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IMPLEMENTATION AND PREPARATION OF A METHODOLOGY FOR A LABORATORY SCALE BIOAUGMENTED MEMBRANE BIOREACTOR (MBR) TREATMENT PLANT FOR THE TREATMENT OF DENIM WASTEWATER

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RESUMEN

Este trabajo se enmarca dentro del proyecto llamado Birreactores de Membrana para la industria textil (TEX-MEM), llevado a cabo en la Norwegian University of Life Sciences (Ås, Noruega), en el departamento de Agua e Ingeniería Ambiental. Surge de la necesidad de conservar la calidad de los ecosistemas acuáticos por la contaminación debida a las industrias del sector textil, uno de los más contaminantes y que más agua consume en el mundo. La producción de tela vaquera se realiza con el colorante indigo, este tinte artificial presenta un color azul intenso que causa daños en los ecosistemas acuáticos. Se propone un tratamiento de estos efluentes industriales mediante el uso de la tecnología de los Biorreactores de Membrana (MBR) y la bioaumentación, esta tecnología está siendo cada vez más utilizada en el tratamiento de aguas, debido a la mejora de la calidad de los efluentes. En este trabajo se ha iniciado un sistema de MBR aerobio a escala de laboratorio. Se ha realizado una revisión bibliográfica de los últimos 10 años de investigaciones en el uso de MBR y la bioaumentación en la remoción de tintes. A partir de la búsqueda bibliográfica, también se ha creado un agua sintética (STW) similar a los efluentes de la industria textil del denim que se utilizará como influente a la planta del laboratorio. El trabajo ha consistido en el montaje y organización de una planta piloto a escala de laboratorio, en la cual se han implantado sistemas de automatización de bombas y lectura de datos de presión a tiempo real. Se han elaborado módulos de ultrafiltración (UF) y se han estudiado sus características de funcionamiento

como la resistividad y permeabilidad, se han controlado las etapas de lavado y los ciclos de limpieza. Además se ha creado una metodología de trabajo de laboratorio que consiste en el estudio de las características del fango de los reactores: tiempo de succión capilar (CST), potencial Z, sólidos suspendidos totales (MLSS), hidrofobicidad, u oxígeno disuelto; así como del permeado de las membranas: demanda química de oxigeno (COD) y absorbancia. Además se han analizado los resultados obtenidos del primer mes de trabajo. El estudio consigue poner en marcha dos biorreactores de membrana aerobios, con las misma características, uno de ellos (MBR1) de control y el otro (MBR2) al que se le han inoculado bacterias específicas (bioaumentación) que degradan el colorante indigo. Los resultados obtenidos permiten continuar el estudio y los trabajos de laboratorio de este proyecto TEX-MEM, que actualmente se encuentra en fase de recogida de resultados. Además cabe comentar, la importancia de comprobar cómo influye la bioaumentación en los MBR y el comportamiento de los módulos de UF.

Palabras clave: Bioaumentación; Birreactor de Membranas; Ultrafiltración; Indigo; Industria Textil; Denim; Pesión Transmembrana; Eliminación del color

ABSTRACT

This work is part of the project called Textile Membrane Bioreactors (TEX-MEM), carried out at the Norwegian University of Life Sciences (Ås, Norway), in the Department of Water and Environmental Engineering. It arises from the need to conserve the quality of aquatic ecosystems due to textile industries emissions, one of the most polluting and water consuming in the world. The production of denim fabric is made with indigo dye, this artificial dye presents a deep blue colour that causes damages in the aquatic ecosystems. It is proposed to treat these industrial effluents through the use of Membrane Bioreactor (MBR) technology and bioaumentation, this technology is being increasingly used in water treatment, due to the improvement of effluent quality. In this work, a MBR aerobic system has been started at laboratory scale. A bibliographical review of the last 10 years of research on the use of MBR and bioaumentation in dye removal has been carried out. From the bibliographic research, a synthetic textile wastewater (STW) similar to effluents from the denim textile industry has been created, which will be used as an influent to the laboratory plant. The work consisted in the assembly and organization of a laboratory-scale pilot plant, in which automated pump systems and real-time pressure data reading were implemented. Ultrafiltration (UF) modules have been developed and their operating characteristics such as resistivity and permeability have been studied, the washing stages and the cleaning cycles have been controlled. In addition, a laboratory work methodology that consists of the study of the characteristics of

reactor sludge has been developed to study: capillary suction time (CST), Z potential, mixed liquor suspended solids (MLSS), hydrophobicity, or dissolved oxygen; as well as membrane permeate characterization: chemical oxygen demand (COD) and absorbance. In addition, the results obtained from the first month of work have been analysed. The study achieves the start up two aerobic membrane bioreactors, with the same characteristics, one of them (MBR1) is the control and the other one (MBR2) has been inoculated with specific bacteria (bioaumentation) that degrade the indigo dye. The results obtained allow the study and laboratory work of this TEX-MEM project to continue, which is currently under data collection phase. In addition, it is important to note the importance of checking how bioaugmentation influences MBR performance and the behaviour of Ultrafiltration (UF) modules.

Keywords: Bioaumentation; Membrane Bioreactor; Ultrafiltration; Indigo; Textile Industry; Denim; Transmembrane pressure; Colour Removal

RESUM

Aquest treball s'emmarca dins del projecte anomenat Birreactores de Membrana per a la indústria tèxtil (TEX-MEM), dut a terme en la Norwegian University of Life Sciences (Ås, Noruega), en el departament d'Aigua i Enginyeria Ambiental. Sorgeix de la necessitat de conservar la qualitat dels ecosistemes aquàtics per la contaminació deguda a les indústries del sector tèxtil, un dels més contaminants i que més aigua consumeix en el món. La producció de tela vaquera es realitza amb el colorant indigo, aquest tint artificial presenta un color blau intens que causa danys en els ecosistemes aquàtics. Es proposa un tractament d'aquests efluents industrials mitjançant l'ús de la tecnologia dels Biorreactors de Membrana (MBR) i la bioaumentación, aquesta tecnologia està sent cada vegada més utilitzada en el tractament d'aigües, a causa de la millora de la qualitat dels efluents. En aquest treball s'ha iniciat un sistema de MBR aerobio a escala de laboratori. S'ha realitzat una revisió bibliogràfica dels últims 10 anys de recerques en l'ús de MBR i la bioaumentación en la remoció de tints. A partir de la cerca bibliogràfica, també s'ha creat un aigua sintètica (STW) similar als efluents de la indústria tèxtil del denim que s'utilitzarà com influent a la planta de laboratori. El treball ha consistit en el muntatge i organització d'una planta pilot a escala de laboratori, en la qual s'han implantat sistemes d'automatització de bombes i lectura de dades de pressió a temps real. S'han elaborat mòduls d'ultrafiltración (UF) i s'han estudiat les seues característiques de funcionament com la resistivitat i permeabilitat, s'han controlat les etapes de llavat i els cicles

de neteja. A més s'ha creat una metodologia de treball de laboratori que consisteix en l'estudi de les característiques del fang dels reactors: temps de succió capil·lar (CST), potencial Z, sòlids suspesos totals (MLSS), hidrofobicitat, o oxigen dissolt; així com del permeat de les membranes: demanda química d'oxigene (COD) i absorbància. A més s'han analitzat els resultats obtinguts del primer mes de treball. L'estudi aconsegueix crear dos biorreactors de membrana aerobis, amb les mateixa característiques, un d'ells (MBR1) de control i l'altre (MBR2) al que se li han inoculat bacteris específics (bioaumentación) que degraden el colorant indigo. Els resultats obtinguts permeten continuar l'estudi i els treballs de laboratori d'aquest projecte TEX-MEM, que actualment es troba en fase de recollida de resultats. A més cal comentar, la importància de comprovar com influeix la bioaumentación en els MBR i el comportament dels mòduls d'UF.

Paraules clau: Bioaumentación; Bioreactor de Membranes; Ultrafiltración; Indigo; Indústria Tèxtil; Denim; Pesión Transmembrana; Eliminació del color

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I INTRODUCTION AND OBJECTIVES

One of the biggest problems of this century is water quality management. Although water is the most abundant element on Earth, fresh water suitable for human's consumption represents only 3% of the total, furthermore, human being only have access to 0.3% of this fresh water present on Earth (Cassardo & Jones, 2011). Due to this scarcity, it is important to maintain the quality of water resources and treat its pollution by all means. A recent estimate shows that 69% of worldwide water use is for agriculture (mainly irrigation), 22% for industries, 1% for recreational purpose and 8% for household purposes (Al Fry, 2006).

Industrial pollution affects the environment and can cause environmental problems. Industry in general and textile industry in particular. The textile industry is one of the most water consuming, as it uses water during all the process for dye application, washing, and finishing.

One of the aims of this work is to study the removal of colour in the wastewater coming from the textile industry, specifically, the denim industry. Denim sector, that uses indigo dye, is spread over the world. Indigo dye is one of the most used dyes in the textile industry nowadays. It is used mainly in the production of blue denim (European, 2003). The volume of water used to produce a pair of jeans is 10.85 litters of water (Chapagain et al., 2006). Current treatment technologies for dye removal can be biological, electrochemical, enzymatic, by chemical oxidation or physical-chemical.

Furthermore, the negative consequences of coloured effluents coming from the treatment with indigo dye are among others, visual impact on the water bodies, as water will turn artificially coloured. Also this may cause oxygen depletion, as colour will avoid sun light pass through the water column and photosynthetic organisms will die and reduce the dissolved oxygen concentration in the water body. As Kant (2012) said “Colour the earth beautiful and kill it with sweet poison”.

The discovery of synthetic dyes by W. H. Perkins in 1856 has provided a wide range of dyes that colour fast and come in a wider colour range and brighter shades. As a result “dye application” has become a massive industry today (Kant, 2012).

The aim of this study is to start up and perform a bioaugmented Membrane Bioreactor (MBR) system for the treatment of textile wastewater under laboratory conditions. The specific objectives of the study are (1) to initiate bioaugmented Membrane Bioreactor (MBR) process, (2) make ultrafiltration (UF) modules in a laboratory scale (3) study and create the composition of the Synthetic Textile Wastewater (STW), (4) to create a methodology for the project, (5) make a literature review update in the topic (6) show some start-up results of the process.

II LITERATURE REVIEW

II.1 TEXTILE INDUSTRY AND WASTEWATER MANAGEMENT

II.1.1 Textile industry

The history of the textile industry sector is one of the oldest in the World, it goes back to around 5000 B.C. starting with linen clothes found in Egyptian caves. It is also, one of the longest and most complicated industrial chains in the manufacturing industry. The main environmental concern in this sector is the chemical load and amount of water discharged (Chequer et al., 2013; Dasgupta et al., 2015; L. A. Quintero & Cardona, 2011). Italy is the leading European producer for textiles by far, followed by Germany, the UK, France and Spain, together accounting for over 80% of the production in the EU (European, 2003). However, as it is shown in Figure 1 the number of textile Industrial Pollution Prevention Control (IPPC) listed facilities and pollutants per country, it is shown that Belgium and Germany lead the number of facilities before Italy. This means that Italian textile production is composed by small companies outside of the IPPC regulation.

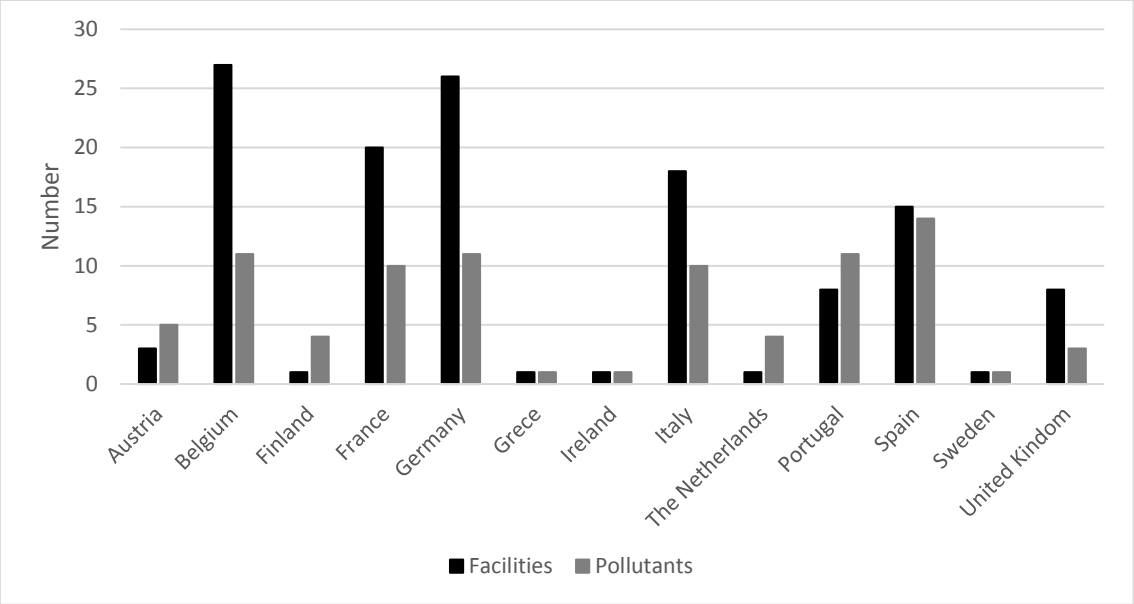


Figure 1. Number of reported textile Industrial Pollution Prevention Control (IPPC) facilities and pollutants by country in 2001 (Christie, 2007)

However, it is known that developed countries are producing its textile products in under-developed or developing countries where the legal regulations are not as strict as in the richer countries. As Figure 2 shows, the major source of imports in the textile industry comes from Asian countries like Turkey or China, with less stricter regulations. Regarding legal regulations in Europe, textile industry is managed by the Directive 2010/75/EU of the European parliament and of the council of 24 November 2010 (European Council, 2010), this directive covers legal arrangements and requires the inspecting authorities to give permits to the industrial facilities and to monitor their environmental performances within this general approach. Moreover, the European Community Regulation (EC) No 1907/2006 – REACH of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) and

establishing a European Chemicals Agency (EC, 2006) is the former legislative framework for chemicals in the EU and it will give more information about the products used in this sector.

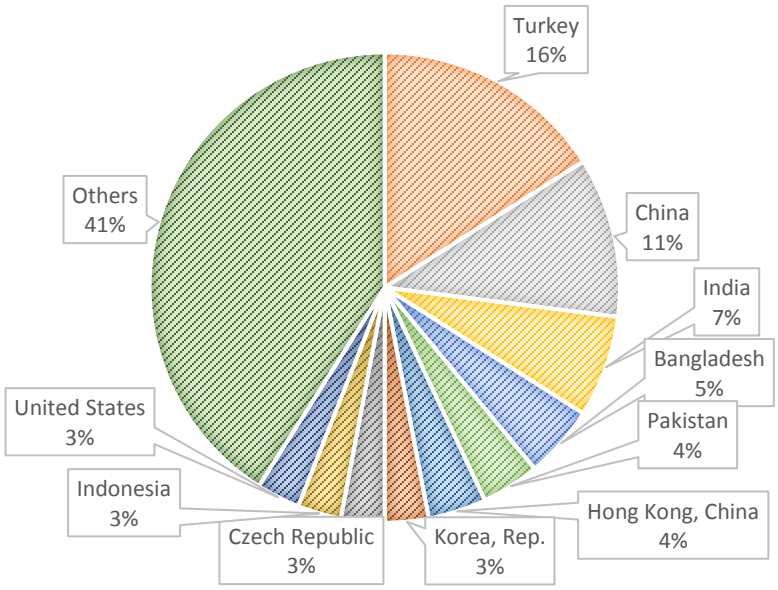


Figure 2. Sources of imports of textile industry in EU (Nordås, 2004)

Regarding Spanish textile industry, it is basically composed of small and medium-sized companies (SMEs), generally familiar factories and national investors. It is remarkable that the industry is distributed specially in the Mediterranean coast especially in Catalonia and the Valencian Community. Nevertheless, it is also developing in other regions as Castilla la Mancha, Andalucía and Galicia (Canales, 2007).

The textile industries are considered as water intensive activities. Regarding the steps of the manufacturing of textile products, this sector is very heterogeneous and fragmented. The products resulting from this industry are mainly clothing, home furnishing

and industrial use. Depending on the raw material used in the textile plant, process operations vary a lot. A general overview of a process chain of the textile industry is given in Figure 3. Moreover, it is showed below the summarized process stages of the textile industry (Arslan et al., 2016):

- Sizing: The process of giving a protective coating on the warp yarn to minimize yarn breakage during the weaving.
- Desizing: The process of removing sizing agent from woven fabric prior to subsequent processes, such as bleaching, dyeing and finishing.
- Scouring: The process of removing impurities.
- Bleaching: The process of removing or lightening coloured materials.
- Mercerization: The process of improving lustre, dye ability, strength of cellulosic material.
- Dyeing: The process of colouring fibres or fabrics.
- Printing: The application of colourants in definite, repeated patterns to fabric, yarns, or sliver by any one of a number of methods other than dyeing.
- Finishing: The final process given to a textile material to give good appearance, functional properties, such as water-proof, shrink resistant, and wrinkle-proof.

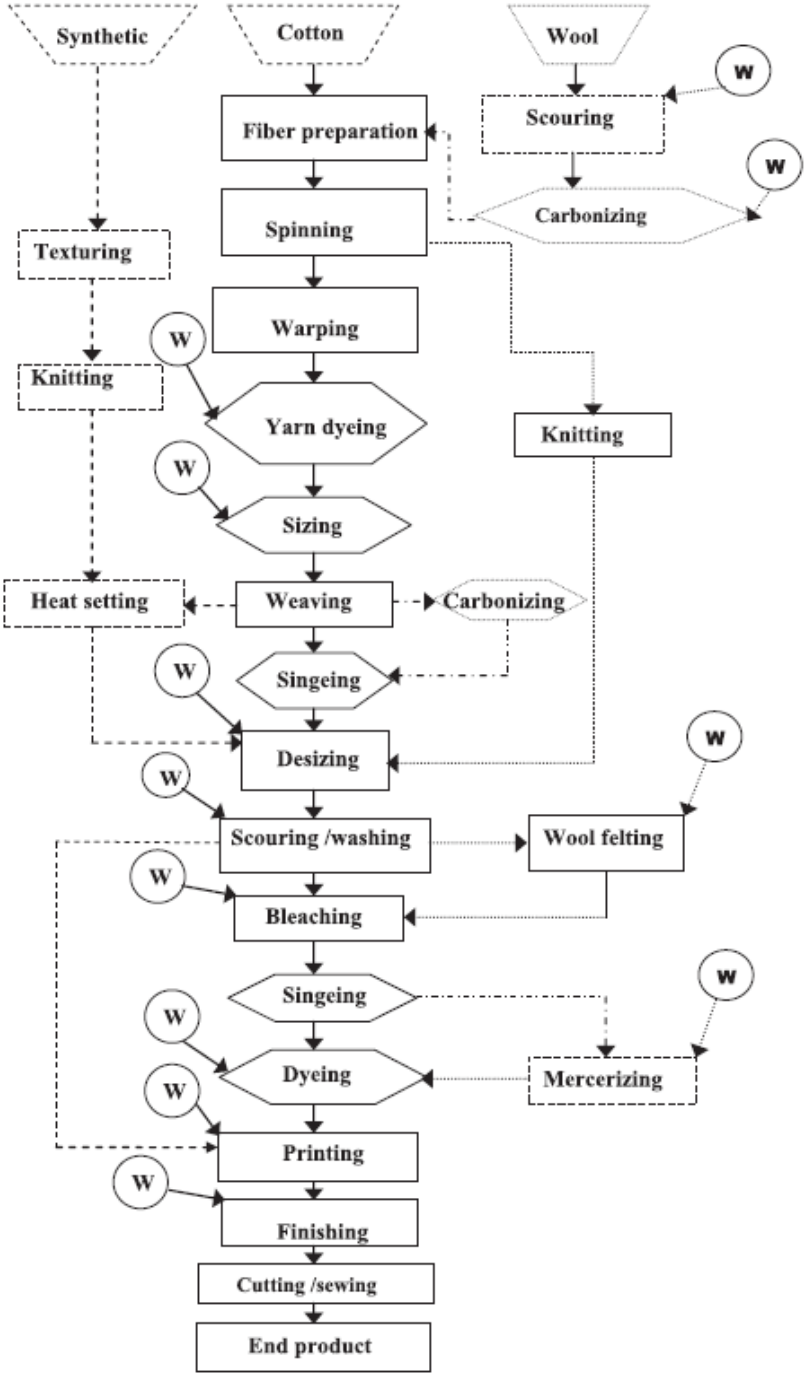


Figure 3. Flowchart for the general steps in the textile fabrication (Dasgupta et al., 2015)

II.1.2 Water use in textile industry

As previously said, textile industry has a great rate in water consumption as well as toxicity in its loads. Wet processing operations, containing preparation, dyeing and finishing, generate the majority of textile water pollution. Water is the principal medium for removing impurities from raw materials, applying dyes and finishing agents. The consumption of water in this sector differs depending on the type of process, raw material used or techniques used. However, for a large industrial chain, working with wet processing operations will consume more than 5000 m^3/d (Ünlü, 2008), further studies say that wastewater generated per ton of finished product in the textile industry is between 200 to 350 m^3 (Dasgupta et al., 2015).

II.1.2.1 Integrated Pollution Prevention and Control

In EU countries, pollution rising from industrial activities is managed by “integrated pollution management” concept. IPPC Directive (10/75/EC), covers legal arrangements and requires the inspecting authorities to give permits to the industrial facilities and to monitor their environmental performances within this general approach. Annex I to the IPPC Directive categorizes the industrial activities covered into six. These are energy production, production and processing of metals, minerals, chemicals, waste management, and others (pulp and paper, textile, tanning, food production and the intensive farming of poultry and pigs) (The European Commission, 2003; Unlu et al., 2009). In this respect, a general approach covering pollution within the production phases

is accepted rather than considering pollution control via end of pipe treatments and setting limit values for the discharges or emissions from industrial facilities. Therefore, a general concept of waste prevention and/or minimization techniques is adopted to all production phases to minimize discharges taking air, water and soil as a whole.

II.1.2.2 Characterization of the wastewater in the textile industry

Textile industry is one of the most significant manufacturing sectors that produce large volumes of highly polluted and toxic wastewater. The World Bank estimates that 17-20% of industrial water pollution is contributed by the textile industry (Kant, 2012). Increasing the discharge of such effluents without proper and adequate treatment has impacted the water bodies, soil and ecosystems adversely.

The composition of effluents from the textile factories are quite complex because of the variation in machines, techniques, type of fibres, and chemicals. Textile wastewater is often rich in colour and also of extreme pH with various types of chemicals (persistent and toxic) like heavy metals. Due to this reason, many countries have now introduced more stringent discharge standards for textile wastewater (European Commission, 2003).

Increasing industrialisation has led to severe environmental pollution and it has now become a global issue. It is recorded that more than 100,000 commercially available textile dyes are present in the market and approximately 700,000–1,000,000 tons of dyes are produced while 280,000 tons are discharged via effluents generated from the textile

industry to the global environment annually (Ali, 2010). Table 1 shows the typical water emission values for a textile industry.

