


DOTTORATO DI RICERCA IN INGEGNERIA CIVILE PER L'AMBIENTE ED IL TERRITORIO
XIV Ciclo - Nuova Serie (2013-2015)
DIPARTIMENTO DI INGEGNERIA CIVILE, UNIVERSITÀ DEGLI STUDI DI SALERNO

ADVANCED MBR PROCESSES FOR WASTEWATER TREATMENT AND ENERGY PRODUCTION

PROCESSI MBR AVANZATI PER IL TRATTAMENTO DELLE ACQUE REFLUE E LA PRODUZIONE DI ENERGIA

ING. LAURA BOREA

Relatore:
PROF. ING. VINCENZO NADDEO

Coordinatore
PROF. ING. VINCENZO BELGIORNO

Correlatore:
PROF. ING. VINCENZO BELGIORNO

In copertina: Wet light glow by Heinz-Trebuth
(https://marketplace.500px.com/photos/133085209/wet-light-glow-by-heinz-trebuth)

ADVANCED MBR PROCESSES FOR WASTEWATER TREATMENT AND ENERGY PRODUCTION

Copyright © 2015 Università degli Studi di Salerno – via Giovanni Paolo, II – 84084 Fisciano (SA), Italy – web: www.unisa.it

Proprietà letteraria, tutti i diritti riservati. La struttura ed il contenuto del presente volume non possono essere riprodotti, neppure parzialmente, salvo espressa autorizzazione. Non ne è altresì consentita la memorizzazione su qualsiasi supporto (magnetico, magnetico-ottico, ottico, cartaceo, etc.).

Benché l'autore abbia curato con la massima attenzione la preparazione del presente volume, Egli declina ogni responsabilità per possibili errori ed omissioni, nonché per eventuali danni dall'uso delle informazione ivi contenute.

A mio padre,
guida ed esempio di vita

CONTENTS

LISTS OF FIGURES

LIST OF TABLES

ABSTRACT

More stringent standards on water quality along with the shortage of water resources have led to the development of advanced wastewater treatment processes, in order to ensure the respect of discharge limits and the reuse of treated water. Membrane bioreactors (MBRs), combining biological processes with membrane filtration, are becoming increasingly popular as wastewater treatment due to their unique advantages such as high effluent quality, low production of excess sludge and small reactor volume. However, membrane fouling is still gaining the research attention for improving the performance of this technology since it still involves high operating costs due to the energy consumption for contrasting this phenomenon. Several factors like the type of influent wastewater, sludge loading rate, sludge age, MLSS concentration and microbial products, such as bound extracellular polymeric substances (bEPS), soluble microbial products (SMP) and, only recently and in few studies, transparent exopolymer particles (TEP), are thought to influence membrane fouling.

Recent studies have proven that the application of electrochemical and bioelectrochemical processes to membrane bioreactors represents a promising technological approach for membrane fouling control. In the last years, electrochemical processes have been applied to membrane bioreactors to limit membrane fouling by integrating these processes into the reactor itself (electro MBR) or applying electrocoagulation as a pre-treatment. These studies, however, did not highlight the mechanisms of nutrient removal, in particular of ammonia compounds, inside the electro membrane bioreactor. Furthermore, the influence of electrochemical processes on activated sludge flocs hydrophobicity and TEP concentration in a membrane bioreactor and the possibility of recovery hydrogen from this system have not been investigated yet.

In wastewater, an internal energy exists which can be extracted as electricity or hydrogen and be used to reduce fouling directly and to lessen input of external energy. Microbial fuel cells (MFCs) and microbial electrolysis cells (MECs) are two types of bioelectrochemical systems (BES) that use exoelectrogenic microbes to produce energy from

wastewater by converting biodegradable organic matter directly into electricity and hydrogen, respectively. Only recently, MBRs have been combined with bioelectrochemical systems (BES), as an internal or external configuration, for cost-effective wastewater remediation, overcoming the problem of high energy consumption of MBR and avoiding dissolved methane that results in anaerobic MBR. However, few studies are available regarding the combination of MBRs with MFCs in an external configuration and they did not assess the main electron transfer mechanism governing the anode electro-active biofilms.

The Ph.D. research project aimed to control fouling in membrane bioreactors and enhance the treatment performance through the integration of electrochemical and bioelectrochemical processes. A further objective was to assess the energy production in the combined systems in terms of electricity and hydrogen.

The experimental activity was divided in following four phases: design and construction of the membrane bioreactor at laboratory scale; integration of electrochemical processes into the membrane bioreactor (electro MBR); application of a microbial fuel cell (MFC), as a down-stream process for treating the excess sludge from a MBR pilot plant; evaluation of the hydrogen production in the electro MBR at anoxic conditions. The first two phases and the last phase of research activity were conducted at the Sanitary Environmental Engineering Division (SEED) of Salerno University (Italy). The third phase was performed for three months at the Laboratory of Chemical and Environmental Engineering (LEQUIA) of the University of Girona (Spain).

Regarding the electro MBR, two intermittent voltage gradients (1 V/cm and 3 V/cm) were applied between two cylindrical perforated electrodes, immersed around a membrane module, with the aim of investigating the treatment performance and the membrane fouling formation. In particular, the impact of electrochemical processes on transmembrane pressure variation over time, on sludge relative hydrophobicity and on TEP, proposed as a new membrane fouling parameter, compared with the conventional precursors such as bEPS and SMP, was investigated. Furthermore, mechanisms of nutrient removal were studied. For comparison purpose, the reactor also operated as a conventional membrane bioreactor. All the results indicate that the integration of electrochemical processes into a membrane bioreactor has the advantage of improving the treatment performance especially in terms of nutrient removal and of reducing membrane fouling through the increase of floc

hydrophobicity up to 71.7%, the decrease of membrane fouling precursors' concentrations and, thus, of membrane fouling rate until to 54.3% at 3 V/cm. The relationship found between the TEP concentration and the membrane fouling rate confirms the applicability of this parameter as membrane fouling indicator.

Closing the electro MBR and working at anoxic conditions like a MEC, hydrogen production was detected in the electro MBR with a maximum volumetric production rate of around 18 $mg(H_2)m^{-3}min^{-1}$, highlighting the possibility of energy production by the combined system.

With reference to the combination of a MFC with a MBR, a potentiostatic controlled microbial fuel cell (MFC) was fed in batch with activated sludge from a membrane bioreactor (MBR), characterized by a different influent total suspended solids (TSS) content, in order to understand the bioelectrochemical response of the system and the impact of the treatment on the sludge characteristics and membrane fouling parameters. An open circuit voltage microbial fuel cell (OCV-MFC) was operated as a control test. Regarding sludge degradation, the MFC showed higher COD removals than the control test and a reduction of the sludge highlighting its stabilization. Electricity production in the MFC increased with the increase in the sludge of the influent COD and TSS content achieving a maximum current density of 2.0 A m^{-2} and a voltage output of 100 mV. The electrochemical characterization indicated that the oxidation of the sludge took place at a formal potential of -0.211 ± 0.040 V vs. SHE with a direct electron transfer (DET) mechanism. An increase of sludge hydrophobicity, a reduction of protein extracellular polymeric substances (EPSp) and carbohydrate soluble microbial product (SMPc), along with an increase of SMPp/SMPc ratio, were obtained in the MFCs which could limit membrane fouling in the case that the treated sludge is recirculated to the MBR reactor. The results observed indicated that sludge reduction, electricity production and a variation of membrane fouling parameters could be obtained in a MFC treating MBR sludge.

Therefore, the combination of membrane bioreactors with electrochemical and bioelectrochemical processes represents an innovative and promising method for the increase of treatment efficiencies, sludge reduction, fouling control and energy production.

SOMMARIO

Normative più restrittive sulla qualità delle acque unitamente alla scarsità della risorsa idrica hanno portato allo sviluppo di processi di trattamento avanzati al fine di garantire il rispetto dei limiti allo scarico ed, al contempo, il riuso delle acque reflue trattate. I bioreattori a membrane (MBRs), combinando i processi di degradazione biologica con la filtrazione su membrane, stanno trovando sempre maggiore applicazione al trattamento delle acque reflue grazie ai vantaggi che li caratterizzano rispetto ai processi convenzionali. Oltre ad un effluente di elevata qualità sostanzialmente disinfettato ed a una ridotta produzione di fanghi, i bioreattori a membrane hanno il vantaggio di ridurre notevolmente gli spazi richiesti grazie al mantenimento di elevate concentrazioni di biomassa all'interno del reattore.
L'attenzione della ricerca scientifica è ancora focalizzata a limitare il fenomento del fouling, ossia il rapido sporcamento delle membrane, al fine di migliorare le performance della tecnologia MBR, a causa degli elevati consumi energetici che caratterizzano tale fenomeno. Differenti fattori influenzano la formazione del fouling di membrana come la tipologia di acque reflue influenti, il fattore di carico organico, l'età del fango, la concentrazione di solidi sospesi nella miscela aerata e i prodotti dell'attività batterica, quali le sostanze polimeriche extracellulari (EPS), i prodotti microbici solubili (SMP) e, recentemente ed in alcuni studi, le particelle esopolimeriche trasparenti (TEP).
Recenti studi hanno dimostrato che l'applicazione di processi elettrochimici e bioelettrochimici ai bioreattori a membrane rappresenta un promettente approccio tecnologico per controllare la formazione del fouling. Negli ultimi anni i processi elettrochimici sono stati applicati ai reattori MBR per limitare il fouling, integrando tali processi direttamente all'interno del bioreattore (elettro MBR) o come pre-trattamento di elettrocoagulazione. Questi studi, tuttavia, non hanno evidenziato i meccanismi di rimozione dei nutrienti ed, in particolare, dei composti ammoniacali, che avvengono all'interno dell'elettro MBR. Inoltre, non è stata ancora investigata l'influenza di tali processi sull'idrofobicità dei fiocchi di fango e sulla concentrazione dei TEP nei bioreattori a

membrane e la possibilità di produrre energia nell'elettro MBR sotto forma di idrogeno.
Nelle acque reflue esiste, difatti, un'energia interna che può essere estratta sotto forma di elettricità o idrogeno ed utilizzata per ridurre direttamente il fouling o per diminuire l'apporto di energia dall'esterno. Le celle a combustibile microbico (MFC) e le celle ad elettrolisi microbica (MEC) sono due sistemi bioelettrochimici (BES) che utilizzano i batteri per produrre energia dalle acque attraverso l'ossidazione e la trasformazione della sostanza organica in energia elettrica e idrogeno gassoso, rispettivamente. Soltanto recentemente gli MBRs sono stati combinati con i processi bioelettrochimici, in una configurazione esterna o interna, al fine di sviluppare un processo efficace dal punto di vista energetico e, pertanto, economico superando i problemi connessi agli elevati consumi energetici degli MBRs ed evitare la dissoluzione del metano che avviene negli MBR anaerobici. Tuttavia, solo alcuni studi riportano la combinazione di MFCs con gli MBRs in configurazione esterna e questi non valutano il principale meccanismo di trasferimento degli elettroni che caratterizza il biofilm elettricamente attivo presente all'anodo.
Il presente progetto di ricerca ha avuto come principale obiettivo il controllo del fouling nei bioreattori a membrane ed il miglioramento delle performance del trattamento attraverso l'applicazione di processi elettrochimici e bioelettrochimici. Ulteriore obiettivo è stata la valutazione della produzione di energia nei sistemi combinati in termini di elettricità e di idrogeno.
L'attività sperimentale è stata suddivisa in quattro fasi: progetto e realizzazione del bioreattore a membrane a scala di laboratorio, integrazione dei processi elettrochimici nel reattore MBR (elettro MBR); l'applicazione di una MFC come post-trattamento del fango proveniente da un impianto pilota MBR e la valutazione della produzione di idrogeno nell'elettro MBR in condizioni anossiche. Le prime due fasi e l'ultima fase dell'attività sperimentale sono state effettuate presso il Laboratorio di Ingegneria Sanitaria Ambientale (SEED) dell'Università di Salerno. La terza fase è stata svolta per un periodo di tre mesi presso il Laboratorio di Ingegneria Chimica Ambientale (LEQUIA) dell'Università di Girona (Spagna).
Per quanto concerne l'elettro MBR, due campi di corrente intermittenti (1 V/cm e 3 V/cm) sono stati applicati tra due elettrodi forati cilindrici e concentrici intorno al modulo di membrane al fine di investigare le

performance del trattamento e la formazione del fouling. In particolare, è stata analizzata l'influenza dei processi elettrochimici sulla variazione della pressione di transmembrana nel tempo, sull'idrofobicità della miscela aerata e sulla concentrazione di TEP, proposto come un nuovo indicatore del fouling in confronto ai suoi precursori convenzionali quali EPS e SMP. Il reattore ha anche operato come bioreattore a membrane convenzionale come test di confronto. I risultati ottenuti indicano che l'integrazione dei processi elettrochimici in un bioreattore a membrane ha il vantaggio di migliorare le performance del trattamento, specialmente per la rimozione dei nutrienti, e di ridurre il fouling attraverso l'incremento dell'idrofobicità, la diminuzione della concentrazione dei suoi precursori e della sua velocità di formazione. La relazione riscontrata tra la concentrazione di TEP e la velocità di formazione del fouling ha confermato l'applicabilità di tale parametro come nuovo indicatore del fouling di membrane.

Chiudendo l'elettro MBR ed operando in condizioni anossiche come una MEC, è stata rilevata una produzione di idrogeno con un tasso massimo di 18 $mg(H_2)m^{-3}min^{-1}$, evidenziando le potenzialità energetiche della combinazione dei due processi.

Per quanto riguarda la combinazione di una MFC con un reattore MBR, una cella controllata potenziostaticamente è stata alimentata in batch con fango attivo MBR caratterizzato da differenti concentrazioni di solidi sospesi totali (SST), al fine di capire la risposta bioelettrochimica del sistema e l'impatto del processo sulle caratteristiche del fango e sui parametri caratteristici del fouling. Una cella a circuito aperto è stata utilizzata come test di controllo. La cella controllata potenziostaticamente ha mostrato maggiori rimozioni del COD rispetto alla cella di controllo ed una riduzione dei solidi sospesi volativi presenti nel fango, evidenziando la sua stabilizzazione. La produzione di elettricità è aumentata all'aumentate nel fango influente del contenuto di COD e TSS raggiungendo un valore massimo dell'intensità di corrente pari a 2.0 A m^{-2} con un voltaggio di 100 mV. La caratterizzazione elettrochimica ha indicato un meccanismo diretto di trasferimento degli elettroni in seguito all'ossidazione della sostanza organica. E' stato, inoltre, riscontrato un incremento dell'idrofobicità del fango, una riduzione degli EPS in termini di proteine (EPSp) e di SMP in termini di carboidrati (SMPc) unitamente ad un incremento del rapporto SMPp/SMPc, fattori che potrebbero limitare il fouling nel caso che il fango trattato venisse ricircolato nel reattore MBR. I risultati osservati

nella MFC alimentata con fango MBR hanno, quindi, mostrato una riduzione del fango, una produzione di elettricità ed una variazione dei parametri caratteristici del fouling.
Pertanto, la combinazione di bioreattori a membrane con processi elettrochimici e bioelettrochimici rappresenta un metodo innovativo e promettente per incrementare le efficienze di rimozione, stabilizzare il fango in eccesso prodotto nel reattore MBR, controllare il fouling e produrre energia dalle acque reflue.

ACKNOWLEDGMENTS

I wish to express my sincere appreciation to those who have contributed to this doctoral thesis and supported me during these three years.
First of all, I would like to thank my advisor and co-advisor, prof. Vincenzo Naddeo and prof. Vincenzo Belgiorno, for believing in my research project, for their support and suggestions and for the insightful discussions about the research. I consider as a great opportunity to have done my doctoral programme under their guidance, learning from their research expertise.
I am also very grateful to prof. Sebastià Puig and the whole LEQUIA research team for welcoming me at the University of Girona, for the help in my research activity and for sharing their knowledge with me.
I also want to thank present and past colleagues of SEED for their support and valuable suggestions: Alessandra C., Anna F., Angela, Anna C., Dina, Giusy, Simona, Tiziano, Davide, Antonino and Stefano. Particularly, I want to thank Paolo for his laboratory assistance and for helping me in the realization of my experimental setup.
Special thanks go to those who shared these years with me, colleagues and even more dear and life-long friends: Alessandra M., Jenny and Roberta.
I owe a lot to my mother and all my family, who encouraged and helped me and longed to see this achievement come true.
Finally, but by no means least, thanks go to Mirco for his almost unbelievable support, encouragement and loving patience.

ABOUT THE AUTHOR

Laura Borea completed her MSc with honors in Environmental Engineering at the University of Salerno discussing a thesis entitled "Wastewater treatment by EGSB reactors and anaerobic ponds". The research activity, related to the MSc thesis, was carried out for 5 months at the Centre for Water Science Institute of Cranfield University (UK). In 2013, she was admitted to the Ph. D. program in Environmental and Civil Engineering at the Department of Civil Engineering of Salerno University. Since then, her research activity has been mainly focusing on wastewater treatment and energy production from wastewater through the innovative combination of membrane bioreactors with electrochemical and bioelectrochemical processes. During the Ph. D., she was a visiting researcher at Laboratory of Chemical and Environmental Engineering (LEQUIA) of University of Girona (Spain). She has been co-advisors of 11 BSc and 3 MSc theses. She is author and co-author of several papers published in national and international journals and conference proceedings.

Laura Borea ha conseguito con lode la laurea specialistica in Ingegneria per l'ambiente ed il territorio nel 2012 presso l'Università degli Studi di Salerno, discutendo una tesi dal titolo "Trattamento delle acque reflue con impianti EGSB e stagni anaerobici", a seguito di un'attività di ricerca svolta presso l'Università di Cranfield (UK). Nel 2013 è stata ammessa al Corso di Dottorato di Ricerca in Ingegneria Civile per l'Ambiente ed il Territorio presso l'Università degli Studi di Salerno. La sua ricerca è focalizzata sul trattamento delle acque reflue e la produzione di energia mediante la combinazione di bioreattori a membrane con processi elettrochimici e bioelettrochimici. Durante il dottorato è stata ricercatrice ospite presso l'Università di Girona (Spagna). È autrice e coautrice di diverse pubblicazioni scientifiche, pubblicate su riviste ed atti di convegni nazionali ed internazionali.

1 INTRODUCTION

The growth in demand and the shortage of water resources along with more stringent effluent regulations have given remarkable impetus to development of advanced technologies for wastewater treatment and reuse. Treatment processes that are reliable, cost efficient and effective in removing a wide range of pollutants are required. One very promising technology involves the utilization of membrane bioreactors (MBRs), which separate the effluent and activated sludge by filtration instead of sedimentation, combining biological processes with membrane filtration. MBRs allow disinfected and high quality effluents, high concentrations of mixed liquor suspended solids (MLSS), low production of excess sludge, high flexibility towards influent fluctuations, improve nitrification and reduce footprint and reactors volume (Lin et al., 2014; Meng et al., 2009). However, membrane fouling represents a major obstacle for the widespread application of membrane bioreactors in wastewater treatment. This phenomena leads to a decrease of membrane permeability over time due to the deposition of soluble and particulate materials which are adsorbed or simply accumulated onto and into the membrane surface during the filtration (Drews, 2010).

Several research has been made to determine in membrane bioreactors the impact on fouling of sludge hydrophobicity (Le-Clech et al., 2006), of "bound" extracellular polymeric substances (bEPS) (Lin et al., 2014) and soluble extracellular polymeric substances (sEPS) or soluble microbial products (SMP) (Drews et al., 2008). Only recently and in a few studies (de la Torre et al., 2010; De la Torre et al., 2008), transparent exopolymer particles (TEP) have been investigated as a new parameter for membrane fouling characterization in membrane bioreactors.

As a result of membrane fouling, the membrane module needs frequent physical and chemical cleaning and supplying of excessive amount of air, increasing energy consumption and operating costs as well as reducing the membrane lifespan. Therefore, over the last years a significant amount of advanced strategies for membrane fouling reduction, in addition to conventional methods, has emerged (Leyva-Díaz et al., 2014; Naddeo et al., 2015a, 2015b).

Recent studies have proven that the integration of electrochemical processes into membrane bioreactors (electro MBR/eMBR) represents an alternative technological approach for membrane fouling control and the increase of the treatment performance. Different electrochemical mechanisms, indeed, occur when a direct current field is applied to a membrane bioreactor such as electrocoagulation, electroosmosis and electrophoresis. Electro-coagulation (EC) could be considered as the main mechanism affecting the removal of organic materials of high fouling potential from the sludge supernatant. Furthermore, the application of the electric field brings the removal of bound water from the microbial flocs electrical double layer due to electroosmosis mechanism, thus increasing sludge dewaterability by decreasing the specific resistance to filtration (Ibeid et al., 2013). Electrophoresis is another electrochemical mechanism for removal of organic materials and reduction of membrane fouling. Indeed, the surface of activated sludge is, generally, negatively charged (Liao et al., 2001; Lee et al., 2003). This means that it may be possible to control the motion of activated sludge by the application of an external electric field, thus controlling membrane fouling (Akamatsu et al., 2010). Electrochemical processes have been applied as a pre-treatment in a separate chamber or integrated directly inside the membrane bioreactor. Although these previously studies have shown the enhancement of treatment efficiencies after the application of the electric field, the mechanisms of nutrient removal, in particular of ammonia compounds, inside the electro membrane bioreactor, have not been highlighted. Furthermore, no papers have been published regarding the influence of electrochemical processes on activated sludge flocs hydrophobicity and TEP concentration in a membrane bioreactor or concerning the possibility of recovery hydrogen from this combined system.

The urgent need to use an energy-efficient and environmental friendly technology for reducing fouling and offsetting the energy consumption deriving from it has also led to the combination of membrane bioreactors with bioelectrochemical systems (BES). Bioelectrochemical systems are a new and promising approach for simultaneously treating wastewater while extracting its internal energy.

