



**Politecnico
di Torino**

Politecnico di Torino

Master Course in Environmental and Land Engineering
Industrial Environmental Sustainability

A.y. 2024/2025

Study of the setup and the optimization of lab-scale Membrane Aerated Bioreactor (MABR)

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ABSTRACT

The growing environmental awareness, increasingly stringent environmental laws related to the discharge into surface waters, the need to reduce GHGs and energy consumption in wastewater treatment plants have led to the research for new and modern technology in this field.

This master's thesis focuses on the configuration, study and optimisation of a Membrane Aerated Bioreactor (MABR) - an innovative system that allows wastewater treatment with higher energy efficiency and much elevated nitrogen and COD removal rate, compared to the Conventional Activated Sludge reactor (CAS). The main principle of this reactor lies on the homogeneous supply of oxygen through a membrane, allowing a constant aeration for the biofilm which ensure the establishment of an aerobic zone for the nitrification and an anoxic zone for the denitrification, enabling the Simultaneous Nitrification and Denitrification (SND).

The experimental analyses were carried out in the biological laboratory at DIATI department in Polytechnic of Turin and the experimentation is divided into three principal phases. The first phase consisted in the inoculation of the reactor for the effective development of a biofilm with a secondary activated sludge rich in microbial communities, fundamental for the growth of the attached biomass. The second phase, or intermediate phase, was inevitable due to issues with the reactor biomass and the holiday closure. Phase three determined the optimisation of MABR operational conditions, and the Oxygen Transfer Rate (OTR) and the Oxygen Transfer Efficiency (OTE) were monitored to determine the effectiveness of the aeration system. This phase was crucial for the improving of nitrification removal rate which increased to a maximum value of 8 ppm/d while the removal efficiency of organic carbon is higher than the 50%.

The results demonstrate how the MABR reactor represents a more sustainable alternative to the conventional treatments thanks to its promising removal performances which can comply with the legislation.

This thesis provides the basis for further and more precise experimentations necessary to determine and evaluate the full potential of the MABR.

Table of contents

ABSTRACT	II
TABLE OF CONTENTS	IV
CHAPTER 1	1
INTRODUCTION.....	1
CHAPTER 2.....	3
BIOLOGICAL TREATMENTS.....	3
2.1. MICROORGANISMS	3
2.2 MAIN PROCESSES.....	5
2.2.1. Nitrogen removal	6
2.2.2 Phosphorous removal	8
2.3. LEGISLATION	9
CHAPTER 3.....	11
MEMBRANE AERATED BIOREACTOR (MABR)	11
3.1. IMPORTANCE OF THE BIOFILM	12
3.2. PARAMETERS	14
CHAPTER 4	15
MATERIALS AND INSTRUMENTS	15
4.1. INSTRUMENTS.....	15
CHAPTER 5	19
EXPERIMENTAL PHASES	19
5.1. PHASE ONE: START-UP-PHASE.....	19
5.1.1 Synthetic wastewater composition.....	22
5.2. PHASE TWO: INTERMEDIATE PHASE	24
5.3. PHASE THREE: OPTIMISATION OF THE REACTOR PARAMETERS AND IMPROVE OF THE REMOVAL EFFICIENCY.	26
5.4. CAS SETUP	28
CHAPTER 6.....	29
RESULTS ANALYSIS	29
6.1. PHASE ONE RESULTS ANALYSIS.	29
6.1.1. Semi-continuous subphase	32
6.2. PHASE TWO: INTERMEDIATE PHASE.....	34
6.2.1 Phase Two: reactor's preparation	34

6.2.2 Phase Two: <i>holyday period</i>	36
6.2.3 Phase Two: <i>post-holyday period</i>	38
6.3. PHASE THREE: OPTIMISATION OF THE PARAMETERS	39
CHAPTER 7	45
CRITICALITIES, FUTURE DEVELOPMENTS AND CONCLUSIONS	45
7.1. CRITICALITIES AND CHALLENGES	46
7.2. FUTURE DEVELOPMENT	47
LIST OF TABLES	49
TABLE OF FIGURES	50
BIBLIOGRAPHY	51

CHAPTER 1

INTRODUCTION

"The capacity of a population to safeguard sustainable access to adequate quantities of and acceptable quality water for sustaining livelihoods, human well-being, and socio-economic development, for ensuring protection against water-borne pollution and water-related disasters, and for preserving ecosystems in a climate of peace and political stability^[1]."

As stated in a United Nations (UN) brief, the role of water has gained several definitions – not merely as a resource but as a key element with a strategic value, essential for life, environmental ecosystems, social and economic aspects. Even though water is apparently abundant, the availability of high-quality water is strictly limited especially since it is important to face the demographic growth and the inhomogeneous distribution of clean water. Hence, climate changes and the increase of the anthropic activities have made necessary the sustainable management of water resources.

European and Italian legislation, and UN 2030 Agenda for Sustainable Development define the directives for water protection. Precisely, the Sustainable Development Goals n. 6^[2] highlights the necessity to guarantee the access to clean water, promoting the quality of water and by consequence the quality of discharge of treated wastewater in surface waters.

Wastewater treatments represent a crucial challenge and an opportunity of the green transition: wastewaters are not anymore recognised as waste but a source for several resources. However, wastewater treatment sector requires a high amount of energy and for this it is necessary to develop innovative technologies which can comply with nowadays sustainability request.

In the context where the knowledge of pollutants and their concentrations is constantly increasing, the development of innovative wastewater technologies becomes essential. Particularly, the purpose of this master thesis is the evaluation of the potential of a Membrane Aerated Biofilm Reactor (MABR). This reactor exploits biological processes to perform Simultaneous Nitrification and Denitrification in a single unit, achieving space, material and energy saving compared to other competing or conventional technologies. The peculiarity of the MABR is the supply of oxygen, which is more precise than other technologies and it allows the reduction and the optimisation of energy consumption in WWTPs.

In the further chapters, the theoretical principles of biological wastewater treatment processes and the scientific basis of MABR reactor will be meticulously discussed.

CHAPTER 2

BIOLOGICAL TREATMENTS

In the field of wastewater treatment, biological processes represent a fundamental approach, as they exploit the metabolic activity of microorganisms to degrade several typologies of compound present in water. In recent years, those processes have been continuously improved especially to mitigate the increase of emerging contaminants that have been recently identified. The aim of this chapter is to outline the main principles of biological processes, describe the essential role of microorganisms for the biodegradation and highlight the applied technologies.

Biological processes are traditionally applied for the biodegradation of organic substances, which are decomposed in simpler compounds through microorganisms, such as bacteria or fungi. In some cases, it results in the complete mineralization in CO_2 and H_2O [3]. These techniques also include the removal of nutrients commonly present in wastewater, such as nitrogen- and phosphorous-containing compounds. The main processes, which will be discussed later in this thesis, are nitrification and denitrification that allow the reduction of ammonium.

2.1. Microorganisms

Microbial activity is essential for the success of biological processes; therefore, it is necessary to understand which type of communities are operating to guarantee their survival. Microorganisms include a wide variety of species such as bacteria, fungi or algae. A fundamental aspect is providing the appropriate nutrients since all the microorganisms need carbon, nutrients such as nitrogen and phosphorous, and energy. It is possible to distinguish organisms considering the way in which they obtain their carbon sources:

- Autotroph: capable of synthesizing carbon from inorganic substances, such as HCO_3^- or CO_3^{2-} ;
- Heterotroph: obtaining carbon from pre-existing organic compounds present in the wastewater.

Another classification can be done based on the source of energy.

- Phototroph: organisms that utilise light as energy;

- Chemotroph: organisms that utilise chemical energy ^[4].

Food sources emerge as a cardinal factor for the maintenance of the microbial communities. The nutrients and the energy enable the occurrence of the chemical reactions within the reactor. Hence, all those parameters are essential to estimate the mechanisms that characterise microbial metabolism which determine the basis for the progress of biological processes. It is possible to distinguish two differentiated metabolic pathways: the anabolic path is an assimilative process determined by energy consumption and the synthesis of cellular material, while the catabolic path is a dissimilative process where the substances are degraded into stable products and the energy is released. All these pathways are defined by oxidation-reduction reactions, which require the electron exchange between an oxidising donor element and a reducing acceptor element. In biological processes the electron donor can be identified as the substrate, which serves as the source of energy, while the electron acceptor drives the reduction reactions ^[5].

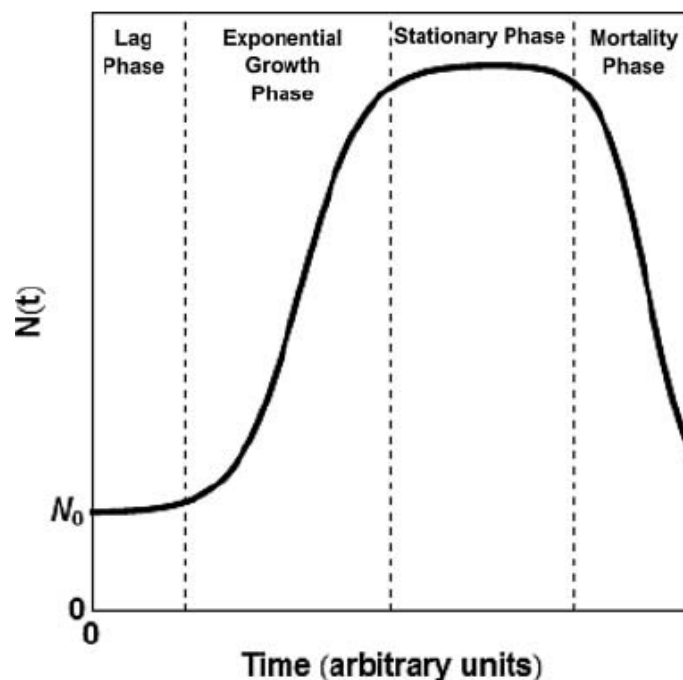


Figure 1 – microorganisms growth curve ^[6]

All these key aspects are characteristic for the development of microbial communities; *Fig. 1* shows how microorganisms grow in a batch reactor. On the x axis the time is reported, while on the y axis it is possible to notice the number of microorganisms present in the system. The curve illustrates four different phases that allow to determine the physiological state of the microbial species, typical for batch reactors.

- Lag phase: first step which demonstrates that microorganisms need a period for acclimatation in the new environment; indeed, during this phase the bacteria adapt to growing conditions without a significant increasing in the cell number.
- Exponential growth phase: second stage determined by a rapid growth. This phase can be further split into two steps, an unlimited growth phase where the number of microorganisms increases rapidly and a limited growth phase during which the species start reaching a stationary level.
- Stationary phase: it occurs when the nutrients are depleted and so death and growth have a similar rate.
- Mortality phase: characterised by the lack of nutrients which result in the death of the microbial population ^[4].

Environmental parameters can significantly affect the microbial activity, especially temperature and pH since they can define the operating conditions of reactors. Considering the temperature, it is possible to establish three optimal range related to the type of bacteria: psychrophilic, mesophilic and thermophilic. As for pH an optimal range is comprised between 6.5 and 7.5, although some bacteria can operate at higher values, up to 9 ^[5].

2.2 Main processes

The availability of free oxygen determines whether a biological process can be categorised as aerobic or anaerobic: by definition, an aerobic process occurs in presence of air (oxygen), while an anaerobic process develops in its absence. These processes depend on the type of microorganism involved in the degradation: aerobic treatments are driven by microbial communities able to utilise the oxygen to oxidise organic compound into carbon dioxide, water and biomass, whereas anaerobic processes are carried out by microorganisms which do not require air, but are capable of degrade the organic impurities into methane, carbon dioxide and biomass ^[7]. Both processes are widely applied for wastewater treatments, since they are necessary for the removal of organic impurities, to comply with legislation limits. A further diversification can be done by the identification of the anoxic processes which occur when the oxygen inside an environment is completely depleted.

2.2.1. Nitrogen removal

Nitrogen removal is a crucial aspect for wastewater treatment plants, since, as a nutrient, the discharge of wastewater and treated water containing nitrogen compound must be monitored. Indeed, it is responsible for the proliferation of algae in surface waters which depletes dissolved oxygen and can lead to eutrophication phenomena. Accordingly to this reason, the removal of nitrogen is fundamental to conform to the European, national or regional legislation standards.

The nitrogen removal is obtained through two chemical reactions that occur in the presence of specific microorganisms: nitrification and denitrification. Nitrification is accomplished by aerobic autotrophic bacteria or Ammonia-Oxidising Bacteria (AOB) that obtain energy from ammonia or nitrite and they are able to oxidise nitrogen compounds into nitrite and nitrate ^[8]. Alternatively, denitrification is led by facultative heterotrophic microorganisms or Nitrites-Oxidising Bacteria (NOB) which reduce nitrate in bimolecular nitrogen, but they also require a carbon source for their growth.

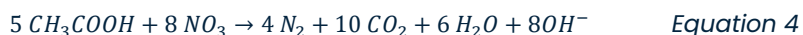
The equations modelling nitrification are as follows:



The complete reaction is:



Concerning the denitrification the chemical reaction is more complex; when the source of carbon is represented by the acetate it is equal to:



Nowadays, wastewater treatment plants widely use nitrification and denitrification processes to ensure the compliance with the increasingly strict environmental policies. In literature, there are a multitude of possible conventional and non-conventional configurations to perform the removal of nitrogen with high efficiency. Fig. 2 shows the conventional pre-denitrification setup, also called Ludzack-Ettinger process, where the denitrification is conducted in an anoxic tank before the nitrification. In this case the influent flow is enriched with the nitrates coming from the recirculation of the activated sludge. The Modified Ludzack-Ettinger (MLE) process is a variation of the previous configuration, which expect an internal recirculation from the aerated flow to the anoxic tank to improve the removal efficiency. The WWTP in Castiglione Torinese, belonging to SMAT group company, which is one of the

most important state-of-art in Europe, implements the MLE for the biological treatment of its wastewater ^[9].

