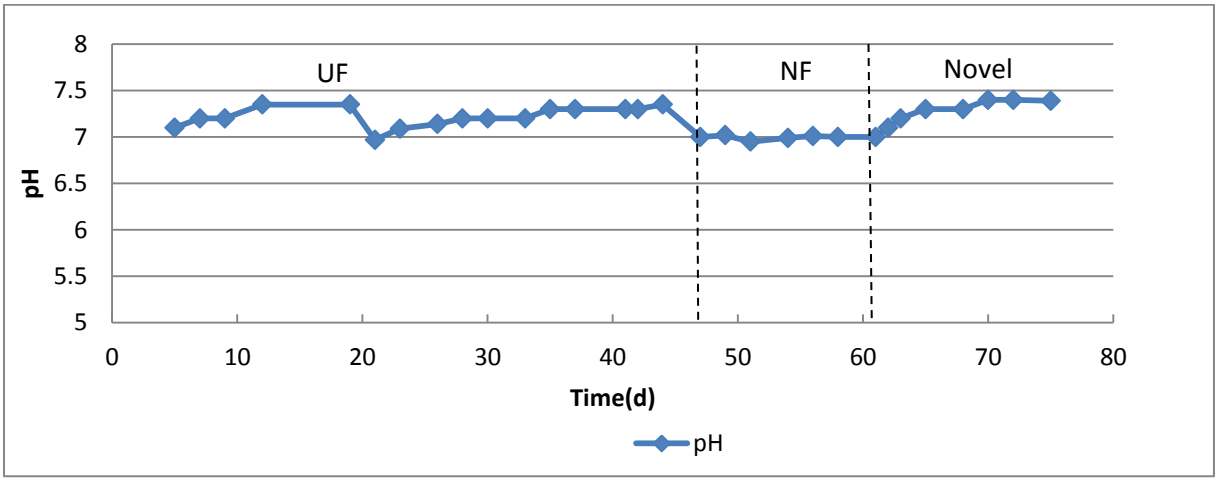


Figure .3.65. pH for the anaerobically pretreated water

3.4.11. CO_2 and O_2 in exhaust air

Figure 3.66 represents CO_2 and O_2 in the exhaust gas during the experimental period. As Figure 3.66 shows O_2 concentration remains stable around 21 Vol% and the CO_2 level fluctuates around 2,6-5 Vol% control. However these values are quite higher than those during the first aerobic treatment part see Figure 3.30. This could be attributed to some technical problems that we faced during this phase with the software.

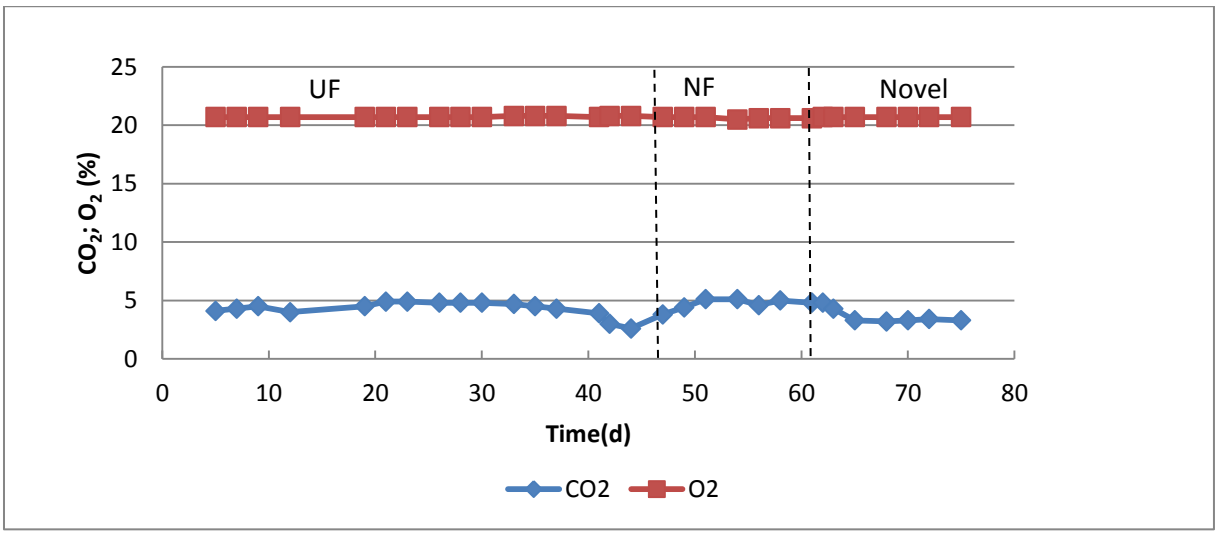


Figure .3.66. CO_2 and O_2 in exhaust gas for the anaerobically pretreated water

Figure 3.67 shows the relation of the COD removal efficiency to the bacterial activity which is represented by the exhausted CO_2 in the reactor. As illustrated in Figure 3.51 the CO_2 concentration in the exhaust gas almost perfectly follows the COD removal efficiency. Only from day 70 CO_2 level remains almost constant whereas COD removal efficiency increases.

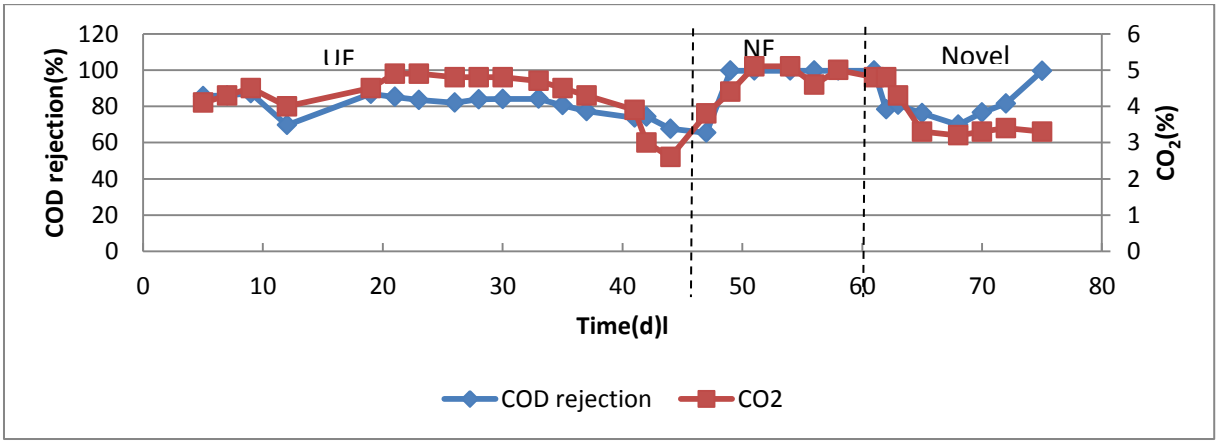


Figure .3.67. The correlation between CO_2 to the COD removal efficiency for the anaerobically pretreated water

3.4.12. Temperature

Figure 3.68 below shows the temperature during the whole experimental period. As can be seen the temperature was perfectly kept slightly lower than 20°C.