Microbial fuel cells (MFCs) and microbial electrolysis cells (MECs) are two types of bioelectrochemical systems (BES) that use exoelectrogenic microbes to produce energy from wastewater by converting biodegradable organic matter directly into electricity and hydrogen,

respectively. Despite the advantages associated with these systems, further treatments are needed before discharging or reusing the effluent of a BES. Therefore, the combination of membrane bioreactors with bioelectrochemical systems (BES) takes advantage of both processes in terms of wastewater treatment and energy recovery. The energy produced can be used for reducing fouling directly and to lessen input of external energy. Recently, different studies have reported about the combination of MFC with MBRs (Ge et al., 2013; Ma et al., 2015; Tian et al., 2015). In most of them, ultrafiltration (UF) membranes have been immersed in the MBR reactor as an internal configuration, even though the external configuration increases the flexibility of the coupled system. However, limited studies are available regarding the combination of MBRs with MFCs in an external configuration and they did not investigate the main electron transfer mechanism governing the anode electro-active biofilms.

1.1 OBJECTIVES

According to what previously reported, the Ph.D. research project aimed to:

- Control fouling in membrane bioreactors and increase the treatment efficiencies through:
  - the integration of electrochemical processes into MBRs, applying an electric field inside the bioreactor (electro MBR/eMBR);
  - the application of a microbial fuel cell (MFC) as a down-stream process for the treatment of the excess sludge from a MBR pilot plant;
- Evaluate the energy production in the combined systems in terms of electricity for the MFC and of hydrogen for the eMBR working at anoxic condition, in order to operate as a microbial electrolysis cell (MEC).

To this extent, a literature review on MBR technology and electrochemical and bioelectrochemical processes for wastewater treatment as well as their combination with membrane bioreactors was undertaken in order to gather background information and define the

experimental activity. Two different experimental setups have been developed. In particular, an electro membrane bioreactor was designed and constructed at laboratory scale along with a microbial fuel cell for the treatment of MBR sludge characterized by different influent solid concentrations.
To achieve the set objectives, the following aspects have been investigated:

- The overall treatment performance of the electro MBR, evaluating, in particular, the mechanisms of nutrient removal and membrane fouling formation in terms of fouling rate, sludge hydrophobicity and membrane fouling precursors (bEPS, sEPS or SMP and TEP) at different electric voltage gradients applied. The results have been compared with those of a conventional membrane bioreactor;
- The influence, in the MFC fed with MBR sludge, of bioelectrochemical processes on concentration of organic matter, sludge content and properties, in particular, on main parameters that influence fouling in membrane bioreactors, in the case that part of the treated sludge is recycled to the MBR;
- Electrochemical characterization of the MFC in order to evaluate the current production and the anode electron transfer mechanism;
- Hydrogen production in the electro MBR at anoxic conditions.

1.2 OUTLINE

The thesis is divided in seven chapters. The principles of MBRs technology are reported in the Chapter 2, highlighting its main aspects, the historical background, the current market, operating parameters and possible configurations.
The Chapter 3 describes the mechanism of membrane fouling formation, the different types of membrane fouling and the factors that influence its formation along with the conventional and innovative strategies for controlling it.
The application of electrochemical and bio-electrochemical processes to wastewater treatment and their combination with membrane bioreactors

for the enhancement of the treatment performance and fouling control are reviewed in the Chapter 4.
In Chapter 5, experimental setups, sampling and analytical methods are illustrated with reference to the experimental research activity which can be divided in four phases:

- Design and construction of the electro membrane bioreactor at laboratory scale;
- Integration of electrochemical processes into a membrane bioreactor (electro MBR);
- Application of a microbial fuel cell (MFC) as a down-stream process for treating the excess sludge from a MBR pilot plant;
- Evaluation of the hydrogen production in the electro MBR at anoxic conditions.

The first two phases and the last phase of the research activity were conducted at the Sanitary Environmental Engineering Division (SEED), Department of Civil Engineering of Salerno University (Italy). The third phase was performed for three months at the Laboratory of Chemical and Environmental Engineering (LEQUIA) of the University of Girona (Spain).
Chapter 6 shows the results and discussion for each of the last three phases of the experimental activity.
Concluding remarks and future perspectives are presented in the Chapter 7. The references are reported at the end of the thesis.

2 MEMBRANE BIOREACTORS

Membrane bioreactors (MBRs), combining biological degradation processes with membrane filtration for biomass retention, are becoming increasingly implemented due to their advantages over conventional wastewater treatment processes (Drews, 2010). Indeed, the growth in demand and the shortage of water resources along with more stringent regulations have led to the development of treatment processes that are reliable, cost efficient and effective in removing a wide range of pollutants. In this way, the respect of discharge effluent standards and, simultaneously, the reuse of treated water are guaranteed.
In the present chapter the principles of MBRs technology are presented, highlighting its main aspects, the historical background, the current market, operating parameters and possible configurations.

2.1 FUNDAMENTALS OF MBR TECHNOLOGY

Membrane bioreactors represent one of the most promising and reliable technology for wastewater treatment and reuse. The biological unit of MBRs allows the degradation of contaminants while the membrane modules, integrated inside in different configurations, permit the physical separation of the treated water from the mixed liquor, replacing the secondary clarifier of the conventional activated sludge plants (CAS)(Figure 2.1).
Membranes are perm-selective barriers since some constituents can pass more readily through them, constituting the permeate, while others are rejected by them becoming the retentate (Judd, 2011). In MBRs, membrane separation contributes to the removal of pollutants, dispersed or dissolved in the mixed liquor, and to the "purification" of wastewater (Stephenson et al., 2000).
Therefore, by using micro or ultrafiltration membranes with pore sizes ranging from 0.01 to 0.4 μm, MBR systems allow small footprint and reactor requirements, high effluent quality, good disinfection capability, high mixed liquor suspended solids (MLSS) concentrations, higher

volumetric loading and less sludge production (Drews and Kraume, 2005; Judd, 2011; Le-Clech et al., 2006). In conventional biological processes, biomass concentrations of only 4-5 kgMLSS m^{-3} are applied since, at higher concentrations, significant volumes of sedimentation tanks would be necessary to settle sludge while floating sludge would be even impossible to settle (Drews and Kraume, 2005).
Application of MBR reactors does not only reduce the required reactor volume but also avoids the use of sand filtration and disinfection due to the high reachable effluent quality (Drews and Kraume, 2005) (Figure 2.1). The upgrading of existing plants with MBRs is an advantageous option in order to improve the performance of the system or to cope with an increase of the influent load, limiting simultaneously the structural modification of the current units.

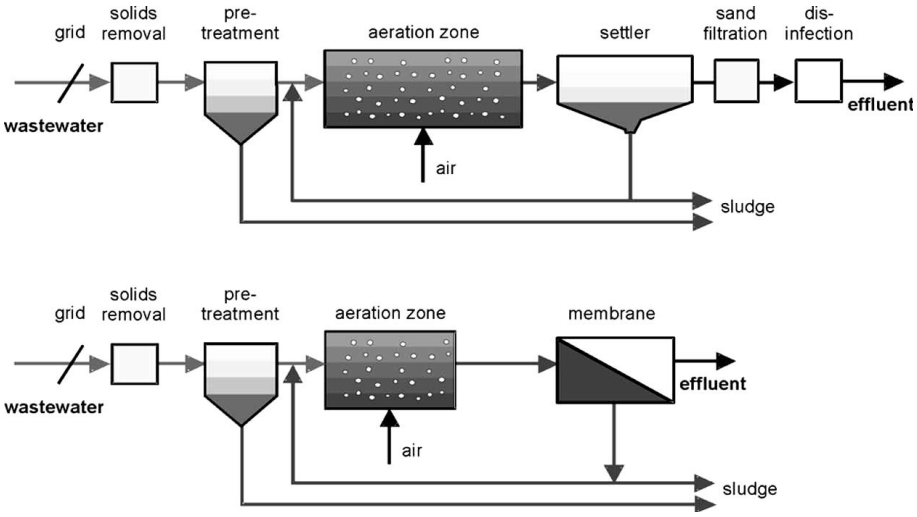

Figure 2.1 Flowchart of an activated sludge plant (CAS, top) and a membrane bioreactor (MBR, bottom) (Drews and Kraume, 2005).

Despite costs for the installation of the membranes have been reduced during the last years, membrane fouling, which will be discussed in the following chapter, still involves high operating costs due to the energy consumption to counter this phenomenon.

2.2 HYDRAULICS OF MEMBRANE BIOREACTORS

Membrane filtration allows the physical separation of certain compounds from a liquid flow in function of membrane pore size. Generally, membranes used for wastewater treatment are pressure driven and, thus, are characterized by a purified effluent flow called permeate (Qp, Cp) and a concentrated retentate waste (Qr, Cr>Cp)(Judd, 2011) (Figure 2.2).

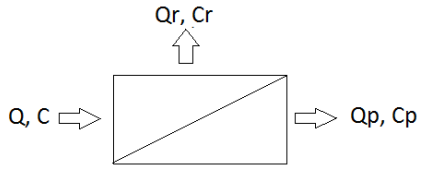

Figure 2.2 Fundamentals of membrane filtration.

The performance of a given membrane process is characterized by the rejection, represented by the ratio of the respective concentrations of the target contaminant in the feed and the permeate effluent and the specific permeate flux (Gander et al., 2000).

The membrane flux is the quantity of materials passing through a unit area of the membrane in the unit of time. Generally, it is expressed as litres for m^2 per hour or LMH (Judd, 2011) rather than in SI units. MBRs operate at fluxes between 10 and 150 LMH (Judd, 2011). The flux is influenced by the driving force, i.e. the transmembrane pressure (TMP), by the total resistance offered by the membrane and the interfacial region adjacent to it (Stephenson et al., 2000). The membrane performance is also related to membrane permeability (*K*), which is calculated as permeate flux per unit of TMP and is usually given as L m^{-2} h^{-1} bar^{-1} (Radjenović et al., 2008). Resistance is the ratio of pressure difference ΔP to the flux and viscosity μ and, thus, is given by $\Delta P/\mu J$ and is inversely related to the permeability.

Since the membrane is a selective barrier, it lets some materials pass through it, rejecting others (Stephenson et al., 2000). Membrane rejection can be expressed as:

$$R = \frac{1 - Cp}{C} \, x \, 100 \qquad (1)$$

Where C is the concentration of the feed and Cp is the concentration of the permeate.

The fraction of the feed flow recovery as permeate is called yield or recovery and it is given by:

$$\theta = \frac{Qp}{Q} x\,100 \quad (2)$$

where Qp is the permeate flow and Q is the feed flow.
Pressure driven membrane processes can operate in two modes. If there is no retentate flow then, the operation is called "dead-end" while it is called "crossflow" when the retentate flows from the membrane outlet and the feedwater flows parallel to the membrane surface (Judd, 2011), removing the accumulated materials from the membrane surface with scouring action (Figure 2.3). More the membrane is perm-selective, higher is the hydraulic resistance and, therefore, greater the propensity for the crossflow operation (Stephenson et al., 2000). Indeed, filtration leads to an increase in the resistance of the flow which increases proportionally to the thickness of the cake layer formed on the membrane surface in the dead-end operation (Judd, 2011). Recovery is normally close to 100% for dead-end filtration, while it varies significantly for cross-flow filtration in function of the nature and design of membrane process (Radjenović et al., 2008).

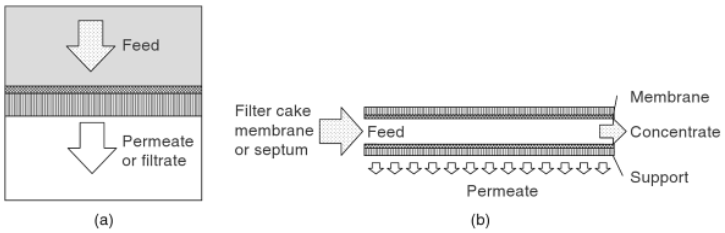

Figure 2.3 a) Dead end and b) cross flow filtration (Stephenson et al., 2000).

2.3 MEMBRANE CLASSIFICATION

The most widely used membrane separation processes are microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO). This classification can be defined according to the pore size which can be expressed in terms of effective equivalent pore diameter in μm or the equivalent mass of the smallest molecule in daltons (Da) the membrane

is able to reject. The separation ranges are: 100 to 1000 nm for MF, 5 to 100 nm for UF, 1 to 5 nm for NF and 0.1 to 1 nm for RO (Radjenović et al., 2008). High degree of selectivity is achievable through membrane with smaller pore size, permeability and, therefore, higher hydraulic resistance (Stephenson et al., 2000).
Figure 2.4 shows the classification of the different types of membrane processes along with contaminants that they are able to remove.
Generally, membranes used in pressure-driven processes are anisotropic with symmetry in a single direction in order to have their pore size variable with membrane depth (Stephenson et al., 2000). Membranes are characterized by a thin surface layer which provides the required perm-selectivity on the top of a thicker porous support that gives the mechanical stability (Judd, 2011).

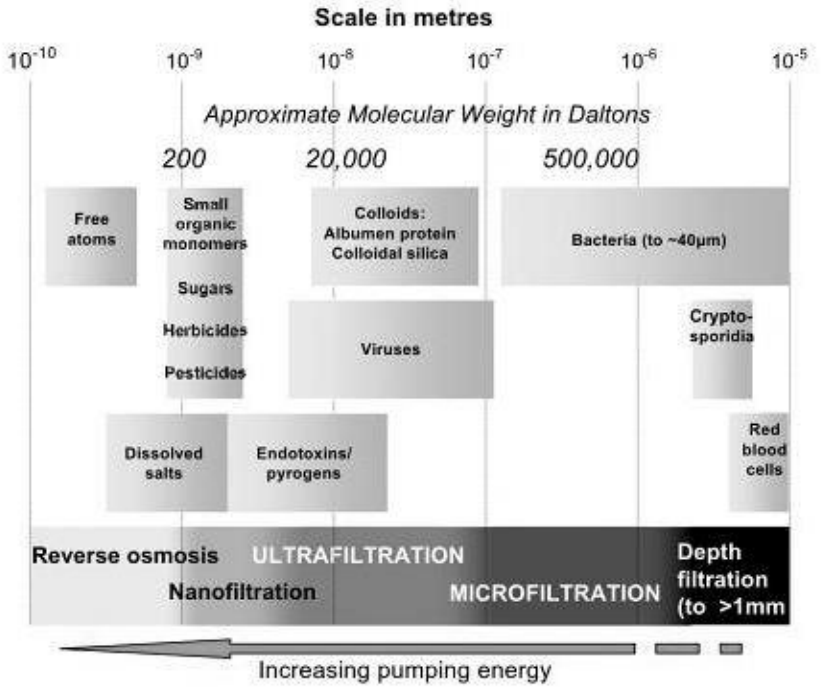

Figure 2.4 Membrane separation processes (Stephenson et al., 2000).

Membranes are usually made of organic (polymeric) and inorganic (ceramic or metallic) materials. Ceramic membranes are not the preferred option for MBR applications due to their high cost, even though they

have superior chemical, thermal and hydraulic resistances. (Le-Clech et al., 2006).
The most widely utilized materials are celluloses, polyamides, polysulphone, charged polysulphone and other polymeric materials such as polyacrylonitrile (PAN), polyvinylidene difluoride (PVDF), polyethylsulphone (PES), polyethylene (PE), and polypropylene (PP)(Radjenović et al., 2008). The combination of a good physical and chemical resistance with the surface structure have determined the prevalence of such polymeric materials.
Most of these materials are also hydrophobic and it is known that hydrophobic membranes are more tending to fouling than hydrophilic ones due to the fact that most interactions between the membrane and the foulants are of hydrophobic nature (Le-Clech et al., 2006; Radjenović et al., 2008). For this reason, all commercially available membranes are modified by chemical oxidation, organic chemical reaction, plasma treatment, or by grafting to achieve more hydrophilic surface (Radjenović et al., 2008).
Lastly, membrane materials should have resistance to thermal and chemical attacks due to extreme conditions of temperature, pH and/or oxidant concentrations in the case of chemical cleaning (Judd, 2011).

2.4 MEMBRANE CONFIGURATIONS

The configuration of membranes, namely its geometry and the way in which they are mounted and oriented respect to the water flow, is important for the performance of the process (Judd, 2011).
Currently, there are six principal configurations used in membrane processes, all of them characterized by their benefits and drawbacks (Judd, 2011). These configurations, based on either planar or cylindrical geometry, are:

- Hollow fiber (HF);
- Plate-and-frame (i.e., flat sheet (FS))
- (Multi) Tubular (MT);
- Pleated filter cartridge (FC);
- Spiral-wound (SW);
- Capillary tube (CT).

Only the first three configurations can be used for MBR technologies due to the possibility of creating turbulence and permitting regular cleaning (Judd, 2011).

As it can be seen in Figure 2.5, the flow in MT is in-out while in FS and HF it is out-in. Therefore, the interstitial is related to the tube diameter for an MT, the distance between the filaments for an HF and the channel width for FS (Judd, 2011).

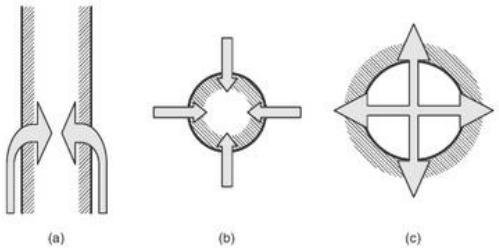

Figure 2.5 Representation of the water flow in FS (a), HF (b) and MT (c) membranes (adapted from Judd, 2011).

The flat sheet modules (Figure 2.6) are characterized by stacked flat – sheet membranes and support plates with the flow passed between the membranes of two adjacent plates and permeate is being collected through pipes emerging from the interior of the membrane module in a process that operates under vacuum (Odendaal et al., 1996; Radjenović et al., 2008). The plates ensure the mechanical support of the membranes. The modules can be easily disassembled to gain access for manual cleaning or replacement of the membranes (Odendaal et al., 1996).

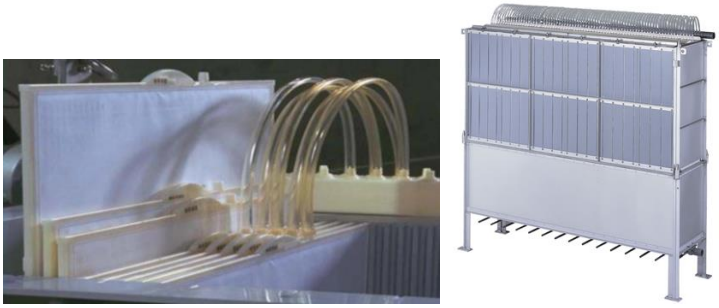

Figure 2.6 Flat sheet membranes (KUBOTA Membrane).

In the HF module (Figure 2.7), large amounts of HF membranes are gathered in a bundle and the ends of the fibers are sealed in epoxy block connected with the outside of the housing (Radjenović et al., 2008).
The water can flow from the inside to the outside of the membrane with IN-OUT configuration, and also from the outside to the inside OUT-IN, which is produced differently by different manufacturers (Radjenović et al., 2008). Operating velocities are very low and modules can be operated without recirculation (dead-end mode), nevertheless shear rates can be high due to the very small flow channels (Odendaal et al., 1996). Another advantage of this configuration is that UF or MF hollow fiber, since they are self-supporting, can be backflushing inverting the flow and detaching the cake layer on the membrane surface (Odendaal et al., 1996).

Figure 2.7 Hollow fiber modules (ZeeWeed, GE/Zenon on the left, PURON membrane modules, Koch Membrane supplies on the right).

In the tubular module (Figure 2.8), the membrane is placed inside the wall of a porous support tube (Odendaal et al., 1996).

Figure 2.8 Multitubular membranes (Sepra Separation process application).

The tubes with diameters from 6 to 40 mm can be placed inside stainless steel or PVC sleeves or PVC sleeves for smaller scale units or bunched together in bundles in a cylindrical housing with appropriate end plates (Odendaal et al., 1996). In MT, mixed liquor is pumped to them, the permeate is collected externally while the retentate flows through the tube (Radjenović et al., 2008). These modules do not need the pre filtration of the feed, can be easily cleaned and velocities up to 6 m s-1 can be achieved if the turbulence is required (Odendaal et al., 1996). They are useful for very viscous fluids although the low packing density increases the capital costs (Odendaal et al., 1996).
They are predominantly used for side-stream configurations (Radjenović et al., 2008) for high fluxes and values of MLSS. They are also characterized by high energy consumption due to cross flow operation mode. Their application is, thus, limited to industrial scale with low flows. HF and FS modules are mostly immersed directly in oxidation tank with permeate drawn through the membranes using vacuum pumps (Radjenović et al., 2008) and favored for MBR processes. In the case of HF membranes, use of 0.8 mm to 1.5 mm fine screen upstream of membranes is encouraged to protect the membranes from hair and other materials that can lead to excessive cleaning frequencies while a fine screen of 2-3 mm is usually employed for FS membrane systems (Radjenović et al., 2008).
HF membranes are characterized by lower energy consumption, high packing density, control of effective permeability losses and high expected membrane life. FS modules, instead, have lower consumptions of chemicals, more plant simplicity, low packing density and do not required backwashing.
Each one of these configurations has the tendency to be more suitable for particular applications.
According to membranes installation mode, there are three alternative system configurations: side stream, immersed or mixed (Figure 2.9).

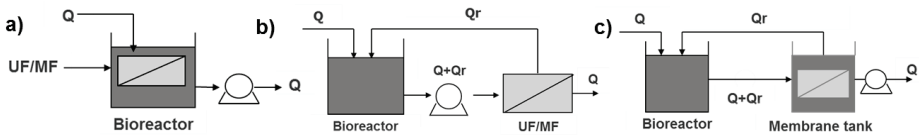

Figure 2.9 Membrane processes configurations: a) side stream; b) immersed; c) mixed configuration.