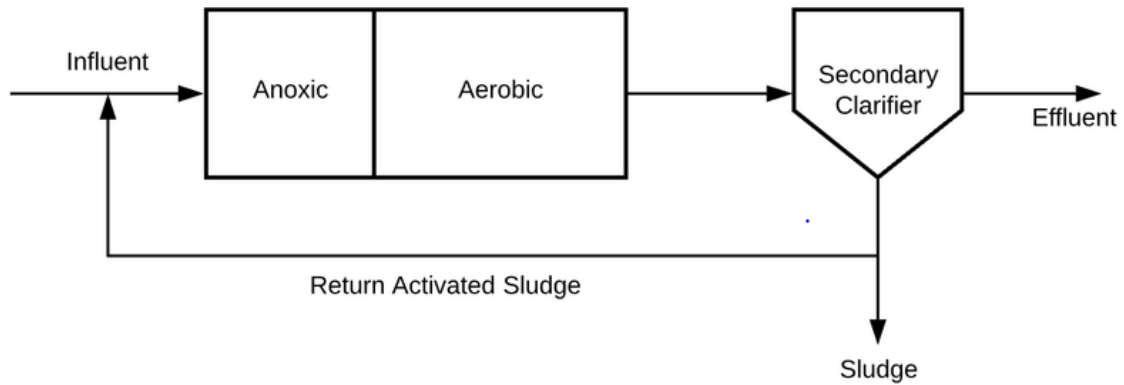


Figure 2 – Pre-denitrification configuration^[10]

Fig. 3 displays the post-denitrification configuration where the nitrification is performed before the denitrification, which occurs respectively in the aerobic tank and in the anoxic tank. This arrangement, designed by Whurman, includes the recirculation of activated sludge which contributes to higher removal efficiency.

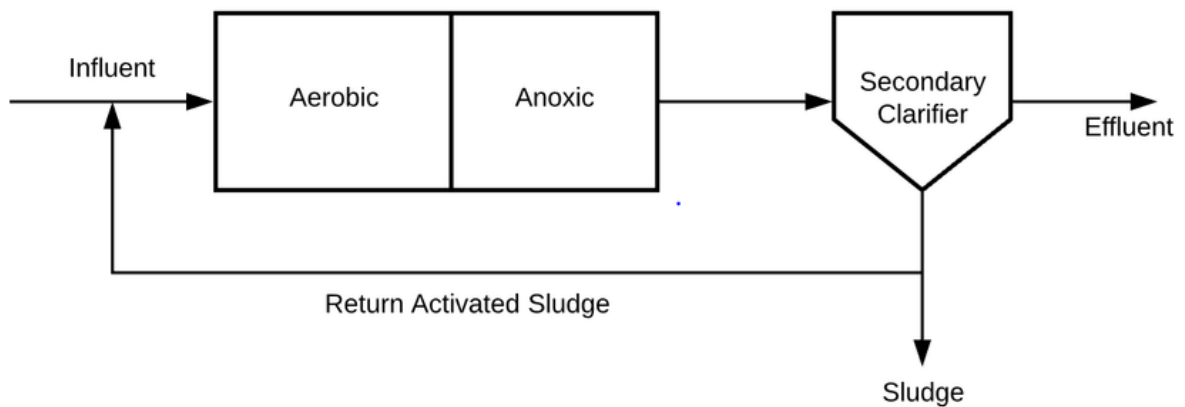


Figure 3 –Post-denitrification configuration^[10]

A further setup is the Simultaneous Nitrification-Denitrification (SND) which allows to remove ammonium in a single bioreactor considering specific conditions. The nitrification and denitrification happen in the same tank, where the nitrifiers bacteria consume the oxygen to oxidise the ammonia into nitrates and nitrites and after the oxygen depletion the denitrification process transform nitrates in diatomic nitrogen. This mechanism, typical of membrane bioreactors,

is suitable for WWTP and it can be a viable alternative to conventional nitrification and denitrification arrangements, as it exhibits the following features:

- Lower carbon demand;
- Lower sludge production;
- Alkalinity is supplied by the denitrification hence the pH maintains its stability;
- No need of recirculation from other tanks to supply nitrates for the denitrification ^[11].

Nevertheless, this technology presents some disadvantages, the two principals are as follows:

- Lower Nitrogen removal;
- Conflict between the different microbial species.

The efficiency of SND can be affected by several environmental factors:

- The pH: for the AOB the optimal pH value falls within the range of 8.2–8.4 while for the NOB the value fluctuates within the range of 7.2 and 7.9 [11];
- Temperature: at temperature higher than 25°C AOB outperforms NOB, while NOB growth is favoured at lower temperatures ^[12];
- The Dissolved Oxygen (DO): the concentration of oxygen must be balanced between the microbial communities because high concentration in the bulk liquid can limit the denitrification and the formation of an anoxic zone, however low level of DO is a constraint for the nitrification ^[11];
- The Carbon to Nitrogen ratio: for stable processes the ratio should be around the value of 4.2 ^[11];
- Salinity: high concentration of salt can inhibit microbial activities.

2.2.2 Phosphorous removal

Phosphorous is another relevant nutrient present in domestic wastewater and, as Nitrogen, it can become one of the main causes of abnormal algal growth and eutrophication when discharged in surface waters. The removal of Phosphorous containing compound is biologically achieved through the Enhance Biological Phosphorous Removal (EBPR) where it is possible to exploit the activity of Phosphorus Accumulating Organism (PAO). Indeed, those bacteria are capable of accumulating exceeding phosphorus. Generally, the process requires three stages:

- Anaerobic phase: where the bacteria release phosphate inside the wastewater;
- Aerobic phase: PAOs store the exceeding Phosphorus;
- Sludge removal: through sedimentation, it is possible to collect and remove sludge rich of Phosphorous.

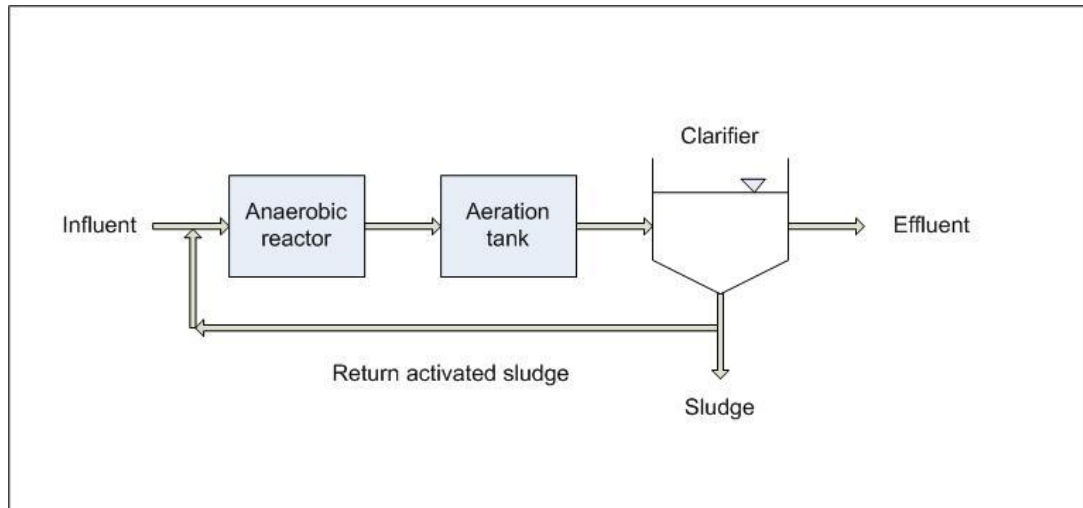


Figure 4 - Biological Phosphorous Removal (BPR) typical configuration^[13]

One of the typical configurations, it is diagrammed in Fig. 4. As previously described, there are an anaerobic tank, an aerobic tank and a secondary clarifier from which the sludge it is collected. The recirculation of the activated sludge increases the removal efficiency.

2.3. Legislation

As already introduced in this thesis, the removal of contaminants and nutrients must comply with the limitation imposed by legislation, especially for the discharge in surface waters. In the wastewater context, legislation follow a pyramidal scheme that defines the responsibilities: from the European Union to each Italian Region.

The European Union issued several laws related to the wastewater treatment and the respective environmental preservation. The Directive (UE) 91/271/CEE focuses on eutrophication, on secondary and tertiary treatment and defines the criteria to detect sensible areas, which could become vulnerable in the future^[14]. Hence, this legislation imposes for all the Union European Member States common regulations on the discharge of treated waters concerning the number of pollutants and all the chemical compounds that can cause abnormal algal proliferation. This Directive has been recently abrogated and it will be

substituted from August 2027 to be succeeded by Directive (UE) 2024/3019 which will also comply with the goals of Green Deals and Action Plan ^[15]. Subsequently, the Directive (UE) 2000/60/CEE, or Wastewater Framework Directive [16], has introduced the concept of integrated approaches, determined the chemical and ecological quality of water bodies and implemented stricter environmental limits.

Thereafter, with respect of European Directive, every UE member state has adopted its own legislation. Indeed, in Italy all the environmental regulations come from D.Lgs 152/2006 - Parte III -, or commonly called "Testo Unico Ambientale" [17]. Therefore, the legal limits are established from each Italian Region or delegated to the respective Competent Authority.

CHAPTER 3

MEMBRANE AERATED BIOFILM REACTOR (MABR)

The purpose of this thesis revolves around the Membrane Aerated Bioreactor (MABR) and its removal efficiency. In recent years, MABR technology has been studied since its performances could become advantageous to modernise wastewater treatment plants and could lead to a more efficient energy management. Indeed, MABR has the capacity to optimise the oxygen utilisation which allow to enhance the nutrients removal efficiency, furthermore its specific configuration determine the appropriate environment for SND. All these characteristics are fundamental especially for the keeping up with the stricter environmental regulations and for the transition to the energy neutrality.

Fig. n°5a represents a typical MABR configuration at laboratory scale [18]. This set up has been used for the analysis at Polytechnic of Turin and the reactor is placed in the biological laboratory of DIATI department. Moreover, this arrangement has been used also for the purposes of this thesis.

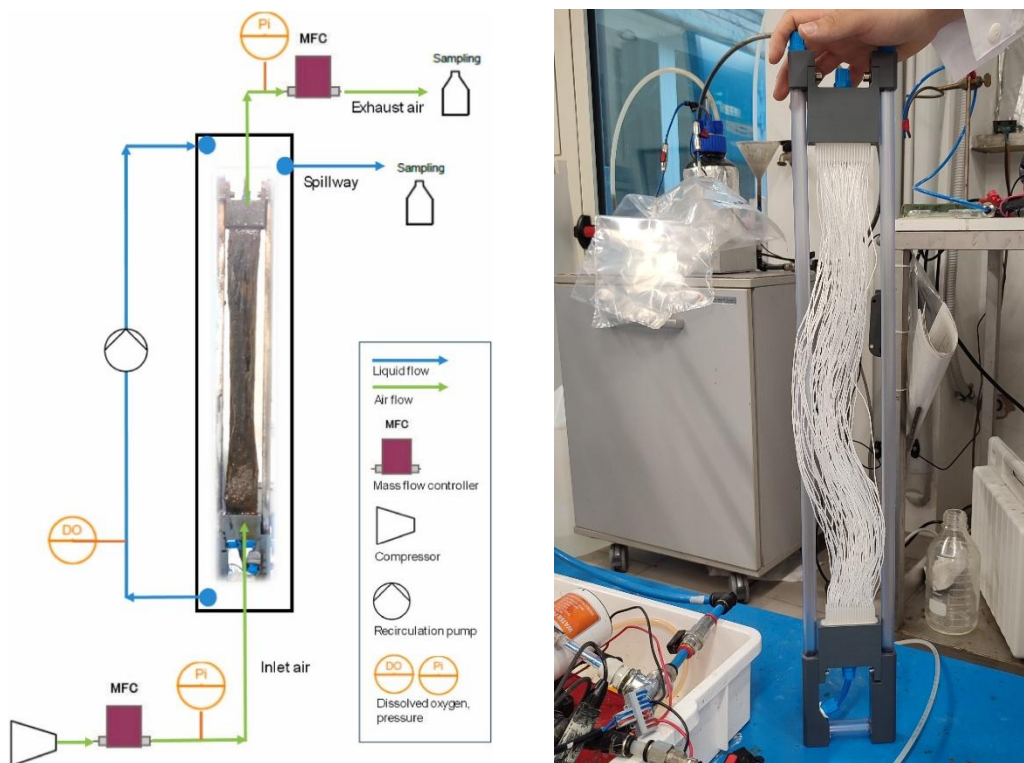


Figure 5 - a) schematic diagram of MABR , b) clean hollow fiber membrane

The MABR reactor is developed around an air-permeable hollow fiber membrane (Fig. 5b) which is employed both for oxygen supply and for the growth of the attached biomass biofilm, fundamental for biological oxidations. There are several typologies of materials and membranes that can be used for the presented purposes; however, the one used in DIATI laboratory consists in porous cords with a multiple number of filaments braided to a polyester support. The membrane determine the division of the reactor into two phases: a gas phases which is located in the lumen side and provide oxygen, and a liquid phase ^[19]. Another crucial aspect that characterised this reactor and distinguishes MABR from conventional biological reactor is the bubbliness aeration. Hence, the inlet air is supplied by a counter-current system which identify the growth of a stratified biofilm.

3.1. Importance of the biofilm

In MABR, the biofilm grows attached to the membrane and it is constituted by trapped microorganisms in gel-like Extracellular Polymeric Substance (EPS) ^[19]. Generally, a biofilm reactor can provide high removal performances than reactor with suspended microorganisms, since in the latter case the microorganisms are suspended in flocs and continuously removed. While, in biofilm reactor the biomass is trapped and consequently the Hydraulic Retention Time (HRT) is significantly higher. Furthermore, biofilm can act as a catalyser for the air transfer and enhance the Oxygen Transfer Rate (OTR) ^[20].