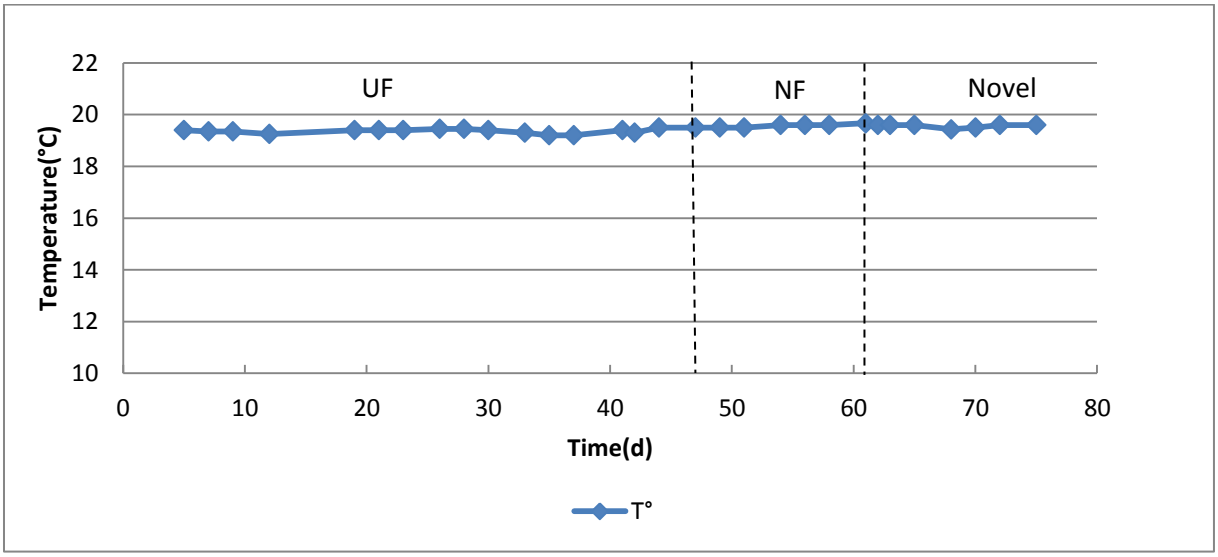


Figure .3.68. Temperature during the experimental period for the anaerobically pretreated water

3.4.13. Colour removal efficiency

No colour rejection measurements have been conducted for the samples collected after the treatment of the combined anaerobic/aerobic treatment since the whole amount of the colour has been removed during treatment under anaerobic conditions (see Figure 3.54 and Figure 3.55). Selected samples have been analysed by photspectrometer at 505 nm and 595 nm, however, concentration of the blue and red colour was always below the detection limit. The efficiency of colour removal can be seen by naked eye on the photos in Figure 3.69.

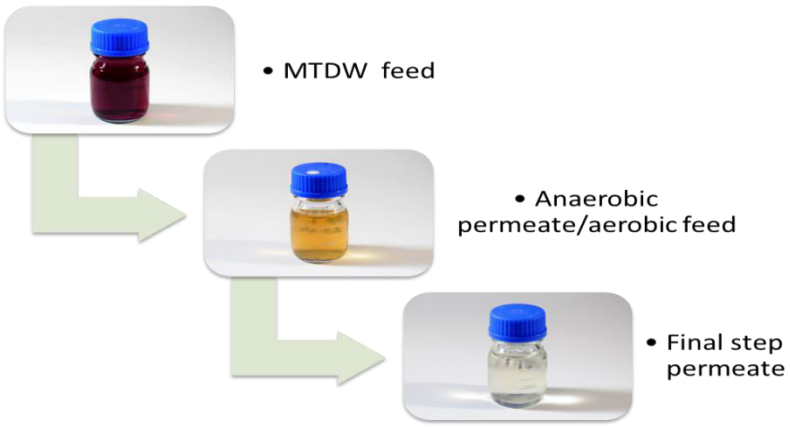


Figure .3.69. Colour rejection from feed to permeate of the combined anaerobic/aerobic process