In the side stream configuration, membrane system is placed outside the biological treatment process tank where the mixed liquor comes in pressure and part of the retentate is recirculated. The mixed liquor is, therefore, pumped through the membranes in cross-flow mode at high pressures (2-3 bar) and the permeate forced through the membrane under the combined action of the pressure and the crossflow.
In the immersed configuration, the membrane modules are placed directly in the bioreactor and operate in dead-end mode. In the mixed configuration, the membranes are installed in a tank that is external to the bioreactor with the recirculation of the mixed liquor to the oxidation tank.
The most favored configuration in terms of volume of treated water is immersed over the more established pumped sidestream technology (sMBR), normally based on multi-tube (MT) membranes for lower energy demand. The lower footprint that characterized the MT membranes, along with their operational flexibility and perceived robustness, make indeed them favored for industrial effluent applications.
Both configurations require a shear over the membrane surface to prevent membrane fouling (Radjenović et al., 2008). Side-stream MBRs provide this shear through pumping whereas immersed processes use aeration in the bioreactor to provide it (Radjenović et al., 2008). Shear enhancement requires also energy demands, which is probably the reason for submerged configuration predominance (Radjenović et al., 2008). The higher permeate flux of side stream processes also increases membrane fouling formation. The mixed configuration combines the benefit of both the configurations.

2.5 DESIGN AND OPERATIONAL PARAMETERS

2.5.1 Transmembrane pressure

The driven force applied for allowing the permeate moving across the membrane is constituted by the pressure gradient, properly called transmembrane hydraulic pressure (TMP).

TMP is defined as the difference between feed and permeate side pressure (Drews, 2010). Considering the pressure drop along a membrane module, it can be written as:

$$\mathrm{TMP} = \frac{p_{\mathrm{Feed}} + p_{\mathrm{Retentate}}}{2} - p_{\mathrm{Permeate}} \tag{3}$$

There are, thus, three pressures need to be measured during a filtration experiment (Drews, 2010). In short modules, the pressure drop is generally negligible, so two will enough (Drews, 2010). Quite often, however, only one pressure transducer on the permeate side is used and the feed pressure is taken as the initially recorded pressure before permeation (Drews, 2010).

2.5.2 Permeate flux

Permeate flux is the ratio between the permeate flow rate and the membrane surface A ($L^3\ L^{-2}\ t^{-1}$).
With cleaned membranes, it can expressed as a function of the TMP, Rm (resistance of cleaned membrane) and viscosity of the fluid according to the Darcy law:

$$J = {}^{TMP}/_{\mu R_m} \tag{4}$$

With fouling, J can be expressed as:

$$J = \frac{TMP}{\mu \cdot (R_m + R_c + R_p)} \tag{5}$$

Where Rc and Rp are the resistances of external and internal fouling.

2.5.3 Design of MBR plant

The design of biological processes can be conducted through Monod kinetics for a limiting substrate, generally, organic carbon or ammonia (Judd, 2011). With reference to the Monod kinetic, the loading rate is determined by the rate of substrate removal and the rate of the reaction

is first order with the respect to a limiting substrate up to a maximum specific growth rate, after that growth is not influenced by an increase of substrate concentration (Judd, 2011):

$$\mu = \frac{\mu_m S}{K_s + S} \quad (6)$$

where μ and μ_m are the growth rate and maximum specific growth rate per day, respectively, S is the limiting substrate concentration and Ks is the saturation coefficient, both in g/m^3. The maximum specific substrate utilization rate is equal to:

$$k = \frac{\mu_m}{Y} \quad (7)$$

Where Y is the biomass yield, the mass of cell formed per mass of substrate consumed in g volatile suspended solid (VSS) per g BOD (Judd, 2011).
Under optimal conditions the biomass is kept as close to a food-limited environment as possible in order to promote endogenous respiration (Gander et al., 2000). In this way, catabolism of substrate continues unhindered while the anabolism of the biomass is restricted resulting in a reduction of the sludge production (Gander et al., 2000).
The effluent dissolved substrate can be obtained substituting the terms of the Monod kinetics into a mass balance of the system (Judd, 2011):

$$S_e = \frac{K_s(1 + k_e\theta_{x,aer})}{\theta_{x,aer}(Yk - k_e) - 1} \quad (8)$$

where $\theta_{x,aer}$ is the sludge retention time or sludge age (STR) in days and ke is the decay rate constant. The STR can be used as a design parameter. In MBR system the SRT can be completely controlled since the biomass is retained in the bioreactor. Ke, i.e. the decay constant rate for the endogenous metabolism, is equal to 0.04-0.075/day in MBRs (Fan et al., 1996; Wen et al., 1999).
In order to obtain the total biomass yield $M_{x,TSS}$, it should be considered the following factors: the growth of heterotrophic biomass, endogenous decay, the growth of nitrifying biomass, the fraction of volatile

particulate non- biodegradable organics nbVSS and inert total suspended solids (iTSS) (Judd, 2011).
Defined the MLSS concentration inside the reactor and the required SRT for the nitrification process, the aeration tank volume can be determined calculating the mass of solids being aerated and, then, using the aerobic MLSS to convert that mass to the volume which solids occupy according to the following equation (Judd, 2011):

$$V_{aer} = \frac{M_{x,TSS}\,\theta_{x,aer}}{X_{aer}} \tag{9}$$

MBR systems, retaining the biomass inside the reactor, allow high SRT without increasing the volume of the reactor since SRT and the hydraulic retention time (HRT) are independent of each other. Increasing SRT increases the MLSS content inside the reactor. High values of MLSS can damage the process since accumulation of inert, high fouling and clogging could occur. The SRT can be controlled discharging a defined quantity of the sludge from the bioreactor. The volume of sludge wasted is (Judd, 2011):

$$Q_w = \frac{V_{aer}}{\theta_{x,aer}} \tag{10}$$

Another important parameter is the food to microorganism ratio F/M, i.e. the rate at which the substrate is fed to the bioreactor respect to the solids present in the reactor itself (Judd, 2011):

$$F/M = \frac{QS}{VX} \tag{11}$$

This can be related to the SRT and the efficiency of the process according to the following equation (Judd, 2011):

$$Y\frac{F}{M}\frac{E}{100} - ke = \frac{1}{\theta_{x,aer}} \tag{12}$$

Since flux and driving force are correlated either one can be fixed for design purpose (Judd, 2011). Generally, for conventional pressure driven water filtration, the value of the flux is fixed (Judd, 2011).
For calculating the overall membrane surface, the maximum flux has to be fixed. In order to not have large membrane surface, it should not be too low and, at the same time, for avoiding severe fouling, not very high. Generally, the design permeate flux Jp is 80% of the critic flux Jcr which will be explained in the following chapter. The total membrane surface can be calculated as follows:

$$A = Q_{MAX} / J_P \quad (13)$$

The range of Jp used for design is 15-35 $L/(m^2\ h)$.
The aeration system, finally, has three purpose: to ensure the aerobic conditions inside the reactor, to maintain complete mixing conditions and limit fouling. These objectives can be achieved through the implementation of two aeration systems, one with large bubbles, suitable for membrane cleaning due to the agitation created from bubble size, and one with fine bubble for oxygen transfer inside the reactor.
For designing MBR aeration system, specific aeration demand SAD can be used, defined as the ratio between aeration flow rate and the overall surface area of the membrane (SADm) or as the ratio between the aeration flow rate and permeate flow (SADp):

$$SADm = Qa / A \quad (14)$$

$$SADp = Qa / Jp\ A \quad (15)$$

In most full-scale immersed MBR installations now in operation, SADp on average exceeds 10 Nm^3/m^3, and can be as high as 50 at some sites while the range of SADm is 0.3-1.5 $Nm^3/(m^2\ h)$.
The aeration for the biological system can be calculated as for CAS plant taking into account an oxygen transfer factor lower than CAS for the greater SST concentrations in the tank.

2.6 MBR HISTORY AND MARKET

The MBR process was introduced in the late 1960s, by Dorr-Olivier Inc. combining activated sludge processes with a crossflow membrane ultrafiltration for the treatment of shipboard sewage (Judd, 2011; Le-Clech et al., 2006). The flat sheet membranes used in this process were polymeric with pore size ranging from 0.003 to 0.01 μm in sidestream configuration (Judd, 2011; Le-Clech et al., 2006). Due to the higher costs related to the first generation MBRs for the energy consuptions, they only found applications in niche areas for isolated cases. The breakthrough for the MBR came in 1989 with Yamamoto et al. (1988) who submerged the membranes in the bioreactor, as well as the development of an FS microfiltration in immersed configuration by the agricultural machinery company Kubota (Judd, 2011). There were, afterwards, pilot scale implementations first at Hiroshima in 1990 (25 m^3/d) and, then, at the company's site at Sakai-Rinkai in 1992 (Judd, 2011). Kubota installed 60 plants in Japan by the end of 1960 for domestic wastewater treatment and, later, for industrial effluent treatment.

At the same time as Kubota industrialized its products, Zenon developed an MBR system patenting by the early 1990s the ZenoGem immersed HF UF MBR (Judd, 2011). At the end of the millennium the installed capacity of the Zenon plants reached 150 MLD (Judd, 2011).

The other key steps in the MBR development were the achievement of modest fluxes (25% or less of those in the first generation), and the idea to use two-phase bubbly flow to control fouling (Le-Clech et al., 2006).

The lower operating cost due to the submerged configuration along with the reduction of membrane cost led to an exponential increase in MBR plant installations from the mid 1990s (Le-Clech et al., 2006). Kubota realized his first municipal wastewater treatment plant outside Japan at Porlock in the United Kingdom in 1997 (Judd, 2011). The first Zenon membrane based plant of similar size was Veolia Biosep plant at Perthes en Gantinais in France in 1999 (Judd, 2011). By the end of 1990s until nowadays, the MBR market has significantly grown with different membrane products and systems. Indeed, as a result of urbanization and water stress, the global market of membrane bioreactors grew to $838.2 million in 2011 and is projected to increase up to $3.44 billion by 2018 with a growth rate (CAGR) of 22.4% over this time period (http://www.waterworld.com/). The number of MBR manufactures is

dramatically increased after that the first technology with submerged configuration was realized by Kubota in 1990 (flat sheet configuration) followed by Zenon in 1993 (hollow fiber configuration).
These two companies still maintain their dominance in the global market for the treatment of domestic wastewater (Figure 2.10) with Kubota, which is among the first eleven MBR suppliers, owns approximately 20-25% of the total number of installation (compared to the installed capacity) and GE Zenon about 40% (Judd, 2011).

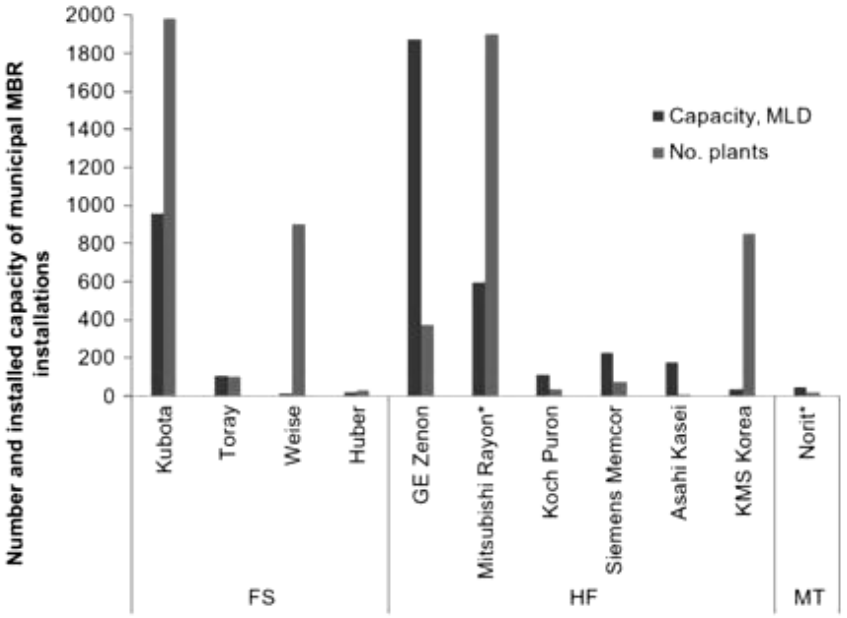

Figure 2.10 MBR market for municipal wastewater treatment (Santos and Judd, 2010).

Mitsubishi Rayon Engineering (MRE) has realized a number of plants comparable with those installed by Kubota but its activity is limited to the Far Est. New suppliers are emerging in numbers and market share. By the end of 2009, indeed, around 45 manufactures have arisen. Table 2.1 reports the main MBR technology suppliers according to the configuration of the membrane modules.

Table 2.1 Main MBR suppliers (Santos and Judd, 2010).

Immersed configuration		Side – stream configuration
Flat sheet	**Hollow fibers**	**Multitubular/ multichannel**
A3-MaxFlow DE **Alfa Laval** - Hollow Sheet SE **Brightwater** - MEMBRIGHT® IRL **Colloide** - SubSnake NIR **Huber** - VRM®; ClearBox®, **Biomem** DE **Jiangsu Lantian Peier Membrane** CN **KOReD** - Neofil KR **Kubota** - ES/EK JP **MICRODYN-NADIR** - BioCel® DE **Pure Envitech** – ENVIS KR **Shanghai Megavision Memb. Eng. & Tech.** CN **Shanghai SINAP Membrane Sci. & Tech**. CN **Toray** -MEMBRAY® TMR JP **Vina Filter** - VINAP CN **Weise Water Systems GmbH** - MicroClear® DE	**Asahi Kasei** - Microza™ JP **Beijing Origin Water Technology** CN **Ecologix** – EcoFlon™, EcoFil™ CN **ENE** – SuperMAK KR **GE Zenon** – ZeeWeed® NA **Hangzhou H-Filtration Memb. Tech. & Eng.** – MR CN **Koch Membrane Systems** – PURON® NA **Korea Membrane Separations** – KSMBR KR **Litree Purifying Technology** – LH3 CN **Memstar Tech**. – SMM SG **Micronet Porous Fibers** – Micronet® SP **Mitsubishi Rayon Eng**. – Sterapore SUR™; SADF™ JP **Tianjin Motimo** – Flat Plat FPII CN **Philos** KR **SENUO Filtration Technology** – **SENUOFIL** CN **Shanghai Dehong Biology Medicine Sci. & Tech. Dev.** CN **Siemens Water Tech**. – MemPulse™ DE **Sumitomo** – POREFLON™ JP **Zena Membranes** – P5 CZ	**Berghof** – HyPerm-AE; **HyPerflux** DE **Norit X-Flow** – F4385, F5385 NL **Orelis Environment** – Kerasep®; Pleiade® FR **MEMOS** – MEMCROSS DE **Hollow fiber** **Ultra-flo** – Ultra-flo® SG **Polymem** – IMMEM FR **Ceramic flat sheet membrane** **Kerafol** DE **Grundfos** – Biobooster DK

3 FOULING IN MBRS

The advantages that characterize membrane bioreactors along with the more stringent discharge standards, steady reduction of membrane cost and needs of water reclamation, have given remarkable impetus to the extensive research and applications of MBR technology for biological wastewater treatment (Lin et al., 2014). Notwithstanding, membrane fouling still inhibits the operational efficiency of MBR processes and limits their widespread application. This phenomena is due to the deposition of soluble and particulate materials which are adsorbed or simply accumulated onto and into the membrane surface during the filtration and leads to a reduction of membrane permeability over time and an increase of the trans-membrane pressure (TMP) (Drews, 2010), depending on operation mode. Fouling has to be distinghished from clogging, which is the filling of membrane channels with solids due to poor hydrodynamic conditions (Judd, 2011). Fouling in MBRs decreases the productivity of the reactors, increase the energy requirement for air scouring and frequency of physical and chemical cleaning which might shorten the membrane lifespan and result in higher replacement costs (Lin et al., 2014). Therefore, causes, characteristics, mechanisms and control strategies of membrane fouling in MBRs are investigated with a great interest (Lin et al., 2014).
In the present chapter, the mechanism of membrane fouling formation, the different types of membrane fouling and the factors that influence its formation, along with the conventional and innovative strategies for controlling it, are reported.

3.1 MECHANISMS OF MEMBRANE FOULING FORMATION

Membrane fouling in MBRs is a result of the interactions between the membrane and the sludge suspension (Le-Clech et al., 2006). Fouling occurs due to the following mechanisms (Meng et al., 2009):

1) adsorption of solutes or colloids within/on membranes;

2) deposition of sludge flocs onto the membrane surface;
3) formation of a cake layer on the membrane surface;
4) detachment of foulants attributed mainly to shear forces;
5) the spatial and temporal changes of the foulant composition during the long-term operation.

Membrane fouling is influenced by the dimension of sludge flocs, colloids e solutes in the mixed liquor. In function of these, there are different mechanisms of membrane fouling formation (Figure 3.1) (Radjenović et al., 2008):

- Complete blocking caused by occlusion of pores by the particles with no particle overlap;
- Intermediate blocking caused by partial occlusion of pores by particles with particle overlap ;
- Standard blocking where particles smaller than the membrane pore size (colloids) deposit onto the pore walls thus decreasing the pore size;
- Cake filtration where particles larger than the membrane pore size deposit on the membrane surface.

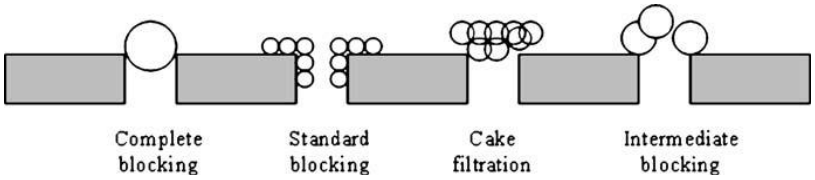

Figure 3.1 Mechanisms of membrane fouling formation (Radjenović et al., 2008).

Meng et al. (2009) report that the measurement of fouling resistance can help to understand the fouling extent or optimize the fouling conditions. Resistance is inversely related to the permeate flux and is equal to (Radjenović et al., 2008):

$$R = \frac{\Delta P}{\eta J} \qquad (16)$$

Where η is the permeate viscosity in kg $m^{-1}s^{-1}$. Considering the resistance in series model, the total resistance is (Rosenberger et al., 2005):

$$R = R_{membrane} + R_{cake} + R_{poreblocking} + R_{adsorption} \qquad (17)$$

According to the mechanisms of membrane fouling formation, the retained components can form a cake layer (*R*cake) on the membrane surface, block the membrane pores (*R*poreblocking) or adsorb (*R*adsorption) at the membrane surface or in the membrane pores, in function of their chemical and physical properties (Rosenberger et al., 2005). Figure 3.2 shows the different resistances.

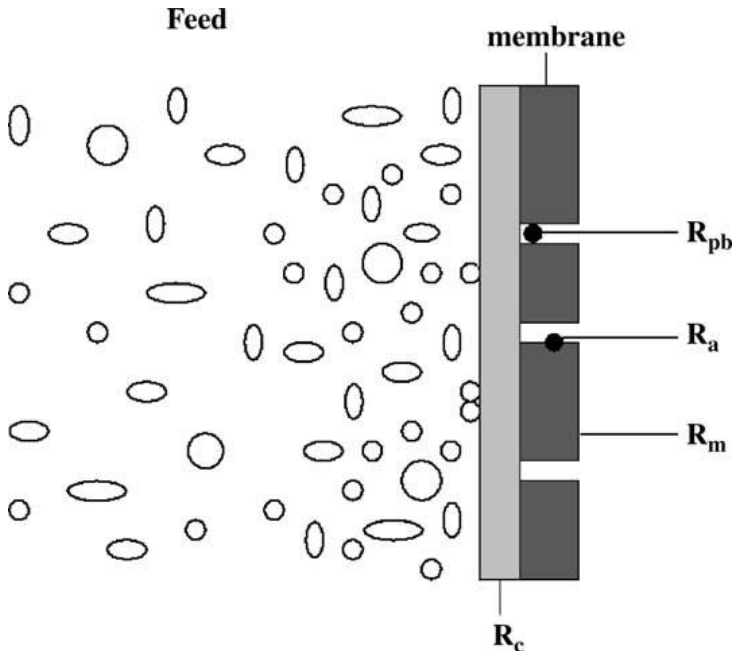

Figure 3.2 Graph of filtration resistances (Rosenberger et al., 2005).

Membrane resistance depends on characteristics of membrane material such as thickness and pore size and it determines the flux through the membrane for filtration of one-component liquid, i.e., clean water (Radjenović et al., 2008). In MBRs, membrane resistance is often given as its inverse value called "clean water permeability", which is normally within the range of a few hundred to a few thousand L m^{-2} h^{-1} bar^{-1} (Radjenović et al., 2008).

In addition, concentration polarization and biofouling can occur. Concentration polarization (CP) is a phenomenon of solute tendency to accumulate within the boundary liquid layer of near-stagnant fluid adjacent to membrane surface (Radjenović et al., 2008). Since the

velocity of the flow within this layer is close to zero, the only mass transport is diffusion, which is significantly slower than convective transport in the bulk solution (Radjenović et al., 2008). CP can increase resistance to liquid flow and, therefore, decrease the permeate flux (Wang et al., 2014). The thickness of the boundary layer is dependent on system's hydrodynamics and can be decreased by promoting the turbulence of liquid flow (Radjenović et al., 2008).
In crossflow operation, the deposition of the particles on the membrane surface continues until that the adhesion force are balanced by the drag force exhibited by the fluid near the membrane. This favours the concentration polarization and, thus, of a gelatinous layer. In the dead-end filtration, the solids on the membrane surface generate a filtering layer that provides a hydraulic resistance greater than the cleaned membrane and that increases in thickness over time.

3.1.1 Critical flux

While most of MBR studies have been carried out under constant pressure conditions, the use of constant flux and monitoring of TMP increase over time have proved to be particularly useful in the context of monitoring fouling in complex fluids (Le Chech et al., 2016). Typically, increasing flux steps are imposed and the TMP monitored at each step (Le Chech et al., 2016). When the TMP is no more stable at each flux step and increases rapidly to point out rapid accumulation of foulants, this is usually referred to as the critical flux (Le Chech et al., 2016). *Critical flux* J_{cr} is the flux below which a decline of permeability with time does not occur, and above which fouling is observed (Field et al., 1995). The critical flux depends on the back transport provided by the crossflow or turbulence produced by imposed liquid flow and/or bubbling as well as the specific solute-membrane interactions, which are influenced by charge and hydrophobicity (Le Chech et al., 2016). For *complex fluid systems*, the most popular procedure for experimentally determining the critical flux is to incrementally increase the flux for a fixed duration by flux-stepping method (Figure 3.3). This leads to relatively stable TMP at low fluxes (indicating little fouling), and an ever increasing rate of TMP rises at fluxes beyond the critical flux values (Chen et al., 1997; Cho and Fane, 2002; Defrance and Jaffrin, 1999). The precise identification of the critical flux value from flux-stepping experiments strongly depends on the conditions used (step duration, step

height, initial state of the membrane) (Le Clech et al., 2003). The most important parameter remains the step height, which needs to be kept as small as possible for higher accuracy in the determination of the critical flux value (Jefferson et al., 2004).