Table 1. Chemical loads of textile industry in the EU (European Commission, 2003)

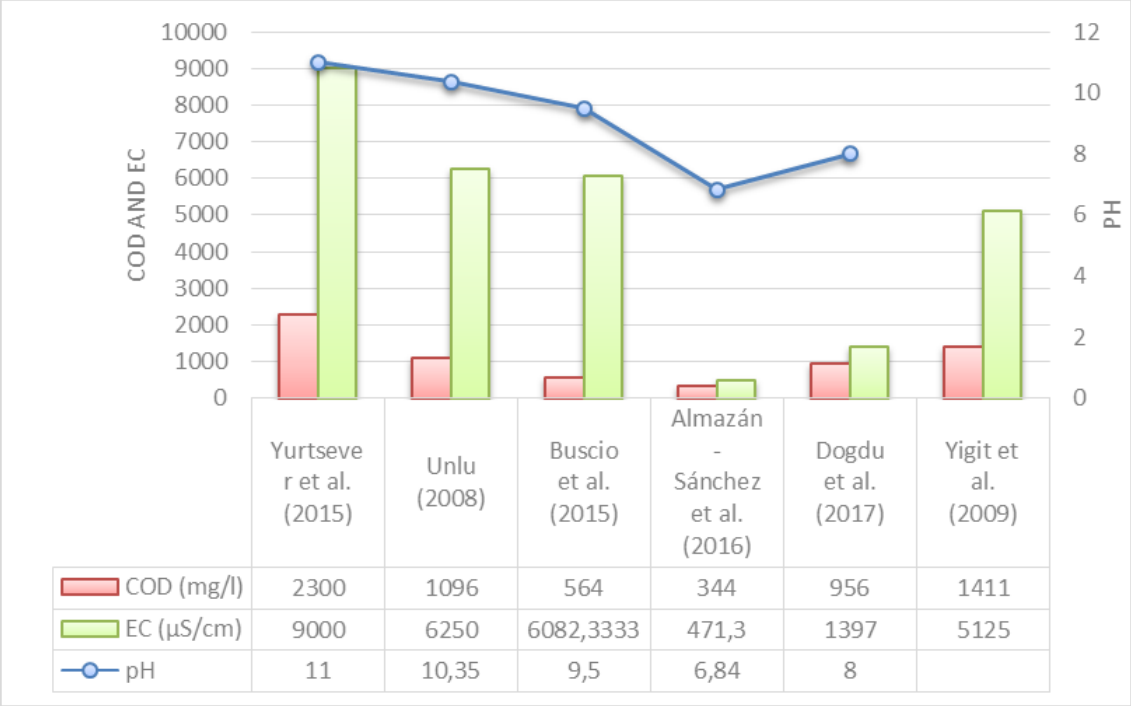
Substances	Environmental load (t/yr.)
Salts	200000 - 250000
Natural fibres impurities (including biocides) and associated material	50000 – 100000
Sizing agents (mainly starch, starch derivatives, but also polyacrylates, polyvinylalcohol, carboxymethylcellulose and galactomannans)	80000 – 100000
Preparation agents (mainly mineral oils, but also ester oils)	25000 – 30000
Surfactants (dispersing agents, emulsifiers, detergents and wetting agents)	20000 – 25000
Carboxylic acids (mainly acetic acid)	15000 - 20000
Thickeners	10000 – 15000
Urea	5000 – 10000
Complexing agents	<5000
Special auxiliaries with more or less ecotoxicological properties	<5000

Raw textile wastewater can be characterised by measurement of BOD (Biological Oxigen Demand), COD (Chemical Oxigen Demand), colour, suspended solids (SS), dissolved solids (DS) and heavy metals etc. Typical characteristics of textile industry wastewater generally include a wide range of pH, COD, dissolved solids and strong colour (Verma et al., 2012) which may be comparable to moderate municipal wastewater. However, the main challenge is to eliminate the colour of wastewater, which is due to the remaining dyes.

Some reviews conducted amongst the characterization of textile effluents reveal the great variation of contents in the textile industry effluents, this results are shown in Figure 4 and Table 2.

Table 2 below, shows a review of the characterization of water effluents coming from the Denim industry. It can be commented that whereas Yurtsever et al. (2015) characterized four different wastewater samples from a mill effluent. In Table 2 it is shown the average composition given from the mill. In their study, although COD of the wastewater was quite high, nitrogen and phosphorus concentrations were not adequate for biological treatment. Hence, NH_4CI and KH_2PO_4 were added to obtain COD/N/P ratio as 100/5/2. Also, the pH of wastewater was adjusted to 6.8–7.3 with concentrated H_2SO_4, this method is applied in this work as well. Moreover, Unlu (2008) gives the values in intervals since the characteristics of the same dyeing recipe may differ due to operating conditions, such as rinsing water flowrate, change in the concentration of the dyes, and auxiliary chemicals used in the dyeing process. In Yigit et al. (2009) it is claimed that the characteristics of influent wastewater was quite variable mainly due to the variations in the textile production program and break offs during weekends for cleanings, however if we compare the characterization with the other authors, they are in the same range. Buscio et al. (2015) states that it can be observed, that effluents from denim industry are mainly characterized by an alkaline pH attributed to the dyeing process, as it requires pH between 11.5 and 12, moreover, it is also characterized by high conductivity due to the

presence of sulphates, which are generated from the oxidation of sodium dithionite. This reagent is used for the indigo reduction during the vat dyeing process. Almazan-Sanchez et al. (2016) made a physicochemical characterization to a textile wastewater according to parameters shown in table below, the wastewater was obtained from the rinse vat of a denim textile manufacturing process, where the denim clothes only receive a finished treatment using products, such as liquid detergents, fabric softeners, sea salt, and pumice stone. Figure 4 shows the variability of compositions of the textile industry wastewater effluents.



	Yurtsever et al. (2015)	Unlu (2008)	Buscio et al. (2015)	Almazán - Sánchez et al. (2016)	Dogdu et al. (2017)	Yigit et al. (2009)
COD (mg/l)	2300	1096	564	344	956	1411
EC (µS/cm)	9000	6250	6082,3333	471,3	1397	5125
pH	11	10,35	9,5	6,84	8	

Figure 4. Main textile wastewater parameters characterization review (own elaboration)

Table 2. Major characteristics of real textile wastewater studied by various researchers

Parameters	Denim textile industry	Denim textile industry	Denim textile industry	Denim industry			Rinse vat of a denim textile manufacturing process	Denim factory
				Cotton1	Lyocell2	Cotton4		
COD (mg/L)	2300±800	1263-929	1411	320	800	572	344	762 - 1150
Colour (PCU)	2347±1200	6850-5120	2447	-	-	-	330	190-590
Indigo (mg/L)	-	-	-	58	118	82	-	-
pH	9–13	9.4-11.3	-	8.6	9.5	10.4	6.84	7.93-8.07
EC (µs/cm)	9000±3	6600-5900	5125	6751	7266	4230	471.3	231- 2563
BOD_5 (mg/L)	-		455	-			91.91	-
TDS (mg/L)	4000–8000	-	2563	-			-	
TSS (mg/L)	150–300	218-230	137	-			-	-
TN (mg/L)	20±3	-	49.2	-			-	
TP (mg/L)	0–3	-	6.3	-			-	
NH_4-N (mg/L)	3.5±0.5	-	-	-			-	2.5-4.5
NH_3-N (mg/L)	-	-	11.2	-			-	
NO_2-N (mg/L)	-	-	0.35	-			0.05	0.27-1.16
NO_3-N (mg/L)	-	-	42.6	-			1.9	4.75-8.7
PO_4-P (mg/L)	-	-	-	-			287.08	1.42-2.59
Cl (mg/L)	-	-	-	-			338.19	-
Sulphate(mg/L)	-	-	-	-			227.06	-
Na (mg/L)	-	-	-	-			44.99	-
K (mg/L)	-	-	-	-			3.08	-
Mg (mg/L)	-	-	-	-			4.39	-

Parameters	Denim textile industry	Denim textile industry	Denim textile industry	Denim industry	Rinse vat of a denim textile manufacturing process	Denim factory
Ca (mg/L)	-	-	-	-	5.65	-
Si (mg/L)	-	-	-	-	5.6	-
Mn (mg/L)	-	-	-	-	1.99	-
Fe (mg/L)	-	-	-	-	0.343	-
References	(Yurtsever et al., 2015)	(Ünlü, 2008)	(Yigit et al., 2009a)	(Buscio et al., 2015)	(Almazán-Sánchez et al., 2016)	(Dogdu et al., 2017)

COD: Chemical Oxygen Demand; PCU: Platinum Cobalt Units of colour measurement; EC: Electrical conductivity; BOD5: Biological Oxygen Demand; TDS: Total Dissolved Solids; TSS: Total Suspended Solids; TN: Total Nitrogen; TP: Total Phosphorus;

II.1.2.3 Dyes history and classification

Colorants have been used by men for many thousands of years. The earliest known use of a colorant was by Neanderthal man about 180,000 years ago. They used red ochre (essentially iron oxide), an inorganic pigment obtained from riverbeds, to daub dead bodies before burial. The first known use of an organic colorant was much later, 4,000 years ago, when the blue dye indigo was found in the wrappings of mummies in Egyptian tombs (Christie, 2007).

By definition, dyes are aromatic compounds; in their structure they include aril rings, which have deallocated electron systems. These are the responsible for the absorption of electromagnetic wavelength, which will be different depending on the energy of electromagnetic clouds. In order to classify dyes three ways can be considered. One systematic classification of colour is the colour index (CI), showed in Table 3 (Wesenberg et al. 2003). Another classification can be depending on the ionization kind, as well as its chromophore boundary or molecular structure (Quintero & Cardona, 2010). The most important groups in this classification are azo dyes, antrachinone, sulphur, triphenilmethane, indigoid and phtalocyanine dyes. In auxocromos groups we can find amine group, carboxylic, sulfonic and hydroxyls (Chequer et al., 2013). The azo dyes are the most used, and represent the 60% of total dye production (Solís et al., 2012). However, indigoid dyes are the second more used dye in the textile industry, as the denim production is widely spread.

At the industrial level, classification according to their application class, is the preferred method. They can be grouped in: direct, disperse, acids, basics, cationic, reactive, vat and sulphurous. From a chemical point of view, vat dyes can be distinguished into two groups: indigoid vat dyes and anthraquinoid dyes. Indigo dyes are almost exclusively used for dyeing warp yarn in the production of blue denim (Buscio et al., 2015; Canales, 2007; European, 2003). Due to the importance of indigo dyes in the actual textile industry, the present work will focus in the treatment of this dye.

Table 3 Classes of synthetic dyes according to colour index (C.I) (Wesenberg et al., 2003)

Code	Chemical Class	Code	Chemical Class	Code	Chemical Class
10000	Nitrose	42000	Triarymethane	53000	Sulphur
10300	Nitro	45000	Xanthene	55000	Lactone
11000	Monoazo	46000	Acridine	56000	Aminoketone
20000	Disazo	47000	Quinoline	57000	Hydroxyketone
30000	Trisazo	48000	Methine	58000	Anthraquinone
35000	Polyazo	49000	Thiazole	73000	Indigoid
37000	Azoic	49400	Indamine/Indophenol	74000	Phthalocyanine
40000	Stilbene	50000	Azine	75000	Natural
40800	Carotenoid	51000	Oxazine	76000	Oxidation Base
41000	Diohenylmethane	52000	Thiazine	77000	Inorganic

In the coloration of cellulosic fibres, vat dyes account for about the 31% of the world market, of which indigo occupies 7%, sulphur dyes account for 7% and other vat dyes account for 17%. This represents about 120,000 tonnes of used indigo dye annually (Roessler et al., 2002). Although only 10 g of indigo is necessary for dyeing one pair of trousers, the world production of indigo is close to 10,000 t/yr due to the vast annual sales of 10^9 blue jeans (Manu & Chaudhari, 2003). Figure 5 shows the world dye consumption

of different dyes. Moreover, in the dyeing process, indigo remains between 5 and 20% without fixing to the textile (O'Neill et al., 1999).

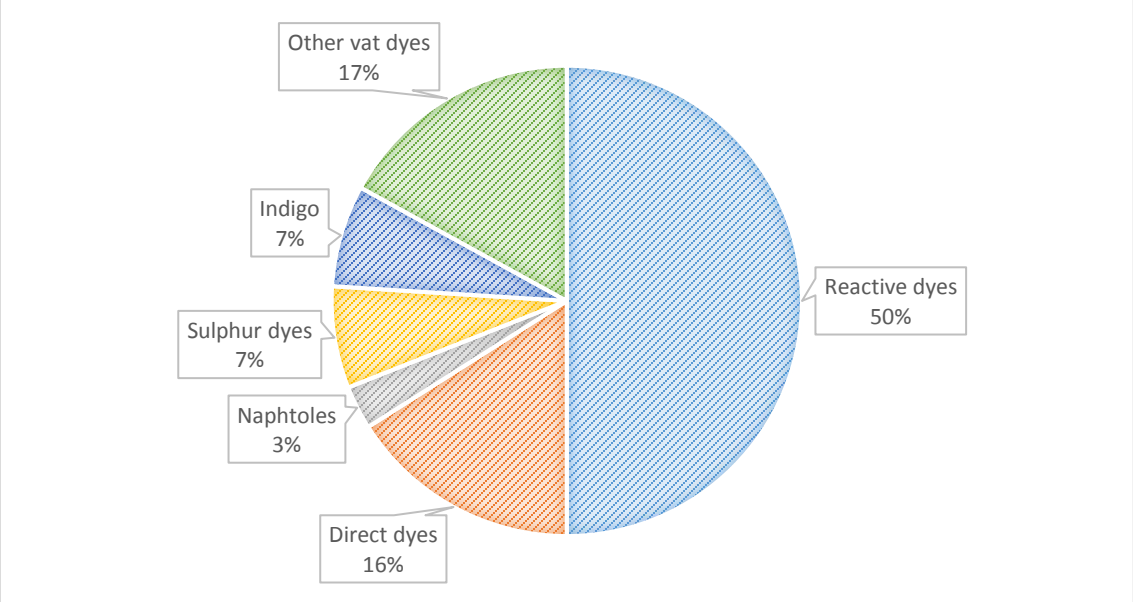


Figure 5. Worldwide dye consumption for cellulosic fibres (Božič & Kokol, 2008)

Vat dyes are one of the most used in the textile industry, especially the indigo dye which is used in the denim industry. One of the main advantages of this dye is its low solubility in water when it is in its oxidized form, however, in the industry, it is reduced into its soluble form. Indigo dye in particular can be natural or synthetic. Natural indigo comes from *Indigofera* plant. Indigo colour (2,2'-bis-indigo), (CI Vat Blue I) or vat indigo, with chemical formula $C_{12}H_{10}O_2N_2$, (Wesenberg et al., 2003), is dark blue crystalline powder. It has a high fusion temperature (390-392 ºC); it is water, alcohol or ether insoluble due to its great intermolecular cohesion force caused by the hydrogen bridges. It is soluble in chloroform, nitrobenzene or strong sulphuric acid. In its solid state, indigo is a polymer in

which each molecule is found united to four molecules around it. Whereas in no polar solvents it is presented as a monomer, in polar solvents intermolecular association takes place and the solution is blue (Buscio et al., 2015; Khelifi et al., 2008a; L. A. Quintero & Cardona, 2011) the following Figure 6 shows the molecule of indigo.

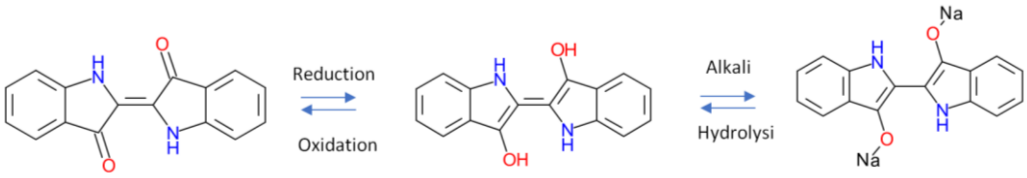


Figure 6. Molecule of indigo

One of the advantages of its water insolubility is that the dye will not wash out of clothing in the washing machine. Unfortunately, however, it also means that indigo cannot be introduced into fabrics by simply immersing them in an aqueous solution of the dye. In order to introduce indigo into fabric a process called vat dyeing must be utilized. Vat dyeing involves reducing the dye to a leuco derivative which is soluble in a dilute alkali solution. The fabric is immersed in this solution which allows the leuco compound to adhere to the fabric by hydrogen bonding. The fabric is then exposed to air which oxidizes the leuco compound into the dye (McKee & Zanger, 1991).

II.1.2.4 Environmental and health impacts of textile wastewater

Textile wastewaters generated from different stages of textile processing contains huge amount of pollutants that are very harmful to the environment if released without proper treatment. The release of textile wastewater to the environment causes aesthetic

problems as the colour change of the water bodies such as lakes and rivers, after releasing of wastewater from the industry. Also, the accumulation of colour, hinders sunlight penetration, disturbs the ecosystem of receiving sunlight, and can cause anoxic conditions, as the photosynthetic organisms of the ecosystem will stop producing oxygen and this will derive in oxygen depletion in the water (Forgacs et al., 2004; Rannug et al., 1992). If this contaminants reach the phreatic system by leaching through the soil layer, ground water may be polluted (Chapagain et al., 2006; Costa et al., 2013).

On the other hand, several dyes and their decomposition derivatives have been proved to be toxic to aquatic life (aquatic plants, microorganisms, fish and mammals). Additionally, fairly intensive studies have inferred that such coloured allergens may undergo chemical and biological assimilations, cause eutrophication, consume dissolved oxygen, prevent reoxygenation in receiving streams and have a tendency to sequester metal ions accelerating genotoxicity and microtoxicity. In a wider sense, sporadic and excessive exposure to coloured effluents is susceptible to a broad spectrum of immune suppression, respiratory, circulatory, central nervous and neurobehavioral disorders presage as allergy, amongst other disease (Verma et al., 2012).

II.1.2.5 Treatments in the textile industry

As it can be concluded by the previous section, wastewater coming from the textile industry is characterized by its variability in its composition. Several physicochemical decolouration techniques have been reported in the literature (e.g. adsorption, membrane

separation, advanced oxidation process); none, however, has appeared as a panacea due to high cost, low efficiency and limited versatility (Hai et al., 2006). It is well known, however, that biodegradation is an environmentally friendly and cost effective treatment.

In the last years, different techniques have been investigated for the treatment of textile effluents. Most of the published studies focus on the elimination of dyes Figure 7.

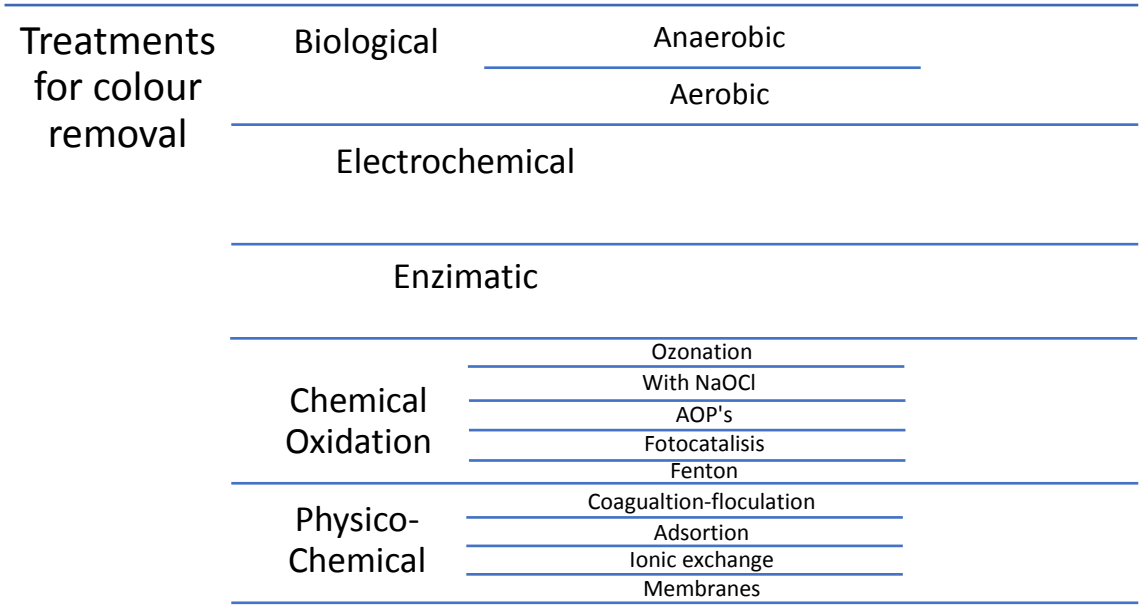


Figure 7. Treatments for colour removal in textile wastewater (Verma et al., 2012)

As more stringent regulations and increasing costs of water is becoming a huge burden for textile industries, membrane processes emerges as the technology-of-choice to provide recyclable water through the treatment of effluents as well as a way to reuse the removed indigo dye. The application of membrane separation processes does provide the industries with a technology to meet water quality limits and produce reusable water,

and has proved to be an effective process in concentrating the bulk of pollutant into small liquid volume for further disposal (Uzal et al., 2009).

The following table 4 has been created to show a literature review of the different techniques used in the denim industry. It also shows the characteristics of each treatment method.

Table 4. Denim wastewater treatment technologies (own elaboration)

Influent Wastewater	Type of treatment	Scale	Volume (l)	HRT (h)	SRT (d)	OLR kg(COD)/m³ day	F/M gBOD/d	Flux l/MH	Pressure (kPa)	COD removal (%)	Colour Removal (%)	(*)
Denim textile industry	AS + NF	Lab	10*	192	8	-	-	-	-	99.62	99.74	1
Denim textile industry	Coagulation	-	-	-	-	-	-	-	-	50	52	2
	MF(0.45µm)	-	-	-	-	-	-	360-1980	70-300	29	62	
	MF + UF	-	-	-	-	-	-		340	31.75	91.99	
	MF + NF	-	-	-	-	-	-		330	96	99	
Denim textile industry	MBR	Pilot	230	14	25	0.03-0.07 **	0.37-1.01	20	14-56	95	97	3
Denim textile industry	UF External	Pilot-	-	-	-	-	-	-	-	40	96	4
	UF -Sub	Pilot	20	-	-	-	-	-	-	80	99	
	Ext + Sub	semi-industrial	-	-	-	-	-	-	-	67	98	
Rinse vat of denim process	Adsorption	-	-	13.27	-	-	-	-	-	90.3	32.4	5
Denim textile industry	Wetlands	Lab	15	144	-	0.042	-	-	-	75.6 -77.8	-	6

(**)The unite value in kg BOD_5/kg MLSS day. (*)References: 1: (Sahinkaya et al., 2008); 2: (Ünlü, 2008; Unlu et al., 2009); 3: (Yigit et al., 2009); 4: (Buscio et al., 2015); 5: (Almazán-Sánchez et al., 2016); 6: (Dogdu et al., 2017); (**)The unite value in kg BOD_5/kg MLSS day.

II.2 MEMBRANE BIOREACTOR TECHNOLOGY

The combination of biological and membrane filtration processes is known as a membrane bioreactor (MBR) system. Figure 8 gives and overview of the membrane filtration process in comparison with tional wastewater treatment.