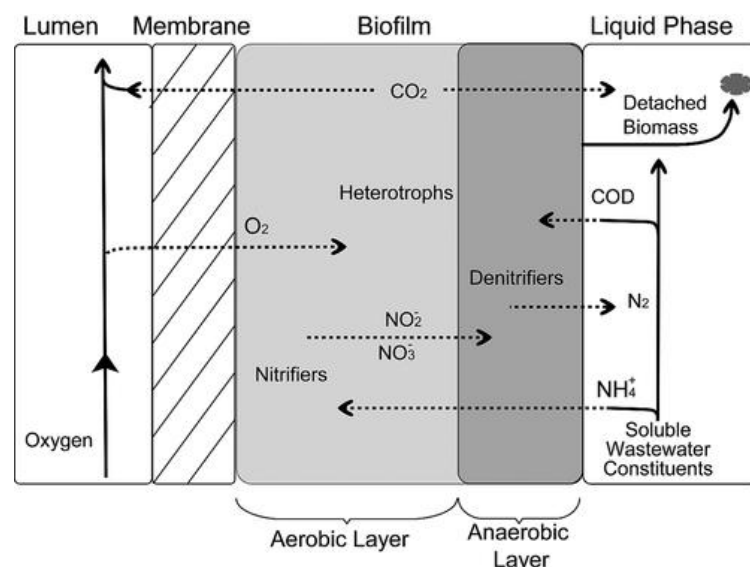


Figure 6 – Schematic diagram of transport fluxes ^[8]

Fig. 6 represents a schematic view of what happens inside a MABR reactor and the role of membrane in the removal of compounds. In the drawing are represented all the fluxes, with dashed lines, and the microbial stratification. The region closest to the membrane is aerobic and characterised by both the presence of oxygen and nutrients. Indeed, the NH_4^+ from the wastewater reaches the aerobic zone and the nitrifiers organism in the biofilm oxidise the nutrient to NO_2^- and NO_3^- . Once the oxygen is depleted and the nitrification has occurred, the nitrates reach the anaerobic area where the denitrifiers transform NO_3^- in N_2 thanks to the presence of acetate in water which is the main source of COD. This configuration enhances the efficiency of simultaneous nitrification and denitrification.

The development of the biofilm represents a crucial and an unpredictable aspect. A proper thickness, provide the optimal conditions for the formation of aerobic and anaerobic regions, however its control is not simple. Excessive biofilm can limit the substrate penetration to the microbial population and can cause flow maldistribution, resulting in unbalanced oxygen transfer rate [19]. Nevertheless, the maintenance of a constant thickness depends on the ratio between the accumulation and the detachment, and the latter is not easily detectable. Indeed, detachment occurs either through erosion or sloughing phenomena but in literature, those mechanisms have not been widely studied [8].



Figure 7 - Biofilm growth. May 15 (left), July 7 (middle), August 35 (right)

Fig. 7 depicts the biofilm growth during the experimentation conducted in DIATI laboratory and it reports the state of the biomass on May 15, July 7 and August 25.

3.2. Parameters

There are several factors that can describe the correct functioning of a MABR reactor, among all the most important are related to the supply of air and oxygen.

The Oxygen Transfer Efficiency (OTE) determines the efficiency related to oxygen consumption and it is computed as follows:

$$OTE = \frac{Q_{IN} * O_2^{IN} - Q_{OUT} * O_2^{OUT}}{Q_{IN} * O_2^{IN}} \quad [-] \quad \text{Equation 5}$$

The Oxygen Transfer Rate (OTR) is a parameter that represents the availability of oxygen for the biomass, mathematically it can be computed as the consumed oxygen in the reactor over the membrane area. It is calculated as:

$$OTR = \frac{Q_{IN} * O_2^{IN} - Q_{OUT} * O_2^{OUT}}{A_M} \quad \left[\frac{gO_2}{d * m^2} \right] \quad \text{Equation 6}$$

In both Equation 5 and Equation 6:

- Q_{IN} and Q_{OUT} represent respectively the inlet and outlet airflow;
- O_2^{IN} and O_2^{OUT} corresponds to the volumetric concentration in the inlet and outlet flow;
- A_M is the membrane surface area [18].

CHAPTER 4

MATERIALS AND INSTRUMENTS

The experimental activities have been conducted inside the laboratories of DIATI department at Turin Polytechnic. Throughout the laboratory work, different instruments and devices have been daily involved to carry out the experiments precisely and to endure the reliability of all the results obtained.

4.1. Instruments

The accuracy of the experiments required the collection of a sample of treated wastewater from MABR reactor outlet to determine the removal efficiency of Nitrogen and COD, particularly during the start-up phase which will be lately discussed in this thesis. The samples, which contained a high concentration of suspended solids, were filtered using two methods depending on the amount of solids content.

When the concentration of suspended solids was too high for the $0.45\ \mu\text{m}$ mesh to be effective, a centrifuge (Fig. 9) was employed to achieve the solids-liquid separation.



Figure 8 – Centrifuge ^[21]

The Spectrophotometer (Fig. 10) is one of the most used devices for the experimentation. This instrument base is functioning on the molecular absorbance; indeed, a ray of UV-visible light is emitted to hit the sample and then the values of absorbance are recorded, from which it is possible to detect the concentration on NH_4^+ . The analysis is conducted using an ammonium kit

which is composed of reagents that react with the samples, previously diluted, and colour the content of the tubes. It is immediately noticeable that higher concentration of NH_4^+ corresponds to greener samples.



Figure 9 – Spectrophotometer [21]

The TOC-TN instrument is capable to distinguish and quantify the concentration of Total Organic Carbon (TOC), Inorganic Carbon (IC), Total Carbon (TC) and Total Nitrogen (TN).



Figure 10 – TOC -TN [21]

The Chemical Oxygen Demand (COD) is calculated through the device showed in Fig. 12, which makes use of already prepared and sealed tubes that reacts with COD present in the sample resulting in an exothermic reaction. Considering the typology of the reactor and previous analysis, the middle-low range has been used to detect COD in the concentration range between 0 to 1500 ppm. To measure the COD, it is necessary to insert 2 mL of the sample inside the kit tube test and then put it inside the heater which heats all the tubes for 2 hours at

150°C. The actual concentration of COD is observed through a photometer since there is a linear correlation between the concentration and the absorbance.



Figure 11 – COD [21]

The Ionic Chromatographer (IC) showed in Fig. 13 is an instrument use to detect the concentration in ppm of anions, such as NO_3^- and NO_2^- , relevant to the outcome of the experiment. The methodology demands the insertion of approximately 1.5 mL or 2 mL, then the instrument build a graph, the chromatogram, with time on the horizontal axis and the conductivity in μS on the vertical axis. The peaks of the plot allow the identification of the different species present in the sample, instead of the area under the curve which determine the effective concentration of anions.



Figure 12 – Ionic Chromatographer (IC) [21]

For the analysis exhausted gas, a Gas chromatograph has been employed. This instrument was fundamental to determine the volumetric concentration of the inlet gases and the concentration of outlet gases, which are all valuable data for the mass balance analysis and the determination of OTR and OTE. The following table (Table 2) represents typical values of two different days: September 22 and September 23.

Table 1 - typical volumetric composition (v/v %)

Date	Inlet			Outlet			
	O_2	N_2	CO_2	O_2	N_2	CH_4	CO_2
09/22	21.3086	78.6086	0.0829	20.2914	78.8361	0.4301	0.4424
09/23	21.4504	78.4828	0.0668	19.8415	78.8515	0.8498	0.4572

Chapter 5

EXPERIMENTAL PHASES

In this thesis's chapter the configuration of MABR for the experimentation will be discussed. The reactor consists of a plexiglass rectangular section, and the working volume is 3.2 L where the Zeelung lab-scale module is submerged, as in Fig. 13.

Table 2 – MABR set up parameters.

Parameter	Unit of measurement	Value
Volume	L	3.2
Membrane Surface Area	m^2	0.025
Surface – to – volume ratio	$\frac{m^2}{m^3}$	83.3
Cords diameter	mm	0.7
Cords length	m	1

Table 1 also highlight the characteristics of the membrane such as the length and the diameter of the chords. On the other hand, Fig. 13 shows the presence of a peristaltic pump used for the liquid recirculation while the air is supplied through a gas meter and set to reach a maximum value of 250 NmL/h. The outlet air is also controlled through another gas meter configured at 100 NmL/h, then the exhaust gases are collected in a gas bag which will be subjected to further analysis.

The experimentation has been divided into two principal phases: the start-up-phase during which the main goal was the growth of the biofilm and a optimisation phase which was fundamental to improve all MABR's main parameters.

5.1. Phase One: start-up-phase

The installation of a MABR reactor involves several issues, since the reactor operates with attached biomass and development of a functional biofilm is

always critical. Indeed, this phase lasted from the May the 6th to July the 16th and it was fundamental for the initialisation of the reactor and its preparation for further analysis and experimentation. Hence, the start-up-phase consists in the commissioning of the reactor with the installation of a new and clean hollow fiber membrane inside the rectangular plexiglass reactor. Then, the reactor has been initially fed with a secondary sludge coming from the WWTP of Castiglione Torinese.. It is principally composed by wastewater and microorganisms which must be periodically removed from the plants to maintain constant the concentration of the aeration tank. Indeed, the secondary sludge is an optimal source of microorganisms and bacteria fundamental for the biomass growth. Fig. 13 shows the reactor right after the inoculum injection and it is possible to notice that the microorganisms are still not attached to the membrane and dark colour is representative for a condition rich of suspended solids.

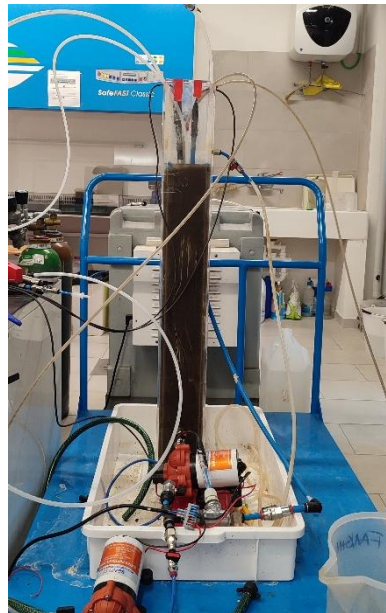


Figure 13 – MABR after inoculum injection.

Other main chemical compounds have been provided as sources of nutrients and to constitute a synthetic wastewater: diammonium hydrogen phosphate ($(NH_4)_2HPO_4$) as source of NH_4^+ and sodium acetate trihydrate ($CH_3COOH * 3H_2O$) as a source for COD . The table below shows the exact mass used for this initial phase.

Table 3 – nutrients amount in 3.2 L of water

$CH_3COOH * 3H_2O$	0.7622 g
$(NH_4)_2HPO_4$	3.0948 g

The peculiarity of MABR reactor, which distinguishes it from other conventional reactor, is the oxygen supply. In this case, environmental air is provided, and its volumetric composition is daily analysed through a gas chromatograph. During this initial phase, the outlet gas meter was arranged at 70 NmL/h while the inlet gas meter was set to reach a maximum value of 150 NmL/h. The collection of exhaust gases has started further this starting period.

The principal parameters are monitored through several sensors which continuously report the value of pH, Dissolved Oxygen (DO) and Oxidising-Reduction Potential (ORP). All those parameters allow to detect the correct functioning and operational conditions of the reactor. Indeed, the pH is a sentinel for the microorganisms' activity and survival and the optimal range is encompassed between 7.2 and 7.9 for NOB and 8.2 and 8.4 for AOB. While DO and ORP identifies aerobic and anaerobic condition in the water medium: a negative ORP stands for an anaerobic system whereas a positive ORP is characteristic of aerobic conditions. One of the main purposes of the overall experimentation is to maintain the optimal conditions of those three parameters since determines a correct removal potential for the microorganisms.

Subsequently to this initial phase, in batch mode, the reactor has been switched into a semi-continuous mode. During this subphase, the configuration of the reactor was the same of the batch mode, however it has been connected to a feed tank filled with synthetic wastewater, with a volume equal to 20L. The water withdrawal has been implemented using a mini peristaltic pump and the outlet has been collected in another tank to establish a dynamic equilibrium into the reactor. The mini pump was able to work in a flux range between 5 mL/min and 150 mL/min ^[22]. Since the inability of the pump to withdraw lower rate fluxes, it has been necessary to implement a semi-continuous mode. A MATLAB code interfaced with an Arduin system was used to control the amount of water withdrawn from the feed tank. Every fifteen minutes the reactor was fed with synthetic wastewater for 1 minutes and 30 second, with a flux flow rate equal to 38.4 mL/h to introduce into the reactor a total volume of wastewater equal to 200 mL every hour. This value was necessary to guarantee a Hydraulic Retention Time equal to 16 h, which complies with the values in literature and with previous experimentation conducted on the same reactor. The composition of synthetic wastewater has been fixed through the literature experimentation on MABR. One of the goals of the semi-continuous set up was finding an adequate wastewater composition to enhance the biological processes and the biofilm growth.

5.1.1 Synthetic wastewater composition

In this master thesis three literature studies will be reported. The synthetic wastewater composition shown in table 4 has been introduced into the reactor to guarantee the correct growth of the biofilm and the development of Extracellular Polymeric Substrate (EPS).

Table 4 – synthetic wastewater composition ^[23]

Chemical compound	Amount	U.M.
Na_2HPO_4	2.77	g/L
KH_2PO_4	1.7	g/L
$(NH_4)_2SO_4$	0.2	g/L
$MgSO_2 * 7H_2O$	0.41	g/L
Ca-Fe solution	2	mL/L
Trace mineral solution	2	mL/L

Another study provided a similar wastewater composition, as highlight in table 5, always to enhance the biofilm growth and determine the effect of aeration on EPS and on the biomass ^[24]. The following wastewater is composed by a Ca-Fe solution and a trace mineral solution.