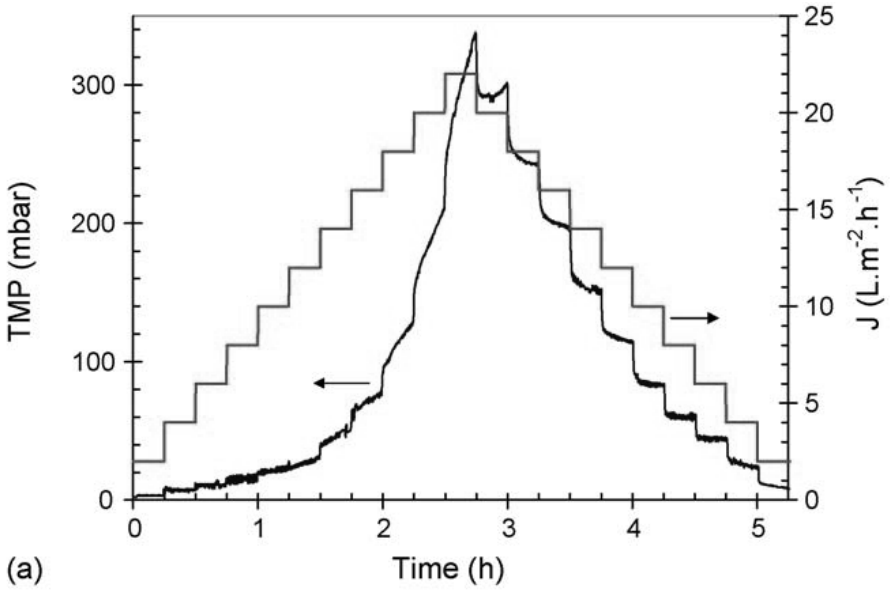

Figure 3.3 Critical flux determination by the flux-stepping method (Le Chech et al., 2006).

Significant differences above and below a clearly defined flux exist, in order to distinguish between high and low fouling rates or to indicate the point of their significant change, the "sustainable flux" has been introduced (Bacchin et al., 2006). It can be defined as the flux above which the rate of fouling is economically and environmentally unsustainable (Bacchin et al., 2006) or for which the TMP increases gradually at an acceptable rate, such that chemical cleaning is not necessary (Le Chech et al., 2006).

The current trend in MBR design is to operate at constant flux (Le Chech et al., 2006), monitoring the variation of TMP over time. In the MBR and other membrane filtration processes at constant TMP, a rapid flux decline is expected to occur during the initial stages of the filtration (Le Chech et al., 2006). The rate of fouling then decreases before reaching a plateau (Le Chech et al., 2006). At constant flux operation, the

transport of foulants on membrane surface does not diminish and fouling phenomena increases resulting in a sharp increase of TMP (Le Chech et al., 2006). With fouling rate, and thus cleaning frequency, increasing with flux, operation conditions favor the MBR to operate at modest fluxes to limit fouling formation (Le Chech et al., 2006).
Therefore, the mechanisms of membrane fouling formations are influenced by membrane flux and transmembrane pressure (TMP): high fluxes lead the particles to adhere on membrane surface more rapidly and high TMPs develop more quickly the cake layer pressing the particles until that membrane pores are occluded.
Generally, as shown in Figure 3.4, the increase of TMP over time has three stage (Cho and Fane, 2002; Meng et al., 2009; Zhang et al., 2006):

- Stage 1: an initial short-term rapid rise in TMP;
- Stage 2: a long-term weak rise in TMP;
- Stage 3: a sharp increase in dTMP/dt, also known as TMP jump (Cho and Fane, 2002).

The TMP jump is a consequence of severe membrane fouling. Cho and Fane (2002) attributed the TMP jump to modifications in the local flux due to fouling eventually causing local fluxes to be higher than the critical flux. Latterly, Zhang et al. (2006) have observed that the sudden jump could be also caused by sudden changes of the biofilm or cake layer structure, since due to oxygen transfer limitation, the bacteria in the inner biofilms tend to die and release more extracellular polymeric substances (EPS) (Meng et al., 2009).

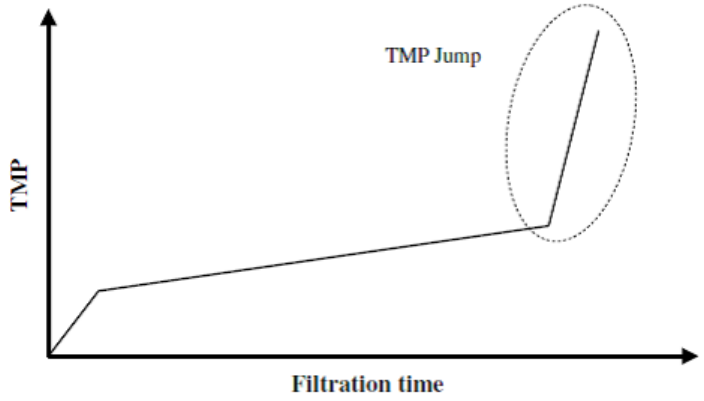

Figure 3.4 Representation of TMP jump (Meng et al., 2009).

TMP also depends on operating parameters and occurs during long term operation (Meng et al., 2009). Therefore, it is important to control fouling, retarding the occurrence of the TMP jump through the modification of sludge characteristics or decreasing the membrane flux in order to operate below critical flux (Meng et al., 2009).

3.2 CLASSIFICATION OF MEMBRANE FOULING

During the past decade, Le-Clech et al. (2006), Meng et al. (2009), Drews (2010) and Wang et al. (2014) carried out comprehensive reviews on the membrane fouling causes and cures by covering all fouling aspects, such as membrane materials, feed-biomass characteristics and operating conditions. Herein, based on these publications, there is an overview of the major types of membrane fouling in MBRs.

3.2.1 Reversible and irreversible fouling: literature definitions

Different definitions are proposed in the literature related to reversible and irreversible fouling making these concepts a bit confused.
Generally, the term reversible fouling refers to fouling that can be removed by physical cleanings such as backflushing or relaxation under crossflow conditions, while irreversible fouling refers to fouling which can only be removed by chemical cleaning (Drews, 2010; Judd, 2011; Le-Clech et al., 2006; Lesjean and Huisjes, 2008).
Drews (2010) highlights that, during long-term operation of a full-scale MBR, beyond irreversible and reversible fouling, two more distinct fouling rates can be observed (Figure 3.5). Reversible fouling is due to external deposition of material (cake filtration) and can be removed during filtration breaks or backflush cycles (Drews, 2010). The slope of the baseline is "irreversible" in that it is alleviated by maintenance cleans, leaving another baseline to be treated by main cleans in order to recovery the membrane permeability. Finally, irrecoverable fouling cannot be removed by any cleaning and happens over long periods (Drews, 2010).

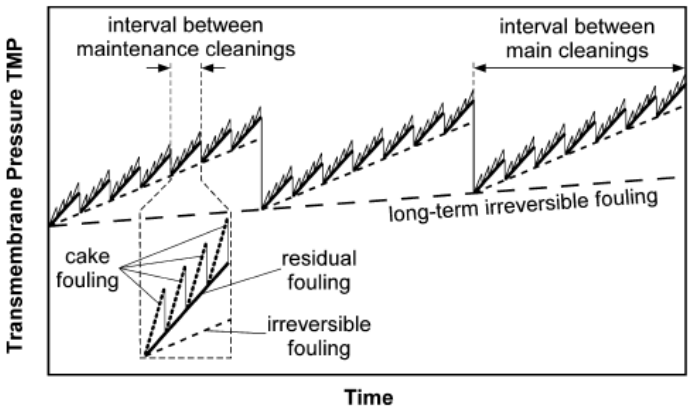

Figure 3.5 Schematic representation of different fouling rates during long-term operation of full-scale MBRs (Kraume et al., 2009).

Meng et al (2009) define three types of fouling: removable fouling, irremovable fouling and irreversible fouling. As shown in Figure 3.6, for the authors, the removable fouling can be easily eliminated by physical cleaning (e.g., backwashing) while the irremovable fouling needs chemical cleaning to be eliminated.

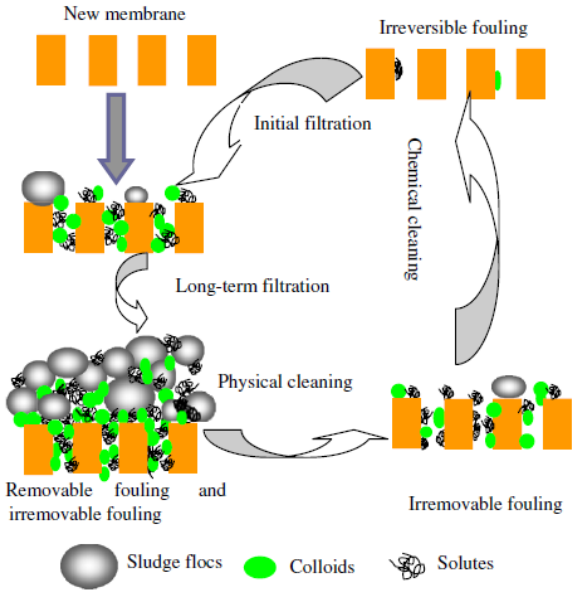

Figure 3.6 Formation and removal of removable and irremovable fouling in MBRs (Meng et al., 2009).

The removable fouling and reversible fouling are the same (Meng et al., 2009). The removable fouling is caused by loosely attached foulants; however, irremovable fouling is caused by pore blocking and strongly attached foulants during filtration (Meng et al., 2009). The irreversible fouling is permanent and it cannot be removed by any approaches. In general, removable fouling is attributed to the formation of cake layer, and the irremovable fouling is attributed to pore blocking (Meng et al., 2009).

Wang et al. (2014) defined the following four types of fouling (Figure 3.7):

- *Reversible fouling*. It results from the loose attachment of fouling materials to membrane surfaces, which can be removed by physical cleaning method, such as relaxation, a strong shear force or backflush (Wang et al., 2014). The authors highlight that other authors call it 'removable' or 'temporary' fouling (Judd, 2011; Meng et al., 2009). In general, cake layer is considered as the main cause of reversible fouling (Wang et al., 2014). Enhanced physical cleaning methods should be implemented to clean the long-term developed reversible fouling (Wang et al., 2014).
- *Irreversible fouling*. Formation of a strong matrix of fouling layer with solutes during a continuous filtration will turn the reversible fouling into an irreversible fouling (Wang et al, 2014). Irreversible fouling is also due to pore narrowing or pore blocking on the membrane. Irreversible fouling cannot be removed by physical or biological cleaning methods, and it is called as physically or biological irreversible fouling (Wang et al., 2014);
- *Residual fouling*. Residual fouling concept is proposed by Kraume et al. (2009) and Judd (2011). As shown in Figure 3.7, residual fouling cannot be removed by chemically enhanced backflush or maintenance cleaning but can be removed by recovery cleaning;
- *Irrecoverable fouling*. Once a membrane is fouled during longterm operation, the original membrane permeability is never recovered. There is a remaining resistance which can be defined as 'irrecoverable fouling', and it is not readily removed by typical chemical cleaning (Judd, 2011; Resosudarmo et al., 2013).

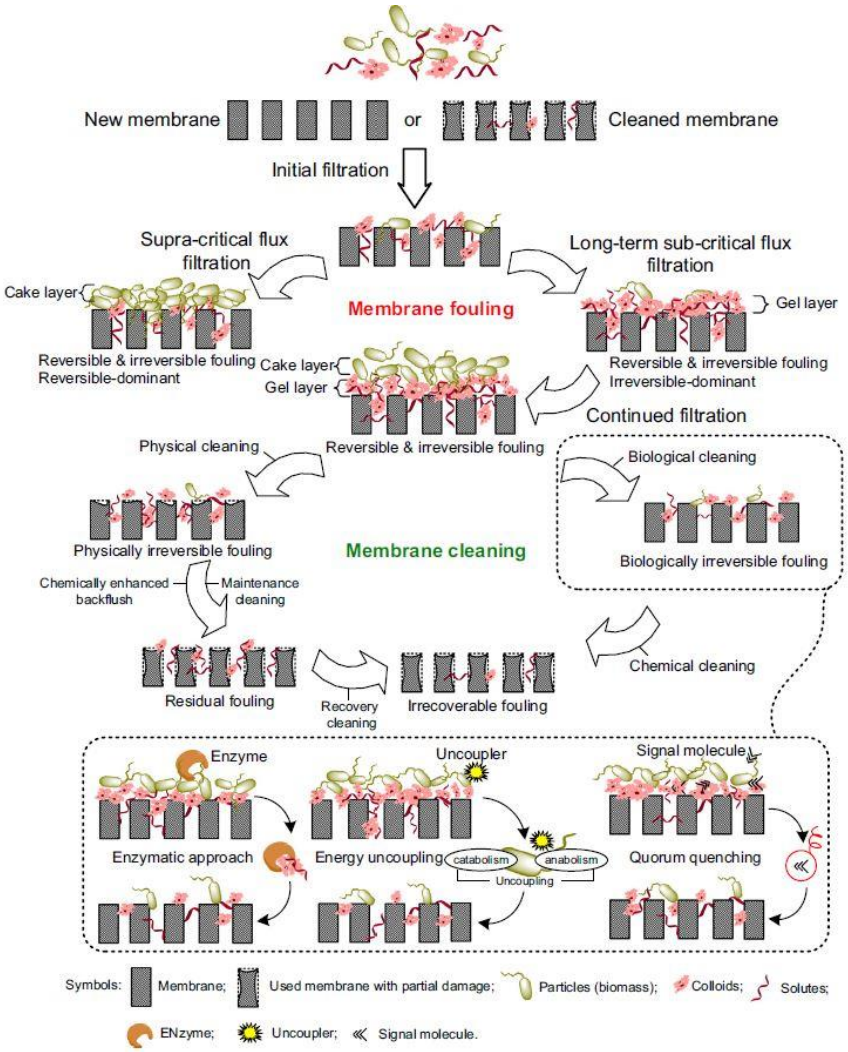

Figure 3.7 Membrane fouling classifications and cleaning strategies (Wang et al., 2014).

3.2.2 Biofouling, organic fouling and inorganic fouling

According to biological and chemical characteristics of membrane foulants, membrane fouling can be classified biofouling, organic fouling, and inorganic fouling (Meng et al., 2009; Spettmann et al., 2007). These

different types of membrane fouling influence the strategies of membrane cleaning (Wang et al., 2014).

Deposition and growth of microorganisms on membrane surface lead to the formation of *biofouling*. Therefore, biofouling process is due to colonization of membrane surfaces with microorganisms (Ma et al., 2013; Malaeb et al., 2013b). Biofouling may start with the deposition of individual cell or cell cluster on the membrane surface, after that the cells multiply and form a biocake (Meng et al., 2009). Zhang et al. (2006) observed that the microbial communities on membrane surfaces could be very different from the ones in the mixed liquor.

Organic fouling is due to the deposition of proteins, polysaccharides, humic acids and other organic substances (either soluble or colloidal) originated from feed water or microbial secretion (Wang et al., 2014). Soluble microbial products (SMP) and extracellular polymeric particle (EPS) are considered as key membrane organic foulants in MBRs. Due to the small size, the biopolymers can occlude easily the membranes pores (Meng et al., 2009). Metal cations can interact with some biopolymers forming chelating polymers and causing severe membrane fouling (Wang et al., 2008).

Inorganic fouling (scaling), as shown in Figure 3.8, can form through chemical precipitation of inorganic crystals and/or biological precipitation of inorganic-organic complexes (Costa et al., 2006; Meng et al., 2009).

Metal ions such as Ca^{2+}, Mg^{2+}, Fe^{3+}, and Al^{3+}, and the anions such as CO_3^{2-}, SO_4^{2-}, PO_4^{3-} and OH^- can react and lead to chemical precipitation if the saturation concentrations are exceeded on the membrane surfaces or other specific site (Wang et al., 2014) due to concentration polarization. Moreover, the inorganic particulates present in the systems can also attach onto membrane surfaces or block membrane pores causing inorganic fouling (Zhang et al., 2012). You et al. (2006) observed that inorganic scaling is not easy to be eliminated by means of chemical cleaning.

Carbonates are one kind of the predominant salts in inorganic fouling since aeration and the CO_2 produced by microorganisms can influence the super-saturation of carbonates and the pH of the sludge suspension (Meng et al., 2009).

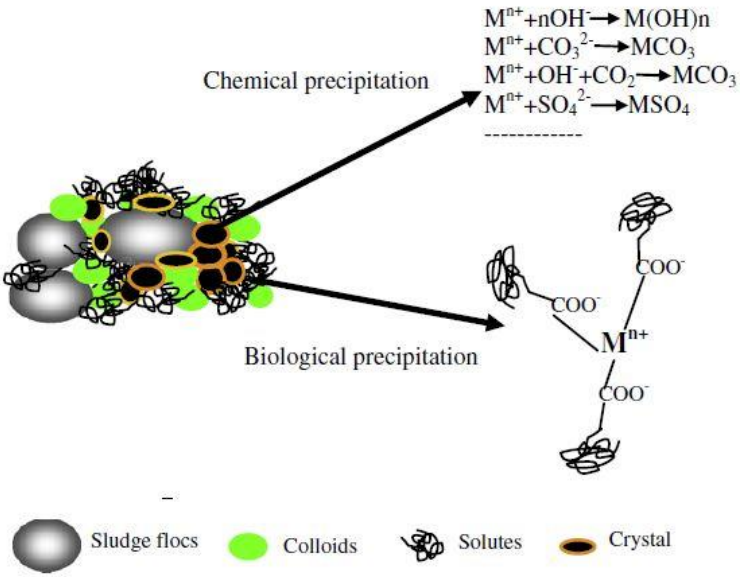

Figure 3.8 Illustration of inorganic fouling formation in MBRs (Meng et al., 2009).

The carbonates of metals such as Ca, Mg, and Fe can increase the potential of membrane scaling (You et al., 2005). Biological precipitation is another contribution to inorganic fouling (Meng et al., 2009). Indeed, biopolymers contain ionisable groups and metal ions can be easily captured by these negative ions. Metal ions present in the permeate can be caught by the bio-cake layer via complexing and charge neutralisation and then accelerate membrane fouling (Meng et al., 2009). Therefore, a synergistic interaction exists among biofouling, organic fouling and inorganic fouling (Meng et al., 2009).

Inorganic fouling can be controlled by pretreatment of feedwater and/or implementation of chemical cleaning (Meng et al., 2009). However, the presence of a small quantity of metal ions such as calcium can be beneficial for the filtration due to its positive effect on sludge flocculation ability (Kim and Jang, 2006).

3.3 FACTORS AFFECTING MEMBRANE FOULING

According to Le-Chech et al. (2006), the factors that influence the formation of membrane fouling in MBR can be classified into four group: membrane materials, biomass characteristics, feedwater characteristics and operating conditions. The complex interactions between these parameters complicate the understanding of membrane fouling (Meng et al. 2009). The relationship between MBR parameters and membrane fouling is shown in Figure 3.9.

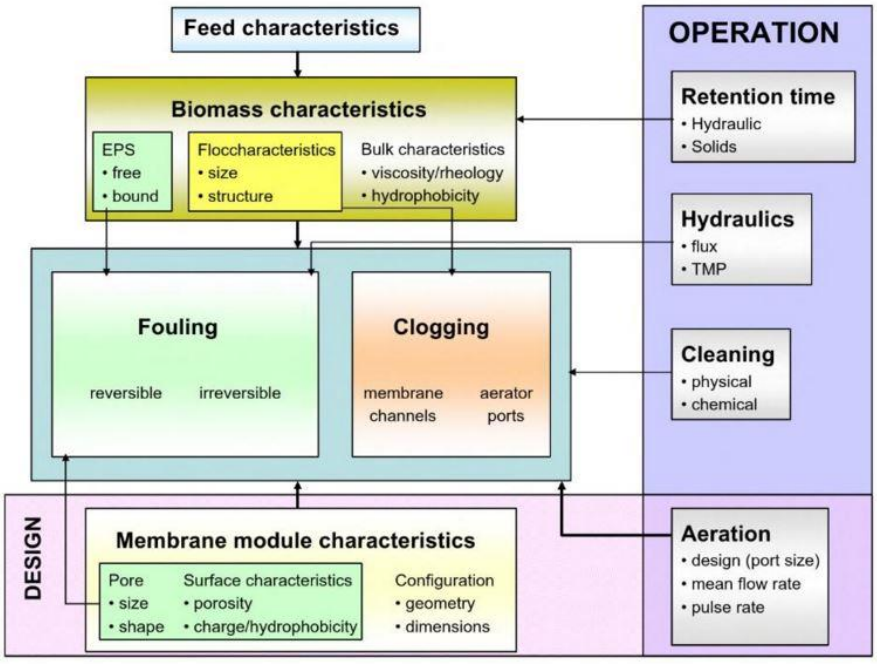

Figure 3.9 Relationship between MBR parameters and membrane fouling (Judd, 2011).

In the following, considering primarily the reviews of Le Chech et al. (2006), the influence that these parameters have on membrane fouling is reported.

3.3.1 Membrane characteristics

The particle size distribution and the feed solution characteristics influence the effects of pore size in a membrane bioreactor (Le Chech et al., 2006). In particular, if particles have dimension smaller than pore size, pore blocking and/or restriction are expected (Le Chech et al., 2006). Considering this, it is expected that large pore membranes like MF would present higher fouling propensity compared to UF membranes (Le Chech et al., 2006). However, the complex structure of biological suspension present in membrane bioreactors and the large pore size distribution of the membrane generally used are the main causes for the undefined general dependency of the flux propensity on pore size (Chang et al., 2002; Le-Clech et al., 2003). Since membrane characterized by smaller pore size retain a wider range of materials, the cake layer formed shows an higher resistance compared to large pore membranes (Le Chech et al., 2006). However, this kind of fouling is more reversible and can be easily removed during the maintenance cleaning respect to fouling due to internal pore clogging, observed in larger pore membrane systems which is the main cause of the poor long-term performances of larger pore size membranes (Le Chech et al., 2006).