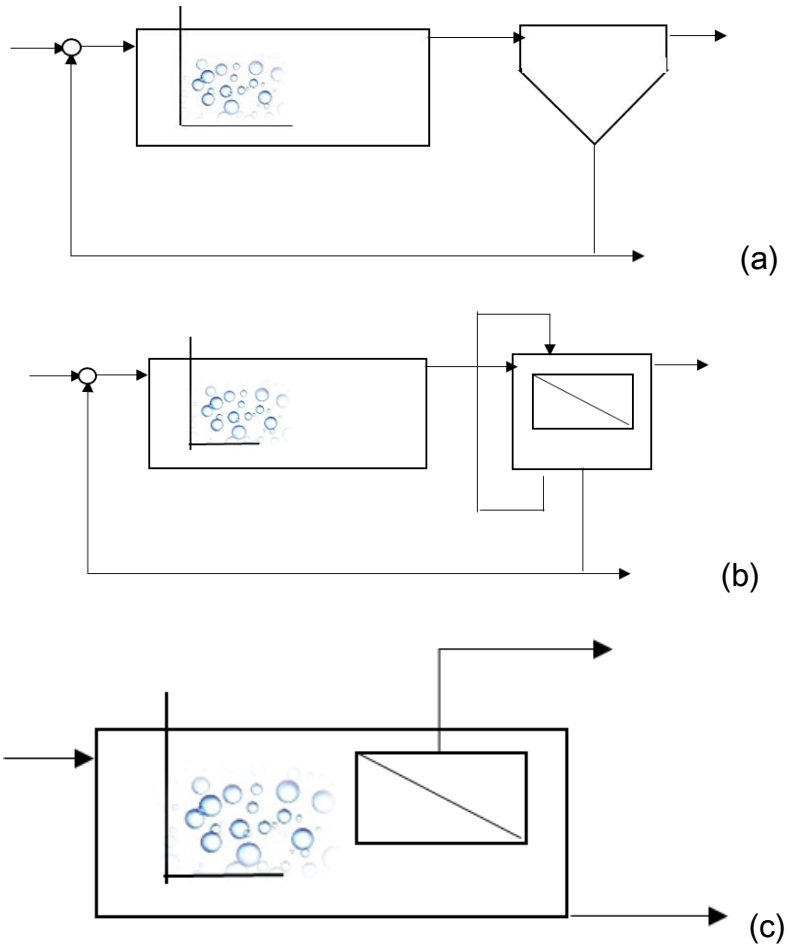


Figure 8. (a) Activated sludge; (b) External membrane bioreactor; (c) Submerged membrane bioreactor.

The benefits of MBR systems in submerged or external cross-flow mode are:

- High microbial quality of effluent water, high removal efficiencies of suspended solids, microorganisms and viruses.

- Greater freedom to vary process parameters, like reduction of excess sludge or the concentration of slowly growing microorganism because MBR systems are independent of the sedimentation behaviour of sludge.
- Volume reduction of the activated sludge tank because of higher biomass concentration and elimination of the sedimentation tank, both resulting in a reduction of the total plant foot print.
- High cellular retention time allows to work under more stable conditions as well as reduction of sludge production. It avoids separation problems with the sludge, moreover with bulking problems.
- It allows treating slow biodegradable organic matter due to the higher retention times.

The financial success of MBR is determined by the process used to restore decreased flux caused by fouling. The resulting disadvantages of MBR are the high investment cost for the needed membrane surface area and high operating costs for cleaning management and the energy demand for cross-flow mode on top of the cost for supping oxygen to microorganisms.

In the submerged mode, the membrane modules are directly installed in the activated sludge bioreactor or immersed in an aerated separate container. Air bubbling plays a significant role in attaining high fluxes and periodic back-flushing is used to reduce fouling.

Industrial wastewater treatment plants are often characterized by low rates and high pollutant concentrations. The benefit of using membranes is the possibility to reuse water in different qualities and the gain of reusable material as well as environmental aspects integrated in the production process (Wiesmann & Choi, 2007).

Membrane technology is one of the most important separation processes and most used in recent years. Despite the fact that the first studies with membranes began in the eighteenth century, it was not until the twentieth century when this technique began to arouse the interest of researchers (Olivera, 2015). The development that has experienced membrane technology in recent decades focuses on the development of new materials for the manufacture of membranes, the modelling of its processes and the effect of the different variables that intervene in it. In a membrane process, the feed stream is divided into two: one permeate or filtrate containing that entire fraction that has managed to pass through the membrane and a concentrate, or refuse, containing species other than they cross.

In general, submerged MBR require higher aeration and initial investment costs, with respect to side-stream membrane configurations. In contrast, pumping and operating costs are lower, requiring lower operating flows and cleaning frequencies. Thus, in the case of sewage treatment, the selection between submerged and external configurations for aerobic MBRs seems somehow settled, in favour of submerged MBRs. Although, nowadays most of the commercial applications are based on the submerged configuration, due to lower associated energy requirements, external configuration is still commonly used for certain industrial applications as well as for tertiary filtration treatment.

The main advantages of the employment of submerged membranes in combination with biological wastewater treatments are the total control of sludge retention time, the

high stability of the process against peak loads and temperature and the high quality of the obtained effluent, which enable water reuse. Besides, the use of the membranes allows the complete retention and development of extremely slow-growth bacteria, such as newly discovered denitrifying methanotrophes, avoiding its wash-out from the biological systems. On the contrary, membrane fouling is one of the main drawbacks associated with the application of membrane technology for wastewater treatment. Fouling decreases the permeability of a membrane, limits flux and shortens the life of membrane modules, thus increasing both the capital and the operating costs of filtration systems.

Regarding the drawbacks of these treatment methods it can be:

- Higher energy costs (you have already commented on the costs of membranes and operation),
- Higher aeration costs by reducing the efficiency of O_2 transfer by increasing the SS concentration and by having to introduce more air to stir the membranes in the case of hollow fibre.
- Need for replacement of membranes over time.

II.2.1 Membrane characteristics and definitions

Membrane processes can be classified according to the driving force, the separation mechanism, membrane structure or particle size which they retain, Figure 9 shows different membrane processes and the main pollutants that they remove depending on the pore size and characteristics of the membrane or process. To date, the most studied

and applied membranes at industrial level are those in which the driving force is the pressure gradient. Depending on the membrane pore size, the membrane will separate different substances in the water. UF and MF are size exclusion membrane processes (physical removal) that reject particles, colloids, pathogens, high molecular weight species, and ultimately lower turbidity. However, Ultra Filtration (UF) and Micro Filtration (MF) do not reject dissolved salts, and only partially dissolved organics or other species like true colour, taste and odour, etc.

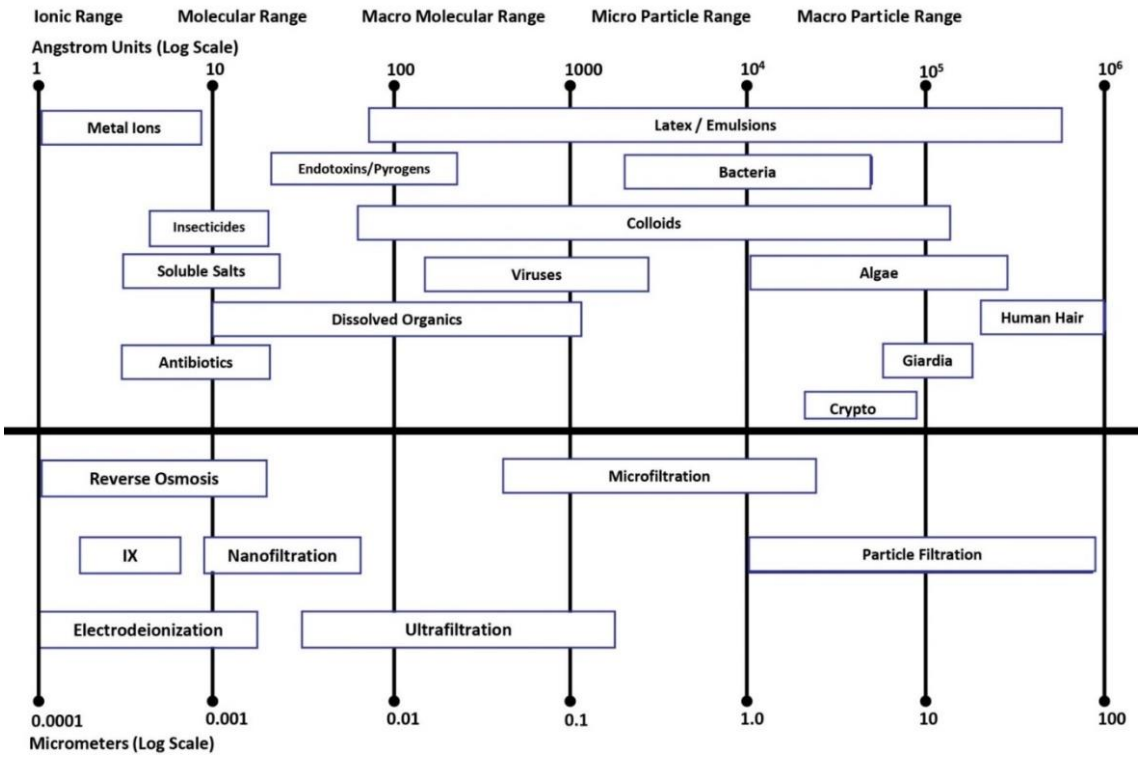


Figure 9. Pore size for Membranes, materials and removal (Maletskyi, 2017)

Membrane technology is focused on the use of different materials for its manufacture. The materials used may be of an organic or inorganic nature. Organic membranes are made from polymers. Table 5 shows the most used in commercial membranes and their application range.

Table 5. Polymers used for the fabrication of membranes and its application (Olivera, 2015)

Acronym	Polymer	MF	UF	NF/RO
CA	Cellulose acetate	*	*	*
PVC	Polyvinylchloride	*		
PVDF	Polyvinylidene Fluoride	*	*	
CN	cellulose nitrate		*	
PPO	Polyphenylene Oxide		*	
PAN	Polyacrylonitrile		*	
PVA	Polyvinyl alcohol		*	
PA	polyamide		*	*
PC	Polycarbonate	*		
PEA	Polyetherimide			*
PES	Polyester sulfone		*	
PE	polyethylene	*		
PPO	Polypropylene	*		
PS	Polysulfone		*	
PTFE	Polytetrafluoroethylene	*		
CTA	Cellulose triacetate		*	*

Cellulose membranes and their derivatives were the first membranes used. Although these types of membranes continue to be manufactured today, their low resistance to chemical agents and temperature, has caused their replacement by other polymers with better performance. Inorganic membranes are more mechanically, thermally and

chemically resistant than organic membranes, however their industrial application is currently limited. Within the inorganic membranes, the ceramics are the most used. Membranes made from glass, coal or metal can also be found.

II.2.1.1 Type of membranes

If Ultra filtration and Microfiltration are compared, it can be stated that due to smaller pore size, UF provides better filtrate water quality if for example SDI (Silt Density Index), TOC (Total Organic Carbon), or turbidity, are compared. Ultrafiltration has higher removal of microorganisms (especially virus). Microfiltration membranes typically operates in a depth filtration pattern with eventual pore blocking, compared to Ultrafiltration's cake filtration pattern that is easily removed by back washing, ultrafiltration has a thin active layer and a high porosity sub structure. And asymmetric membrane will have higher stable permeability and better backwash efficiency.

Depending on the direction of flow relative to the membrane, two types of filtration are distinguished: conventional and cross-flow. In conventional filtration, the effluent to be treated is perpendicular to the surface of the membrane. However, in the cross-flow filtration, the flow circulates tangentially to the surface of the membrane so, while the filtration is performed, the membrane is cleaned.

Dead-end filtration (Figure 10a) refers to filtration at one end. The entire fluid flow is forced through the membrane under pressure. As particles accumulate on the membrane

surface or in its interior, the pressure required to maintain the required flow increases, until at some point the membrane must be replaced. A problem with these systems is frequent membrane clogging (Baker, et al., 2000). Dead-end filtration is generally suitable for concentrated suspensions, and not appropriate for the filtration of very fine and dilute suspensions or production of very pure filtrates (Ünlü, 2008).

In **cross-flow filtration** (Figure 10b) the feed solution is circulated across the surface of the filter, producing two streams: a clean particle-free permeates and a concentrated containing the particles. The equipment required for cross-flow filtration is more complex, but overcoming the problem of membrane clogging lets membrane lifetime be longer than with in-line filtration and it is widely used in water and wastewater treatment (Baker et al., 2000; Cheremisinoff, 2002). Figure 10 shows the schematic representation of dead-end and cross-flow filtration mode.

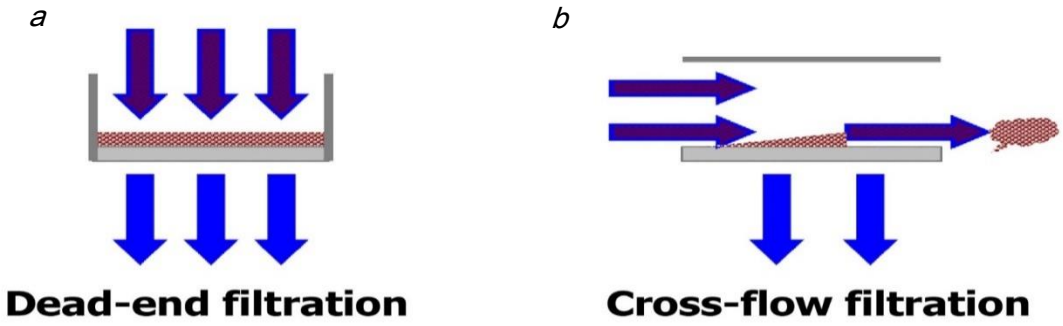


Figure 10. a) Dead end filtration, b) cross-flow filtration (Maletskyi, 2017)

II.2.2 Design and operating parameters in MBR

II.2.2.1 Membrane process operation

The performance of a membrane unit is defined by the following main parameters: Flux, pressure, resistance and permeability.

The **volumetric flux** is volume divided by surface (m^3/hm^2 of membrane surface), is modelled using a modified form of Darcy's law (AWWA, 2005). Pure water transport across a clean porous membrane is directly proportional to the transmembrane pressure (TMP) and inversely proportional to the dynamic viscosity.

$$J = \frac{Q}{A} = \frac{\Delta P}{\mu * R_m}$$

Equation 1

Where:

$J = volumetric\ water\ flux\ through\ membrane, \frac{m^3}{h * m^2}\ or\ \frac{m}{h}$

$Q = volumetric\ flow\ rate\ of\ pure\ water, \frac{m^3}{h}$

$A = surface\ area\ of\ clean\ membrane, m^2$

$\Delta P = transmembrane\ pressure, kPa$

$\mu = dynamic\ viscosity\ of\ water, Pa * s$

$R_m = membrane\ resistance\ coefficient, m^{-1}$

Whereas in the Darcy's law it is used the pressure gradient, in this form it is used the absolute value of pressure differential.

The volumetric flow rate of water across a single pore can be modelled using Poiseuille's law:

$$Q_{pore} = \frac{\pi\, r^4}{8\,(\mu)} * \frac{\Delta P}{\Delta z}$$

Equation 2

Where:

Q_{pore} = volumetric flow rate of pure water across a single pore, m^3/h

$r = radius\ of\ pore, m$

$\Delta P = transmembrane\ pressure, kPa$

$\mu = dynamic\ viscosity\ of\ water, Pa * s$

$\Delta z = pore\ length, m$

Because pores in commercial water treatment membranes are not perfectly cylindrical, a dimensionless tortuosity factor is added to Equation 3. To represent the total flow rate, Equation 3 is multiplied by surface area and pore density per unit area (Ho & Sirkar, 1992):

$$Q = A\rho_{pore} = \frac{\pi\, r^4}{8\,(\mu)\tau} * \frac{\Delta P}{\Delta z}$$

Equation 3

Where:

$\rho_{pore} = pore\ density\ per\ unit\ area, \frac{pore\ number}{m^2}$

$\tau = tortuosity\ factor, dimensionless$

This equation provides some insight into the factors that influence the design of a membrane filter. The flow rate is directly proportional to pore density and inversely proportional to water viscosity, tortuosity, and thickness of the membrane. The most important factor affecting flow rate is the pore size because flow rate is directly proportional to the 4th power of pore radius. Therefore, small increase in pore radius can result in large increase in filtered water flow. Perhaps more importantly, because commercial membranes employed in water treatment have distribution of pore sizes, the larger pores will transport a disproportionate quantity of water and particles.

Operating pressure. In wastewater treatment, transmembrane pressure AP varies from 0.1 bar up to 120 bar (Wiesmann & Choi, 2007) for pressure systems. To minimize the fouling the transmembrane pressure should be limited to 100 kPa in real treatment plants scale (AWWA, 2005; Bergman, 2005).

For the direct filtration mode, the transmembrane pressure may be calculated as:

$$\Delta P = P_i - P_p$$

Equation 4

Where:

$\Delta P = transmembrane\ pressure, kPa$

$P_i = pressure\ al\ inlet\ to\ module, kPa$

$P_p = permeate\ pressure, kPa$

II.2.2.2 Fouling phenomena and cleaning

Membrane fouling is caused by the deposition of organic and inorganic substances on the membrane surface or within the pores.

Fouling of MF/UF membranes may be defined as the gradual reduction in filtrate water flow rate at constant pressure, or an increase in transmembrane pressure to maintain a constant flux. Fouling may be caused by particulate matter, dissolved organic matter, or biological growth. It may be *reversible* or *irreversible.* The fouling is termed irreversible if the loss on flux cannot be recovered by backwashing and cleaning operations (Jacangelo et al., 1997). These are illustrated in Figure 12. There are a number of models that have been developed in an attempt to describe the decline in permeate flux.

Membrane bioreactor (MBR) technology has been used widely for various industrial wastewater treatments due to its distinct advantages over conventional bioreactors. Treatment of textile wastewater using MBR has been investigated as a simple, reliable and cost-effective process with a significant removal of contaminants. However, a major drawback in the operation of MBR is membrane fouling, which leads to the decline in

permeate flux and therefore requires membrane cleaning. This eventually decreases the lifespan of the membrane.

Fouling factors need to be taken seriously because they are the major problems affecting the performance of the MBR and quality of the effluent. There are specific methods to reduce and clean the clogging membrane depending on the level of severity of the fouling. Besides that, the performance of MBR soluble organic waste can be increased by adding a fouling reducer such as powdered activated carbon (PAC). (Sánchez & Garrido, 2013).

Organic fouling is mainly caused by colloidal and soluble organic matter as well as by the sludge itself, which forms the so-called sludge cake layer. Different strategies can be adopted in order to minimize membrane fouling. Reversible fouling can be counteracted by physical means such as backwashing or relaxation and air scouring (biogas in case of AnMBR), whereas irreversible fouling can only be removed by chemical cleaning. Finally, irrecoverable fouling refers to the phenomena which cannot be recovered using either physical or chemical cleaning strategies (Sánchez & Garrido, 2013).

This operation consequence, called fouling can be due to different causes and it affects membrane performance, commonly caused by raw water characteristics and inappropriate pre-treatment. There are several types of fouling:

- Colloidal and particle fouling – caused by solids from the pretreatment entering the first stage elements

- **Biofouling** – occurs due to high bio-growth potential in feed water, improper operation and procedures, dead legs in system
- **Organic fouling** – caused by natural organic matter in the feed water, polluted raw water, polyelectrolytes in flocculation/coagulation pre-treatment
- **Inorganic fouling** – scaling of salts due to concentration polarization requires proper pre-treatment, dosing of reagents, chemical cleaning.

The factors affecting the fouling of membrane in an MBR and their operational conditions are shown in Figure 11 for example, MLSS in a MBR can vary from 10 to 40 g/l (Jegatheesan et al., 2016).

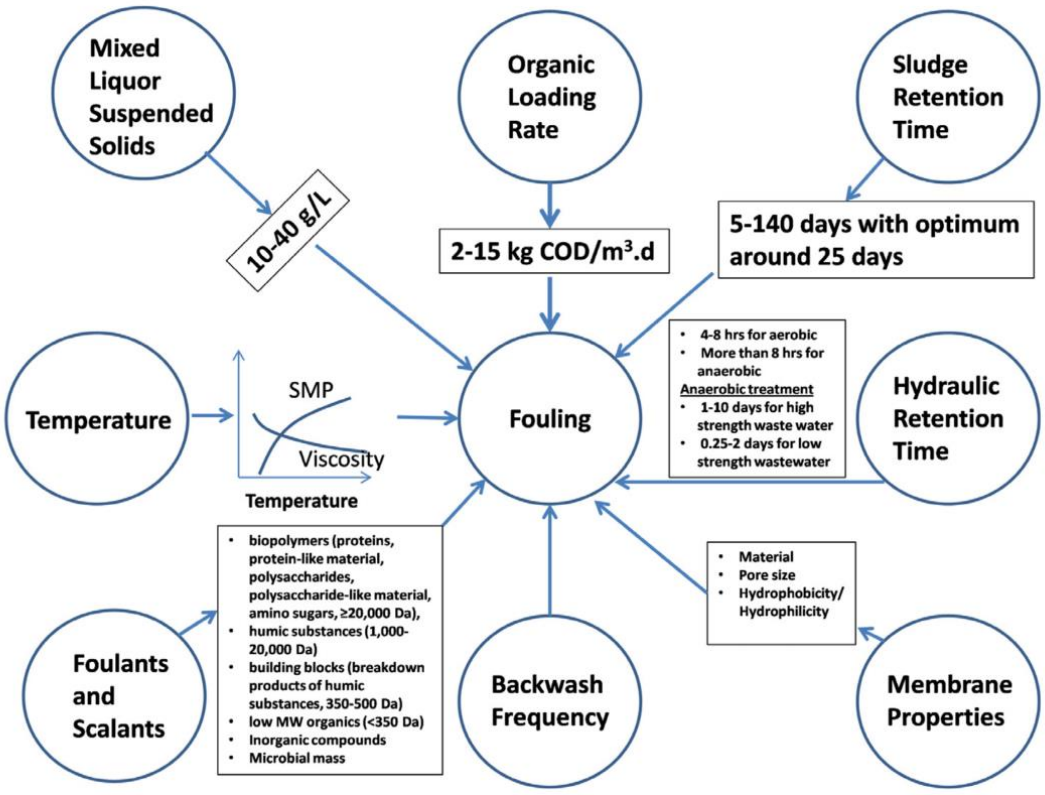


Figure 11. Factors affecting the fouling of membranes in a MBR (Jegatheesan et al., 2016)

Membrane cleaning

Membranes can be cleaned physically or chemically depending on various factors, below some cleaning methods are presented.

Backwashing. The backwashing cleaning cycle is automatically controlled. All modules in a rack are washed simultaneously. Backwashing occurs at some present interval ranging from 30 to 90 minutes and it lasts 1 to 5 minutes, in the real scale reactors. The off-line time for a rack may be longer that 5 minutes because of the time inherent in valve sequencing for shut down and start up. MF systems may be backwashed with either air (in hollow-fibre membranes) or permeate water. UF systems are backwashed with permeate water. Adding chlorine to backwash water aids in reducing biofouling.

