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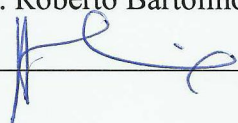
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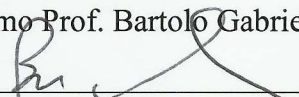
**Preparation and characterisation of polymerisable bicontinuous
microemulsion membranes
for water treatment application**

Settore Scientifico Disciplinare CHIM/06 – Chimica Organica

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Riassunto

I cambiamenti climatici in atto, la crescita della popolazione mondiale e l'urbanizzazione sono tra le principali cause della carenza di acqua in molti Paesi del mondo. L'acqua rappresenta una risorsa essenziale per la vita per tutti gli organismi viventi e la sua tutela ed un suo responsabile uso sono urgenti sfide che l'umanità dovrà affrontare nel prossimo futuro. Al fine di ottenere uno sviluppo sostenibile per la corretta gestione e sfruttamento dell'acqua, il trattamento delle acque reflue, sia industriali che municipali, risulta pertanto essere di fondamentale importanza.

Attualmente, il progresso tecnologico ha portato allo sviluppo di una serie di tecnologie che rendono il processo di trattamento delle acque reflue sempre più concreto ed efficiente. Tra di esse, i processi a membrana, rappresentano una valida alternativa grazie ai numerosi vantaggi offerti quali il basso impatto ambientale, l'alta efficienza ed i bassi costi correlati. Lo scopo del presente lavoro di tesi è stato la preparazione di membrane polimeriche ottenute mediante la tecnica di polimerizzazione di microemulsione bicontinua (PBM). Le microemulsioni bicontinue sono costituite da una rete interconnessa di canali acquosi e oleosi (rappresentati da un monomero) stabilizzati dalla presenza di un tensioattivo o surfattante. I canali oleosi possono essere polimerizzati per formare la matrice polimerica della membrana, mentre i canali acquosi rimangono inalterati e sono responsabili della formazione della parte porosa della membrana. Nel presente lavoro di tesi, membrane ottenute mediante PBM sono state utilizzate, per la prima volta, come materiale di rivestimento (coating) di membrane commerciali in polietilene sulfonato (PES) sulla cui superficie è stata polimerizzata la microemulsione. La prima parte del lavoro è stata incentrata sulla sintesi del surfattante polimerizzabile bromuro di acrililossidodeciltrietilammonio (AUTEAB) che è stato successivamente utilizzato per la formulazione della microemulsione. È stata, inoltre, valutata la possibilità di utilizzare un surfattante non polimerizzabile commerciale come il bromuro di dodeciltrimetilammonio (DTAB) per la preparazione della microemulsione. Le membrane così preparate sono state caratterizzate, nella seconda parte del lavoro, al fine di identificare le membrane con le migliori proprietà e caratteristiche. I test di caratterizzazione condotti sulle membrane rivestite con PBM hanno chiaramente mostrato le importanti potenzialità che queste innovative membrane possono rivestire nell'applicazione dei bioreattori a membrana (MBR) per il trattamento delle acque reflue. Infatti, la superficie particolarmente liscia, l'alto livello di idrofilicità e la tipica struttura bicontinua, rendono le membrane rivestite con PBM altamente resistenti allo sporco (fouling) della loro superficie. Questo aspetto è di fondamentale importanza soprattutto alla luce del fatto che lo sporco è uno dei maggiori svantaggi di quasi tutti i processi a membrana. Esso è principalmente legato all'accumulo di materiale organico e/o

inorganico sulla superficie della membrana causandone una diminuzione delle prestazioni, un aumento del consumo di energia e (in casi più gravi) un danno strutturale della membrana stessa. Inoltre, le membrane PBM, in seguito alla presenza di surfattanti cationici, hanno mostrato un'interessante attività antimicrobica. La possibilità di avere membrane dotate di attività antimicrobiche previene il fenomeno del biofouling causato dall'adesione e dall'accumulo di microorganismi sulla superficie della membrana. Per tutte le potenzialità mostrate, le membrane rivestite con PBM sono state testate con successo, nell'ultima parte del presente lavoro, nel processo MBR per il trattamento di acque reflue modello dell'industria tessile. Le membrane PBM, raffrontate alle membrane commerciali, hanno mostrato soddisfacenti risultati per un lungo periodo di tempo (6 mesi) in termini di permeabilità e reiezione ai coloranti. Ulteriormente, l'applicazione delle membrane PBM ha permesso di operare con minori costi legati alla manutenzione e alla pulizia delle membrane. Le nuove membrane sviluppate possono essere dunque utilizzate anche ad altri processi a membrana per il trattamento delle acque reflue.

Abstract

Climate changes, population growth and urbanization are some of the causes of water shortage in many countries of the world. Water is essential to the life of all living organisms and its preservation and responsible use are some of the challenges that humanity will face in the near future. In particular, the possibility of treating and re-using municipal and industrial wastewaters can represent an important solution to water scarcity. Technological breakthroughs have led to the development of a number of technologies that can be efficiently applied in wastewater treatment. Among them, membrane applications are receiving an increasing attention thanks to their versatility, low environmental impact, easy scale-up and high product quality. Aim of this thesis was to produce polymeric membranes obtained through the polymerisation of a polymerisable bicontinuous microemulsion (PBM). Bicontinuous microemulsions consist of an interconnected network of oil and water channels stabilised by a surfactant. Oil channels can be polymerised, forming the membrane matrix, while water channels remain unaffected, forming the pores. In the present work, for the first time PBM membranes were applied, by polymerisation, as coating material for commercial polyether sulfone (PES) membranes. In the first part of the work, the polymerisable surfactant acryloyloxy undecyltriethylammonium bromide (AUTEAB) was synthesised and used for microemulsion formulation. The possibility of using a non-polymerisable surfactant such as dodecyltrimethylammonium bromide (DTAB) was also evaluated. In the second part of the work, novel membranes prepared by microemulsion polymerisation were characterised in order to select the proper membrane with suitable characteristics and properties. Characterization tests carried out on PBM membranes showed the great potential that these membranes could have on wastewater treatment in membrane bioreactor (MBR) applications. In particular, the very smooth surface, the relatively high hydrophilicity and the channel-like structure (typical of the bicontinuous microemulsion) make PBM membranes less prone and highly resistant to fouling. This aspect is the key point if we consider that fouling is one the major drawbacks affecting almost all membrane processes. Fouling is mainly due to the deposition of organic and/or inorganic matter on the surface of the membrane, causing therefore a decline in membrane performance, an increase in energy consumption and (in severe cases) damage of the membrane structure. Furthermore, PBM membranes, due to the presence of a cationic surfactant, present an interesting antimicrobial activity. The possibility of having membranes with antimicrobial properties prevents the phenomenon of biofouling caused by the adhesion and the accumulation of microorganisms at membrane surface. PBM coated membranes were, then, successfully applied to the MBR process for the treatment of wastewater from textile dyeing. PBM coated membranes, when compared with

commercial PES membranes, showed superior results for a long time (6 months) in terms of permeability and dye rejection. Moreover, less cleaning efforts were required leading to lower costs. Novel PBM coated membranes developed can be, thus, also applied to other membrane processes for wastewater treatment.

Thesis outlines

The present work is organised in 6 different chapters assembled in 3 sections:

Section 1 “General introduction” contains the first two chapters. Chapter 1 starts with a brief introduction and the discussion of the scope of work. The main objectives are reported and a schematic description of the work carried out is illustrated. In chapter 2 the state of the art on polymerisable microemulsions with particular remarks on bicontinuous microemulsions polymerisation (PBM) is reported. Furthermore, the main concepts on membrane technology and membrane processes are underlined.

Section 2 “Material and methods” comprises Chapter 3. In this chapter the materials, equipment and instruments used to perform this work are described in details. The methodologies and routes that have been followed in order to accomplish the work are reported.

Section 3 “Results and discussion” contains the experimental work together with a discussion of the results obtained. In particular, Chapter 4 focuses on the preparation of membranes through a bicontinuous microemulsion polymerisation (PBM) technique. The organic synthesis of the surfactant and preliminary characterization tests (such as conductivity measurement) are reported. In chapter 5 the characterisation tests carried out on the PBM membranes produced are widely discussed and in chapter 6 the application of the produced membranes within a Membrane Bio-Rector (MBR) process is described. Chapter 7 deals with the conclusions and final discussion.

Chapter 1

Introduction

1.1 Work objectives

Nowadays membranes are gaining more and more attention in different fields due to their versatility, low energy requirement, low operational costs, environmental compatibility and high efficiency, showing their huge potential in a wide spectrum of applications. There are several methods used for membrane preparation, depending upon the application in which the membrane has to be used. Phase inversion process is certainly the most widely used technique in membrane preparation. It consists in the precipitation of the polymer (dissolved in a suited solvent) with the subsequent formation of the membrane. The precipitation of the polymer can be induced by evaporation of the solvent, by using a non-solvent in which the polymer is not soluble (NIPS technique) or by thermal- or vapour-induced phase separation (TIPS or VIPS techniques). In the present work, novel membranes have been prepared by the polymerisation of a bicontinuous microemulsion.

The synthesis of polymeric membranes obtained by bicontinuous microemulsion polymerization (PBM) has a significant technological importance and it has been the main objective of this work. The possibility to control the permeability and the structure of the membrane depends on the opportune modifications in microemulsion composition and polymerization conditions. Furthermore, the possibility of dispersing nanoparticles and nanocatalysts into the starting microemulsion and to incorporate them within the polymerised membrane matrix allows to obtain functionalised membranes broadening their application in different fields.

Usually, the aim of polymerizing a microemulsion is to keep the original size of the microemulsion structure, which is also one of the main issues deeply studied in this work. Polymerised final latex particles, in fact, have a diameter of around 50 nm, while the original microemulsion particles have a diameter of 7-10 nm. The growth of the particles is due to the monomer diffusion and to the collision and coalescence of particles during the polymerization [1].

The aim of the present work is to produce hydrophilic membranes through the polymerisation of polymerisable bicontinuous microemulsions (PBM).

Microstructured and nanostructured materials obtained by PBM have been widely investigated in the course of the last 30 years. The interest in microemulsion lies mainly in the possibility of dissolving larger amounts of oil and water by using polymerisable and non-polymerisable

surfactants. By polymerising the bicontinuous microemulsion it is possible to produce transparent porous polymeric solids [2,3,4]. The polymerisation in microemulsion gained an increasing attention due to the possible application of the derived materials in catalyses, separation processes or as drug delivery systems [5]. In the present thesis a polymerisable surfactant was synthesised and applied to microemulsion preparation. The use of the polymerisable surfactant, acryloyloxy undecyltrimethylammonium bromide (AUTMAB), for microemulsion preparation is very well known and largely documented in literature [6,7,8]. Instead of the traditional AUTMAB, a novel surfactant, acryloyloxy undecyltriethylammonium bromide (AUTEAB), was synthesised due to its lower synthesis cost and easier reproducibility. Furthermore, the possibility of using a commercial surfactant was also evaluated by exploring the surfactant dodecyltrimethylammonium bromide (DTAB) for PBM preparation. PBM membranes, produced as coating material for ultrafiltration commercial membranes, were applied for wastewater treatment.

The wastewater treatment and water reuse represent a possible answer in the logic of sustainable water management. Water, in fact, is essential for the life of all living organisms and its preservation and responsible use is one of the global challenges that humanity will face in the next future. In under developed countries in Africa, the scarcity of freshwater is one of the most important causes of death for children under 5 years. But the problem affects some European countries as well, such as Cipro, the southern part of Italy, Spain and Portugal, which suffer from insufficient freshwater supply. Within this context, the European Union has promoted and financed several research projects in order to explore new solutions that can face the incumbent problem of water shortage by treating industrial wastewater. The project “Bionexgen” (Development of the Next Generation Bioreactor system-Grant agreement no: 246039), within our work has been performed, is a clear example of this strategy.

The United Nations estimated that by 2025 one third of humanity will face the problem of water scarcity. The question of water scarcity is directly linked to the evidence that the world’s water resources are not unlimited and the increasing demand of water due to urbanization and population growth together with global climate changes have a very strong effect on water availability [9].

The increasing worldwide demand for clean water is pushing more and more the market to find new strategies and innovative alternatives that can be applied for water reuse. The development of efficient wastewater treatment technologies can, thus, give complete answers to many of the problems related to water purification.

Wastewater treatment has a double purpose: producing high quality water from contaminated resources and transforming wastewater in water able to be reused in agriculture and industry.

In particular, membrane processes devoted to wastewater treatment are gaining more and more attention thanks to their high efficiency, energy saving systems, easy scale-up, and flexibility. In the membrane field, membrane bioreactors (MBRs) initiated during the early 1990s and represent today one of the most important technologies on the market for municipal and industrial wastewater treatment. MBRs combine a biological process, operated by specialized bacteria, with a physical separation, operated by selective membranes. Other advantages of MBRs are a small environmental footprint (thanks to the tight compaction of membranes that reduces the surface area) together with good effluent quality and high hygienic standards [10].

Nevertheless, one of the major drawbacks of MBR technology is the fouling and biofouling phenomena that occurs at membrane surface. Fouling is characterised by the deposition and accumulation, at membrane surface, of material of different nature (organic and inorganic matters); while biofouling is due to the deposition of biological material, such as bacteria, proteins or lipids that create a biofilm at membrane surface. Both phenomena cause a decline in membrane performances in terms of water permeability and decrease drastically the membrane life.

Aim of the present work is to provide a technological breakthrough in the field of water treatment by using innovative PBM membranes. For the first time, PBM have been successfully used as coating material for the preparation of flat sheet membranes applied in MBR technology (Figure 1.1.1).

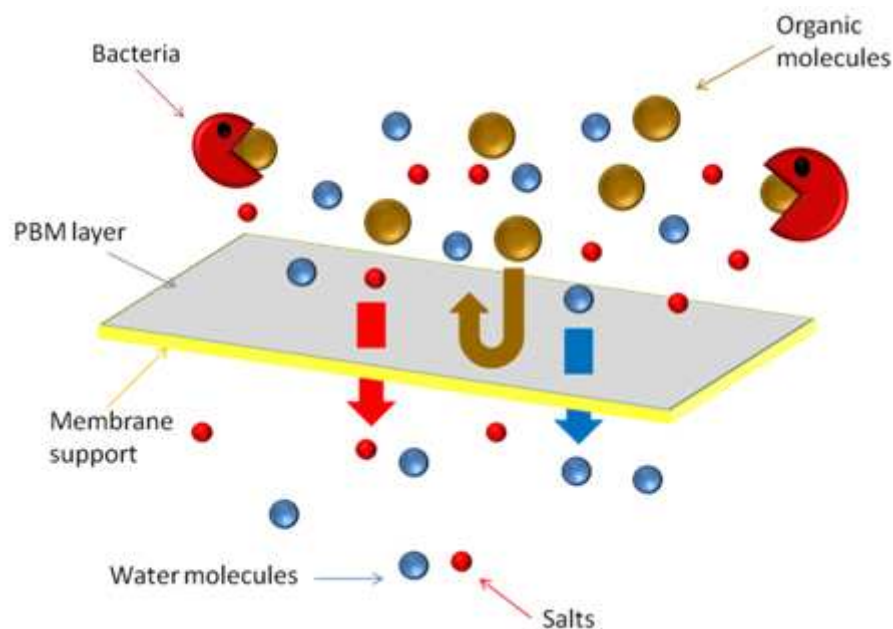


Figure 1.1.1 PBM membranes separation mechanism in MBR technology

PBM membranes were produced in order to lower fouling and improve rejection of low-molecular micro-pollutants of existing commercial membranes. Optimization of the prepared PBM membranes allowed extending the MBR operation efficiency from high biodegradable organic compounds to wastewaters containing stress-inducing substances.

The new-developed PBM membranes presented numerous advantages when applied in an MBR system such as: constant water permeability in time, good quality of the filtrate by rejection of organic compounds, modest oxygen consumption and an increase in the efficiency and durability of the membranes and reduced use of cleaning agents.

The above mentioned goals were achieved by overcoming or reducing some of the conventional limitations related to MBRs application. The main benefits brought by the PBM membranes produced were:

Anti-fouling properties

As described, fouling represents a major bottleneck for MBR technology. In the present work two different approaches were applied in order to reduce membrane fouling:

- Increasing membrane hydrophilicity: PBM coating allowed to enhance the hydrophilic moiety of commercial membranes used as support. Higher hydrophilicity resulted in better performances in terms of water permeability and foulant rejection. The attachment of various substances to the membrane surface is, in fact, mainly due to hydrophobic interactions. Hydrophilic membranes present a very low affinity with dissolved organics so that a lower water permeability decline, due to the fouling phenomenon, can be observed.
- Increasing membrane smoothness: membrane surface roughness plays an important role in the fouling process by increasing the “affinity” between the membrane surface and foulants. The troughs created by rough membranes are, in fact, preferred sites of accumulation of particles in comparison to smoother surfaces. The PBM coating allowed to reduce membrane roughness, therefore limiting the fouling layer formation.

Antimicrobial activity

Biofouling is formed by the sorption and subsequent colonization of microorganisms at membrane surface. It tends to occur in all the membrane processes where microorganisms and nutrients are present. It is predominant in MBRs where a population of bacteria is responsible for organic matter degradation. The consequence of biofouling are: reduction in permeability,

increase in energy consumption and in membrane maintenance costs. Thanks to their antimicrobial activity, due to the presence of a cationic surfactant, PBM membranes showed good antimicrobial properties for a long time.

Possibility of tuning the pore size

Pore size of produced PBM membranes could be finely tuned by modifying the temperature of microemulsion polymerization and its chemical composition. Thanks to this property, membranes with different pore size could be obtained, extending their application in several membrane processes (microfiltration, ultrafiltration, nanofiltration, in water filtration and membrane bioreactor).

Pollutants rejection

Good quality of the filtrate by rejection of organic compounds was achieved when, for instance, membranes were applied in a MBR process (COD rejection higher than 97%).

Enhancement of biological degradation (in an MBR process) due to the permeation of salts was also achieved. Furthermore, the water produced was not demineralized, offering therefore an opportunity for the subsequent production of drinking water.

Nanoparticles incorporation

Nanoparticles and nanocatalysts were dispersed into the starting microemulsion and incorporated by polymerization within the membrane matrix, allowing to obtain functionalised membranes. In the present work, this property was demonstrated by incorporating polyoxometalates (POMs) nanoparticles well known for their strong oxidant and catalytic activity [11].

Low operational costs

From MBR tests it was demonstrated how the lifecycle of PBM membranes was significantly enhanced in comparison to pristine uncoated commercial membranes. Lower cleaning efforts (due to the anti-fouling and anti-biofouling properties) are also required, reducing, consequently, the related costs.

The work carried out in the present thesis can be summarized as follows:

1. A bicontinuous microemulsion was prepared by dispersing an oil phase into an aqueous phase by means of a surfactant. A cross-linking agent was also added to the system in order to strengthen the matrix of the final latex, and redox initiators were finally used in order to promote the polymerization process.
2. The microemulsion so prepared was, then, used as coating material for a commercial polyethersulphone (PES) membrane by polymerization at membrane surface. The coating obtained had a thickness of 0.2-3 μm .
3. Preliminary characterization tests were carried out at lab scale in order to study membrane structure and membrane performances.
4. The membranes prepared were, then, assembled into a MBR module and tested at pilot scale, under simulated MBR conditions. All the results were compared with the ones obtained by using, under identical conditions, membranes without PBM coating. The lab scale MBR prototype was developed and successfully tested for model textile wastewater treatment.

All the steps followed in this work are schematically presents in Figure 1.1.2 (a-f):

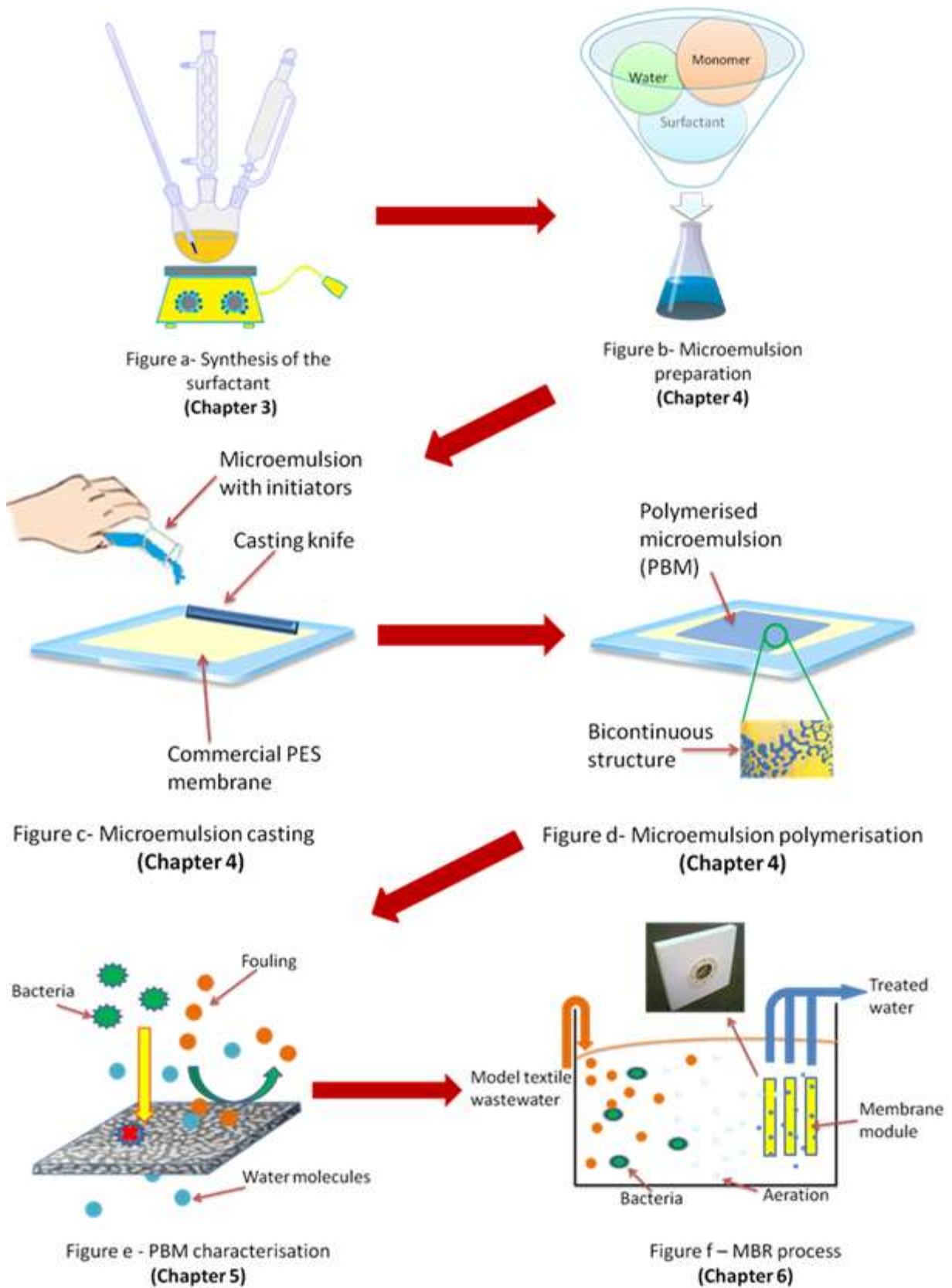


Figure 1.1.2 Schematically illustration of the work carried out in this thesis

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Chapter 2

Polymerisable bicontinuous microemulsions (PBM) and membranes

2.1 Microemulsions - Introduction

A microemulsion is a thermodynamically-stable dispersion consisting of two immiscible liquids (oil and water) stabilized by a surfactant. Often a cosurfactant, usually represented by a short-chain alcohol, is required for the formation of the microemulsion. The cosurfactant, in fact, along with the surfactant, lowers the interfacial tension to a very small (and sometimes even negative) value. However, the use of cosurfactant may not be necessary when non-ionic surfactants, some cationic surfactants or double-chain surfactants are used.

In contrast to emulsions, microemulsions form spontaneously, are optically transparent and thermodynamically stable, have smaller droplet size and lower interfacial energy.

Microemulsions are conventionally divided in three different types:

1. Oil-in-water (O/W) microemulsions: they are formed at low oil concentrations. The oil-swollen micelles are dispersed in a continuous water phase;
2. Water-in-oil (W/O) microemulsions: they are formed at low water concentration. The water droplets are dispersed in a continuous oil phase;
3. Bicontinuous microemulsions: they are formed at balanced conditions in which the oil and water domains are randomly dispersed in two phases giving a sponge-like structure.

At low surfactant concentrations, different multi phase equilibria, known as Winsor systems, arise :

1. Winsor I (O/W): surfactant-rich water phase coexisting with surfactant-poor oil phase;
2. Winsor II (W/O): surfactant-rich oil phase coexisting with surfactant-poor water phase;
3. Winsor III (bicontinuous): surfactant-rich hybrid phase coexisting with poor phases of water and oil, respectively [1].

Microemulsions can provide reaction sites for some inorganic/organic reactions and for polymerization. Nanoparticles, microlatexes and nanoporous polymeric materials can be obtained by polymerizing, respectively, W/O microemulsions, O/W microemulsions and bicontinuous microemulsions [2]. Microemulsions are suitable to solubilise hydrophilic and lipophilic materials that are relatively non soluble in water or organic solvents. This is due to the presence of water and oil microdomains within the same single-phase solution. Furthermore, thanks to their versatility and

thermodynamic stability, microemulsions are applied to different fields such as pharmaceutical, cosmetics, agrochemicals, oil recovery, as food additive and as reaction media.

In bicontinuous microemulsions the surfactant is located at the interface between the oil and water microdomains, forming a network of interconnected water and oil channels. The oil channels can be polymerized to form the matrix of liquid membranes, while the aqueous phase remains unchanged. For this reason, the microemulsions may be used for all purposes as membranes. Their tendency to organize themselves into stable structures, depending on the initial ratio between oil, water and surfactant, allows the adjustment and control of membrane morphology (size and pore distribution) in the range of nanometers.

The study of microemulsion properties includes different experimental approaches, such as viscosity measurements, conductivity measurements, phase behaviour, static and dynamic light scattering, NMR self-diffusion [3].

2.2 Microemulsions - State of the art

The term microemulsion was first coined by Schulman et al. in 1959 to describe a multiphase system containing oil, water, surfactant and alcohol, leading to the formation of a clear solution. A quaternary solution of water, benzene, hexanol, and k-oleate was, then, prepared. The system was stable, homogenous and slightly opalescent. In the years between 1943 and 1965 Schulman and co-workers described how to prepare these transparent systems. They found that by mixing the right combination of four components (water, oil, surfactant and cosurfactant), a clear single-phase solution could be obtained [4].

In 1980 Stoffer and Bone [5] studied the polymerization of methyl acrylate (MA) in water/oil systems (W/O) opening this field to an increasing number of investigations [6].

From that time on, many works were published on polymeric membranes obtained by microemulsion polymerization using both polymerisable and non-polymerisable surfactants.

Gan et al. [7-10], for instance, studied the polymerization of methyl methacrylate (MMA) using different types of polymerisable and non polymerisable surfactants. Microporous polymeric transparent materials were, thus, obtained and characterized. The zwitterionic surfactant (acryloyloxyundecyldimethylammonium) acetate (AUDMAA), the anionic surfactant 11-(N-ethylacrylamido)undecanoate (Na11-EAAU) and the nonionic surfactant ω -methoxy poly(ethylene oxide)₄₀ undecyl- α -methacrylate (PEO-R-MA-40) were applied in three different works to prepare bicontinuous microemulsions using different chemical concentrations. The differences between the use of polymerisable and non polymerisable surfactants were also investigated [9]. The anionic

surfactant sodium dodecyl sulphate (SDS) and the cationic surfactants of n-alkyltrimethylammoniumbromide (C_n TAB) allowed to obtain opaque polymer composites with different structures. The effect of the alkyl chain length of C_n TAB ($n=12, 14$ and 16) was evaluated and its strong effect on bicontinuous microemulsion structure was found. By increasing the length of the alkyl chain (from C_{12} to C_{16}), in fact, the morphology of polymerized microemulsions varied from a globular shape to a worm-like microstructure. The microstructure presented a dimension ranging from a few hundred nanometers to a few micrometers as the alkyl chain length was increased. This was probably related to the stronger interactions established by C_{16} TAB with the thicker hydrophobic layer that limited the formation of fluid interfacial films. On the contrary, when a surfactant with a shorter alkyl chain was used, as C_{12} TAB, the formation of more fluid interfacial films led to a globular microstructure. The above mentioned non-polymerisable surfactants were suitable to obtain open-cell microstructures even if the composites prepared were not transparent but opaque. For this reason, in order to obtain transparent latexes, polymerisable surfactants such as sodium 11-(N-ethylacrylamido)-undecanoate (SEAAU), acryloyloxyundecyltrimethyl ammonium chloride or bromide (AUTMAC or AUTMAB), AUDMAA and (PEO-R-MA- n) were applied. The produced polymer composites showed a promising application in the field of liquid separation as selective membranes. By adjusting, in fact, the composition of the microemulsion, the permeability of the membranes could be controlled.

When polymerisable surfactants are used to prepare the microemulsion, as shown above, all the components are polymerisable. After the polymerization, in fact, the surfactant results chemically bonded to the membrane matrix enhancing the hydrophilicity of the overall membrane [11].

As reported in literature, cationic and anionic surfactants are generally the most used surface active agents. Chieng et al. [12] in 1996 produced porous polymeric membranes using the anionic SDS and the cationic dodecyltrimethylammonium bromide (DTAB) surfactants.

Membranes obtained with SDS showed higher opacity when compared to membranes prepared with the cationic surfactant DTAB, indicating the larger pore size of the former ones (from 100 nm to 3 μ m). DTAB, on the other side, allowed to obtain transparent membranes with a smaller pore size (less than 100 nm), and, furthermore, it showed a better efficiency in stabilizing the copolymers particles of MMA and of 2-hydroxyethyl methacrylate (HEMA), used as cosurfactant, due to their strong interaction of the surfactant with these.

Burban et al. [13-14] used didodecyldimethylammonium bromide (DDAB) a double-chained surfactant, for the polymerization of MMA and silica gels eliminating the need of a cosurfactant that was normally applied for microemulsion preparation.

Bicontinuous microemulsions were, also, successfully used to prepare hollow-fiber membranes by coating and polymerizing them on to the fiber's internal surface. Li et al. [15] used bicontinuous microemulsion to coat pre-fabricated polyethersulfone/diethylene glycol/N-methyl-2-pyrrolidone (PES/DES/NMP) hollow-fiber membranes of different pore size by in situ polymerization. Prepared coated hollow-fiber membranes showed different performances on polyethylene glycol (PEG) separation and permeation that was found to be strongly dependent on the composition of the bicontinuous microemulsion precursors.

Over the past decades an increasing interest was devoted to microemulsion application as reaction media [16-17], for polymerization [18-21] and enzymatic [22-23] reactions, and as drug delivery systems [24-26].

Microemulsion polymerization, however, remains one of the most active field in microemulsion application. The 2001 paper by Capek [27], discusses the radical polymerization of styrene in the three and four component microemulsions stabilized by a cationic surfactant. Polymerization in the o/w microemulsion was defined as a new polymerization technique, which allowed to prepare polymer latexes with a very high particle interface area and narrow particle size distribution. Subsequently, in 2003 Stromberg et al. [28] studied the electropolymerization of 3,4-ethylenedioxythiophene (EDOT) from a highly concentrated bicontinuous microemulsion using a nonionic surfactant, while in 2006 Lim et al. [29] produced a proton exchange membrane by bicontinuous microemulsion photo-polymerization. A novel application was proposed by Figoli [30,31], where PBMs were applied as liquid membranes and used in the immobilization of porphyrin in the nanostructured bicontinuous microemulsion for the oxygen-facilitated transport.

In the last few years, bicontinuous microemulsions started to play an increasingly important role as drug delivery systems. Krauel et al. [21] in 2005 used different structure types of microemulsion for the preparation of nanoparticles by interfacial polymerization. Nanoparticles were prepared by selecting w/o droplet, bicontinuous- or solution-type microemulsions with ethyl-2-cyanoacrylate. Morphology of the particles and entrapment of the water-soluble model protein ovalbumin was investigated. This study clearly showed how the entrapment of proteins was dependent on the amount of the monomer used. The advantage of using bicontinuous microemulsion lay in the larger aqueous fraction and in the possibility to entrap bigger amounts of proteins, although entrapment efficiency was lower than in w/o droplet and solution-type microemulsions.

Another similar work was carried out by Graf et al. [32] in 2008. Poly(alkylcyanoacrylate) nanoparticles based on microemulsions for insulin-controlled release were studied. Even in this case, a low entrapment efficiency of the peptide in the nanoparticles was observed that could be compensated by administering a higher dose of the formulation.

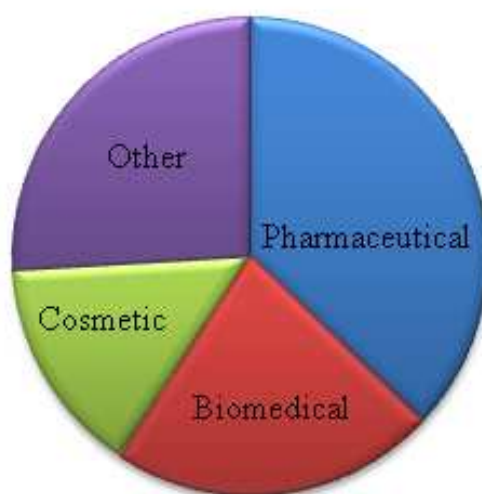
Table 2.2.1 Summary of microemulsion literature data

MONOMER (wt%)	WATER (wt%)	SURFACTANT (wt%)	COSURFACTANT (wt%)	INITIATOR	APPLICATION	REFERENCE
MMA (6-57)	4-40	SDS (1-14 wt%)	HEMA (20-54 wt%)	DBK, UV	Not reported	33
MMA (18 wt%)	30-36	SDS (4-10 wt%)	HEMA (42%)	APS-TMEDA, redox	Not reported	12
MMA (18 wt%)	28-33,2	DTAB (6.8-12 wt%)	HEMA (42%)	APS-TMEDA, redox	Not reported	12
MMA (30-48 wt%)	20-50 wt%	AUDMAA (17.5-28 wt%)	HEMA (30-48 wt%)	APS-TMEDA, redox	Not reported	34
MMA (30-48 wt%)	20-50 wt%	AUTMAB (17.5-28 wt%)	HEMA (30-48 wt%)	APS-TMEDA , redox	Not reported	34
MMA (20-60 wt%)	20-40 wt%	AUDMAA (20-40 wt%)	-	DMPA, UV	Not reported	8
AN (32.5-45 wt%)	10-35 wt%	PEO-R-MA-40 (32.5-45 wt%)	-	APS-TMEDA, redox	Pervaporation EtOH/H2O	11
MMA (7.5-20 wt%)/ NiPAAm (0-25 wt%)	23-33 wt%	C1-PEO-C11-MA-40 (35 wt%)	HEMA (5-20 wt%)	DMPA, UV	Potential construction of dressings and cell-delivery systems for wound healing	35
MMA (28-34 wt%)	15-30 wt%	Nall-EAAU (21-25.5 wt%)	HEMA (21-25.5 wt%)	DBK, UV	Not reported	7

MMA (8 wt%)	48-54 wt%	C12TAB (6-12 wt%)	HEMA (32 wt%)	DBK, UV	Not reported	9
MMA/HEMA (30-48 wt%)	20-50 wt%	AUDMAA (17.5-28 wt%)	MMA/HEMA (7:3) (30-48 wt%)	APS-TMEDA,redox	Not reported	9
MMA/HEMA (7:3) (30-48 wt%)	20-50 wt%	AUTMAB (17.5-28 wt%)	MMA/HEMA (7:3) (30-48 wt%)	APS-TMEDA,redox	Not reported	9
MMA (13-38.6 wt%)	55.9-81.8 wt%	AOA/SDS (5.2-10.2 wt%)	-	γ -ray	Not reported	36
Isopropyl Myristate	10-50 wt%	Caprylocaproyl Macrogolglycerides	Polyglycerol Oleate	Interfacial polymerization	Possibility to serve for encapsulation processes for oral delivery of insulin	32
Ethyloleate	Water	Polyoxyethylene 20 Sorbitan Mono-oleate/Sorbitan Monolaureate	Butanol	Interfacial polymerization	Protein entrapment	37
Isopropyl myristate (8-18 wt%)	10-60 wt%	PEG-8 caprylic/capric glycerides	Polyglyceryl-6 dioleate	Not polymerised	Potential drug delivery systems	24
Tetradecane (12,5 wt%)	35 wt%	CTAB (17,5 wt%)	1-Pentanol (35 wt%)	Not polymerised	Enzymatic hydrolysis of (R,S)-ketoprofen ethyl ester	22
MMA /21-32 wt%)	29-41 wt%	AUTMAB (25-37 wt%)	HEMA (0-10 wt%)	Polymerised	Gas separation	30

AN: acrylonitrile; AOA: 12-acryloxy-9-octadecenoic acid; APS: Ammonium persulfate; DBK: Dibenzyl Ketone ; DMPA: 2,2-dimethoxy-2-phenylacetophenone; NiPAAm: N-isopropylacrylamide; TMEDA: N,N,N,N-tetramethylethylenediamine

In Figure 2.2.1 the different fields of application of bicontinuous microemulsions, from registered patents, are reported.