Although all membranes have similar nominal pore size, polyvinylidene fluoride (PVDF), mixed cellulose esters (MCE) and polyethersulfone (PES) membranes show different fouling behaviours (Le Chech et al., 2006). While fouling was mainly due to cake formation for PVDF and MCE membranes, pore blocking was responsible for 86% of the total hydraulic resistance in the case of PES membrane (Le Chech et al., 2006). Overall, the PES membrane presented a 50% higher fouling resistance than the PVDF and MCE membranes (Le Chech et al., 2006). He et al. (2005) stated that the large "filling-in points" present on rougher membranes are more prone to the formation of fouling layers, compared to the fewer and smaller "crevices" observed on smoother membranes.

Regarding membrane configuration, hollow fiber modules are generally characterized by low costs, high membrane density and can tolerate vigorous backwashing, while flat plate and tubular membranes can control more easily fluid dynamics and distributions since they have well defined the membrane channel width (Cui et al., 2003; Le-Clech et al., 2006). As a result, hollow fibers may be more inclined to fouling and, thus, need more frequent physical and chemical cleaning (Le Chech et

al., 2006). Günder and Krauth (1998) observed better hydraulic performance of the flat plate in their studies.
Another parameter for submerged hollow fibers that can influence membrane fouling is packing density (Le Chech et al., 2006). The distance between adjacent membranes can influence the mass transfer and, thus, the shear and aeration demands (Le Chech et al., 2006). Furthermore, high packing density can result in severe clogging and slower rise of bubbles, limiting their control of fouling formation (Le Chech et al., 2006). According to Yeo and Fane (2005), in hollow fibers membranes characterized by low packing density configurations, cake layers from adjacent fibers do not interfere with each other and the effect of cross flow velocity (CFV) can be more distributed, controlling overall fouling.
With regards to the chemical characteristic of the membranes, membrane fouling is expected to be more severe with hydrophobic rather than hydrophilic membranes due to the hydrophobic interactions occurring between solutes, microbial cells and membrane material (CHANG et al., 1999; Kang et al., 2006; Yu et al., 2005). However, once initially fouled the membrane's chemical characteristics would become less important than the sludge materials covering the membrane surface (Le Chech et al., 2006).
Considering membrane materials, ceramic membranes exhibit less fouling beyond that higher chemical, thermal and hydraulic resistances, but they are not preferred due to their high cost (Le Chech et al., 2006). However, the membranes conventionally used in MBRs are polymeric-based (Le Chech et al., 2006). A direct comparison between polyethylene (PE) and PVDF membranes clearly showed that the later leads to a better prevention of irreversible fouling and that PE membrane fouled more quickly (Yamato et al., 2006). Furthermore, the same authors observed that some fractions of the organic matter present in the biomass presented a higher affinity with certain polymeric materials.

3.3.2 Feed and biomass properties

Fouling in membrane bioreactors is mostly affected by the interactions between the membrane and the biological suspension rather than the influent wastewater characteristics (Choi et al., 2005). The wastewater nature influences the physico-chemical changes in the biological suspensions (Jefferson et al., 2004; Le Clech et al., 2003). Le Chech et al.

(2003) also found that the fouling rate was higher using synthetic wastewater. For these reasons, the fouling propensity of the wastewater is indirectly taken into account during the characterization of the biomass (Le Chech et al., 2006).

The concentration of mixed liquor suspended solids (MLSS) has a complex interaction with MBR fouling and controversial findings about the effect of this parameter on membrane filtration have been reported (Le Chech et al., 2006). The increase in MLSS concentration seems to have a mostly negative impact (higher TMP or lower flux) on the MBR hydraulic performances (Chang and Kim, 2005; Çiçek et al., 1999) while some authors have observed positive impact (Brookes et al., 2006; Defrance and Jaffrin, 1999) or insignificant impact (Hong et al., 2002; Lesjean et al., 2005).

MLSS does not appear to have significant effect on membrane fouling between 8 and 12 g/l (Le Chech et al., 2006). While MBR performances are expected to decrease for higher MLSS at flux higher than the critical flux, the MLSS concentration may not play a significant role in fouling propensity when the MBR is operated at low fluxes (Le Chech et al., 2006). The lack of a clear correlation between MLSS concentration and any other foulant characteristics shows that the MLSS concentration is a poor indicator of biomass fouling propensity (Jefferson et al., 2004).

Biomass viscosity is considered as a foulant parameter and it is closely correlated to its concentration (Lee and Yeom, 2007).

There is a critical MLSS concentration under which the viscosity remains low and rises only slowly with the concentration (Le Chech et al., 2006). Above this critical value, viscosity increases exponentially with the solids concentration (Itonaga et al., 2004). The same behavior was observed for the capillary suction time (CST), another parameter closely related to viscosity (Brookes et al., 2003). Viscosity can modify bubble size and dampen the movement of hollow fibers in submerged bundles (Wicaksana et al., 2006), increasing fouling rate and reducing the transfer of oxygen in the mixed liquor (Germain and Stephenson, 2005).

Temperature affects permeate viscosity which is generally corrected in order to make comparable permeabilities or resistances obtained at different temperatures (Drews, 2010). Indeed, to avoid the interference of the temperature effects on MBR fouling, non-linear regression between critical flux and temperature was obtained (Fan et al., 2006):

$$J_{c,t} = J_{c,20} \times 1.025^{\,t-20} \qquad (18)$$

Parameters such as sludge viscosity and in turn shear stress/forces close to the membrane surface, deflocculation, release of EPS, diffusitivity, biodegradation and adsorption all depend on temperature (Drews, 2010). In a study, Lyko et al. (2008) observed that temperature has different effects on permeability in a full scale plant over 2 years. Indeed, as temperature was increased, CST decreased, while at the same time, filterability (measured in terms of a filtration index in lab scale) was not clearly correlated.

The greater resistances observed at low temperature were explained by four phenomena occurring in the system: (1) the sludge viscosity was calculated to increase by 10%, (2) intensified defloculation tend to occur at low temperature, reducing biomass floc size and releasing EPS to the solution, (3) particle back transport velocity is less at low temperature and (4) biodegradation of COD was also reduced at decreased temperature, resulting in a higher concentration of solute and particle COD in the reactor (Jiang et al., 2005). According to Miyoshi et al. (2009), reversible fouling was more significant in the low temperature period, while irreversible fouling developed more rapidly in the high temperature period.

Regarding dissolved oxygen, low levels of DO lower the cell hydrophobicity and, thus, cause floc deterioration (Le Chech et al., 2006). Therefore, deflocculation, increased SMP concentrations and a deterioration in filterability can be the result of oxygen stress (Drews, 2010).

Generally, higher DO tends to lead to better filterability and lower fouling rate (Le Chech et al., 2006). This was explained by the lower specific cake resistance of the fouling layer which leads to larger particle sizes and greater porosity (Kang et al., 2003; Kim et al., 2006). In a study obtained with anoxic and aerobic sludges (Jang et al., 2006), floc deterioration was observed and used as a possible explanation for the higher fouling rates obtained at anoxic conditions.

With regard to floc characteristics, the aggregation of the microorganisms and the formation of large floc is important for an effective separation of suspended biomass from the treated water (Le Chech et al., 2006).

Hydrophobic flocs lead to high flocculation propensity and low interaction with the (generally) hydrophilic membrane (Le Chech et al., 2006). Relative hydrophobicity of floc can be directly measured by bacterial adhesion to hydrocarbons (hexane) (Rosenberg et al., 1980) or

estimated by contact angle determination (Yu et al., 2005). Hydrophobicity measurement of sludge and EPS solutions revealed that the decrease of EPS relative hydrophobicity may cause floc deterioration (and consequent increase of *R*c) (Jang et al., 2006). Furthermore, low hydrophobicity of flocs is typically assumed to cause higher fouling due to floc deterioration and stronger interactions with the typically hydrophilic membrane (Drews, 2010).
Given the large number of recent publications dealing with the fouling of MBRs by bio-polymeric substances such as extracellular polymeric substances (EPS), soluble microbial products (SMP) and transparent esopolymeric particles, another paragraph is focused on their characteristics and influence on MBR fouling.

3.3.3 Operating conditions

In MBR systems, aeration allow to induce flow circulation and shear stress on the membrane surface (Le Chech et al., 2006). Aeration used in MBRs has three major roles: providing oxygen to the biomass, maintaining the activated sludge in suspension and mitigating fouling by constant scouring of the membrane surface. Mainly, the bubbles flowing due to aeration near to the membrane surface lead to local shear transients and liquid flow fluctuations, increasing back transport phenomenon and preventing large particle deposition on the membrane surface (Le Chech et al., 2006). However, the effect of tangential shear depends on function of particle diameter, with lower shear induced diffusion and lateral migration velocity for smaller particles, leading to more severe membrane fouling by fine materials (Choo and Lee, 1998).
In hollow fibers MBR systems, aeration leads to the movement of the fibers and the bubble can help to overcome the problems related to high packing density in hollow fiber bundles (Wicaksana et al., 2006; Le Chech et al., 2006).
On the other hand, intense aeration rate may also damage the floc structure reducing their size and releasing EPS in the bioreactor (Ji and Zhou, 2006; Park et al., 2005). These phenomena have been similarly observed in the sidestream MBR configuration in which the circulation pump is responsible for the break up of bacterial flocs (Tardieu et al., 1999; Wisniewski and Grasmick, 1998).
SRT (and consequently the F/M ratio) is one of the most important operating parameters impacting on membrane fouling formation in

MBRs (Grelier et al., 2006). Operating an MBR at higher SRT leads inevitably to increase of MLSS concentration, but this does not mean that there will be an increment of membrane fouling (Jinsong et al., 2006). Extremely low SRTs (down to 2 days) have shown fouling propensity (Trussell et al., 2006). There is no reason to run MBRs at these extreme conditions and F/M ratio is recommended to be maintained below 0.5 gCOD/gMLVSS/day (Le Chech et al., 2006). The reasons for that the fouling rate increases when SRT decreases include the increased levels of production of EPS (Le Chech et al., 2006). At the other end of the spectrum, MBRs operate at very long SRT, which is the advantage of this process over CASP in order to minimize sludge production as well (Le Chech et al., 2006). The increase in MLSS concentration due to long SRT could also result in higher fouling propensity even with the aeration raised significantly (Le Chech et al., 2006). Too short SRT might do harm to membrane performance while too long SRT, however, was also found to result in excessive membrane fouling (Meng et al., 2009). Lee et al. (2003) reported that increasing SRT from 20 days to 40 and 60 d, the overall fouling resistance increased. Therefore, there could be an optimal SRT, between the high fouling tendency of very low SRT operation and the high viscosity suspension prevalent for very long SRT (Le Chech et al., 2006).

3.4 MEMBRANE FOULING PRECURSORS

The biomass in a membrane bioreactor is characterized by different amounts of particulate, colloidal and dissolved fractions which are responsible for membrane fouling (Drews, 2010). In particular, extracellular polymeric substances (EPSs) are considered as the main origin of membrane fouling in membrane bioreactors (Drews et al., 2008). Another group, which until recently have only been studied in the formation of biofilms in marine and freshwater environments and considered as cause of biofouling on RO membrane surface (Berman and Holenberg, 2005), is rapresented by transparent exopolymer particles (TEP).

3.4.1 Extracellular polymeric substances (EPS) and soluble microbial products (SMP)

The term "EPS" is generally used to identify different classes of macromolecules such as polysaccharides, proteins, nucleic acids, (phosphor) lipids and other polymeric compounds which have been found at or outside the cell surface and in the intercellular space of microbial aggregates (Flemming and Wingender, 2001). They can be generated from cell-lysis, microbial metabolites or unmetabolised wastewater components (Drews et al., 2006). A distinction should be made between "bound" EPS (bEPS), embedded in the floc matrix, which derives directly from the active cell wall and are bound to the flocs and the "soluble EPS" or soluble microbial products (SMP) freely suspended in the supernatant and unassociated with the cell (Le-Clech et al., 2006). Generally, polysaccharides and proteins are considered as the major fractions that contribute to fouling. Thus, the determination of bEPS or SMP concentrations is based almost exclusively on polysaccharides and proteins measurements (Drews, 2010). The gel structure of bEPS and SMP makes them able to block the membrane pores, reducing the filtration and constituting a possible nutrient for biofilm formation (Rosenberger et al., 2005).

Extracellular polymeric substances (EPSs) have complex interactions or relationships with all membrane foulants and fouling mechanisms in MBRs (Figure 3.10).

In order to understand and control membrane fouling, it is important to study these interactions or relationships in MBRs (Lin et al., 2014).

Despite the substantial variation of the data, bound EPSs of sludge in MBRs generally fall in the range of 20–250 g/kg MLSS (Massé et al., 2006; Meng and Yang, 2007; Mishima and Nakajima, 2009; Su et al., 2013a; Zuriaga-Agustí et al., 2013). The EPSs matrix retains the sludge cells together determing the mechanical stability of the formed sludge flocs and providing a protective layer against adverse influences from the environment for the cells (Lin et al., 2014). EPSs possess large surface area and carry numerous functional groups, exerting great influences on the physico-chemical characteristics of sludge flocs, such as hydrophobicity, adhesion, settling, flocculation and dewatering properties and, therefore, significantly affecting membrane fouling in MBRs (Lin et al., 2014).

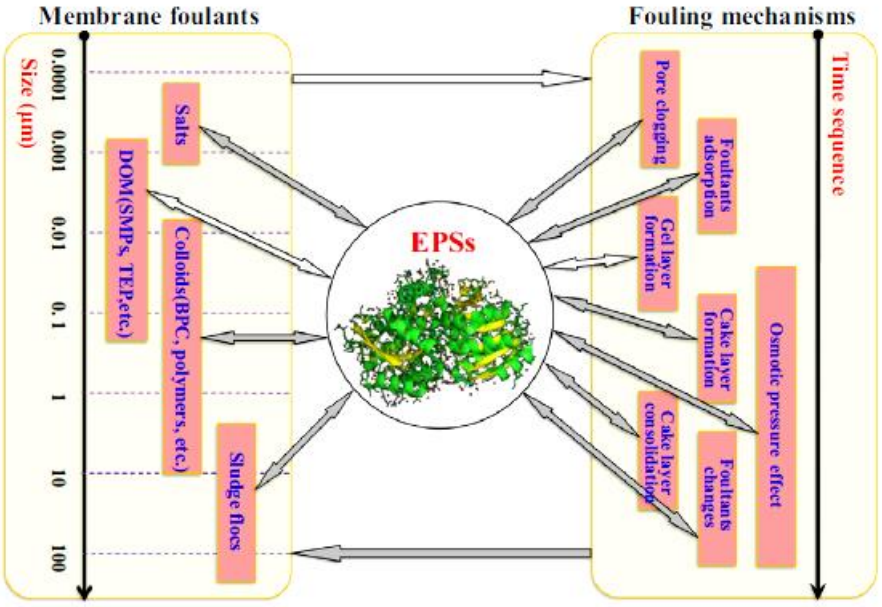

Figure 3.10 Interactions or relationships between EPSs and other membrane foulants and fouling mechanisms in MBRs (Lin et al., 2014).

EPSs show a three-dimensional, gel-like, highly hydrated matrix (Figure 3.11a), where the microorganisms are embedded and more or less immobilized (Wingender et al., 1999).

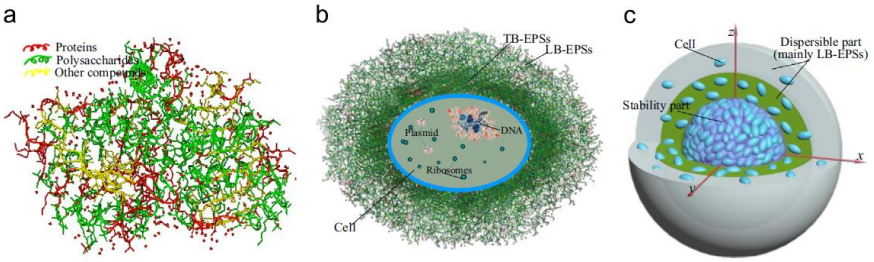

Figure 3.11 Representation of EPSs structure (a), cell structure (b) and sludge flocs structure (c) (Lin et al., 2014).

EPSs surrounding bacteria or in sludge flocs likely have a dynamic double-layered structure which is characterized by tightly bound EPSs (TB-EPSs) form inner layer and loosely bound EPSs (LB-EPSs) diffuse

in outer layer (Figure 3.11b-c) (Jorand et al., 1995; Poxon and Darby, 1997). LB-EPSs are of highly hydrated matrix and tend to form a dispersible and loose slime layer without an obvious edge (dispersible part) (Figure 3.11c). It was reported that LB-EPSs are more significantly correlated with membrane fouling in MBRs respect to TB-EPSs (Ramesh et al., 2006a; Wang et al., 2009).
EPSs are made of proteins, polysaccharides and other macro- molecules, carrying ionizable functional groups such as carboxyl, phosphoric and hydroxyl groups (Lin et al., 2014). These functional groups dissociating make EPSs negatively charged at near neutral pH (Lin et al., 2014). Hydrophobicity is usually considered as the tendency of non-polar molecules forming aggregates in order to decrease their surface of contact with water molecules, while hydrophilicity is a concept opposite to hydrophobicity (Meyer et al., 2006). EPSs present in the mixed liquor typically contain abundant charged groups and non-polar groups (Lin et al., 2014). EPSs show high ability of adhesion to substratum surfaces since, as shown in Figure 3.12, their chain is typically flexed and contains both hydrophilic and hydrophobic sites, allowing deposition of EPSs or sludge flocs on both hydrophilic and hydrophobic surfaces (Lin et al., 2014).

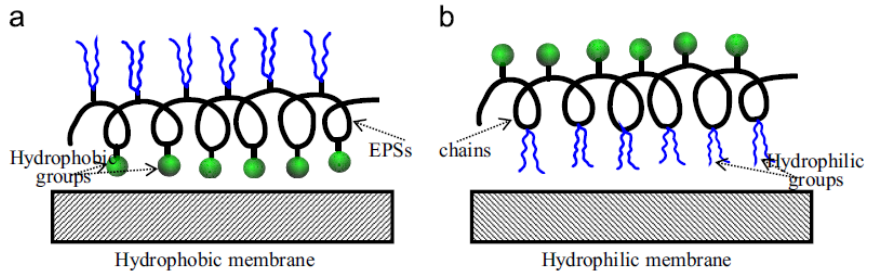

Figure 3.12 Adhesion of EPSs on surface of (a) hydrophobic membrane and (b) hydrophilic membrane (Lin et al., 2014).

They can block membrane pores, adhere to membrane surface, influence cake structure and, in general, membrane fouling formation. Laspidou and Rittmann (2002) developed a unified theory to elaborate interrelashionships between SMP and bound EPSs. Accordingly to these authors, SMP can be subdivided into biomass-associated products (BAP) and substrate-utilization-associated products (UAP). UAP and BAP were mostly made of small and large molecules, respectively (Boero et al.,

1996). Electron-donor substrate can be used for biomass synthesis to directly produce active cells, bound EPSs and UAP (Lin et al., 2014). BAP can be formed through bound EPSs hydrolysis and cell lysis (Lin et al., 2014). UAP and BAP can be recycled as electron-donor substrate due to their biodegradability (Lin et al., 2014). Some SMP can be adsorbed by the sludge flocs and become bound EPSs (Lin et al., 2014). SMP could significantly affect the fouling propensity of EPSs (Lin et al., 2014). It was suggested that initial adhesion of SMP and biopolymer matters colonized membrane surface and, then, facilitated the following adhesion of sludge flocs and, in particular of EPSs (Hong et al., 2013; Q. Wang et al., 2013).

Cho et al. (2005) observed a close relationship between the bound EPS and the specific cake resistance and reported a functional equation in which the specific cake resistance was proportional to the EPS concentration. Ahmed et al. (2007) also found that as bound EPS concentration incresed, the specific cake resistance rose, resulting in an rise of TMP. Ramesh et al. (2006b) fractionated bound EPS into loosely bound EPS and tightly bound EPS and observed that the fouling formation was primarily caused by the loosely bound EPS but not by the tightly bound EPS. Despite these results, several studies reported that bound EPS had little correlation with membrane fouling (Meng et al., 2009). Rosenberger and Kraume (2003) found that, contrary to some literature, no impact of bound EPS on the filterability could be observed. Instead, the soluble EPS or SMP was found to have great impact on the filterability of sludge (Meng et al., 2009). Another study (Yamato et al., 2006) reported no clear relation between bound EPS and membrane fouling as its concentration was smaller than 10 mg/g SS.