Chemical cleaning. Even with frequent backwashing, membrane performance will deteriorate over time. The cleaning procedure may take a few hours. The module may be cleaned in place (CIP) or may be removed for cleaning. (Figure 12).

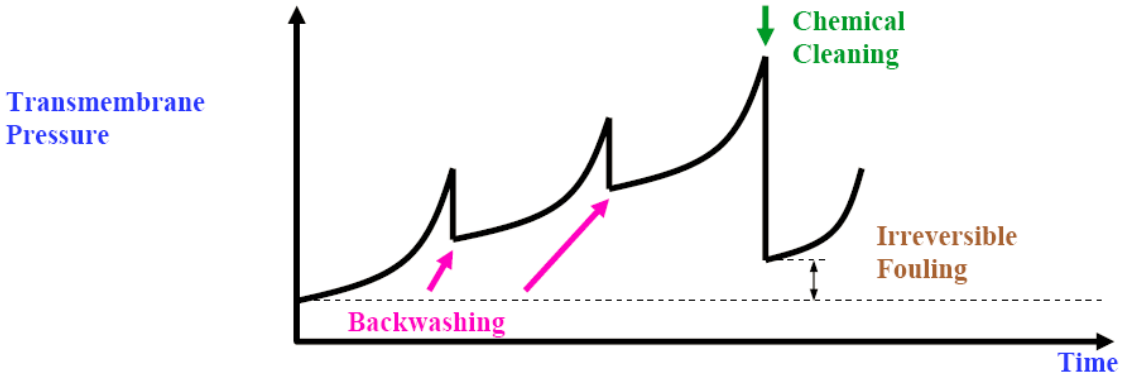


Figure 12. Theoretical variation of transmembrane pressure and influence of cleaning in MBR (Maletskyi, 2017)

II.2.2.3 Configuration of membrane modules

The membranes, for their operation, are coupled to a unit called module. In general, four modules can be distinguished: the **flat module** is the oldest and simplest configuration. It is a leaf or semipermeable sheet in which the water to be treated falls on only one side of the membrane. Its main disadvantage is its low surface area, which is why several membranes are generally arranged in the form of a stack or column. In **spiral winding**, several sheets of flat membrane are wound separating by a spacer. Its main advantage is its low cost of operation. In the **tubular module**, the membrane is arranged in the form of a tube with its active layer on the inside. The permeate flows radially from the inside to the outside and the concentrate is collected at one end of the tube. Finally, in the **hollow fibre module** the active membrane layer is in the exterior, whereby the permeate flows from the exterior to the interior and is collected in the end of the fibre. This type of configuration has certain advantages over the rest: occupies less volume, has more active surface and is more resistant (Olivera, 2015).

Hollow fibre membranes are the most common configurations of MF and UF filtration applications. Unlike nanofiltration (NF) and reverse osmosis (RO), the MF membrane filters operate over a repeating filtration cycle like granular filters. After filtration for a set duration, the accumulated solids are removed by backwashing with air and/or water. Once clean, the filter is put back into service.

All of the hollow fibre membranes fall into one of two categories: positive pressure driven and negative pressure driven (vacuum driven). The positive pressure driven systems are configured in pressure vessels. The vacuum systems are submerged in basin containing the feed water.

II.2.3 MBR treatments for indigo colour removal

Some remediation techniques employ microbial degradation, which uses microorganisms such as bacteria and fungi, phytoremediation using plants, and remediation through specific enzymes. Bioremediation modes applied to dye discoloration include crop mixtures, isolated organisms and isolated enzymes. Extracellular enzymes such as laccase and peroxidase are produced by fungi.

At pilot scale and on a large scale, effluents can be treated in bioreactors with cultures of one or more isolated microorganisms or a mixture of populations, also called consortia. In a culture mix, where a consortium of different species is present, dye discoloration may be the result of the synergy of several microorganisms (Mittal et al., 2006).

In general, mixtures of populations have the highest stabilities in stress environments, caused by changes in effluent characteristics, such as temperature, pH or composition (Kandelbauer & Guebitz, 2005), The types of microbial growth are of two types: suspended and with immobilized cells, depending on the type of reactor. For example, the fluidized bed reactor contains free and mobile pellets covered with layers of

immobilized biomass, whereas packaged bed reactors contain organisms which are fixed in a carrier material (Zheng et al., 1999).

There are physical-chemical, chemical, physical and biological technologies for the treatment of indigo textile wastewater. The choice of treatment depends on the water quality of the effluent, the use, and the costs of the technology, advantages and disadvantages. The non-biological treatments applied to indigo dye, although they have excellent removal results, lack economic studies, pollution transfer studies and many laboratory scale results have not been used at pilot scale, so many factors that intervene in scale dimensioning have not been evaluated. Treatment systems using microorganisms are able to degrade recalcitrant dyes to mineralize them. The effectiveness of these treatments depends on the survival and adaptability of the microorganisms during the treatment process. Biological treatments have been more frequently scaled and increasingly targeted to cells immobilized with microbial consortia. Table 6 summarizes some aerobic and anaerobic biological treatments, evaluated at pilot scale, of textile effluents for indigo removal (Luz Quintero & Cardona, 2010).

Table 6. Summary of MBR bibliographic review for treatment of textile wastewater for the past 10 years

Influent	Process description	Scale	Config	Vol (l)	Flux lMH	TMP (kPa)	HRT (h)	SRT (day)	F/M (kg COD/m^3MLSS d)	MLSS (g/l)	*
Anthraquinone dyes synthesis	Aerobic MBR	L	Sub	10	-	10-30	50-20	-	-	2.0-3.0	1
	Ae Bioaugmented MBR	L	Sub	10	-	10-30	15-24	-	-	2.0-3.0	
Textile mill	Aerobic MBR	P	Sub-HF		2-8	5-10	6-22.5	>30	-	9-11	2
Denim textile wastewater	Sub MBR/Aerobic CSTR	P	Sub-HF	230	11-18	14-56	13.29	25	0.030.07 kg	13.9-17	3
Treat. plant (reactive blue 4)	Fenton oxidation and AeMBR	L	Sub-HF	6	7.5	<35	10-25	30	0.007-0.035	6	4
Synthetic, anthraquinone	MBR-IE	L	Sub HF	18	-	<53	20	30	-	4-5.5	5
Commercial laundry and textile factory	MBR+RO	I	Sub MF	$126*10^3$	-	5-10	-	-	-	3-10	6
	MBR	P	Sub HF	90	8-10	-	6-22.5	-	0.05-0.15	-	
Industrial	Aerobic MBR	L	Sub	28,00	2	<43	11	60d	1.4-1.7	6-9	7
Synthetic TW, red dye	Aerobic MBR	L	Sub-HF	22		2.8-13	4-48	-	-	1-3	8
STW	Aerobic MBR	L	Sub-FS	57	2-4	3-5	100	NSR	0.05-0.1	8-12	9
Textile wastewater	Aerobic MBR	P	Sub FS UF	60	-	7-35	24-62.4		0.8-2.1	5.22-10	10
Textile wastewater	MBR	P	Sub-HF	6000	-	25	-	-	0.36-1.25	6-14	11

Influent	Process description	Scale	Config	Vol (l)	Flux lMH	TMP (kPa)	HRT (h)	SRT (day)	F/M (kg COD/m^3MLSS d)	MLSS (g/l)	*
Dyeing and finishing wastewater	2 phase An CSTR/aerobic CSTR+M aerobic CSTR	L	Sub	60	-	-	-	-	-	5.64-4.8	12
Synthetic azo dye	sequential An & A MBR	L	Sub-FS	18L	-	-	24	-	-	2.1	13
Textile dyeing wastewater	HCMBR	P	Sub	1670			-	-		6.05-8.32	14
Synthetic textile wastewater	Anaerobic MBR	L	Sub-FS	5.7	9		24-48	NSR	-	10	15
	Aerobic MBR	L		4.3	20		12-24	30d	-	20	
STWW (Remazol Brilliant Violet 5R)	Sequential AnMBR	L	Sub-FS	5.7-4	4.22-8.51		30.7-54.2	30-NSR	-	-	16
STWW (Remazol Brilliant Violet 5R)	Sequential AeMBR	L		4.3-2.5	87.7-10.15		37.2-25.44	30-NSR	-	-	17
STWW (Red and blue anthraquinone dye)	AeMBR	L	Sub	57	2-4	3-5	25-150	NSR	0.05-0.1	8-12	18
	AeMBR	L	Sub	57		3-5	25-150	NSR	0.05-0.1	8-12	
	AeMBR UF	L	Sub	57	-	3-5	25-150	NSR	0.05-0.1	8-12	
STW	AeMBR (2 membranes)	L	Sub	60-47	1.2-2.5	4-6	70-30	-	0.1-0.25	4-14	19
STW	AeMBR MF	L	Sub-HF	12.5	-	-	15	-	-	2	20

Influent	Process description	Scale	Config	Vol (l)	Flux lMH	TMP (kPa)	HRT (h)	SRT (day)	F/M (kg COD/m^{3}MLSS d)	MLSS (g/l)	*
STW	SMBR	L	Sub	30	2-4	3-5	40-90	-	0.05-0.1	8-12	21
	SSMBR		Side-Stream	57	5-15	3-5	145-400	-	0.02-0.06	6-8	
STW	SMBR	L/P	Sub-FS	170	-	-	48	-	-	-	22

References: 1: (Qu et al., 2009); 2: (Huang et al., 2009) 3: (Yigit et al., 2009b); 4:(Feng et al., 2010); 5: (Qin et al., 2012); 6: (Hoinkis et al., 2012); 7: (Thanh et al., 2012); 8: (Thanh et al., 2012); 9: (Konsowa et al., 2013); 10: (Konsowa et al., 2013); 11: (Bouhadjar et al., 2015); 12: (Es Friha et al., 2015); 13: (Lubello et al, 2007); 14:(Gao et al., 2008); 15: (You & Teng, 2009); 16: (Yan et al., 2009); 17: (Yurtsever et al., 2015); 18: (Shamming et al., 2016); 19: (Luong et al., 2016); 20: (Hossain et al., 2016); 21: (Bouhadjar et al., 2015); 22: (Taylor et al., 2017); P: Pilot scale; L: laboratory scale; I: Industrial Scale; Sub: Submerged membrane bioreactor: NSR: No sludge was removed; HF: Hollow Fibre; FS: Flat Sheet; IE: internal micro-electrolysis; HCMBR: hybrid coagulation/membrane bioreactor; MF: micro filtration.

Conventional aerobic biological treatments are recognized for their low costs, feasibility and ability to reduce BOD and COD (Forgacs et al., 2004; Kornaros & Lyberatos, 2006). The aerobic processes have recently been used for the treatment of wastewater and have been confirmed to be efficient and effective for the treatment of industrial residual water (Sandhya et al., 2005; Sudarjanto et al., 2006). In Khelifi et al., (2008a) a sequence of continuous aerobic reactors for indigo discoloration was evaluated, however, in this study it is desired to continue the investigation of indigo discoloration and the use of Ultra Filtration technology is proposed.

Table 7, coming from the same literature review as the previous Table 6, is presented in order to show the characteristics of the membranes used in different experimental performances. The parameters that were taken into account were the membrane cleaning periodicity, as well the effluent characteristics of each study. This table shows that the common materials used in PVDF (Polyvinylidene Difluoride) and that membrane cleaning procedures can be backwashing and chemical cleaning.

Table 7. Membrane characteristics used in different papers

Configuration	Material	Pore size (μm)	Membrane cleaning	COD(%) removal	Colour(%) removal	Reference
Submerged	-		backwash-3d chemical-2months	50	65	Qu et al. (2009)
Submerged	-		backwash-3d chemical-2months	50	90	
Submerged-Hollowfiber	PVDF		no chemical	85-92	60-75	Huang et al. (2009)
Submerged-Hollowfiber	-	0.04	chemical after 35 d	>95	>97	Yigit et al. (2009)
Submerged-hollowfiber	PVDF	0.2	Chemical (35 Kpa TMP)	TOC removal 88.2	91.3	Feng et al. (2010)
Submerged-hollowfiber	A self- made PVDF	0.05	-	93	98	Qin et al. (2012)
Submerged microfiltration plate and frame	chlorinated polyethylene	0.4	1 year no cleaning	90	-	Hoinkis et al. (2012)
Submerged hollowfiber	PVDF	0.2	No needed	90	60-75	
Submerged	PVDF	0.2	-	91	86.3	Bui Xuan et al. (2012)
Submerged-hollowfiber	MF polyethylene (PE)	0.4	sodium hypochlorite NaOCl	90.9-95.6%	-	Konsowa et al. (2013)

Configuration	Material	Pore size (μm)	Membrane cleaning	COD(%) removal	Colour(%) removal	Reference
Submerged-membrane sheets	UF-novel low fouling membrane-	0.03-0.05	no chemical	90-95	40-55	Deowan et al. (2013)
Submerged crossflow flat sheet UF	-		-	98	100	Friha et al. (2015)
Submerged-Hollowfiber	MF	0.2	-	91%	-	Lubello et al. (2007)
Submerged	Hollowfiber			-		Gao et al. (2008)
Submerged-Flat sheet	PTFE	0.22		5.2	9.1	You et al (2009)
Submerged	PVDF, hollowfiber	0.2		90.72	-	Yan et al (2009)
Submerged-Flat sheet	MF-PES	0.45	Chemical	-	100	Yurtsever et al. (2015)
		0.45	Chemical	97	30-50	
Submerged-Flat sheet	Flat sheet microfiltration polyethersulfone (PES)	0.45	Chemical	80-85	>99	Yurtaever et al (2016)
	Flat sheet microfiltration polyethersulfone (PES)	0.45	Chemical	86-65	>99	Yurtaever et al (2016)
Submerged	UF with antifouling coating-polymeraseble bicountinuous microemulsion (PBM)		no chemical cleaning regular back flush with permeate was applied (every 9 min for 0.5 min)	95±1	40-50/55	Shamin et al (2016)

Configuration	Material	Pore size (μm)	Membrane cleaning	COD(%) removal	Colour(%) removal	Reference
Submerged	PES UF	0.04	day 27-replacement physical cleaning water-chemical cleaning 1% H2O2	90±1	40-50	
Submerged	PES UF	0.04	day 27-replacement physical cleaning water-chemical cleaning 1% H2O3	95±1	23-45	
Submerged	flat UF membrane		-	95	20-60	Tan et al. (2016)
Submerged-Hollowfiber	MF polyethylene	0.4	Off-site manual cleaning with water	50-67	98	Kaizar et al. (2016)
Submerged	Flat sheet UF cross flow	0.04	-	90	20-40/50-90	Saadia et al. (2016)
side stream	Flat sheet NFandUF		-	97	20-40/	
Submerged-flat sheets	flat-sheet membranes (PVDF + PET)	0.08–0.3	-	87-90	90.71-80.84	C. Acikgoz et al. (2016)

II.3 BIOAUGMENTATION

Bioaugmentation, bacterial augmentation, biomass enhancement or inoculum addition is a process which attempts to improve biological wastewater treatment by increasing diversity and/or activity through direct introduction of either selected naturally occurring micro-organisms or genetically altered micro-organisms to the treatment plant

It is the process of adding selected strains/mixed cultures to wastewater reactors to improve the catabolism of specific compounds, as for example removal of colour.

Options of bioaugmentation:

- Addition of pre-adapted pure bacterial strains
- Addition of pre-adapted consortia
- Introduction of genetically engineered bacteria
- Addition of biodegradation-relevant genes packed into a vector to be transferred into microorganisms already there

The reasons why we use bioaugmentation are:

- MBR deficiencies in colour removal
- Bioaugmentation reduce energy consumption as it will reduce HRT time
- Indigo removal with bioaugmentation has not been reported

In the Table 8 below, it is shown the past 10 years review of papers working on Bioaugmentation. Most of the papers are studying azo dye removals by bioaugmentation, whereas few of them studied the removal of indigo dye. It can be seen in the table, the microorganisms (bacteria or fungi) that are used to bioaugment the laboratory experiment

in each case, as well as the place where this stain was taken and isolated, normally this bacteria are isolated from activated sludge form an specific industrial reactor (Khelifi et al., 2008a; H. Lin et al., 2012; Qin et al., 2012) or from fungi organisms as the studies of Manai et al. (2016) and F.I. Hai et al. (2011). It is also remarkable that most of the studies are conducted using synthetic medium, due to the advantages to work in stable conditions, it is also important to highlight that the review made shows that most of the bioaugmentation studies made up to this date are made in small volume reactors around 1 l.

Table 8. Past 10 year review of papers working on Bioaugmentation; system characteristics

Dye	Microorganism Isolated from	Reactor	Volume (l)	Scale	Medium	Ref
Xylidine Ponceau 2R (XP2R)	Shewanella marisflav Marine sediment	Aerobic	0.5	L	Synthetic	1
2, 4-Xylidine		Anaerobic				
Indigo	Bacillus cereus & Bacillus pumilus Ae reactor textile wastewater		0.250	L	sterile textile ww	2
Indigo	Fungal Strains (*Aspergillus alliaceus* (KF-3)) Ae reactor textile wastewater		0.251	L	10% (v/v) sludge sample	3
Indigo	Activated sludge Ae reactor textile wastewater	Combined CSTR/FFB	0.7	L	WWTP (Tunisia),	4
		CSTR	0.7	L		
		FFB	0.7	L		
Azo dyes	white-rot fungi *Coriolus versicolor* NBRC 9791	(MBR) GAC-packed An zone	0.85	L	STW	5
Indigo	Isolated fungal *Chaetomium globosum* IMA1. Ae tank WWTP	Activated Sludge	2	L	Real TW (Tunisia)	6
-	Providencia sp., Brevibacillus sp., Alcaligenes sp. and Pseudomonas sp.	Sequential reactor	10 Anox 5 Ae	L	Soil sample	7
Acid Red B (ARB)	Magnusiomyces ingens LH-F1	(BAFs)	2	L		8

Dye	Microorganism Isolated from	Reactor	Volume (l)	Scale	Medium	Ref
Acid Red B (ARB)	Candida tropicalis TL-F1 Sea mud	MBR hollow (PVDF)	14	L	Simulated azo dye WWr	9
Brilliant Scarlet GR		(AnSBRs)	0.125	L	Synthetic	10
C.I. Direct Blue 71	genetically engineered strain *Escherichia coli* JM109	AnSBRs		L	SW	11
1-amino-4-bromoanthraquinone-2-sulfonic acid	Sphingomonas xenophaga sludge samples Chemical Plant (China)	(SMBR)	10	L	SW	
CI Reactive Violet 5 (CIRV5)	Staphylococcus aureus TW	in vitro	Small	L	Synthetic	12
Quinoline and phenol removal	Comamonas testosteroni bdq06 WWTP Petrochemical Company (China)	stirred tank reactors	1	L	Dye wastewater	13
Reactive brilliant red X-3B (X-3B in abbreviation)	Electrochemical methods for enhancement of microbial degradation	anaerobic reactor Fe-graphite plate electrodes		L	Artificial azo dye wastewater	14
Acid Orange 7	Shewanella sp. XB quinone-reducing consortium enriched from activated sludge	AMBR	2	L	SW	15

REFERENCES: 1: (Xu et al., 2016); 2: (Khelifi et al., 2012) 3: (Khelifi et al., 2009); 4: (Khelifi et al, 2008b); 5: (F. I. Hai et al., 2011); 6: (Manai et al., 2016); 7:(Chattaraj et al., 2016); 8: (Hongjun Lin et al., 2012); 9: (H. Lin et al., 2012); 10: (Qu et al., 2009); 11: (Qu et al., 2009); 12: (Qu et al., 2009); 13: (Qin et al., 2012); 14 y 15: (H. Lin et al., 2012); STW: synthetic textile wastewater; SW: synthetic wastewater.

III METHODOLOGY

This chapter describes the research methodology followed in this master thesis. The working plan is shown in Figure 13. Firstly, the system set-up was carried out by installing the reactors, the pumps, the tubing, the sensors and the controllers of the laboratory experiment. Moreover sludge for the reactors was collected from an industrial wastewater treatment plant. Different works were carried out in order to find the appropriate composition of Synthetic Textile Wastewater (STW). Membrane modules were also made and they were characterized and monitored their performance. Especial attention is given to the methodology related with the performance of the membrane. Conventional parameters such as flux or permeability are described, but also theoretical explanation of the resistance to filtration determination. Moreover, methodology related with the determination of different hydrophobicity and capillarity suction time. Bioaugmented bacteria were studied in parallel to the laboratory system performance, this bacteria were grown in STW media in order to observe if they keep their ability to degrade indigo colour dye. Finally the process was started up. About the results of the process of study, coming from the laboratory plant, pressure of the membranes was monitored and collected the data in a personal computer (PC). Sludge on the reactors was characterized periodically in order to study its characteristics variations along the time of the experiment. Effluent or permeate of the membranes was collected and measured the COD (Chemical Oxygen Demand), Colour and EC (Electrical Conductivity). Finally results were studied and discussed.

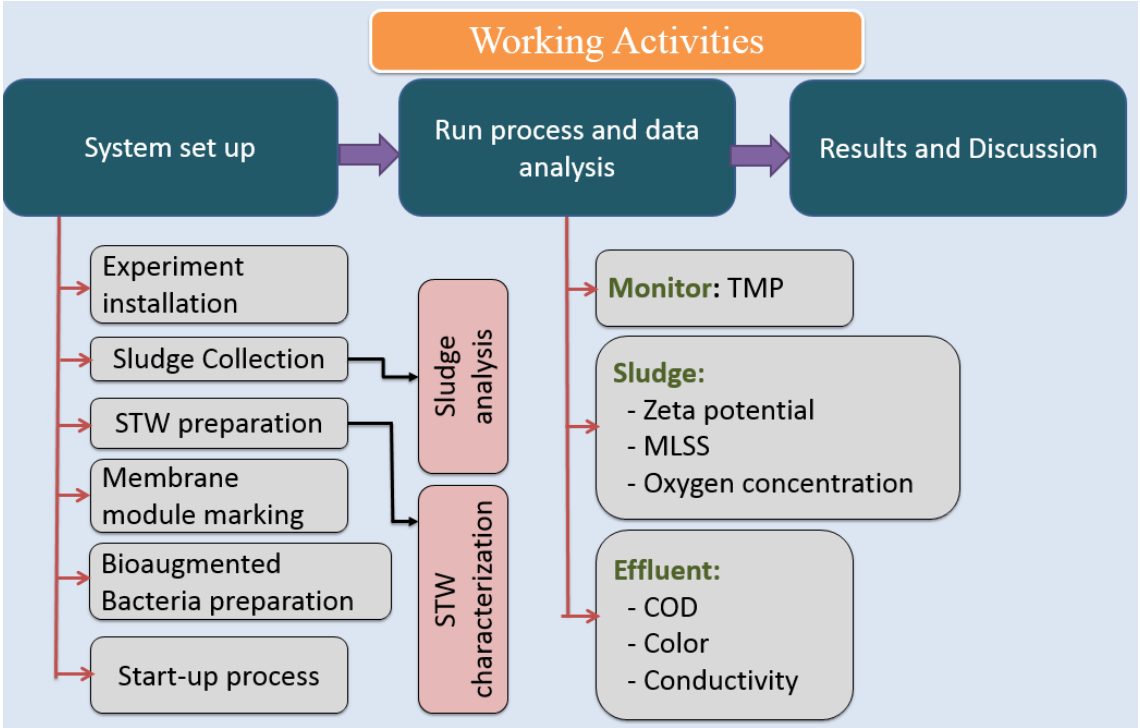


Figure 13. Working plan

III.1 EXPERIMENTAL SET-UP AND OPERATING STRATEGY

III.1.1 Laboratory-plant MBR

The laboratory-scale set-up consists of two cylindrical PVC reactors (Diameter 10.6 cm, Height 44 cm) with a working volume of 2.5 l and containing submerged membrane hollow fibre modules. The diagram (Figure 14), shows how STW will be used as the influent of the process, this water will be pumped by two multichannel pumps and will enter MBR1 (membrane bioreactor 1, control) and MBR2 (bioaugmented membrane bioreactor). This to reactors are aerated by a diffusor that is placed in their bottom and is connected to the blower by tubing and a mechanical controller of the air in order to keep the same oxygen concentration in both reactors. Water will come out of the reactors by the

membrane modules, these are connected to a pressure gauge that will register data of pressure in the PC every 6 seconds. The out-pump that will allow water flow from the membrane into the permeate tanks is controlled by Arduino in order to keep certain characteristics of the sucking-backwashing cycle. Moreover, green arrows in the figure show that permeate water will be recirculated to the reactor to avoid water level in the reactor to decrease, this is controlled by a mechanical sensor level and the tubes are gravity driven.