Pharmaceutical field: Ref. [38], [40], [41], [46], [53], [55], [56], [57], [60], [61]; Biomedical field: Ref. [38], [40], [43], [47], [48]; Cosmetic field: Ref. [50], [51], [52], [54]; Other: Ref. [39], [41], [44], [45], [49], [58], [59], [32]

**Figure 2.2.1 Diagram of microemulsions main fields applications
(Patents references)**

According to patents data (Figure 2.2.1), the pharmaceutical field is the predominant area (almost 40%) of microemulsion applications. In particular, microemulsions are used as drug delivery systems (transdermal, oral, transmucosal and extra-vascular administration) due to their high solubilisation capacity for lipophilic drugs as well as for their potential effect on topic and systemic drug bioavailability [61].

The biomedical field follows with almost the 20% of applications. In this area, microemulsions formulations suitable for artificial cornea, for contact lens application [43], for blood gas controls and calibrators production [47] have been developed. The cosmetic field represents the 15% of applications. Microemulsions are mainly used for preshampoos formulations [50] and general cosmetic skin care products [53, 54].

Microemulsions are also used in other fields such as: thinner paint production [58], porous composites, catalytic materials [44], fluoropolymers production [39] and in some diesel fuel compositions in order to reduce harmful diesel emissions [49].

To the best of our knowledge, for the first time, in this work, a bicontinuous microemulsion was successfully employed as coating material for the preparation of composite membranes applied in wastewater treatment.

2.3 Oil-in-water (O/W) microemulsions

In O/W microemulsions the polymerization of styrene and MMA was mainly studied. These systems were prepared using nonionic, cationic (e.g. CTAB) and anionic (e.g. SDS) surfactants. One of the limitations of these systems was the very low solubility of the monomer, normally not exceeding the concentration of 8-10 wt%. For this reason, high concentrations of surfactants were required, making this process highly expensive. Furthermore, the latexes often showed instability and turbidity as a result of the incompatibility between the polymer formed and the cosurfactant. Often, in fact, the alcohols used as cosurfactants were solvent for the monomer but nonsolvents for the final polymer.

Latexes obtained were usually in the range of 20 to 60 nm in diameter [62].

2.4 Water-in-oil (W/O) microemulsions

Acrylamide (AM), HEMA and acrylic acid (AA) were the most used water-soluble monomers for W/O (or inverse) microemulsion preparation. The latexes obtained were formed by swollen water polymer particles dispersed in the continuous organic phase [63]. The water-soluble monomers usually played also the role of cosurfactant with the enhancement of the monomer solubilisation through the increase of the flexibility and the fluidity of the interfaces [62]. Hydrocarbons solutions of dialkyl sulfosuccinates surfactants, for instance, where the oil phase was toluene, benzene, decane or heptanes, did not require any addition of cosurfactants [63].

2.5 Bicontinuous microemulsions

In bicontinuous microemulsions, the amount of monomer that can be incorporated in the microemulsion can reach 25 wt%, producing stable and clear microlatexes with very small particle size. The organic and aqueous phases coexist in an interconnected network with surfactant molecules localized at the interface of water-oil domains. MMA and styrene are the most used monomers for bicontinuous microemulsion preparation. Cosurfactant, such as AA and HEMA, are commonly used and nonionic, cationic, zwitterionic and anionic surfactants are applied. A crosslinking agent, such as ethylene glycol dimethacrylate (EGDMA), can be included into the

bicontinuous microemulsion to consolidate the final structure. Since all the components of the microemulsion are polymerisable, they can be copolymerised forming a strong and resistant network [64].

2.6 Phase diagram

The construction of a phase diagram allows the determination of water dilutability of the system and the range of compositions constituting a monophasic region [1].

As shown in figure 2.6.1, microemulsions can be in the form of oil-swollen micelles dispersed in a continuous water phase (O/W), or water-swollen droplets dispersed in an oil phase (W/O). In the intermediate region, the structure is not globular anymore but it has a sponge-like structure (bicontinuous microemulsion) where the oil and water domains coexist in interconnected domains. At low surfactant concentrations Winsor phase equilibria can be identified: Winsor I (O/W), Winsor II (W/O) and Winsor III (bicontinuous microemulsion).

The different phases and coexistence regions occurring in a three-component water, oil and surfactant system can be represented in a triangular phase diagram (ternary phase diagram).

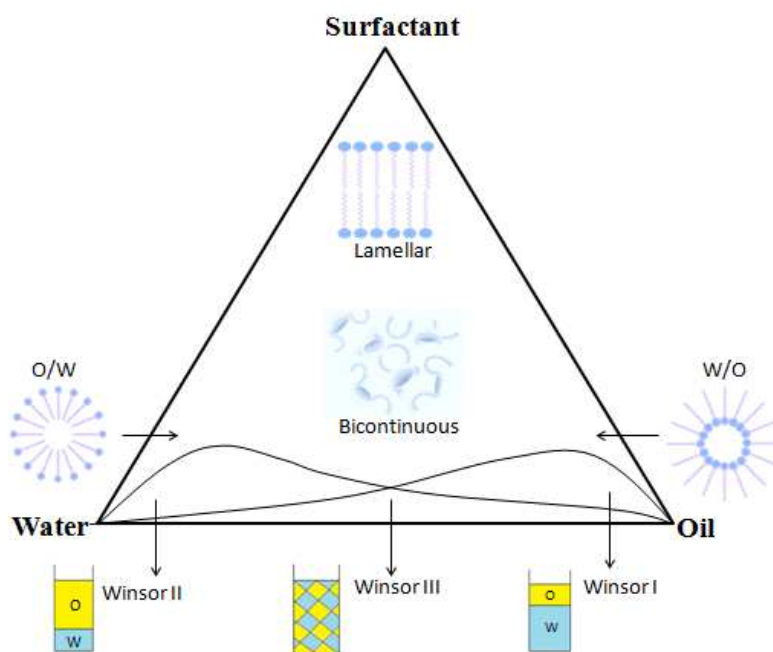


Figure 2.6.1 Ternary phase diagram representing some phase equilibria in multicomponent systems

As shown in Figure 2.6.1, at high oil concentration reverse micelles capable of dissolving water molecules are formed. W/O microemulsions are formed in consequence of the further addition of

water to the system. Here, water exists in the oil phase as droplets surrounded by the surfactant molecules.

Upon further dilution with water, a crystalline liquid region may be observed with the formation of double layers of surfactant (lamellar structure). Finally, as the amount of water increases, water forms a continuous phase containing droplets of oil stabilized by surfactant molecules (O/W microemulsions). The bicontinuous microemulsion forms in the middle phase, which is in equilibrium with almost pure water and oil phases, respectively.

2.7 Microemulsion polymerisation

Free radical polymerization has been widely investigated over the past few decades. Most of the studies focused on the O/W microemulsion polymerization. The basic sequence of the events describing the general mechanism of O/W microemulsion polymerization is reported in Figure 2.7.1. Two stages (defined as Intervals) can be identified in microemulsion polymerization: Interval I in which particle nucleation occurs, Interval II in which particle growth occurs.

Interval I: Once initiators are added to the microemulsion, they produce, by their decomposition in the aqueous phase, radical species able to promote a reaction (Figure a). Thus, initiator radicals start reacting with water-soluble monomer molecules dispersed in the aqueous phase to form oligomeric radicals. At this point, particle nucleation occurs (Figure b).

Interval II: In the second stage, the oligomeric radicals, being more hydrophobic than the monomer from which they originated, enter more favourably into the monomer-swollen micelles present in the aqueous phase. Polymerization propagates within the monomer-swollen micelles starting the process formation of latex particles. The growth of latex particles is due to the diffusion of monomer molecules from monomer-swollen micelles (Figure c) and to the collision and subsequent coalescence between two particles (Figure d).

If the transfer of a radical from the propagating polymer to a monomer molecule occurs, the monomeric-formed radical can continue to propagate within the latex particle or it can exit the particle and enter a micelle starting a new propagation event and a new latex particle formation. Polymerization continues until the monomer is totally consumed. The final latex consists of surfactant-stabilized polymer particles and empty micelles formed by the excess surfactant [64] (Figure e).

Figure a Formation of initiating radicals in the aqueous medium

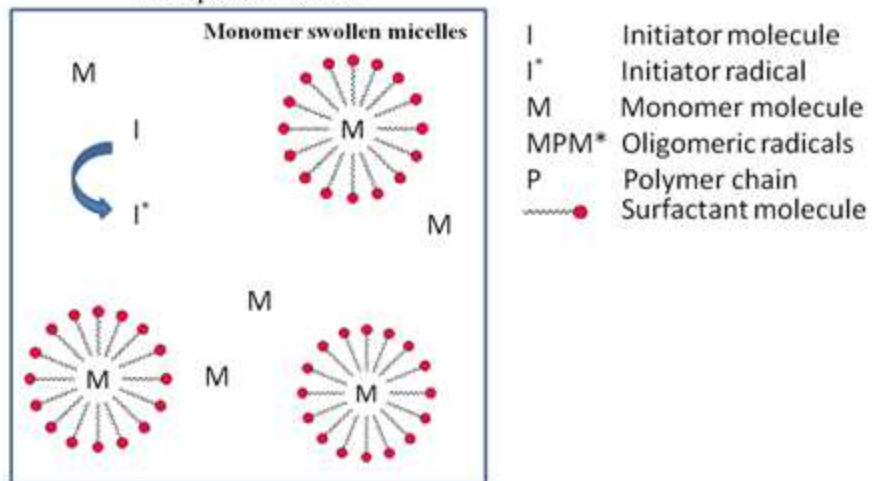


Figure b Nucleation of monomer swollen micelles

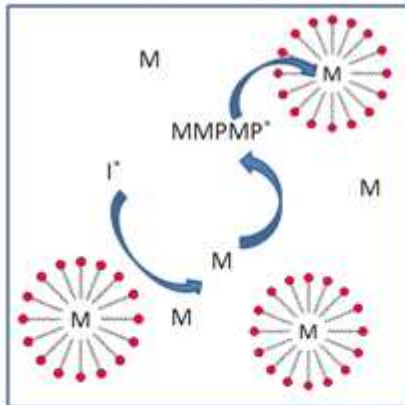


Figure c Growth of latex particles by diffusion of monomer molecules

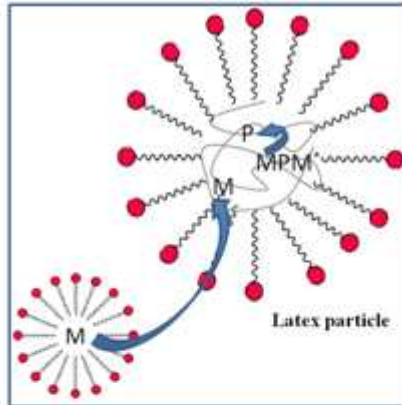


Figure d Growth of latex particles by collision and coalescence of two particles

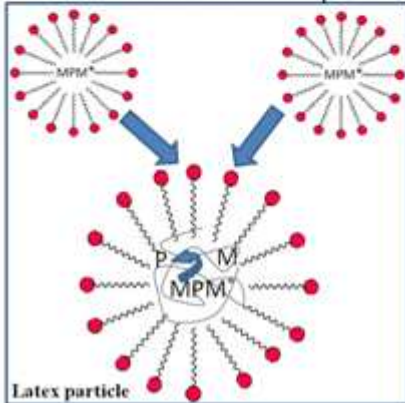


Figure e Polymer particles formation

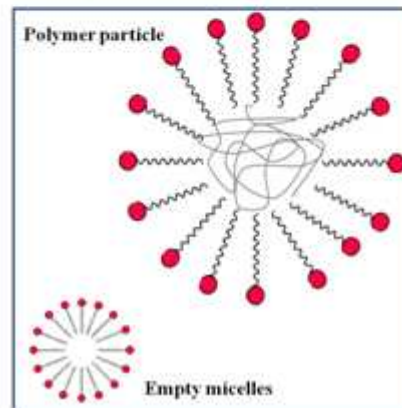


Figure 2.7.1 Schematic representation of O/W microemulsion polymerization (figure adapted from [64])

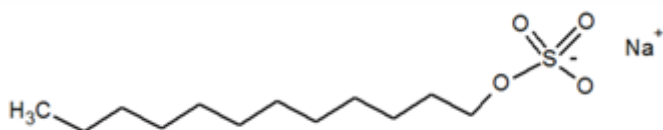
2.8 Surfactants

Surfactants are amphiphilic molecules consisting of a hydrophilic water-soluble head and a hydrophobic oil-soluble tail. They are able to lower the surface tension of a liquid, facilitating the wetting of surfaces or the miscibility among different liquids. The stabilizing behaviour of surfactants depends on their molecular structure (geometry), the interactions they undergo with water and/or oil and the elastic properties of the interfacial film they form.

Surfactants can be divided into ionic and non-ionic surfactants depending on the presence of a charge.

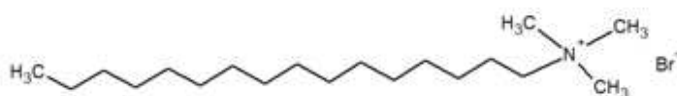
Generally, ionic surfactants consist of an anionic headgroup, such as SO_3^- , or a cationic headgroup like $-\text{N}^+(\text{Me})_3$. Surfactants that bear both a positively and a negatively charged group are zwitterionic and thus overall neutral. Non-ionic surfactants consist generally of an AB block copolymer type structure. Those most commonly used are built up of ethylene blocks (hydrophobic moiety) and ethyleneoxide blocks (hydrophilic moiety) (Figure 2.8.1).

Anionic surfactant



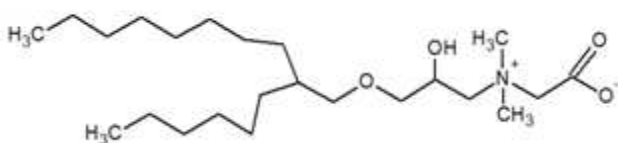
Sodium dodecyl sulphate
(SDS)

Cationic surfactant



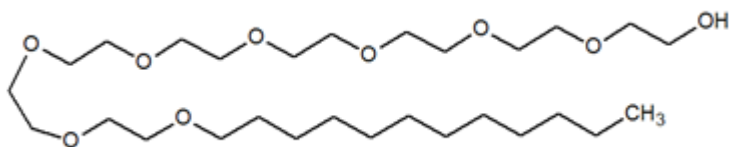
Cetyltrimethylammonium
bromide (CTAB)

Zwitterionic surfactants



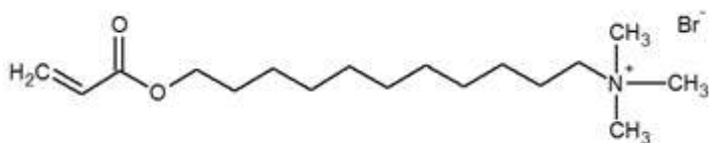
Guerbet alcohol hexadecyl glycidyl
ether glycine betaine

Non-ionic surfactants



Octaethylene glycol
monododecyl ether

Polymerisable (cationic) surfactant



Acryloylundecyltrimethylammonium
bromide (AUTMAB)

Figure 2.8.1 Different structures of surfactants

In microemulsion preparation both types of polymerisable and non-polymerisable surfactants are used for the production of nanostructured materials. However, the structures of the materials obtained with non-polymerisable surfactants can be easily destroyed by chemical or physical forces. For this reason, the use of polymerisable surfactants is generally preferred. Polymerisable surfactants can be, in fact, polymerized and cross-linked with other microemulsion components thanks to the presence of their double bond. In this way a strong and resistant network can be obtained, which is able to keep its original structure [65].

In the present work both types of polymerisable (AUTEAB) and non-polymerisable (DTAB) cationic surfactants have been used for bicontinuous microemulsion preparation.

2.9 Generality on membranes

Membrane operations in the last years have gained more and more attention due to their characteristics of efficiency, simplicity, eco-friendly applications, low impact costs, low energy requirements, good selectivity and permeability. Membrane applications have, thus, been used in a large variety of processes such as water desalination, water treatment, gas separation, centrifugation, clarification, crystallization, etc..

A membrane can be defined as a selective barrier that separates or puts in contact two phases allowing the exchange of matter, energy or information between them in a specific or non-specific way [66].

Polymeric membranes lead the membrane separation industry market because they are very competitive in performance and economics. Depending on the type of separation, different membranes, with different properties, can be produced. Based on their morphology, polymeric membranes are classified in isotropic (or symmetric) and anisotropic (or asymmetric) membranes. Depending on the size of separated molecules, membranes can be also classified in dense or porous membranes. Dense membranes are generally used in applications where very small molecules need to be retained or separated, such as pervaporation, gas separation or reverse osmosis. In other processes such as microfiltration, ultrafiltration or nanofiltration, where large molecules (suspended colloids, cells, biomolecules) are separated, porous membranes find their use.

The phase inversion technique is one of the most widely used methods for membrane preparation. A selected polymer is dissolved in a suitable solvent at a certain temperature and the membrane is prepared through one of the following procedures:

- Non-solvent induced phase separation (NIPS): the cast film is immersed into a coagulation bath containing a nonsolvent and the precipitation of the polymer occurs through the exchange between solvent and non-solvent;
- Solvent evaporation: the volatile solvent is evaporated from the cast film containing two or more solvents with different dissolution properties;
- Vapour-induced phase separation (VIPS): the cast film is exposed to a non-solvent vapour (generally water) for a fixed time and then immersed into a coagulation bath;
- Thermally induced phase separation (TIPS): the cast film, prepared at elevated temperature, is cooled down causing phase separation and polymer precipitation.

Figure 2.9.1 shows the generic casting method to prepare membranes at laboratory scale as well as the different phase inversion techniques.

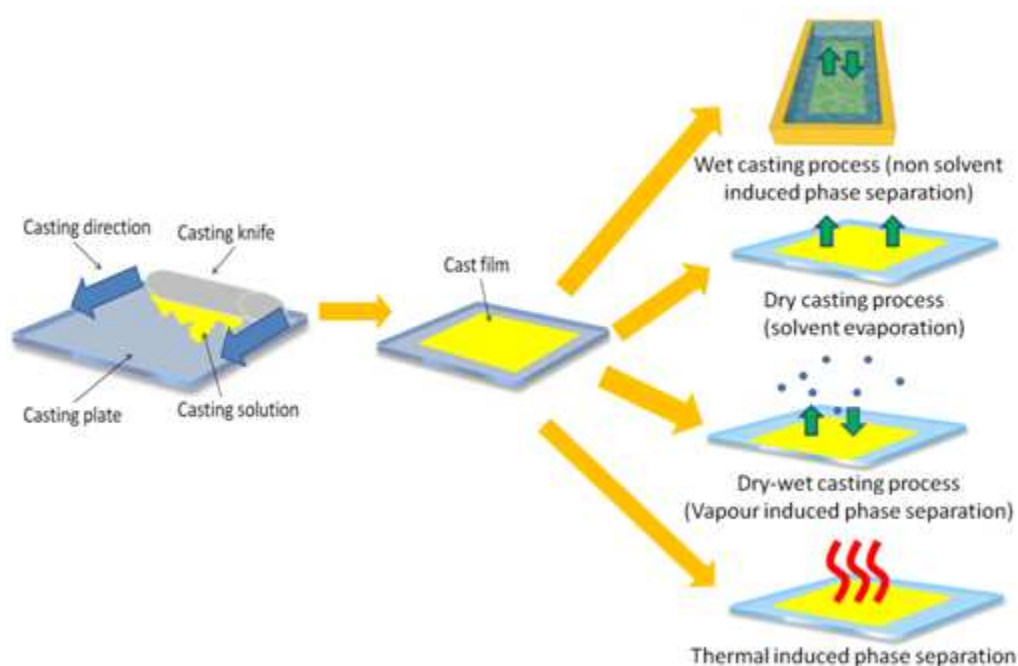


Figure 2.9.1 Procedure for casting flat sheet membranes at lab scale and methods for inducing phase-separation

Other techniques such as track-etching, sintering or melt extrusion are also used for the preparation of different membranes, depending on the desired membrane structure and on the final application.

In some membrane processes such as pervaporation [67, 68], reverse osmosis or gas separation, where dense membranes are applied, the mass transfer is governed by the solution-diffusion model. This model is based on the dissolution of target molecules into the polymeric membrane matrix and their subsequent permeation and desorption through the membrane's permeate side. In order to achieve an acceptable flux, the membrane should be as thin as possible. For this reason, asymmetric membranes are generally used. Unfortunately not all the available polymers can be used for the production of asymmetric membranes by phase inversion technique. This had led to the development of composite membranes obtained by the deposition of a very thin layer of dense coating material on a porous membrane support. The membrane's surface acts as a selective barrier, while the porous sublayer acts as support for the overall membrane.

In the present work, composite membranes, with a tuneable pore size, were obtained by casting a polymerisable bicontinuous microemulsion on the surface of commercial polyether sulfone (PES) membranes. The result was a thin coating layer polymerised on the surface of a porous support.

Produced membranes were thus characterised by different techniques in order to study and to evaluate membrane properties and performances. Microscopic analyses (atomic force microscopy and scanning electron microscopy), pure water flux, molecular weight cut-off, contact angle

measurements, antimicrobial activity and organic molecules rejections were some of the characterization techniques applied in the present work and usually reported in literature.

At the industrial level, where hundreds or thousands of square meters of membrane are required, membranes are assembled together in order to form modules with different configurations. Plate-and-frame modules were one of the first modules developed by the industry. In this configuration, flat-sheet membranes and permeate spacers are layered with spacers forming feed flow channels and clamped together between two end plates. The feed is forced across the permeate that is collected through a central permeate collection manifold.

In spiral-wound configuration, flat sheet membranes are wound like an envelope with feed spacers around a central collection tube. The feed is pumped into the space outside the envelope and the permeate is, then, collected inside the envelope and directed to the central tube.

Tubular membrane modules are used for hollow fibre, capillary and tubular membranes. Hollow-fibre membrane modules are made up of several tubular membranes arranged in parallel in two types of configuration. In the shell side configuration, the feed is in contact with the external fibre surface. Thus, the permeate passes through membrane walls and exits through the open fibre ends where it is collected. In the second configuration, the feed is circulated through the lumen of the fibres and the permeate is collected on the shell side.

Pressure-driven membrane processes such as microfiltration (MF), ultrafiltration (UF) and nanofiltration (NF) are widely used in membrane purification applications. Because of the driving force, solvent or water passes through the membrane together with small molecules, while the molecules larger than the pore size of the membrane are rejected. Going from MF to NF the size of membrane pores becomes smaller (from 10 μm in MF to 2 nm in NF) and consequently also the dimension of the particles rejected decreases. Denser membranes are used in reverse osmosis (RO) applications where the pore size is in the order of a few nm. RO membranes are used when low molecular weight solutes such as inorganic salts or glucose have to be separated from the solvent. RO membranes requires high pressures to operate (ranging from 15 to 80 bar) and they are often applied for the desalination of brackish water or seawater.

In concentration-driven processes, on the contrary, dense membranes are used. The transport across the membrane occurs by the dissolution and adsorption of a target molecule through the membrane material. The affinity between the polymer and the permeating molecule is therefore of primary importance in order to achieve the separation. The chemical gradient formed by the difference in concentration between the two sides of the membrane represents the driving force in this type of membrane separation. Pervaporation, gas separation and vapour permeation are among the membrane separation processes based on the concentration difference [69].

Among the several membrane applications, over the last 40-50 years an increasing attention was devoted to the development of membranes to be applied in the field of wastewater treatment [70]. Nowadays, the highest number of installations are for industrial wastewater application and municipal wastewater treatment [71].

Recent technological developments resulted in clear breakthroughs where membranes covered a prominent role in the field of wastewater treatment. Membrane technologies for wastewater treatment include:

- NF and RO: they represent the starting point of membranes applied to wastewater [72]. They are high-pressure driven processes and are mainly applied as the final step of the treatment in order to produce high quality effluent.
- MF and UF: they are low-pressure driven processes effective for the removal of suspended solids and for clarification. They are also able to remove bacteria and viruses (UF).
- Membrane Bioreactor (MBR): MF or UF membranes are immersed in a reactor tank or placed in a external unit. The membrane filtration process is associated with a biological treatment using an activated sludge.

2.10 MBR technology and fouling

Among the several membrane processes, the membrane bioreactor (MBR) technology is receiving an increasing attention, in particular for the industrial and municipal wastewater treatment application. The MBR process combines a biological treatment with a membrane purification. The first step is operated by bacteria through the digestion of organic compounds, nitrification and denitrification. In the second step, the separation of biomass is achieved by membranes. Generally MF and UF membranes are applied in an MBR process operating by sieving or surface filtration. Recently, however, many NF MBR plants took place [73-74].

Two main types of MBR configuration are available (Figure 2.10.1):

1. Submerged MBR: the membrane module is totally submerged within a tank containing the wastewater and the activated sludge. An aeration system provides oxygen for microorganism survival and generates a cross-flow at membrane surface limiting the fouling formation. This configuration was also used in the present work.
2. Side-stream MBR: the membrane unit is located outside the activated sludge tank. The mixed liquor (representing the concentration of suspended solids) is then pumped through the membrane module generally formed by tubular membranes.

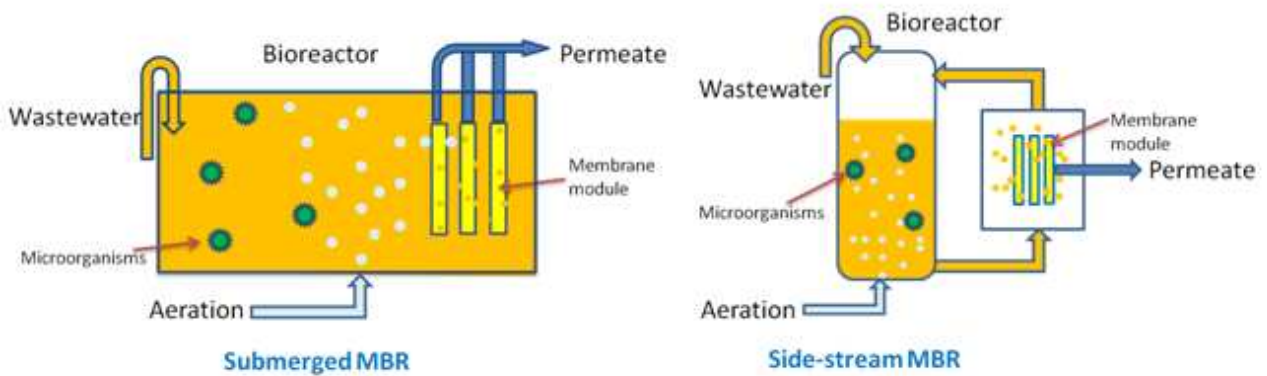


Figure 2.10.1 Submerged and side-stream MBR

The main operating parameters in an MBR system are:

Trans-Membrane Pressure (TMP): it represents the pressure across the membrane and is the driving force for the permeate production. TMP is created by a vacuum pump at permeate side.

Aeration: it is of fundamental importance in MBR. It is used to supply oxygen to microorganisms and to prevent fouling by scouring membrane surface. The dimensions of the air bubbles, the intensity and the aeration rates are also controlled in order to reach the best MBR performances.

Hydraulic Retention Time (HRT): it affects the reactor volume and the filtration process. It represents the time length that the feed solution stays in the reactor before it turns into permeate.

Mixed Liquor Suspended Solid (MLSS): it represents the concentration of dissolved solids within the reactor. The possibility to use high concentrations of solids results in a reduced footprint but many authors reported an increase of fouling with increasing MLSS.

Oxygen consumption: it is the oxygen consumed by microorganisms to enable their degradation work.

Permeability: it is the amount of liquid treated by the membrane normalized by pressure, time and area.

Food to Microorganisms (F/M) ratio: it is the organic loading rate measured by the amount of food provided to a unit amount of biomass for a unit period of time.

The biological performances of an MBR process are:

Chemical Oxygen Demand (COD): it is used to measure the amount of organic compounds dissolved in water. The higher is the COD removal efficiency, the better is the permeate quality.

Biological Oxygen Demand (BOD): it is the amount of dissolved oxygen needed by aerobic biological organisms to degrade the organic material contained in the reactor.

MBR can operate under aerobic or anaerobic conditions. The anaerobic MBR has the main advantage of reducing operative costs of aeration since no oxygen is required by microorganisms. However, in aerobic MBR the productivity is higher and better performances can be obtained.

Fouling is one of the major drawbacks occurring in MBR processes. In MBR the feed is represented by activated sludge. For this reason, a large part of the fouling is represented by the components originating from the sludge and from their interactions with the membrane surface. Activated sludge has many different components such as extracellular polymeric substances (EPS), soluble microbial products, and colloids which are responsible of fouling [75]. In addition, the formation of a biofilm caused by microorganisms is one of the major factors of membrane biofouling. Biofouling and fouling cause a decline in membrane performance and in membrane durability. Although biofouling created by microorganisms at membrane surface is not desirable at all, microorganisms, in order to accomplish their degradation work, have to be healthy and sustainable. For this reason, the conditions of the reactor must be suitable for their growth and survival. The community of bacteria in MBR is varied and diversified. The dominant group of bacteria is generally represented by Protobacteria followed by Nitrosomonas and Nitrospira which are autotrophic ammonia oxidising bacteria. Nitrobacter and Nitrospira are nitrite-oxidising bacteria and represent a minor group of the microorganism population [76].

Membrane fouling is generally observed through a decrease in permeability and an increase in trans-membrane pressure (TMP). Two different types of fouling can be identified:

1. reversible fouling: it is the fouling occurring at membrane surface that can be removed by physically washing the membranes;
2. irreversible fouling: it is represented by fouling occurring within membrane pores, which is only removable through chemical cleaning.

Fouling can be caused by physical and chemical interactions between the fouling particles and the membrane surface. Membrane fouling is determined by the feed composition and concentration, pH, temperature, hydrodynamic conditions and membrane properties (hydrophilicity, roughness) [77]. Foulants can be classified in four different categories:

1. Particulates: formed by inorganic or organic particles that can physically interact with membrane surface;
2. Organic: they deposit at the membrane surface by adsorption (such as humic acid);
3. Inorganic: they tend to precipitate on the membrane surface due to pH variation or oxidation;
4. Microorganisms: bacteria, algae and fungi that can adhere to the membrane causing biofouling [78].

Many strategies can be applied in order to control the fouling such as reducing the flux, increasing the aeration rate, back-flushing the membrane, using physical or chemical cleaning [79]. The approach adopted in the present work was to produce a novel coating (made by PBM) , applied on commercial PES ultrafiltration membranes, highly resistant to fouling. PBM membranes thus prepared were used for the treatment of model textile dye wastewater. The textile industry is, in fact, an intensive water-consuming sector where large amounts of water are needed. It is estimated that for each ton of fabric produced, 20-350 m³ of water are necessary [80]. Textile wastewater contains a wide range of contaminants such as salts, enzymes, dyes, surfactants and oxidizing agents. Because of the toxicity and poor biodegradability of many of these compounds, an effective technology, such as MBR, has to be applied. It is estimated that about 10% of the dye used in the industry is lost during the colorization process [81]. Azo dyes represent the majority of dyes (65-70%) encountered in textile wastewater [82]. They are characterized by the presence of the azo bond (-N=N-) and their wide application can be attributed to the fact that these dyes provide a wide range of brilliant colors. Due to their high solubility in water, dyes can react with water rather than the hydroxyl groups of cellulose and they are, thus, discharged in wastewater. The presence of dyes into wastewater can create several problems since they can originate toxic compounds and affect the normal process of photosynthesis of aquatic plants. For this reason, a treatment of produced wastewater is required. Biological, physical and chemical methods are usually applied for the treatment of textile wastewater. Recently, MBR technology, thanks to the high quality of the filtrate that can be obtained and to the efficient removal of pollutants, are of high interest for many industries as an innovative technology for wastewater treatment and reuse of water in their industrial processes. In the present work, the novel PBM membranes developed were applied for the treatment of a model dye textile wastewater in an MBR process. The removal efficiency of two representative dyes (Remazol Brilliant Blue and Acid Red 4) was used for the evaluation of membrane performances.

2.11 References

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Chapter 3

Materials and methods

In the present chapter the materials and methods adopted to accomplish this work are reported. The chapter is organised in 3 paragraphs and a final appendix. In the first paragraph particular relevance is given to the synthesis of the surfactant acryloyloxyundecyltriethyl ammonium bromide (AUTEAB). The surfactant was then applied for the preparation of a polymerisable bicontinuous microemulsion (PBM) that was used as coating material for a polyether sulfone (PES) ultrafiltration commercial membrane. The methodologies and materials adopted for microemulsion preparation and polymerisation are described in detail. In the second and third paragraph, the instruments, materials and method used for membrane characterisation and application in MBR are reported. The chapter ends with an appendix covering the characterisation tests (NMR, IR) carried out on the synthesised surfactant AUTEAB.

3.1 Development of novel PBM membranes

Synthesis of the surfactant AUTEAB

Surfactants are amphiphilic molecules consisting of a hydrophilic water-soluble head and a hydrophobic oil-soluble tail. They are able to lower the surface tension of a liquid, thus facilitating the wetting of surfaces or the miscibility among different liquids. The synthesis of a pure polymerisable surfactant is a key step in the formation of microporous materials from bicontinuous microemulsions, since some of them are not commercially available. All the chemicals used for the AUTEAB synthesis were purchased from Sigma-Aldrich with purity higher than 98% (analytical grade).

AUTEAB has been synthesized by following a two-step procedure:

1° step: Esterification

Acryloyl chloride (2.26 g, 24.9 mmol) was dissolved in anhydrous CH₃CN (110 ml) under nitrogen atmosphere and added to a stirred solution of 11-bromoundecanol (5 g, 19.9 mmol). 3A molecular sieves (4.3 g) were also added to the solution under nitrogen atmosphere. The solution was stirred for 24h at 90°C. After cooling, the mixture was filtered in order to remove molecular sieves, the solvent was removed by vacuum and the product was purified by column chromatography (silica

gel, hexane: ethyl acetate 9:1). Yield: 5.35 g (17.5 mmol); 88% based on starting 11-bromo-1-undecanol.

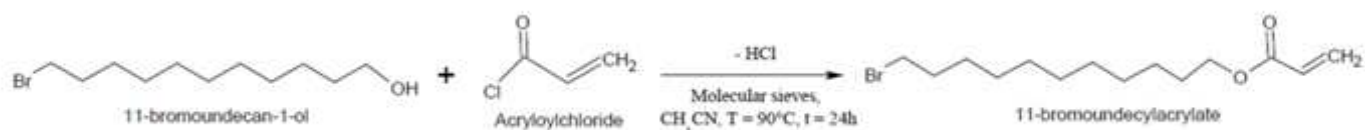


Figure 3.1.1 Esterification reaction for AUTEAB synthesis

2° step: Quaternization

11-bromoundecylacrylate was dissolved in anhydrous chloroform (8 mL) under nitrogen atmosphere. Triethylamine (1.96 g, 19.4 mmol) was added to the mixture and then the solution was stirred for 72h at 60°C. After cooling, the solution was filtered and under stirring diethyl ether (80 mL) was added dropwise. The resulting white precipitate was filtered and washed with diethyl ether. Yield: 4.74 g (11.7 mmol); 67% based on starting 11-bromoundecylacrylate

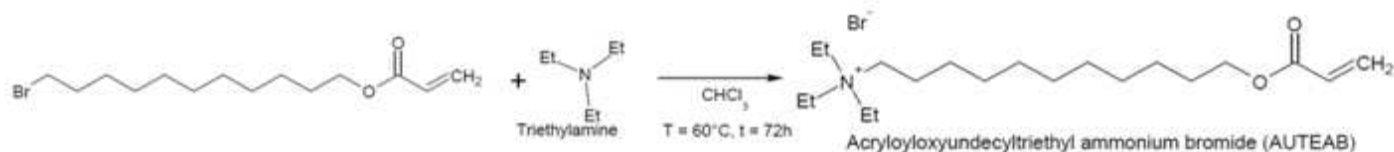


Figure 3.1.2 Quaternization reaction for AUTEAB synthesis

Characterizations tests (NMR and IR reported in the appendix at the end of the chapter) confirmed that the synthesis was successful and that the expected surfactant had been synthesised.