Table 5 – synthetic wastewater composition ^[24]

Chemical compound	Amount	U.M.
Na_2HPO_4	2.773	g/L
KH_2PO_4	0.169	g/L
$(NH_4)_2SO_4$	0.202	g/L
$MgSO_2 * 7H_2O$	0.41	g/L
$CaCl_2 * 2H_2O$	1	g/L
$FeSO_4 * 7H_2O$	1	g/L
$ZnSO_4 * 7H_2O$	0.1	g/L
$MnCl_2 * H_2O$	0.03	g/L
H_3BO_3	0.3	g/L
$CoCl_2 * 6H_2O$	0.2	g/L
$CuCl_2 2H_2O$	0.01	g/L
$NiCl_2 6H_2O$	0.01	g/L
$Na_2MoO_4 * 2H_2O$	0.03	g/L
Na_2SeO_3	0.03	g/L

The last study implemented a growth media that was necessary for the development of EPS on the membrane, since they can affect negatively the performance of a MABR reactor. Indeed, EPS can be responsible for the operating conditions because they can cause fouling of the membrane and for that reason their growth have been studied to prevent problems ^[25]. Table 6 shows the wastewater composition used for this study.

Table 6 – synthetic wastewater composition ^[25]

Chemical compound	Amount	U.M.
Na_2HPO_4	2.77	g/L
KH_2PO_4	0.169	g/L
$(NH_4)_2SO_4$	0.2	g/L
$MgSO_2 * 7H_2O$	0.41	g/L
$CaCl_2 * 2H_2O$	1	g/L
$FeSO_4 * 7H_2O$	1	g/L
$ZnSO_4 * 7H_2O$	0.1	g/L
$MnCl_2 * H_2O$	0.03	g/L
H_3BO_3	0.3	g/L
$CoCl_2 * 6H_2O$	0.2	g/L
$NiCl_2 6H_2O$	0.01	g/L
$Na_2MoO_4 * 2H_2O$	0.03	g/L
Na_2SeO_3	0.03	g/L

From all those studies, the wastewater composition used for the experimentation has been extracted and it is reported in Table 6. The synthetic wastewater is principally composed of nutrients which are extremely fundamental for feeding the reactor and let the biological processes happen. Then the addition of micronutrients enhanced the growth of the biofilm.

Table 7 – Synthetic wastewater composition used for the semi-continuous mode

Chemical compound	Amount	U.M.
$MgSO_4 * 7H_2O$	0.06	g/L
$FeSO_4 * 7H_2O$	0.01546	g/L
$ZnSO_2 * 7H_2O$	0.00414	g/L
$MnSO_4 * 7H_2O$	0.00244	g/L
$CaCl_2 * 2H_2O$	0.01632	g/L

The micronutrients were introduced in a Becher of 1 L of volume to create a unique stock solution. The preparation of the synthetic wastewater consisted in solution composed of 20 L of distilled water, nutrients and micronutrients in a

concentration equal to 5 mL/L, taken from the stock solution. Therefore, the concentration of nutrients was variable during all the experimentation, since it was necessary to try different C/N ratio to find the most efficient one for the attached biomass development. The following table shows the concentration of nutrients used for the first part of the experimentation with the semi-continuous mode with a C/N ratio equal to 5.

Table 8 – concentration of nutrients with C/N ratio equal to 5

Chemical compound	Amount	U.M.
$CH_3COOH * 3H_2O$	0.9526	g/L
$(NH_4)_2HPO_4$	0.1576	g/L

5.2. Phase Two: intermediate phase

The intermediate phase started involuntarily on July the 16th because a problem with the reactor occurred. The pressure sensor detected a dangerous variation of pressure inside the membrane, and it detached, which consequently caused the reactor to empty. Therefore, this technical issue resulted in the loss of part of the biomass attached to the membrane's fibre and for this reason the semi-continuous mode ended in favour of a batch mode. The reactor has been inoculated again, and more nutrients were added to guarantee new feed and bacteria. The purpose of this phase was the refurbishment of the biofilm and the monitoring of the biological activity which decreased a lot its efficiency. Indeed, even though the nutrients removal efficiency decreased, the reactor was still unstable and for this period, the C/N ratio was lowered from 5 to 4 for the compliance with the literature values.

Another challenge of this phase was the closure of the Polytechnic of Turin, and its laboratories, for the Italian summer holydays. The closure period lasted from August the 9th to August the 20th and the reactor needed to be prepared to guarantee the survival of the microorganisms and their proliferation. For the three days before the closure, the reactor has been fed daily considering a C/N ratio equal to 4 and the mass of nutrients is defined in the following table.

Table 9 – concentration of nutrients used for the preparation of the reactor

Chemical compound	Amount	U.M.
$CH_3COOH * 3H_2O$	0.7659	g/L
$(NH_4)_2HPO_4$	0.1576	g/L

For the last day before the vacation, the concentration of Sodium acetate and Diammonium hydrogen phosphate (DAP) remain the same, but the mass has been quintuplicated. The nutrients overload has been done to guarantee the biofilm growth during the period in which the reactor was not physically reachable. The other parameters of the reactor configuration have been checked, indeed it was extremely important to ensure the air feeding of the reactor and to do so the inlet gas meter has been set to 100 NmL/h while the outlet gas meter air flow was at maximum 250 NmL/h.

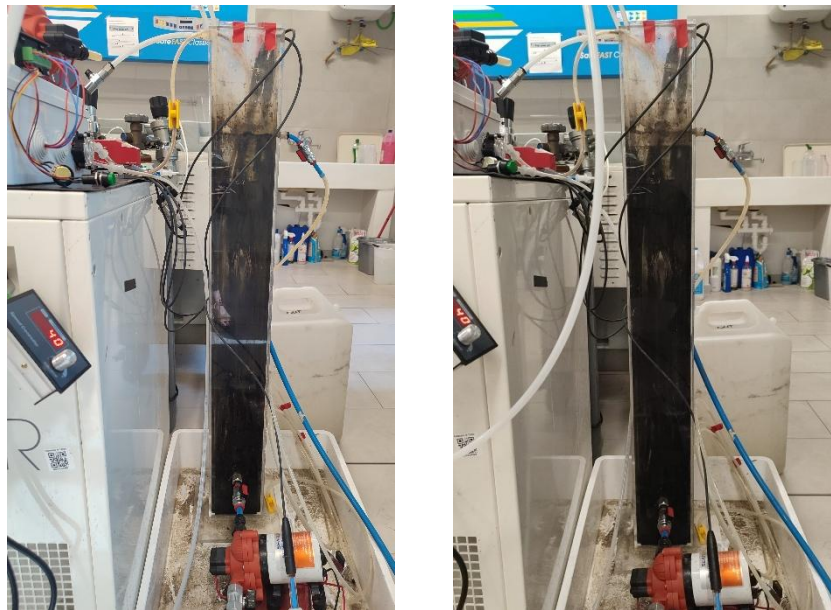


Figure 14 – comparison of the reactor before and after the closure August the 8th (left) and August the 20th (right)

As show in Fig. 14 the comparison between the two stages of the reactor is not easily comprehensible. The image on the left presents the reactor before the overloading of nutrients, while the picture on the right displays the reactor after the Holydays period and even though the growth of the biofilm is not appreciable from the images, the performance of the reactor stayed constant and the reactor worked correctly during the closure period.

Another subphase lasted till September the 1st. The reactor has been emptied and then filled with new wastewater with the same C/N ratio equal to 4. This procedure was necessary since the pH was too elevated and it could have been not advantageous for the microbial activities. The reactor has been kept into a batch mode, since it was important to improve its performance that were still unstable.

5.3. Phase Three: optimisation of the reactor parameters and improve of the removal efficiency.

Phase Three has been extremely crucial for the optimisation of the reactor parameters, the improvement of the Oxygen Transfer Rate (OTR) and the enhance of the nitrification and NH_4^+ removal efficiency. The issues caused by the problematics presented in the previous paragraph, considerably stressed the reactor and the microorganism communities. The consequences can be noticed in the removal efficiency, since the nitrification rate was unstable and the amount of ammonium in the reactor was still high. The analyses have been daily conducted: samples were extracted from the reactor and gases collected in gas bags were analysed through the gas chromatograph. The reactor was still connected trough sensor and Arduin system to a Matlab code that permitted to collect daily data inside a file Excel. The code registered the values of the ORP, the Dissolved Oxygen, the pH, the inlet pressure, the outlet pressure, the inlet air flow rate and the outlet air flow rate every 1.5 seconds or 2 seconds, it depended on the sensors. Those data will be used for the analyses, and the results will be discussed in the following chapter.

This phase is characterised by a trial and errors procedure, necessary to find the optimal conditions. Initially, the reactor has been half emptied on August 27th, and the water inside has been replaced with new synthetic wastewater. In this case the ratio between the carbon and ammonium has been maintained consistent with the previous experimentation but since the reactor needed nutrients the concentration of both sodium acetate trihydrate and DAP have been doubled. The results of the analyses showed immediately that the concentration of $N - NH_4^+$ was too high and the rate of removal was slow. However, the removal of COD was efficient, and the concentration of the acetate decreased with a percentage removal that ranges from 31.9 % to 78.8 %, computed from addition of nutrients to the subsequent addition of nutrients. Considering this condition, in which the reactor showed acceptable rate of removal of COD but issues with the removal of ammonium, it has been decided to add only sources of COD to replenish the lack. The COD has been added in the following days, with the reported masses:

- 6 g of sodium acetate trihydrate on September the 2nd,
- 3 g of sodium acetate trihydrate on September the 3rd,
- 2 g of sodium acetate trihydrate on September the 5th,
- 2 g of sodium acetate trihydrate on September the 9th,
- 2 g of sodium acetate trihydrate on September the 11th,
- 1 g of sodium acetate trihydrate on September the 26th.

These measures allowed the decrease of nitrogen, but it was important to evaluate also the other operational parameters: the ORP, the pH and the OTR. This phase, with the discontinuous addition of COD sources, was not advantageous for the operational condition. The addition of acetate increased the denitrifies activity at the expense of the nitrification, this condition has been evaluated trough different factors:

- the ORP which was extremely negative with values under -400 mV, which stands for an anaerobic water medium,
- the high concentration of $N - NH_4^+$ in the water medium,
- the production of methane, through methanogenesis inside the reactor. The biological methane production is a process that must be conducted under anaerobic conditions.

Another problem has been found in the pH which was almost equal to 9. In fact, the elevated pH likely reflects chemical or biological processes in the reactor, possibly related to the degradation of organic matter and nitrogen compounds. For this reason, it was decided to replace the synthetic wastewater in the reactor to lower the pH and raise the ORP. Concerning the OTR analyses, this period was crucial because it was noticeable that the addition of COD in the reactor resulted in a decrease the inlet gas flow.

For this purpose, the composition of the wastewater has been modified, and the new composition is shown in the Table 10.

Table 10 – wastewater composition with ratio

Chemical compound	Amount	U.M.
$CH_3COOH * 3H_2O$	0.0324	g/L
$(NH_4)_2HPO_4$	0.144	g/L

The C/N ratio was equal to 0.31, which is extremely low compared to conventional values reported in the literature. This low C/N was chosen to enhance ammonium removal in the reactor by promoting nitrification under limited organic carbon conditions, rather than by increasing aeration, which could have affected the overall process balance. The concentration shown in Table 10, allowed the introduction in the reactor of almost 38 ppm of NH_4^+ and in this way it was possible to better monitor the daily and weekly removal. Indeed, when the concentration of $N - NH_4^+$ inside the reactor was under a certain threshold, lower than 25 ppm, more nutrients were added in order to reach again the concentration of 38 ppm. The nutrients ratio has not been kept constant, but it was gradually raised to reach a C/N value equal to 3 under stable conditions.

The results obtained will be later exploited in the following chapters of this master thesis.

5.4. CAS setup

To determine the activity of the microorganisms respirometry tests have been conducted simultaneously to MABR's phase three, through a Conventional Activated Sludge reactor. The reactor configuration consisted in a Becher of 2L capacity filled with 1L of activated secondary sludge, a constant source of aeration supplied by an aeration pump placed inside the reactor, a pH sensor and a DO sensor. To avoid the sedimentation of the suspended solids, a constant mixing was provided from a magnetic stirrer which unfortunately resulted in an unstable system.

The data related to this reactor have been collected with the same Matlab code of the Phase three, the values considered were pH and DO. The dissolved oxygen trend has certainly been a crucial parameter for the respirometry test. The experimentation consisted in the instauration of different cycles:

- Introduction of a source of COD,
- Analysis of the DO curve.

Right after the injection of the nutrient, the DO inside the reactor rapidly decreased to reach a stability where the aeration and the endogenous respiration stayed in equilibrium till the total consume of the acetate and then the profile of oxygen increased to reach again the stability at 8 ppm of DO, which is the typical value of equilibrium of DO in a water medium in contact with the external environment.

The analyses have been effectuated with a Python code which took in input the profile of oxygen, computed the total time during which the cycle run and determined the area over the curve from the cycle starting point, identified at the end of the stability, to the cycle ending point, represented from the start of the stability after the decrease.

CHAPTER 6

RESULT ANALYSES

This chapter of master thesis presents and discusses the results obtained from the laboratory analyses, focusing on the purposes of each experimental phase. As already described in the previous chapter, the laboratory period is divided in three phases is representative for a specific goal:

- Phase One: inoculation and biofilm growth,
- Phase Two: intermediate phase that faced the Italian summer holidays closure,
- Phase Three: optimisation of the nitrification rate and maximisation of the Oxygen Transfer Rate.

6.1. Phase One results analysis.

The main purpose of this phase is the development of the biofilm. This is the most complicated and delicate stage, since the high instability of the reactor which still does not constitute the optimal environmental condition for the microorganisms. The progression of the attached biomass was registered through pictures, representative for this initial period and the results are shown in Fig. 15.