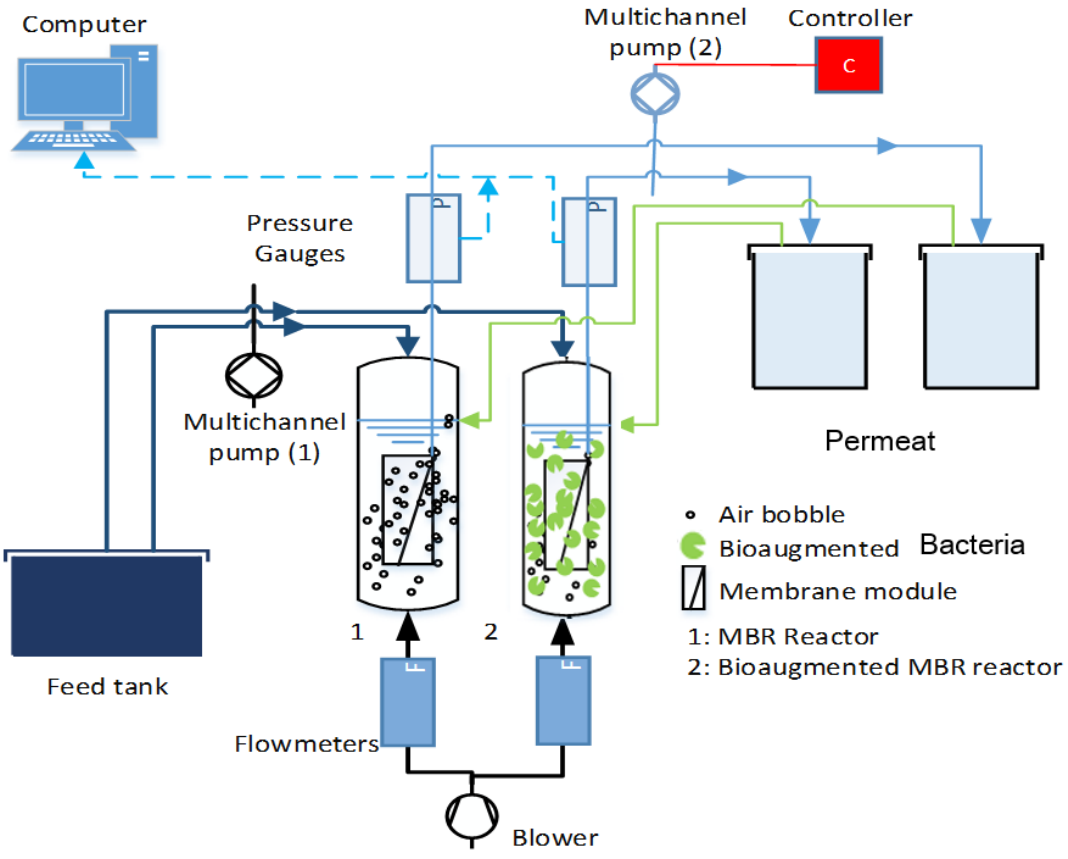


Figure 14. Laboratory set up flow diagram

III.1.1.1 Bioreactors and pumps

As it is shown in Figure 15. Laboratory display, two multichannel peristaltic pumps model BT100LC cr-pump, were installed. One on them, pumps the water from the synthetic textile water tank into the reactors, the income flow to the system was fixed in 1.157 ml/min during this first period of the experiment. Regarding the second multichannel pump, it sucks the water from the membranes into the effluent tanks. Moreover, this second pump is controlled by Arduino controller in order to work certain time sucking, then certain time of relaxation and certain time of backwashing. The controller characteristics are shown below. As it is shown in the figure the pressure gauges are connected to the tubing, connecting the membranes to the pump, more details are given below.

One air blower was installed and supplied air to the base of the reactors, where a diffuser was set up. The control of the aeration was manual, with a controller of the air at the entrance of the tubes. However, the Dissolved Oxygen was measured in order to maintain the same aeration in both tanks.

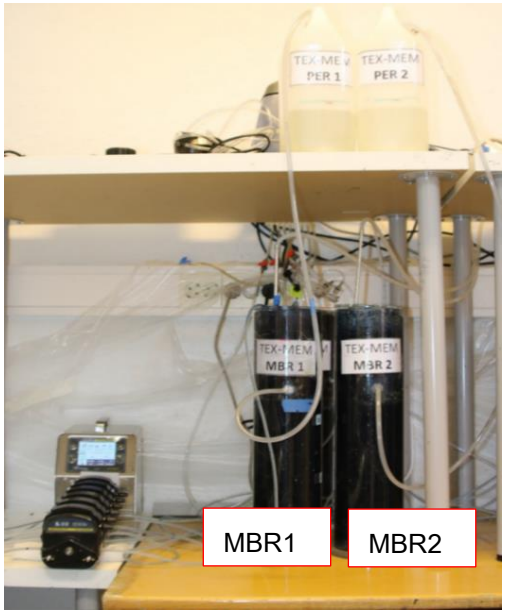


Figure 15. Laboratory display

III.1.1.2 Sensors and automation

Level sensor. A level sensor was included in the reactor in order to maintain the water level and the volume of water in 2.5 l. This sensor consists on a ball (orange ball in Figure 16) that will float in the water when the level is high and will block the entrance of water. This water comes from the permeate tanks by gravity. If sludge level in the reactor goes down, the ball will go down too, and this will allow the water from the permeate flow to the reactor and fill it until its fixed level again. Reactor water level sensor shown in Figure 16, is responsible to maintain the same water level in both reactors, water will be recirculated by gravity from the permeate tanks and pass through the white plastic when the ball goes down.

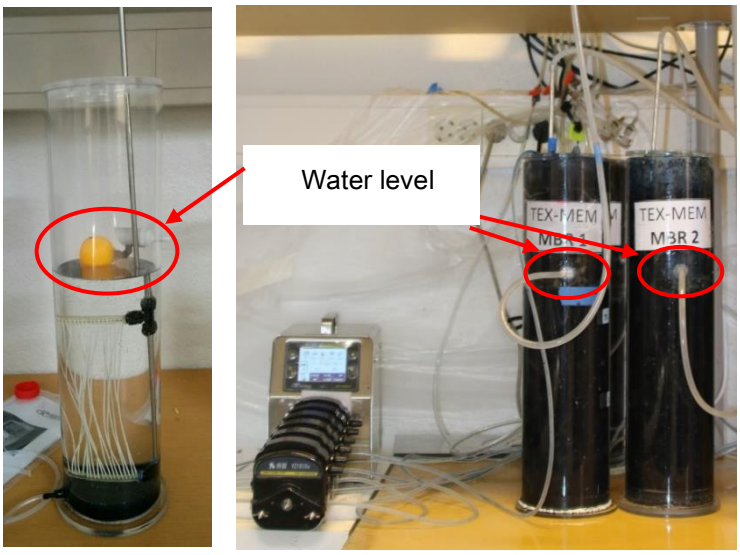


Figure 16. Water level mechanical control

Control and automation: Arduino. In order to control one of the multichannel peristaltic pumps it was necessary to add an external control chip. This will allow the pump to work during 9.5 min sucking form the membrane, 1 min of delay, then 30 s of backwash and then other minute of delay. This cycle will be repeated continuously. The technical datasheet of Arduino controller is showed in the Table 9. Pictures bellow show the connections of the chip (Figure 17).

Table 9. Technical datasheet of Arduino controller

Characteristics	**Specifications**
Microcontroller	ATmega328P
Operating Voltage	5V
Input Voltage (recommended)	7-12V
Input Voltage (limit)	6-20V
Digital I/O Pins	14 (of which 6 provide PWM output)
PWM Digital I/O Pins	6
Analog Input Pins	6
DC Current per I/O Pin	20 mA
DC Current for 3.3V Pin	50 mA
Flash Memory	32 KB (ATmega328P) of which 0.5 KB used by bootloader

Characteristics	Specifications
SRAM	2 KB (ATmega328P)
EEPROM	1 KB (ATmega328P)
Clock Speed	16 MHz
LED_BUILTIN	13
Length	68.6 mm
Width	53.4 mm
Weight	25 g

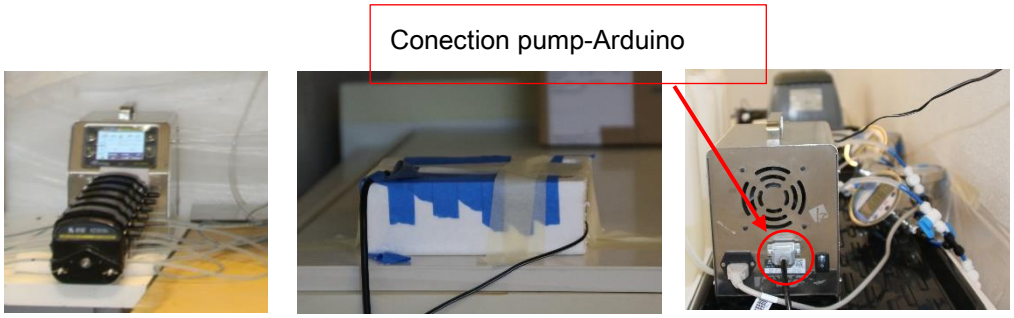


Figure 17. Pump control

Next Figure 18 shows the writing of the programme. It can be seen the temporal series of performance is 12 min long and 9.5-1-0.5-1min different activities will be ordered to the controller and consequently, to the out-pump.

Figure 18. Programme writing, cycle specifications

III.1.1.3 Manometers

Pressure Gauges. The pressure in the tubes coming from the membrane modules to the effluent tanks is measured by two pressure gauges from xaancn.com, these pressure gauges are connected to software called KaciseView Intelligent transmitter motoring, in this software the results from the pressure gauges will be collected, and can be exported to excel sheets.

This sensor it collecting the data into a PC where they can be exported to an excel file in order to study the results. One of the main challenges of this methodology is the great amount of data that are collected (one value of pressure every 6 seconds approximately).

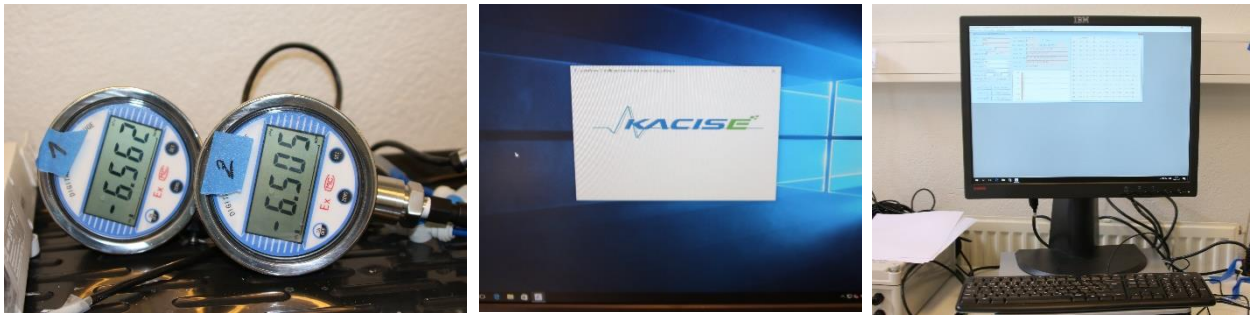


Figure 19. Pressure gauges and associated pc programme

III.1.1.4 Membrane modules

Membrane modules. The characteristics of the membranes used in this laboratory set up are the following. Ultra-filtration membranes made of PVDF (Polyvinylidene Difluoride), the manufacturer is Siemens, the pore size of the membranes is 0.04 µm, and the surface area 150 cm^2.

Chemical cleaning. In order to establish a cleaning protocol to clean the membranes in the beginning of the functioning of the system, as well as when the pressure reach a determined level, the membrane modules will be cleaned and the pressure resistance will be measured again. This will give information about the state of the membrane as well as the influence of the bioaugmentation into the reactor, comparing the results of the membrane cleaning of the control reactor to the bioaugmentation reactor. The cleaning procedures are listed below.

- In a small beaker, submerge the membrane modules in 50 ml distilled water and shake it manually for 2 min to remove weakly adsorbed fraction.
- To remove the intermediate fraction backwash the membrane with 50 ml of distilled water at 65 l/m^2h
- To remove the most strongly bound fraction, soak the membrane in 50 ml of 0.02 % Sodium Hydroxide solution for 24 h with slow sitting.

- During the experimental running it is fixed in the bibliography that when a certain pressure is set around 40 kPa the membranes have to be cleaned.
- They can also be cleaned in a 1000 ppm solution of sodium hypochlorite during 4h, after that, the Resistance of the membranes is measured again to check the results of the cleaning.

There is a procedure that can allow the assessment of cleaning efficiency; this procedure does not aim to replicate cleaning strategies applied in the industry, but to obtain three fouling layers in a well-controlled environment for further characterisation by analytical tools.

Membrane modules elaboration. In order to produce the modules, the procedure explained below was followed:

Materials for one membrane module:

- 1 T tubing with 3 exits
- 1 T tubing with 2 exits
- Metal tube
- 2 PVC plastic tubes
- 20 cm UF fibres
- Epoxy glue

Procedure: A module containing 19 lumens with working length of 20 cm was prepared.

1. Cut 19 pieces of 35 cm of hollow fibre. Hollow fibre membrane is easy to be stretched or damaged, this membranes where handled carefully while working with them. The required length of the membrane is measured with addition of few cm for both ends for potting purpose.

2. To assemble the materials EPOXI resin glue was used as shown in Figure 20.
3. Cut two plastic PVC one-end tube with 19 small holes
4. Add the fibres to the PVC tube (Figure 21)
5. Connect the tube to the pipe connector
6. Cut 35 cm of the metal tube and 20 cm for the union Metal bars of 32.8 cm were connected to plastic connectors and these to a hard plastic bar with holes into which the PVC fibres were attached.
7. Let the module dry
8. Cut three membrane hollow fibres into 22 cm lengths.
9. The calculations to obtain the surface area of each module is shown in Equation 5. Membrane modules surface area calculation.

$$S\ (cm^2) = Nfibers * \pi * Dfiber * L$$

Equation 5

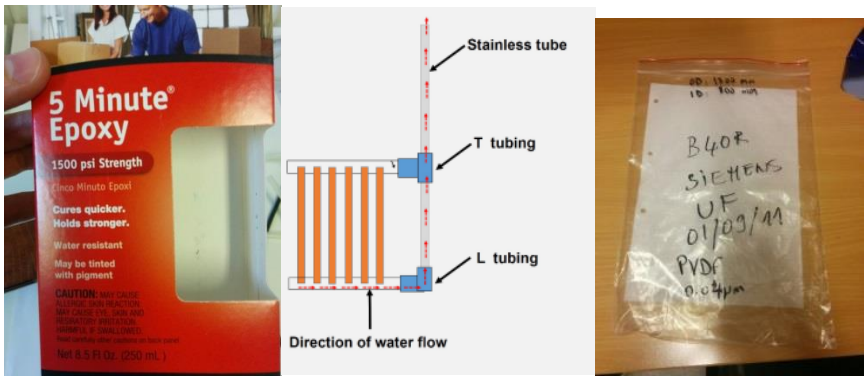


Figure 20. Epoxy glue; Membrane module diagram; Membrane fibres UF

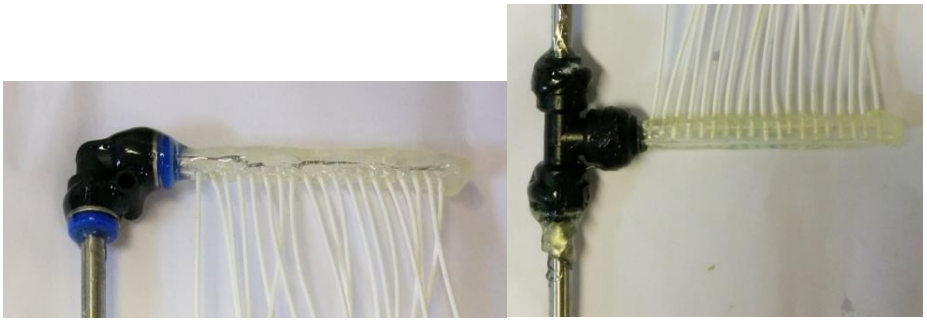


Figure 21. Tubing connection with two exits and tubing connection with 3 exits

Membrane module first checks in. In order to check the correct functioning of the membrane modules, once 24 h of drying, the membrane modules were introduced in distilled water and air blew by the air blower. This will give an idea of the points that were not well assembled. Small leaks were located by the bubbling in the water. If a leak was detected, the epoxy glue was removed and added again in order to achieve no leaks in the modules as they will cause functioning problems. This procedure was repeated until no leaks were detected.

III.1.2 Bioaugmentation

Bioaugmented bacteria used in this work were collected from SITEX denim industry in Tunisia. Bacteria were isolated and kept under -20ºC conditions for one year. External studies were conducted in order to make this stains viable again. Later on, the bacteria were introduced into synthetic textile wastewater in order to check their availability to degrade indigo dye. Figure 22 shows the result of the batch experiment after 24 h of mixing of synthetic textile wastewater (STW) with the decolorizing bacteria, the flask in the right shows the colour of the original STW. Finally these bacteria were added into the MBR2 reactor.

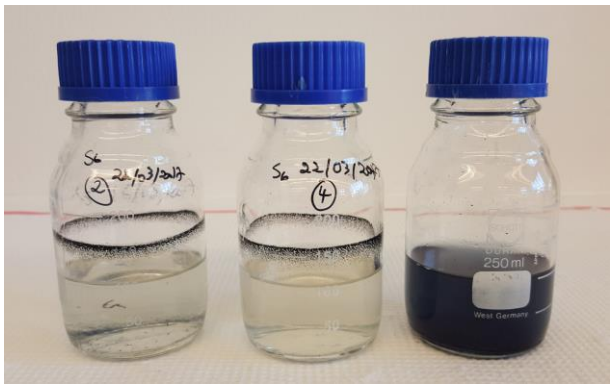


Figure 22. Two flasks containing decolorizing bacteria after 24 h in STW media

III.2 CLEAN WATER TEST

Membrane module resistance calculation. The procedure followed in order to measure the resistance of the membrane is called “Clean water test”.

Clean Water Testing. The Clean Water Test allows the assessment of the membrane hydraulic performances, i.e. Permeability (K) and Resistance (Rm). The aim of the clean water test is to perform the system using permeate pumps and pressure gauge by following the steps below:

1. Connect rig, Figure 24 shows the rig set-up.
2. Activate pump to begin circulation while observing pressure on the software-computer interface.
3. After circulating at constant flux until the pressure stabilizes stop the pump and when the pressure stabilizes record the value (P_0).
4. Set the pump at known fluxes 10, 20, 40, 80 l/m²h (suggested values) and allow the pressure to stabilize at each flux step. At each flux step record the set flux (J) and corresponding stable pressure (P_t).
5. Record Results in the format of Table 10.

As for the constant pressure operation, K (and R_m) should remain relatively constant over the range of flux tested. As it was exposed in page number 32 while reviewing the membrane process operation equations 1 to 4, the following Table 10 sums up the calculations made in order to obtain permeability and resistance of the membrane modules.

Table 10. Flux steps method for assessment of membrane resistance

Flow (l/h)	Flux (J) (L/m²h)	Suction Pressure (SP) (kPa)	Trans Membrane Pressure TMP (kPa)	Permeability (K) (L/m²h/kPa)	Resistance Rm (m^{-1})
DW Volume of a glass cylinder that will be filled up in certain fixed time	$\frac{\text{Flow}}{\text{Module area}}$	Raw data coming from the pressure gauge and exported by Kacise viewer	$TMP = P_0 - P_t$ P_0: SP when flow is 0 P_t: SP at each t time	$\frac{\text{Flux}_t}{TMP_t}$	$\frac{1}{Permeability}$

DW: Distilled water

During Clean Water Tests, if R_m increases with increasing flux/volume it may indicate the presence of contaminants in the system. Further cleaning of the tank and elements and use of deionised water is recommended. If R_m decreases with increasing flux the membrane may not be fully wetted or there may have an integrity issue.

For test to be valid, K and R_m are expected to remain constant (+/- 10-20%). If significant increase in K is observed, this could indicate incomplete wetting of the membrane, and wetting procedure should be repeated. This trend could also indicate a loss of integrity from the membrane (which should be checked for glue

default). It is also possible for K to decrease for higher heights; this could indicate improper potting or deposition of impurities on the membrane surface. In that case, membranes and tanks should be cleaned.

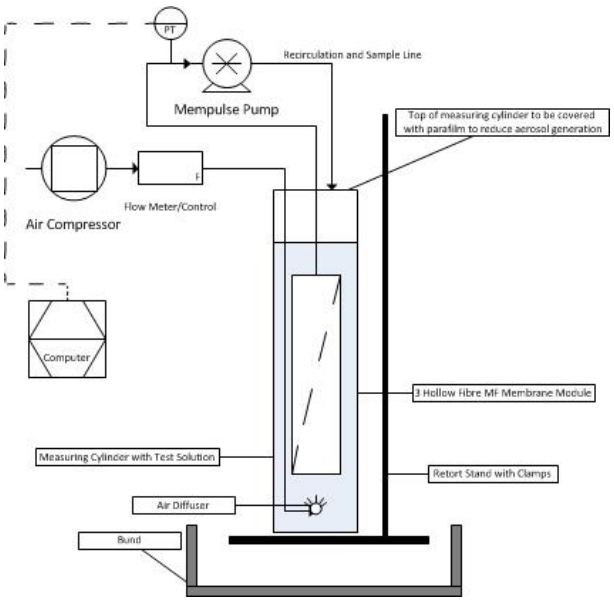


Figure 23. Rig set-up, theoretical set-up proposed by the methodology

III.3 ANALYTICAL METHODS

In the following section the laboratory work is exposed.