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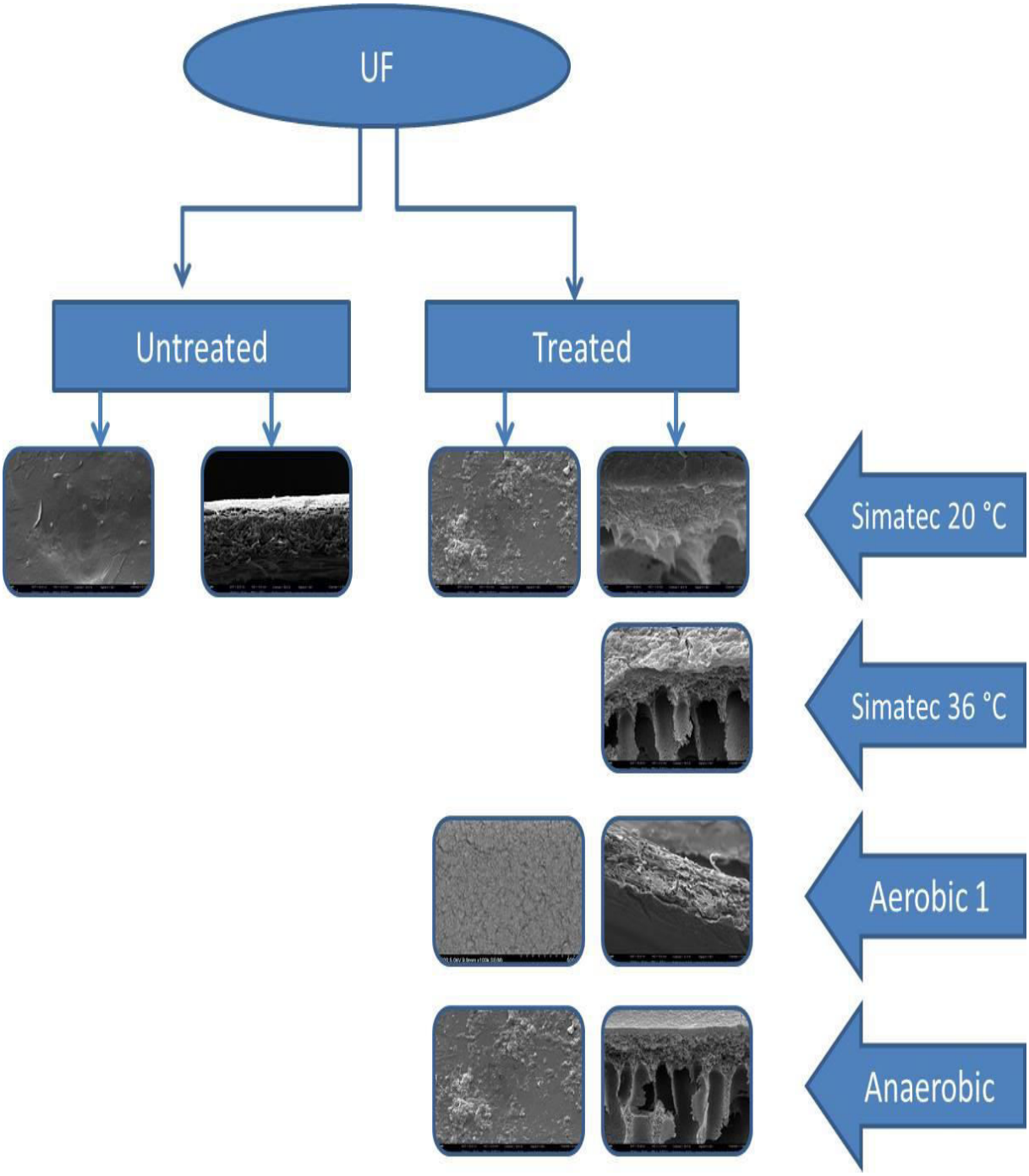
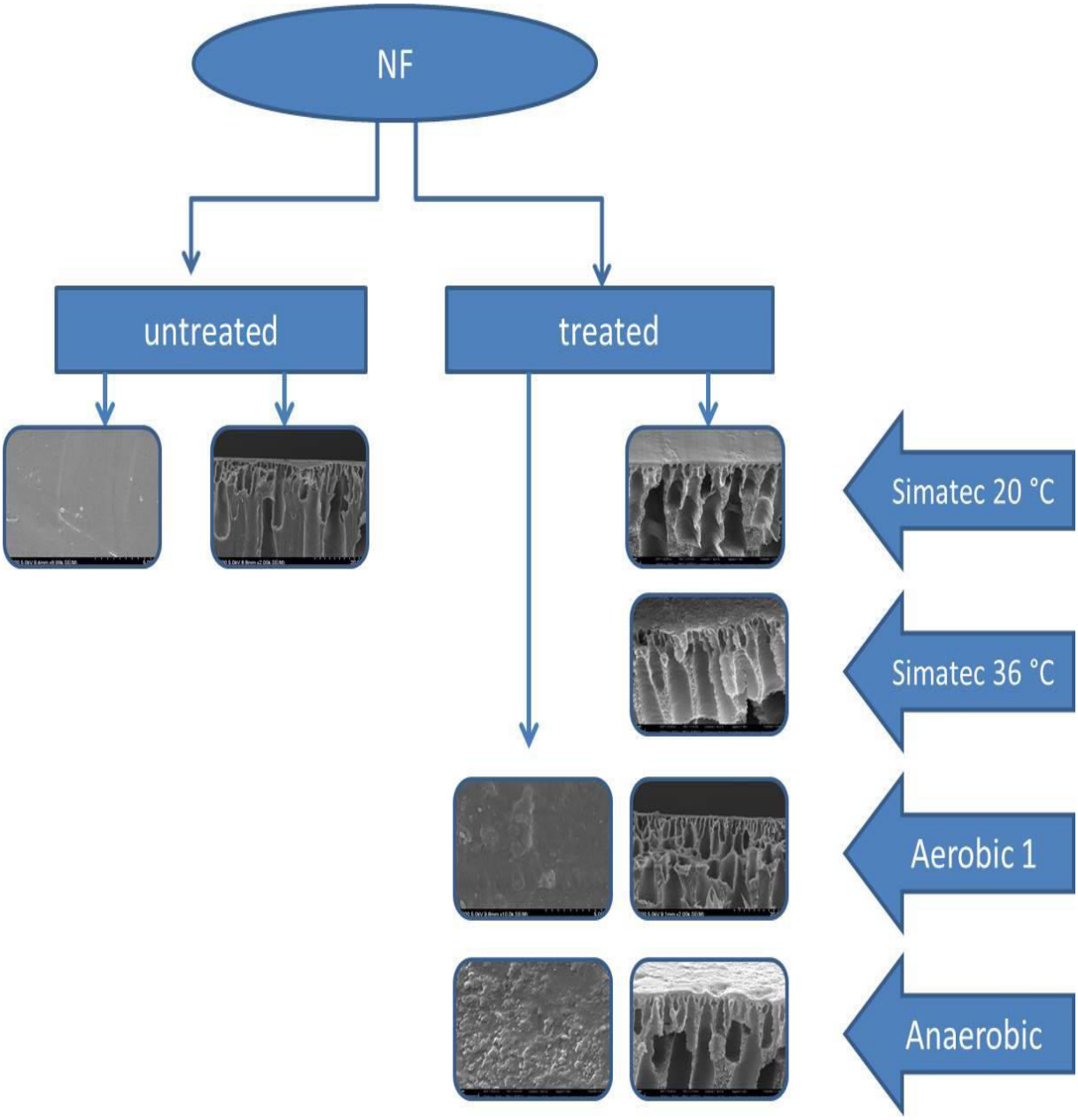
APPENDIX