For melting point determination Linkam TH600 Microscope Leitz 12 POL was used.

Spectrometer FT-IR Perkin Elmer Paragon 1000 PC was used for IR analyses.

Spectrometer NMR Briker-500 was used for NMR analyses.

Microemulsion composition and polymerisation

A preliminary literature survey was carried out to better understand the microemulsion's composition and polymerisation. A microemulsion is a liquid dispersion containing water and oil with characteristics of uniformity, transparency and thermal stability by adding a corresponding

quantity of surfactant and co-surfactant. The microstructure of a microemulsion depends on the composition of the system, e.g. water-in-oil (w/o) droplets at low water content, oil-in-water (o/w) droplets at high water content, and a bicontinuous structure at intermediate water content. Aim of the thesis was the production of highly hydrophilic flat membranes by PBM to be used as coating material for PES commercial membranes for water purification. All the chemicals used for preparing microemulsions were purchased from Sigma-Aldrich with purity higher than 98% (analytical grade).

The composition of the microemulsion was:

- 1) Methyl methacrylate (MMA), used as monomer constituting the oil phase of the microemulsion;
- 2) Water, used as the aqueous phase of the microemulsion;
- 3) Lab-made surfactant AUTEAB and the commercial surfactant dodecyltrimethylammonium bromide (DTAB), used to lower the surface tension of the microemulsion facilitating the formation of a single phase;
- 4) 2-hydroxyethyl methacrylate (HEMA), used to enhance the dispersion of the oil and water phase;
- 5) Ethylene glycol dimethacrylate (EGDMA), added as cross-linker;
- 6) Ammonium persulfate (APS) and N,N,N',N'- tetramethyl ethylenediamine (TMEDA), added as initiators.

The optimal concentration of chemicals used for microemulsion preparation together with conductivity measurements, that allowed to identify the bicontinuous range, are reported in Chapter 4.

The preparation of the microemulsion was carried out as follows: the monomer and the water were first added within a flask in the proper amount. The surfactant was then added and the immediate and spontaneous formation of a transparent and homogenous dispersion (without mixing) was observed. The cosurfactant HEMA and the cross-linker EGDMA were also added.

The solution was then kept at the desired temperature (between 20°C and 30°C) and finally redox initiators (APS and TMEDA) were added to the microemulsion that was purged with nitrogen gas for at least 1 minute. When the microemulsion, depending on the set temperature, reached the suitable viscosity, it was cast on PES membrane in a chamber under nitrogen atmosphere and controlled temperature. Microemulsion was cast using a casting knife of 250 µm, as shown in figure

3.1.3. The PBM coating was left to polymerise overnight and it was totally transparent. Its thickness was measured and it was about 0.2-3 μm .

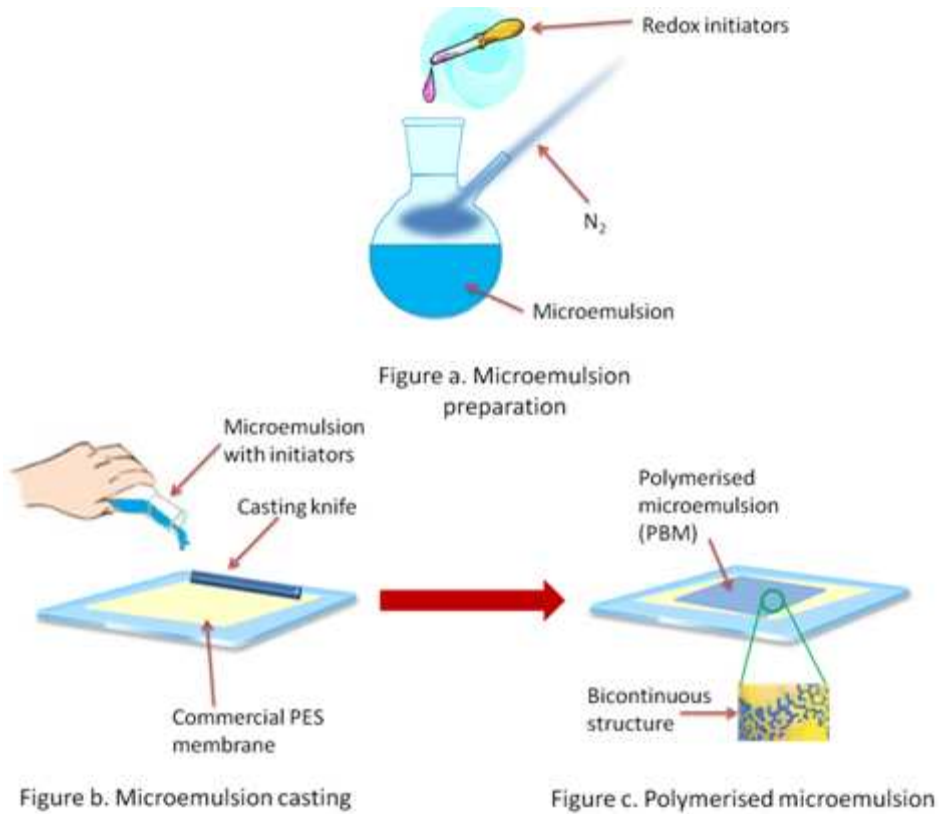


Figure 3.1.3 Microemulsion preparation and casting

The microemulsion casting and polymerisation occurred in a nitrogen chamber under controlled temperature (Figure 3.1.4).

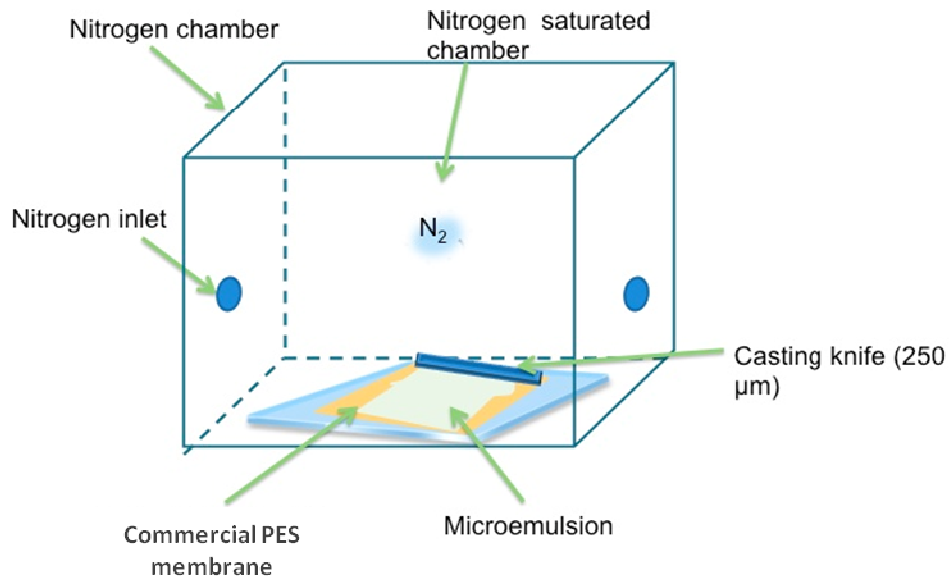


Figure 3.1.4 Nitrogen chamber used for PBM preparation

PES commercial membranes used as support for PBM coating were supplied by the company Microdyn Nadir (Germany).

3.2 Microemulsion and PBM membrane characterisation

Microemulsion conductivity

Conductivity measurements were carried out by Eutech Instruments PC2700. Different microemulsion compositions (with DTAB and AUTEAB surfactants) were prepared at different water content. The initiators were not added to the microemulsion. The measurements were taken at room temperature (about 22°C) and each measurement was repeated three times and the average of the results obtained was considered.

Weight loss determination

In order to calculate the weight loss of PBM membranes, the polymerised membrane was first weighed and then dried overnight in the oven at 50°C in order to remove the water. The membrane was then soaked for 2h in toluene in order to extract the unpolymerised MMA and finally PBM was treated with water at 50°C for 3h in order to remove the unreacted surfactant. The amount of water and unreacted material was determined by measuring the weight loss after each extraction. Tests were carried out both for membranes prepared with DTAB and AUTEAB at their optimal concentrations. The loss was calculated by using the following equation:

$$W_l = \frac{W_i - W_f}{W_f} \cdot 100$$

Where:

W_l is the weight loss, W_i is the initial weight of the membrane before each drying or extraction and W_f is the final weight of the membrane after each drying or extraction.

Scanning electron microscopy (SEM)

The SEM used for the morphology investigation of PBM and PES commercial membranes was Hitachi Field Emission SEM (model S-4800). The characteristics of the instrument are:

Resolution of SEM (model S-4800):

Accelerating voltage 15 kV

Working distance = 4 mm -1.0 nm

Accelerating voltage 1 kV

Working distance = 1.5 mm -2.0 nm

The surface and cross-section of membranes were evaluated. Membrane cross sections were prepared by freeze fracturing the samples in liquid nitrogen, to produce a clean brittle fracture. The specimens were then mounted on a sample holder to be analysed.

SEM measurements were carried out by Dr. Daniel Johnson at Swansea University (CWATER), United Kingdom.

Atomic Force Microscopy (AFM) and surface roughness

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

AFM and roughness measurements were carried out by Dr. Daniel Johnson at Swansea University (CWATER), United Kingdom.

Pore size measurement

Pore size measurements were performed by a PMI capillary flow porometer which provided fully automated through-pore analysis including bubble point, pore size distribution and mean flow pore size (PMI, porous materials, Inc. USA).

Molecular weight cut-off

Molecular weight cut-off was measured by using a mixture of three polydispersed dextrans with molecular weight of 11KDa, 70 KDa and 480 KDa. Dextrans (5 g/L) that were dissolved in 0.02 M buffer phosphate solution. Filtration tests were, then, carried out at room temperature and the pressure was adjusted in order to have a flux lower than 40 L/m² h. Feed and permeate were collected after about 10 minutes of filtration. Both samples were then analysed by gel permeation chromatography (GPC) (Accela-RI detector- Thermo Scientific) equipped with three columns (Varian, Inc. GPC/SEC PLaquagel –OH 8 µm 300x7.5 mm, Lab Service Analytica) connected in series and using buffer phosphate 0.02 M as eluent phase at the flow rate of 100 µL/min. Chromatograms obtained were integrated and set with the calibration curve previously prepared with narrow dextrans.

Contact angle measurements(CAM)

Contact angle measurements were performed using ultrapure water by the method of the sessile drop using a CAM200 instrument (KSV Instrument LTD, Finland). The resolution of the instrument was 800 × 600 pixel. For each sample, at least 10 measurements were taken; the average value and the corresponding standard deviation were, then, calculated. Water CAM were performed for the active side of PES commercial membranes and for the coating side of PBM coated membranes.

Antimicrobial activity

The following protocol was used for the determination of the surfactants' antimicrobial activity. Antibacterial tests were started by preparing growth media using Mueller-Hinton broth and agar.

Prepared agar, which was sterilized at 121°C, was cooled to appropriate temperature, then poured to the petri dishes in 15 ml amounts and left for drying overnight. On the next day, petri dishes were checked for contamination. Then *E.coli* bacteria was applied onto four of them by using a needle holder and *E.coli* bacterial cultures were grown on nutrient agar plates at 37°C overnight. Then, sufficient amount of *E.coli* colonies was dissolved in 0.9 % NaCl-water to adjust the turbidity to Mcfarland no. 0.5 which corresponds to 10⁸ CFU (Colony-Forming Unit)/ml. Sterile tissue culture plates (6 well with 10 ml volumes) were obtained from Becton Dickinson Labware Company. 0.1 ml of bacteria suspension and 1.9 ml of Mueller-Hinton broth were added into the well containing different amounts of antibacterial material (surfactant) and they were incubated for 24 h. After that, 0.1 ml of liquid sample was added on nutrient agar plates and spread over the plates. Plates were incubated at 37°C for 24h. Finally, grown cells were counted on the plates.

For the determination of PES commercial and PBM coated membranes antimicrobial activity, 60 CFU of *E.coli* were seeded on the membranes which were imprinted on Mueller-Hinton agar plates for 24h and incubated at 37 °C. After the 24 h incubation period had elapsed, the number of CFU present on the membrane surfaces was counted.

Antimicrobial activity tests were carried out by Prof. Sacide Alsoy Altinkaya at Izmir Institute of Technology, Turkey.

Nanoparticles incorporation

Polyoxometalates (POMs) nanoparticles linked to AUTEAB were incorporated within the membrane matrix by dispersing them into the microemulsion with a concentration of 2 wt% and their activity was evaluated. The dispersion was allowed by alternating sonication and magnetic stirring for 24h. When the nanoparticles were completely dispersed into the microemulsion, redox initiators were added and the microemulsion was polymerized on a PES membrane.

In order to measure the activity of POMs nanoparticles, an aqueous solution containing 4 wt% of H₂O₂ 30 w/v% (purchased from Panreac) was used. POMs nanoparticles were synthesized and bounded to AUTEAB by Prof. Mauro Carraro at ITM CNR at the University of Padua, Italy.

The EDX analyses on PBM membranes to verify the incorporation of POMs nanoparticles were performed by using SEM (Cambridge Stereoscan 360).

Fouling tests

Fouling tests were carried out by using humic acid (HA) (purchased from Aesar GmbH & Co KG, Germany) as model foulant with a concentration of 100 mg/L. Filtration tests were carried for 24h both for PES and PBM membranes by using an auto-controlled ultrafiltration (UF) cross-flow testing cell manufactured by company SIMAtec GmbH, Germany. The dimensions of the active membrane area used were 21.4 cm × 4.0 cm covering 85.6 cm². The feed solution from the feed tank was pumped at room temperature into the membrane module and through the membrane at desired pressure (in order to have the same flux among the coated PBM and the PES membrane). The permeate and concentrate coming out of the membrane module were recirculated back to the feed tank. After treatment with HA, the membranes were backflushed with water at 0.5 bar for 3h and finally removed from the testing cell. The decrease and regain in water permeability and the appearance of the membrane after backflushing were an indication of the membrane's fouling propensity. Furthermore, the fouling layer thickness was measured by SEM analyses.

Water permeability and dye rejection

Water permeability and dye rejection were measured at room temperature (22°C) by using a laboratory ultrafiltration cross-flow testing cell at the pressure of 1 bar. Water or model-dye solution was pumped, by means of a peristaltic pump, through the membrane on an area of 11.6 cm².

Water permeability (P) was calculated by collecting the permeate during a fixed time and then by applying the following equation:

$$P: \frac{Q}{A t p}$$

Where:

Q is the volume of permeate expressed in liters, A is the area of membrane expressed in m², t is the time expressed in hours and p is the pressure expressed in bar.

In case of a dye solution, the rejection toward both dyes was calculated by the UV spectrophotometer UV-160A Shimadzu. Permeate samples to be analysed were collected after 30 min of filtration. The concentration of dyes was 50 mg/L for each dye. Acid Red 4 and Remazol Brilliant Blue dyes were purchased from company BOC Sciences (USA) and Chemos (Germany),

respectively. The absorbance of both dyes was firstly measured by spectrophotometer and it was 505 nm for Acid Red 4 and 593.5 for Remazol Brilliant Blue.

The calibration curve of the Remazol Brilliant Blue solution was prepared by spectrometric analysis of the mixed solution at a 593.5 nm wavelength. The amount and concentration of the dye in the solutions were known. Table 3.2.1 shows that the absorbance of the dye solution increases while its volume increases.

Table 3.2.1 Data for calibration curve of Remazol Brilliant Blue in the mixed solution (50 mg/L)

Blue (ml)	Blue (Abs 593.5 nm)	Red (ml)	Red (Abs 505 nm)	Blue Concentration Detected
0.25	0.122	2.75	2.273	4.21
0.50	0.169	2.50	2.115	7.80
0.75	0.214	2.25	1.973	11.20
1.00	0.264	2.00	1.806	14.95
1.25	0.305	1.75	1.655	18.09
1.50	0.350	1,50	1.499	21.56
1.75	0.416	1.25	1.269	26.56
2.00	0.497	1.00	0.991	32.72
2.25	0.552	0.75	0.806	36.92
2.50	0.611	0.50	0.607	41.38
2.75	0.669	0.25	0.408	45.77

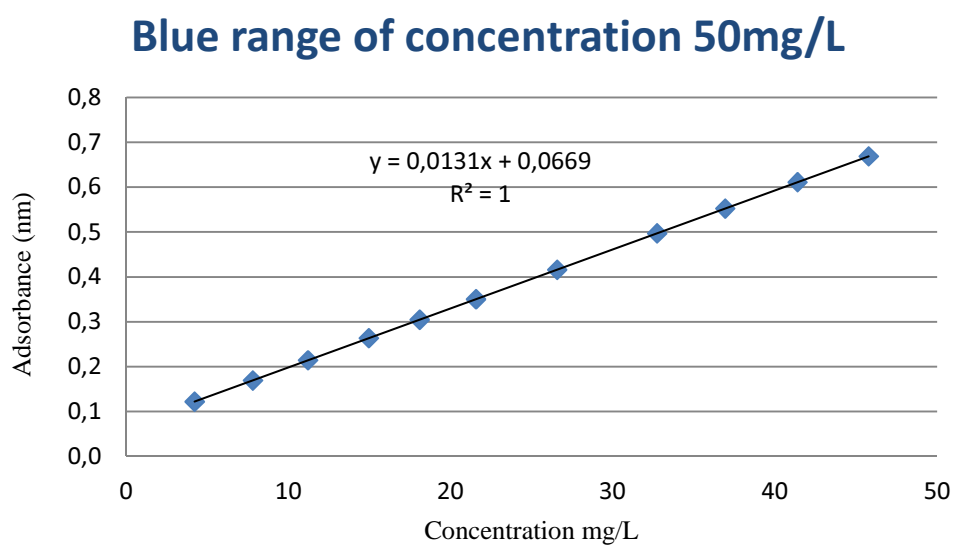


Figure 3.2.1 Remazol Blue calibration curve

Similarly, a calibration curve for the Acid Red 4 solution was developed by spectrometric analysis of the mixed solution at 505 nm wavelength.

Table 3.2.2 Data for calibration curve of Acid Red in the mixed solution (50 mg/L)

Red (ml)	Red A1 (Abs 505 nm)	Blue (ml)	Blue A2 (Abs 593,5 nm)	Red Concentration Detected
0.25	0.408	2.75	0.669	4.46
0.50	0.607	2.50	0.611	8.91
0.75	0.806	2.25	0.552	13.39
1.00	0.991	2.00	0.497	17.54
1.25	1.269	1.75	0.416	23.76
1.5	1.499	1.50	0.350	28.91
1.75	1.655	1.25	0.305	32.42
2.00	1.806	1.00	0,264	35.77
2.25	1.973	0.75	0.214	39.53
2.50	2.115	0.50	0.169	42.73
2.75	2.273	0.25	0.122	46.27

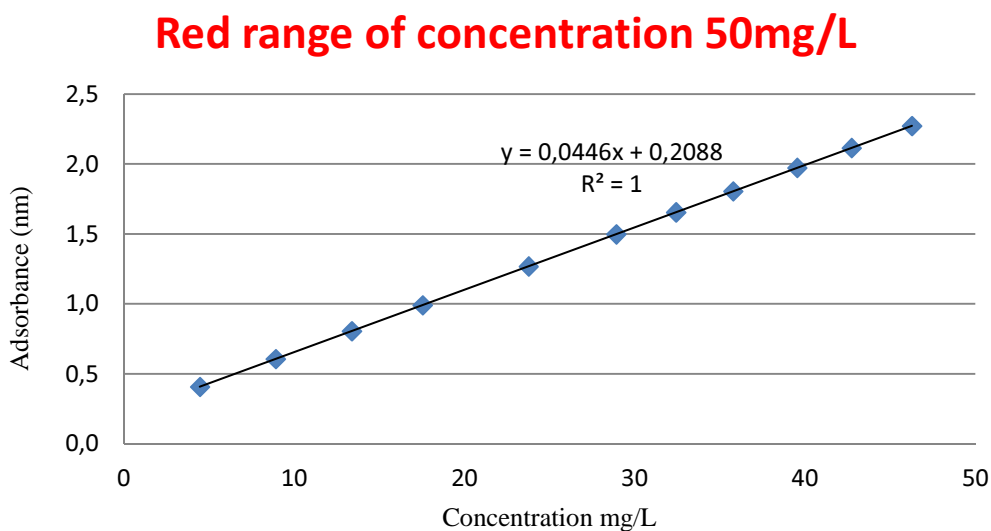


Figure 3.2.2 Acid Red 4 calibration curve

This data were used to calculate the blue and red dye concentration in the membrane permeate solution.

The dye rejection (R) was then calculated by using the following equation:

$$R = 1 - \left(\frac{C_p}{C_f} \right) \cdot 100$$

Where:

C_p is the concentration of the dye in the permeate and C_f is the concentration of the dye in the feed solution.

Intensive chemical cleaning test

Intensive chemical cleaning tests were based on basic and acid treatment on the membrane surface in order to check the resistance of PBM coating to cleaning. Filtration tests were carried out for 1h for both PES and PBM membranes by using an auto-controlled ultrafiltration (UF) cross-flow testing cell manufactured by company SIMAtec GmbH (Germany). The base cleaning tests were carried out in order to simulate the oxidation cleaning to remove biofouling, while the acid cleaning tests were carried out in order to simulate the treatment used to remove inorganic fouling/scaling. For the basic cleaning tests, H_2O_2 (purchased from Sigma Aldrich) was used with a concentration of 1 w/v% and pH 10.3. In the case of acid cleaning, citric acid (purchased from Sigma Aldrich) was used with a concentration of 0.2 w/v% and pH of 2.6. The variation in permeability before and after the chemical cleaning was used as an indication of PBM coating stability and chemical resistance. The permeability data obtained were then compared with that obtained with a PES commercial membrane.

Salt rejection

Salt rejection was measured by using a laboratory ultrafiltration cross-flow testing cell at the pressure of 0.5 bar and at room temperature (22°C). NaCl and $MgSO_4$ were added to an aqueous solution with a concentration of 500 ppm and 2000 pm, respectively. The rejection was measured by conductivity measurement of the feed and the permeate by using Eutech Instruments PC2700.

Salt rejection (R) was calculated applying the following equation:

$$R = 1 - \left(\frac{Cond_p}{Cond_f} \right) \cdot 100$$

Where:

$Cond_p$ is the conductivity of the permeate and $Cond_f$ is the conductivity of the feed.

3.3 PBM membranes application in MBR

MBR reactor

Once the novel PBM coated membranes had been prepared and characterised, they were assembled by the company Microdyn Nadir (Germany) by gluing two membranes together by lamination from the support side with a spacer between them for permeate collection. A total of six membranes with a total area of 0.33 m² were used for the production of one module. In the centre of the module an inlet, from where the permeate was sucked, provided the connection to the vacuum pump (figure 3.3.1).

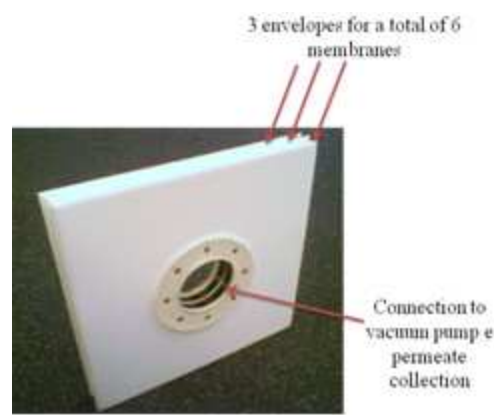


Figure 3.3.1 MBR module

The module prepared was then set in a suitable cassette and immersed in the MBR tank containing the model textile wastewater to be treated.

The MBR reactor was designed in accordance to MBR systems usually present on the market and shown in figure 3.3.2.

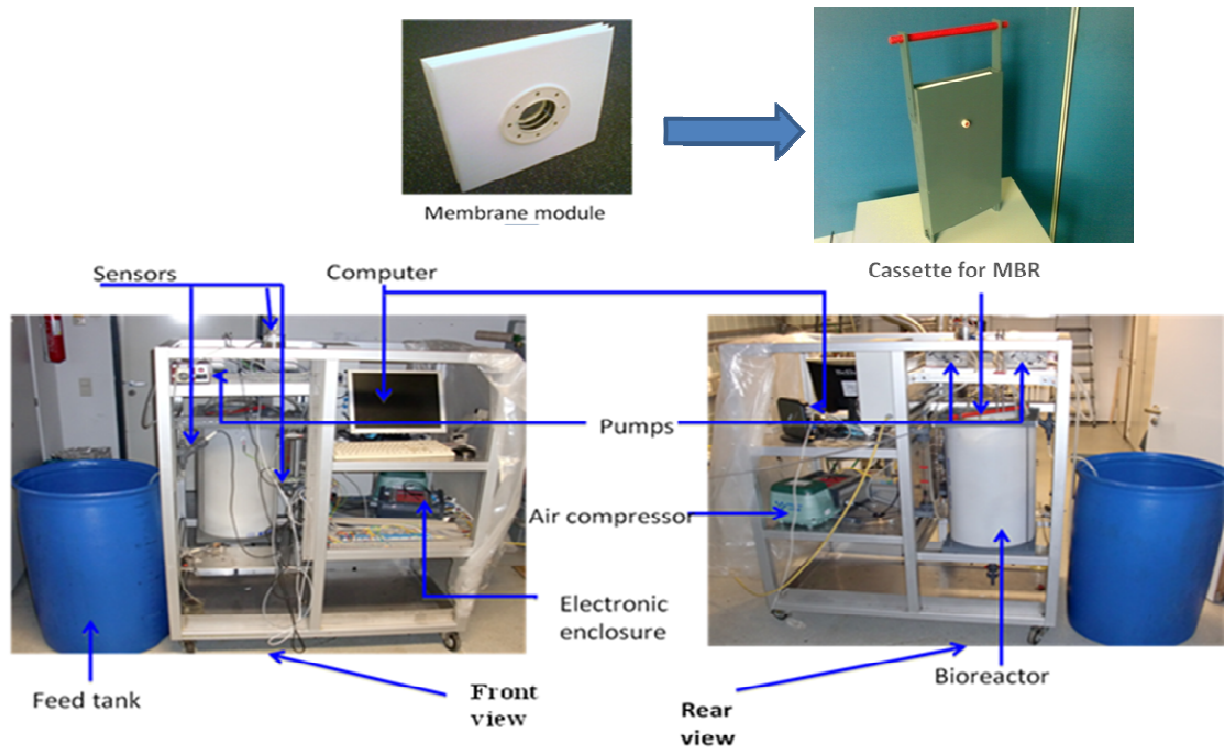


Figure 3.3.2 MBR reactor

The front view and the rear view of the MBR reactor are shown in figure 3.3.2. A feed tank of 57 L was used as model textile wastewater storage. The wastewater was then pumped inside the bioreactor filled with the industrial sludge as a source of microorganisms and in contact with the membrane module, which was also located inside. An air compressor provided the air supply from the bottom of the bioreactor in order to create a cross-flow of air bubbles at membrane surface limiting the fouling phenomenon and providing oxygen for bacteria survival. A computer allowed to set and control all the parameters (feed pump velocity, trans-membrane pressure (TMP), aeration rate) and a series of sensors (level sensor, differential pressure sensor, feed pump, permeate pump, foam pump, foam sensor, flow sensor, pH sensor, temperature sensor, conductivity sensor and air flow meter) collected all the information during MBR experiment. The operating TMP was kept at about 40-60 mbar and fine bubbles were used as aeration. Two aeration rates were applied: 0.5 m³/h and 1 m³/h. The HRT was maintained in the range 70-120 h with a flow rate ranging from 0.5 to 1 L/h. The operation mode of the MBR was as follows:

1. 8.5 minutes of filtration (in this phase the permeate was sucked by a pump);
2. 30 seconds of relaxation phase (the pump was stopped);
3. 30 seconds of backwashing (the flux was inverted from the permeate to the feed in order to clean the surface of the membrane);
4. 30 seconds of relaxation phase (the pump was stopped again) [1].

Carbon Oxygen Demand (COD)

The COD was analysed by COD cell tests (Method 1.14541) from Merck KGaA (Germany). The measuring range of this method was 25 - 1500 mg/L of COD.

Red and Blue dyes

The concentration of the dyes, Remazol Brilliant Blue and Acid Red 4 was analysed by UV spectrophotometer (Model: UV-1800) from Shimadzu (Japan) as described above. Red and Blue were purchased from company BOC Sciences (USA) and Chemos (Germany) respectively.

Dissolved Oxygen

The DO concentrations were determined with an oxygen sensor (Model: Oxi 340i meter and CelloX[®] 325 O₂ electrode) from WTW GmbH (Germany).

Permeability

The permeability was measured by collecting the permeate in time and applying the equation reported above.

Model textile dye wastewater

The model textile wastewater composition, reported in table 3.3.1, was prepared according to literature data.

Table 3.3.1 Chemical and concentrations used for textile wastewater formulation

Chemicals	Concentration (mg/L)	Reference
Remazol Brilliant Blue	50	
Acid Red 4	50	
NaCl	2500	[2]
NaHCO ₃ /Na ₂ CO ₃	1000	[3]
Glucose	2000	[3]
Albatex DBC (Detergent)	50	[4]

Red and Blue dyes were selected on the basis of their chemical structure. Azo and anthraquinone dyes such as Acid Red 4 and Remazol Brilliant Blue are, in fact, among the most common dyes encountered in textile wastewater. They can originate carcinogenic compounds and can cause

problems to the photosynthesis of the aquatic plants if they are directly discharged into the environment. NaCl, NaHCO₃ and Na₂CO₃ were added as salts in order to mimic the real textile wastewater composition. Glucose was added as a nutrient for microorganisms while the detergent Albatex DBC, usually applied in laundries and textile industries, was also used in order to reproduce the typical textile wastewater.

The parameters applied to the model textile wastewater are reported in table 3.3.2.

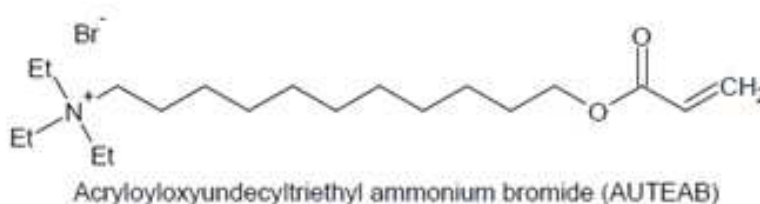
Table 3.3.2 Parameters applied to model textile wastewater

Parameters	Value
pH	7.5-8.2
Temperature	20°C
COD	2400 mg/L
BOD ₅	50 mg/L
Chloride	1756 mg/L
Total Nitrogen	5.9 mg/L
Conductivity	6.6 mS/cm

All the experiments performed with MBR were carried out in collaboration with the Karlsruhe University of Applied Sciences (HSKA, Germany) under the supervision of Prof. Jan Hoinkis.

3.4 Appendix

AUTEAB characterization



Colorless solid

PM: 374.4443 g/mol

Melting Point: 43-44°C

NMR and IR analysis were used in order to characterize AUTEAB.

IR (KBr): ν/cm^{-1} = 2328 (m), 2852 (m), 1719 (s), 1636 (m), 1456 (w), 1384 (m), 1295 (w), 1202 (m), 1056 (w).

^1H NMR (500 MHz, DMSO): δ = 6.29 (dd, j = 17.6, 1.4, 1H, $\text{CHH}=\text{CH}$), 6.15 (dd, j = 17.6, 10.2, 1H, $\text{CHH}=\text{CH}$), 5.92 (dd, j = 10.2, 1.4, 1H, $\text{CHH}=\text{CH}$), 4.08 (t, j = 6.5, 2H, COOCH_2), 3.23 (q, j = 7.2, 6H, $3\text{N}^+\text{CH}_2\text{CH}_3$), 3.08-3.13 (m, 2H, CH_2N^+), 1.52-1.62 (m, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2\text{N}^+$), 1.21-1.34 (m, 14H, $\text{N}^+\text{CH}_2\text{CH}_2\text{CH}_2(\text{CH}_2)_7\text{CH}_2\text{O}$), 1.15 (t, j = 7.2, 9H, $3\text{N}^+\text{CH}_2\text{CH}_3$).

^{13}C NMR (125 MHz, DMSO): δ = 165.4, 131.3, 128.3, 64.0, 55.9, 51.9, 28.8, 28.73, 28.69, 28.5, 28.4, 28.0, 25.7, 25.2, 20.8, 7.1.