III.3.1 Synthetic Textile Wastewater - Influent

The purpose of this study was to elaborate representative wastewater, with similar characteristics to the real one, coming from the denim textile industry, using indigo dye in their process. First of all, bibliographic review was done using formal database in order to review the last 10 years research papers in this topic. As shown in the previous chapter of this thesis, literature review, textile waste water is very variable in their composition due to different process taking account in the textile mills. Moreover, in order to stablish constant characteristics of the

inflow to the membrane process of study, and the long distance to the closest textile mill, it was decide to produce our own waste water.

It has to be said that two recipes were followed because in the first step of the experimental set up it was noticed the non-solubility of the indigo dye in the waste water. Due to this problem, a second recipe was used based on the literature review. Simulating the colour of textile effluents.

The generation of synthetic wastewaters of different composition is necessary for research but there is little information available on simulating the colour of textile effluents, specifically in indigo dye. The base composition of the wastewater used in this study was taken from O'Neill et al. (1999), this wastewater was previously used by co-supervisor's department and took it as a reference. However, the dye used in this literature was azo dye, while the dye used in this experiment is vat dye indigo.

Table 11 shows the main characteristics of the STW used in this experiment based on (O'Neill et al., 1999), it is underlined the compound that presents changes along the study. The rest remained constant.

Table 11. Synthetic textile water composition

Chemical	Concentration 1 l
NaCl (Sodium Cloride)	0,15 g/l
Acetic acid	0,53 g/l or 0.5067 ml
$(NH_4)_2SO_4$	0,28 g/l
NH4Cl	0,23 g/l
Na_2HPO_4 (M=201,91 g/mol)	0,0504 g/l
Trace metal solution	1 ml
Stock starch solution	50 ml
Stock dye solution	Indigo solution
H_2SO_4	Adjust pH

Composition of Trace metal solution is shown in Table 12. It is remarkable the importance of adding the trace metal solution as they constitute micronutrients to the bacteria.

Table 12. Trace metal solution composition

Chemical	Concentration1 l
$MgSO_47H_2O$	5 g/l
$FeCl_24H2O$	6 g/l
$COCl_2$	0,88 g/l
H_3BO_3	0,1 g/l
$ZnSO_47H_2O$	0,1 g/l
$CuSO_4$* M=159,612 g/mol	0,0782 g/l
$NiSO_4$* M=154,7594 g/mol	1,697 g/l
$MnCl_2$* M=125,8434 g/mol	7,8607 g/l
$(NH_4)6Mo_7O_244H_2O$	0,64 g/l
$CaCl_22H_2O$	5 g/l

Preparation of Starch solution. The purpose of adding starch into the waste water is because it has been reported its use in the denim wastewater mills, as well as it is one of de carbon sources of the bacteria in order to grow. It is important to say that starch was selected instead of glucose, as it is a slower carbon source and it allows bacteria to choose between this carbon source and indigo dye as part of their metabolism. The process of cooking the starch is listed below, as well as the chemical composition is presented in Table 13.

1. Weight the solids
2. Add 250 ml of DW and the Starch that is very soluble in water
3. Use magnetic stirrer and hot plate
4. Add NaOH into 1l beaker and mix
5. Combine both mixtures into one flask
6. Wait for 2h at 80ºC
7. Add DW to complete 1 l

Table 13. Stock starch solution preparation

Chemical	Concentration 1 l
Starch	20 g/l
NaOH (4%)	40 g/l
Distilled water	1 l

Preparation of indigo dye solution I. Indigo dye stock solution was prepared by cooking NaOH and indigo powder during 4 h at 80ºC until complete mixing. In this first step 10% concertation was prepared.

Preparation of indigo dye solution II. Due to the non-solubility of the previous indigo dye solution I, a new methodology was applied, in order to reduce indigo dye into its soluble form. Indigo ($C_{16}H_{10}N_2O_2$), Sodium dithionite ($Na_2S_2O_4$) and Sodium Hydroxide (NaOH) were used following Diagne et al. (2014) the procedure for cooking the dye solution was to add all the reagents and cook them for two hour at 80 ºC. The chemical composition is presented in Table 14 below.

Table 14. Chemical composition of indigo dye solution II

Compound	Weight
Indigo	2.62 g/l
Sodium dithionite	17.4 g/l
Sodium Hydroxide	6 g/l

Characterization of the synthetic textile wastewater. Systea Easy Chem Plus discrete Analyzer (Figure 24) was used to measure the following parameters: NO_2^-, NO_3^-, NH_4^- and total Phosphorus, also pH and Electrical Conductivity was measure with pHmeter WTW pH3110 was measured with Conductimeter WTW 3310. Results are shown in the results chapter. Synthetic Textile Water (STW) was also brought to an external laboratory in order to compare characterization data, results are pending to arrive.

Figure 24. Systea Easy Chem Plus discrete Analyzer apparatus set up

III.3.2 Effluent characterization

The effluents were characterized following the Standard Methods 22nd edition (Rice et al., 2012).

III.3.2.1 Chemical Oxygen Demand and Colour

For the COD measurement the method 5220 C (Mohr salt titration) and 5220 D (colorimetry) from the Standard Methods (Rice et al., 2012) COD values were measure with HACH Lange KITs. Colour was measured with Spectrophotometer HACH LANGE 3900 (Figure 25).

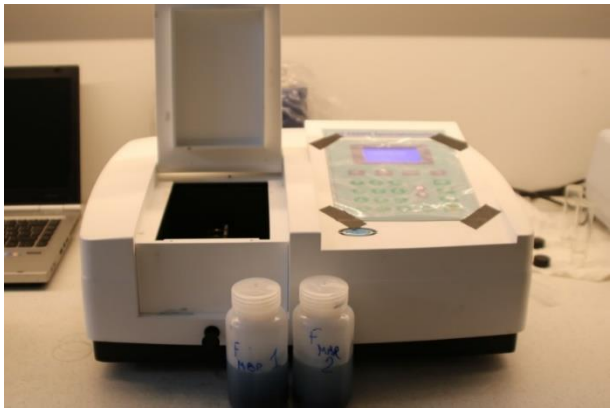


Figure 25. Spectrophotometer

Curve of Absorbance for measuring the colour. Colour was measured by spectrophotometric absorbance at 661 nm where the dye presents its maximum absorbance. In order to know the absorbance range that we have to work, an absorbance curve was done with spectrophotometer and programme, (MetaSpec Pro – [Wavelength Scan]). Using glass cuvettes for the visible spectra, this precision cells are made of optical glass, with light path 50 mm (brand: Hellma Analytics). A standard curve was generated. Once the spectrophotometric curve of the synthetic textile water was done, one wavelength was set up as the highest point, of absorbance, and this was set up as the absorbance wavelength for measuring the colour. The percentage of colour removal will be calculated as shown in the following equation.

$$\%\ Removal = \frac{i_{abs} - sample_{abs}}{i_{abs}}$$

Equation 6

Where:

$\%\ Removal = is\ the\ removal\ eficiency\ of\ the\ system$

$i_{abs} = is\ the\ result\ of\ the\ absorbance\ of\ the\ synthetic\ wastewater$

$sample_{abs}$
$= is\ the\ result\ of\ the\ absorbance\ of\ the\ permeate\ at\ certain\ wavelenght$

III.3.2.2 Conductivity, pH and DO

The pH and conductivity were measured according to methods 2510 B y 4500 H^+B, respectively (Rice et al., 2012). , measured with pHmeter WTW pH3110 (Figure 26) and Electrical Conductivity with Conductimeter WTW 3310.

Figure 26. Hatch HQ30d (left) and pHmeter 3110 (right)

III.3.3 Sludge samples

The sludge samples were taken from the Industrial water treatment plant of the company Norske Skog Saugbrugs-Halden, this company is located near the border with Sweden, and it is a paper production plant. Two samples were taken, one form the sludge coming from the aeration system just before decantation and other from the recirculation, taken in the centrifuge of the Waste Water Treatment Plant (WWTP).

It has to be noticed, that this sludge, due to timing delay and also space limits, was kept in two 2.5 l reactors and acclimated during 3 months. Later on, it was mixed with sludge coming from urban wastewater treatment plant. So we can call Sludge I to the one coming from the paper industry. Sludge II to the one mixed of

sludge I and sludge coming from WWTP. Moreover, due to certain factors yet to conclude, and not determined yet, there was a loss of biomass during the running of the sludge II for the period of 15 days, so it was settled and mixed with sludge coming from pilot plant (MLSS 5000 mg/l), and we call it sludge III. Sludge III was considered as the appropriate to start the experimental phase. So in reactor MBR1 sludge III was stablished and in MBR2 it was added the bioaugmentation bacteria.

Sludge acclimatization. This process consisted on applying every two days 100 ml of STW 10% concentration of indigo into the reactor, previously 100 ml of supernatant were removed before 30 min of settlement without aeration. After 10 days, the periodicity of the addition of STW was increased to everyday.

III.3.4 Characterization of sludge

To determine the sludge properties, different analysis have been carried out pH, TSS, VSS, CST. The concentration of **solids (TSS and VSS)** in the sludge compartments was determined according to APHA standard method 2540D. The dewaterability of the different mixed liquor samples was evaluated by measuring the **capillary suction time** with CST papers and the 5 ml of sludge sample. Physical parameters as temperature, pH and dissolved oxygen (DO) were also analysed during the study.

The different procedures carried out during the study are shown below

III.3.4.1 Mixed Liquor Total Suspended Solids

Mixed Liquor Total Suspended Solids (MLSS) and Mixed Liquor Volatile Suspended Solids (MLVSS) concentration Solids present in water can be organic or inorganic. The determination of MLVSS concentration is especially useful in the control of wastewater treatment plant operation because it offers a rough approximation of the amount of organic matter present in the solid fraction of wastewater, activated sludge or industrial wastes. MLSS and MLVSS are determined following the methods 2540B and 2540D described in Standard Methods for the Examination of Water and Wastewater (APHA-AWWA-WPCF, 1998), whereas MLVS and MLVSS are determined following the method 2540E.

III.3.4.2 Capillary Suction Time

The dewaterability of the different mixed liquor samples was evaluated by measuring the **capillary suction time** *(Triton electronics Ltd., type 304 B*) with CST papers and the 6 mL of sludge sample.

Definition: CST method was developed to measure the dewatering properties of activated sludge. This method is essentially measuring how quickly the activated sludge wet a filter paper. When sludge contact with filter paper, water from the sludge starts to wet the paper due to capillary suction phenomena of the spaces among the hydrophilic fibers that consist of the filter paper. Once the water in the sludge-paper interface is absorbed by paper, the sludge that contacts directly with paper becomes compact and acts as a barrier for further water loss

to the paper. If macromolecules and fine particles are abundant in the sludge, the compact sludge formed in the interface would act as more efficient barrier.

This is a convenient quick test method, but the direct correlation with membrane fouling is questionable. The CST test conditions are quite different from actual filtration condition, where crossflow exists that can discourage particle deposition and TMP induces cake layer compaction.

Apparatus (Figure 27 and 29):

- Filtration unit
    - Automatic time counter.
    - Chromatography paper
    - Sludge reservoir
- Pipet

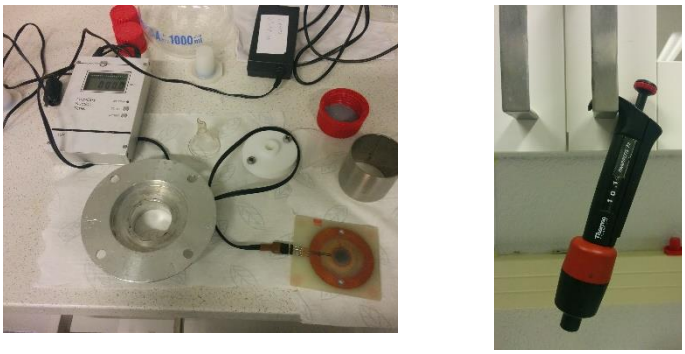


Figure 27. Apparatus for CST measurement

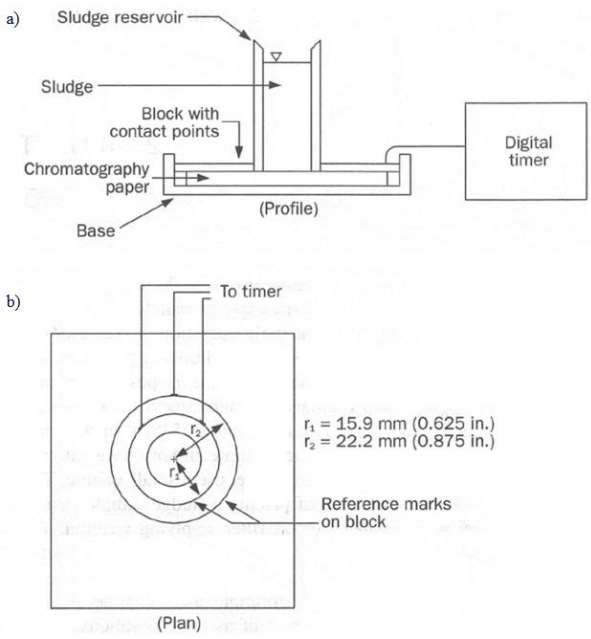


Figure 28. CST measurement scheme

Procedure

1. According to the Standard Method, sludge is poured in the test cell reservoir located in the center as shown in Figure 28.
2. As soon as sludge contacts with a filter paper in the bottom, it starts to wet the filter paper and the water proceeds radially.
3. The time required for water to proceed from r1 to r2, which is called CST, is measured using a conductivity sensor.
4. CST can be normalized by dividing the reading by MLSS (g/L) in order to reduce the effect of MLSS in a narrow MLSS range.

III.3.4.3 Z-potential

Zeta potential represents the charge density of colloids, which give the inter-molecular interaction by long-range repulsive forces. Thus, it is typically used to assess the potential of colloids and particulates in water and wastewater. For the membrane filtration, measurement of zeta potential are used to predict a long-term colloidal stability of the macromolecules in the concentration polarization

(CP) layer formed on the membrane surface (L. Quintero & Cardona, 2012). The zeta potential in this study is measure by Zetasizer Malvern (Figure 29).

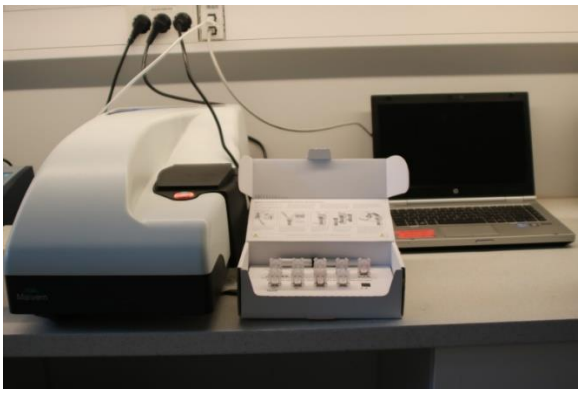


Figure 29. Z-sizer

III.3.4.4 Temperature, pH and Dissolved Oxygen

Physical parameters as temperature, pH and dissolved oxygen were also analysed during the study. **Temperature** and **pH** of the mixed liquor and d**issolved oxygen**.

Dissolved Oxygen

Definition: **Dissolved oxygen** (DO) refers to microscopic bubbles of gaseous **oxygen** (O_2) that are mixed in water and available to microorganism for respiration—a critical process for almost all organisms. Primary sources of DO include the atmosphere and aquatic plants.

III.3.4.5 Hydrophobicity

An important parameter for activated sludge characteristics in MBRs is the relative **hydrophobicity.** Various functional groups of proteins and polysaccharides, which are the main components of Extracellular Polymeric

Substances (EPS), are exposed to the surface of sludge flocs. The more hydrophobic the flocs are, the more prone they are to be adsorbed to the membrane surface. The flocs' hydrophobicity is decided by balance of the hydrophilic and hydrophobic nature of the functional groups on the floc's surface (Park et al. 2015). Chang et al. (1999) reported that the relative hydrophobicity of a normal activated sludge has a percentage value of around 56-60% (57% average), while foaming sludge would have 62-93% (81% average), which was quite higher than normal sludge values. The determination of flocs relative hydrophobicity is explained below:

Materials and equipment:

- Phosphate buffered saline (PBS-buffer), pH 7.4, V~10 ml;
- N-hexadecane, 95%, V=3 ml;
- Hach Lange DR 3900 spectrophotometer;
- Separatory funnel, V=50 ml (Figure 30);
- Filters (VWR international), 1.2μm pore size.

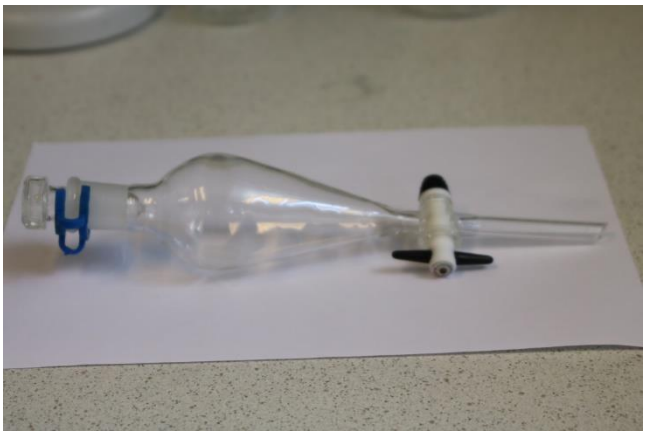


Figure 30. Separatory funnel

Sludge relative hydrophobicity (RH) of the flocs is measured according to Rosenberg's method.

Procedure:

- Calculate the volume of sludge sample you have to take out of the reactor, as well as the volume of Phosphate Buffer you have to use. Then divide the volume of sludge extracted from the reactor in 3 small Erlenmeyer flasks.
    - Sludge samples are diluted and washed twice with a phosphate buffered saline (PBS-buffer) to 2.5 g MLSS/L.
    - Add the buffer and wait for 15 or 20 min until the sample will settle.
    - Remove the supernatant of the flask after waiting 15 or 20 min and repeat again the buffer addition and waiting.
    - Then add 1.5 ml of n- hexadecane and 1.5 ml of the settled and washed sludge into the funnel, make sure it is closed. Close it and mix it powerfully during 2 min.
    - Wait for 5 min the mix in the funnel.
    - Drain the settled part and keep it. Take the water in the down part out
    - Repeat this 5th step twice
    - This diluted sample is measured as the initial value at 650 nm (Dubois et al., 1956) in a spectrophotometer (DR5000, Hatch Lange) with the filtrate from this sample as a blank.
    - After that, the sample is allowed to separate again for 5 min. The absorbance in the aqueous phase is then measured at 650 nm (Abs f)

and compared to the absorbance of the dilution sample (blank). The RH can then be calculated as follows:

$$RH = 1 - \frac{Abs\ f}{Abs\ i} * 100$$

Equation 7

Where:
Abs f: is the absorbance of the aqueous phase sample after the extraction in the separatory funnel;
Abs i: is the absorbance of the initial specimen that underwent dilution and the washing with PBS-buffer.

III.3.4.6 Microbiology observations

Microscopic examinations were done using a *Nikon model Eclipse E200* microscope and the microscope pictures were recorded using the *Zeiss KS100.3* software (Figure 31).

Bioaugmented bacteria observation. Gram staining was conducted of the bioaugmented bacteria in order to observe them in the microscope. However no results were taken from this step due to lack of time.

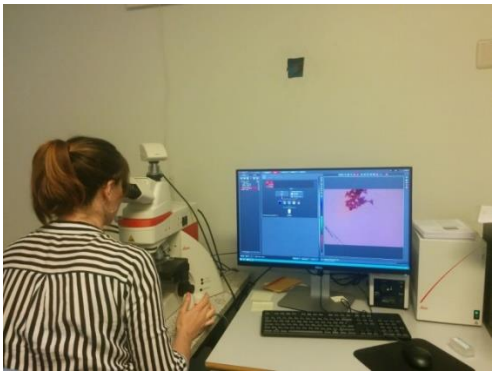


Figure 31. Microscopic observation procedure in Image Centre Norwegian University of Live Sciences

IV RESULTS AND DISCUSSION

IV.1 MEMBRANE BIOREACTOR PROCESS

Figure 33 shows the result of the membrane bioreactor set up. It shows 6 bioreactor, in this experiment two of them where used. The MBR tanks are feed with STW pumped by a multichannel pump, the left pump in the figure. The permeate coming from the suction of the membranes, is collected in the white bottles. Moreover the aeration of the reactors is provided by a blower shown in the top left corner of the figure. It is also important to comment the pump used for sucking and backwashing, this multichannel pump is controlled by Arduino and pumps the water out of the reactors through the membranes and into the permeate bottles where it is collected for its analysis. As it was commented on the methodology, permeate is backwashes from the bottles into the reactors again in order to provide physical cleaning.

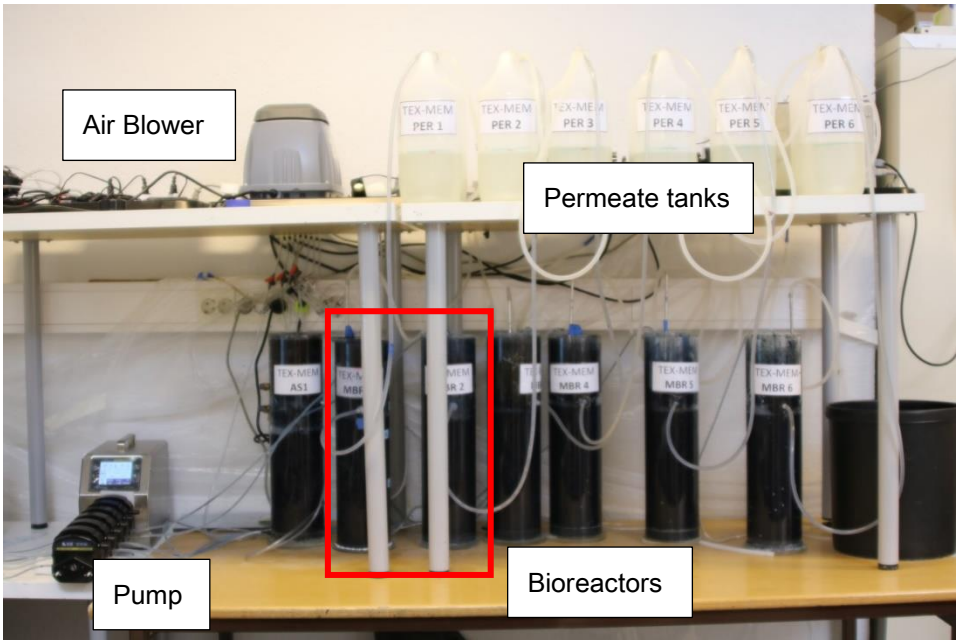


Figure 32. Laboratory set up

The performance characteristics of this laboratory plant are show in Table 15. Hydraulic retention time is fixed in 36 h and sludge retention time in 30 days, in order to keep good performing conditions. Oxygen in the reactors is manually controlled by a valve in the tubes connecting the blower with the diffusor in the bottom of the reactor and it is kept in 6 mg O_2/l. TMP is maintained between 3 and 40 kPa. When TMP raises to 40 kPa chemical cleaning is performed. Operational flux was maintained at 15 l/m^2/h (lMH). Bioaugmented MBR2 reactor has the same design as the MBR tank but with the addition specific decolorizing bacteria, these bacteria were added to MBR2 after one week of steady state performance of both reactors in order to start from the same conditions. The operation condition of the experiment is showed in Table 15.