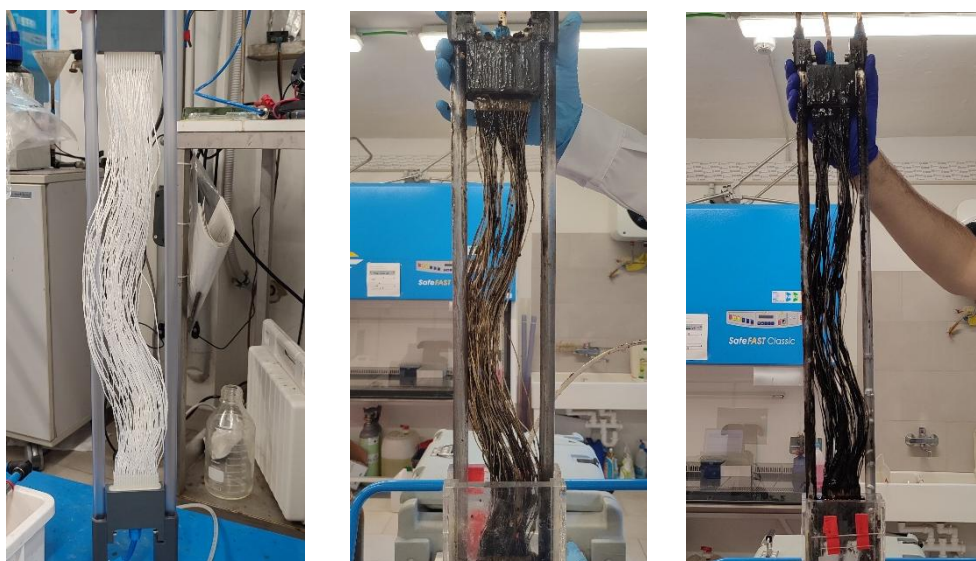


Figure 15 – progression of the biofilm growth. May the 6th (left), May the 15th (middle) and June the 16th (right)

From Fig. 15 is immediately noticeable the effectiveness of the biological processes. The experimental phase started in a batch mode with a new and clean hollow fibre membrane installed on May the 6th and just ten days later, on May the 15th, microorganisms were attached to the module. Since the obtained results were good, the same conditions have been maintained. The reactor was fed with nutrients to enhance and at end of this phase, on June the 16th, it was possible to observe the formation of a thin strata of biofilm in certain area of the membrane. It was recognizable, since there were some regions in which microorganisms were trapped in gel-like strata, immediately observable. However, the biofilm present in the reactor was still not enough to guarantee efficient biological activity and nutrients removal.

The high instability of this phase can be demonstrated through the analysis carried on the concentration of nitrogen-species and COD inside the reactor. The study of the amount of nutrients has been carried out on a daily basis: samples were taken from the bottom outlet of the reactor and analysed with the COD photometer, the spectrophotometer for the NH_4^+ concentration, and the IC for the detection of nitrites and nitrates. To determine the Total Nitrogen (TN) inside the reactor, it was important to compute the concentration of nitrogen in the ammonium, nitrites and nitrates. To do this, the following consideration were applied:

- $N - NH_4^+$ corresponds to the 77.79 % of the total molecular weight of the ammonium,
- $N - NO_3^-$ corresponds to the 22.59 % of the total molecular weight of the nitrates,
- $N - NO_2^-$ corresponds to the 30.45 % of the total molecular weight of the nitrites.

Table 11 illustrates the results of the laboratory analyses. The inoculum has been added on May the 5th and on May the 15th whereas nutrients were supplied on May the 5th, on May the 20th, on June the 3rd, on June the 9th and on June the 13th.

Table 11 – laboratory results for the start-up phase

Date	$N - NH_4^+$	$N - NO_2^-$	$N - NO_3^-$	COD
	[ppm]	[ppm]	[ppm]	[ppm]
5-May	14,15	0,65	0,39	152
6-May	36,45	0,66	0,39	337
7-May	91,45	0,84	0,35	251
8-May	54,64	1,21	0,36	193
9-May	72,32	1,49	0,36	146,5
12-May	21,74	1,49	0,36	369,5

14-May	103,36	1,60	0,37	298
15-May	78,68	1,60	0,37	334,5
19-May	56,86	1,19	0,17	107
20-May	157,30	0,63	0,40	151,5
21-May	170,95	0,35	0,38	421
23-May	120,86	0,36	0,41	359,5
26-May	109,26	0,82	0,37	260,5
27-May	104,15	0,83	0,37	168
28-May	117,42	2,05	0,62	145,5
29-May	133,41	2,02	0,32	116
30-May	132,84	1,90	0,49	74,5
3-Jun	126,79	0,47	0,77	56
5-Jun	66,74	0,57	1,67	390,5
9-Jun	60,35	1,48	0,13	75
11-Jun	57,60	1,70	0,04	568,5
12-Jun	42,61	1,87	0	462
13-Jun	43,16	1,84	0	447

The previous table and Fig. 16 demonstrate the instability of the reactor during the start-up phase. Indeed, both concentration trends present peaks or unexpected increases even not right after the addition of new nutrients or inoculum. The obtained data enable some considerations on the reactor performances. The trend's irregularities can be caused by several factors:

- The instability of biological processes since the microbial communities are still in phase of development and growth,
- The progression of the biofilm growth is in an initial stage and still not stratified. Hence, the biological speciation of the microorganisms is not precisely organised in strata, as MABR requires.
- The possibility of apparent removal during the start-up phase, especially for the COD. It could happen that only a part of the COD is consumed to produce the biomass whereas the other amount is trapped on the microorganisms through adsorption mechanisms. The COD is lately released in the water medium, and this implies an unexpected concentration increase in the wastewater samples.

The fluctuations in concentration are particularly evident for the COD vales; notably, towards the final stage of the inoculation period the ammonium removal rate was still unstable, as plotted in Fig. 16. However, during this final period the ammonium concentration started lowering, without any other peaks.

For the regularisation of the nutrient's addition and the monitoring of the main parameters, the reactor has been switched to the semi-continuous subphase, which will be meticulously examined in the following paragraph.

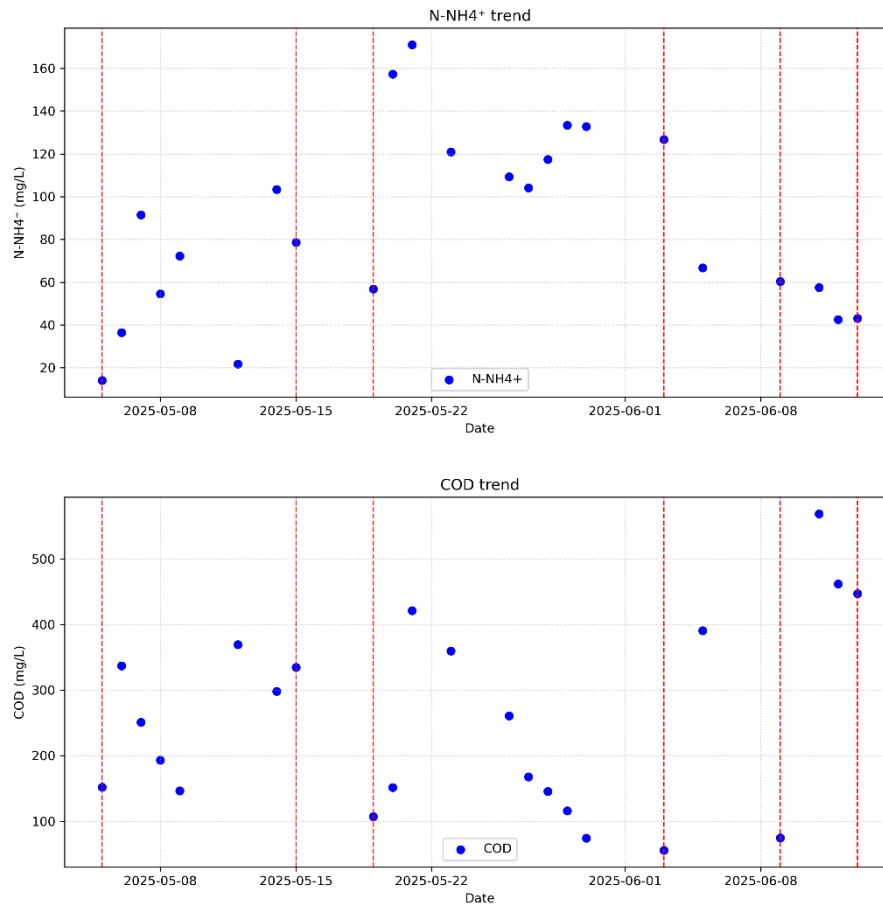


Figure 16 – trend of $N - NH_4^+$ concentration (top), trend of COD concentration (bottom). The dashed lines represent the addition of nutrients

6.1.1. Semi-continuous subphase

The switch to the semi-continuous mode determined a much stable conditions inside the reactor, with respect to the previous subphase. The aim of this stage coincided with the one of the previous subphase: the growth of the biofilm and the development of stratified microbial communities. The operational conditions of the semi-continuous mode, already exploited in Chapter 5, enabled the instauration of a dynamic equilibrium between the inlet and the outlet. Moreover, the addition of nutrients became more standardized and therefore also the amount of nitrogen and COD does not present unexpected peaks.

During this phase, samples were taken both from the inlet tank and from the outlet, then laboratory analyses were applied to determine the concentration of COD, NH_4^+ , NO_3^- , NO_2^- and TOC. On average, during the semi-continuous subphase, the measured concentrations are equal to:

- 195.2 ppm of COD in the inlet,
- 36.5 ppm of $N - NH_4^+$ in the inlet,
- 89.1 ppm of COD in outlet,
- 34.2 ppm of $N - NH_4^+$ in the outlet.

With respective average removal efficiency:

- 58.3 % removal efficiency of the COD,
- 10.9 % removal efficiency of $N - NH_4^+$,

From this data is already noticeable that the removal of COD is quite high, reaching almost 90%, while the removal of $N - NH_4^+$ is still not consistent with the literature removal efficiency.

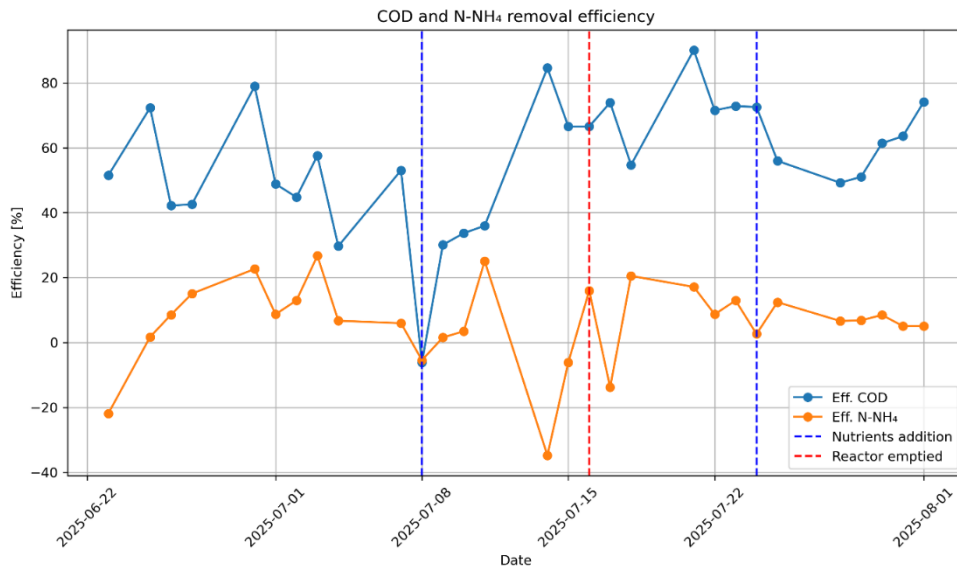


Figure 17 – removal efficiency of COD and $N - NH_4^+$

Fig. 17 shows the removal efficiency related to the COD and $N - NH_4^+$ concentration. The efficiencies are computed as follows:

$$\eta = \frac{[COD]_{IN} - [COD]_{OUT}}{[COD]_{IN}} * 100 \quad \text{Equazione 7}$$

$$\eta = \frac{[N-NH_4^+]_{IN} - [N-NH_4^+]_{OUT}}{[N-NH_4^+]_{IN}} * 100 \quad \text{Equazione 8}$$

The graph demonstrates the hypotheses; hence, the removal of COD is remarkably higher than the removal of $N - NH_4^+$ and on average the removal of COD is equal to 56% with peaks of 90%. The results from IC analysis showed no detectable nitrate accumulation. This may indicate that either nitrate formation was negligible due to weak nitrification, or that any formed nitrates were rapidly reduced. Consequently, the observed COD removal cannot be directly attributed to denitrification but is likely due to other metabolic processes in the reactor. The plot showed in Fig. 17 has three dashed lines: the blue lines correspond to the change of the wastewater composition while the red line highlights the day during which the reactor has emptied. Immediately following the change in wastewater composition, COD removal efficiency decreased, which could be explained by the presence of residual nutrient concentrations in the reactor.

6.2. Phase two: intermediate phase

Phase two became crucial for the biofilm growth and the survival of the microorganisms' communities. For the analysis results, this phase has been divided into three separate cycles, aiming to better understand the operational performance of the reactor during the closure period.

As already described in the previous chapter, the reactor needed to be prepared for the department closure. Hence, the main goal was the overloading of nutrients to have alimentation even during the unmonitored days. Throughout this stage, it was impossible to collect the exhaust gases and by consequence the computation of the OTR. Indeed, the main analysis carried on are only related to the COD and $N - NH_4^+$, to evaluate the removal rates. The operational conditions of the reactor are evaluated through the data registered by the sensors, mainly ORP, pH and gas flow difference. In the following paragraph, the three steps will be exploited

6.2.1 Phase Two: reactor's preparation

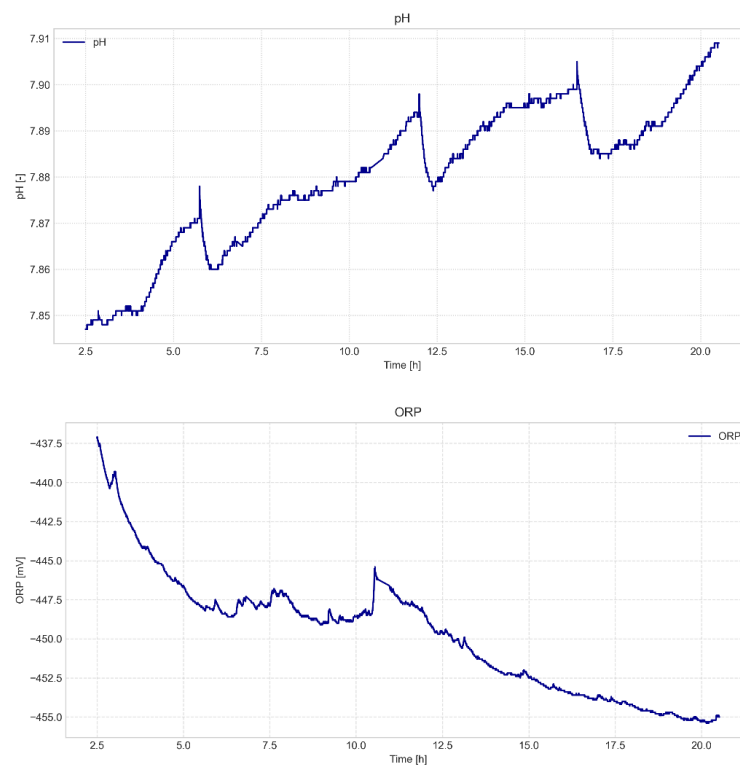
Considering what already outlined in Chapter 5, this passage was necessary to adapt the reactor to batch mode. The preparation consisted in the daily addition of nutrients with a C/N ratio of 4. The principal data obtained are the concentration of COD and $N - NH_4^+$, from samples of the water medium taken at the bottom outlet of the reactor.