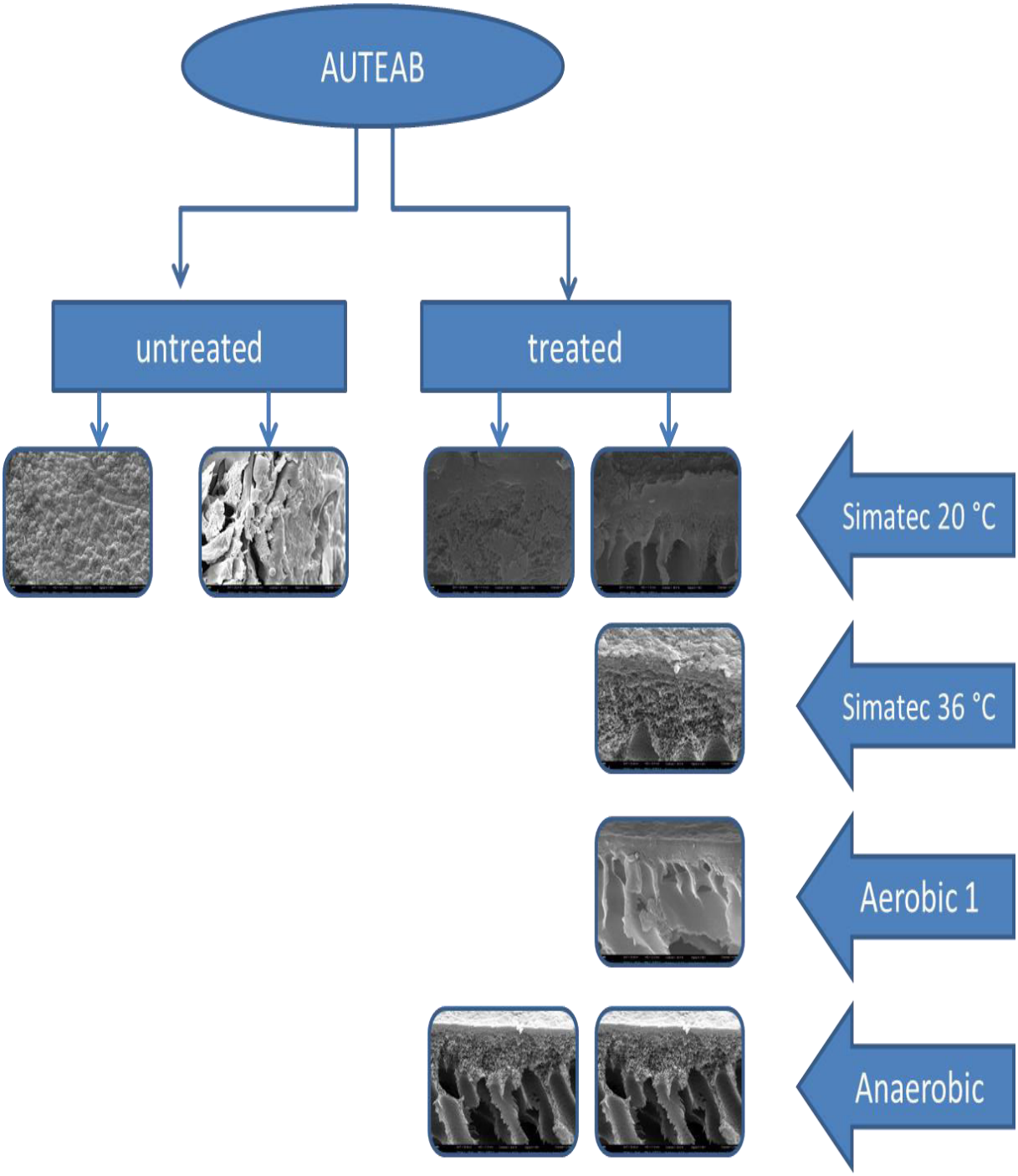
SEM



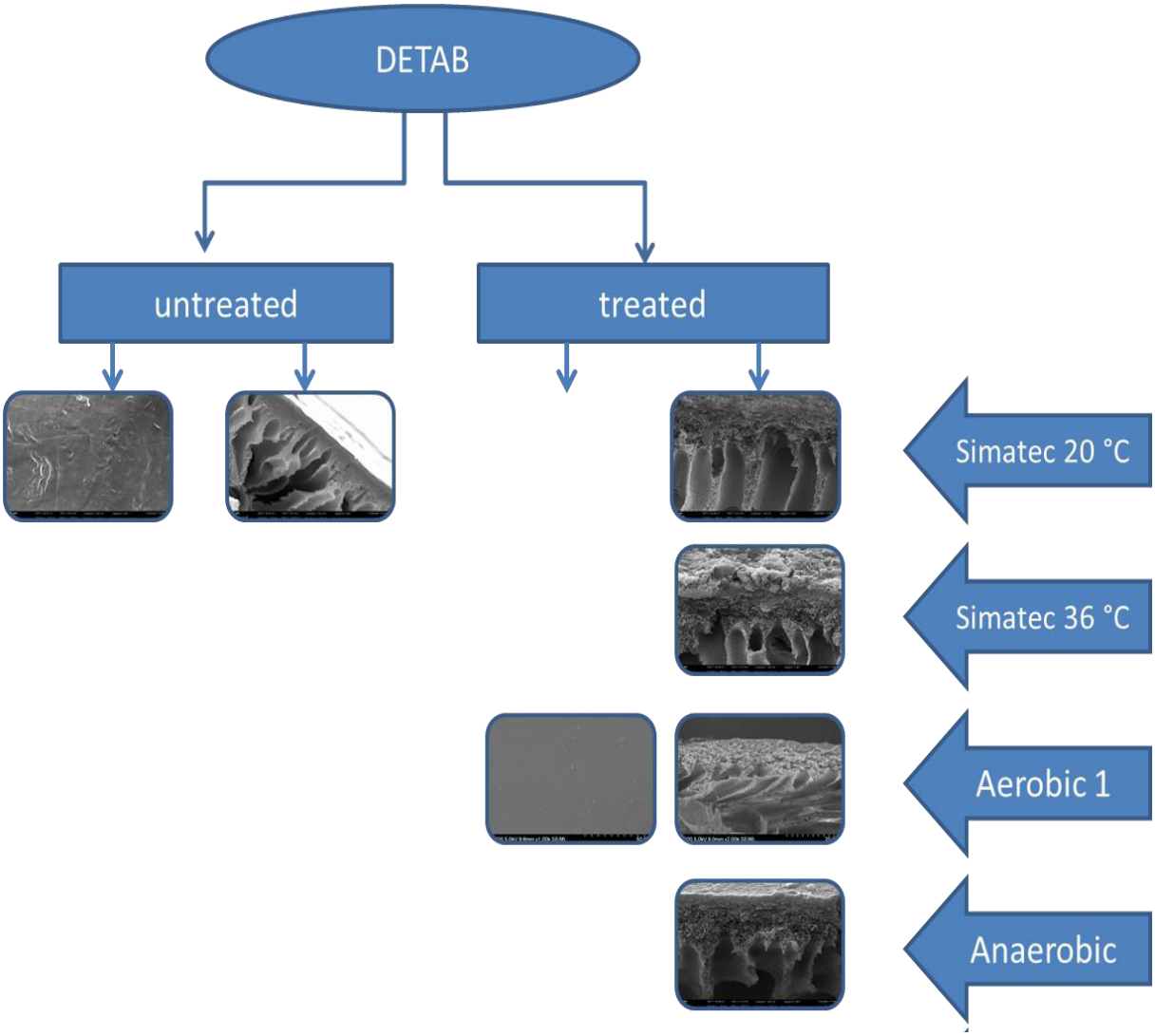
A.1. SEM images for the UF membrane under the different conditions of temperature for anaerobic and aerobic trials.



A.2.SEM images for the NF membrane under the different conditions of temperature for anaerobic and aerobic trials.