Table 15. Procedure parameters

Parameters	Value
HRT	36 h
SRT	30days
Active value of reactor	2.5 l
Oxygen supply	6 mgO_2/l
Temperature	27-28 ℃
Permeate	15 l/m^2/h (lMH)
TMP	3-40 kPa

IV.1.1 Pump Calibration

The influent pump calibration results are shown in Table 16 and in the Figure 33, the STW containing tank and the pump that transports the influent into the reactors is shown. In the beginning of the experimental procedure the flowrate of the effluent pump is 2.5 l/36 h, however it is expected to increase this flow in order to study different hydraulic retention times.

Table 16. Influent pump calibration

Flowrate	Original Speed (ml/min)	Multichannel Pump (ml/min)
2.5 l per 36 hours	1.157	1.703

Figure 33. Synthetic textile water influent tank and multichannel pump

IV.1.2 Clean water test results

As a part of the clean water test procedure, a calibration of the pumps was done. The procedure is explained below.

1. Run the pump, pumping deionized water from 1 beaker to another, at 4 rotational speed set points and collect water in a beaker for 2 minutes at each stable set point.

2. Measure the volume of the water collected in a glass cylinder from each set point to determine a flow rate and create a calibration curve using the data (Figure 34 and Figure 35).
3. Use the resultant calibration curve to set the pump at the correct rotation speed to get the desired flux. Due to the different results coming from the pump, it was decided not to create a curve from the result data, instead the objective value was calibrated in order to obtain the seek volume.

On the other hand, regarding the out pump, which sucks and backwashes the membranes, the calibration results are shown below. The r^2 adjustment in the graphs show that data have a lineal trend.

Table 17. MBR1 pump calibration results

Pump Speed (rpm)	Flux l/m²/h (lMH)
0	0
30	16.78
60	34.48
120	58.42
180	81.85

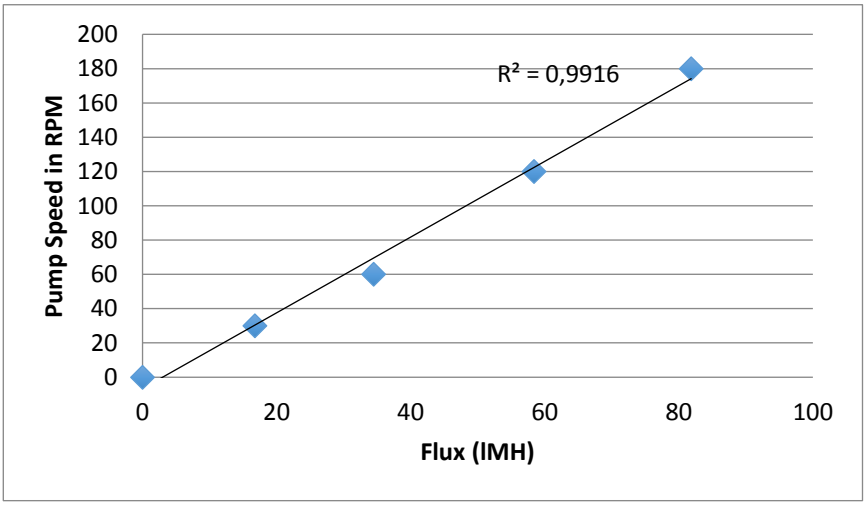


Figure 34. MBR1 pump calibration graph

Table 18. MBR2 pump calibration

Pump Speed (rpm)	Flux L/m²/h (IMH)
0	0.00
30	26.02
60	47.70
120	95.40
180	130.65

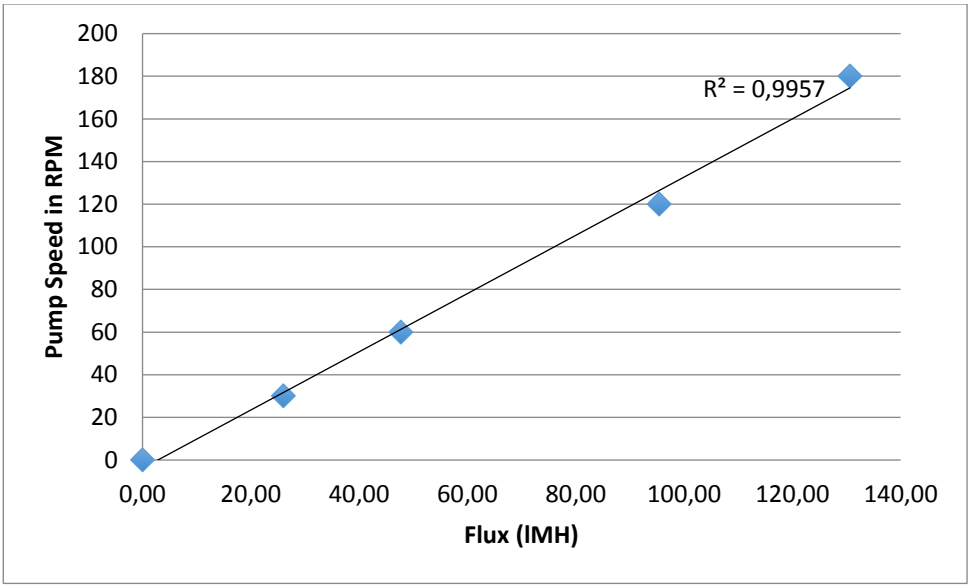


Figure 35. MBR2 pump calibration graph

As it is said in the methodology, for the test to be valid, Test is valid if K and R_m are expected to remain constant (+/- 10-20%). In this case, for MBR1 it is 9.34% and for MBR2 is 8.25%, so data from this test are considered valid, for MBR1 and 2, the results are close to 10%, Table 19 and Table 20 show the results for the clean water test respectively.

Table 19. Membrane 1 control reactor

Pump speed (rpm)	Flow (l/h)	Flux l/m2/h (lMH)	TMP (kPa)	Permeability (lMH/kPa)	Resistance (1/m)
0	0	0.00	0		
30	0.24	16.78	16.51	1.02	3.54E+12
60	0.50	34.48	27.66	1.25	2.89E+12
120	0.85	58.42	49.05	1.19	3.02E+12
180	1.19	81.85	68.38	1.20	3.01E+12
Mean					3.11E+12
Relative Standard Deviation					9.34 %

Table 20. Membrane 2 Bioaugmentation reactor

Pump speed (rpm)	Flow (l/h)	Flux l/m2/h (lMH)	TMP (kPa)	Permeability (lMH/kPa)	Resistance (1/m)
0	0.00	0.00	0	0.00	0
30	0.47	26.02	12.20	2.13	1.69E+12
60	0.86	47.70	24.80	1.92	1.87E+12
120	1.71	95.40	52.10	1.83	1.97E+12
180	2.35	130.65	74.50	1.75	2.05E+12
Mean					1.89E+12
Relative Standard Deviation					8.25 %

IV.1.3 UF modules

Figure 36 shows the final result of the ultrafiltration modules. It has to be notice the importance of this technique before starting the experiment. It is also important to keep the membranes always wet once they have been put into water for the first time. Even though, there were some gluing problems on the first time, they were solved thanks to the procedure of trying the membranes with the air blower before introducing them into the reactors. Attention must be given to them when storing

the membranes while waiting for the reactor or sludge to acclimate. The membranes modules should be kept in water media with disinfection treatment in order to avoid biological growing in the membrane surface. The module area of the ultra-filtration modules is 0.0145 m^2.

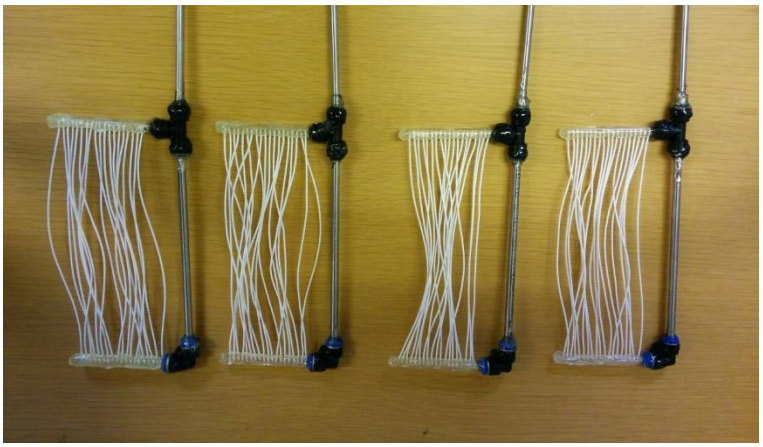


Figure 36. Final result of membrane modules

IV.1.4 Transmembrane pressure

Results of the membrane modules, pressure measured in reactor MBR1 and MBR2 with bioaugmentation. The TMP results show the fixed control of the outflow pump, this means that every 12 minutes there will be a cycle, including 9.5 min of sucking, 30 s of stop, 1.5 min of backwashing, that will help to avoid biofouling and the creation of a biomass cake in the membranes, and finally 30 s of stop before starting the sucking again. Next Figures 38 and 39shows the performance of the pressure gauges during one hour for control MBR1 and MBR2.

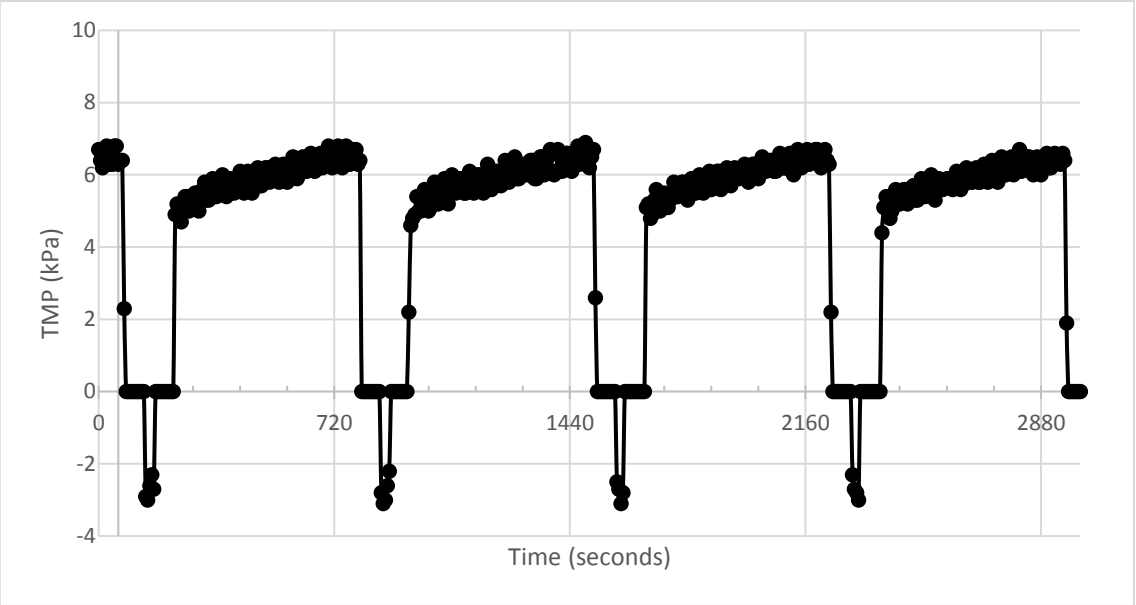


Figure 37. TMP (kPa) of 14th of June at 15:00 h of MBR1

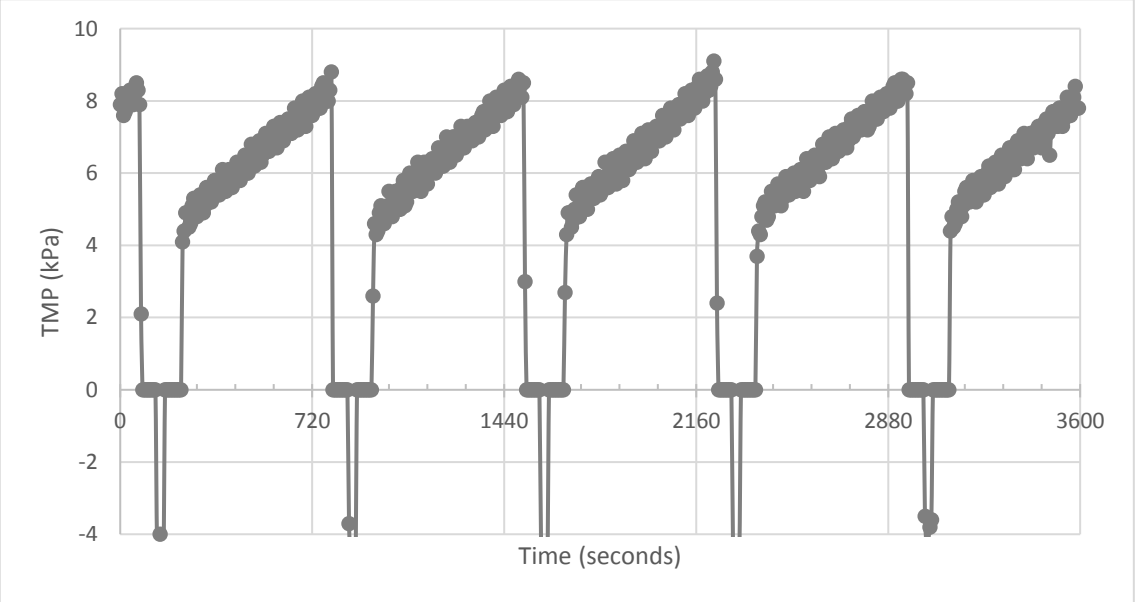


Figure 38. TMP (kPa) of 14th of June at 15:00 h of MBR2

If a comparison is made of one hour performance at the end of the time period of both membrane modules show similar variations. However, MBR2 shows higher difference of pressure during the sucking period, as it will start from 4 kPa but it reaches 8 kPa in the end of the period. MBR1 starts from a higher pressure than

4 kPa, but it only reaches between 6 and 7 kPa at the end of the sucking period. This can mean that bioaugmentation reactor has more biomass in the sludge and will present fouling easier (Figure 39).

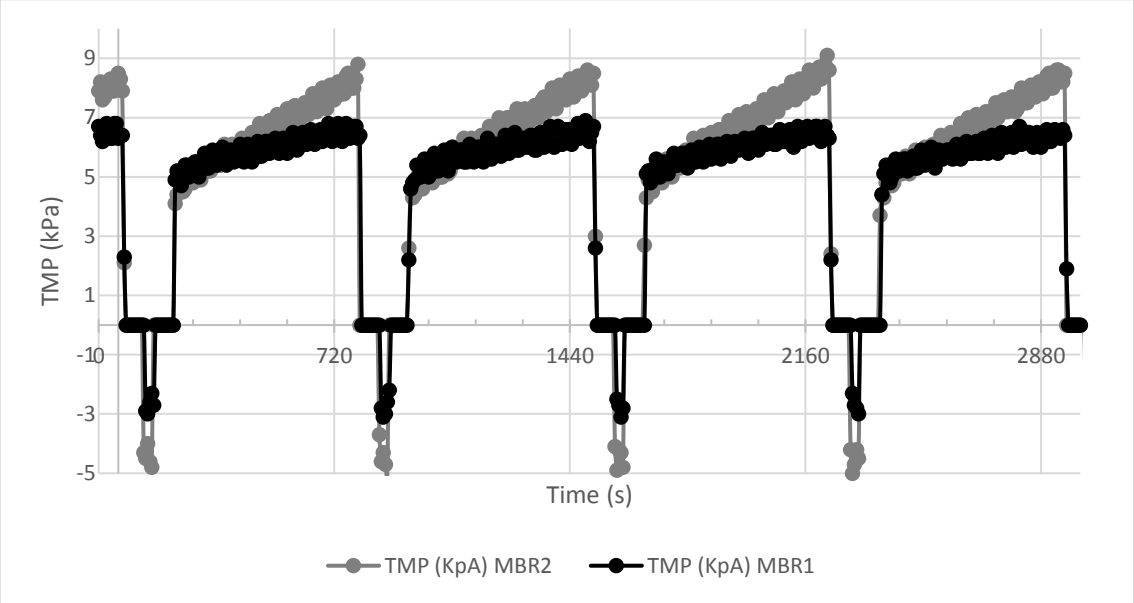


Figure 39. Comparison TMP (kPa) of 14th of June at 15:00 h of MBR1 and 2

Results exported from Kacise view from a temporal series from the 21st of June until the 15th of July. This data are presented to show the TMP variation during the functioning period. The objective of measuring the pressure was to study the fouling in the membranes and to determine the chemical cleaning periods.

Regarding the fouling study of the membranes of the control Figure 40 can be observed. Data were collected every 6 seconds by Kacise viewer, however this graph shows the maximum value of each hour in order to show the cleaning periods of each membrane module and the fouling phenomena. It has to be said that for control membrane data are not collected in the period between 4th and 7th (hours 306 until 397) of July due to pressure gauge error display (Figure 40).

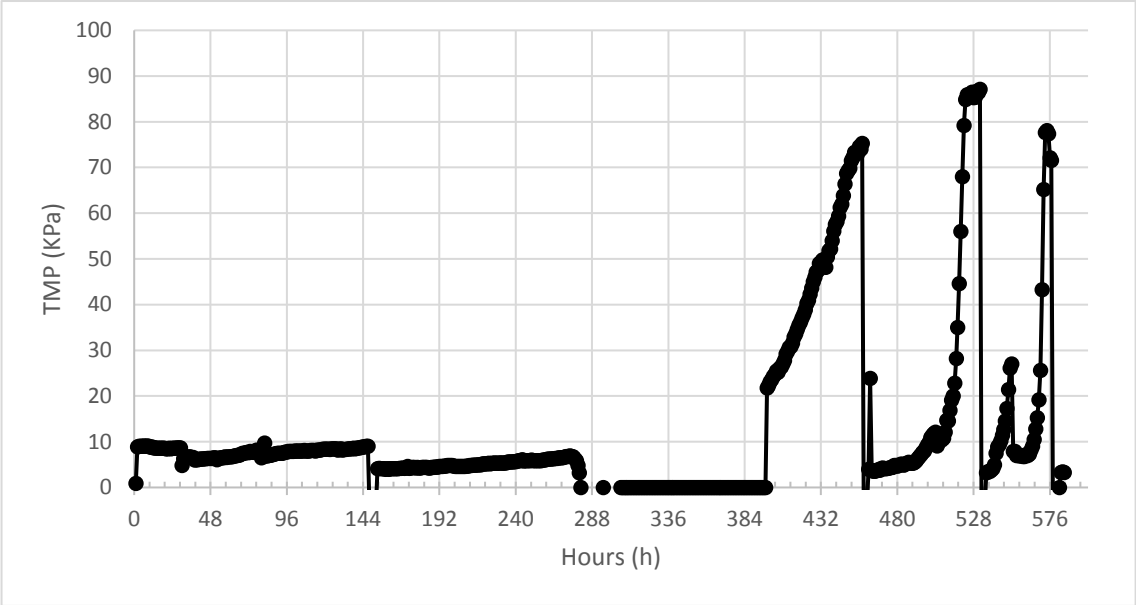


Figure 40. Transmembrane pressure change during long-term constant flux in the membrane bioreactor 1

On the other hand, membrane number 2, with Bioaugmentation, shows the following values for TMP in Figure 42.

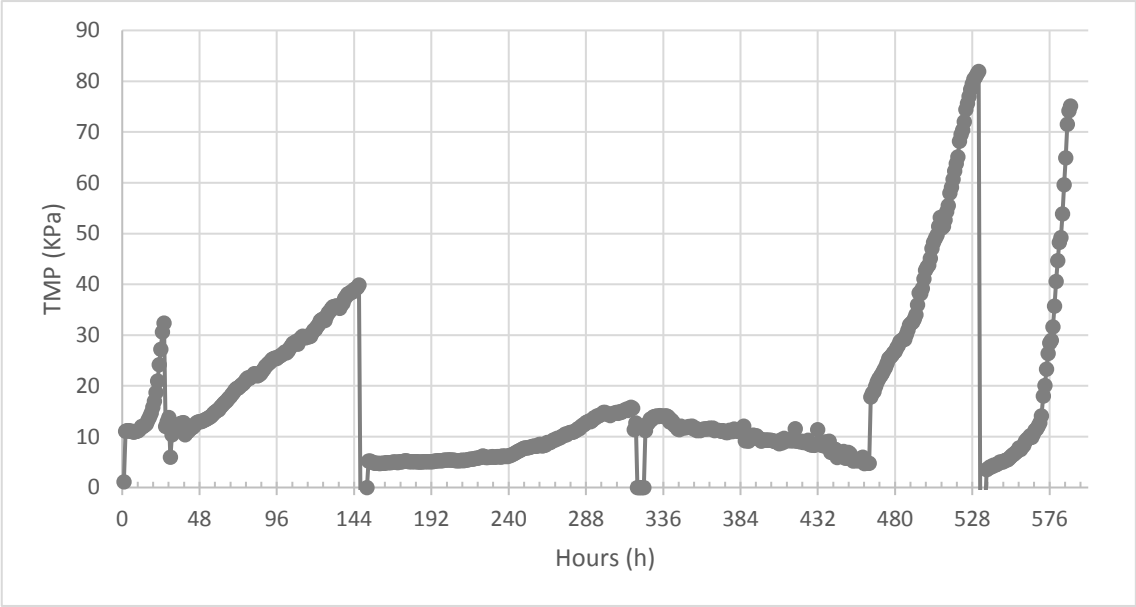


Figure 41. Transmembrane pressure change during long-term constant flux in the membrane bioreactor 2

If both membrane performances are compared as Figure 42 shows. It can be seen that control membrane reaches maximum TMP faster than MBR2. This can occur due to the faster methabolitation of organic matter and substances that cause fouling of the sludge with Bioaugmentation. Regarding the values equal to cero in the graphs, they occur due to the stop of the process and removal of the membrane for chemical cleaning. As the figure below shows, six periods can be differentiated. It is important to say that bioaugmented bacteria were added on the 30th of June (216 h) of performance. However, membrane modules MBR1 and MBR2 did not reach stationary conditions.

- The first period corresponds with the first 24h of functioning of the membrane and it shows how MBR2 module reaches more than 30 kPa in one day while MBR1 remains in 10 kPa, due to this strange behavior, MBR2 was stoped and cleaned with water in order to remove any fouling problems.
- During the second period, that is five days long, it is observed the same behaviour of MBR2 compared to MBR1, increases its pressure faster.
- During the third period, seven days long, MBR2 performance is more constant as it reaches 20 kPa while MBR1 pressure gauge has some performance problem and data are not available.
- The forth period lasts 6 days during which MBR1 reaches 75 kPa very fast, and MBR2 remains in low pressure values.
- Two last periods show how high pressure values are achived by bothe membranes in a sort time interval, this can be due to membrane fouling.