Concerning the nutrients, as showed in Table 12, it is difficult to evidence the removal rate specifically because the nutrients were added daily and the microorganisms did not have enough time to adjust to the new conditions and start operating efficiently again.

Table 12 - $N - NH_4^+$ and COD concentrations during phase two – reactor's preparation

Date	$N - NH_4^+$	COD
	[ppm]	[ppm]
6 - Aug	35.91	84.5
7 - Aug	62.90	142
8 - Aug	90.81	222.5

The plots below illustrate the pH, ORP and the flow difference trends. All the plots have the time in hours on the y axis.



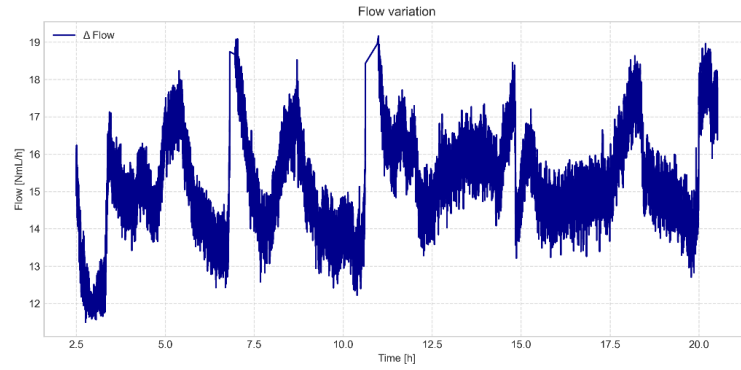


Figure 18 – pH, ORP and flow difference variation of phase two – reactor's preparation

As observed in Fig. 18, it is possible to notice that the increasing concentration of nutrients effects the operational parameters of the reactor. Indeed, it is evident the variation of pH and ORP.

As expected, the ORP profile shows a decrease since the addition of a source of COD entails its oxidation through the dissolved oxygen and it results in the instauration of a reducing environment. These conditions effect also the biofilm because a low value of ORP is advantageous of the denitrification part of the SND biological process. The pH increase is always related to the denitrification process; indeed, when the acetate is used to produce more biomass, it determines a decrease of the pH since the reaction develops acids, that can release H^+ ions. However, when the source of COD it is consumed for the denitrification, the reaction consumes H^+ resulting in a more basic pH condition.

The last plot figures the gas flow difference. It is computed as difference between the inlet air flux and the outlet air flux. Generally, a high difference can be translated with an effective microbial activity and a good rate of nitrification while a low difference means that the oxygen is not diffusing correctly through the biofilm. This value will be important in the further phase.

6.2.2 Phase Two: holyday period

Throughout this subphase the reactor has been left not monitored for 12 days, even though it was still attached to the sensors that allow the collection of the principal parameters. The removal rate of this period can be computed but before it was necessary to estimate the theoretical initial concentration, considering the final concentration of the previous subphase.

The NH_4^+ is computed as follows:

$$C_{NH_4^+} = C_{0,NH_4^+} + \left(\frac{M_{DAP} * \frac{MM_{NH_4^+}}{MM_{DAP}}}{V_R} \right) [ppm] \quad \text{Equazione 9}$$

While the concentration of COD is evaluated through the demand of oxidation needed to oxidise the acetate:

$$COD_{th} = \frac{MM_{O_2}}{MM_{acetate}} [ppm] \quad \text{Equation 10}$$

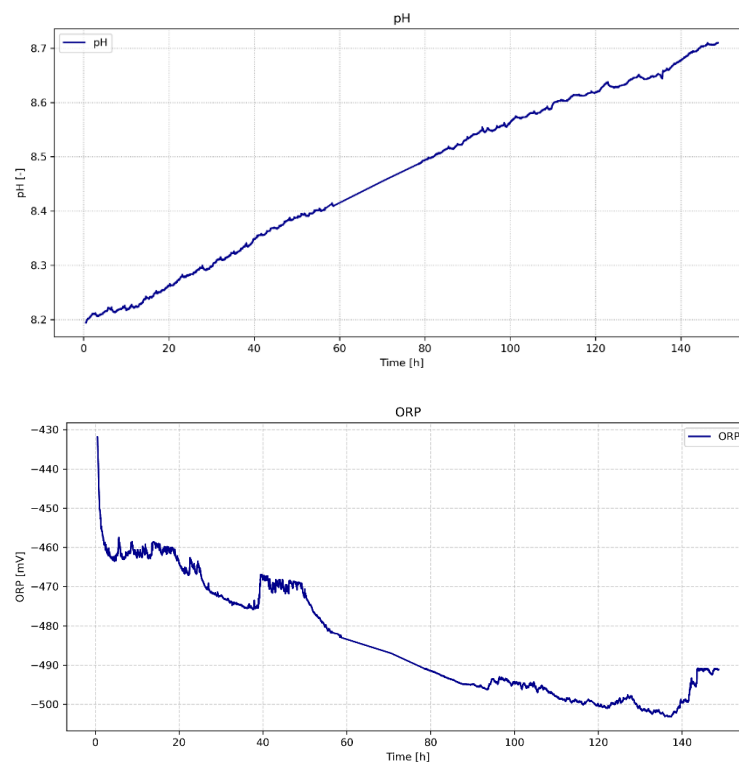
$$COD = COD_0 + \frac{COD_{th} * m_{acetate}}{V_R} [ppm] \quad \text{Equation 11}$$

As a result, the concentration right before the closure and the concentration right after are listed below in Table 13:

Table 13 - $N - NH_4^+$ and COD concentrations during phase two – holyday period

Date	$N - NH_4^+$	COD
	[ppm]	[ppm]
8 - Aug	258.1	2002.4
20 - Aug	174.8	81.5

The removal rate can be computed, and it is immediately noticeable that the removal of COD was high. Hence, the removal rate of the COD is equal to 6.67 ppm/h and the efficiency corresponds to 95.9%. However, the removal of nitrogen as effective as the COD. The removal rate was equal to 0.23 ppm/h and efficiency was 32.2%. Those data demonstrate that the nitrification part of the biological process is still not efficient as expected.



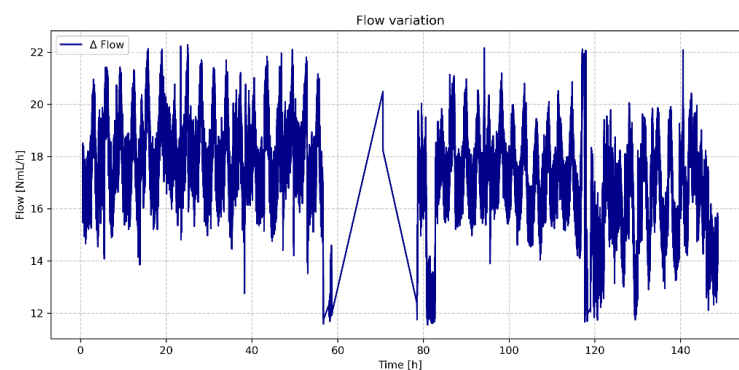
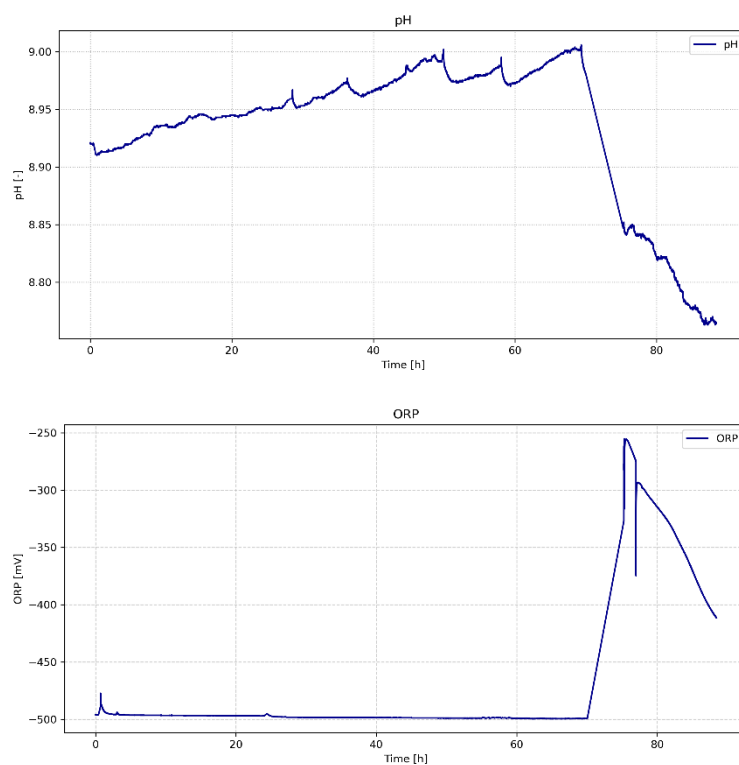


Figure 19 – pH, ORP and flow difference variation of phase two – holyday period

As the previous subphase, Fig. 19 illustrates the increase of pH and the decrease of the ORP, while on average the gas flow difference is a little bit higher, meaning a more homogenous diffusion through the biofilm.

6.2.3 Phase Two: post-holyday period

As phase two – holyday period, the ORP was highly negative and the pH was increasing, and Fig. 20 showed the trend of this period.



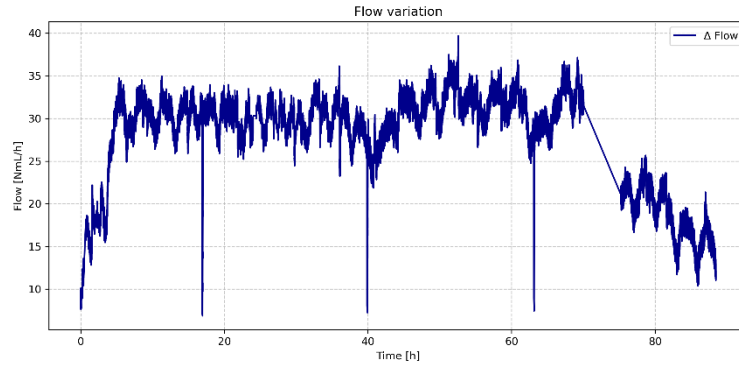


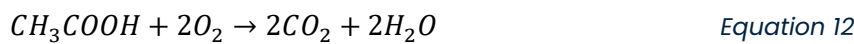
Figure 20 – pH, ORP and flow difference variation of phase two – post-holyday period

The sudden decrease of the pH and the increase of the ORP is determined from the replace of the water medium inside the reactor, necessary to start the optimisation phase.

6.3. Phase Three: optimisation of the parameters

The aim of the experimentation is the maximisation of the OTR and OTE and the improvement of the nitrification toward all the phase, considering different COD/N ratio. Due to some issues related to the instrumentation, it was not possible to measure the COD but instead the evaluation of the removal will be carried out through the TOC. The TOC measures the concentration of Total Organic Carbon present in the water medium. To be consistent with the previous data the TOC is converted into COD, thanks to the calculations below.