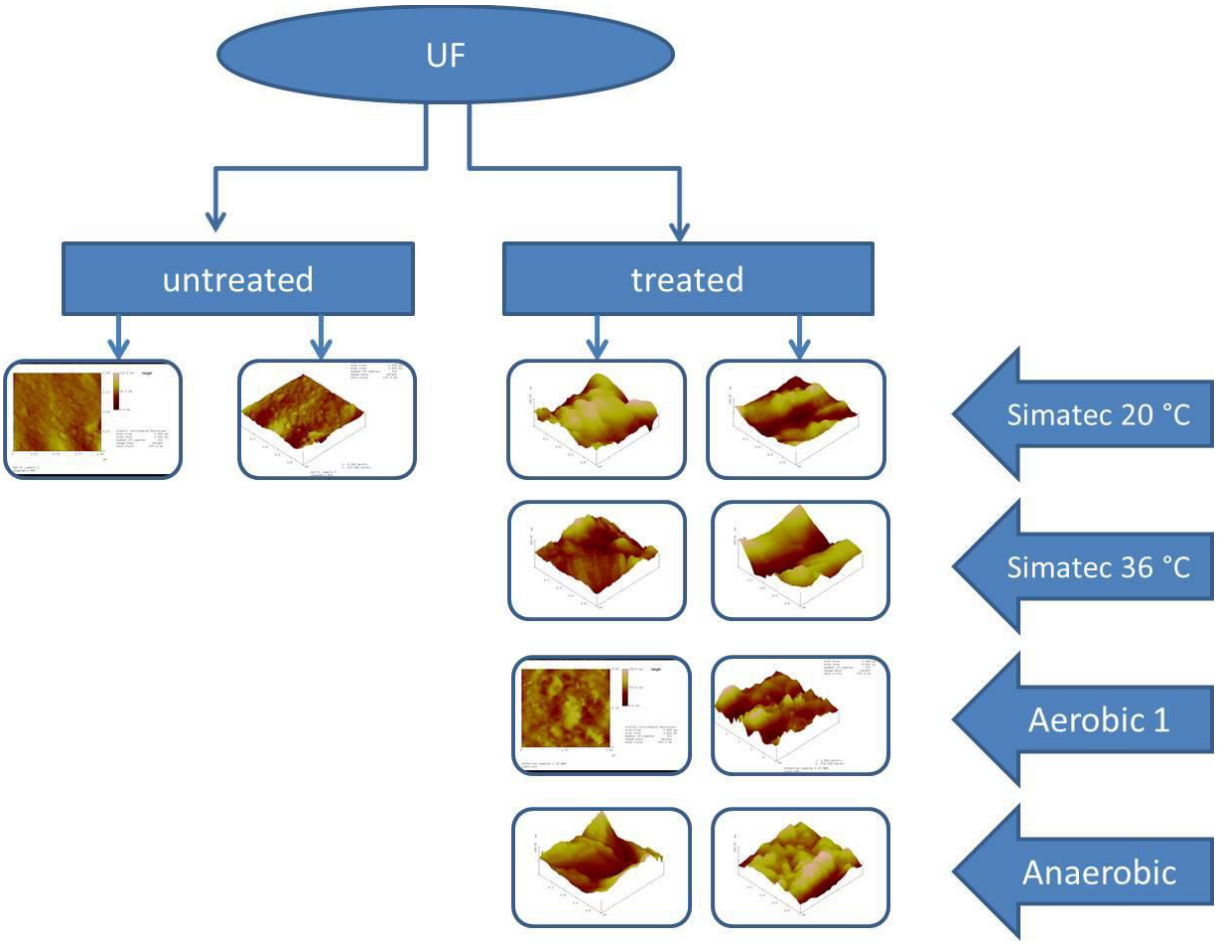


A.3.SEM images for the AUTEAB membrane under the different conditions of temperature for anaerobic and aerobic trials.