Ng et al. (2006) found that membrane fouling rate rose with increasing SMP and bound EPS concentrations, both of which increased with decreasing SRT. The increase of F/M ratio also led to high bound EPS concentration and sludge viscosity (Meng et al., 2007). Cho et al. (2005) found a relationship between specific resistance, MLVSS, TMP, permeate viscosity and EPS. In particular, EPS was found to have no influence on the specific resistance below 20 and above 80 mgEPS/gMLVSS, but had a significant role on MBR fouling between these two limits. This was confirmed by another study reporting no clear relation between bound EPS and membrane fouling for concentrations lower than 10 mg/gSS (Yamato et al., 2006). However, considering the significant roles of bound EPS in sludge characteristics and membrane

fouling, they should be controlled in order to limit membrane fouling more efficiently (Meng et al., 2009).
Laspidou and Rittmann (2002) reported that the formation of bound EPS is in direct proportion to substrate utilisation. Therefore, the increase of organic loading rate or F/M ratio will lead to the generation of more bound EPS (Meng et al., 2009).
Regarding SMPs, they can accumulate on the membranes or penetrate into membrane pores (Meng et al., 2009), adsorb on the membrane surface, form a gel structure on the membrane surface where they can be a possible nutrient source for biofilm formation and a hydraulic resistance to permeate flow (Rosenberger et al., 2005).
SMP can easily accumulated in MBRs due to the rejection of the membrane decreasing the filterability of the sludge suspension (Meng et al., 2009). Geng and Hall (2007) found that the floc size distribution and soluble EPS or SMP in the mixed liquor were the most important properties that significantly influenced the fouling formation in a MBR, but the content of bound EPS was not observed to be directly associated with membrane fouling. Furthermore, diffent studies have shown that polysaccharide SMP contribute to fouling more than protein substances (Rosenberger et al., 2006; Yigit et al., 2008), since direct relationships between the carbohydrate level in SMP solution with fouling rate (Lesjean et al., 2005), filtration index and CST (Evenblij et al., 2005; Grelier et al., 2006; Tarnacki et al., 2005), critical flux tests (Le-Clech et al., 2005), have been clearly observed (Le Chech et al., 2006).
As for EPS, SMP levels decreased with increasing SRT (Lee and Yeom, 2007). For SRT ranging from 4 to 22 days, SMPp and SMPc levels were reduced by factors of 3 and 6, respectively (Grelier et al., 2006).The control of SMP concentration in MBRs is diffucult due to the small size of these substances (Meng et al., 2009). In general, the control of SMP can be achieved by adjustment of operation parameters (i.e., SRT, HRT, DO concentration, temperature, aeration) and addition of adsorbents or coagulants to reduce SMP concentration (Meng et al., 2009).

3.4.2 Transparent exopolymer particles (TEP)

Regarding the TEP, they are very sticky, transparent, discrete particles (operationally defined as being >0.4 μm in diameter) that show the characteristics of gels and are considered as the acid fraction of

polysaccharides (Alldredge et al., 1993; Arruda Fatibello et al., 2004; Passow, 2002). They are large organic particles commonly found in sea water, surface water and, according to recent studies (Bar-Zeev et al., 2009; de la Torre et al., 2010; De la Torre et al., 2008), in wastewater. Passow (2002) proposed two possible pathways of TEP formation by the degradation of organic matter in acquatic enviroment (Figure 3.13).

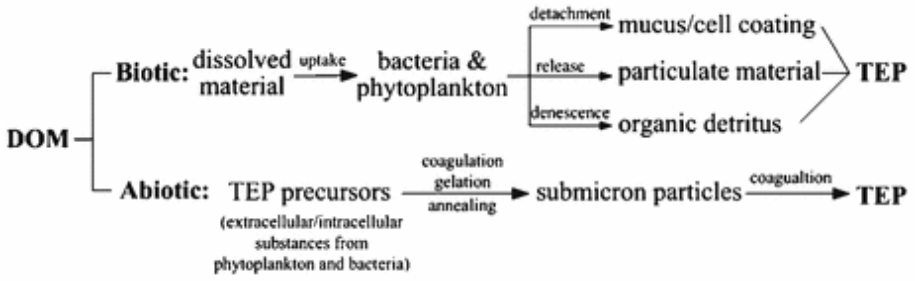

Figure 3.13 Formation of TEP from the degradation of the organic matter (Passow, 2002).

Many phytoplankton and bacteria can directly generate TEP from membrane mucous, cell coating surface and organic debris (Meng et al., 2013). TEP can be also generated from precursors (extracellular and intracellular substances) as a result of specific environmental conditions such as turbulence or ion density, especially in the marine environment (Meng et al., 2013). TEP can be considered as a kind of suspended extracellular polymeric substances (EPS) which are in the form of discrete particles instead of surface-attached or dissolved EPS (Berman, 2010; de la Torre et al., 2010; Passow, 2002). Thus, TEP not only contain polysaccharides but also may include proteins, lipids, amino acids, trace elements, and heavy metals (Passow 2002). This suggest that TEP can be a source of both nutrients and attachment sites for microorganisms (Meng et al., 2013). However, the transparent character of TEP had complicated earlier studies to investigate its abundance in aquatic systems (Villacorte et al., 2009).

As surface-active acidic polysaccharides, TEP can attach onto or be easily adsorbed by other solid surfaces including membranes. It has been reported that TEP can be colonized by bacteria (Passow 2002) and, consequently, these bacteria can be transport to solid surfaces through attachment of TEP due to their high stickiness (Meng et al., 2013). This in turn suggests a possible mechanism by which TEP can contribute to

membrane biofouling (Meng et al., 2013). The TEP-associated membrane biofouling has been reported in membrane filtration of seawater, surface water and wastewater (Bar-Zeev et al., 2012, 2009; de la Torre et al., 2010; De la Torre et al., 2008; Van Nevel et al., 2012; Wu et al., 2012). Berman and Holenberg (2005) first described the potential link of TEP with membrane fouling due to biofilm formation in reverse osmosis systems. Many study highlight the relationship between TEP and membrane fouling in RO membranes for desalination of seawater or drinking water (Bar-Zeev et al., 2012, 2009; Villacorte et al., 2009).

Nevertheless the focus on the role of TEP on membrane fouling formation, there are few reports dealing with the influence of this parameter on membrane fouling in wastewater treatment.

De la Torre et al. (2008) first studied the influence of these particles on the membrane fouling in a membrane bioreactor observing a linear correlation between the TEP concentration, the critical flux and the capillary suction time and showing the potential of this parameter as a membrane fouling indicator for MBR systems. They determined TEP by the method developed by Arrunda et al. (2004) through the dye alcian blu, in mg/L of xanthan gum. In addition, the method for the analysis of TEP is simpler and quicker than the conventional method for the analysis of the polysaccharide in the MBR fouling characterization, the dye is not toxic and no strong acids are used (De la Torre et al., 2008).

Wu et al. (2012) observed in a membrane bioreactor that, when the soluble substances (e.g., EPS and TEP) in the MBR suddenly increased, cleaned membranes were more inclined to be fouled than the membranes with the initial cake layers formed at a low fouling rate. They stated that soluble substances were major foulants in MBRs and that effective fouling control strategies could be: facilitating microbial flocs to form first loose structured cake layers on the membranes at a low flux; or adding coagulants or flocculants into the MBRs to adsorb or co-precipitate with the soluble substances (Wu et al., 2012).

All of the studies reported suggest that TEP may play a role in membrane biofouling.

3.5 STRATEGIES FOR CONTROLLING MEMBRANE FOULING

Control of fouling and clogging is commonly limited to the five principle strategies (Judd, 2011):

- Applying an appropriate pre-treatment to the influent wastewater;
- Employing appropriate physical or chemical cleaning protocols;
- Decreasing the flux;
- Increasing aeration intensity;
- Chemically or biochemically changing the characteristics of the mixed liquor.

3.5.1 Feed pre-treatment

While an MBR can displace primary sedimentation, oxidation process and secondary clarifier as well as tertiary effluent polishing, classical screen of 6 mm bar interspace is not enough for MBR, since it increases the potential of clogging of the membrane channel (Judd, 2011). In HF membranes, aggregates of hair are generally formed and tend to deposit at the top of the membrane module which are not able to be removed with backwashing or other cleanings (Judd, 2011). Clogging occurs in MBR due to the inhomogeneous fouling deposition, causing sludging in the membrane channels and at the channel inlet (Judd, 2011). If the pre-treatment are not appropriate, aeration system can be also damage due to the deposition of materials on it and, thus, its air scouring function is compromised.

3.5.2 Membrane cleaning

Membrane cleaning is typically classified into in-situ (on line cleaning) and ex situ cleaning (offline cleaning or cleaning out of place (COP)) according to the position of membrane modules within membrane bioreactor or out of bioreactor during cleaning (Wang et al., 2014). Membrane cleanings can be physical, chemical and biological/biochemical based on fouling removal mechanisms or cleaning agents used (Wang et al., 2014). Figure 3.14 schematically summarizes the protocols of 'in-situ' and 'ex-situ' cleaning adopted in MBRs (Wang et al., 2014). Ex-situ cleaning needs the removal of

membrane modules from membrane tank, and physical cleaning combined with chemical cleaning can be carried out (Figure 3.14) (Wang et al., 2014). In general, in-situ cleaning is preferred in MBRs during operation compared to ex-situ membrane cleaning and in-situ cleaning is performed more frequently than ex-situ cleaning (Wang et al., 2014). The time interval for ex-situ cleaning is typically once every 1-3 years (Brepols et al., 2008), while in-situ cleaning can be conducted every 10 min, or weeks, or several months in function of membrane fouling conditions and cleaning strategies used (Judd, 2011).

Physical cleaning

Physical cleaning is normally and widely carried out either by backflushing, i.e., reversing the flow, or relaxation, which is simply ceasing permeation whilst continuing to scour the membrane with air bubbles (Judd, 2011, Wang et al., 2014). Generally, physical cleaning, which is used to remove reversible fouling (e.g., deposited biosolids and cake layer), is less effective compared to chemical cleaning. However, it does not require chemical reagents and, thus, is less likely to cause membrane degradation/damage except for some harsh mechanical cleaning (Wang et al., 2014). Other physical methods, such as intermittent aeration and water flushing, are also used in MBRs (Judd, 2011). Tap-water flushing or moderate-pressure water flushing is usually used during ex-situ membrane cleaning (Wang et al., 2014).
Physical cleaning can be classified into hydraulic, mechanical, ultrasonic, and other cleaning, among which hydraulic cleaning is the most used approach for eliminating reversible fouling in MBRs (Wang et al., 2014). Hydraulic cleaning can be carried out either in situ or ex situ in case of needed (Wang et al., 2014). Air scouring, backflushing and relaxation (intermittent filtration) for in-situ membrane cleaning in submerged MBRs are included in hydraulic cleaning (Judd, 2011). Intermittent aeration and water flushing are also used in MBRs (Judd, 2011). Tap-water flushing or moderate-pressure water flushing are usually conducted during ex-situ membrane cleaning (Wang et al., 2014).
Air-scouring or aeration is commonly used for membrane cleaning since the cross flow velocity or shear stress induced by aeration can lead to the elimination of CP and/or remove reversible fouling (Qin et al., 2010; Ratkovich et al., 2009; Xia et al., 2013). Aeration intensity, bubble size,

bubble shape, and location and geometry of diffusers can influence membrane cleaning efficiencies (Wang et al., 2014).

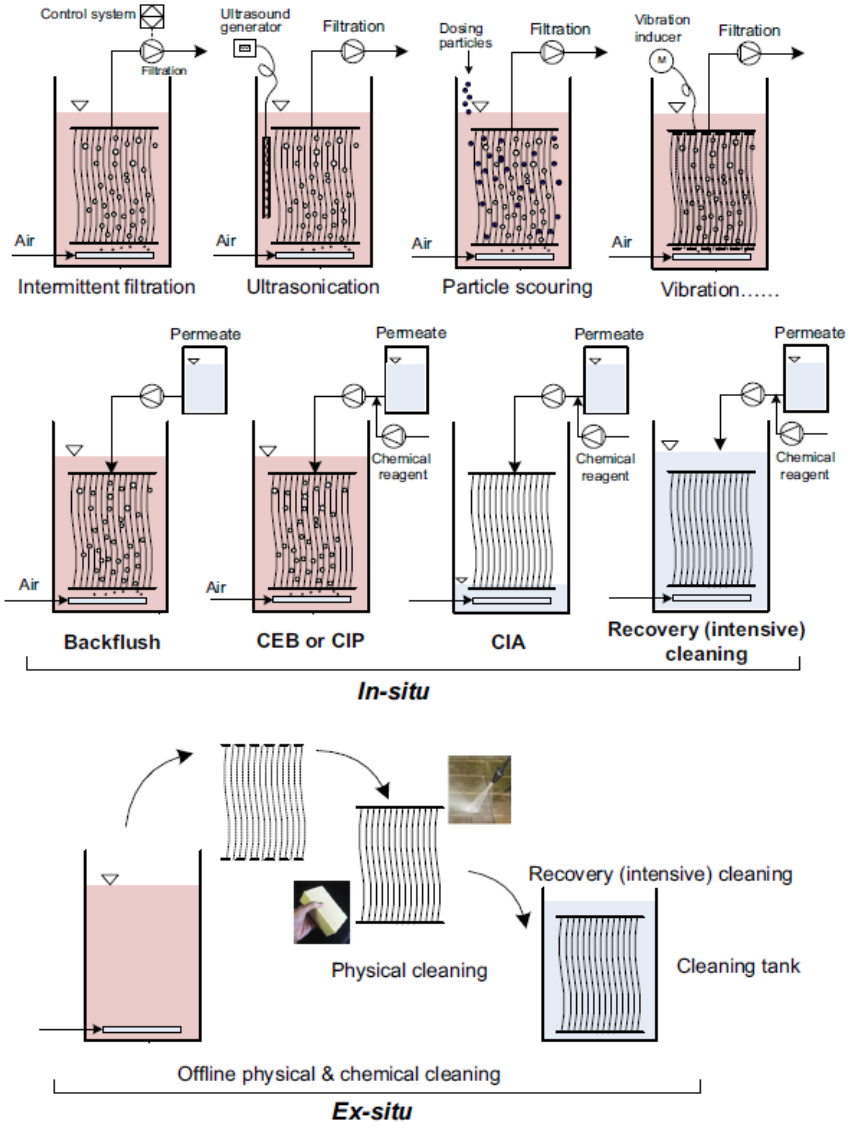

Figure 3.14 In-situ and ex-situ membrane cleanings where CEB is chemically enhanced backwash; CIP is cleaning-in-place; CIA is cleaning in air (in the drained membrane tank) (Wang et al., 2014).

Bubble flow velocity, channel gap width (FS membrane), membrane module geometry, sludge concentration (viscosity) and reactor geometry also influence the hydrodynamic conditions affecting membrane cleaning (Liu et al., 2000; Nagaoka et al., 2006; Prieske et al., 2010; Yamanoi and Kageyama, 2010).

Backflush flux, duration and frequency are the most important cleaning parameters for *backflushing* using permeate (Hwang et al., 2009; Raffin et al., 2012). Generally, there are less frequent and longer backflushing (7-16 min filtration/30-60 s backwashing), and more frequent and shorter backflushing (5-12 min filtration/ 5-20 s backwashing) for HF and MT membranes (Wang et al., 2014). It seems that the full-scale MBR plants tend to use more frequent backwashing (i.e., short filtration cycle) respect to scientific studies (Itokawa et al., 2008). An optimization of cleaning protocol, such as backwashing frequency and duration, is dependent on operational parameters (permeate flux, temperature, etc.), foulant properties and backwashing flux (Smith et al., 2006). Monitoring TMP profile during the filtration, the backwashing also in terms of duration can be automatically adjusted (Wang et al., 2014). Studies regarding backwashing have generally revealed that net permeability increases more with backwash flux and frequency than with duration (Decarolis et al., 2001; Kim and DiGiano, 2006; Smith et al., 2006; Zsirai et al., 2012). Backwash flux is another significant factor influencing cleaning efficiency (Wang et al, 2014). According to the same authors, the main backwashing flux, that is often used, is mainly ranging from 25 L/(m^2 h) to 40 L/(m^2 h) at the filtration flux 10–30 L/(m^2 h) in MBRs, although much higher backwash fluxes have been also applied, e.g., 48 L/(m^2 h) (Smith et al., 2005), 50 L/(m^2 h) (Raffin et al., 2012; J. Wu et al., 2008), and 58 L/(m^2 h) (Ivanovic and Leiknes, 2008). It has been reported that about 400% increase in the flux over that attained from continuous operation is achieved using air backflush if the scenario, 15 min of air backflush every 15 min of filtration, is used (Visvanathan et al., 1997).

Regarding *relaxation*, it allows in situ associated with air scouring the diffusive back transport of membrane foulants away from the membrane surface driven (Wang et al., 2014). Membrane fouling can be controlled with an intermittent filtration mode (filtration coupled with relaxation) (Le Chech et al., 2006, Wu et al., 2008). For aerobic MBR, relaxation is generally performed for 1-2 min every 7-15 min of filtration for both HF and FS membranes (Judd, 2011). Researches also reported that relaxation

combined with backwashing can enhance cleaning efficacy (Diez et al., 2012; Martinez-Sosa et al., 2011). Using relaxation, instead of backwashing, eliminates the need for additional permeate storage tanks, valves and piping (DeCarolis and Adham, 2007). Furthermore, the frequent backwashing can cause the damage of membrane integrity (DeCarolis and Adham, 2007). Other hydraulic methods, such as cyclic aeration and water flushing, are also available (Wang et al., 2014). *Cyclic aeration* (high/low aeration) can enhance the cleaning efficiency since low aeration results in the loose attachment of large particles (reversible fouling) (Wang and Wu, 2009) and high aeration can enhance the scouring of the membrane surface .

Water forward-flushing is also used for offline cleaning of membranes (Wang et al., 2014). Some studies (Jeison and van, 2007; Sofia et al., 2004) reported that flushing with tap water under moderate pressure can remove cake layer in MBRs. Initially deposited layer on the membrane surface can be easily removed by water flushing while further filtration might result in a compact fouling layer (Wang et al., 2014).

Chemical cleaning

Chemical cleaning is used in order to remove irreversible fouling by means of chemical reagents, such as bases (caustic soda), acids (hydrochloric, sulfuric, citric, oxalic, etc.), and oxidants (hypochlorite and hydrogen peroxide). As shown in Figure 3.7 and Figure 3.14, chemical cleaning can have several protocols based on the cleaning process, such as in-situ maintenance cleaning and in-situ recovery (intensive) cleaning. In situ maintenance cleaning includes clean in place (CIP), i.e., cleaning membrane in situ without draining the membrane tank, and clean in air (CIA), which is to clean membrane with the membrane tank drained (Wang et al., 2014). Recovery cleaning, which consists in soaking the membranes in cleaning reagent with higher concentration in the drained membrane tank (Figure 3.14), can be conducted either in situ (in-situ recovery cleaning) or ex situ during offline cleaning of membranes (Wang et al., 2014).

Chemical reagents applied in membrane cleaning can be generally divided into four categories: acids, bases, oxidants and other chemicals (chelating agents, surfactants, etc.) (Wang et al., 2014). Specific reagents can be applied in order to effectively clean the membrane fouled by given substances (Wang et al., 2014). Generally, various chemical

reagents are combined since the membrane foulants of MBRs are always a complicated mixture of organic, inorganic and biological species (Wang et al., 2014).

Acid cleaning eliminate inorganic fouling (crystals), which are caused by chemical precipitation of inorganic matters (multivalent cations) and biologically induced mineralization between biopolymer and salts (Malaeb et al., 2013; Meng et al., 2009). The widely-used acids include oxalic, citric, nitric, hydrochloric, phosphoric, and sulfuric acids (Wang et al., 2014).

Alkaline cleaning is used in order to remove organic foulants deposited on membrane surfaces (Wang et al., 2014). Sodium hydroxide (NaOH) is widely used as the cleaning reagent (Wang et al., 2014). Using this reagent, at caustic conditions, large organic particles such as colloids and microbes can be disintegrated into fine particles and/or soluble organic matters (Yu et al., 2013). Organic matters, such as proteins and carbohydrates, can be hydrolyzed and solubilized into small molecules (Wang et al., 2014). Oxidants aim to remove organic and biological foulants through oxidation and/or disinfection. The commonly-used oxidants are sodium hypochlorite (NaClO) and hydrogen peroxide (H_2O_2) for membrane cleaning, while other kinds of oxidants have been also used, e.g., polyvinyl pyrrolidone (PVP)-iodine, peracetic acid and sodium perborate .

Maintenance cleaning is designed to maintain membrane permeability and reduce the frequency of recovery cleaning and offline cleaning [cleaning out of place (COP)] (Wang et al., 2014). In general, it is thought that maintenance cleaning is routinely employed for HF membranes (Judd, 2011) but it can be also conducted for FS membranes (Wang et al., 2014). The CIP is performed in the mixed liquor without draining the tank (Wang et al., 2014). Sometimes, the water level in the tank is decreased to a lower level prior to CIP through extracting permeate and stopping the influent (Wang et al., 2014). The major difference between FS and HF CIPs is that FS CIP feeds the cleaning solution into the membrane and soaks the membrane for 1-2 h while HF CIP usually backwashes the membranes. After soaking, the FS MBR plant starts normal operation (Wang et al., 2014). The cleaning reagents remaining in the membrane go out through the permeate lines, and then can be sent to the head of works. During chemical cleaning, aeration intensity can be reduced in the case of sludge foaming due to the release of cleaning reagents into mixed liquor (Wang et al., 2014). In general, maintenance

cleaning is performed more frequently compared to recovery cleaning (Wang et al., 2014). The range of maintenance cleaning interval is 3-120d (Wang et al., 2014). NaClO is the most used cleaning reagents in full-scale MBRs, which is often combined with citric acid during cleaning (Wang et al., 2014). The popular NaClO and citric acid concentrations for maintenance cleaning are 300-2000 mg/L and 0.2-1.5 wt%, respectively (Wang et al., 2014).

Recovery cleaning is commonly performed when further filtration is no longer sustainable due to a diminished permeability (Le Chech et al., 2006). Compared with maintenance cleaning, recovery cleaning frequency is 1 month to 3 years and, thus, once or twice a year (Wang et al., 2014). Recovery cleaning also takes a relatively longer time to complete the cleaning process from 8 h to 24 h (Wang et al., 2014). The cleaning reagents are similar to maintenance cleaning with higher concentration than those of maintenance cleaning (Wang et al., 2014). In particular, the concentrations of NaClO and citric acid that predominantly adopted are 500-3000 mg/L (average 2000 mg/L) and 0.4-2 wt% (average 1.1 wt%), respectively (Wang et al., 2014).

Physical-chemical cleaning

One of the typical physico-chemical cleaning methods is chemically enhanced backflush (CEB) (Wang et al., 2014). The cleaning efficiency of backwashing is enhanced by adding a low concentration of cleaning agents into the backwash water (Wang et al., 2014), resulting in a maintenance cleaning. CEB is carried out less frequently than normal backwashing but more often compared to regular maintenance cleaning (CIP and CIA). CEB can be carried out daily or up to every 7-14 d, but usually on a daily basis (Gabarrón et al., 2013; Zsirai et al., 2012). The concentration of chemical reagents used in CEB is generally lower than that of maintenance and recovery cleaning (Wang et al., 2014). The typical concentration for CEB using sodium hypochlorite is in the range of 100–500 mg/L.