It is necessary to consider the reaction:



$$COD_{th} = TOC * \frac{32 \frac{g_{O_2}}{mol}}{12 \frac{g_{C}}{mol}} = TOC * 2.67 \quad [ppm] \quad \text{Equation 13}$$

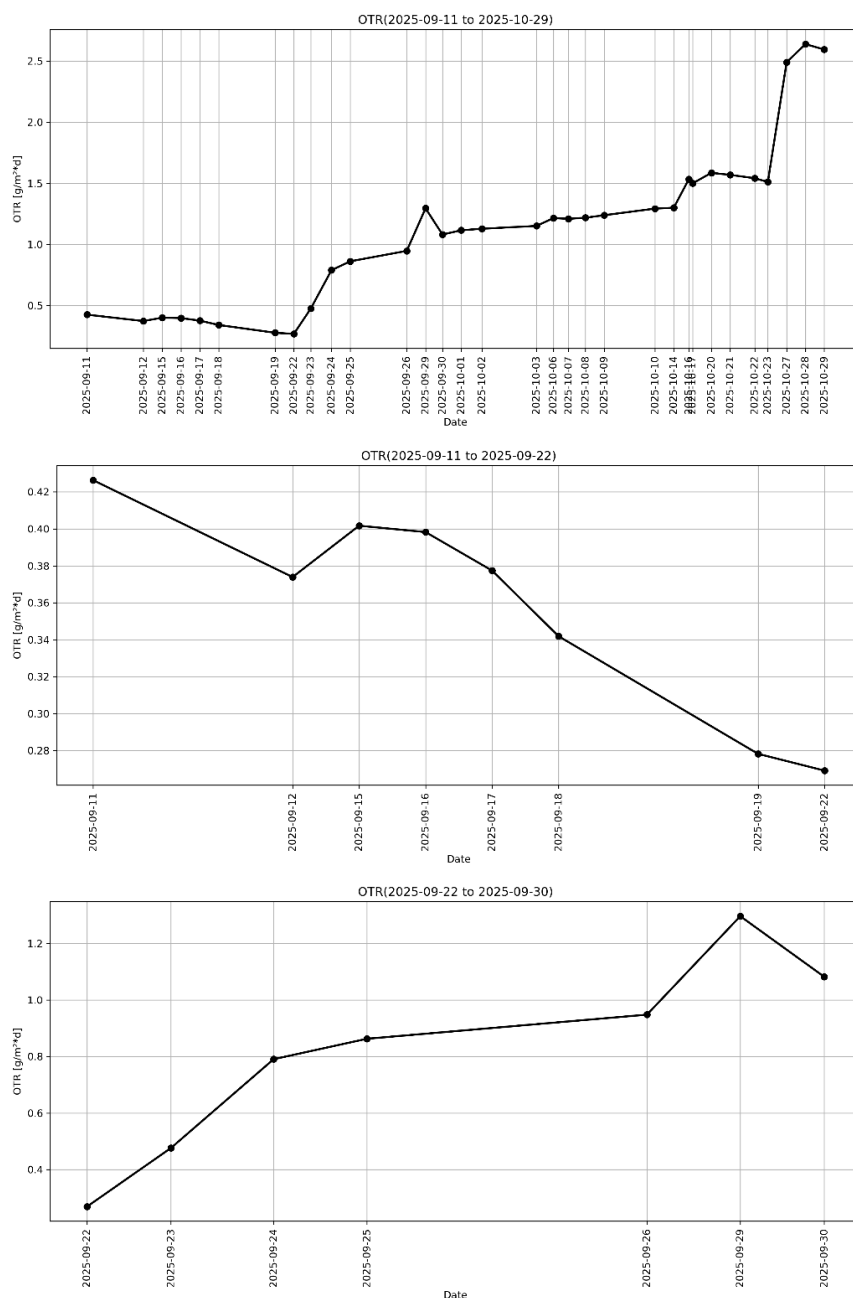
This experimentation has been split into different subphases related predominantly to the change of the COD/N ratio which varied from 0.5 to 2.5. However, the first and second subphases were evaluated primarily to understand the any residual issues from the intermediate phase. Below are listed the temporal window considered:

- Subphase 1: from September the 11th to September the 22nd,
- Subphase 2: from September the 23rd to September the 30th,
- Subphase 3: from October the 1st to October the 7th,
- Subphase 4: from October the 8th to October the 15th,
- Subphase 5: from October the 16th to October the 24th,
- Subphase 6: from October the 25th to October the 27th

- Subphase 7: from October the 28th to October the 30th.

The data of the inlet and outlet flow rate and the composition of both the inlet air and the exhaust gases are needed for the determination of the OTR and OTE. The OTR corresponds to the velocity at which the oxygen is transferred from a gaseous medium to a liquid medium. For a MABR reactor is a fundamental parameter since it allows to understand how the oxygen is moved through the membrane. The values of the OTR are influenced by the configuration of the gas meter: indeed; increasing both the inlet and the outlet air determine an increase of the OTR whereas the OTE decreases with this trend [18].

The following images in Fig. 21 illustrate the results obtained with the monitoring of the OTR during all the phases.



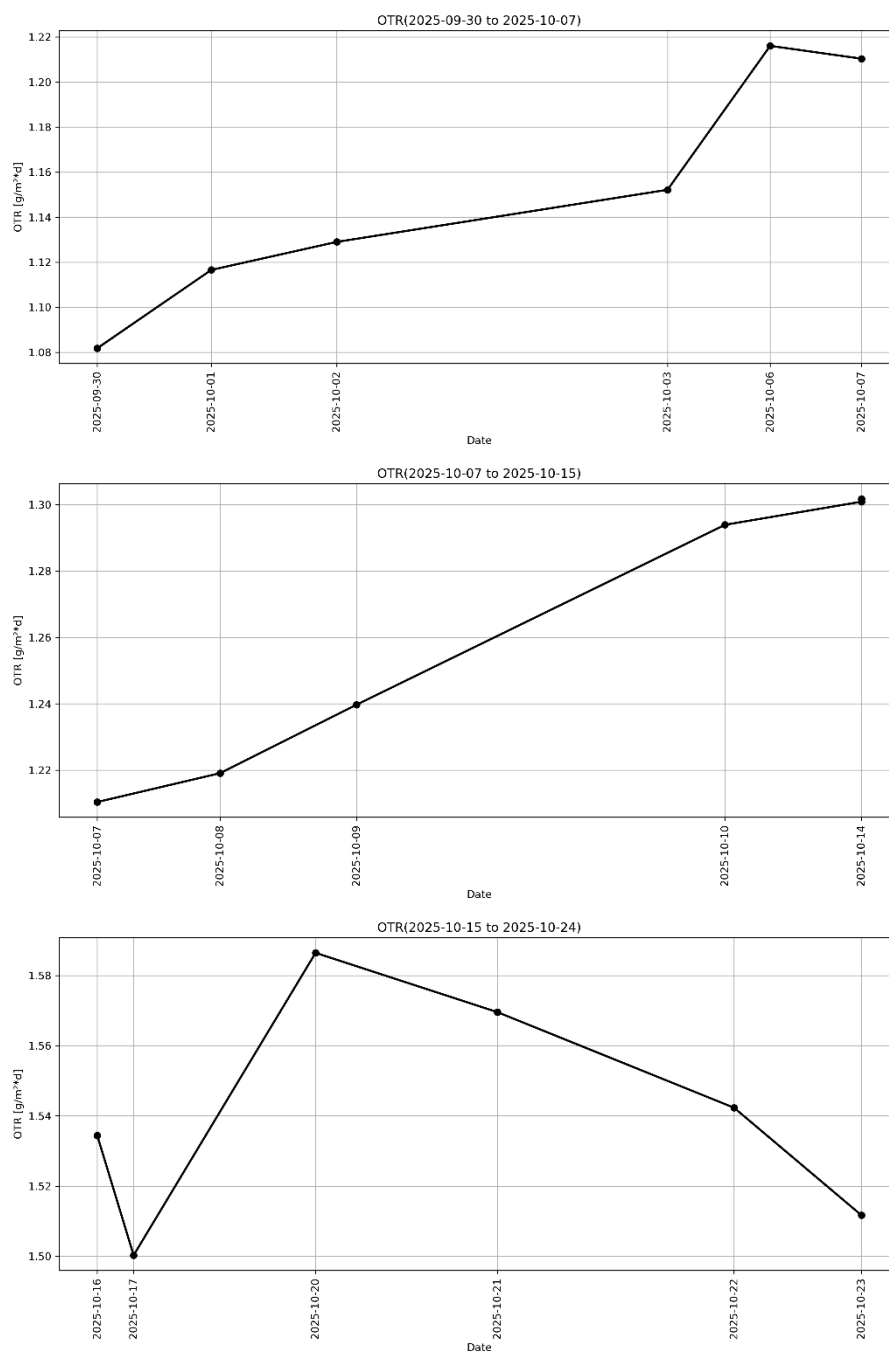


Figure 21 – graphical representation of the OTR. A) OTR of the all period. B) OTR of subphase 1. C) OTR of subphase 2. D) OTR of subphase 3. E) OTR of subphase 4. F) OTR of subphase 5

The figures above are all plotted with the same structure: the x-axis represents the date during which the file excel have run and the y-axis shows the OTR in $\frac{g_{O_2}}{d \cdot m^2}$. These graphs have been constructed thank to a Python code which computes the OTR with this equation, considering the oxygen consumed inside the reactor:

$$OTR = \frac{Q_{IN} \cdot O_2^{IN} - Q_{OUT} \cdot O_2^{OUT}}{A_M} \left[\frac{gO_2}{d \cdot m^2} \right] \quad \text{Equation 14}$$

Fig. 21.a is representative of all the phase three, it is immediately noticeable that after the intermediate phase the OTR has decreased reaching its lowest values – related to all the experimentations. For the maximisation, it was important to understand which conditions were not appropriate. After the analyses of gas flow difference, it was evident that the addition of acetate decreased the inlet flow. However, there were also some other evidences that the system was not still working well.

- Subphase 1, showed in Fig. 21.b, started after the addition of 3 g of COD source into the reactor and the OTR decreased almost constantly. The inversion of the trend is due to the addition of the 10% of the inoculum into the reactor, to stimulate the microorganism communities.
- Subphase 2, showed in Fig. 21.c, figures an increase. This part of the experimentation foresaw the monitoring of the COD introduction. Indeed, only 1 g was added.
- Subphase 3, showed in Fig. 21.d, it was crucial for the maximisation of the OTR and the improvement of the removal efficiencies. The water medium inside the reactor was replaced with new synthetic wastewater since the pH was too high and the ORP was too negative, a value representative for a very reducing environment, not advantageous for the nitrification and the development of the nitrifiers. Moreover, also the addition of the nutrients was monitored because the COD/N ratio was reduced to 0.5.
- Subphase 4, showed in Fig. 21.e, is representative for a COD/N equal to 1 but still demonstrate that the controlled increment of nutrients is fundamental for helping the stabilisation of the reactor.
- Subphase 5, showed in Fig. 21.f, is representative for a COD/N equal to 1.5. but still demonstrate that the controlled increment of nutrients is fundamental for helping the stabilisation of the reactor.
- Subphase 6, showed in Fig. 21.g, presents a COD/N ratio equal to 2.
- Subphase 7 is not showed in the figures, due to the lack of values, but from Fig. 21.a it is possible to highlight that the OTR reached its highest value from the start of the experimentation.

There are several possibilities that can translate the reduction of the OTR. It was important to understand why the addition of COD source was so negatively impacting on the system. During the intermediate phase the reactor has been subjected to different form of stress and the overloading of the nutrients may have stimulated the uncontrolled growth of the biofilm, creating a substrate constituted by EPS. In literature has been studied that the fouling of the membrane could decrease both the OTR and OTE efficiency [26]. The biological matter, coming from the secretion and the death of the microbial communities,

enters inside the pores of the membrane resulting in lower diffusion through the module. During the experimentation, the change of the wastewater between the Subphase 2 and the Subphase 3, removed part of the suspended solids in the water medium allowing the membrane to clean itself and to discharge some of the materials that causes fouling. The outcome was an almost instant increase of the OTR, even though it needed a stabilisation. To reach this effect, monitoring the COD/N ratio was important. Indeed, the gradually addition of acetate with ratios lower than the previous experimentation could have determined the stabilisation of the biofilm and by consequence the almost linear increase of the Oxygen Transfer Rate. For all this phase, the inlet flow rate and the outlet flow rate were respectively set to 250 NmL/h and 100 NmL/h, adjusting the inlet at higher values might have increased the OTR value, but at the expense of the OTE.

The OTE has been investigated towards phase three. As the OTR, it was unexpectedly at low values, in a range between 5% - 10%, meaning that the oxygen is not efficiently consumed. As before, the gradual addition of nutrients, allowed a more controlled consumption of the oxygen and at the end of the Subphase 7 the OTE reached almost the 70%.

Another factor that was hampering the system is highlighted by the high rate of denitrification at the expense of the nitrification. This could be highlighted by the much negative value of ORP that installed very anaerobic conditions that were impacting the stratification and the growth of nitrifiers. The COD/N ratio was also useful to monitor the effectiveness of the nitrification and the ammonium removal. Inside the subphases, it is possible to identifies different cycles with the introduction of new nutrients. The plot below illustrates the removal efficiencies of both COD and $N - NH_4^+$.

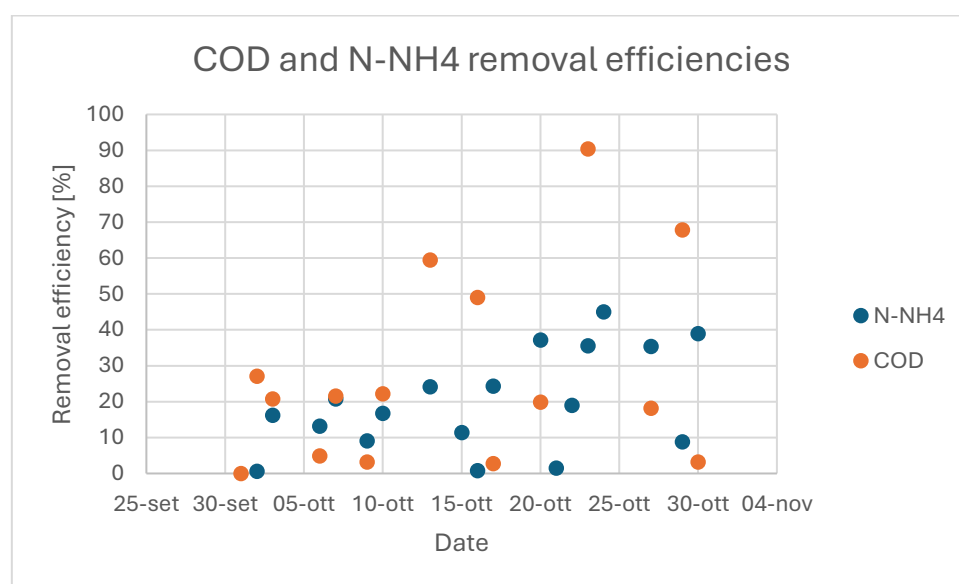


Figure 22 – COD and $N - NH_4^+$ removal efficiencies

It is clearly noticeable that the removal presents an increasing trend during the experimentation. Generally, the removal of the nitrogen ammonium was always under 50% while the COD removal reaches peaks of 80%.

The subphase can be divided into cycles due to the addition of nutrients. The nutrients were added when the concentration of $N - NH_4^+$ was equal or under 20 ppm in the water medium. The new nutrients allowed to reach again the initial concentration of $N - NH_4^+$ of 38 ppm, with the desired COD/N.