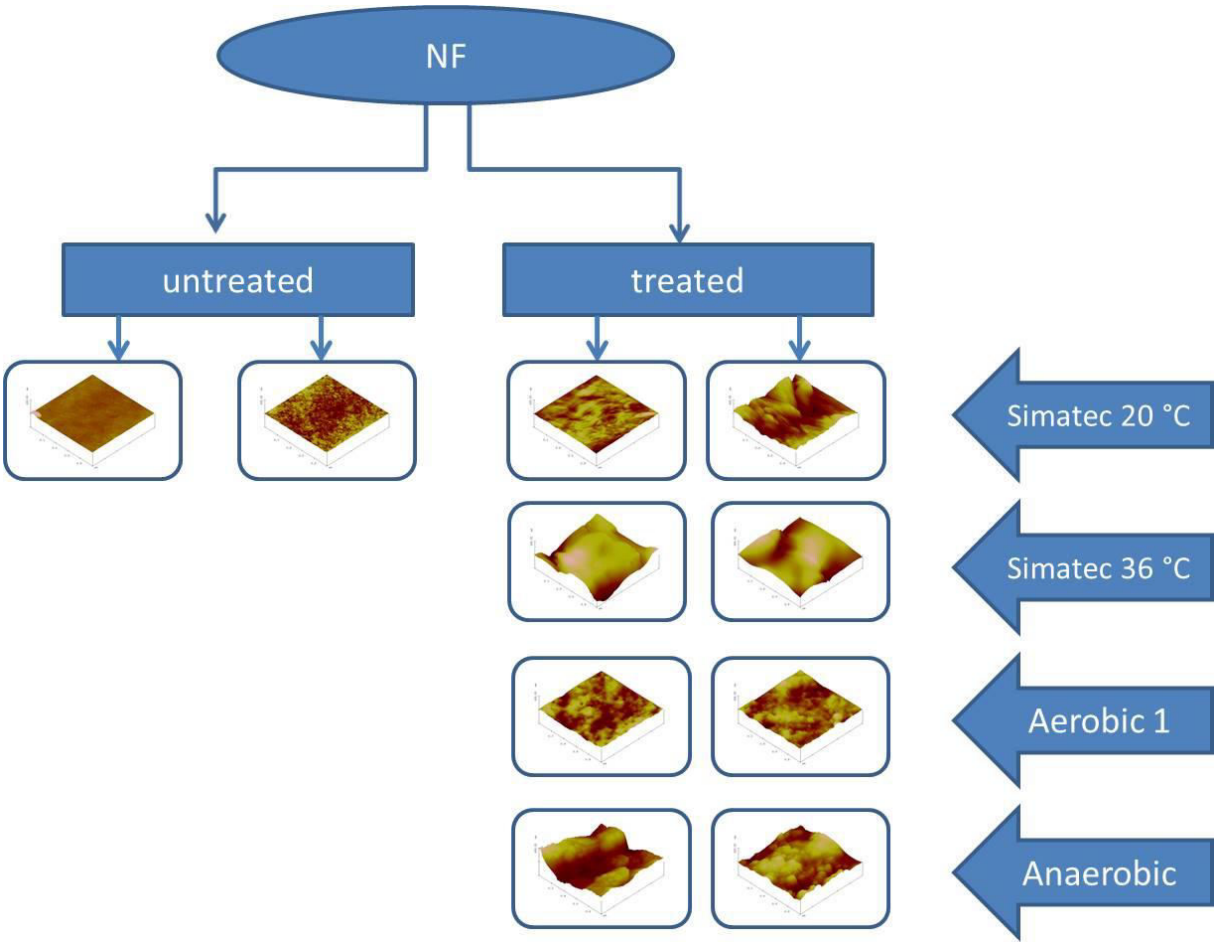


A.4.SEM images for the DTAB membrane under the different conditions of temperature for anaerobic and aerobic trials.

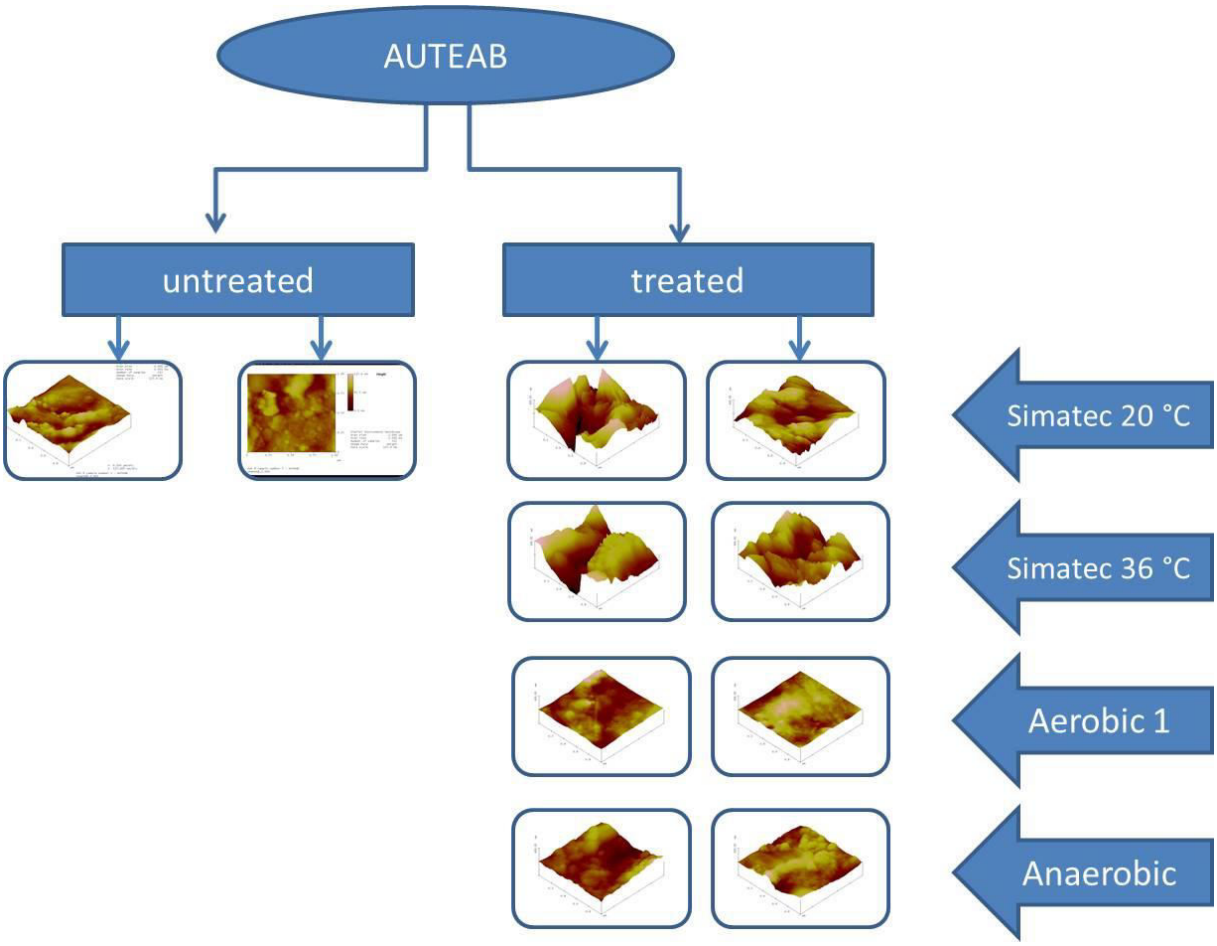
AFM



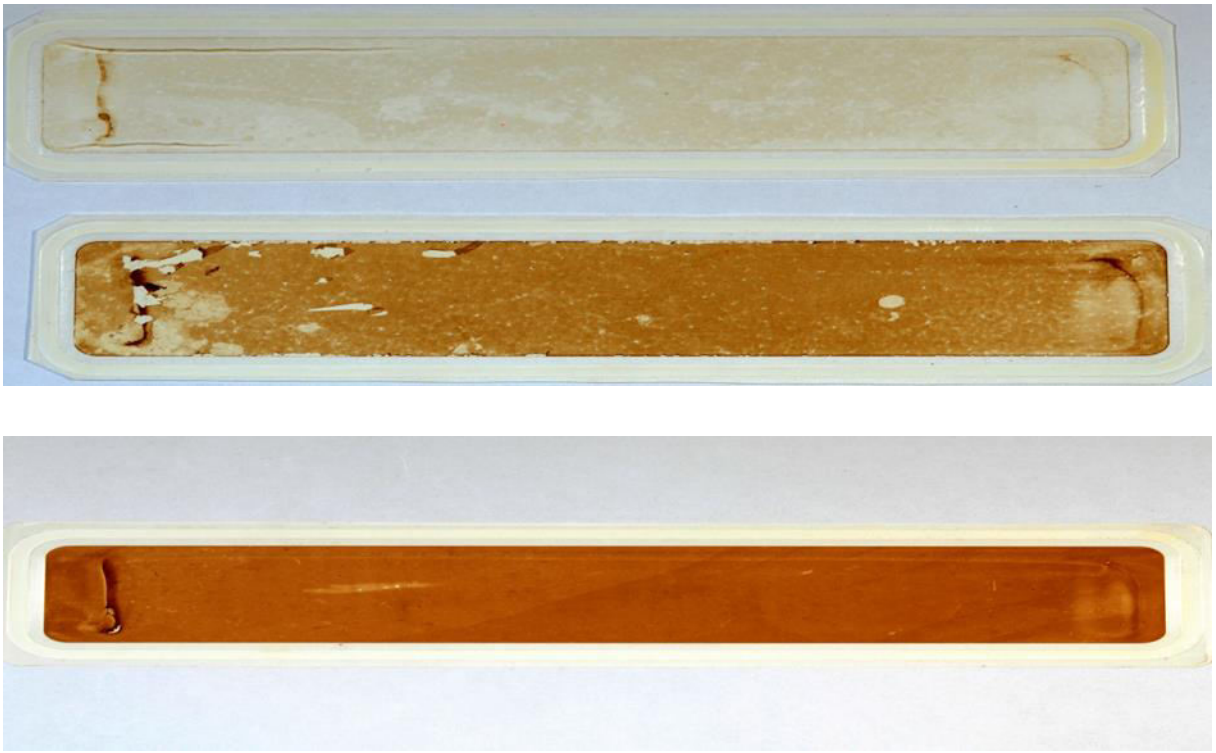
A.5.AFM images for the UF membrane under the different conditions of temperature for anaerobic and aerobic trials.