3.5.3 Innovative cures for membrane fouling

Addition of additives/particles/carriers

Addition of the additives, such as adsorbent agents, carriers, coagulants and other chemical agents, can alter the sludge properties (Lin et al.,

2013) They will adsorb SMP and colloids, increase EPSs content in flocs, enlarge flocs size, and thus control membrane fouling (Lin et al., 2014). Adsorbent agents such as powdered activated carbon (PAC) (Jamal Khan et al., 2012; Lin et al., 2011; Satyawali and Balakrishnan, 2009), zeolite (Yuniarto et al., 2013), bentonite, vermiculite, Moringa oleifera (Damayanti et al., 2011; Malamis et al., 2009) and clay (Yi et al., 2013), and coagulants including ferric chloride, aluminum sulfate, polyacrylamide (PAM), polyaluminum chloride (PACl), polyferric sulfate (PFS) and chitosan (Ji et al., 2010; Song et al., 2008; Wu et al., 2006), have been applied in order to limit membrane fouling. Once dissolved in water, aluminum tends to form hydroxide precipitates which adsorb materials such as suspended particles, colloids and soluble organics (Le Chech et al., 2006). Holbrook et al. (2004) reported that the addition of alum led to a significant reduction of the SMPc concentration, along with an improvement in membrane hydraulic performances. Due to back transport and shear induced fouling control mechanisms, large microbial flocs are expected to have a lower impact on membrane fouling (Le Chech et al., 2006). Zeolite has also been applied in MBRs and allowed the fromation of rigid flocs that have lower specific fouling resistance (Le Chech et al., 2006). Addition of adsorbents into biological treatment systems reduces the concentration of pollutants and, in particular, of organic compounds (Le Chech et al., 2006). When PAC is mixed with the activated sludge, biologically activated carbon forms and is responsible for significant uptake of soluble organics (Le Chech et al., 2006).

Particles and carriers have been also used in MBRs since they can mechanically scour the membrane surface, enhance the foulant back-transport away from the membrane surface due to the turbulence created and vibrate HF membranes (Huang et al., 2008; Rosenberger et al., 2011; Yang et al., 2006; Zhong et al., 2007). The particle should be regular and without sharp edges for avoiding damage to membranes (Wang et al., 2014).

The particle size should be less than the distance/diameter of fluid channel of membranes and the density close to or a little higher than water density in order to facilitate their distribution and recirculation in mixed liquor (Wang et al., 2014). It has been reported that MLSS concentration might be a significant factor for determining the dosage (Huang et al., 2008). For GAC/PAC, the dosages adopted in aerobic MBR are mainly in the range of 1–5 kg/m^3 (Kim et al., 2011). Mechanical

cleaning through the addition of particles/granulates has been commercialized (Wang et al., 2014). For example, a commercial process, Bio-Cells-Mechanical Cleaning Process (Bio-Cells-MCP) for continuous mechanical cleaning, has been produced by MICRODYN-NADIR GmbH by adding granulates in MBRs (Wang et al., 2014).

Addition of nanomaterials

Chae et al. (2009) recently developed a novel measure which used fullerene C60 nanoparticles addition to alleviate membrane fouling. It was demonstrated that C60 decreased the zeta potential and increased hydrophobicity, and then impeded attachment of Escherichia coli (Lin et al., 2014). Copper-based nanoparticles and magnesium or titanium oxide can be other potential additives to alleviate fouling (Chae et al., 2009).

Vibration/rotation

Vibration and rotation of membranes can generate high shear or turbulence at the membrane surface, resulting in an on-line cleaning of membranes (Beier et al., 2006; Kimura et al., 2000; Prip Beier and Jonsson, 2009). Presently, the reported vibration systems include the Vibratory Shear Enhanced Process (VSEP) and Vibrating Hollow Fiber Modules (VHFM) (Bilad et al., 2012).
Rotating membrane modules have been also industrialized and applied in MBRs (Wang et al., 2014). Wu et al. (2008) constructed a rotating aerobic MBR utilizing round FS membrane fixed on the axes of an electric motor. A commercial product, Grundfos BioBooster-Rotation Cross-flow (RCF) MBR system, has been available in MBR market (Bentzen et al., 2012).

Ultrasonic cleaning

Ultrasonication has been utilized for membrane cleaning in various membrane filtration processes (Juang and Lin, 2004; Muthukumaran et al., 2004; Naddeo et al., 2015a, 2015b). Ultrasonic cleaning can be carried out either in situ or ex situ (Lim and Bai, 2003; Sui et al., 2008). The parameters influenced cleaning efficiencies are ultrasonic frequency, power density, and duration (Wang et al., 2014). The membrane cleaning efficiency is lowered as the frequency is increased for any type of

membrane and materials (Wang et al., 2014). In particular, in the range of 20 to 100 kHz, the flux recovery rate decreases much significantly with the increase of frequencies (Wang et al., 2014). Application of ultrasound for membrane cleaning can also influence the sludge properties in MBRs, which will in turn impact membrane fouling and cleaning (Wang et al., 2014).

Biological/biochemical cleaning

Physical and chemical cleaning methods can damage membrane integrity, impact on microbial viability and generate chemical waste reagents (Lin et al., 2013). Less aggressive cleaning, such as biological cleaning methods have been gradually developed to remove foulants from membranes and to recover the permeability (Wang et al., 2014). Bioactive agents (enzymes or signal molecules) have been used to enhance the removal of membrane foulants (Maartens et al., 1996; Muñoz-Aguado et al., 1996). Enzymatic cleaning, energy uncoupling and quorum quenching are more intensively studied and used in MBRs (Wang et al., 2014). *Enzymatic approach* is one of the most prevalent biological/ biochemical cleaning methods (Argüello et al., 2003; Petrus et al., 2008). Enzymatic agents are highly specific for the biopolymers with which they interact and efficient in breaking the fouling layer on the membrane surface, thus avoiding the physical and chemical destruction of the membrane materials (Wang et al., 2014). Generally, proteases can remove proteins and protein-like substances from the membrane surface, and the biological depolymerization of alginate (polysaccharides) can be catalyzed by alginatelyase through the β-elimination mechanism (Chen and Columbia, 2011). Amylase has been found to be effective in removing humic acid fouling (Yu et al., 2010). Quorum quenching is innovative strategy for biological/ biochemical cleaning of fouled membranes (Wang et al., 2014). The formation of biofilm induced by quorum sensing demonstrates negative impacts on filtration process in MBRs (Khor et al., 2007; Yeon et al., 2009). In light of these results, Yeon et al. (2009) applied the concept of bacterial quorum sensing to MBRs as a new biofouling cleaning strategies.

4 ELECTROCHEMICAL AND BIO-ELECTROCHEMICAL PROCESSES IN WASTEWATER TREATMENT

Membrane bioreactors represent a promising technology for wastewater treatment and reuse, as highlighted in the second chapter. Membrane fouling, however, restricts their wider use. The application of an electric field to a membrane bioreactor was proven to increase the treatment performance as well as reduce fouling. In wastewater, an internal energy exists which can be extracted as electricity and be used to reduce fouling directly or to lessen input of external energy. Microbial fuel cells (MFCs) and microbial electrolysis cells (MECs) are two types of bioelectrochemical systems (BES) that use exoelectrogenic microbes to produce energy from wastewater by converting biodegradable organic matter directly into electricity and hydrogen, respectively. Just recently, MBRs have been combined with bioelectrochemical systems (BES) for cost-effective wastewater remediation.
This chapter reports the application of electrochemical and bio-electrochemical processes for wastewater treatment and their combination with membrane bioreactors in order to enhance the treatment performance and control fouling.

4.1 WASTEWATER TREATMENT BY ELECTROCHEMICAL PROCESSES

Biological processes are the most widely used method for wastewater treatment. They have significant advantages since they are cost effective, well studied and can be adapted to different needs (Esplugas et al., 2004; Ganzenko et al., 2014; Oller et al., 2011). However, they have some limits related to the degradation of toxic and/or refractory organic pollutants (Ganzenko et al., 2014). In order to remove refractory compounds and dewater the sludge, electrochemical technologies have been applied to wastewater treatment.

They are considered as benign technologies due to the fact that chemicals are rarely applied during treatment and the main reagent to simulate reaction is electron (Khandegar and Saroha, 2013). Electrochemical treatment methods have high efficiency, easy operation and compact facilities. The different electrochemical processes used for wastewater treatment are discussed below.

4.1.1 Electrocoagulation

Electrocoagulation (EC) is a complex process characterized by many chemical and physical processes that use anodic dissolution of consumable metal electrodes to supply ions into the wastewater stream (Mollah et al., 2004). This process involves the application of an electric current to sacrificial electrodes inside a reactor tank where the current generates a coagulating agent and gas bubbles (Emamjomeh and Sivakumar, 2009). In addition, electrocoagulation/flotation leads to the electrolytic addition of coagulating metal ions directly from sacrificial electrodes (Emamjomeh and Sivakumar, 2009). Therefore, the fundamental of electrocoagulation is the formation in situ of a coagulant species that can remove various pollutants from the water and wastewater (Emamjomeh and Sivakumar, 2009). There are three main mechanisms in the whole of electrocoagulation/flotation process: electrode oxidation, gas bubble generation, flotation and sedimentation of flocs formed (Emamjomeh and Sivakumar, 2009). The metal ions, at an appropriate pH, can form wide ranges of coagulated species and metal hydroxides that destabilize and aggregate the suspended particles or precipitate and adsorb dissolved or suspended contaminants (Chen, 2004). In an electrocoagulation process, the electrode assembly is usually connected to an external DC source and the important parameter is the selection of the electrode material and the mode of combination of anode and cathode (Khandegar and Saroha, 2013). The electrodes should be non-toxic to human health and environment (Khandegar and Saroha, 2013). The electrode materials generally used are aluminium, iron, stainless steel, mild steel and graphite since they are cheap, readily available, nontoxic and very effective (Mollah et al., 2001, 2004; Emamjomeh and Sivakumar, 2009). In particular, the most widely used electrode materials in EC process are aluminium and iron because of the trivalent form of the metal (Attour et al., 2014). In the case of aluminium, main reactions are as:

- Oxidation reaction takes place at the anode:

$$Al(s) \rightarrow Al^{3+}(aq) + 3e^{-} \quad (19)$$

- Reduction reaction takes place at the cathode:

$$3H_2O + 3e^{-} \rightarrow (3/2)H_2\,(g) + 3OH^{-} \quad (20)$$

Al^{3+} and OH^{-} ions generated by electrode reactions (19) and (20) react to form various monomeric species which transform finally into $Al(OH)_3(s)$ according to complex precipitation kinetics (Bayramoglu et al., 2004):

$$Al^{3+} + 3H_2O \rightarrow Al(OH)_3(s) + 3H^{+} \quad (21)$$

The amorphous $Al(OH)_3(s)$ "sweep flocs" have large surface areas which are beneficial for a rapid adsorption of soluble organic compounds and trapping of colloidal particles (Bayramoglu et al., 2004). Finally, these flocs can be removed easily from aqueous medium by sedimentation or H_2 flotation (Bayramoglu et al., 2004). In the case of iron electrodes:

- Oxidation reaction takes place at the anode:

$$Fe\,(s) \rightarrow Fe^{2+}(aq) + 2e^{-} \quad (22)$$

$$Fe\,(s) \rightarrow Fe^{3+}(aq) + 3e^{-} \quad (23)$$

- Reduction reaction takes place at the cathode:

$$2H_2O + 2e^{-} \rightarrow H_2(g) + 2OH^{-} \quad (24)$$

- Overall reaction during electrolysis:

$$Fe^{2+}(aq) + 2OH^{-} \rightarrow Fe(OH)_2\,(s) \quad (25)$$

$$Fe^{3+}(aq) + 3OH^{-} \rightarrow Fe(OH)_3\,(s) \quad (26)$$

These metal hydroxide species neutralize the electrostatic charges on suspended solids and oil droplets, allowing the agglomeration or

coagulation and resulting in the separation from the aqueous phase (Mollah et al., 2001).

EC is cost effective and easily operable since it needs simple equipment and can be designed for any capacity of effluent treatment plant (Khandegar and Saroha, 2013). Secondary pollution, caused by chemical substances added at a high concentration when chemical coagulation is applied, can be avoid in the EC since no chemical addition is required in this process due to the generation of the coagulants by the electro-oxidation of a sacrificial anode (Aouni et al., 2009). For that reason, it can be considered as an environmental friendly technology, since the 'electron' is the main reagent and does not require addition of the reagents/chemicals (Khandegar and Saroha, 2013). EC allows the removal of smallest colloidal particles: the smallest charged particles can get coagulated due to the electric field that sets them in movement. (Aouni et al., 2009). It has also the advantage of producing a relatively low amount of sludge with low current application, eliminating some of the harmful chemicals used as coagulants in the conventional effluent treatment processes (Khandegar and Saroha, 2013). The advantages of electrocoagulation, compared to chemical coagulation, are as follows:

- EC does not need an addition of chemicals and provides better removal capabilities for the same species than chemical coagulation;
- EC removes many species that chemical coagulation is not able to remove;
- EC produces less sludge, thus lowering the sludge disposal cost;
- EC sludge is more readily filterable and can be utilized as a soil additive;
- EC technique needs minimal start-up time.

Some of the limits that characterize the electrochemical coagulation are the following (Mollah et al., 2001, 2004; Khandegar and Saroha, 2013):

- The sacrificial anodes require to be replaced periodically;
- Electrocoagulation needs a minimum solution conductivity in function of reactor design, limiting its use with effluent containing low dissolved solids;
- In case of the removal of organic compounds, from effluent containing chlorides, there is a possibility of formation of toxic chlorinated organic compounds;

- Impermeable oxide film may be formed on the cathode which may provide resistance to the flow of electric current;
- High cost of electricity can result in an operational cost increase.

The efficiency of the electrocoagulation process depends on many operational parameters such as conductivity of the solution, arrangement of electrode, electrode shape, type of power supply, pH of the solution, current density, distance between the electrodes, agitation speed, electrolysis time, initial pollutant concentration, retention time and passivation of the electrode (Khandegar and Saroha, 2013). The solution needs to have a minimum conductivity for the flow of the electric current (Khandegar and Saroha, 2013). If the conductivity is low, salts can be added to the solutions, such as sodium chloride or sodium sulphate. The current density increases with the increase of the conductivity of the solution at constant cell voltage (Khandegar and Saroha, 2013). Regarding the shape of the electrodes, it is expected that the punched holes type electrodes will result in higher removal efficiency compared to the plane electrodes (Khandegar and Saroha, 2013).

Another important operation parameter is the pH of the solution. The maximum pollutant removal efficiency is obtained at an optimum solution pH for a particular pollutant (Khandegar and Saroha, 2013). Current density defines the coagulant dosage rate, bubble production rate, size and growth of the flocs, affecting efficiency of the electrocoagulation (Khandegar and Saroha, 2013). An increase in current density above the optimum current density does not necessarily lead to an increase in the pollutant removal efficiency since a sufficient number of metal hydroxide flocs are available for the sedimentation of the pollutant (Khandegar and Saroha, 2013). Furthermore, in order to have the maximum pollutant removal efficiency, it is necessarily maintaining an optimum distance between the electrodes. At the minimum inter-electrode distance, the pollutant removal efficiency is low due to the fact that the generated metal hydroxides, which act as the flocs and remove the pollutant by sedimentation, get degraded by collision with each other due to high electrostatic attraction (Daneshvar et al., 2004).

Electrocoagulation has been applied in order to remove heavy metals (Kobya et al., 2011), suspended solids (Sadeddin et al., 2011), emulsified oils (Fouad, 2014) and dyes (Merzouk et al., 2009) from water and wastewater, especially of industrial origin. It was found to effectively remove chromium from tannery wastewater (Elabbas et al., 2015), total petroleum hydrocarbon (TPH) from oil refinery wastewater (Perez et al.,

2015), Al and Zr from can manufacturing wastewater (Kobya and Demirbas, 2015), color from sugar beet molasses (Tsioptsias et al., 2015) and textile wastewater (Ghanbari and Moradi, 2015), Mn, Cu and Zn from oil refinery wastewater (Gatsios et al., 2015) and phosphate from mining wastewater (Kuokkanen et al., 2015).

4.1.2 Electrochemical oxidation

For the removal of non-biodegradable organic compounds, advanced oxidation processes are applied using, as the main agent, the hydroxyl radical which has the second highest redox potential after fluorine and, thus, it is strongly oxidizing (Ganzenko et al., 2014). Since hydroxyl radicals have a short life (Ein-Mozaffari Farhad, 2009), they can be easily self-eliminated from the system (Ganzenko et al., 2014). Among different AOPs processes, the electrochemical advanced oxidation processes (EAOPs) have been increasingly attracting attention due to their perspective applications (Martínez-Huitle and Ferro, 2006; Oturan et al., 2011; Quan et al., 2013; Rosales et al., 2012). The main drawback of EAOPs, which limits up-scaling, is its relatively high costs (Oller et al. 2011), related to energy consumption during extensive treatment time until the complete mineralization. Therefore, they can be combined with biological processes, applied as post-treatment, for the removal of the biodegradable compounds produced or as a final step after biological treatment in order to remove residual refractory pollution and to make the effluent comply with discharge limits (Ganzenko et al., 2014).

In electrochemical processes, pollutants can be oxidized by direct oxidation through electron exchange between the pollutants and the electrode surface, or by indirect oxidation through the formation of powerful oxidizing species, such as hypochlorite, ·OH, H_2O_2 and O_2 (Quan et al., 2013). Direct or anodic oxidation (AO) occurs due to direct electron transfer between the electrode and the pollutant molecule or by oxidation through reactive species formed on the surface of the electrode.

In AO, water is electrooxidized at the anode surface (MOx) leading to the formation of physically sorbed active species (·OH) (Eq. 27) which cause the complete oxidation of the pollutants (R) into water and CO_2 (Eq. 28) (Chen, 2004; Sopaj, 2013).

$$MO_x + H_2O \rightarrow MO_x(\cdot OH) + H^+ + e^- \quad (27)$$

$$MO_x(\cdot OH) + R \rightarrow MO_x + mCO2 + nH2O + nH^+ + ne^- \quad (28)$$

In indirect electrooxidation, strong oxidizing species are produced in situ resulting in the degradation of organics in the bulk solution. One of the most commonly used electrochemical oxidants are chlorine and hypochlorite produced in situ upon addition of salts (e.g. sodium chloride) or when the wastewater has high chloride concentration (> 3 g/L) (Chen, 2004). However, possible formation of chlorinated organic by-products, which are highly toxic compounds, hinders its wide application. Other oxidants such as ozone, peroxodisulfate, hydrogen peroxide and silver (II) ion are also studied (Chen, 2004; Ganzenko et al., 2014).

Electrochemical oxidation (EO) is an adequate tool for treating wastewater containing organic compounds (Mouli et al., 2004). It has been employed in the removal of toxic and persistent pollutants like pharmaceutical products (Brillas et al., 2010; Feng, 2013; Sopaj, 2013), municipal solid waste leachate (Quan et al., 2013; Urtiaga et al., 2009), degradation of dyes in wastewater (Martínez-Huitle and Brillas, 2009) and olive wastewater (Cañizares et al., 2006). The non-addition of large amount of chemicals, no tendency of producing secondary pollution and fewer accessories required are just among the advantages of anodic EO respect to indirect oxidation.

4.1.3 Electrokinetic processes for sludge treatment

Electrokinetic processes have been used for the extraction of surfactants and heavy metals (Gao et al., 2013) from wastewater sludge and for its dewatering, realizing an improved liquid/solids separation (Mahmoud et al., 2011). Electrokinetic (EK) process combines the effects of motion and electrical field in the removal of contaminants from wastewater. It is defined as the application of a low level current between two electrodes to facilitate movement of the fluid and charged particles within the porous media. Electrochemical reactions play a significant role in the species transport. Upon application of electricity, water electrolysis occurs producing oxygen gas and protons (H^+) at the anode and hydrogen gas and hydroxyl anion (OH^-) at the cathode (S. O. Kim et al.,

2002; Mahmoud et al., 2010). As a result, acid and alkali fronts are formed at the anode and cathode, respectively, which then migrate towards the oppositely charged electrodes, according to a process called electromigration (Ferri et al., 2009). The movement of H^+ and OH^- in the solution causes pH variation which can affect physicochemical processes such as adsorption-desorption, precipitation-dissolution and oxidation-reduction (Liu et al., 2013). These physicochemical processes facilitate extraction and removal of the organic and inorganic pollutants from wastewater.

Aside from electromigration, two important mechanisms are also considered in the electrokinetic treatment of wastewater. These are the electrophoresis and electroosmosis. Electroosmosis occurs when bulk liquid is drifted towards the oppositely charged electrode as a result of an applied electric field (Mahmoud et al., 2010). The direction of electroosmotic flow is generally towards the cathode since bulk liquid is commonly positively charged. Electrostatic velocity is governed by the following equation:

$$\upsilon_{eo} = \frac{D\zeta}{4\pi\mu}\nabla\phi \tag{29}$$

where, D is the dielectric constant of the medium, ζ the zeta potential (V), $\nabla\phi$ is the electric field strength of gradient in a direction parallel to the electroosmotic flow and μ is the dynamic viscosity of the medium.

Colloidal particles in an electrolyte solution usually possess negative surface charge and have large surface area relative to its volume. This renders electrostatic repulsions to dominate between suspended solids rather than the Van der Waals force, hence, preventing the particles to agglomerate. Upon DC application, the charged particles interacts with the electric field and move towards the electrode of opposite charge, according to a process known as electrophoresis (Ferri et al., 2009). The magnitude of electrophoresis flow is analogous to that of electrostatic velocity but only in different direction, hence, the negative sign:

$$\upsilon_{ef} = -\frac{D\zeta}{4\pi\mu}\nabla\phi \tag{30}$$

Where υ_{ef} is the electrophoretic velocity.