Table 14 $N - NH_4^+$ removal of each COD/N cycle

ID	$\frac{COD}{N}$	$N - NH_4^+$ removal [%]	Days
Subphase 3	0.5	42.75	6
Subphase 4	1	64.04	7
Subphase 5	1.5	82.05	5
Subphase 6	2	45.09	4
Subphase 7	2.5	55.71	4

Table 14 defined the removal efficiency, for a batch mode reactor, is surely dependent on the time. Indeed, it is possible to observe that lower values of COD/N slowed the nitrogen removal and the removal of the 40% is reached after 6 days. However, a higher COD/N ratio allows a 45% decrease of ammonium in 4 days. These considerations are consistent with the literature where higher ratio determines higher removal ^[27].

In conclusion, with phase three the purposes of the experimentation were achieved, and the reactor reached a good level of stability.

CHAPTER 7

CRITICALITIES, FUTURE DEVELOPMENTS AND CONCLUSIONS

To conclude, the present master's thesis has highlighted the potential of the MAMB reactor. Even at the laboratory scale, the reactor proves to be an excellent and viable alternative to conventional systems. Owing to its capability of perform both nitrification and denitrification in the same liquid medium, it can be distinguished from classical reactor configuration, already applied in the wastewater treatment sector. The necessity of performing SND represents a crucial aspect for this reactor, since its capability remove nitrogen with high efficiencies, complying to the updated environmental legislation to prevent eutrophication from treated wastewater discharge in water bodies.

However, the development of MABR reactor also present its difficulties since the biological processes are effective thanks to the biofilm. The purpose of the thesis was the configuration, the start-up and the optimisation of a MABR reactor in a lab-scale. The study has been divided into three different phases, each one with its main goal. Phase 1 was important for the installation of the reactor and the growth of the biofilm, after the inoculation of secondary sludge it was almost immediately observed, the microbial communities started attaching to membrane's chord. Nonetheless, the growth of an effective biofilm requires time. To achieve the main potentiality of SND, the biofilm needs also to be correctly stratified: indeed, the area near to the membrane is aerobic since it is close to the diffusion of oxygen and the nitrification occurs while the denitrification happens subsequently after the depletion of oxygen. Monitoring the development was not simple. The only way to determine whether the biofilm is forming it throughout the observation of the material attached to the membrane: the formation of a gel-like strata is representative for the biofilm. Concerning the removal efficiency of TN and COD, this phase is highly unstable and for this reason the reactor has been switched from a batch mode to a semi-continuous mode to regulate the introduction of nutrients inside the reactor. The semi-continuous mode seems to stabilise the biological processes inside the reactor. Unfortunately, any kind of stress has negative effects to the reactor due to the instability of the microbial communities at this very early stage of the reactor. Phase 2 was mandatory to guarantee the survival of the reactor during the closure period. During this phase few analyses were carried out, nevertheless the removal efficiency of both nitrogen and COD was studied. Hence, the

removal of nitrogen ammonium was equal to 0.23 ppm/d and the removal of 6.69 ppm/h, corresponding to a percentage removal of 32.2% and 95.9%. This intermediate phase strongly effected Phase 3. The goal of this experimentation was the optimisation of the Oxygen Transfer Rate and the increase of the nitrification part of the biological process. After the closure period, the reactor reached value of ORP extremely negative, damping the nitrification. Moreover, the overload of nutrients of the intermediate phase has determined an increase of secretion and dead microorganisms that constituted a form of fouling for the membrane. This type of fouling is a blockage for the oxygen transfer, since it obstacles the diffusion of the oxygen through the membrane, inhibiting the nitrification. The replace of the wastewater and the monitoring of the nutrient's addition, adding gradually acetate and DAP with an increasing COD/N ratio. This operation allowed the improvement of a better stratified biofilm and enhance the removal efficiencies of both COD and $N - NH_4^+$, reaching respectively maximum removal of almost 90% and almost 50%. After these phases the reactor achieved stable conditions, and it was ready to initialise new experimentation.

7.1. Criticalities and challenges

As is common to experimental research, laboratory activity has encountered various issues. The problematics were mainly related to the uncertainty of the biological processes, especially the liability of the development of stratified biofilm and any kind of stress can highly affect the biofilm causing a loss of attached biomass. This is what happened between Phase 1 and Phase 2, the reactor stopped working due to the issues with the pressure's sensor and the reactor suddenly emptied causing the loss of a part of the biomass. Other challenges characterised the accuracy of the research:

- Issues with calibration of the laboratory instruments,
- Fragility of the instruments and extended waiting time to achieve new instrumentation and materials,

A significant challenge in this experiment was ensuring the proper functioning and adaptation of the reactor throughout the holiday period. Hence, the reactor was not reachable for a long period and any intervention to restore its performance was not possible.

7.2. Future development

The effective potential of the MABR reactor still must be exploited. The biological process – simultaneous nitrification and denitrification and the removal of the COD – could be the basis to treat several types of wastewaters, complying with the strict legislation.

The MABR reactor has already been tested to improve the removal of contaminants in wastewater originating from the pharmaceutical industry, which is typically rich in organic substances and nutrients content. Therefore, the possibility of applying the MABR reactor to different types of pollutants – including the emerging contaminants that are currently attracting significant attention – could represent a turning point in wastewater treatment. This is because it would enable the removal of multiple contaminants within a single treatment unit, improving the sustainability of the WWTP.

List of Tables

Table 1 – typical volumetric composition (v/v %)	18
Table 2 – MABR set up parameters	19
Table 3 – nutrients amount in 3.2 L of water	20
Table 4 – synthetic wastewater composition [22]	22
Table 5 – synthetic wastewater composition [23]	22
Table 6 – synthetic wastewater composition [24]	23
Table 7 – Synthetic wastewater composition used for the semi-continuous mode	23
Table 8 – concentration of nutrients with C/N ratio equal to 5	24
Table 9 – concentration of nutrients used for the preparation of the reactor	24
Table 10 – wastewater composition with ratio	27
Table 11 – laboratory results for the start-up phase	30
Table 12 – $N - NH_4^+$ and COD concentrations during phase two – reactor's preparation	35
Table 13 – $N - NH_4^+$ and COD concentrations during phase two – hollyday period	37
Table 14 – $N - NH_4^+$ removal of each COD/N cycle	44

Table of figures

Figure 1 – microorganisms growth curve [5]	4
Figure 2 – Pre-denitrification configuration: [9].....	7
Figure 3 –Post-denitrification configuration [9].....	7
Figure 4 – Biological Phosphorous Removal (BPR) typical configuration[12]	9
Figure 5 – a) schematic diagram of MABR , b) clean hollow fiber membrane.....	11
Figure 6 – Schematic diagram of transport fluxes [7]	12
Figure 7 – Biofilm growth. May 15 (left), July 7 (middle), August 35 (right).....	13
Figure 8 – Centrifuge [20]	15
Figure 9 – Spectrophotometer [20]	16
Figure 10 – TOC -TN.....	16
Figure 11 – COD [20]	17
Figure 12 – Ionic Chromatographer (IC) [20]	17
Figure 13 – MABR after inoculum injection.	20
Figure 14 – comparison of the reactor before and after the closure August the 8 th (left) and August the 20 th (right).....	25
Figure 15 – progression of the biofilm growth. May the 6 th (left), May the 15 th (middle) and June the 16 th (right).....	29
Figure 16 – trend of $N - NH_4 +$ concentration (top), trend of COD concentration (bottom)	32
Figure 17 – removal efficiency of COD and $N - NH_4 +$	33
Figure 18 – pH, ORP and flow difference variation of phase two – reactor's preparation.....	36
Figure 19 – pH, ORP and flow difference variation of phase two – holyday period	38
Figure 20 – pH, ORP and flow difference variation of phase two – post-holyday period.....	39
Figure 21 – graphical representation of the OTR. A) OTR of the all period. B) OTR of subphase 1. C) OTR of subphase 2. D) OTR of subphase 3. E) OTR of subphase 4. F) OTR of subphase 5	41
Figure 22 – COD and $N - NH_4 +$ removal efficiencies.....	43

Bibliography

- [1] «UN-Water Brief», United Nations. [Online]. Disponibile su: <https://sdg.iisd.org/news/un-water-brief-defines-water-security/>
- [2] «United Nations – Sustainable Development». [Online]. Disponibile su: <https://sdgs.un.org/goals/goal6>
- [3] A. Garcia-Rodríguez, V. Matamoros, C. Fontàs, e V. Salvadó, «The ability of biologically based wastewater treatment systems to remove emerging organic contaminants—a review», *Environ. Sci. Pollut. Res.*, vol. 21, fasc. 20, pp. 11708–11728, ott. 2014, doi: 10.1007/s11356-013-2448-5.
- [4] Material from the course of "Applied Environmental Engineering". Prof. Barbara Ruffino, prof. Alberto Tiraferri, prof. Mariachiara Zanetti.
- [5] Material from the course of "Fixation and recycle of CO₂ for greenhouse effect mitigation". Prof. Samir Bensaid, prof. Vincenzo Riggio
- [6] M. Peleg e M. G. Corradini, «Microbial Growth Curves: What the Models Tell Us and What They Cannot», *Crit. Rev. Food Sci. Nutr.*, vol. 51, fasc. 10, pp. 917–945, dic. 2011, doi: 10.1080/10408398.2011.570463.
- [7] A. Mittal, «Biological Wastewater Treatment».
- [8] E. Syron e E. Casey, «Membrane-Aerated Biofilms for High Rate Biotreatment: Performance Appraisal, Engineering Principles, Scale-up, and Development Requirements», *Environ. Sci. Technol.*, vol. 42, fasc. 6, pp. 1833–1844, mar. 2008, doi: 10.1021/es0719428.
- [9] "Quaderno depurazione" SMAT. Disponibile [Online]
- [10] G. Orman, «A Study on the Simultaneous Nitrification and Denitrification Process of a Membrane Aerated Bioreactor Augmented by BiOWiSH Aqua», California Polytechnic State University, San Luis Obispo, California, 2019. doi: 10.15368/theses.2019.112.
- [11] F. Di Capua, F. Iannacone, F. Sabba, e G. Esposito, «Simultaneous nitrification–denitrification in biofilm systems for wastewater treatment: Key factors, potential routes, and engineered applications», *Bioresour. Technol.*, vol. 361, p. 127702, ott. 2022, doi: 10.1016/j.biortech.2022.127702.
- [12] T. Liu, G. Jia, J. Xu, X. He, e X. Quan, «Simultaneous nitrification and denitrification in continuous flow MBBR with novel surface-modified carriers», *Environ. Technol.*, vol. 42, fasc. 23, pp. 3607–3617, ott. 2021, doi: 10.1080/09593330.2020.1735526.
- [13] "Phosphorous removal", Lennitech. [Online]. Disponibile su: <https://www.lennitech.it/rimozione-fosforo.htm>
- [14] Directive (UE). [Online]. Disponibile su: <https://eur-lex.europa.eu/eli/dir/1991/271/oj/ita>

- [15] *Directive (EU)*. [Online]. Disponibile su: <https://eur-lex.europa.eu/eli/dir/2024/3019/oj/ita>
- [16] *Directive (EU)*. [Online]. Disponibile su: <https://eur-lex.europa.eu/legal-content/IT/TXT/?uri=celex%3A32000L0060>
- [17] *Decreto Legislativo*. 2006. [Online]. Disponibile su: <https://www.normattiva.it/uri-res/N2Ls?urn:nir:stato:decreto.legislativo:2006-04-03;152!vig>
- [18] G. Campo, A. Cerutti, M. Zanetti, e B. Ruffino, «Membrane aerated biological reactors (MABRs) to enhance the biological treatment process at a WWTP», *J. Environ. Manage.*, vol. 371, p. 122921, dic. 2024, doi: 10.1016/j.jenvman.2024.122921.
- [19] U. W. R. Siagian *et al.*, «Membrane-aerated biofilm reactor (MABR): recent advances and challenges», *Rev. Chem. Eng.*, vol. 40, fasc. 1, pp. 93–122, gen. 2024, doi: 10.1515/revce-2021-0078.
- [20] C. Pellicer-Nàcher, C. Domingo-Félez, S. Lackner, e B. F. Smets, «Microbial activity catalyzes oxygen transfer in membrane-aerated nitrifying biofilm reactors», *J. Membr. Sci.*, vol. 446, pp. 465–471, nov. 2013, doi: 10.1016/j.memsci.2013.06.063.
- [21] «DIATI laboratories», Polito. [Online]. Disponibile su: https://www.diati.polito.it/il_dipartimento/strutture_interne/laboratori/air_water_waste
- [22] «Amazon». [Online]. Disponibile su: <https://www.amazon.it/Peristaltica-Laboratorio-Bioingegneria-Biochimica-Controllato>
- [23] E. Clements, Y. Nahum, P. Pérez-Calleja, B. Kim, e R. Nerenberg, «Effects of temperature on nitrifying membrane-aerated biofilms: An experimental and modeling study», *Water Res.*, vol. 253, p. 121272, apr. 2024, doi: 10.1016/j.watres.2024.121272.
- [24] P. Perez-Calleja, M. Aybar, C. Picioreanu, A. L. Esteban-Garcia, K. J. Martin, e R. Nerenberg, «Periodic venting of MABR lumen allows high removal rates and high gas-transfer efficiencies», *Water Res.*, vol. 121, pp. 349–360, set. 2017, doi: 10.1016/j.watres.2017.05.042.
- [25] B. Kim, C. S. Madukoma, J. D. Shrout, e R. Nerenberg, «Effect of EPS production on the performance of membrane-based biofilm reactors», *Water Res.*, vol. 240, p. 120101, lug. 2023, doi: 10.1016/j.watres.2023.120101.
- [26] L. Wang, Y. Wu, Y. Ren, Y. Wang, Y. Wang, e H. Zhang, «Transition of fouling characteristics after development of membrane wetting in membrane-aerated biofilm reactors (MABRs)», *Chemosphere*, vol. 299, p. 134355, lug. 2022, doi: 10.1016/j.chemosphere.2022.134355.
- [27] H. Ravishankar *et al.*, «Factors impacting simultaneous nitrification and denitrification in a membrane aerated biofilm reactor (MABR) system treating municipal wastewater», *J. Environ. Chem. Eng.*, vol. 10, fasc. 5, p. 108120, ott. 2022, doi: 10.1016/j.jece.2022.108120.