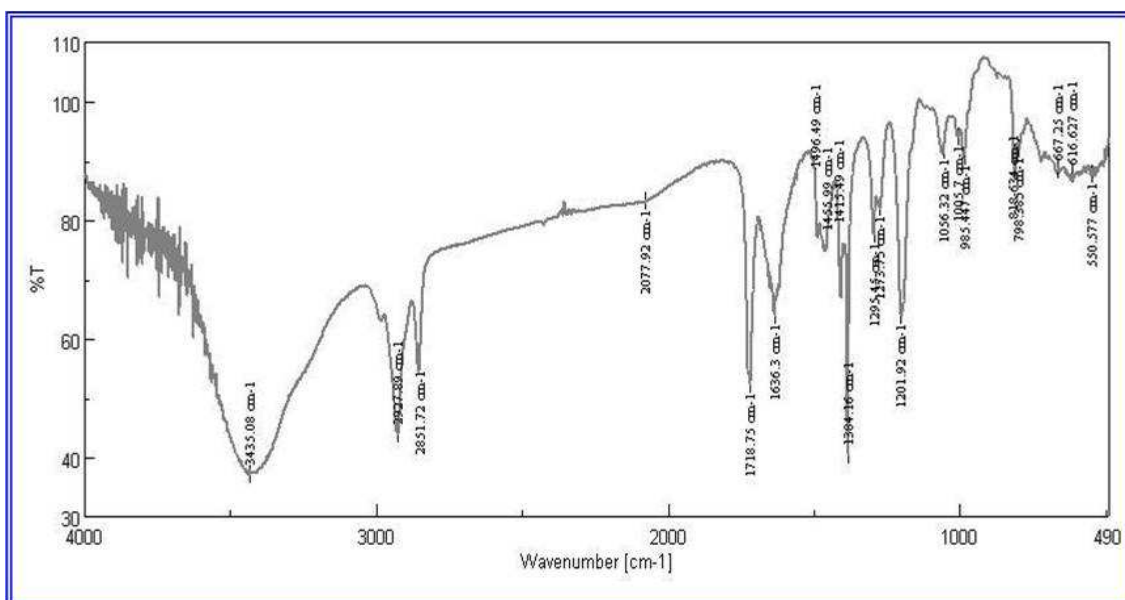


Figure 3.4.1 AUTEAB FT- IR spectrum

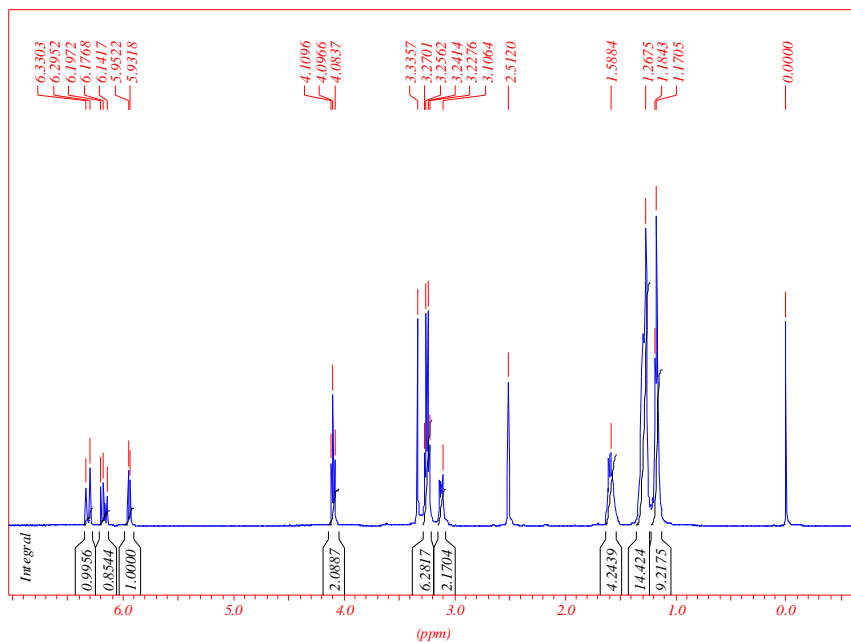


Figure 3.4.2 AUTEAB ¹H NMR spectrum

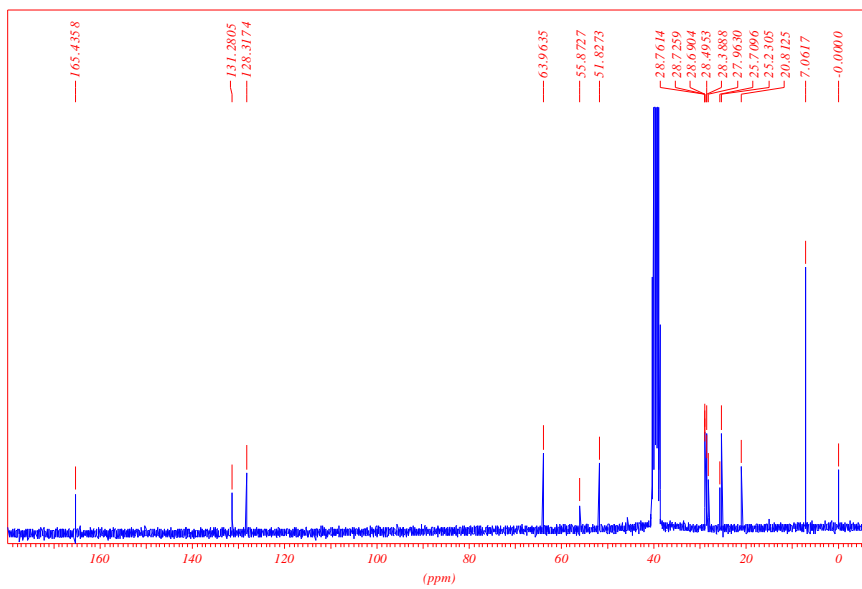


Figure 3.4.1 AUTEAB ¹³C NMR spectrum

3.5 References

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Chapter 4

Preparation of novel PBM membranes

Membranes are usually prepared by classic techniques such as phase inversion (the most common), melt extrusion, track-etching, sintering, etc.. In the present work, an alternative approach was proposed for preparing polymeric membranes from a polymerisable bicontinuous microemulsion (PBM). This technique consists in the polymerisation of two immiscible phases (oil and water) stabilised by a surfactant. The main advantage is that the structural characteristics of the bicontinuous microemulsion can be conserved and transferred to the polymeric matrix. Different types of surfactants can be applied to the microemulsion formulation and, in particular, polymerisable reactive surfactants are of high interest due to the possibility of covalently binding them with polymer domains producing polymers with a well-defined and controlled structure. The possibility of mastering the membrane structure, depending on the final application, is of primary importance in membrane separation processes.

In the present work, polymerisable microemulsions were prepared and characterised in order to identify, by conductivity measurements, the bicontinuous range. Two surfactants were applied: the lab-made cationic reactive polymerisable surfactant AUTEAB and the commercial cationic surfactant DTAB. The microemulsion prepared was, then, polymerised on a PES ultrafiltration commercial membrane in order to obtain a thin-coating PBM layer. Finally, weight loss determination tests were carried out on the PBM membranes obtained in order to investigate the amount of unreacted material.

4.1 Commercial and lab-made surfactants

The preparation of PBM membranes was carried out according to literature. Alternatively to the use of AUTEAB, a commercial surfactant, sodium dodecyltrimethylammonium bromide (DTAB), was employed for the preparation of bicontinuous microemulsion membranes. A new AUTEAB surfactant was synthesized by following the two-step procedure reported in Chapter 3. AUTEAB was synthesized instead of the traditional surfactant AUTMAB (acryloyloxyundecyltrimethyl ammonium bromide) usually reported in literature. The main advantages of this new surfactant are:

1. Reduced cost (about 4 times lower than AUTMAB);
2. Easier way to produce it (liquid triethylamine is used instead of the gaseous methylamine).

By looking in detail at the cost estimations (reported in table 4.1.1 and in table 4.1.2) related to the synthesis of either surfactants, a clear difference in price can be noted. The cost of synthesising the AUTEAB surfactant was, in fact, about 4 times lower than AUTMAB.

Table 4.1.1. AUTMAB cost analysis

BU (11-Bromo-1-undecanol) (cost, €)	Acryloyl chloride (cost, €)	Et ₃ N (TEA) (cost, €)	BUA (11-Bromoundecylacrylate)	Me ₃ N (TMA) (cost, €)	AUTMAB (total cost, €)
100 g (€ 23480)	111.8 g (€ 174.80 quant. 200g)	51 g (€ 21.60 – quant. 1L)	64 g	155 g (€ 124.20)	28.7 g (€ 555.40)

**Cost analysis based on Sigma-Aldrich Catalogue*

Table 4.1.2. AUTEAB cost analysis

BU (11-Bromo-1-undecanol) (cost, €)	Acryloyl chloride (cost, €)	Molecular sieves 3A (cost, €)	BUA (11-Bromoundecylacrylate)	Et ₃ N (TEA) (cost, €)	AUTEAB (total cost, €)
100 g (€ 234.80)	111.8 g (€ 174.80 quant. 200g)	86 g (€ 26.30 – quant. 250g)	107 g	39,1 g (€ 21.60 – quant. 1L)	94.7 g (€ 457.50)

**Cost analysis based on Sigma-Aldrich Catalogue*

The commercial surfactant AUTEAB has the following molecular structure:

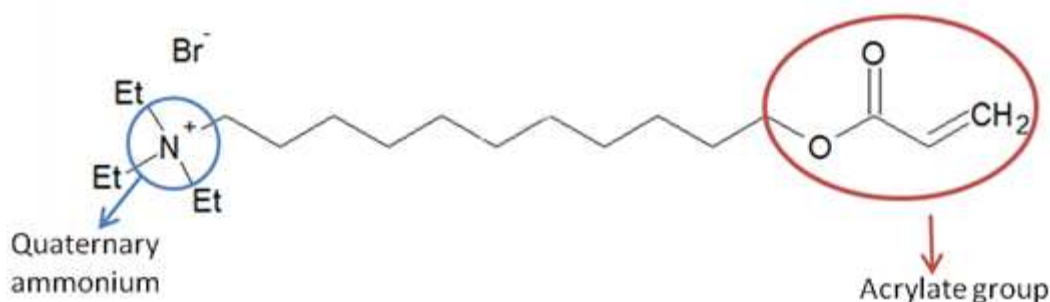


Figure 4.1.1 AUTEAB molecular structure

Based on its molecular structure, AUTEAB is a cationic surfactant with a quaternary ammonium group. It is well known in literature that quaternary ammonium salts have an important

antimicrobial activity. As it will be discussed in the next chapter (Chapter 5, paragraph 5.6), AUTEAB showed an interesting antimicrobial activity against the bacterium *E. Coli*, which was maintained even after the polymerisation of the microemulsion to form the final membrane. Antimicrobial properties are of primary importance when membranes are applied in such processes as membrane bioreactors (MBR), where a population of bacteria is in contact with the membrane surface. Their adhesion and growth on the membrane surface can cause the so-called “biofouling”, which is responsible for the decline of membrane performances. For this reason, a membrane with antimicrobial activity can operate at a higher and more constant flux for a longer period of time.

In AUTEAB’s structure the carbon chain is made up of 11 atoms of carbon. The chain length can also affect the antimicrobial activity of ammonium salts. The antimicrobial activity, in fact, increases with the increase of the alkyl chain length but only up to a certain limit. The presence of the acrylate group makes the AUTEAB surfactant reactive and polymerisable. Acrylates, in fact, easily form polymers because the double bonds are very reactive. The possibility of polymerizing the surfactant within the polymer matrix allows to obtain materials with constrained geometries by preventing the restructuring of the interfacial film during the polymerization, which is often observed if conventional (non- polymerisable) surfactants are used.

The commercial surfactant DTAB has the following molecular structure:

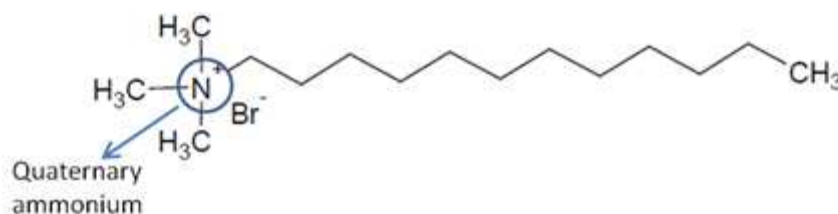


Figure 4.1.3 DTAB molecular structure

As it can be seen from its molecular structure, DTAB is also a cationic surfactant with a quaternary ammonium group. The antimicrobial tests carried out on *E. coli* showed an important antimicrobial activity, slightly higher than in the case of the AUTEAB surfactant, justified by the longest carbon chain (12 atoms of carbon instead of 11). Unlike AUTEAB, DTAB is not a polymerisable surfactant (due to the absence of the acrylate group). For this reason, its embodiment within the polymeric matrix can also be achieved by a physical entrapment of the surfactant and not by a chemical binding (as in the case of AUTEAB). Its release in the surrounding environment is,

therefore, more pronounced (as also demonstrated by weight loss determination tests reported in paragraph 4.4).

DTAB, in the present work, was applied and selected for its commercial availability and reasonable price. The surfactant was widely used for the screening of the best conditions of temperature, surfactant concentration range and membrane morphology. Nevertheless, due to the better and more reliable results obtained with AUTEAB, together with the possibility of covalently binding it into the microemulsion, the latter surfactant was used for the scaling-up of PBM membranes to be applied in the MBR process.

4.2 Microemulsion preparation and polymerisation

The microemulsion with either surfactants was prepared in agreement with literature data [1,2] and microemulsion conductivity measurements allowed to determine the bicontinuous range. The monomer methyl methacrylate (MMA) was used as oil phase of the system, water was used as aqueous phase and the surfactant (either DTAB or AUTEAB) was used to disperse the two immiscible phases. The cross-linking agent ethylenglycol dimethacrylate (EGDMA) was also added so to strengthen the final polymer matrix, while the short-chain alcohol 2-hydroxyethylmethacrylate (HEMA) was used as co-surfactant in order to facilitate the dispersion of the oil phase and the aqueous phase.

The molecular structures of polymerisable components (other than the surfactant) are shown in Figure 4.2.1:

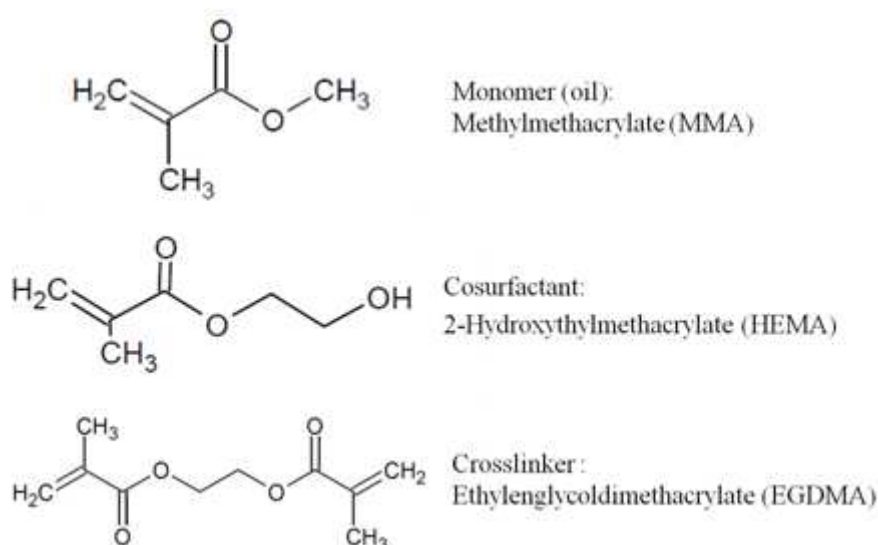


Figure 4.2.1 Molecular structure of polymerisable components of the microemulsions

All the compounds used for microemulsion preparation (when AUTEAB was used as the surfactant) were polymerisable. Preliminary tests were focused on the determination of the best concentration of chemicals within the microemulsion. At balanced concentrations the microemulsion formed spontaneously (without mixing or mechanical stirring) and they appeared homogeneous and optically transparent. The transparency of the solution is a prerogative of microemulsions (thermodynamically stable) in contrast with emulsions that present a milky and turbid appearance (Figure 4.2.2).



Figure 4.2.2 Optical appearance of an emulsion and a microemulsion

The possibility of using different initiators, in order to promote the polymerization, was also evaluated. PBM membranes were produced by using two different types of initiators:

1. 2,2-dimethoxy-2-phenylacetophenone (DMPA) photoinitiator, under UV-Light in inert nitrogen atmosphere;
2. ammonium persulfate (APS) and N,N,N,N-tetramethylethylenediamine (TMEDA) as redox initiators in inert nitrogen atmosphere.

Even if the first route (UV-light) allowed to polymerize the microemulsion prepared, having in mind the final purpose of the work (coating commercial PES membranes with the bicontinuous microemulsion), redox initiators were selected to be used for microemulsion polymerization. With redox initiators, in fact, it was possible to control the polymerization rate and to cast the microemulsion at the desired viscosity. The viscosity represented a very crucial aspect in the production of the PBM coating. A microemulsion, in fact, has a very low viscosity. Casting it immediately after the addition of redox initiators on the porous PES membrane, caused its infiltration within the porous membrane matrix with no coating deposited on the PES surface. It was noticed that, after the addition of initiators and depending on the operating temperature, the

viscosity of the microemulsion gradually increased. Based on this observation, depending on the selected temperature, an optimal microemulsion viscosity, suitable to be cast on the PES membrane, was found. The effect of temperature on microemulsion polymerization rate is reported in Table 4.2.1:

Table 4.2.1. Effect of temperature on microemulsion polymerization rate

Temperature	Polymerization rate
20°C	7-8 minutes
25°C	3-4 minutes
30°C	2 minutes

As shown in Table 4.2.1, polymerization time decreases with increasing temperature (from 7-8 minutes at 17°C to 2 minutes at 30°C). At 20°C, the optimal temperature was found. At this temperature it was possible to control the polymerization process and produce reproducible PBM membranes as demonstrated by water permeability measurements.

In particular for AUTEAB, different problems were encountered when the temperature was increased up to 25°C. The viscosity of microemulsion, in fact, drastically increased in the range of a few seconds, causing the polymerization of the microemulsion within the test tube. In case of DTAB, on the contrary, various membranes were prepared at higher temperature (30°C) producing PBM membranes with a more dense structure (as shown in Chapter 5, paragraph 5.9).

First attempts on microemulsion polymerization were carried out by polymerizing the microemulsion on a petri dish or between two glass plates. In Figure 4.2.1 a PBM membrane polymerized between two glass plates is shown:



Figure 4.2.3 Optically transparent PBM after polymerization

As it can be seen in Figure 4.2.3, the polymer materials obtained were totally transparent. They appeared tough and fragile in dry conditions but more elastic and flexible in wet conditions. The next step was to coat a commercial membrane. Once the microemulsion had been prepared, it was polymerised on the surface of a commercial PES membrane under nitrogen atmosphere. The PBM coating obtained had a thickness ranging from 0.2 to 3 μm .

The optimal microemulsion composition for PBM membranes prepared with AUTEAB and DTAB surfactant is reported in Table 4.2.2:

Table 4.2.2 Optimal microemulsion composition for AUTEAB and DTAB surfactants

MICREMULSION COMPOSITION (wt%)						MICROEMULSION CONDITIONS	
MMA	HEMA	H ₂ O	SURFACTANT	EGDMA	INITIATORS	T (°C)	ATMOSPHERE
21	10	41	AUTEAB 25	3	APS TMEDA	20	Inert nitrogen atmosphere
10	40	40	DTAB 10	4 (MMA+HEMA)	APS TMEDA	20	Inert nitrogen atmosphere

For the DTAB surfactant different microemulsion compositions were also evaluated and reported in Table 4.2.3:

Table 4.2.3 Microemulsion compositions with DTAB surfactants

MICREMULSION COMPOSITION (wt%)						MICROEMULSION CONDITIONS	
MMA	HEMA	H ₂ O	DTAB	EGDMA	INITIATORS	T (°C)	ATMOSPHERE
8	50	34	8	4 (MMA+HEMA)	APS TMEDA	20	Inert nitrogen atmosphere
12	34	42	12	4 (MMA+HEMA)	APS TMEDA	20	Inert nitrogen atmosphere

The concentration of DTAB was varied in the range of 8-12 wt% and the concentration of water was varied in the range 34-42 wt%. From SEM measurements (see chapter 5, Figure 5.1.8) it was clear that different microemulsion compositions produced different PBM structures in which DTAB and AUTEAB concentrations play an important role.

4.3 Microemulsion conductivity measurements

To find the bicontinuous range, microemulsions were investigated in terms of conductivity measurements with both AUTEAB and DTAB surfactants.

In the case of DTAB, as shown in Figure 4.3.1, the bicontinuous range in the microemulsion was found between 20-90 wt% water content.

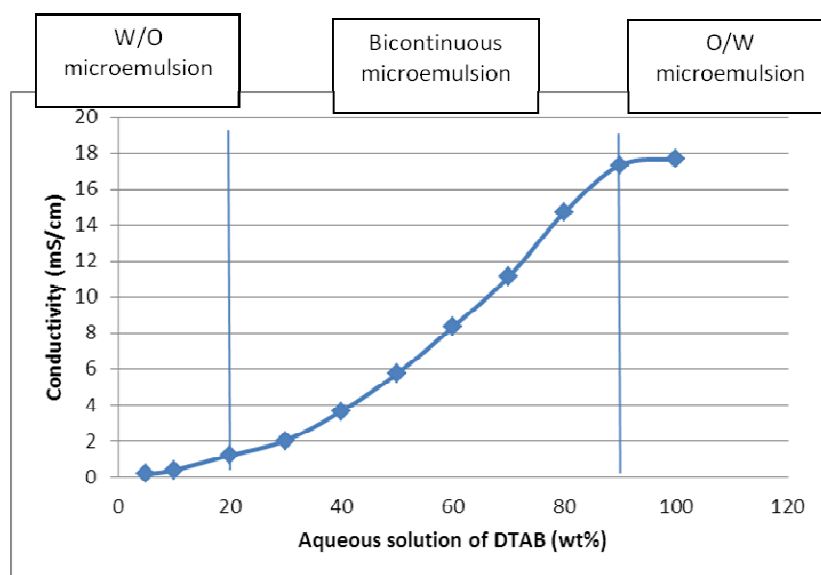


Figure 4.3.1 DTAB conductivity measurements at different aqueous solutions

In the case of AUTEAB, the bicontinuous range in the microemulsion was found between 30-60 wt% water content, as shown in Figure 4.3.2.

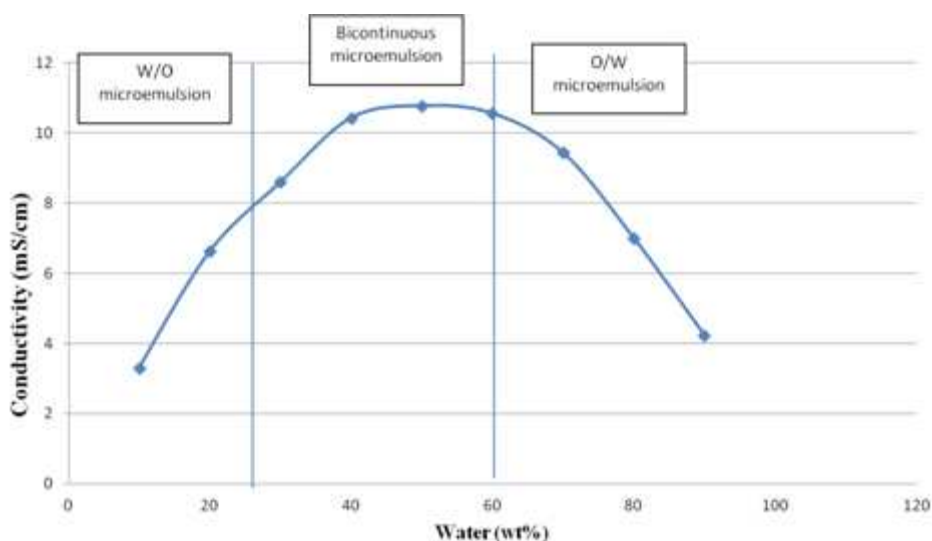


Figure 4.3.2 AUTEAB conductivity measurements at different aqueous solutions

Conductivity measurements allowed to differentiate the o/w droplets, the bicontinuous microemulsion and the w/o systems. It is known that systems with a low conductivity are associated with w/o microemulsions while systems with high conductivity are associated with o/w microemulsions. The transition from a w/o to a bicontinuous microemulsion is shown by a sharp increase in the conductivity value [3].

4.4 Weight loss determination test

In order to determine if all the materials used for microemulsion polymerization were polymerised in an interwoven network, membranes were dried up and exposed to subsequent extractions. First, the polymerised membrane was dried up in order to remove the water, then it was extracted with toluene for 2h in order to remove unpolymerised MMA and finally it was extracted with water at 50°C in order to remove the unreacted surfactant. The amount of unreacted material was determined by measuring the weight loss after each extraction. Tests were carried out both for membranes prepared with DTAB and AUTEAB at their optimal concentrations.

Table 4.4.1 Weight loss determination of prepared PBM membranes

Surfactant	Drying-Loss of water (wt%)	Toluene extraction-Loss of MMA (wt%)	Hot H₂O extraction-Loss of surfactant (wt%)
DTAB	7	0	16
AUTEAB	22	0	5

The weight loss after toluene extraction is null for both DTAB and AUTEAB surfactants, indicating that the whole MMA was fully copolymerised. After hot water extraction, membranes prepared with the lab-made surfactant AUTEAB presented a lower loss of surfactant (5 wt%) in comparison to the membranes prepared with the commercial surfactant DTAB (16 wt%). This behaviour can be explained by the fact that AUTEAB is a polymerisable surfactant (due to the presence of a double bond in its chemical structure) and, unlike DTAB, it copolymerizes in the membrane matrix and cannot be easily removed. This aspect is very important because AUTEAB can guarantee its presence for a long time within the polymerized polymer accomplishing therefore its function of antimicrobial agent when the membranes are applied, for instance, in an MBR process.

4.5 Conclusions

In the first part of the present work, the optimal microemulsion compositions for DTAB and AUTEAB surfactants were found. By means of conductivity measurements and literature data, the bicontinuous range was also identified. The temperature of 20°C was found to be the best polymerization temperature due to the slower and gradual increase in microemulsion viscosity, which is crucial for microemulsion casting on a porous PES support. Weight loss determination tests proved that the oil phase (MMA) totally polymerized forming the matrix of the membrane. AUTEAB's loss rate was less pronounced than DTAB's, due to the possibility of covalently binding the surfactant with the other polymerisable microemulsion components.

4.6 References

- [1] A Figoli, PhD thesis “ Synthesis of nanostructured mixed matrix membrane for facilitated gas separation”, 2001, ISBN 90-365-1673-0
- [2] T H Chieng, L M Gan, W K Teo, “Porous polymeric membranes by bicontinuous microemulsion polymerization: effect of anionic and cationic surfactants”, *Polymer* (1996) 37, 5917-5925
- [3] L M Gan, J Liu, L P Poon, C H Chew, “Microporous polymeric composites from bicontinuous microemulsion polymerization using a polymerizable nonionic surfactant”, *Polymer* (1997) 38, 5339-5345

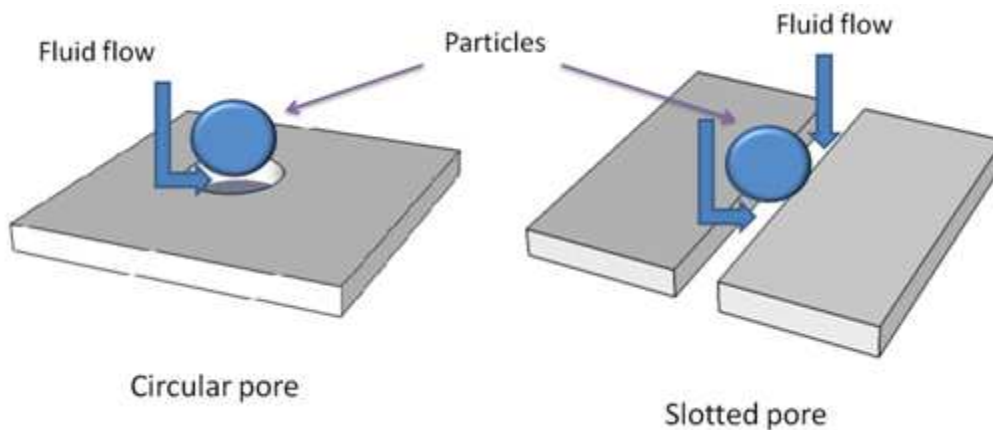
Chapter 5

Characterization tests of the novel PBM membranes

Membrane characterisation relates membrane structure and morphology to its performances. Once the membranes have been prepared, in fact, it is important to characterise them in order to select the proper membrane with the suitable characteristics for a specific separation process. For this reason, a wide number of techniques (SEM, AFM, contact angle, permeability...) are available in order to determine the main properties of a membrane. In this chapter, the characterisation tests carried out on coated PBM membranes (prepared with AUTEAB and with DTAB surfactants) are reported and compared with the ones achieved with uncoated PES commercial membrane. First characterisation tests focused on the evaluation of membrane surface morphology by SEM and AFM analyses. Afterwards, the pore size and the wettability of commercial and PBM membranes were measured by capillary flow porometer and contact angle measurements, respectively. Antimicrobial activity, nanoparticles incorporation, water permeability, antifouling and dyes rejection tests were also investigated. On the basis of the results obtained in terms of performances and structural properties, the most suitable membranes were selected and scaled up to be applied in MBR process for wastewater treatment.

5.1 Scanning electron microscopy (SEM)

The morphology of the PBM membranes prepared was evaluated by means of scanning electron microscopy (SEM) measurements. The existence of a bicontinuous microstructure was revealed for both types of surfactants used in microemulsion preparation and is clearly visible in the Figures 5.1.4 and 5.1.6. This was a direct evidence that the microemulsion was polymerised in the bicontinuous state. During the polymerisation, the water channels remained unchanged, while the oil channels formed the polymer matrix of the membrane, giving, as final result, an interconnected network of oil and water channels. This particular configuration can reflect the important antifouling properties exhibited by PBM membranes. Pore geometry has a big influence on the decline of filtrate flow and cake layer formation at membrane surface due to the fouling phenomenon. Holdich et al [1] studied the effect of pore geometry on fouling formation by comparing both membranes with circular and slotted pores (Figure 5.1.1).



**Figure 5.1.1 Fouling and fluid flow behaviour on the basis of different pore geometries
(Figure adapted from [2])**

From the results obtained by filtration tests containing particles of a specific diameter, it was found that the critical flux for slotted pores membrane was much greater than the one observed with circular pore membrane. In circular pore membrane, the particles deposit at the pore entrance hindering the fluid flow to pass through the pore. In the case of slotted pore membrane, on the contrary, the fluid can flow through the open regions of the pore not coated by the particle deposition. The experiments showed that slotted pores are able to limit the particle bridging over the pores responsible of cake deposition and fouling formation.

This observation can be also assumed for the channel like (bicontinuous) structure presents in the PBM membranes made in the present work. The oil polymerised channels are comparable to slotted pores and they can ideally work in the same way. The proved antifouling properties of PBM membranes can, thus, be also justified by their morphological structure.

In this paragraph SEM pictures of PBM membranes prepared with either surfactants (AUTEAB and DTAB) are shown. The SEM data obtained with PBM membranes were compared with the ones obtained with commercial PES membrane.

PES commercial membrane

In Figure 5.1.2, the surface of commercial PES membrane, used as support for PBM coating, is shown. The membrane surface appears homogenous and porous. The membrane pore size was about 0.1 μm (ultrafiltration range) as indicated by the company supplier (Microdyn Nadir) and confirmed by capillary flow porometer analysis.

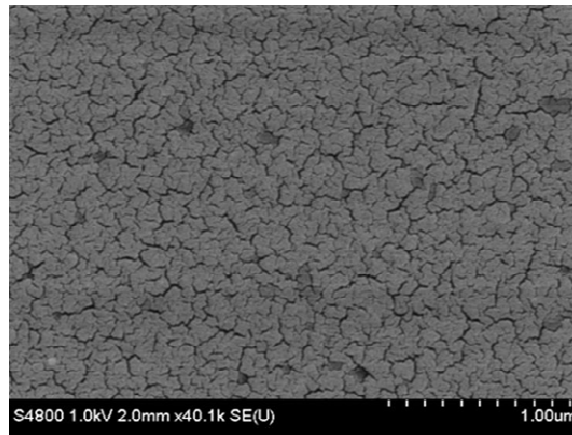


Figure 5.1.2 SEM surface image of PES commercial membrane

A PES membrane is a composite membrane made up of two layers: a top porous active polyethersulfone (PES) layer and an underlying support of polyethylene terephthalate (PET) responsible for the mechanical resistance of the membrane. This structure is clearly visible in Figure 5.1.3 where a cross-section of the PES membrane is depicted.

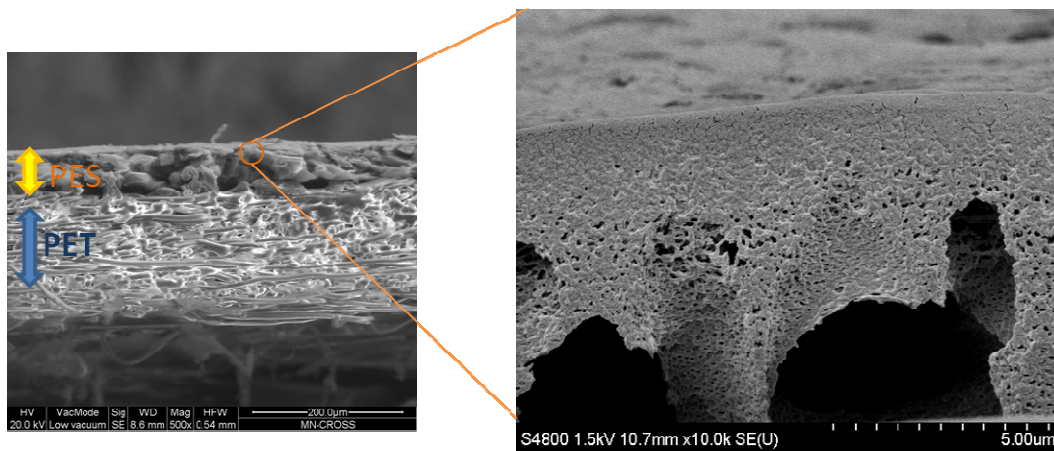


Figure 5.1.3 SEM cross-section of PES membrane with magnification

PBM coated membrane with AUTEAB surfactant

As it can be seen in Figure 5.1.4, PBM membranes present the typical bicontinuous structure made up of an interconnected network of polymer channels (white strips) and water channels (dark strips). SEM pictures of PBM membranes with AUTEAB refer to the microemulsion composition containing 40 wt% of water. The dimensions of the channels (estimated by SEM pictures) were in

the range of 130-240 nm in length and 30-50 nm in width. These structures were randomly distributed across the overall membrane surface.

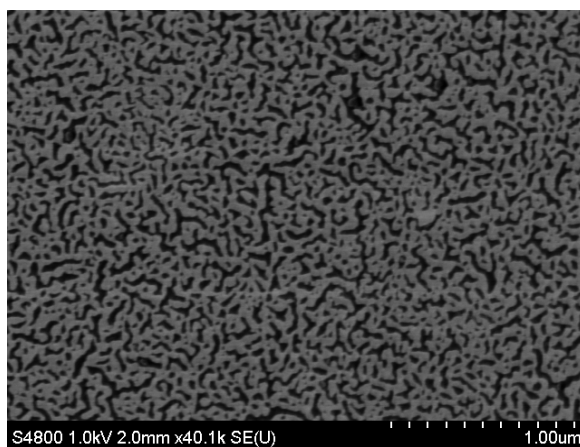


Figure 5.1.4 SEM surface image of a PBM coated membrane

From cross-section images (Figure 5.1.5) the PBM coating on PES membrane is clearly visible. The measured thickness of the coating was less than 1 μm. For all PBM membranes prepared the PBM coating ranged from a minimum of 0.2 to a maximum of 3 μm.

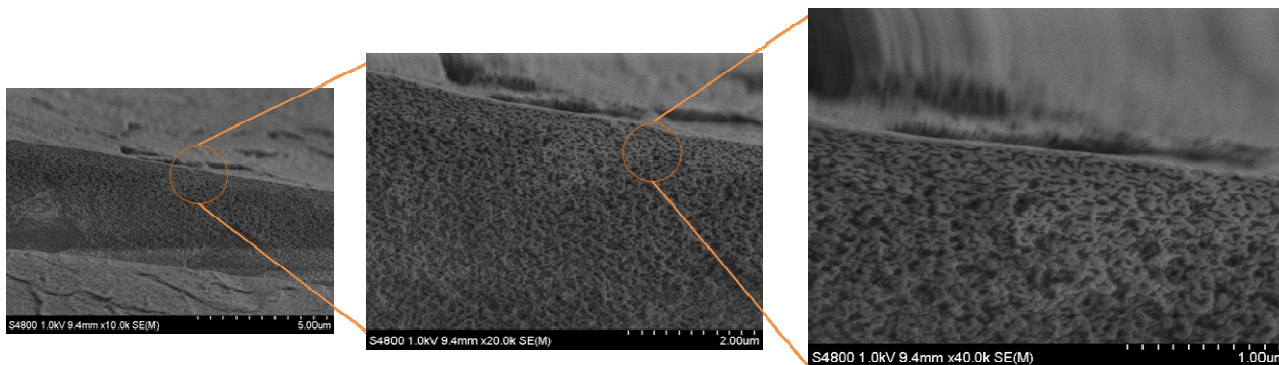


Figure 5.1.5 SEM cross-section of PBM membrane with magnification (magnification from x10 to x40)

PBM coated membrane with DTAB surfactant

PBM membranes prepared with DTAB showed similar morphology than the membranes prepared with AUTEAB. As it can be observed in SEM magnification pictures (Figure 5.1.6), the

polymerised bicontinuous structure is clearly visible as from 2 μm of magnification (x20). Even in this case, the white islets are representative of the polymerised oil phase, while the dark strips are representative of the unpolymerised water channels forming the porous matrix of the PBM membrane. The PBM surface appears uniform and homogenous with a random distribution of the bicontinuous structure.