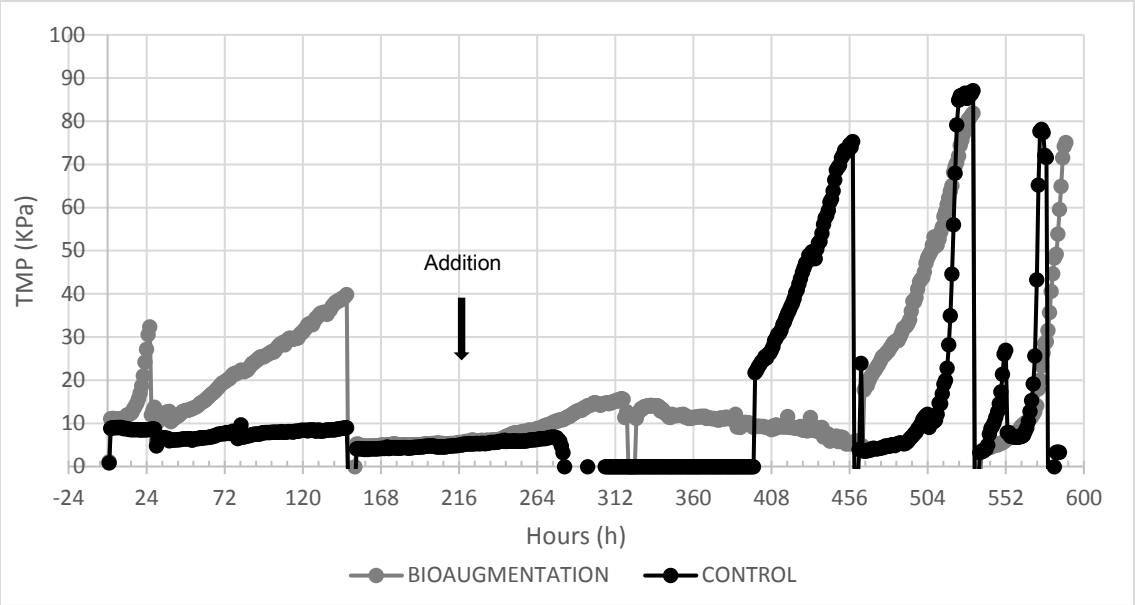


Figure 42. Transmembrane pressure change during long-term constant flux MBR 1 and 2

IV.1.5 Bioaugmentation

Once the conditions of both reactors reach a stable state a week after they have been started, the Bioaugmentation bacteria were added to MBR2. The process of adding the bacteria is commented in the methodology. Before adding the bacteria data of MLSS and MLVSS were measured, and it is important to keep the record of the effluent coming out of the two different reactors.

IV.2 CLEANING PROCEDURE

Membrane is cleaned when the TMP reaches 40 kPa. There are many procedure of membrane cleaning. The cleaning procedure for this laboratory scale membrane modules is listed below:

1. Preparing a cleaning solution of NaCl with 1000 mg/l concentration.
2. Taking out the membrane modules from the MBR tank

3. Soaking them into the NaCl solution during 4 h.

The following Figure 43 shows the membrane module when it is taken out from the reactor tank and after the chemical cleaning.

a) (b) ..... (c)

Figure 43. Fouling of membrane before cleaning (a) and (b) and after chemical cleaning (c).

The following Figure 44 shows both temporal performance of TMP for MBR 1 and 2, red arrow marks the cleaning event for MBR1 and 2, however some days cleaning of the membrane was done at different times of the day depending on the membrane module.

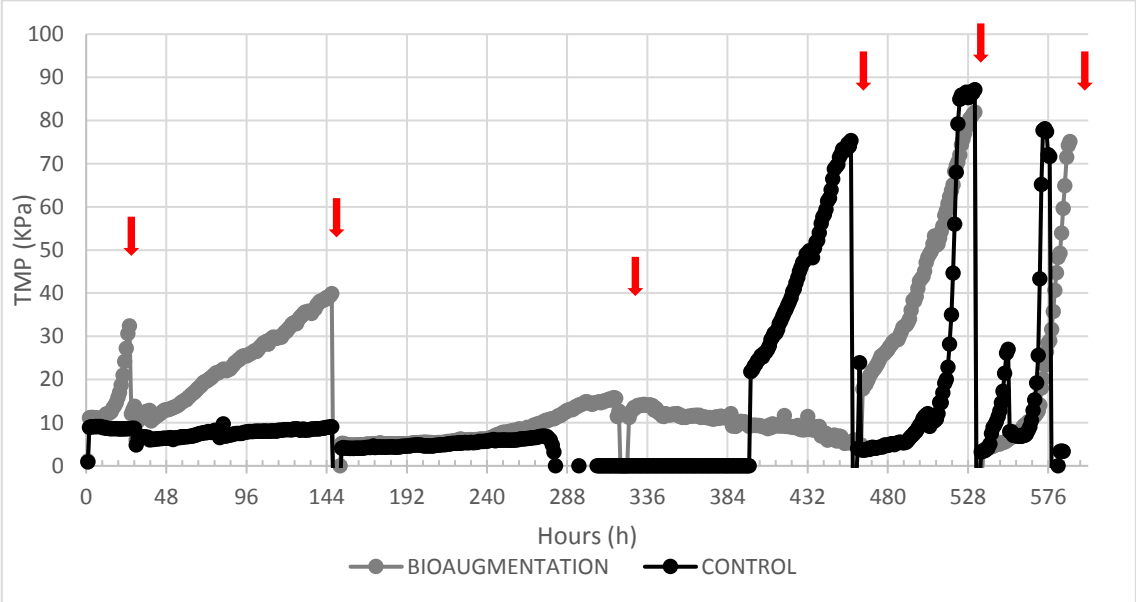


Figure 44. Working periods of the membranes 1 and 2 and localization of the chemical cleaning events

IV.3 SYNTHETIC TEXTILE WASTEWATER (STW)

IV.3.1 Production of Synthetic Textile Wastewater

Denim STW of this study is prepared according to the procedure of O'Neill et al. (1999). The chemicals used to produce the STW are showed in the methodology. The final STW will be adjusted pH to 6.8-7. The stock starch solution (20g/l) is prepared by hydrolysing the starch in 4% of NaOH and heating for 2 hours with the temperature of 80 degrees Celsius.

Trace metal solution is made by (g/l) $MgSO_4 7H_2O$: 5 g, $FeCl_2 4H_2O$: 5 g, $COCL_2$: 0.88 g, H_3BO_3: 0.1 g, $ZnSO_4 7H_2O$: 0.1 g, $CuSO_4$: 0.05 g, $NiSO_4$: 0.1 g, $MnCl_2$: 5 g, $(NH_4)_6MO_7O_2$: 0.64 g and $CaCl_2 2H_2O$: 5 g.

Indigo stock solution prepared according to Diagne et al. (2014). Indigo dye is insoluble in water. In order to dissolve, indigo needs to be solubilized in alkaline medium in the presence of sodium hydrosulphite. In industrial uses, indigo is solubilized in water at the concentration of 0.1 mM in the presence of 1.0 mM and 1.5 mM of sodium dithionite and sodium hydroxide, respectively. The solution, leucocratic, initially turns dark blue after several minutes of agitation. The following Table 21 shows the results of the characterization of the STW before and after changing the stock dye solution of indigo I.

As one of the objectives of this work was the optimization of STW, next Table 21, shows the different STW characteristics, which were studied. However it has to be said that MBR tanks were feed only with STW II.

Table 21. STW characterization

Parameters	STW-I	STW-II	Units
NO^{-}_{2}	1.410		ppm
NO^{-}_{3}	0.821	0.687	ppm
TP	2.531	-	ppm
NH^{-}_{4}	110.414	118.476	ppm
BOD_5	766	152	mg O_2/l
COD1 (not so accurate) d	1500	1550	mg O_2/l
pH	6.5	7.3	
Temperature	22	22,7	ºC
Conductivity	7090	6800	µS/cm
TSS		350	g/l
Colour (10 times dilution)		1130	Abs (660 nm)

IV.4 LABORATORY PLAN SCHEDULE

As a consequence of this study a laboratory plan schedule is proposed in order to optimize the laboratory work. The management of the laboratory work and planning of the experiment would contain the following parameters.

1. Production of STW
2. MLSS and MLVSS
3. COD and absorbance
4. Z-potential and CST
5. TMP control management – Membrane cleaning

IV.5 EXPERIMENTAL RESULTS

IV.5.1 Absorbance

As Figure 45 and Figure 46 show, the highest wavelength value for absorbance of STW is 660 nm. So this would be the wavelength at which absorbance of the permeate samples would be measured. This result shows similarities with the bibliographic review (Khelifi et al., 2008a) of other studies. Absorbance of the Synthetic Textile Water at 660 nm is 1.130 at 10 times dilution. Khelifi et al. (2008a) measured the colour by an UV–vis spectrophotometer at a wavelength of 620nm in which maximum absorbance spectra was obtained, they obtain 0.98 absorbance as a maximum. The absorbances that are obtained from the first month of performance of the effluent of the system are shown in Figure 48, it can be see that the trend is that the permeate's colour is increasing.

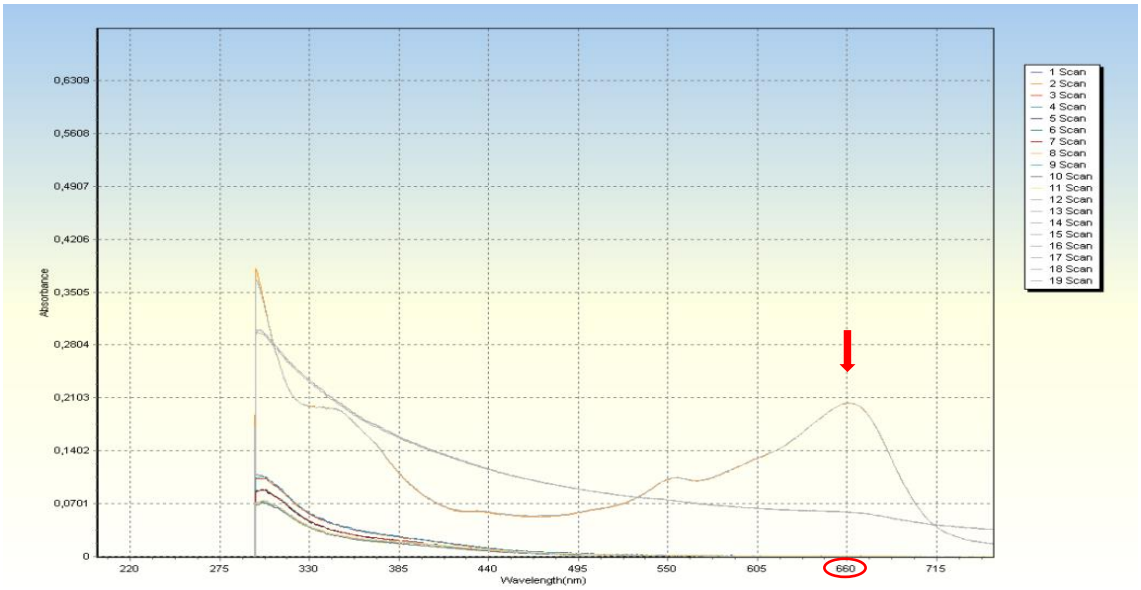


Figure 45. Synthetic Textile Wastewater absorbance curve

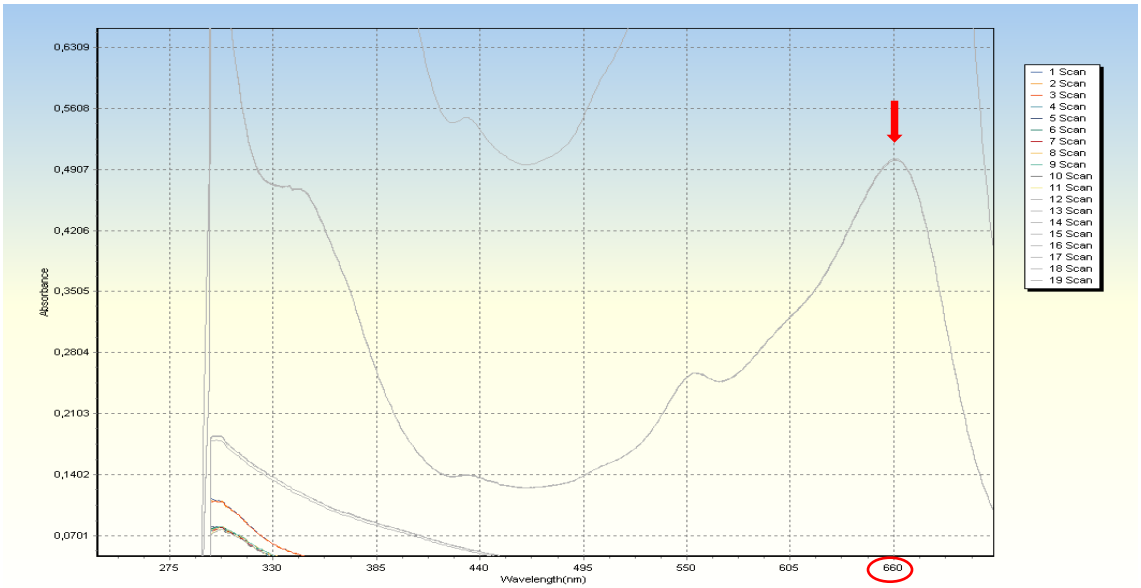


Figure 46. STW Absorbance zoom-in

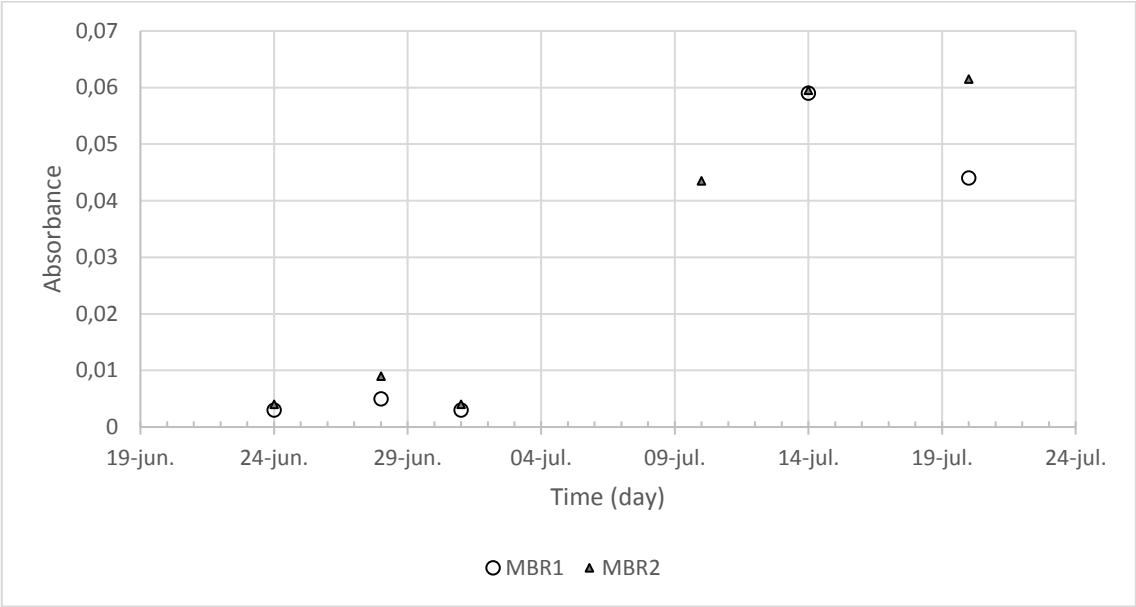


Figure 47. Results of the absorbance measurements

IV.5.2 Chemical Oxygen Demand

Results of the permeate COD measurements show low values, the results are shown in the Figure 48. From this results it can be seen that MBR2 permeate results after 20 days of performance are starting to reduce the amount of COD in the permeate comparing to the control reactor.

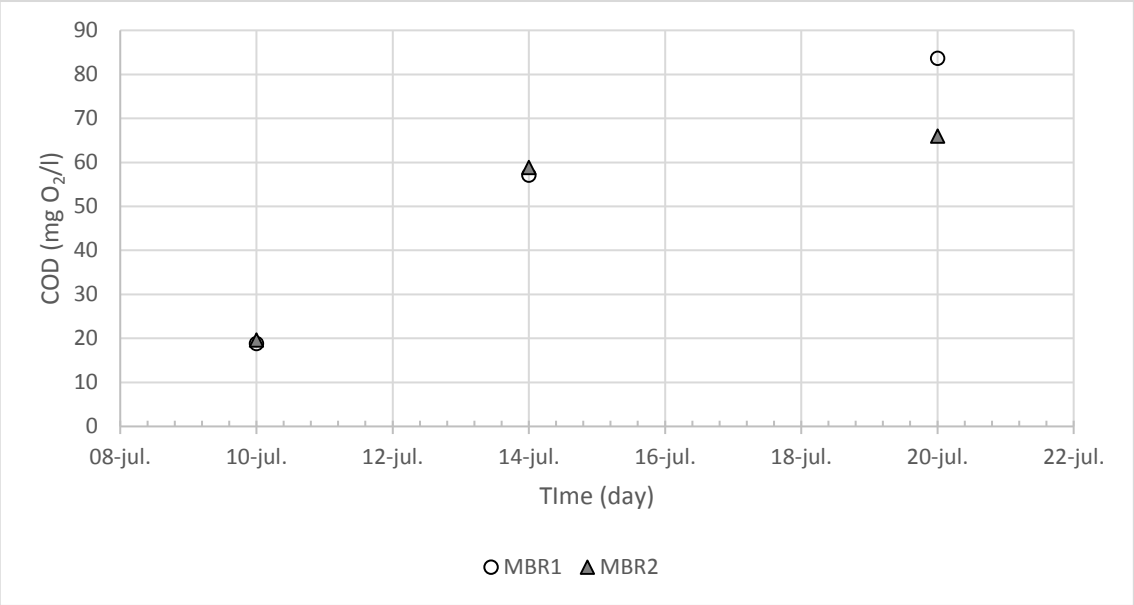


Figure 48. Chemical Oxygen Demand results

IV.5.3 Mixed Liquor Suspended Solids (MLSS)

Due to previous results is was suggested by co-supervisor to mix the biomass in all the reactors. After 30 min of settlement, the supernatant was eliminated and the concentrate in the bottom of the reactor was mixed with sludge coming from pilot plant of Urban wastewater treatment MLSS = 5000 mg/l. The firs analysis of the MLSS in the beginning of the experiment 20/06/17 is 4973.33 ± 176.

In the figure 50 below MLSS results are shown, this results come from the first week of functioning of the system and they show a decreasing trend in the MLSS content, however, more data have to be taken in order to make a better conclusion.

It is importance to take into account that the bioaugmentation was done on the 30th of June, 10 days after the sludge was introduced in the reactor. Results show that the trend is that MLSS results are being reduced gradually. However, on the

9th of July, the result form control reactor can be avoided, because the value is too low and in the next measurement is it high again.

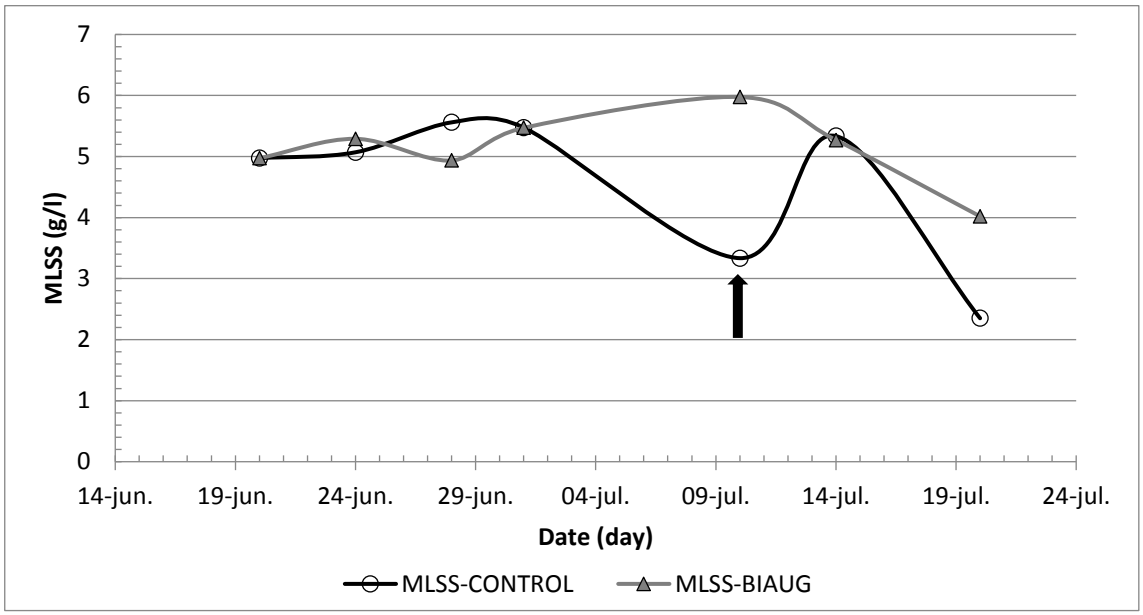


Figure 49. MLSS results

V CONCLUSSIONS, RECOMMENDATIONS AND PERSPECTIVES

This work contributes to the creation of a methodology and the set-up of a laboratory scale MBR for the study of indigo dye removal. The elaboration of this MBR plant is presented, from the purchase of all the equipment until the final functioning of the plant, ready for data collection, within five months duration stay in the laboratory of Water and Environmental engineering of the Norwegian University of Life Sciences. Furthermore, it can be concluded the following:

- On the one hand, the importance of the elaboration of a good literature review update as the first step in an experimental project, to establish a strong database and literature references in order to compare results from the MBR performance.
- Secondly, she significance of elaborating a methodology is well funded due to the complexity of the study and need to characterize the sludge with the following parameters: Z-potential, capilarity suction time, hydrophobiciy, mixed liquor suspended solids; as well as, the characteristics of the permeate: chemical oxygen demand and absorbance.
- Moreover, it has to be highlighted the proposal of a new hand made model of ultra filtation membranes in a laboratory scale. As well as the importance of the characterization of this membranes. Permeability and resistance of the membranes are studied and it is presented the relationship between the results of the “clean water test” and the performance of the membrane modules.
- The importance of testing the UF modules is demonstrated, once the UF modules are elaborated, a method to detect possible glueing feilures is proposed.
- The importance of studing transmembrane pressure in order to establish a good performance of the membrane module comes through thanks to this work. Furthermore, it is determined how TMP gives information about the situation of the membranes inside the reactor while operation.

- As TMP has been detected as a critical parameter, it is evident to highlight the importance to control and automate the data collection from this performance in order to determine possible operating problems.
- Finally, one of the critical issues in the study was the elaboration of the Synthetic Textile Wastewater. The composition of the Synthetic Textile wastewater was studied and characterized. The wastewater that has been created is similar to the one used in the textile industry as previously reviewed in the literature.

On the other hand, thanks to his work, it will be possible to study:

- The performance of the bioaugmented MBR system for the treatment of textile wastewater under different operating conditions changing hydraulic and organic loadings.
- Key parameters that influence fouling for the application of bioaugmented MBR wastewater systems and its optimum operating conditions.
- The microbial population structure, dynamics and the survival of the added microorganisms, differences of the bacterial community structure and microbial population involved in membrane fouling.

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