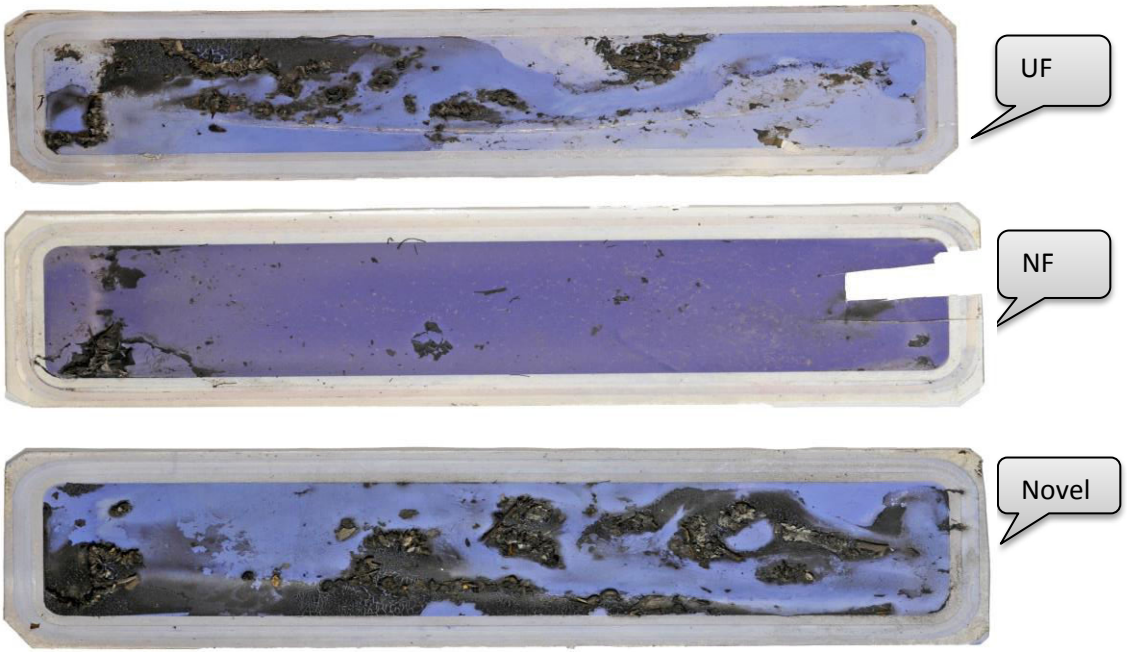
A.6.AFM images for the NF membrane under the different conditions of temperature for anaerobic and aerobic trials.



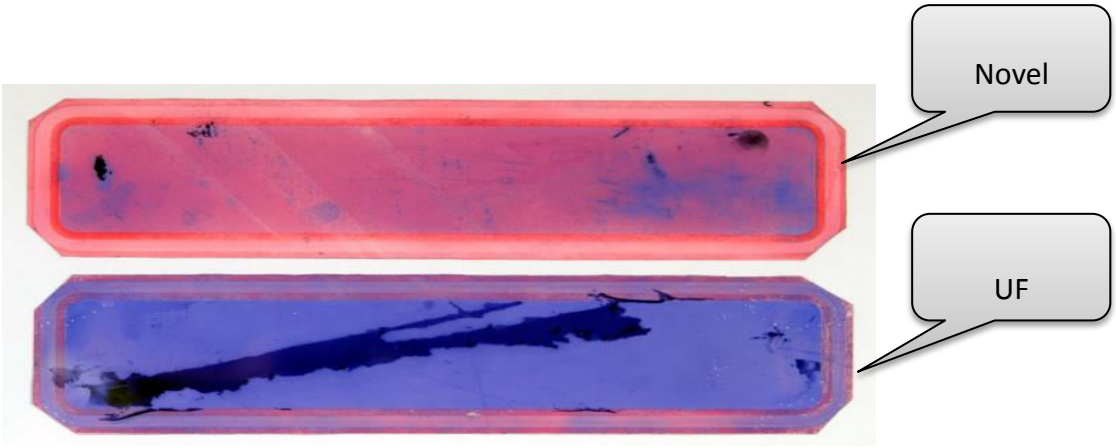
A.7. AFM images for the AUTEAB membrane under the different conditions of temperature for anaerobic and aerobic trials.



A.8.Resistance to humic acid fouling layer on membranes tested in the cross flow unit, Simatec.



A.9.UF, NF and novel membranes after use in the fermenter under the anaerobic condition



A.10. UF and novel membranes after use in the fermenter under the aerobic conditions.

CHAPTER 04

CONCLUSIONS AND OUTLOOK

CONCLUSIONS

This thesis has analyzed the performance of two types of commercial membranes (UF and NF) and novel membranes developed at ITM, Italy and coated at the laboratory at Karlsruhe University of Applied Sciences. The novel membranes were prepared by the Polymerisable Bicontinuous Microemulsion (PBM) technique using two different surfactants. The research was carried out in a laboratory flat sheet cross flow membrane unit and in a sensor controlled side-stream laboratory membrane bioreactor (MBR) unit with working volume of 20 L.

Due to flourishing textile industry its wastewater is of great concern in Algeria. Therefore a Model Dye Textile Wastewater (MDTW) was selected for this work. Within this study the cross flow membrane unit was used to study pure water permeability as well as influence of model foulant whereas in the side-stream MBR experiments were conducted by use of activated sludge under aerobic and anaerobic conditions. Finally also aerobic treatment of anaerobically pretreated wastewater was carried out.