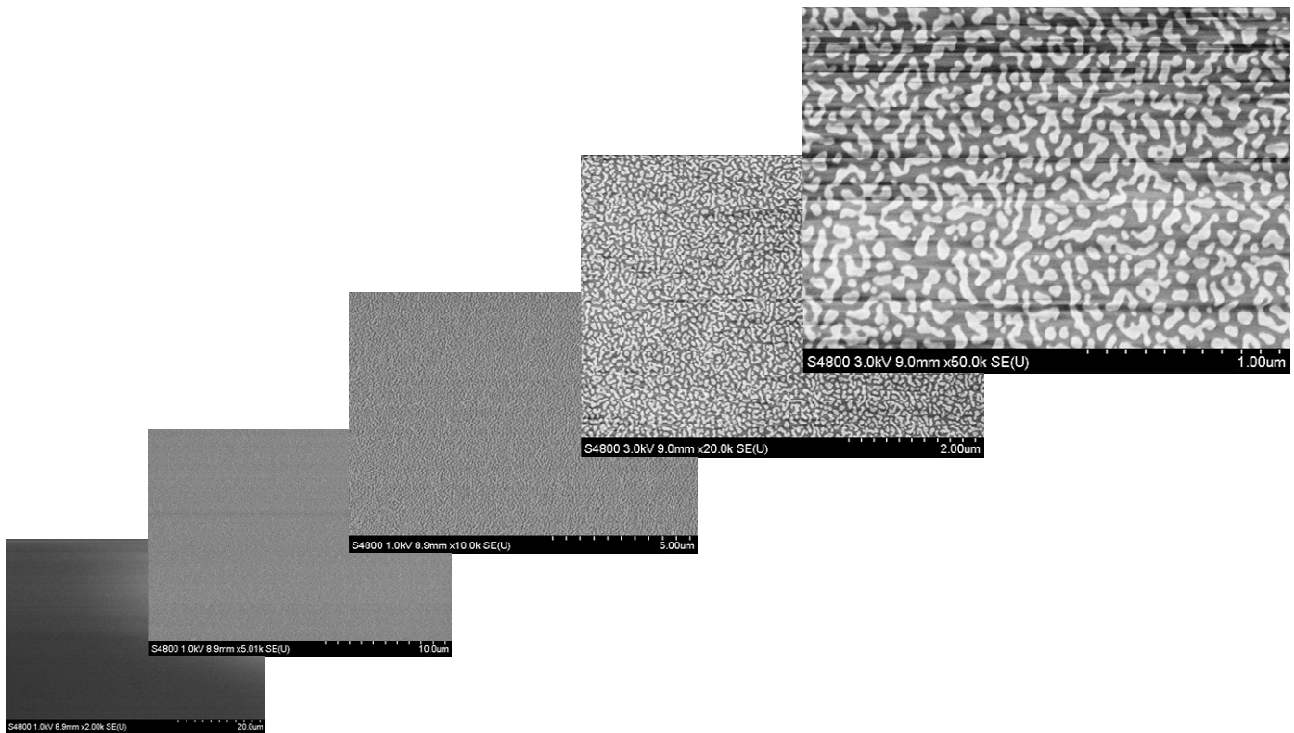


Figure 5.1.6 SEM surface of PBM membrane with magnification (magnification from x2 to x50)

In Figure 5.1.7 the PBM cross-section is shown. A thickness of PBM coating of about 3 μm was observed.

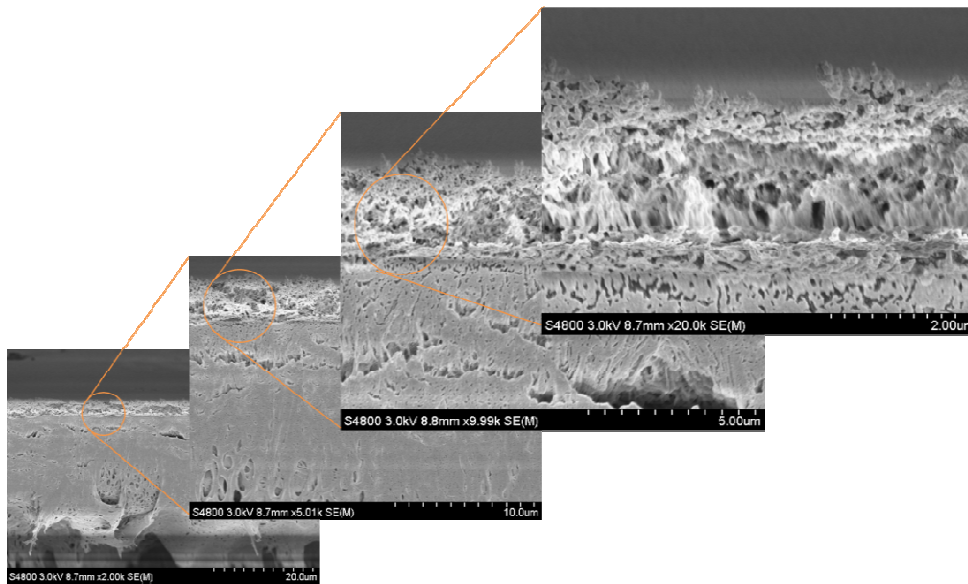


Figure 5.1.7 SEM cross-section of a PBM membrane with magnification (magnification from x2 to x20)

In the case of membranes prepared with the commercial surfactant DTAB, the effect of microemulsion composition on membrane morphology was investigated. In Figure 5.1.8 the impact of microemulsion composition on membrane morphology is shown.

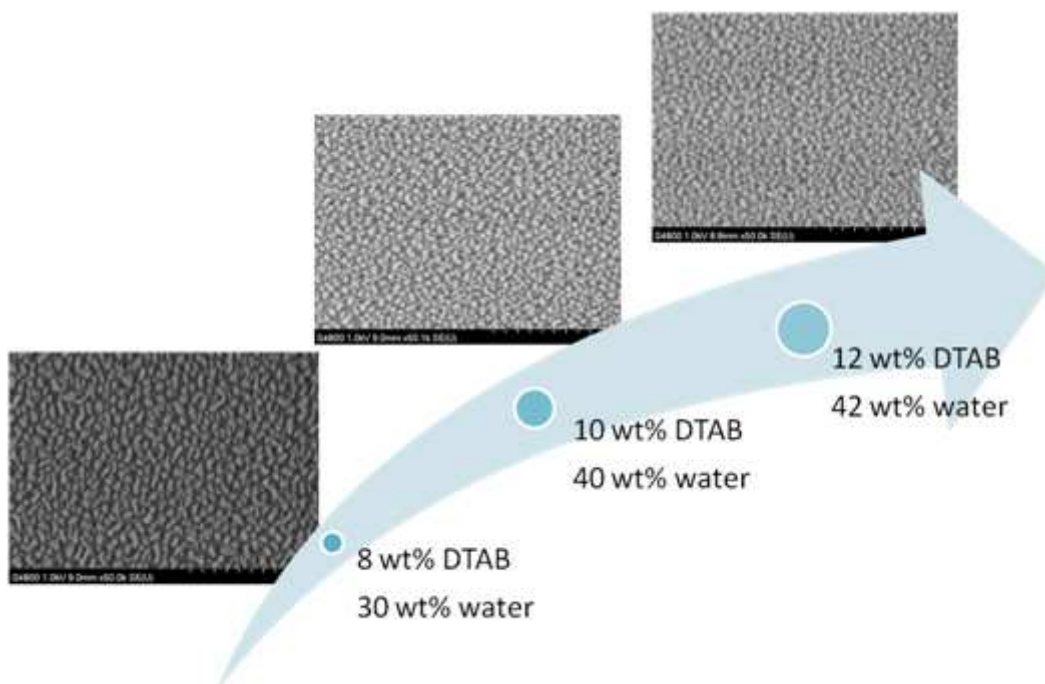


Figure 5.1.8 Effect of microemulsion composition on membrane morphology

By varying microemulsion composition, in particular surfactant and water concentration (Figure 5.1.8), different PBM structures can be obtained. This aspect is of particular relevance because it allows to tune and modulate the membrane structure on the basis of the desired pore size and the final application of the membrane.

Increasing the amount of DTAB (from 8 wt% to 12 wt%), for instance, enabled the dispersion of the oil phase (methyl methacrylate) in the aqueous phase (water) reducing the length and the dimension of the water channels responsible for the formation of the porous matrix of the membrane. For this reason, the membrane prepared with the highest concentration of surfactant (12 wt%) presented a denser structure in comparison to PBM membranes prepared with the lowest amount of surfactant (8wt%). Furthermore, it is supposed that, with increasing water concentration, the oil micro-globules (present in the microemulsion before polymerisation) become larger due to extensive coalescence of growing polymer of lower solubility [3]. This aspect was also in agreement with SEM pictures shown in Figure 5.1.8. By increasing water concentration (from 30 wt% to 42 wt%) the structure of PBM membranes became denser due to the coalescence occurring during polymerisation. In fact, as the SEM images show, the water channels, abundant at lower surfactant and water concentrations, are gradually replaced by monomer islands when the concentration of water and DTAB, within the microemulsion, is increased.

Water permeability and dye rejection tests (reported in paragraph 5.9) further confirmed the trend observed in SEM analyses.

5.2 Atomic force microscopy (AFM)

PES commercial membrane

3D AFM images of PES commercial membrane show a very rough and porous surface.

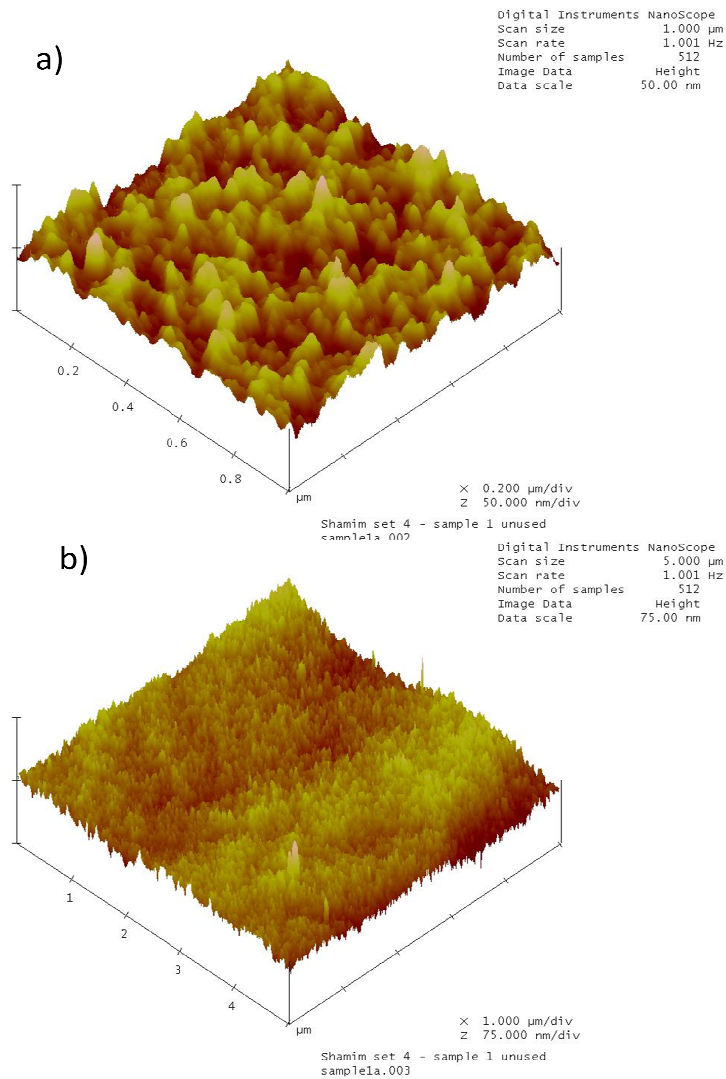


Figure 5.2.1 AFM surface of PES commercial membrane

PBM coated membrane with AUTEAB surfactant

The membrane surface appears flat, homogenous and smooth. By comparing the AFM surface of a PES commercial membrane with the surface of PBM coated membrane, it can be clearly noticed that the latter presents a smoother surface as also proved by roughness measurements reported in the next paragraph.

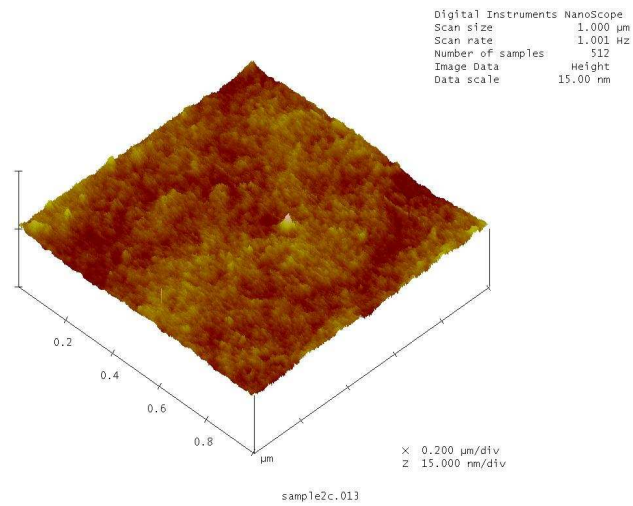


Figure 5.2.2 AFM surface image of PBM coated membrane (with AUTEAB)

PBM coated membrane with DTAB surfactant

Even for PBM coated membrane prepared with DTAB, the AFM shows a very flat and smooth surface. The smoother surface of PBM membranes gave a better wettability towards water (as proved by contact angle measurements) and an improvement in antifouling properties by limiting the adhesion of organic compounds at membrane surface.

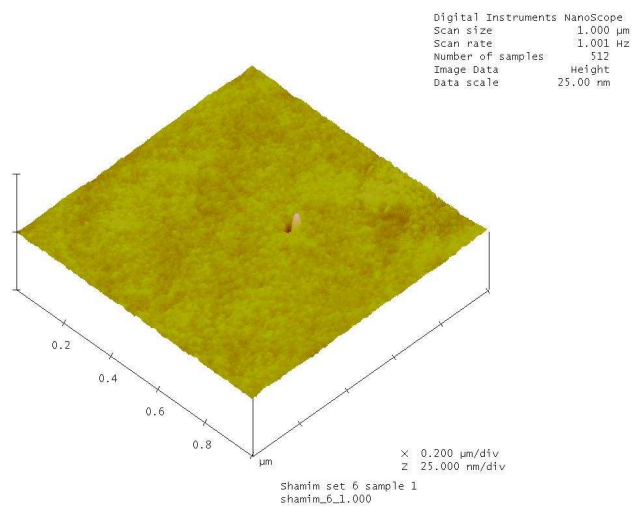


Figure 5.2.3 AFM surface image of a PBM coated membrane (with DTAB)

5.3 Surface roughness

Figure 5.3.1 shows the surface roughness of PES commercial membrane and PBM membranes prepared with both surfactants. In the case of PBM membranes, the addition of a PBM layer led to a reduction in the measured surface RMS roughness. Membrane roughness decreased by more than 60% for PBM coated membranes in comparison to commercial uncoated PES membrane.

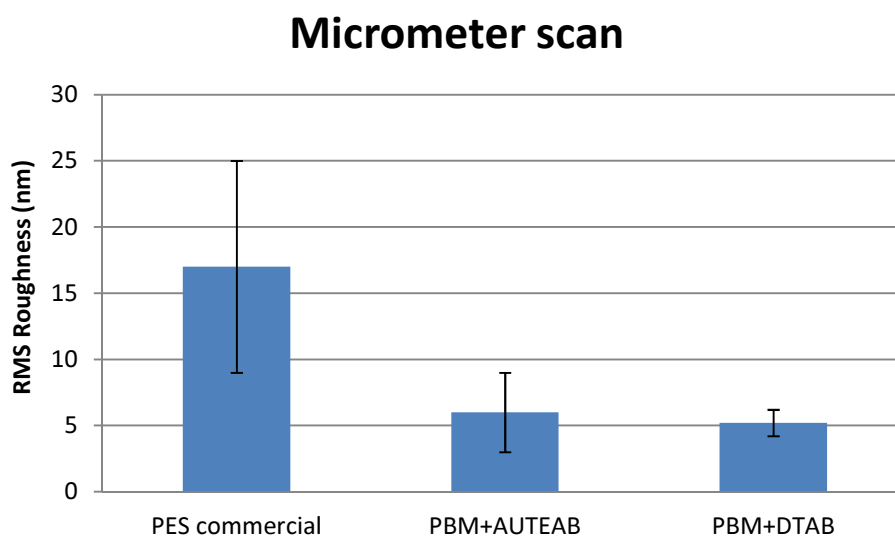


Figure 5.3.1 Surface roughness of uncoated PES and PBM coated membranes

The addition of a PBM layer, in fact, led to a reduction in the measured surface roughness from 17 nm (for PES membrane) to 7 nm (for PBM membrane with AUTEAB) and to 5nm (for PBM prepared with DTAB).

The smoother surface shown by PBM coated membranes was strictly related to their antifouling properties. It is well known, in fact, that the adhesion of organic compounds, that are usually the main responsible of fouling formation, is favoured by rough surfaces. The “throughs” created by rough membranes are, in fact, preferred sites of accumulation of particles in comparison to smoother surfaces. PBM coating allowed to reduce membrane roughness, thus limiting the fouling layer formation (as proved by the antifouling tests reported in paragraph 5.8).

5.4 Pore size measurement

Capillary flow porometer analysis was used to determine the pore size distribution of both PES and PBM coated membranes (Figure 5.4.1). The pore size of PBM coated membranes can be tuned and adjusted (as previously shown in Figure 1.5.8) by varying microemulsion composition and microemulsion polymerisation temperature depending on the final membrane application. In the graph below the pore size of PES and both PBM coated membranes (at the optimal microemulsion composition) is reported. As expected, pore size distribution decreased of about 25% for PBM membrane (prepared with AUTEAB) due to the presence of PBM coating on the top-layer of the membrane. Pore size, in fact, decreased from a value of 0.1 μm for PES membrane to 0.075 μm for PBM coated membrane. In case of DTAB used as surfactant, the average pore size of prepared membranes was about 0.04 μm . Even in this case there was a decrease in pore size of about 60%.

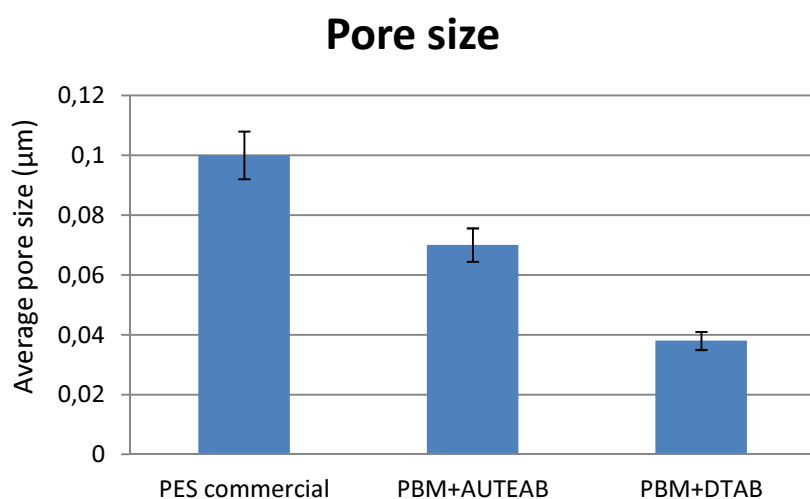


Figure 5.4.1 Pore size of PES commercial and PBM membranes

From capillary flow porometer data, it was shown that PBM coating causes a decrease in membrane pore size and together with the increase of overall membrane thickness (due to the presence of PBM coating) was responsible for the lower water permeability of novel membranes.

5.5 Molecular weight cut-off (MWCO)

MWCO is defined as the lowest molecular species retained at 90% by the membrane. MWCO is characterised by solute molecular weight but other factors can affect the permeation of these molecules through the membrane such as the shape of the molecule (linear or globular), the pH of the solution and the filtration pressure. In this work, the MWCO was calculated by using a mixture of three dextrans of different molecular weights (11 KDa, 70 KDa and 480 KDa) which was applied as feed solution for filtration tests. The feed and the permeate were, then, analysed by gel permeation chromatography (GPC). As expected, MWCO was reduced when PBM was applied as coating for PES commercial membranes.

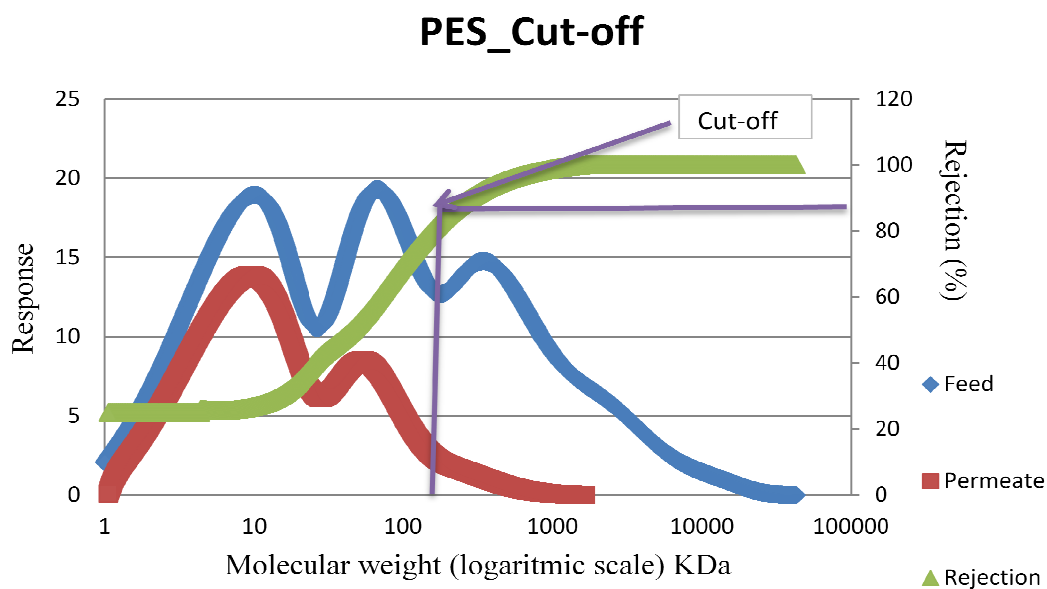


Figure 5.5.1 Molecular weight cut-off of PES membrane

As shown in Figure 5.5.1, the MWCO for PES commercial membrane was about 270KDa.

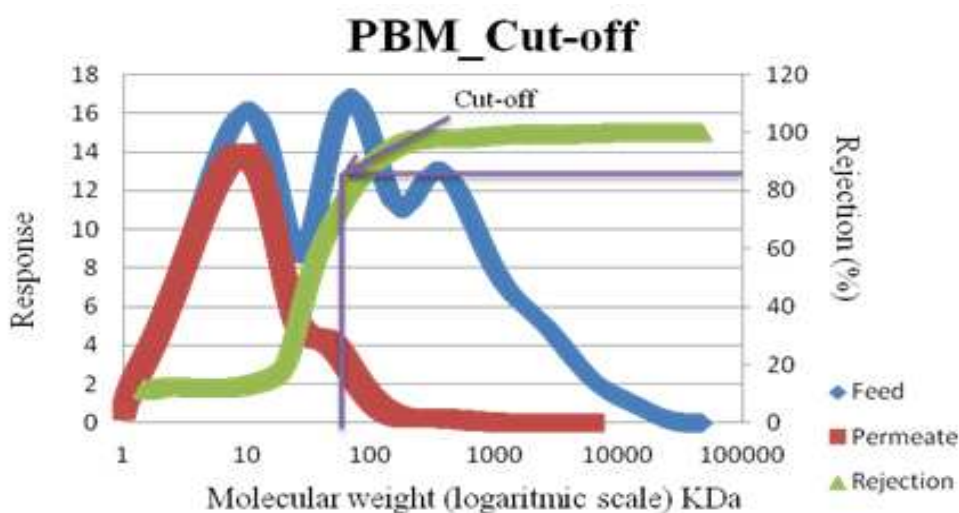


Figure 5.5.2 Molecular weight cut-off of PBM coated membrane

The MWCO for PBM membranes, at the optimal microemulsion composition was about 100KDa (Figure 5.5.2). The reduced MWCO can be attributed to the decreased pore size of PBM coated membranes due to the presence of the microemulsion polymerised on the top. A lower MWCO means a reduced pore size and an increased rejection toward target compounds.

5.6 Contact angle measurements (CAM)

Based on the chemical characteristics of the membranes, membrane surfaces show hydrophobic or hydrophilic moiety. The relative wettability of PBM coated and PES commercial membranes was measured by sessile drop contact angle. All the membranes (coated and commercial) exhibited hydrophilic nature, however, this was more pronounced in the case of membranes with a PBM layer. As shown in Figure 5.6.1, PBM coated membrane showed a higher affinity for water droplet in comparison to PES commercial membrane.

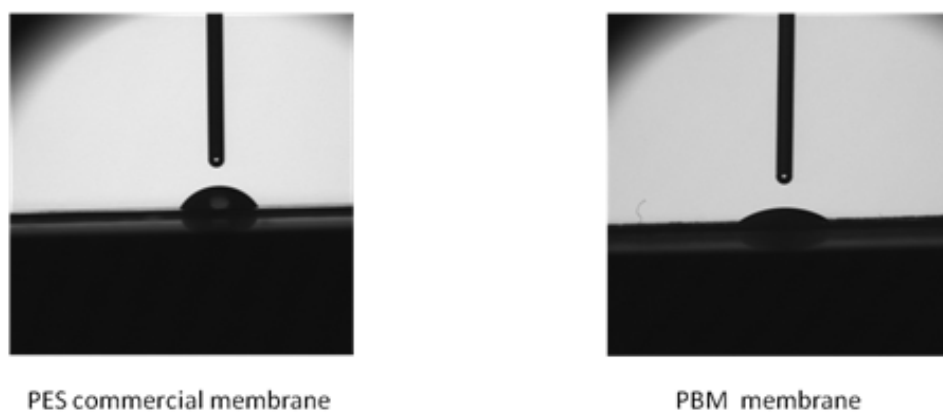


Figure 5.6.1 Water droplet on PES commercial and PBM membrane surface at t =0

PES commercial membranes presented an average contact angle of 68° while PBM+AUTEAB membranes showed an average contact angle of 47°. Therefore, a reduction of about 30% in contact angle values was found when AUTEAB was used (Figure 5.6.2). Even when DTAB was used as surfactant, a decrease of the contact angle in comparison to PES commercial membrane (from 68° to 58°) was observed. The different microemulsion composition and chemical structure of both surfactants explain the difference of the contact angle between the PBM coated membranes prepared with DTAB (58°) and AUTEAB (47°). AUTEAB, in particular, present an acrylate group that can enhance its hydrophilic moiety with respect to the DTAB molecule.

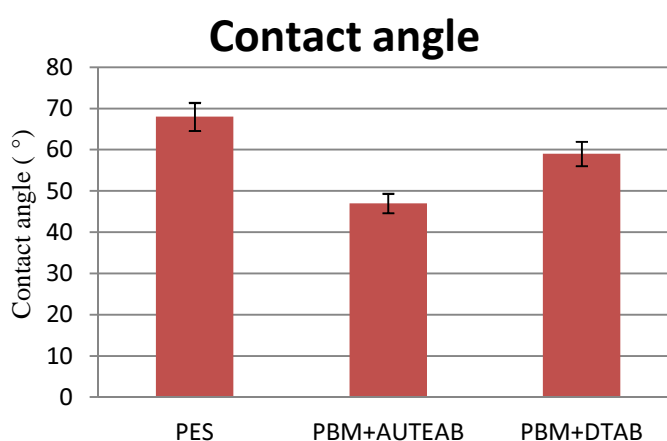


Figure 5.6.2 Contact angle for PES and PBM membranes

As mentioned in Chapter 1, a higher degree of hydrophilicity usually results in better performances in terms of water permeability and foulant rejection. The antifouling potential of hydrophilic membranes is due to the lower binding affinity of organic compounds to membrane surface. Organic matters, in fact, are more inclined to establish hydrophobic interactions at membrane surface causing their accumulation and a cake layer formation.

In this case, PBM coated membranes, due to their relative high degree of hydrophilicity, are more resistant and less prone to fouling, allowing them to operate at higher and more constant permeability for longer time (as proved by MBR experiments).

The evolution in time (5 measurements, one every 10 seconds) for a water droplet was measured for both PES and PBM coated membranes. 5 measurements, one every 10 seconds were automatically taken and the image sequence is reported in Figure 5.6.3 and 5.6.4.

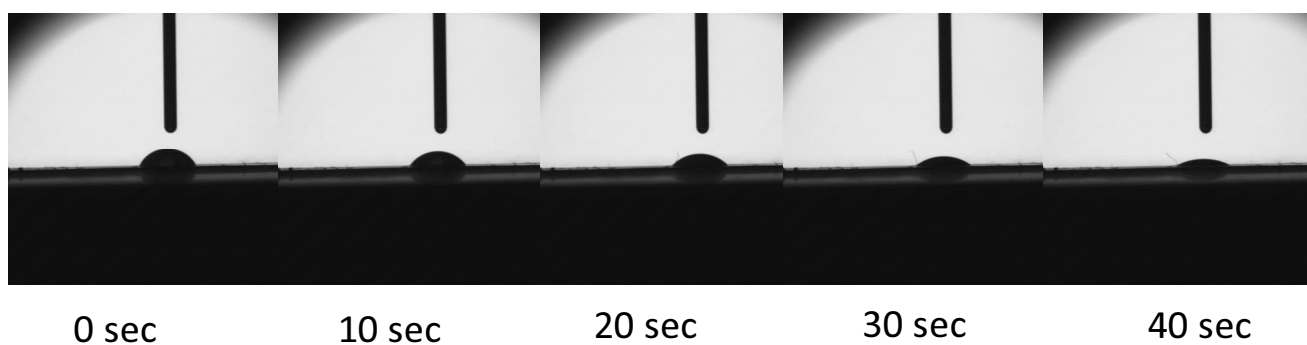


Figure 5.6.3 Contact angle frames of a water droplet on a PES membrane at different times

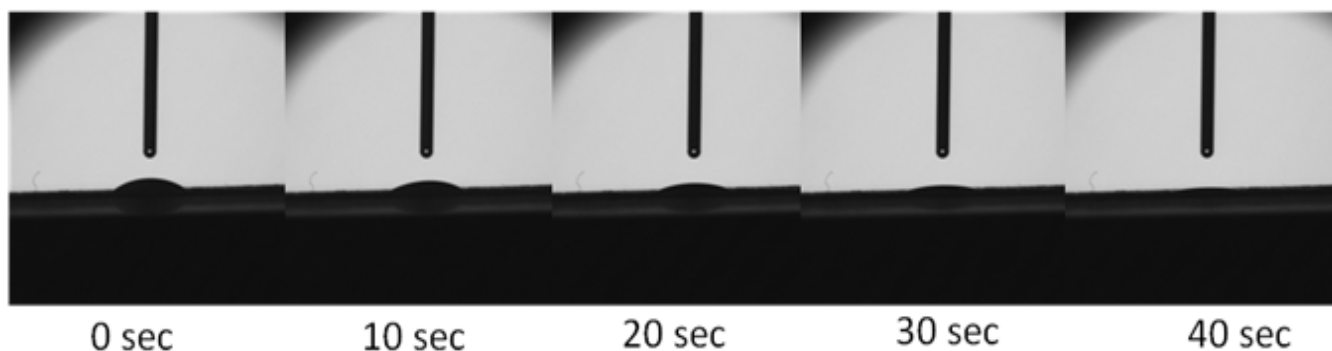


Figure 5.6.4 Contact angle frames of a water droplet on a PBM membrane at different times

As it is possible to notice from Figure 5.6.3, the surface of the PES membrane presented a higher repulsion towards the water droplet. The droplet is not immediately adsorbed by membrane surface indicating a modest degree of affinity with membrane material. The water droplet on the PBM

membrane, on the contrary, was almost immediately adsorbed by the membrane surface (Figure 5.6.4) due to a much greater affinity towards the membrane material . The water droplet totally disappeared within 30 seconds.

The higher hydrophilicity of PBM membranes, in comparison to PES commercial membranes, can be explained with the following two reasons:

1. PBM surface structure: as proved by roughness measurements carried out by AFM analyses, coated membranes presented a smoother surface in comparison to commercial PES membranes. From literature data, in fact, it is well known that the membrane surface morphology can affect the contact angle value. In particular, it is possible to refer to a phenomenological method proposed by Wenzel [4] relating the surface roughness to the membrane contact angle. In general:

$$\text{Cos}\theta^* = \text{Cos}\theta \times r$$

Where θ is Young's angle and r is the surface roughness.

From the equation it can be seen that the contact angle to water of a smooth surface is, in general, lower than the one of a rough membrane. For this reason, the lower contact angle measured for PBM membranes can be attributed to their smoother surface in comparison to commercial PES membranes.

2. PBM chemical composition: it is demonstrated that the presence of particular functional groups on membrane surface such as -OH and -NH₂ decrease the contact angle and it is, thus, favorable for improving the hydrophilicity of the membrane. In microemulsion composition, in particular, the cosurfactant HEMA is a short-chain alcohol presenting an OH group (Figure 5.6.5).

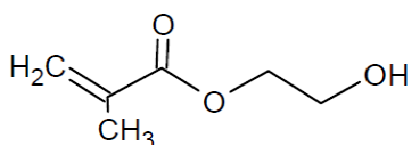


Figure 5.6.5 Molecular structure of the cosurfactant HEMA

The presence of PBM coating on the membrane surface was confirmed by IR analyses where the spectrum of a PES commercial membrane surface was compared with the one of a PBM coated membrane (Figure 5.6.6).

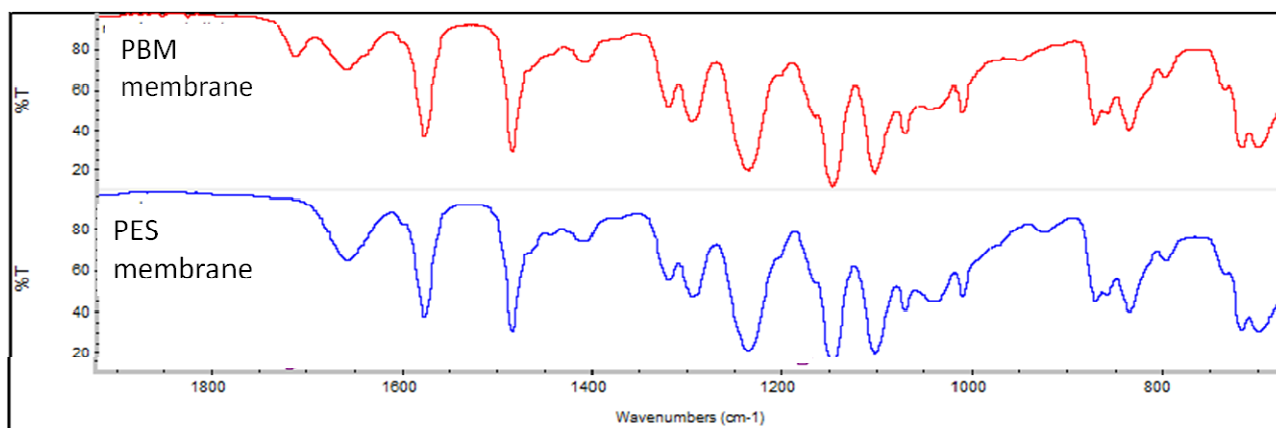


Figure 5.6.6 IR spectra of PES and PBM coated membrane

Spectra of both membranes are perfectly comparable in terms of peaks intensity. It means that the PES membrane structure was not altered by the coating of the PBM (polymerized on the top). The main difference between the two spectra is the presence of the peak with absorbance at about 1731 cm^{-1} given by the double bond $\text{C}=\text{O}$, specific of the molecules containing acrylates (such as MMA, HEMA and EGDMA used for microemulsion preparation). The absence of this functional group in the PES molecule indicates the presence of PBM coating on the membrane surface. For this reason, we can assume that HEMA, which was copolymerized within the microemulsion with the other components, is also present in the coating. HEMA, due to the presence of $-\text{OH}$ group, can thus enhance the affinity of the membrane surface to water molecules improving the hydrophilicity and consequently exhibiting a relatively lower contact angle.

In conclusion, the improvement on hydrophilicity of the PBM coated membranes can favor permeate flux through the membrane itself due to the increasing interaction between membrane surface and water molecules via hydrogen bond and/or electrostatic attraction [5], limiting, at the same time, the fouling phenomenon (paragraph 5.9 and 5.10).

5.7 Antimicrobial activity

Quaternary ammonium salts belong to the group of compounds which exhibit a strong antimicrobial activity. This activity is especially effective against gram-positive bacteria and fungi [6]. The antimicrobial activity is mainly due to the interaction of the ammonium salt with the cell membrane of microorganisms. The antimicrobial activity is more pronounced with the increase of the alkyl chain length but only up to a certain limit. If the length of the alkyl chain overcomes this limit, the antimicrobial activity decreases.

Even surfactants applied in this thesis work, AUTEAB and DTAB, as quaternary ammonium salts, exhibited a strong antimicrobial activity.

Since the activity of quaternary ammonium salts is well known against gram-positive bacteria such as *S. aureus*, the activity of both surfactants was tested against the gram-negative bacterium *E.coli*.

From antimicrobial tests carried out on the surfactant AUTEAB, it was seen that 1.8 mg of surfactant was enough to inhibit the growth of *E.coli*. However, a lower surfactant quantity (1.3 mg) was not enough to inhibit the bacterial growth (as shown in Table 5.7.1). For the surfactant DTAB, viceversa, 1.3 mg of surfactant were sufficient to inhibit the growth of *E.coli*.

Table 5.7.1 Cell counts in 10 ml well plates for AUTEAB and DTAB surfactants

AUTEAB amount (gr)	Count	DTAB amount (gr)	Count
0,0012	too many	0,0011	Too many
0.0013	too many	0,0012	0
0.0018	0	0.0013	0
0.0022	0	0.0018	0
0.0041	0	0.0022	0
0.0076	0	0.0041	0
0.0104	0	0.0076	0
0.0115	0	0.0104	0
0.0165	0	0.0115	0
0.0200	0	0.0165	0
		0.0200	0

The DTAB surfactant showed a slightly higher antimicrobial activity in comparison to AUTEAB, even if, generally speaking, the antimicrobial activity of both surfactants is comparable.

Antimicrobial tests were also carried out on the PBM coated membrane and the results were compared with the uncoated PES membranes. As shown in Figure 5.7.1, the PBM coated membranes had a strong antimicrobial activity. On the contrary, PES membranes did not show any antimicrobial activity.

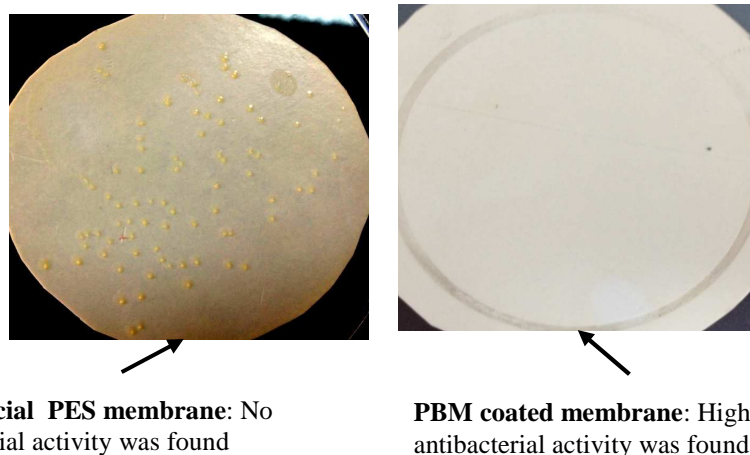


Figure 5.7.1 Antimicrobial activity of commercial PES and PBM membranes

The average number of CFUs grown on the surface of commercial PES membrane was of about 77, while no bacterial growth was observed on the surface of PBM coated membranes. Bacteria are the main responsible of biofouling. Their attachment to the membrane surface is followed by the adsorption of organic compounds (used as nutrients) with the following generation of polysaccharides promoting their anchorage to the membrane surface and protection from the surrounding environment. Biofouling tends to occur in many membrane processes but it is prevalent in wastewater treatment processes and in bioreactors. As it will be illustrated in Chapter 6, PBM produced membranes were applied for textile wastewater treatment in submerged MBR. In this process, a biological degradation of organic compounds (operated by bacteria) is coupled with a physical purification process (operated by membranes). For this reason, in MBR, the biofouling represents one of the major drawbacks being responsible for the loss of membrane performances, increase in energy and cleaning costs. The possibility of having membranes with antimicrobial properties (such as PBM membranes produced in the present work) prevented the phenomenon of biofouling maintaining satisfactory results for a long time in terms of water membrane performances (constant water permeability and good dye rejection). Furthermore, no need of additives (such as biocides) used to inhibit bacteria growth and no need of cleaning chemicals (in order to remove the formed biofouling), made PBM membranes attractive also from the cost-saving point of view.

5.8 Nanoparticles incorporation

POMs nanoparticles are compounds based on polyanionic metal oxides with a great potential in different fields such as catalysis and medicine [7]. Some transition metals such as Nb, V, Mo, W are

able to form polyanions, at their maximum oxidation state and under specific conditions of temperature, pH and concentration, with the dimension of a few Å to some nanometers. POMs can be formed by a transition metal (M) and oxygen (O) with formula $[M_mO_y]^p$ or by a M, O and another metal (X) such as Pb, Si, As, Sb with formula $[X_nM_mO_y]^q$. The structure of POMs is generally represented by octahedrons MO_6 .

In order to guarantee the entrapment of POMs within the polymerized microemulsion, they were encapsulated (by the ITM CNR at the University of Padua were POMs were produced) with the synthesised surfactant AUTEAB forming a complex that can be copolymerized within the microemulsion. The formation of electrostatic interactions between the negative POMs surface and the positive head of AUTEAB avoided the phenomenon of complexes leaching.

Polyoxometalates (POMs) nanoparticles were incorporated into the membrane matrix by dispersing them into the microemulsion and their activity was evaluated. In particular, the biomimetic activity of the POMs containing ruthenium (RuPOMs) (Figure 5.8.1) and linked to AUTEAB surfactant (AUTEAB-RuPOM) was studied.

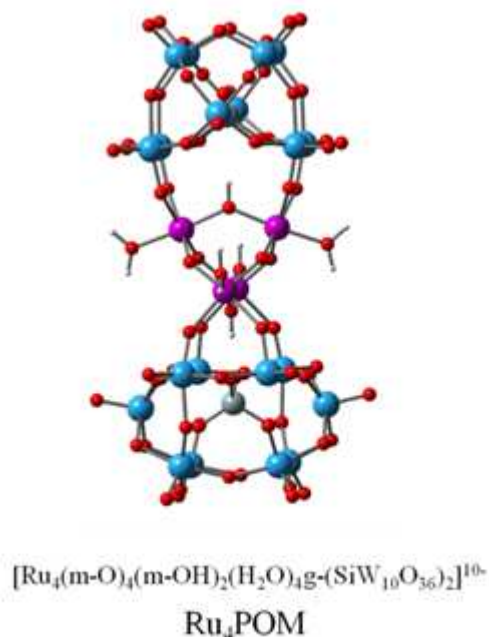


Figure 5.8.1 Structure of Ru-POM

RuPOMs find application in water oxidation processes (water splitting) and in the reaction of H_2O_2 dismutation, miming respectively the activity of oxidase and catalase enzymes. The effective entrapment of POMs nanoparticles into the PBM matrix was evaluated by means of EDX analysis (Figure 5.8.2).

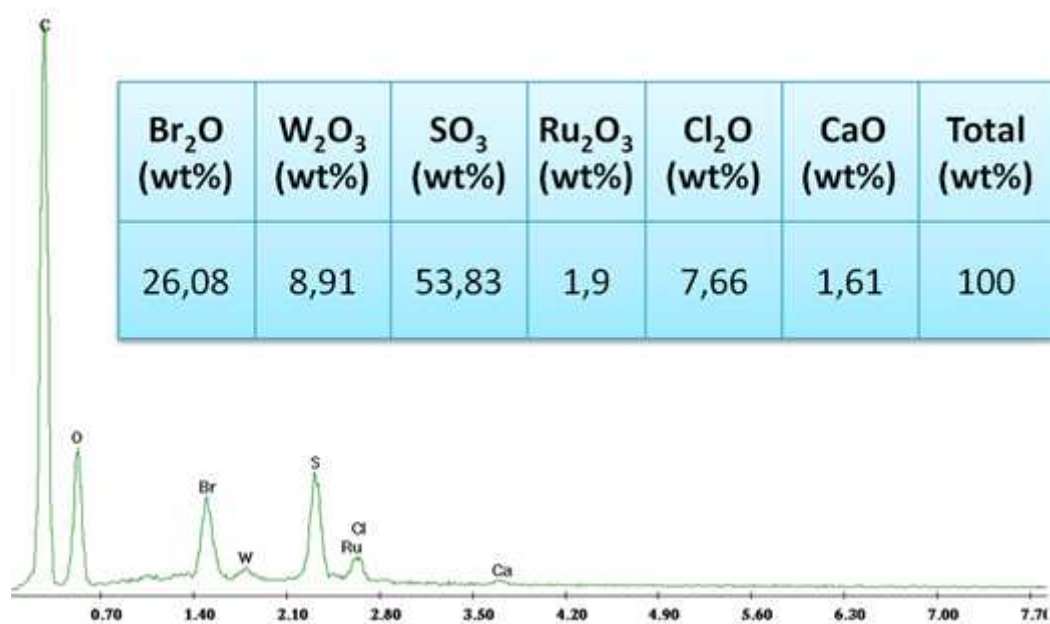


Figure 5.8.2 Percentage of elements detected on PBM membrane surfaces loaded with POMs

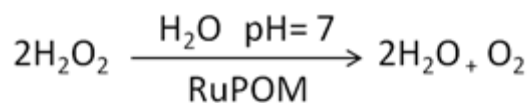
The EDX results show the presence of Ru and W in the membranes, proving the actual embodiment of the nanoparticles within the polymerised microemulsion.

The activity of RuPOMs nanoparticles after microemulsion polymerization was also evaluated. It was found that the catalytic activity of the nanoparticles was still maintained, as shown in Figure 5.8.3, even after incorporation in the polymerized microemulsion.



Figure 5.8.3 Oxygen formation at surface of PBM membrane with AUTEAB-RuPOMs nanoparticles in contact with H₂O₂

When the PBM+RuPOM coated membrane was soaked into an aqueous solution of H₂O₂, the formation of oxygen bubbles at membrane surface was immediately observed. The oxygen formation derived from the dismutation of H₂O₂ is in agreement with the following reaction:



The possibility of oxygen evolution on the membrane surface in presence of H₂O₂, could represent an innovative method able to remove the fouling from the membrane (membrane self-cleaning). Furthermore, POMs are good oxidant agents towards organic substrates.

The antifouling properties of PBM coated membranes with RuPOM nanoparticles was evaluated by bringing in contact the membrane with a model dye solution (Remazol Brilliant Blue and Acid Red). The results were then compared with ones obtained, under the same conditions, with PES commercial membranes and with PBM membranes without POMs nanoparticles (Figure 5.8.4).

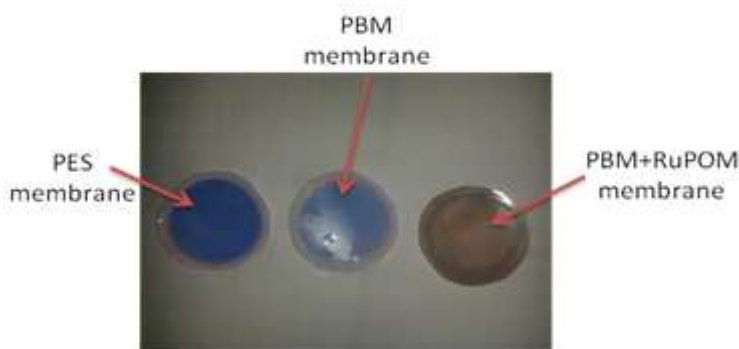


Figure 5.8.4 Visual comparison of PES commercial membrane, PBM membrane (with and without AUTEAB-RuPOM) after treatment with model dye solution

The intensity of the color deposited on membrane surface was considered as index of dye deposition and as an indication of membrane fouling propensity.

As it can be seen from Figure 5.8.4, the PBM coated membrane is less affected by fouling phenomenon in comparison to commercial PES membrane. In fact, the dye color is less pronounced on PBM surface while it is more marked on PES commercial surface. If we look at the PBM+RuPOM coated membrane, considering that the brown color is due to the natural aspect of POMs nanoparticles, all color deposition has been removed from its surface. This means that POMs can play an important role in membrane cleaning and fouling prevention and their combination with PBM membranes, on a larger scale, can be of great interest for future works. Furthermore, the previous results demonstrated the possibility of entrapping and incorporating, by polymerization, different nanoparticles (with different functions) into a bicontinuous microemulsion.

5.9 Fouling tests

Antifouling properties of PBM coated membranes were measured by using the model foulant humic acid (HA). HA comprises a group of heterogeneous organic compounds produced by the biodegradation of organic matter (plants and animals). The typical molecular weights range from a few hundred to a few thousands Dalton depending on the HA source [8]. Its abundance in soil, in natural water and in wastewater brought many researchers to investigate its removal and its effect in membrane processes [9-11]. HA is a mixture having both aromatic and aliphatic components and containing three main functional groups: carboxylic acids (COOH), phenolic alcohols (OH) and methoxy carbonyls (C=O) [12]. During filtration processes, HA can cause serious fouling problems leading to a reduction of membrane performances (in particular flux decline). In the present work, HA was used to test the antifouling properties of PBM membranes and the results were compared with uncoated PES membranes.

Tests were carried out for 24h and the water permeability of the coated PBM membrane (prepared with AUTEAB) and of the commercial PES membrane was measured before and after treatment with HA. The data obtained with both membranes were, thus, compared, and shown in Figure 5.9.1.

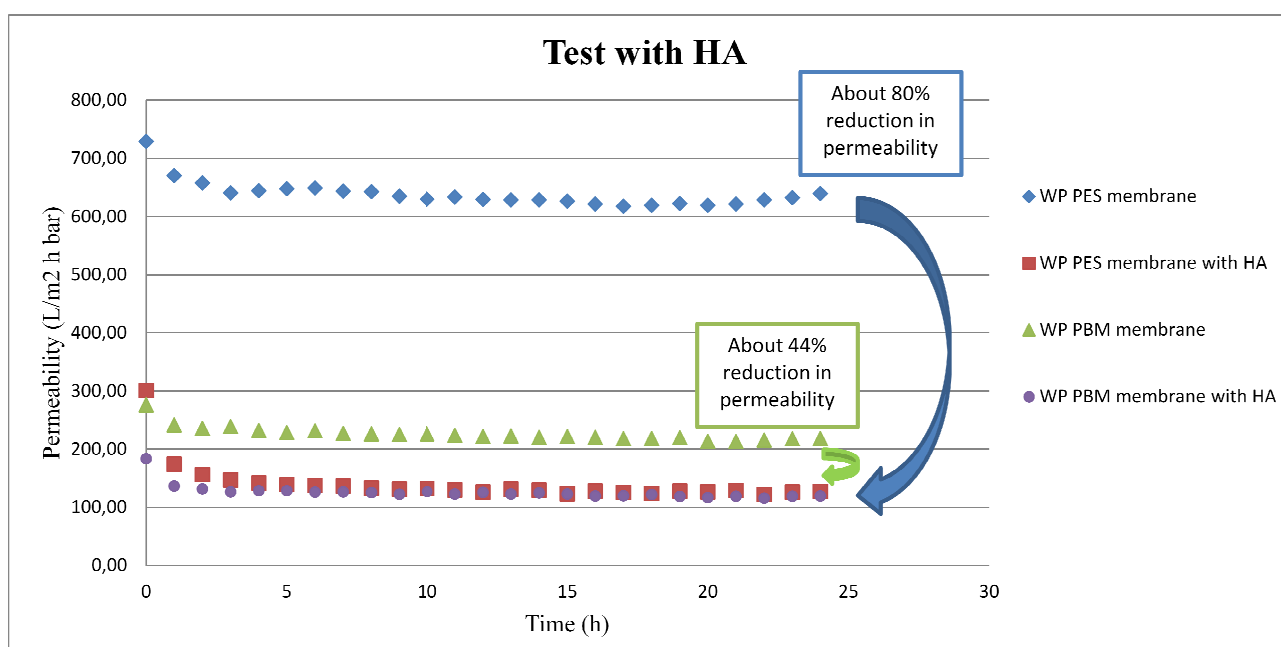


Figure 5.9.1 Permeability of commercial and PBM membranes before and after treatment with HA

As it can be seen from Figure 5.9.1, PES membranes have a water permeability (WP) of 620 L/m² h bar, that is three times higher than PBM coated membrane (about 200 L/m² h bar). This is due to the “extra resistance” given by the PBM layer on the commercial membrane. However, during treatment with HA, the permeability of both membranes decreased and it became comparable (about 150 L/m² h bar). The reduction in permeability before and after HA was about 80% for the PES commercial membrane, while it was about 44% for the PBM coated membrane. This behaviour can be easily explained considering the antifouling moiety of the PBM coating layer. Because of its smoother and relatively higher hydrophilic surface (in comparison to the PES commercial membrane), the PBM membrane is more resistant to fouling. A lower reduction in permeability, when the HA is applied was, thus, observed.

Very interesting results on regain (%) in permeability, after cleaning of the membranes, are underlined in Figure 5.9.2. In fact, both types of membranes after the treatment with HA were cleaned by backflushing (water was sent from the permeate side through the membrane to the feed side).

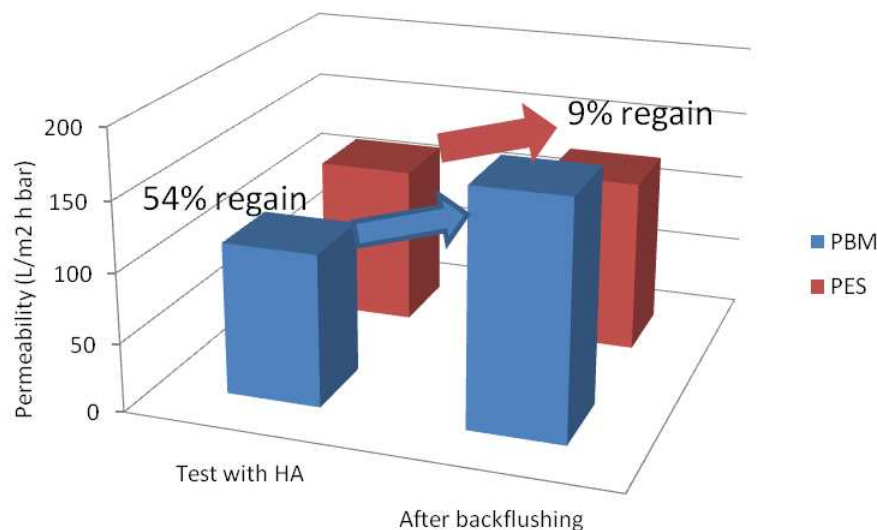


Figure 5.9.2 Regain in permeability of commercial and PBM membranes after treatment with HA

As it can be seen from the Figure 5.9.2, the regain in water permeability for PBM coated membranes was about 54%, while PES commercial membrane showed a water permeability regain of just 9%. This result emphasizes the lower propensity of PBM coated membranes to fouling.

Moreover, the fouling occurred at the PBM membrane surface was reversible and it could be easily removed by washing the membrane with water.

In Figure 5.9.3 two pictures of PES commercial and PBM coated membranes are clearly shown after treatment with HA and subsequent cleaning by backflushing.

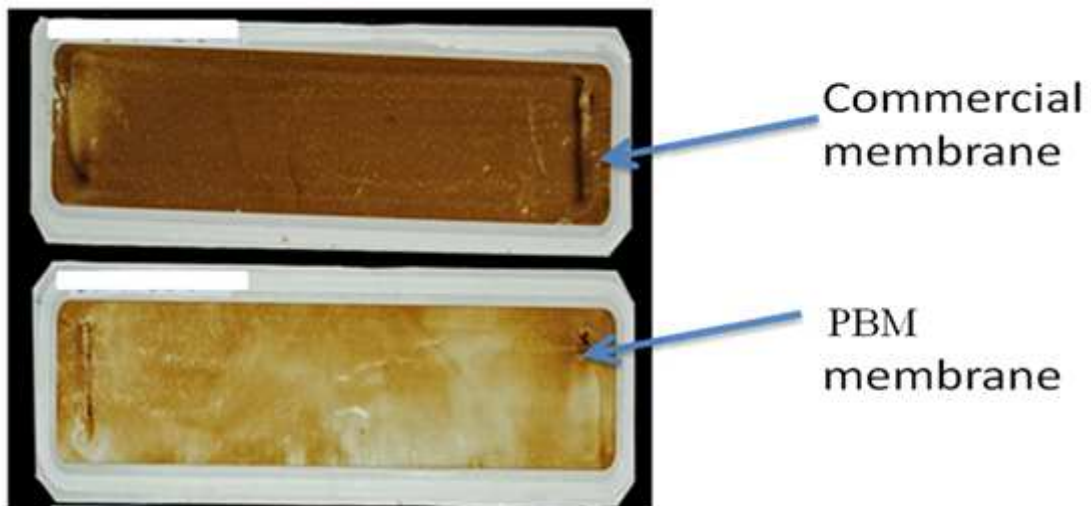


Figure 5.9.3 Comparison of fouling effect on PES commercial and PBM coated membrane

The surface of PES commercial membrane appears more dark and fouled in comparison to PBM coated membrane due to the deposition of a consistent layer of HA. The PBM coated membrane, on the contrary, looks clean and less fouled due to a lower HA accumulation on its surface. As proved by characterization tests reported above, the reasons of PBM coated membranes antifouling properties are given by the sum of different factors, such as the channel-like structure, the smoother surface and higher hydrophilic nature, in comparison to commercial PES membrane.

An estimation of the thickness of the fouling HA layers, deposited on commercial and PBM membrane surfaces, was measured from the cross section SEM imaging data (Figure 5.9.4 and Figure 5.9.5).

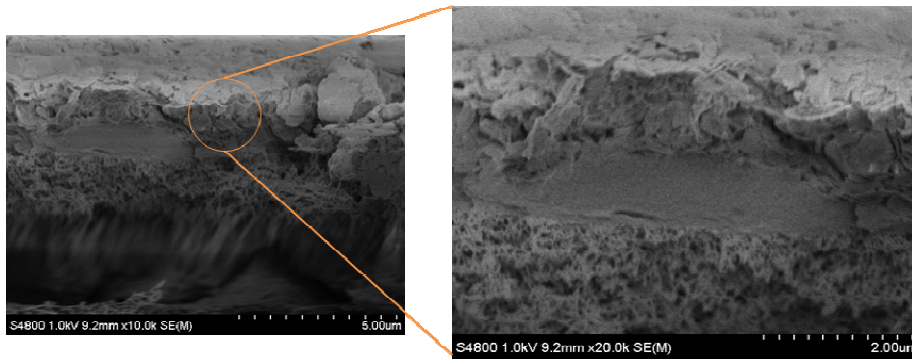


Figure 5.9.4 HA layer on commercial PES membrane

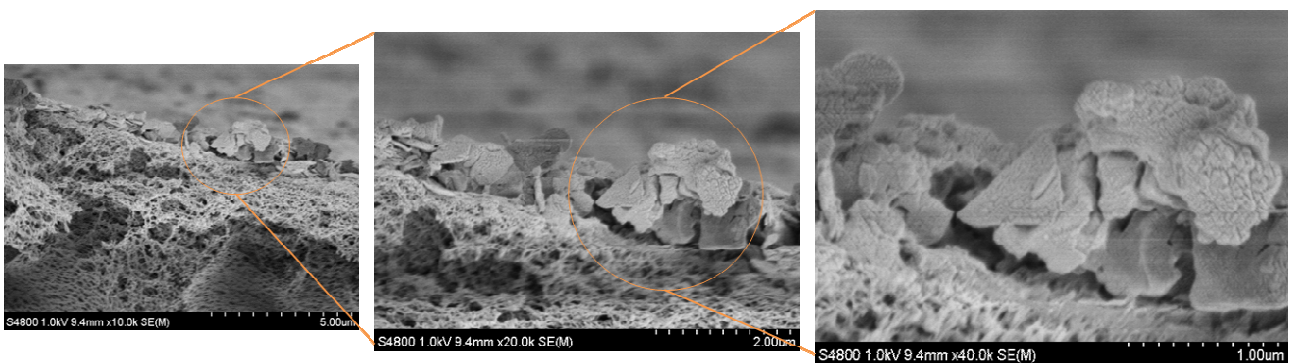


Figure 5.9.5 HA layer on PBM coated membrane

By measuring the thickness of the fouling layer deposited on the surface of both membranes, the data obtained by visual inspection and water permeability tests were confirmed. PES commercial membrane showed, in fact, a HA layer of about 1.7 μm , while PBM coated membrane showed a HA layer of 1.18 μm (with a reduction of about 30% in fouling deposition).

It can be concluded that PBM coated membranes were more resistant to fouling by humic acid than the commercial membranes, but this effect could be extended to other foulants, and it may be implied that coated membranes are likely to have a longer operating lifetime.

5.10 Water permeability and dye rejection

As previously shown in the paragraph 5.1, different PBM coated membranes based on different microemulsion compositions can be produced. By varying, in fact, the type of surfactant, its

concentration in the microemulsion or by modifying the polymerization temperature, different PBM membranes with different structures and performances can be obtained.

Water permeability and dye rejection data were the most important parameters that were taken into account in order to select the proper PBM coated membrane to be applied to the final MBR application. The data obtained were compared with the ones achieved with PES uncoated commercial membranes. A model dye solution using two dyes (Acid Red 4 and Remazol Brilliant Blue) was prepared and their rejection was measured. In all cases the rejection for Remazol Brilliant Blue was higher in comparison to Acid Red 4 due to larger size of the molecule that made more difficult its permeation through the membrane pores.

Since different formulations in microemulsion preparation were used for DTAB and AUTEAB surfactants (due to specific reasons linked to the bicontinuous range in the phase diagram, Chapter 2, Paragraph 2.6) it would not be appropriate to make a direct comparison between PBM membranes prepared with both surfactants. For this reason, the results of permeability and dye rejection obtained are reported in two different paragraphs. The commercial availability of DTAB, in comparison to the lab-made AUTEAB, made it an ideal candidate to be used as a screening surfactant. Due to the large amount of DTAB available, it was possible to widely investigate different parameters, such as polymerization temperature and microemulsion composition, and how they influenced the final PBM structure and performances. Nevertheless, the AUTEAB surfactant was used for the final PBM membranes scaling-up and subsequent application in MBR process.

PBM coated membrane with DTAB surfactant

- Effect of microemulsion composition

The effect of surfactant concentration on membrane performance was evaluated by using different amounts of DTAB for microemulsion preparation and keeping constant the polymerisation temperature (30°C). By increasing the concentration of surfactant from 8wt% to 12 wt%, the water permeability decreased (Figure 5.10.1) from 4 L/m² h bar to 1.4 L/m² h bar. This was mainly attributed to the decreased pore size of produced PBM membranes at higher DTAB concentration (as proved by SEM analyses and showed in Figure 5.1.8). Larger amounts of surfactant, in fact, enabled the dispersion of the oil phase into the aqueous phase producing a membrane with a denser structure.

Water permeability

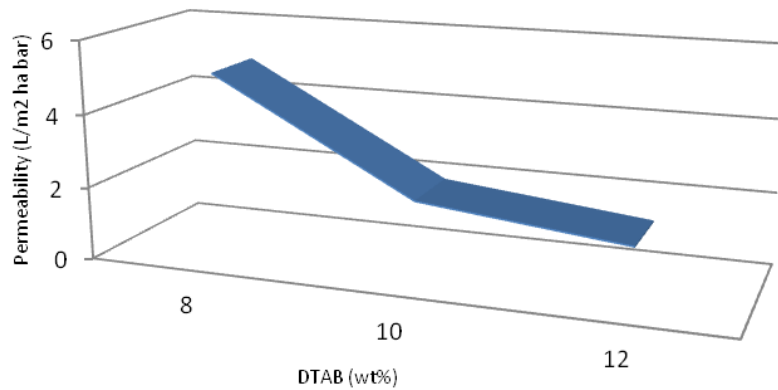


Figure 5.10.1 Water permeability and dye rejection at different DTAB concentrations

On the contrary, dye rejection toward both dyes (Remazol Brilliant Blue and Acid Red 4) increased as the concentration of surfactant increased. Blue rejection increased from 70% (at 8 wt% of DTAB) to 90% (at 12 wt% of DTAB). Red rejection increased from 32% (at 8 wt% of DTAB) to 96% (at 12 wt% of DTAB).

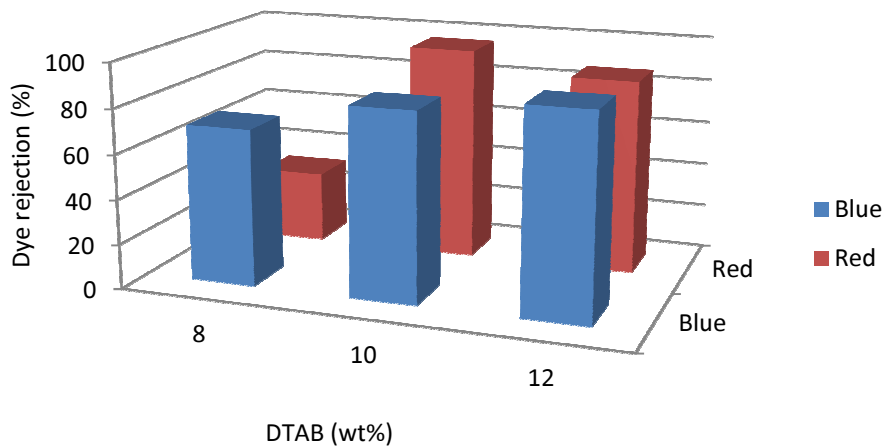


Figure 5.10.2 Dye rejection at different DTAB concentrations

- Effect of microemulsion polymerization temperature

A big gap in terms of performances between membranes prepared at 30°C (reported in the paragraph above) and 20°C was observed. While membranes prepared at higher temperature presented low water permeability (ranging from 1.5 to 12 L/m² h bar), membranes prepared at 20°C showed higher permeability (more than 100 L/m² h bar) accompanied, however, by a lower rejection toward both dyes applied. In this work, the best compromise between water permeability and dye rejection was found for the membranes prepared at 20°C, with a water concentration of 40 wt% and a surfactant concentration of 10 wt% (optimal composition reported in Table 4.2.2 of Chapter 2). Water permeability of PBM coated membranes was lower in comparison to PES commercial membrane permeability. Nevertheless, PBM membranes showed a better antifouling performance (as measured by running the PBM membranes for a longer time without any need for intensive chemical cleaning).

Permeability and dye rejection data for the both above mentioned membranes are presented in Figure 5.10.3.

As we can see from the graph, water permeability was about 400 L/m² h bar for PES commercial membrane while it was about 126 L/m² h bar for PBM coated membrane. PBM membrane, however, presented a more constant water permeability in time in comparison to PES commercial membrane.

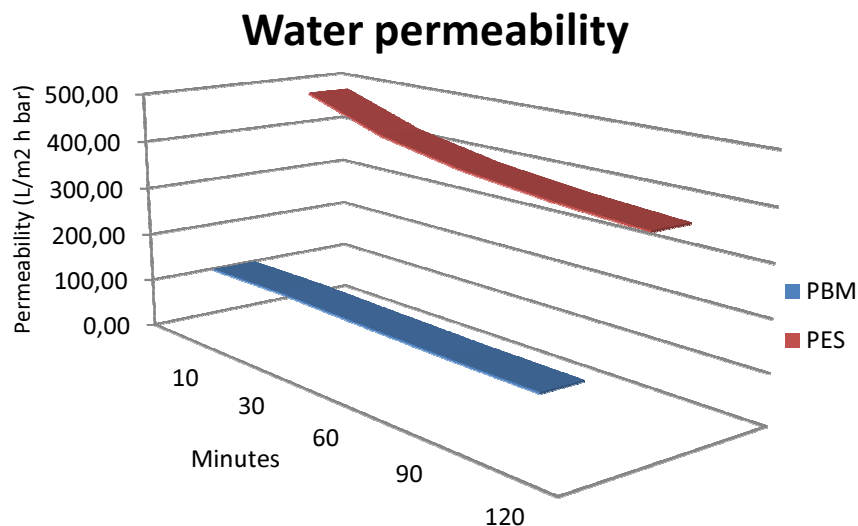


Figure 5.10.3 Water permeability for PES commercial and PBM membrane

A very low reduction in permeability (about 2%) was observed for PBM membranes when the filtration tests were carried out with a model textile dye solution (containing Remazol Brilliant Blue and Acid Red 4 as model dyes). In case of PES membrane, on the contrary, the reduction in permeability was more pronounced (about 26%) confirming once again its higher propensity to fouling (Figure 5.10.4).

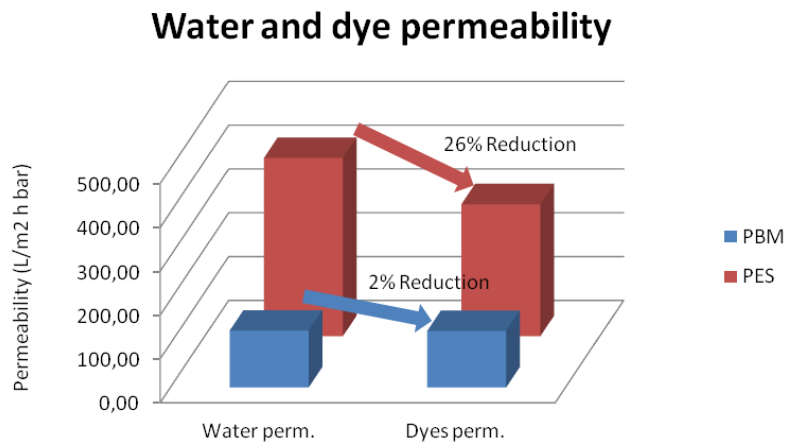


Figure 5.10.4 Water and dye permeability for PES commercial and PBM coated membrane

Regarding rejection to both dyes, PBM membranes presented an increased rejection of about 38% towards the blue and of 30% towards the red dye (Figure 5.10.5).

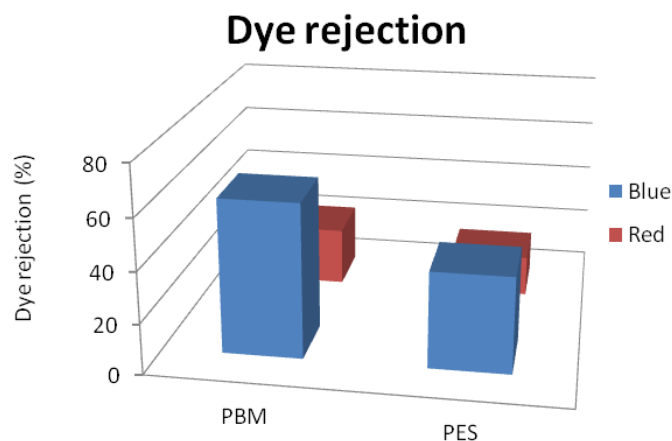


Figure 5.10.5 Dye rejection for PES commercial and PBM coated membrane

In Figure 5.10.6 the affinity among the model textile dye solution toward PES and PBM membrane surface is shown.

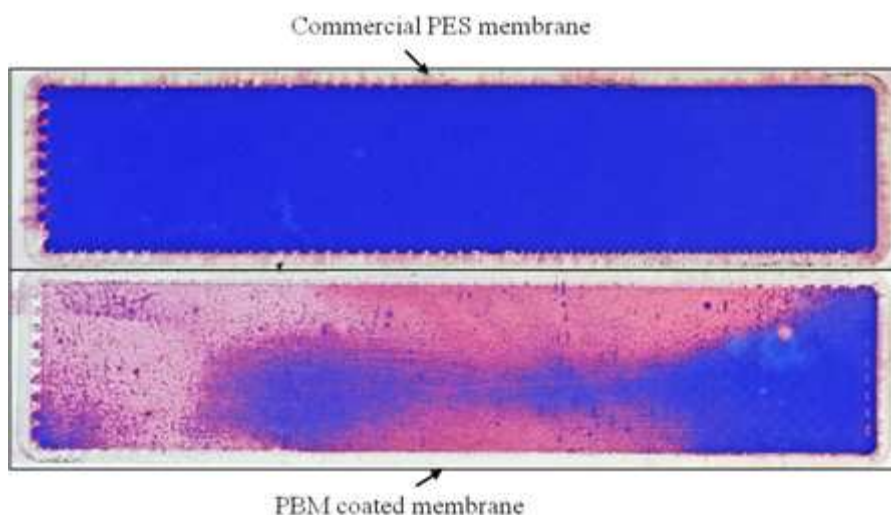


Figure 5.10.6 Affinity of model textile dye solution toward PES and PBM membrane surface

As it can be clearly seen, PBM membrane presented a reduced affinity for model dyes in comparison to commercial PES membrane due to their greater antifouling properties.