The testing with the cross flow unit generally carried out at two temperatures (20°C, 36°C) showed higher water permeability at the higher temperature for all tested membranes with DI water and with the model foulant. As expected the commercial UF exhibited much higher water permeability and higher fouling rate than the commercial NF membrane. The novel PBM coated membranes onto the commercial UF showed no significant lower fouling compared to the untreated commercial one which is not in line with findings of previous works and what needs to be further studied within a follow up work..

The comparison of commercial UF and novel PBM membranes using a side stream MBR under aerobic conditions showed more or less constant water permeability for all tested membranes with no significant drop due to fouling. For the novel PBM membrane based on surfactant AUTEAB water permeability was higher (ca. 35 L/(m^2.h.bar)) than for the commercial ones. For the DTAB based PBM membranes water permeability was significantly lower (1-18 L/(m^2.h.bar)). The lowest permeability of approximately 1 L/(m^2.h.bar) corresponds to a dense DTAB (N3) prepared under higher temperature, which lead to a close membrane pore structure, what explains the low permeability. However, use of DTAB as surfactant is interesting (and should be further studied) for later upscaling to industrial scale

since DTAB is a commercially available surfactant and the production cost of coating is significantly lower than for AUTEAB based PBM membranes.

The experiments under the aerobic conditions showed a very high and relatively constant COD removal efficiency under various operating parameters (93%-95%). Only for the commercial NF membrane, COD removal efficiency was slightly higher (up to 97%). All commercial and novel membranes showed similar low rejection of 20-40% for the red model dye, Acid Red 4. Rejection of the blue model dye (Remazol Brilliant Blue R) was generally higher (50-90%) whereas being significantly higher for the commercial NF (ca. 90%) and the dense PBM DTAB (N3) membrane (ca. 80%). It has been also noticed that this higher colour rejection might affect the biodegradation process due to the significant decrease in the COD removal efficiency when using the dense PBM DTAB (N3) membrane. Among the commercial membranes the NF showed higher COD and colour removal compared to the UF membranes, however, at the cost of lower water permeability.

Regarding colour and COD removal efficiency, the novel PBM membranes showed similar results as the commercial UF membrane. Only if the density of the PBM layer is tuned up by changing conditions of polymerisation (mainly higher temperature) the rejection of the blue dye can be increased but at the cost of unacceptable low water permeability.

A complete nitrification has been noticed during the entire experimental time for all the commercial as well as the novel membranes what can be attributed to the high sludge age and what is in line with literature on aerobic MBR.

Similar experiments under anaerobic condition using the same membranes have been studied with the overall aim to finally study a combined anaerobic/aerobic MBR process for the model textile wastewater treatment.

The fluctuations of water permeability and flux of the membranes under the anaerobic conditions were generally higher than the permeability under the aerobic trials being most notable during the acclimation period of the sludge. Although the NF membrane was only run for a short period of time, the flux dropped significantly which was expected due to the denser porous structure of the membrane. It is necessary to highlight that the water permeability values for the anaerobic trials were generally higher than those for the aerobic trials. This can be explained by the effect of the higher operating temperature under the anaerobic conditions. This was already proved by testing (UF, NF and the novel membranes) in the cross-flow unit when operating under 20°C and 36°.

The COD removal efficiency generally fluctuated much more than for the trials under aerobic conditions. The findings showed that the COD degradation rate depends more on the conditions of the biocenosis than the MWCO of the membrane. In this regard most critical is the final methanogenesis reaction which could be hampered by toxic by-products and what is well know from other publications. For the novel membrane, which were tested under the same conditions of the biosludge the COD removal efficiency was obviously higher at around 95-97%. However, a commercial UF4 which followed the novel membranes in succession showed similar high COD degradation rates and what indicates that rather condition of biosludge is responsible for the removal efficiency.

As expected, the TOC rejection basically shows the same trend as the COD removal efficiency. It can be noticed that the TOC rejection rate is approximately 10% higher than for the COD. The findings for COD and TOC rejection generally indicate that the AnMBR process is more governed by the biological degradation than the membrane MWCO properties.

The colour rejection results were in line with literature and demonstrated that a very high decolourisation was achieved. The results showed that wastewaters containing high azo dye concentrations can be successfully treated by an AnMBR with UF membrane and that no dense membrane is needed. For the AnMBR system this is particularly important because the azo dyes tend to be an inhibitor for methanogenesis, so minimizing dye concentration in permeate is vital for successful biogas production.

The main sources of nitrogen (N) in the MDTW were NH_4Cl as well as to smaller extend the red and blue dyes. However, due to high Total N of the fermenter sludge the Total N in permeate always spiked up after having adding fresh sludge and was only slowly washed-off in the following. Only in the final phase of the experimental series Total N dropped below Total N of feed and this was the most stable period of the experimental period with satble and high COD removal efficiency.

Throughout the experimental period in general, the MLSS steadily decreased and in order to keep it constant sludge was refilled. The aim was to keep the MLSS in the range of 15 g/L without it dropping too severely and in general this was achieved.

The methane production throughout the experimental period was generally low, particularly for the UF2 and the novel membranes. This could be attributed to the fact that azo dyes adversely affected the methane production due to intoxication of methanogens. Lower methane production is in line with higher VFA concentration which generally indicates low methanogenic activity.

By moving back to the aerobic conditions as the third step, we could notice a complete COD removal efficiency especially during the NF, UF4 and the novel membranes trials except the UF1 which has been running during the acclimation period. We could notice also a complete nitrification, hence we can conclude that the target was reached by combining the two processes, namely the anaerobic to the aerobic conditions, we could not only discard the color from the feed solution, but also achieved a complete nitrification.

OUTLOOK

Through this PhD thesis, a deep study regarding the treatment of the model textile wastewater under aerobic as well as anaerobic conditions in a sidestream unit has been accomplished with the aim of preselecting suitable membranes for further studies. Since this work was conducted only by use of MTDW the use of real textile wastewater is needed to get closer to reality in the textile industrial discharge.

In addition, performance of the NF membrane in long-term proved to be an interesting option since it offers higher removal efficiency for low molecular weight compounds. Moreover PBM coating of NF membrane may offer low-fouling propensity in a later phase.

Since N1 based AUTEAB under the aerobic conditions showed outstanding results. It is necessary to repeat these trials in the next coming future, under the same operating conditions.

By considering the results got through testing the novel membranes in the cross-flow unit (SIMATEC). These experiments still have to be repeated for adequate and exact results that explain better the fouling layer on the surface of these membranes. This could be explained by the different coating conditions followed for the preparation of these, than the one followed for the preparation of the novel membranes tested in the sidestream unit.

Besides testing the real wastewater, this study could serve as a platform to find out the best performing membrane for long trials in a submerged unit, being closer to the industrial scale having more or less the same operating conditions.