PBM coated membrane with AUTEAB surfactant

As mentioned in Chapter 4, the optimal AUTEAB concentration for microemulsion formulation was about 26 wt%. At this concentration, in fact, an optimal balance between water permeability and dye rejection was found. The effect of polymerisation temperature effect was also evaluated. It was found that temperatures higher than 25°C caused a very quick increase in microemulsion viscosity hindering solution casting on PES commercial membrane. For this reason, 20°C was chosen as the optimal polymerisation temperature. AUTEAB was used as surfactant for the scaling-up of flat-sheet coated membranes for the final application in MBR process (Chapter 6). The possibility of chemically binding and polymerising the surfactant into the polymeric matrix, ensures its entrapment within the polymerised microemulsion. This was of primary importance in order to preserve the surfactant antimicrobial activity for longer time. Furthermore, the risk of surfactant release in the surrounding environment can be avoided or drastically limited. PBM membranes prepared with AUTEAB surfactant showed, moreover, a higher reproducibility in terms of membranes performances in comparison to membranes prepared with the DTAB surfactant.

The water permeability for PBM membrane was about 200 L/m² h bar (Figure 5.10.7). Permeability was, therefore, about one third lower in comparison to PES commercial membrane (600 L/m² ha bar).

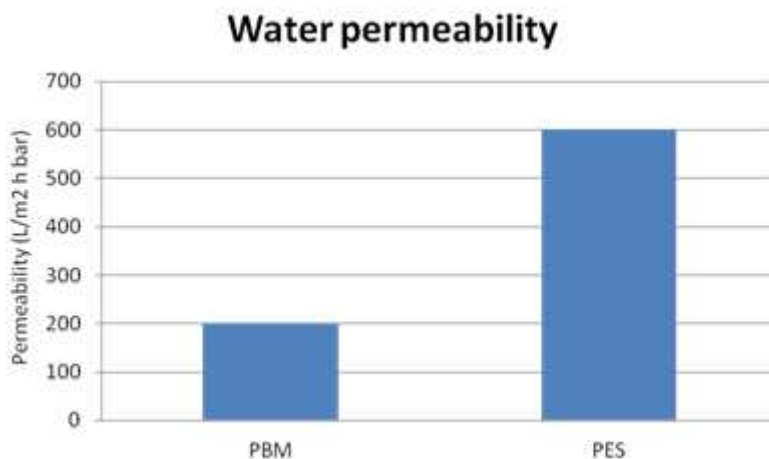


Figure 5.10.7 Water permeability for PES commercial and PBM membrane

In Figure 5.10.8 the rejection toward both dyes for PBM coated and PES membrane is reported.

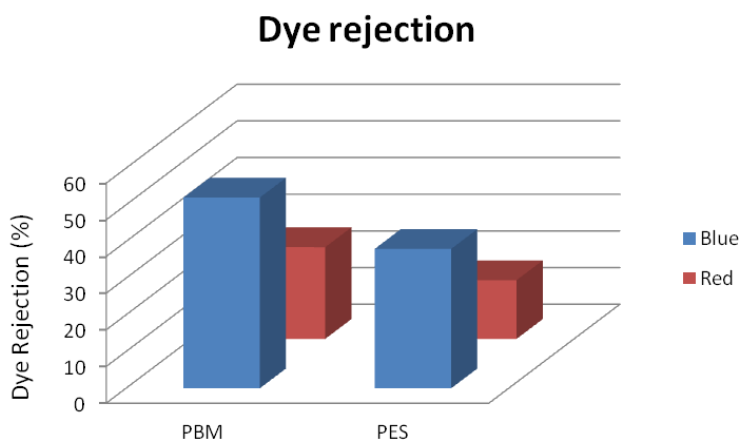


Figure 5.10.8 Dye rejection for PES commercial and PBM membrane

The rejection of PBM membrane toward dyes was about 36% higher for red dye and 27 % higher for the blue dye in comparison to commercial PES membrane.

Due to their antifouling properties, antimicrobial activity, good rejection toward model dyes and constant water permeability, PBM membranes prepared with AUTEAB were successfully scaled up

and used in MBR systems for the treatment of model textile wastewater. The results obtained are shown in Chapter 6 of this thesis.

5.11 Intensive chemical cleaning test

The ultimate target of the PBM coated membranes was to be tested in MBR experiments. The membranes generally applied in MBR applications require mechanical or chemical cleaning to face the severe fouling propensity. When the membrane becomes severely fouled and flux can not be restored, intensive chemical cleanings are needed. The intensive chemical cleanings include base cleaning to remove bio-fouling and acid cleaning to remove inorganic fouling/scaling. The chemicals used for these types of cleaning are very harsh and reduce the life span of the membranes. Sometimes, these kinds of cleanings damage the active surface of the membranes. The stability towards harsh cleanings of the PBM coated membranes was proved by using base and acid cleanings compounds, as already described in Chapter 3. The results of base and acid cleaning tests carried out with PBM coated membrane prepared with DTAB are shown in Figure 5.11.1.

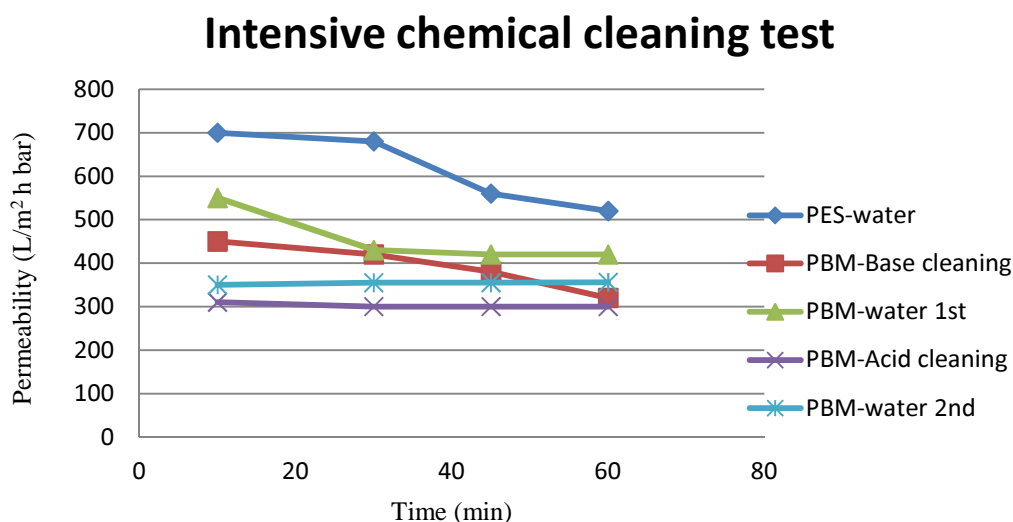


Figure 5.11.1 Base and acid cleaning effect on the permeability of PBM coated membrane

The following procedure was carried out in order to perform the intensive cleaning test:

1. The water permeability of PES commercial membrane was measured and used as a reference;
2. A base cleaning test on the PBM membrane was carried out;
3. The PBM membrane was washed with water (PBM-water 1st)
4. The acid cleaning test on the PBM membrane was carried out;
5. The PBM membrane was finally washed again with water (PBM-water 2nd)

As it was previously reported, the water permeability of PBM coated membrane is lower than that of PES membrane. In fact, the PBM membrane layer on top of PES membrane surface creates an extra resistance layer, which is responsible for the reduction in water permeability compared to pristine PES membrane. Therefore, in case of removal of the PBM layer, the water permeability is supposed to rise up to the value of the original PES membrane. Although the water permeability of PBM coated membranes increased somewhat after base cleaning and acid cleaning, the values went by no means back to the initial water permeability values of PES membrane. This suggested that the PBM coating was still present on the commercial PES membrane. This experiment proved the stability of the PBM coating even under intensive chemical cleaning.

5.12 Salt rejection tests

The rejection towards two different salts (MgSO_4 and NaCl) was evaluated for PES commercial and PBM membranes. A negligible rejection of salts was observed for PES membrane and also for PBM membranes prepared with both surfactants at the optimal microemulsion composition (as reported in Chapter 4, Table 4.2.2). This aspect was of particular relevance since the permeation of salts through the membrane enables an enhancement of biological degradation in the MBR process (where PBM membranes have been applied). In fact the high concentration of salts in the reactor, may decrease the biodegradation of the sludge resulting in toxic disposal. Literature results indicate that high salinity greatly affects the physical and biochemical properties of activated sludge, as well as decreasing membrane permeability [13]. Furthermore, the filtrate produced by MBR treatment was not demineralized, offering therefore an opportunity for the subsequent production of drinking water.

Nevertheless, when more dense PBM coated membranes were produced with the surfactant DTAB (at the higher temperature of 30°C) the rejection toward salts was very high as shown in Figure 5.12.1.

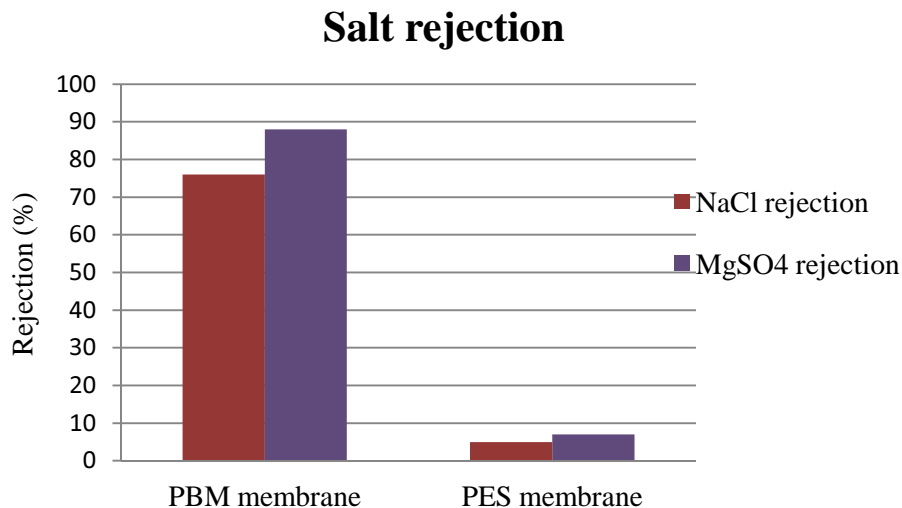


Figure 5.12.1 Salt rejection of PBM and PES membrane

From the graph it can be noticed that for PBM coated membranes a rejection of about 75% for NaCl and about 90% for MgSO₄ was achieved in comparison to commercial PES membranes where the salt rejection was lower than 10% for both salts. The rejection for MgSO₄ is generally higher in comparison to NaCl due to its bigger molecular structure.

5.13 Conclusions

Characterisation tests carried out on PBM membranes prepared with both surfactants (AUTEAB and DTAB), allowed to investigate their morphology and performances.

It is clearly proved that the bicontinuous structure, under specific conditions of microemulsion composition, was maintained after the polymerisation as demonstrated by SEM analyses. The smoother surface of PBM coated membranes, in comparison to commercial PES membranes, was determined by AFM analyses. Roughness measurements as well as contact angles are considered important aspects contributing to the antifouling property of the novel membrane coating. PBM coated membranes prepared with both surfactants showed better resistance to fouling in comparison to commercial PES membranes when treated with HA and with a model dyes solutions. This is due to the very smooth and hydrophilic surface of the PBM coating produced. This resulted in a longer lifecycle of PBM membranes in comparison to uncoated membranes. PBM membranes resulted very resistant to chemical and acid treatment offering the opportunity of chemical cleaning without significant damages to the PBM coating layer. Notwithstanding the lower water permeability, PBM

membranes showed a more constant water flux in time and a higher rejection toward organic compounds. Furthermore, the proved antimicrobial activity was of great interest in preventing the biofouling phenomenon occurring during many membrane operations such as MBR. The AUTEAB surfactant, in particular, due to the possibility of polymerisation within the microemulsion, was selected and successfully applied for the scaling-up of PBM membranes used for the preparation of an MBR module. In the next chapter, the results obtained with an MBR process for the treatment of model textile wastewater are reported.

5.14 References

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Chapter 6

Application of the novel PBM membranes: pilot-scale tests

The novel hydrophilic coated PBM membranes showed their great potential in water treatment (Chapter 5) and they will be tested in water purification by Membrane Bioreactor (MBR). In particular, their relevant antifouling properties, antimicrobial activity and the possibility of tuning the membrane structure make the PBM membranes ideal candidates to be tested in an MBR process. PBM membranes prepared with AUTEAB, at the optimal composition found, have been selected for submerged aerobic MBR experiments.

Today, the textile industry is responsible for a substantial share of water usage and wastewater production worldwide. Different organic compounds, such as dyes and detergents, as well as inorganic solids, such as heavy metals and salts, can be encountered in wastewater effluents originating from the textile industry. It is essential, for this reason, to treat the wastewater for further reutilisation within the industrial process and before its final discharge, as per the more stringent regulations recently adopted by the European Union. A model textile dye solution containing two dyes (Acid Red 4 and Remazol Brilliant Blue) was used as model wastewater. PBM membrane performances in terms of COD (carbon oxygen demand), permeability, trans-membrane pressure (TMP), oxygen consumption, aeration rate and dye rejection were evaluated.

The MBR system with commercial PES membranes was run for more than 6 months. During the period of the experiment, the membrane module was first cleaned and then replaced due to a drastic decrease in membrane performances caused by the excessive fouling. The same procedure was carried out with coated PBM membranes. In this case, too, the MBR system was run for more than 6 months, during which no cleaning or membrane replacement (due to fouling or loss in performance) was needed.

The results obtained with either membranes are compared in the following paragraphs.

All the experiments performed with MBR were carried out in collaboration with the Karlsruhe University of Applied Sciences (HSKA, Germany) under the supervision of Prof. Jan Hoinkis.

6.1 PBM membranes scale-up

PBM membranes were first produced on a smaller scale (about 15x15 cm) in order to be characterized at laboratory level. Afterwards, in order to be tested in an MBR system, PBM

membranes were scaled up and prepared with a 30x30 cm dimension. The membranes prepared were assembled in a module made up of 6 flat-sheet membranes where two membranes were glued together by lamination. The active area of the overall module was 0.33 m². The modules were prepared at Microdyn Nadir Company in Germany.

The module produced (Figure 6.1.1) was tested in submerged MBR with a model textile wastewater. The same operation was carried out with commercial PES membranes and the results were compared under identical operating conditions.

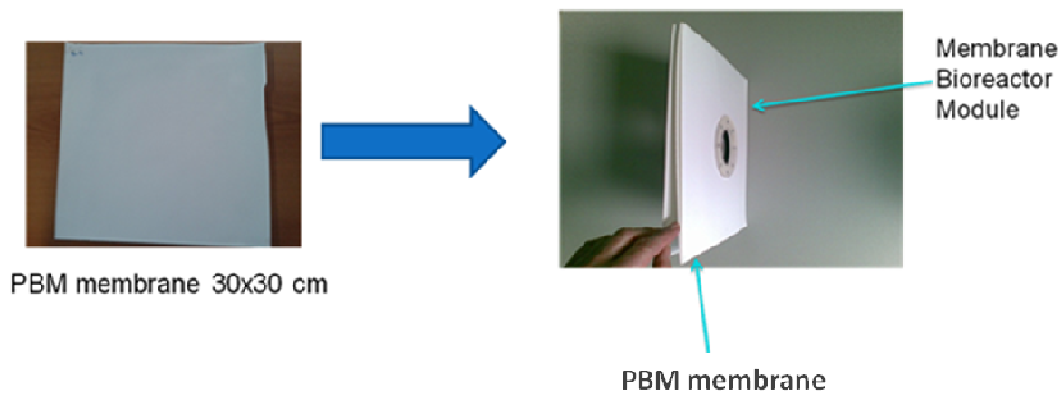


Figure 6.1.1 From flat-sheet membrane to MBR module

The textile wastewater usually contains azo and anthraquinone dyes that can originate benzoic groups, which are carcinogenic and can cause problems to the photosynthesis of the aquatic plants. For this reason, in order to reproduce textile wastewater, two dyes, with the chemical characteristics above mentioned, were used: one from the azo group (Acid Red 4) and one from the anthraquinone group (Remzol Brilliant Blue).

The two applied dyes used for textile wastewater formulation have the following molecular structure:

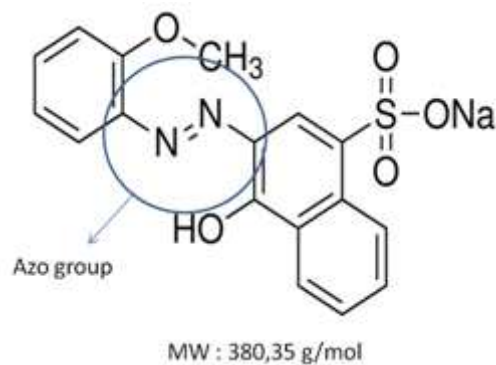


Figure 6.1.2 Molecular structure of Acid Red 4

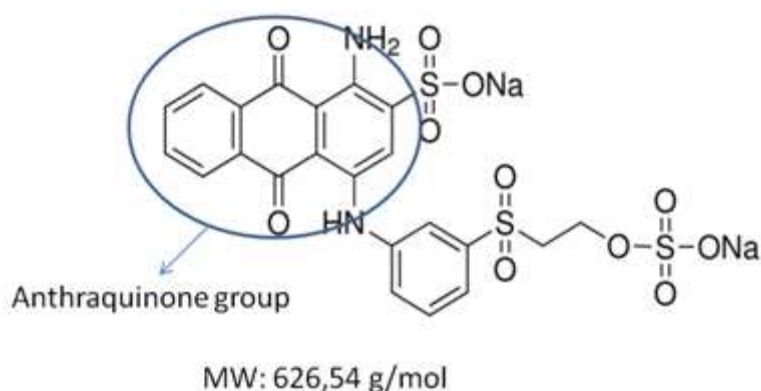


Figure 6.1.3 Molecular structure of Remazol Brilliant Blue

These reactive dyes are able to bind their substrates by a chemical reaction forming covalent bonds between the dye and the fibers. In particular the azo dyes, such as Acid Red 4, are very difficult to break down due to the presence of the very stable azo bond (R-N=N-R'). They are also very stable in acidic and alkaline conditions and resistant to high temperatures and light.

After azo dyes, anthraquinone dyes (such as Remazol Brilliant Blue) are used extensively in the textile industry due to their variety of colour shades and easyness of application.

6.2 Membrane bioreactor (MBR) results

Commercial PES membranes

- Permeability and TMP

Permeability and trans-membrane pressure (TMP) are two of the main parameters in an MBR system, describing the productivity of the process.

From MBR results, PES commercial membrane permeability was almost constant (Figure 6.2.1) for the first 3 months (140-160 L/m² h bar), then a rapid decrease in permeability (due to membrane fouling) was observed (10-40 L/m² h bar). The module was, then, cleaned and reinstalled with a regain in permeability (50 L/m² h bar) . After another month (about 4 months and half in total), the module was cleaned again due to the very low permeability (10 L/m² h bar) and finally it was totally replaced. At the beginning of the process, the water permeability was very high due to the fact that model textile dye wastewater composition was not completely formed. Real conditions were created gradually during the first three months (by adding step by step both dyes and detergents). The average of the PES membrane's permeability during the period of experiment was about 60 L/m² h bar.

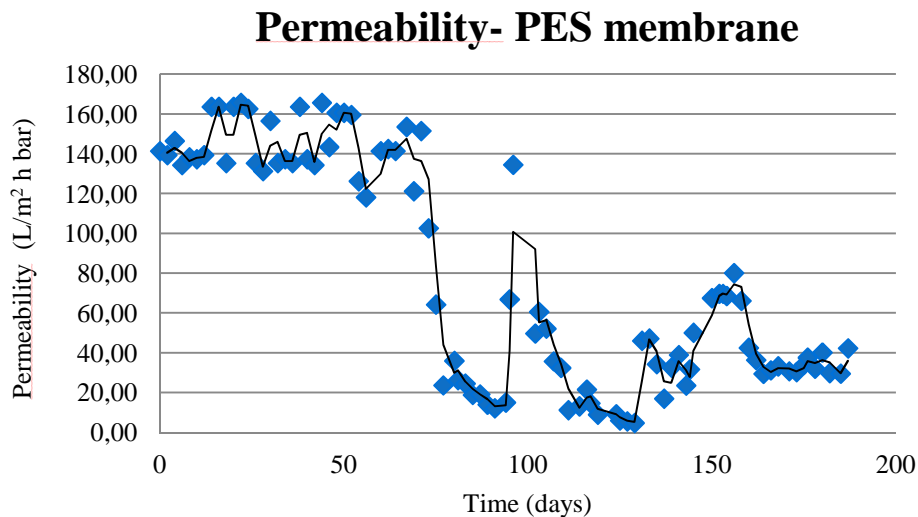


Figure 6.2.1 Permeability of commercial PES membrane

TMP, as shown in figure 6.2.2, is strictly related to permeability. TMP is the pressure (in mbar) across the membrane and gives a indirect indication of the extent of fouling insurgence. As TMP increases, due to the pores occlusion of the membrane, a consequent reduction of permeability was observed.

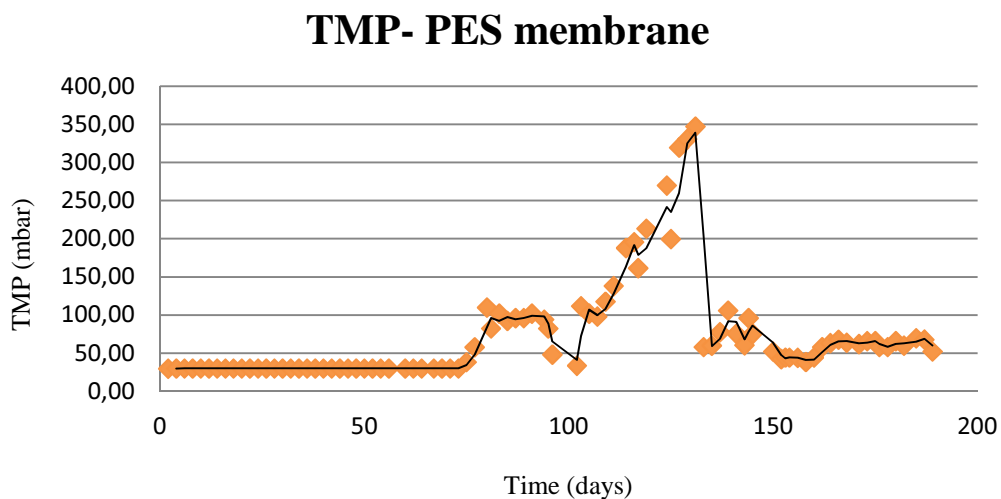


Figure 6.2.2 TMP of PES commercial membrane

During the first 3 months of the experiment, the TMP value was constant at about 40 mbar. When fouling started to affect the membrane's surface, however, an increase in TMP was observed. When TMP reached 100 mbar, in order to re-establish the flux, the membranes were cleaned using a cleaning protocol. A decrease in TMP, that returned to the initial value, was, then, observed.

However, after a few more days, a sharp increase in TMP (more than 300 mbar) forced to remove the module from the submerged MBR and to replace the membranes.

- COD reduction

COD is one the parameters that allows to define the performance of an MBR system in terms of biodegradability. COD is used to measure the amount of organic matter in water and represents a very useful method for the determination of the water quality. The lower is the COD value the higher is the water quality. It essentially depends on the biological activity of the bacteria (responsible for the degradation of the organic compounds) and on the performances of the membranes applied. The amount of COD was measured both in the feed and in the permeate. Then the percent reduction was calculated and plotted in the graph below (Figure 6.2.3).

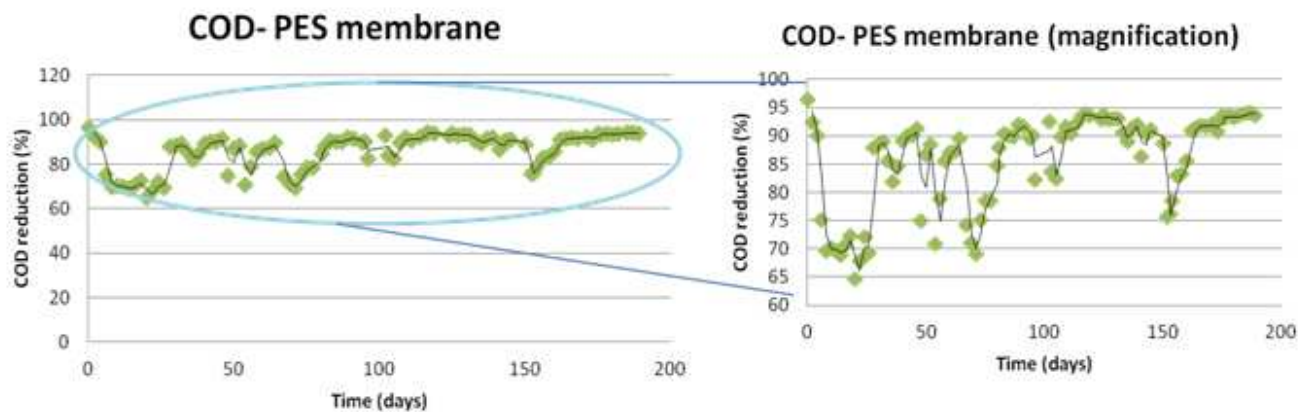


Figure 6.2.3 COD reduction of commercial PES membrane with magnification

As Figure 6.2.3 shows, the COD was fluctuating during the first period due to the acclimation of bacteria to the set conditions of the MBR. After about one month the COD reduction stabilised at about 90%. After 3 months, due to the fouling effect, already observed in the permeability and TMP graph, the COD reduction decreased to 70%. After the module was replaced, the COD reduction was almost constant for the rest of the period (at approximately 93%). The average of COD for PES membrane reduction was about 90%.

- Aeration and oxygen consumption

The aeration has two important effects in an MBR system: it creates a cross-flow of air at membrane surface working as a cleaner, thus avoiding the deposition of substances and removing

those already deposited, and it supplies oxygen for bacteria survival. It represents one of the most costly aspects of the MBR process.

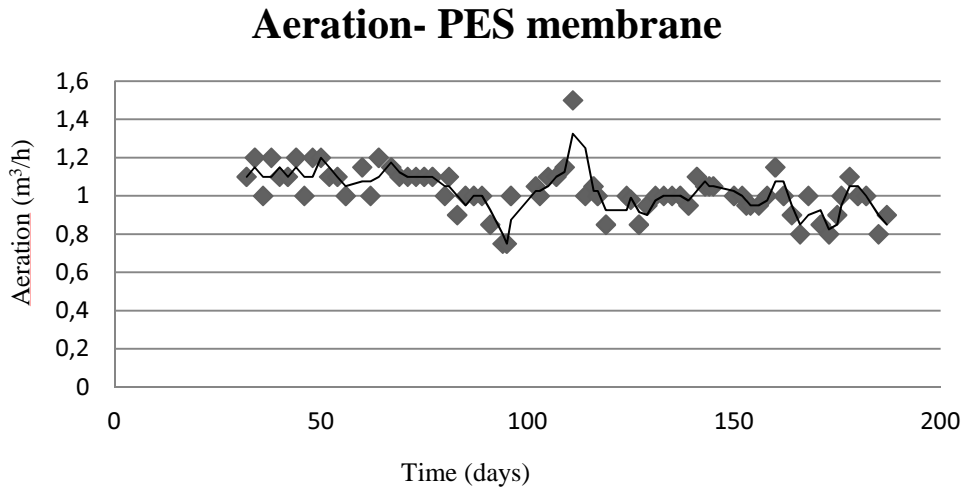


Figure 6.2.4 Aeration rate in the reactor

As shown in Figure 6.2.4, the aeration was maintained between 0.9 and 1.2 m³/h for the overall period, in order to provide the sufficient amount of oxygen to microorganisms and to prevent fouling at membrane surface.

The oxygen consumption, shown in Figure 6.2.5, represents a proxy for the biological activity of the bacteria. The oxygen consumption for PES membranes ranged between 0.1 and 0.5 mg/ L min.

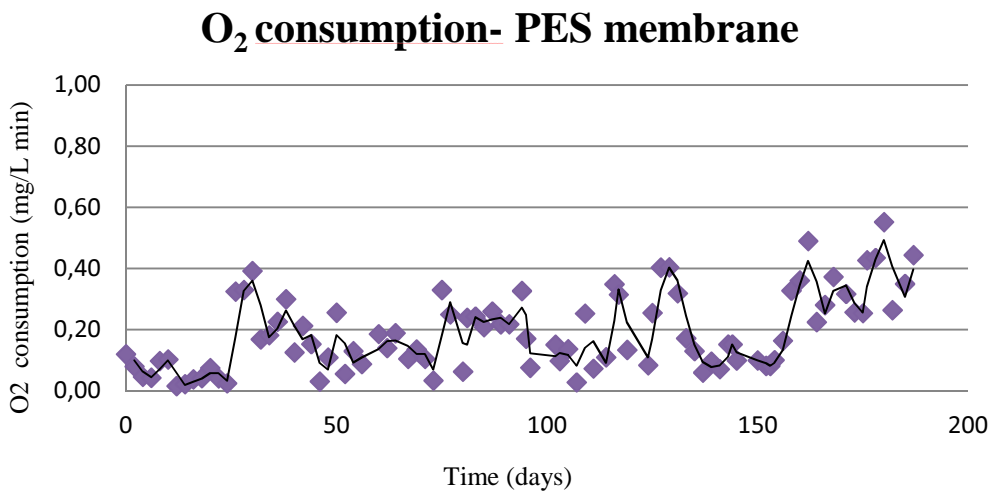


Figure 6.2.5 Oxygen consumption in the reactor

- Dyes rejection

Dye rejection was used in order to evaluate membrane performance in terms of organic compound retention and to evaluate microorganism activity. For commercial PES membranes the rejection to blue dye was very much fluctuating for the first 3 months (10-65 %); then after the fourth month, it was almost stable (about 40 % rejection) and finally decreased during the last month. Red dye rejection was also not constant over time, with a rejection rate ranging between 40-60 %.

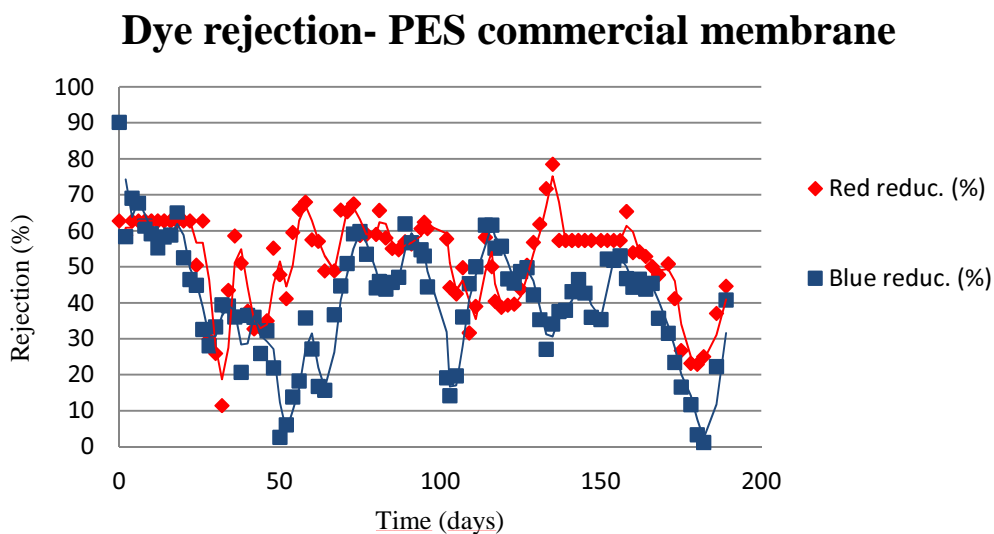


Figure 6.2.6 Dye rejection for PES commercial membranes

Coated PBM membranes

- Permeability and TMP

Coated PBM membranes showed a very constant permeability (Figure 6.2.7) for the first 4 months (35-45 L/m² h bar). After that time, a slight decrease in permeability was observed (20 L/m² h bar) but it was not necessary to clean or replace the membranes during the overall operation time (more than 6 months).

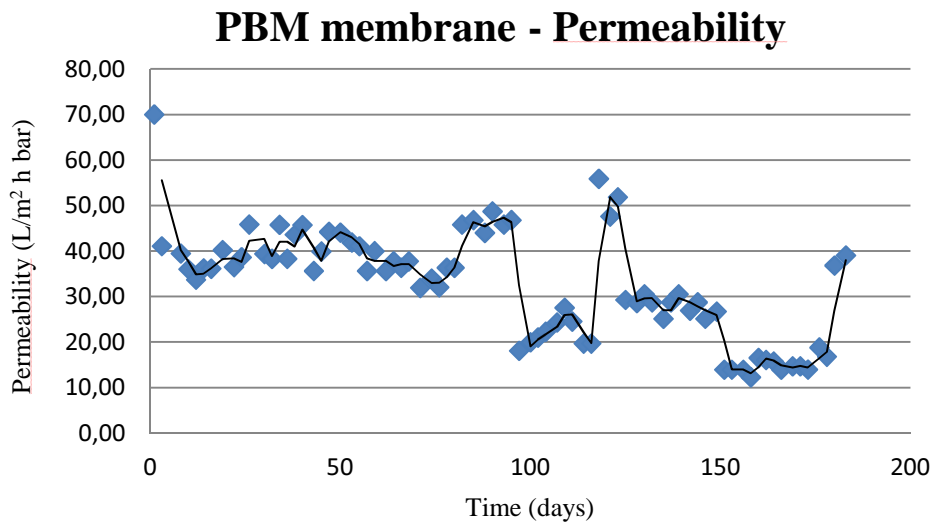


Figure 6.2.7 Permeability of PBM membrane

TMP for PBM membrane was almost constant during the first 3 months (at about 40 mbar). Thanks to PBM's antifouling properties, the values of TMP did not exceed 86 mbar (the peak observed on day 100 was due to a mechanical problem occurred at the set-up).

TMP started to increase after the fifth month due to the intentional decrease of the aeration rate. The aeration rate, as will be explained afterwards, was decreased in order to evaluate the possibility of reducing operation costs, maintaining, at the same time, high standards of filtrate. However, by decreasing the aeration rate, the membranes are more exposed to fouling. Fouling caused an increase in TMP, which was accompanied by a decrease in permeability.

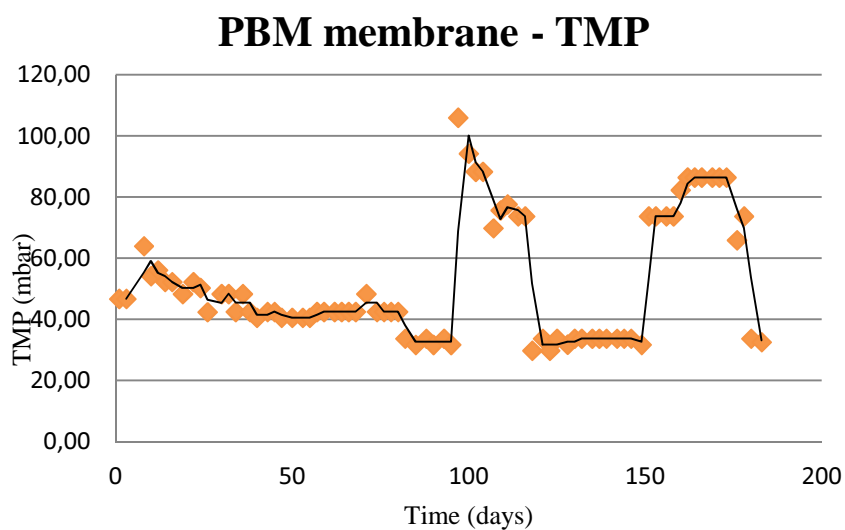


Figure 6.2.8 TMP of PBM membrane

- COD reduction

The COD reduction of PBM membranes increased during the 6 months of experiment. It started from a value of about 90% during the first month. Then, after the acclimation of bacteria, the COD stabilised at about 95-96%.

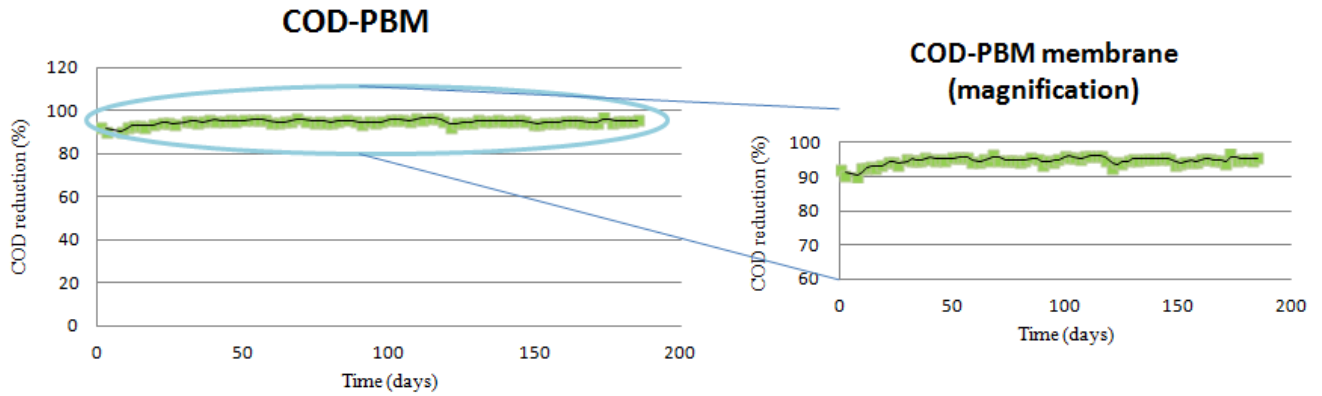


Figure 6.2.9 COD reduction of PBM membrane with magnification

- Aeration and oxygen consumption

The aeration rate for PBM membranes was kept between two ranges (Figure 6.2.10):

- The first range was $1 \pm 0.1 \text{ m}^3/\text{h}$
- The second range was $0.5 \pm 0.05 \text{ m}^3/\text{h}$

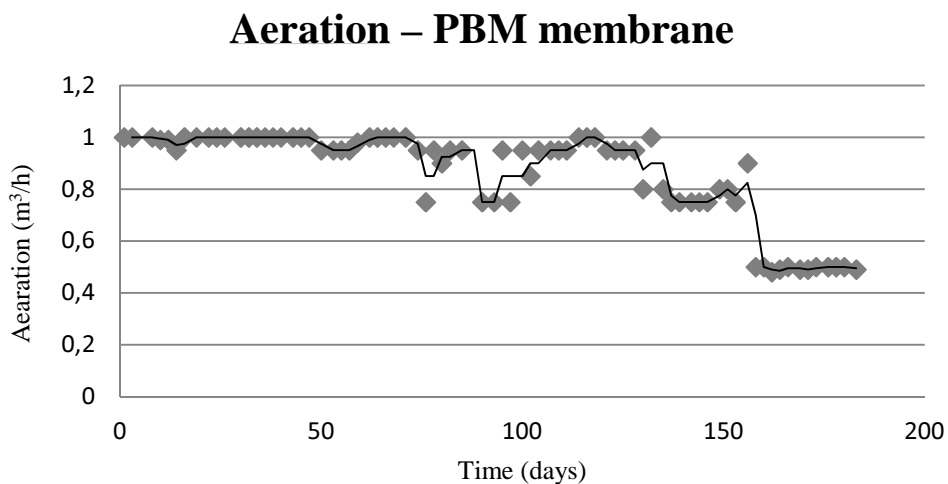


Figure 6.2.10 Aeration rate in the reactor

During the last month of the experiment, the aeration rate, with PBM membranes, was decreased from 1 to 0.5 m³/h, in order to evaluate the possibility of operating with lower energy consumption without drastic effects on membrane performances and permeate quality. It was found that the performances, at this range, were still high with a COD reduction of 96%.

The oxygen consumption for PBM membranes, at the beginning, was comprised between 0.1 and 0.4 mg/L min. After 3 months, a gradual decrease in O₂ consumption was observed (from 0.1 to 0.3 mg/L min), with a further decline during the experiment's last month, due to the intentional decrease of the aeration rate. However, the performances (COD removal efficiency) of PBM membranes in the last stage were still high.

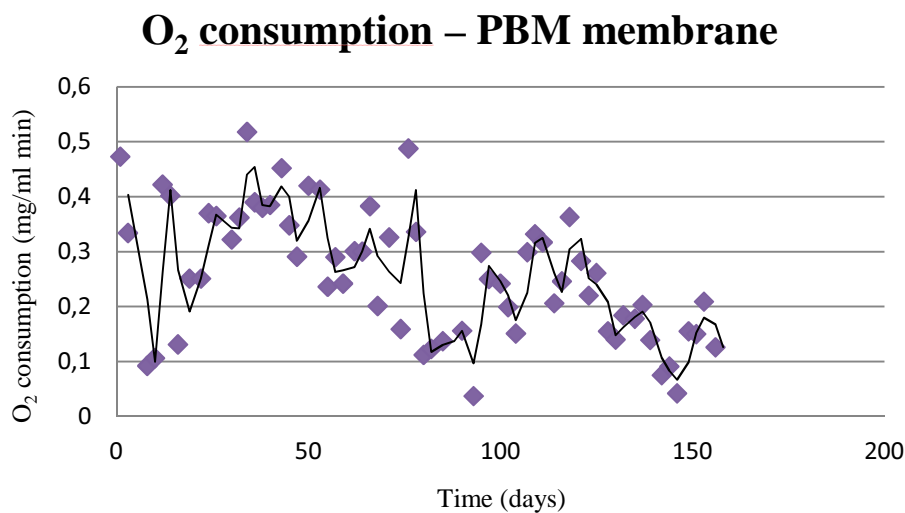


Figure 6.2.11 Oxygen consumption in the reactor

- Dyes rejection

Blue rejection for the first 3 months ranged from 40 to 60% with small variations. Afterwards, blue rejection increased up to 80% and it was almost constant for the overall period (about 70%). The fluctuation of the first 3 months was linked to the acclimation phase of bacteria to the reactor conditions. The rate of red rejection was more fluctuating, from 20 to 80% for the overall period.

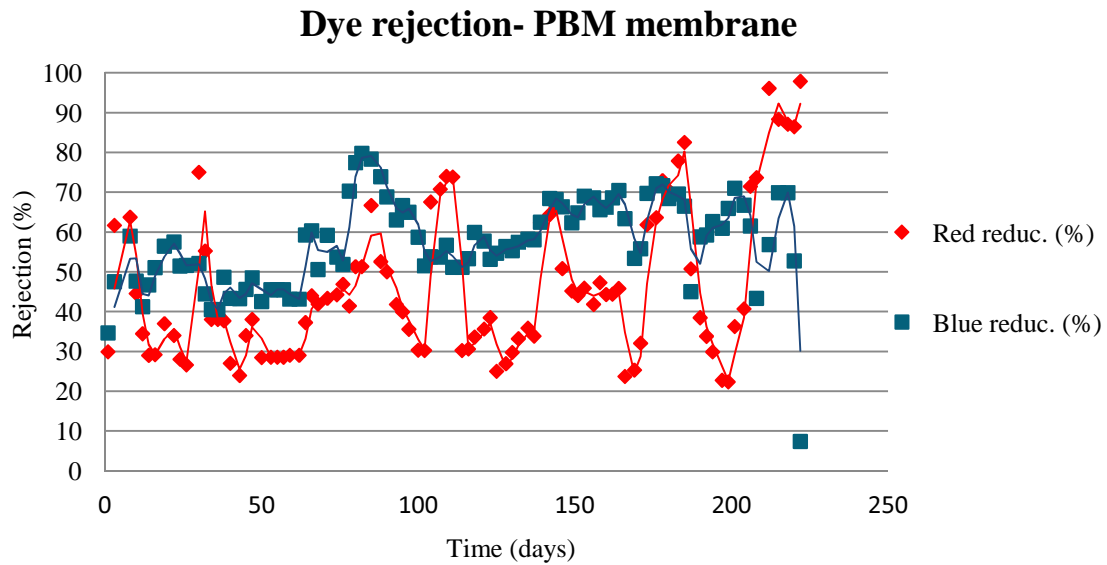


Figure 6.2.12 Dye rejection for PES commercial membranes

Comparison between PES and PBM membranes

After 6 months of MBR experiments, the results obtained with both membranes were compared and reported below:

- Permeability and TMP

As regards permeability PES membranes ranked higher, in particular during the first 3 months of the experiment, during which the real conditions of MBR process were gradually set. A sharp decrease in permeability was then observed and a cleaning process and a subsequent replacement of the membrane module was needed after the third month of the experiment. The permeability of PES commercial membranes was about 60 L/m² ha bar. PBM membranes showed, on the contrary, a very constant permeability over time for the entire period examined. A permeability of about 40 L/m² h bar was achieved with a slight decrease during the last month.

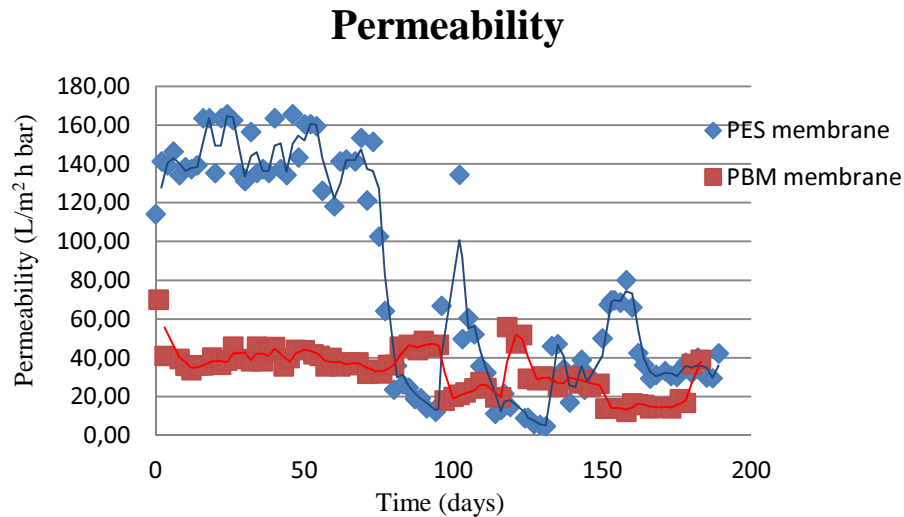
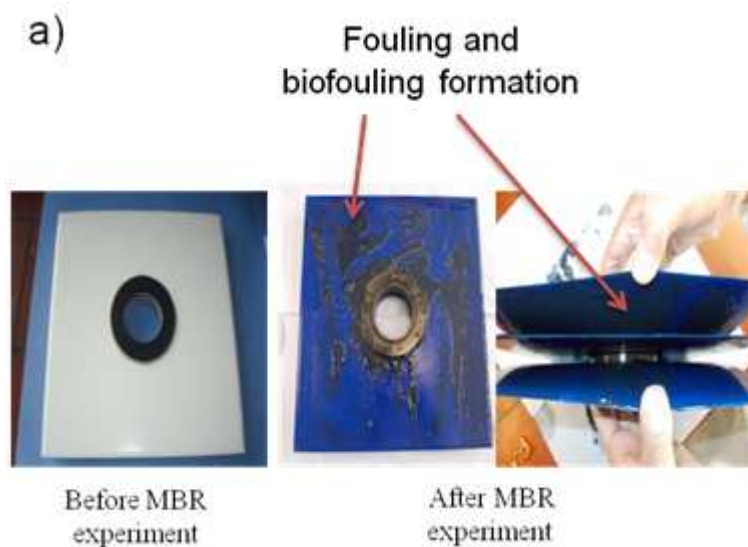


Figure 6.2.13 Permeability of commercial PES and coated PBM membrane

Based on the results obtained, it can be stated that PBM coated membranes were more resistant to the fouling and biofouling phenomenon (as previously demonstrated by the several characterization tests reported in Chapter 5). For this reason, no cleaning and no replacement of the membranes was needed during the MBR experiment and a very constant permeability over time was recorded.

In Figure 6.2.14, the modules of commercial PES (Figure a) and coated PBM membranes (Figure b) after treatment with MBR are shown.



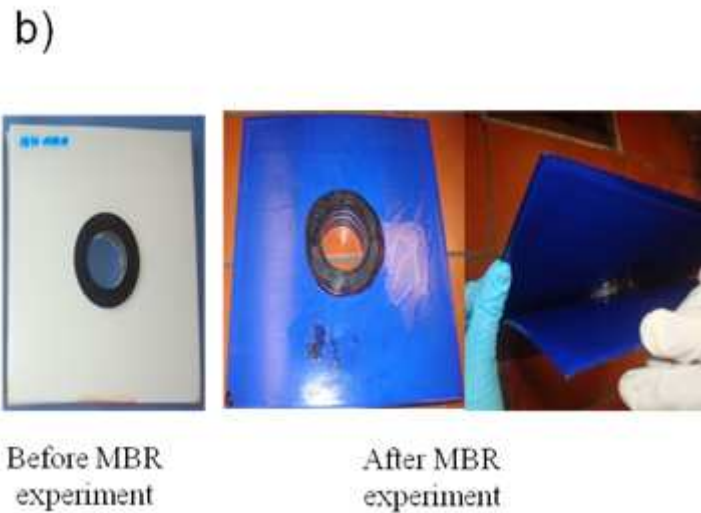


Figure 6.2.14 PES (a) and PBM (b) module before and after MBR treatment

Dark layers owing to the fouling deposition and biofouling formation are clearly visible at PES membrane surface (Figure 6.2.14 a). PBM membranes, on the contrary, showed a lower propensity to fouling due to the antifouling and anti-biofouling properties, owing to the smoother surface, higher hydrophilic moiety, antimicrobial activity and channel-like structure.

The antimicrobial activity at the surface of PES and PBM membranes was also evaluated after 6 months running in MBR in order to check if PBM membranes still maintained their antimicrobial activity. Figure 6.2.15 shows the pictures of film samples after subjection to 3h of preincubation followed by overnight incubation on Mueller Hinton agar plates at 37°C.

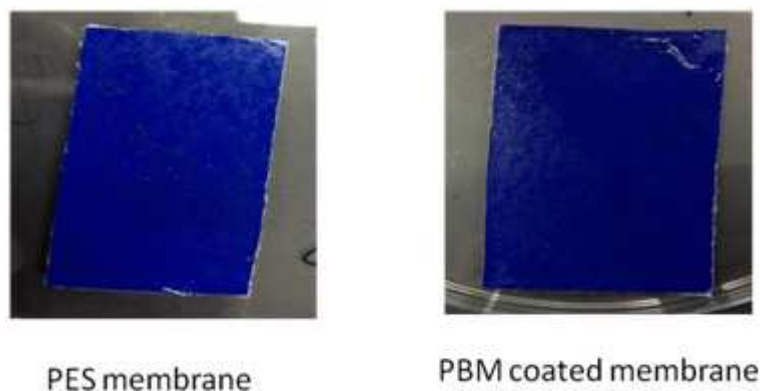


Figure 6.2.15 PES and PBM membrane antimicrobial activity test after MBR experiment

The surface of the PES membrane was covered with bacteria while no bacteria growth was observed on the surface of the PBM membrane. This result indicated that PBM membranes still maintained their antimicrobial activity exhibited by the cationic surfactant AUTEAB copolymerized within the PBM matrix.

The TMP of PES and PBM coated membranes is shown in Figure 6.2.16.

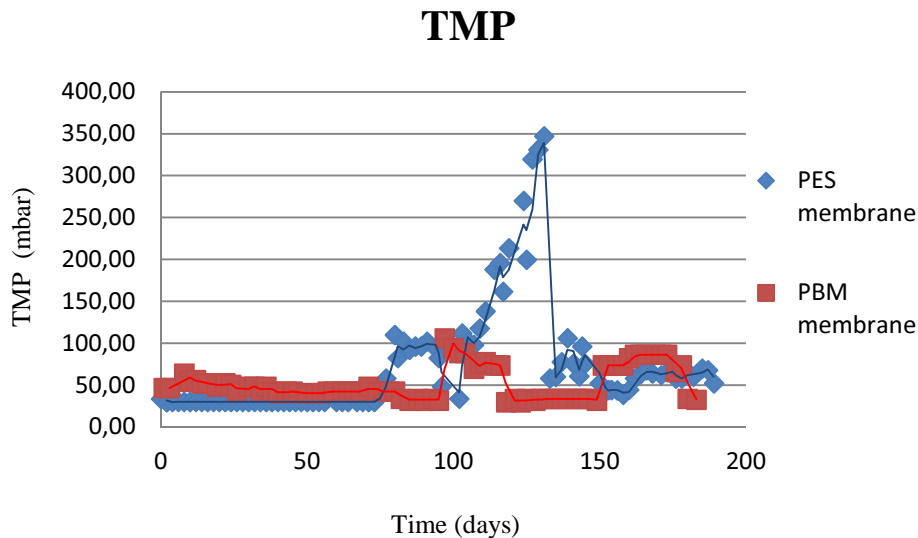


Figure 6.2.16 TMP of PES and PBM coated membrane

TMP was almost constant for both membranes during the first 3 months. A drastic increase in TMP was observed for the PES membrane after 3 months (100 mbar) due to the fouling formation. At this point the membrane was cleaned and reinstalled. However, after a short period, the full replacement of the module was needed due to a new increase in TMP (350 mbar).

The TMP for PBM membranes was more constant in time (50 mbar) with narrower fluctuation during the overall period of experiment.

- COD reduction

The COD reduction for both membranes is plotted in the graph 6.2.17.

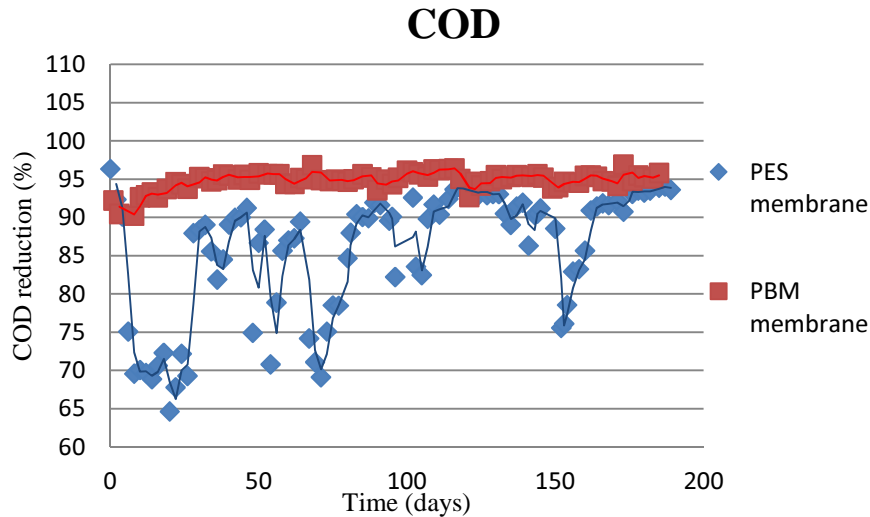


Figure 6.2.17 COD reduction of PES and PBM coated membrane

COD reduction for PBM membranes was constant and high during the overall period with an average of reduction of about 96%. In the case of PES membranes, the COD reduction was not constant, ranging from 70% to 95% (with an average of 90%). The high value of COD reduction obtained with PBM membranes is an indication of the healthy conditions of bacteria and of the better performances of PBM membranes in comparison to commercial ones.

- Aeration and oxygen consumption

Aeration and oxygen consumption for both membranes is plotted in Figures 6.2.18 and Figure 6.2.19.

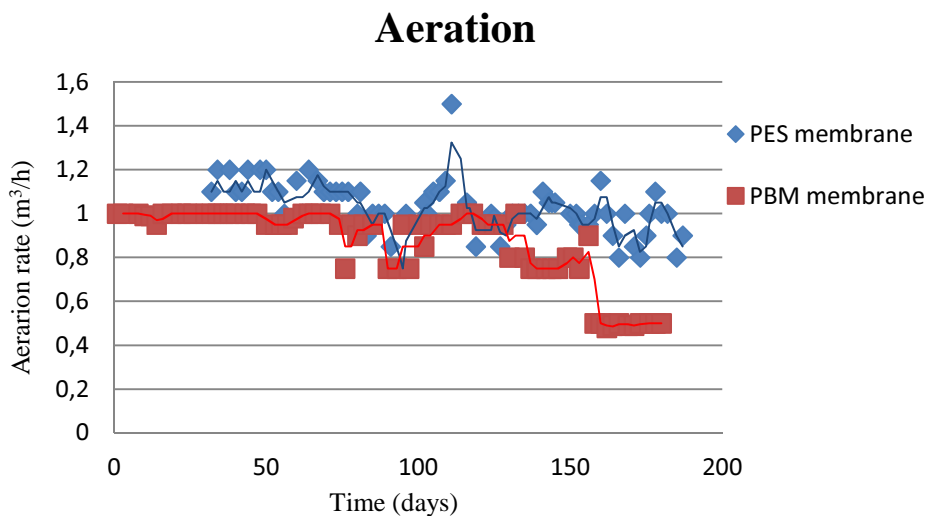


Figure 6.2.18 Aeration of the reactor for PES and PBM coated membranes

As it can be seen in Figure 6.2.18, the aeration rate was higher in the case of PES membranes in comparison to PBM membranes. PBM membranes, in fact, showed the possibility to work at lower aeration rates maintaining, at the same time, good performances in terms of permeability and COD reduction. Furthermore, during the last month, the aeration was further decreased from 0.8 m³/h to 0.5 m³/h with no effects on COD reduction. This means that the constant process observed in PBM membranes induces less stress on microorganisms, so that they can carry out their work even at lower oxygen concentration. This aspect is very important since aeration has one of the biggest impact in terms of costs on MBR process.

The oxygen consumption is the oxygen consumed by microorganisms for enabling their degradation work. It was measured at regular intervals and the results are shown in Figure 6.2.19.

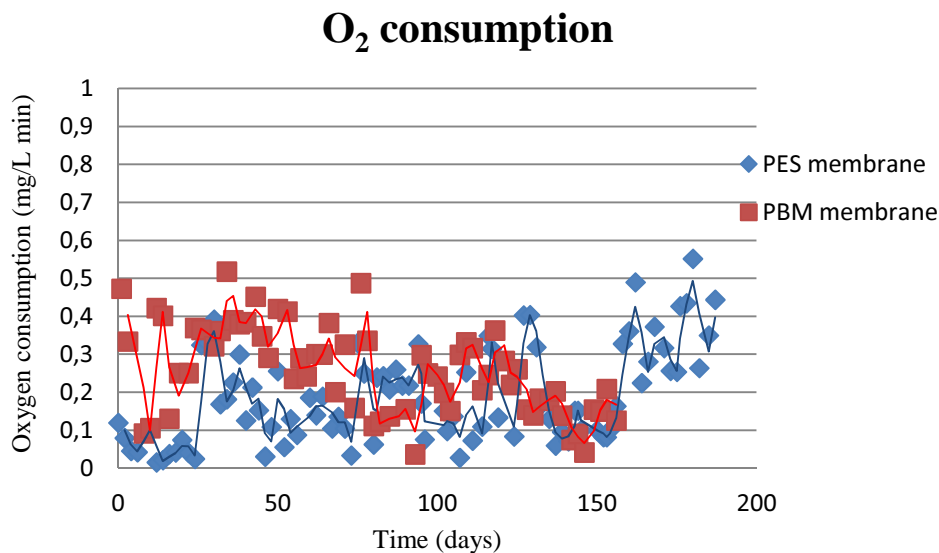


Figure 6.2.19 Aeration of the reactor for PES and PBM coated membranes

For both types of membranes the oxygen consumption ranged from 0.05 to 0.5 mg/L min. In particular, for PBM membranes a decrease in time of oxygen consumption was observed especially during the last month when the aeration rate was intentionally decreased. Nevertheless, good results were obtained and no stress for bacteria, due to the less oxygen available, was observed.

- Dye rejection (Red)

Red rejection was very fluctuating for both membranes. Acid Red 4 dye is a small molecule that could easily permeate through the membranes, giving a similar rejection of about 50% for both

membranes. Furthermore the presence, in the chemical structure, of an azo group makes it more resistant to be degraded by microorganisms.

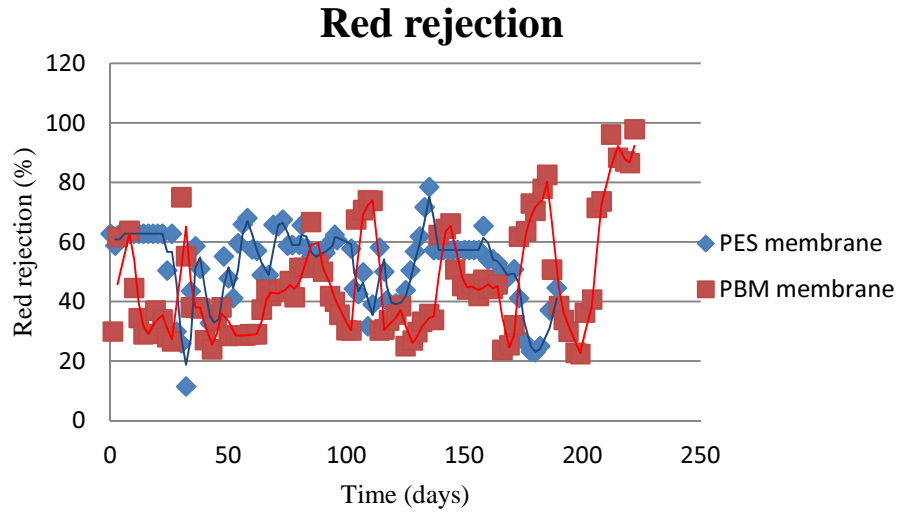


Figure 6.2.20 Aeration of the reactor for PES and PBM coated membranes

- Dye rejection (Blue)

In case of Remazol Brilliant Blue, on the contrary, a clear difference in rejection was observed by comparing both membranes (Figure 6.2.21).

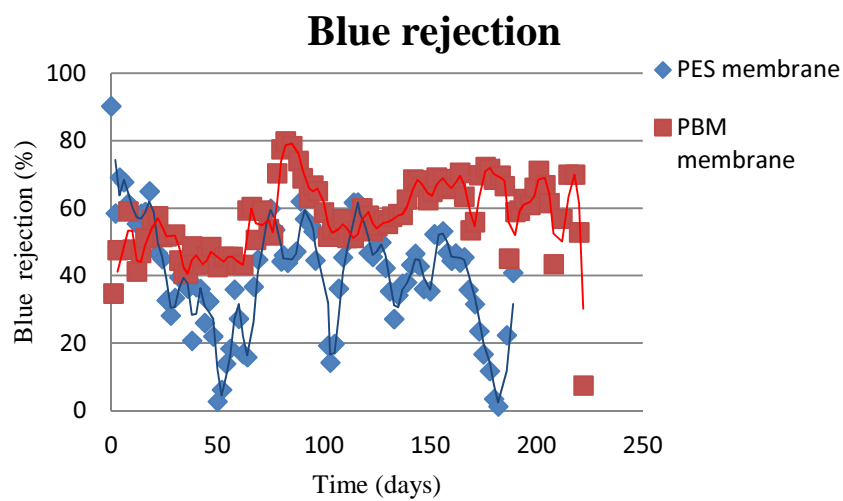


Figure 6.2.21 Aeration of the reactor for PES and PBM coated membranes

PBM coated membranes presented a Blue rejection about 20% higher than PES commercial membranes. Remazol Brilliant Blue has a higher molecular weight in comparison to Acid Red 4 and its chemical hindrance is more pronounced. For this reason, its rejection was more enhanced. PBM membranes, due to their denser structure, in comparison to commercial PES membranes, showed, thus, better performances in rejection.

6.3 Conclusions

MBR results showed some clear benefits of using the novel PBM coated membranes in comparison to uncoated commercial PES membranes. The intrinsic antimicrobial activity (due to the presence of a cationic surfactant) made the PBM membranes highly resistant to biofouling and ideally applicable to a membrane bioreactor (MBR) process where a biological sludge is used. The constant water permeability was an indirect proof of membrane resistance to biofouling. Furthermore, no evidence of formation of microorganisms colonies was observed on the PBM membrane surface after their removal from the MBR. From MBR tests it was demonstrated how the lifecycle of PBM membranes was significantly enhanced in comparison to uncoated membranes. Furthermore, less cleaning efforts (due to the anti-fouling and anti-biofouling properties) were required, reducing, consequently, the related costs. A constant water permeability over time and a good rejection of organic compounds were important benefits achieved by PBM membranes. An increase in the efficiency and durability of the membrane was also obtained. The good quality of the filtrate was proved by COD rejection that was higher than 96% for PBM membranes in comparison to about 90% for commercial PES membranes. Moreover, due to antifouling properties, PBM membranes required a lower aeration rate, thus allowing a reduction in operation costs.

Chapter 7

Conclusions

The main goal of this thesis was to produce hydrophilic membranes by the polymerisation of polymerisable bicontinuous microemulsions (PBM) applied as coating material on PES commercial ultrafiltration membranes. PBM coated membranes were, then, characterised and assembled in modules to be used for textile wastewater treatment in MBR technology. The wastewater treatment represents nowadays an important opportunity within the logic of sustainable water management. Water is essential for the life of all living organisms and its preservation and responsible use is one of the global challenges that humanity will face in the near future.

PBM coated membranes produced present numerous advantages and benefits that can make them very attractive not only from a scientific and speculative viewpoint but also for the real potential application in water treatment. Main objectives attained and the outstanding benefits obtained by applying PBM membranes to an MBR technology are summarised here below:

- Bicontinuous microemulsions were successfully prepared with both surfactants. The optimal microemulsion composition and the best operating conditions were found;
- The pore size of the PBM membranes produced can be fine-tuned by modifying the temperature of the microemulsion polymerization and its chemical composition. Thanks to this property, membranes with different pore size can be obtained, enabling their application to several membrane processes (from microfiltration to nanofiltration);
- PBM membranes were successfully cast and polymerised on PES commercial membranes in order to form a thin coating layer;
- The existence of a bicontinuous microstructure was revealed by SEM analyses. This was a direct evidence that the microemulsion was polymerised in the bicontinuous state;
- Nanoparticles were dispersed into the microemulsion and incorporated by polymerization within the membrane's matrix, so to obtain functional materials giving specific properties to the final membrane;
- The fouling phenomenon (as demonstrated by humic acid and model dyes rejection tests) was drastically reduced thanks to the very smooth and hydrophilic surface of the coating produced, as determined by roughness and contact angle measurements, respectively;
- The intrinsic antimicrobial activity (due to the presence of a cationic surfactant) made the PBM membranes highly resistant to the biofouling phenomenon and ideally applicable to MBR

processes where a biological sludge is used;

- MBR tests demonstrated how the lifecycle of commercial PES membranes was significantly enhanced coating them with a PBM. Furthermore, less cleaning efforts (due to the anti-fouling and anti-biofouling properties) were required, leading to a reduction in maintenance costs;
- A time-constant water permeability and a good rejection to organic compounds were additional important benefits achieved by PBM coated membranes. An increase in the efficiency and in the lifetime of the membrane was also recorded. The good quality of the filtrate (permeate) was proved by a COD rejection that was higher than 96% for PBM membranes in comparison to about 90% for commercial membranes;
- Due to antifouling properties, PBM coated membranes required a lower aeration rate, saving operation costs;
- A lab scale module prototype was developed and successfully tested for model textile wastewater treatment attesting the effective possibility of PBM coated membrane to be scaled-up;
- The developed PBM coated membranes applied in the MBR technology can help to protect the natural resources and contribute to a sustainable development and improved living conditions of human communities, particularly in North-African and Middle-Eastern countries where the need of fresh water becomes ever more pressing.

List of publications and seminars

Patent

- The patent application has been filed on 27/09/2013 with the application number IT GE2013A000096

A. Figoli, J. Hoinkis, B. Gabriele, G. De Luca, F. Galiano, S. A. Deowan, “Bicontinuous microemulsion polymerized coating for water treatment”

Books (Chapters)

- A Figoli, P Vandezande, F Galiano, S Zereshki, “Pervaporation as sustainable process”, in Membrane processes for sustainable growth, Editors by A Basile and A Cassano, Nova publishers, 2013, Chapt 3, 65-100
- A Cassano, A Figoli, F Galiano, P Argurio, R Molinari, “Membrane operations in wastewater treatment: complexation reactions coupled with membranes, pervaporation and membrane bioreactors”, in Handbook of Membrane Reactors, Edited by A Basile 2013, Woodhead Publishing Limited, Chapter 19, 729-760

Articles

- S Simone, A Figoli, S Santoro, F Galiano, S M Alfadul, O A Al-Harbi, E Drioli, “Preparation and characterization of ECTFE solvent resistant membranes and their application in pervaporation of toluene/water mixture”, Separation and Purification Technology 90 (2012) 147-161
- C R Mason, M G Buonomenna, G Golemme, P M Budd, F Galiano, A Figoli, K Friess, V Hynek, “New organophilic mixed matrix membranes derived from a polymer of intrinsic microporosity and silicalite-1”, Polymer 54 (2013) 2222-2230
- S A Deowan, F Galiano, J Hoinkis, A Figoli, E Drioli, “Submerged Membrane Bioreactor (SMBR) for Treatment of Textile Dye Wastewater towards Developing Novel MBR Process”, APCBEE Procedia 5 (2013) 259 – 264

Conference abstracts

- F Galiano, A Figoli, S A Deowan, J Hoinkis, L Veltri, B Gabriele, “PES ultrafiltration modified membranes for wastewater treatment”, Nanomemwater-International conference on application of nanotechnology in membranes for water treatment, 8-10th October 2013, Izmir, Turkey (Poster presentation)
- A Figoli, F Galiano, S A Deowan, J Hoinkis, L Veltri, B. Gabriele, “A new class of functional membranes to lower fouling and improve rejection of pollutants”, Nanomemwater-International conference on application of nanotechnology in membranes for water treatment, 8-10th October 2013, Izmir, Turkey (Oral presentation)
- S A Deowan, F Galiano, L Jahan, S E Bouhadjar, C Aresipathi, B Gabriele, J Hoinkis, A Figoli, E Drioli, “Novel Nano-structured Membrane Materials for Membrane Bioreactor (MBR) Applications”, 2nd Training workshop on “Functionalized membranes for wastewater treatment- nanoparticles and surface modifications”, 15-17th May 2013 Cetraro, Italy (Poster presentation)
- F Galiano, A Figoli, S A Deowan, J Hoinkis, L Veltri, B Gabriele, “Novel hydrophilic membranes for wastewater treatment”, 2nd Training workshop on “Functionalized membranes for wastewater treatment- nanoparticles and surface modifications”, 15-17th May 2013, Cetraro, Italy (Poster presentation)
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- A Figoli, S Santoro, F Galiano, P Bernardo, F Bazzarelli, F Tasselli, J C Jansen, G Clarizia, V G Dzyubenko, P Vdovin, E Drioli, “Ethanol removal from water by Pervaporation using SBS membranes in both flat and spiral wound module configuration”, Workshop : Nanostructured and Nanocomposite Membranes for Gas and Vapour Separations, 15-18th May 2012, Cetraro, Italy (Poster presentation)
- F Galiano, A Figoli, L Veltri, B Gabriele, E Drioli, “Membranes prepared by microemulsion polymerization”, XXVIII Membrane Summer School, 11-15th September 2011, Smardzewice, Poland (Poster Presentation)

Courses and seminars

- “Nanomemwater-International conference on application of nanotechnology in membranes for water treatment”, 8-10th October 2013, Izmir, Turkey
- “Membrane Course for Water Technologies”, 05-06th June 2013, RWTH Aachen, Germany
- “International Scientific Conference on Pervaporation, Vapor Permeation and Membrane Distillation”, Toruń, Poland 12 - 15th May 2013
- “1st WATERBIOTECH conference”, 9-11th October 2012, Il Cairo, Egypt
- “Euromembrane 2012”, Queen Elisabeth II Conference Centre, London, UK, 23-27th September 2012
- “Nanostructured and Nanocomposite Membranes for Gas and Vapour Separations”, 15-18th May 2012, Cetraro, Italy
- XXVIII Membrane Summer School, 11-15th September 2011, Smardzewice, Poland
- “International Conference on Pervaporation, Vapor Permeation and Membrane Distillation”, 8-11th September 2011, Torun, Polonia

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