As per above equations, both electroosmosis and electrophoresis velocities are directly proportional to the zeta potential and electric field strength. In an electrolytic solution, the negative charges adsorbed on the surface of the colloids attract cations from the bulk liquid producing a region of non-zero net charge density. This phenomenon was first proposed by Hermann von Helmholtz in 1850's who named the region as electrical double layer (EDL). According to Stern model, an EDL exists as two separate layers: a) an inner layer of strongly bound ions known as the Stern layer and b) an outer layer of loosely associated ions called the diffuse layer (Figure 4.1). In the diffuse layer, a zone which contains the immobile ions is called slipping plane and the potential that exists in this region is called as zeta potential, ζ. Zeta potential plays a crucial role in determining the stability of a colloidal suspension which can be achieved at high zeta value. It is controlled by the pH of the medium and the ionic strength of the solution. The decrease of solution pH and increase in cationic concentrations due to migration of acid front to the anode during electrokinetic process cause a decrease in zeta potential, hence, reducing the velocity of electroosmosis and electrophoresis flow (Weng et al., 2013).

Addition of electrolyte shrinks the diffuse double layer causing Van der Waals interactions to dominate and coagulation of suspended solids to occur (Mahmoud et al., 2010). Lack of electrolyte supplement builds up electric resistance in the system, therefore, decreasing the electric current and slows down water and particle transport towards opposite charged electrodes.

Electrokinetic method is one of the most promising technologies that can help improve the handling and disposal of sludge which has been considered as one of the most challenging issues affecting wastewater treatment. It is found to be faster, more efficient and has lower operational costs in removing chemically water from sludge as compared to mechanically and thermally driven sludge dewatering techniques (Glendinning et al., 2007; Mahmoud et al., 2011, 2010; Weng et al., 2013). It is also known to enhance treatment of xenobiotic components such as surfactants and heavy metals (e.g. Cd, Ni, Zn, etc.) from contaminated soils and sewage sludge (Ferri et al., 2009; Gao et al., 2013; S. O. Kim et al., 2002; Wang et al., 2005; Yang et al., 2009; Yuan and Weng, 2003).

Figure 4.1 shows how electro dewatering can improve the removal of the water.

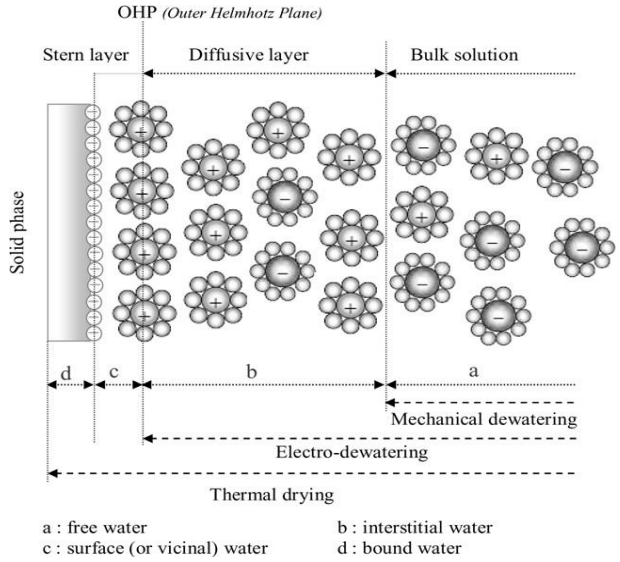

Figure 4.1 Dewatering methods in relation to water distribution in the materials (Mahmoud et al., 2010).

Since the fine-particle suspensions possess a surface charge, usually negative, they are surrounded by a layer with a higher density of positive charges, the electric double layer (Mahmoud et al., 2010).
When an electric field is applied, the usually negative charged particles move towards the electrode of the opposite charge (Mahmoud et al., 2010). The water, commonly with cations, is driven towards the negative electrode (Mahmoud et al., 2010). Electro-dewatering, thus, comprises electrophoresis, electro-osmosis and electromigration (Mahmoud et al., 2010). The mechanical dewatering techniques such as filtration/ compression, gravitational settling and centrifugation are effective in removing free water (Figure 4.1). Electrically-assisted mechanical dewatering can remove a significant proportion of the water that cannot be removed using mechanical dewatering technologies (Mahmoud et al., 2010).

4.2 WASTEWATER TREATMENT BY BIO-ELECTROCHEMICAL PROCESSES

The urgent need to use an energy-efficient and environmental friendly technology for offsetting the energy consumption of wastewater treatment plants has led to the development of bioelectrochemical systems (BES). These are a new and promising approach for simultaneously treating wastewater while generating electricity (Puig et al., 2011) or hydrogen. They should be considered as leading edge innovations for sustainable technology which are currently gaining attention from scientific community due to its capability to extract energy from wastewater during treatment. A BES consists of two electrodes; an anode and a cathode which are often separated by an ion selective membrane and connected by an external wire to complete an electrical circuit. At the anode, exoelectrogenic bacteria oxidize organic matter in anaerobic conditions and produce electrons, carbon dioxide and proton. The bacteria are called exoelectrogenic since they can exogenously transfer electrons to a terminal electron acceptor (TEA) such as a metal oxide like iron oxide. The electrons are transferred to the anode, then flow to the cathode, through an external circuit characterized by a conductive material containing a resistor, and combine with oxygen and protons produced at the anode side, thus, generating electricity (Logan et al., 2006). Electrons can be transferred by exoelectrogenic bacteria outside the bacterial cell to the anode either through direct contact, using outer membrane proteins or self-produced conductive pili called nanowires, or through indirect contact with self-produced electron shuttles such as flavins and phenazines or some artificial redox mediators (Sharma et al., 2014) such as neutral red or anthraquinone-2,6-disulfonate (AQDS). The protons travel through the solution in the cell to the cathode while the carbon dioxide can be captured and reused.

Two major types of BES exist depending on the cathode configuration. These are the microbial fuel cells (MFCs) and microbial elelctrolysis cells (MECs) (Figure 4.2). In case of a MFC, aerobic condition is maintained at the cathode chamber and the electrons combine with the protons and oxygen to form water. In a MEC, oxygen is not supplied at the cathode side, therefore, the electrons arriving at the cathode combine with the protons to produce hydrogen. This reaction, however, does not occur spontaneously so a small amount of external energy (in addition to that

generated by the bacteria) needs to be added to the system in order to drive this process. Thus, MFCs are electricity producing while MECs are electricity requiring for hydrogen production. Both MFCs and MECs are innovative methods for simultaneous renewable energy production and wastewater treatment.

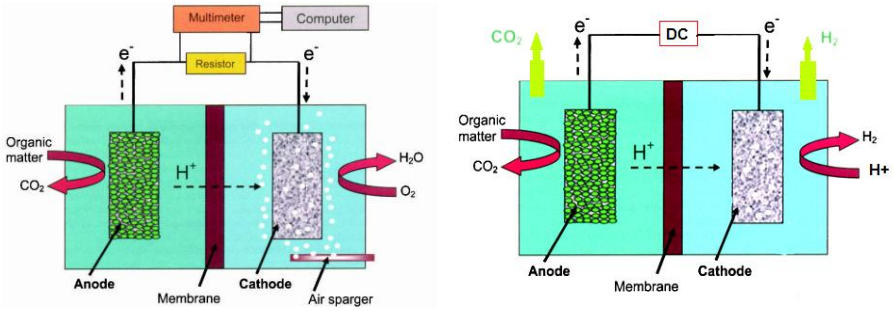

Figure 4.2 Microbial fuel cell (MFC) on the left, microbial electrolysis cell (MEC) on the right adapted from Logan (2008).

4.2.1 Microbial fuel cell (MFC)

A representation of a microbial fuel cell is reported in Figure 4.2. The oxygen in the anode chamber will inhibit electricity generation since it is an electron acceptor, the bacteria should be keep away from the oxygen. This can be achieved by placing a membrane that allows charge transfer between the electrodes, resulting in the formation of two separate chambers (Logan, 2008): the anode chamber, where the bacteria grow and the cathode chamber, where the electrons react with the catholyte.
Dissolved oxygen is provided in the cathode chamber for allowing the reaction. Oxygen is the most suitable electron acceptor for a MFC due to its high oxidation potential, availability, low cost, sustainability, and the lack of a chemical waste product (water is formed as the only end product) (Logan et al., 2006). The two electrodes are connected by a wire containing a load (i.e., the device being powered), but in the laboratory a resistor is used as the load (Logan, 2008). The membrane is permeable to protons produced at the anode, so that they can migrate to the cathode where they, combing with electrons transferred via the wire and oxygen, form water (Logan, 2008). Therefore, the following reactions take place at the anode and cathode chamber in presence of acetate as organic substance:

- Oxidation at the anode chamber:

$$C_2H_4O_2 + 2\ H_2O \rightarrow 2\ CO_2 + 8\ e^- + 8\ H^+ \quad (31)$$

- Reduction at the cathode chamber:

$$O_2 + 4\ H^+ + 4\ e^- \rightarrow 2\ H_2O \quad (32)$$

The current produced by a MFC is typically calculated in the laboratory by monitoring the voltage drop across the resistor using either a voltmeter (intermittent sampling), a multimeter or potentiostat hooked up to a computer for essentially continuous data acquisition (Logan, 2008).

For MFC different configurations exist. The most widely used, since inexpensive, is a two chamber MFC built in a traditional "H" shape, consisting usually of two bottles connected by a tube containing a separator which is usually a cation exchange membrane (CEM) (Logan et al., 2006) such as Nafion (Logan et al., 2005; Min et al., 2005) or Ultrex (Rabaey et al., 2003), or a plain salt bridge (Min et al., 2005).

The membrane should allow the protons to pass between the chambers, indeed, the membrane is also called proton exchange membrane (PEM), but the passage of the substrate to the cathode chamber or electron acceptor, generally oxygen, to the anode chamber should avoid.

An inexpensive way to join the bottles is to use a glass tube that is heated and bent into a U-shape, filled with agar and salt, as a cation exchange membrane, and inserted through the lid of each bottle (Logan et al., 2006). The salt bridge MFC, however, produces low power due to the high internal resistance observed (Logan et al., 2006).

When oxygen is used as an electron acceptor, it is not necessary to place the cathode in water or in a separated chamber. The cathode can be placed in direct contact with air, either in the presence or absence of a membrane (Liu and Logan, 2004). Higher power densities have been observed using oxygen as the electron acceptor when aqueous-cathodes are replaced with air-cathodes (Logan et al., 2006). In the simplest configuration, the anode and cathode are placed on either side of a tube, with the anode sealed against a flat plate and the cathode exposed to air on one side, and water on the other (Logan et al., 2006). The utilization of oxygen by bacteria in the anode chamber can lead to a lower Coulombic efficiency, which is the fraction of electrons recovered as current versus the maximum possible recovery (Liu and Logan, 2004). In

order to increase the overall system voltage, MFCs can be stacked with the systems shaped as a series of flat plates or linked together in series (Aelterman et al., 2006).

The materials utilized for the anodes must be conductive, biocompatible, and chemically stable in the reactor solution (Logan et al, 2006). Non-corrosive stainless steel mesh can be utilized. The most versatile electrode material is carbon, available as compact graphite plates, rods, or granules, as fibrous material (felt, cloth, paper, fibers, foam), and as glassy carbon (Logan et al, 2006). Carbon has several advantages such as good conductivity, biocompatibility and versatility in morphologies, sufficiently low over-potentials and low costs. Indeed, reports showed porous carbon produced higher current density than metals. The simplest materials for anode electrodes are graphite plates or rods since they are relatively inexpensive, easy to handle, and have a defined surface area (Logan et al, 2006). It has been shown that current increases with overall internal surface area in the order carbon felt > carbon foam > graphite (Chaudhuri and Lovley, 2003). Cathode material greatly affects performance and its choice depends on the application (Logan et al, 2006). In bioelectrochemical systems, the surface area of the anode affects the production of current density. This is mainly because larger specific surface area provides more chance of biofilm formation and direct extracellular electron transfer (Sharma et al., 2014). Several surface modifications are being done on the anode material. Moreover, electrodes with a rough surface also proved to produce higher current density than smooth ones.

The reaction takes placed in a MFC is evaluated in terms of the overall cell electromotive force (emf), *E*emf (V), defined as the potential difference between the cathode and anode.

$$E_{emf} = E_{cat} - E_{an} \quad (33)$$

where the minus sign is a result of the definition of the anode potential as reduction reaction (although an oxidation reaction is occurring) (Logan et, 2006). The open circuit voltage (OCV) is the cell voltage that can be measured after some time in the absence of current (Logan et al., 2006). Theoretically, the OCV should approach the cell emf, however, the OCV is lower than the cell emf, due to various potential losses (Logan et al., 2006). Indeed, the maximum MFC voltage (emf) that can be theoretically reached is on the order of 1.1 V (Logan et al., 2006). However, the measured MFC voltage is considerably lower due to a

number of ohmic, activation, bacterial and concentration losses. In an open circuit, when no current is flowing, the maximum MFC voltage achieved thus far is 0.80 V (Liu et al., 2005). During current generation, voltages achieved up to now remain below 0.62 V (Rabaey et al., 2005b).
MFC experiments can require specialized electrochemical instrumentation (Liu et al., 2004). In most cases, cell voltages and electrode potentials are measured with commonly available voltage meters, multimeters and data acquisition systems connected in parallel with the circuit (Logan et al., 2006). Cell voltages can be determined directly from the voltage difference between the anode and cathode (Logan et al., 2006); electrode potentials can only be determined against a reference electrode that needs to be included in the electrode compartment (Bard and Faulkner, 2000). Current is calculated using Ohm's law, $I=Ecell/R$, using the measured voltage (Logan et al., 2006). The potentiostat is used in order to control either the potential or the current of an electrode and study, in this way, the electrochemical response of the electrode at that specific condition (Logan et al., 2006). The potentiostat typically operate in a three-electrode-setup consisting of a working electrode (anode or cathode), a reference electrode, and a counter electrode (Bard and Faulkner, 2000). In MFC experiments, the potentiostat is often used for voltammetry tests in which the potential of the working electrode (anode or cathode) is varied at a certain scan rate (expressed in V s^{-1}) (Logan et al., 2006). Voltammetry can be applied for evaluating the electrochemical activity of microbial strains or consortia (H. J. Kim et al., 2002; Rabaey et al., 2004), determining the standard redox potentials of redox active components (Rabaey et al., 2005a), and testing the performance of novel cathode materials (Zhao et al., 2005).
The potential of an electrode (anode or cathode) can only be determined by measuring the voltage against an electrode with a known potential, i.e., a reference electrode (Logan et al., 2006). The standard hydrogen electrode (SHE) or normal hydrogen electrode (NHE), consisting of a platinum electrode in a hydrogen saturated acidic solution, has a potential of 0 V (Logan et al., 2006). Since the NHE is not a very practical reference electrode to work with in an experimental setup, other reference electrodes are often used such as the silver-silver chloride (Ag/AgCl) reference electrode, due to its simplicity, stability, and non toxicity (Logan et al., 2006). In a saturated potassium chloride solution at 25 °C the Ag/AgCl reference electrode has a potential of +0.197 V against the NHE (Logan et al., 2006). Also practical, but less common in

MFC experiments, is the saturated calomel electrode (SCE, 0.242V against the NHE) (Logan et al., 2006). Electrode potentials are influenced by the pH, that should be monitored in the experiments. The overall performance of an MFC is evaluated principally through power output and Coulombic efficiency. Power is calculated as (Logan et al., 2006):

$$P = I E_{cell} \quad (34)$$

Where the voltage is measured across a fixed external resistor *(Rext)* and the current is calculated from Ohm's law.

4.2.2 Microbial electrolysis cell (MEC)

Microbial electrolysis cell (MEC) is an electrochemical device which generates hydrogen gas from biomass through microbial catalysed process in an anaerobic cathode chamber via the application of a small external voltage. The production of hydrogen at the MEC cathode is shown by the following reaction :

$$2H^+ + 2e^- \rightarrow H_2\,(g) \quad (35)$$

Theoretically, the standard redox potential for this reaction to occur is -0.414 V. The bacteria at the anode can produce as much as -0.3 V. With oxygen, the cathode potential in a MFC is 0.2 V (vs. NHE), achieving an overall cell voltage approaching 0.5 V [0.2 V - (-0.3 V) = 0.5 V)]. In order to form hydrogen at the cathode, however, the oxygen should be removed and a cathode potential at pH = 7 and 298 °C of -0.414 V should be overcome (Logan, 2008). Therefore, an additional potential greater than -0.11V is needed to yield H_2 at the cathode (Cusick et al., 2010). The cell voltage is negative, so the reaction is not spontaneous. Power source is required to initiate the reaction at the electrodes since no oxidant is allowed on the cathode (Escapa et al., 2016).
The voltage needed to achieve H_2 gas production in a MEC can be applied using a MFC or any power source (Logan, 2008). While 0.114 V in theory is required with acetate as a substrate, in practice larger voltages have to be applied due to overpotential at the cathode (Logan, 2008). Experiments have shown that in practice -0.25V have to be applied to the circuit in order to reach reasonable current densities and rates of hydrogen (Logan, 2008). In the MEC process, loss of hydrogen due to its

diffusion through the membrane into the anode chamber or its degradation by bacteria that might grow in the cathode chamber, are primary challenges (Logan, 2008). Hydrogen needs to be generated in a manner that reduces its diffusion back into the anode chamber (Logan, 2008).

The following are just among the different advantages of using MEC in wastewater treatment:

a) The specific energy requirement (>-0.2V) is relatively low compared to 1.23 V applied voltage for conventional hydrogen production via water electrolysis (Logan, 2004; Rozendal et al., 2008, 2007);
b) Since MECs operate under anaerobic conditions, additional costs brought by aeration, a requirement when using MFCs, can be eliminated resulting in large energy savings;
c) Production of sludge is much lower as compared to activated sludge process, thus, reducing additional costs for sludge treatment and disposal;
d) MEC is suitable for treating low concentrations of organic matter in wastewater;
e) MEC has higher hydrogen recovery and can utilize more diverse substrate than the fermentative method (Hu et al., 2008);
f) MEC can operate below 20°C which other anaerobic methods failed to do (Pham et al., 2006).

Hydrogen represents an interesting option since it is a critical resource in many strategic industrial sectors (metallurgy, fertilisers, chemical and petrochemical industry, etc.) (Scholz, 1993), and for its high energy yield (142.35 kJ $g^{-}1$) could be considered the energy carrier of the future (Gómez et al., 2011).

Like the anode for the microbial fuel cell, the cathode material in a MEC significantly affects its ability to reduce protons into hydrogen. Plain carbon based material alone is seldom used as cathode material since it requires high overpotential to drive hydrogen production. Most of the carbon-based materials used for anodes can be used as cathode materials, although some modifications are usually required, the most important being the need for a catalyst to drive the hydrogen evolution reaction (HER) at low over-potentials (Escapa et al., 2016). This reaction is identical to that occurring in conventional electrolysis systems, which usually use noble metals (e.g. platinum, palladium) due to their stability and excellent catalytic activity (Escapa et al., 2016). Usually, metal

catalysts are added for better performance. Metal catalysts are one of the most critical materials and also one of the most expensive in the construction of elecrochemical system (Tenca et al., 2013). Pt catalysts are commonly used as cathode, however, Pt is expensive and mining or extraction of this metal incurs negative impact to the environment. Several alternative materials have, therefore, been proposed including stainless steel (SS) (Call et al., 2009; Munoz et al., 2010; Zhang et al., 2010), palladium (Huang et al., 2011), nickel alloys (Manuel et al., 2010) and iron (Xiao et al., 2012). Nickel and stainless steel are currently the most promising materials identified so far. Both metals are cheap, easily available, have low overpotentials and are highly stable in alkaline solution (Selembo et al., 2009). First row transition metals are also better alternative due to their stability, abundance in nature, low cost and low toxicity to living organisms. Several studies also showed the potential of a biotic cathode which uses microorganisms to catalyze hydrogen production (Jeremiasse et al., 2010; Rozendal et al., 2007).

For the past decade, these two bioelectrochemical systems have been extensively reviewed. Substantial research on microbiology, substrates and reactor configuration and operation have been done which help to improve the performance of the reactor and increase its potential for future scale-up projects. Among the many types of wastewaters that have been examined using MFCs and MECs are brewery (Feng et al., 2008), domestic (Heidrich et al., 2012), food processing (Oh and Logan, 2005; Tenca et al., 2013), meat processing (Heilmann and Logan, 2006), paper recycling (Huang and Logan, 2008), real urban (Rodrigo et al., 2007), starch processing (Lu et al., 2009) and swine wastewaters (Min et al., 2005).

The energy that could be captured from domestic wastewater is enough to run a treatment plant (Logan, 2008). The most significant energy savings of MFCs for wastewater treatment, besides electricity generation, result from the removal/reduction of aeration and solids handling since the sludge yields for an anaerobic process are approximately one-fifth of that for an aerobic process (Logan, 2008).

The major drawback of using BES technologies is that the effluent from the anaerobic anode needs to be treated further before discharge because the turbidity, ammonia, phosphate and organic matters in anaerobic effluent cannot meet the discharge standards. To enhance the effluent qualities, hybrid systems integrating BES with membrane bioreactor had

been proposed. Such integration also contributes to membrane fouling control.

4.3 INTEGRATION OF ELECTROCHEMICAL AND BIO-ELECTROCHEMICAL PROCESSES INTO MEMBRANE BIOREACTORS

4.3.1 Electro membrane bioreactors (eMBRs)

In addition to traditional methods for fouling mitigation, such as physical and chemical cleaning, which increase energy demand and operating costs as well as reduce the membrane lifespan, over the last years a significant amount of advanced strategies for membrane fouling reduction has emerged (Leyva-Díaz et al., 2014; Naddeo et al., 2015a, 2015b).

Recent studies have proven that the integration of electrochemical processes into membrane bioreactors represents an alternative technological approach for membrane fouling control (Giwa et al., 2015; Hosseinzadeh et al., 2015; Keerthi et al., 2013; Zhang et al., 2015). When an electric field is applied to a membrane bioreactor, the anode and the cathode are exposed to oxidative and reductive conditions respectively, which influence the sludge proprieties in the bioreactor (Hasan et al., 2012).

Two novel types of electro membrane bioreactor (eMBR) have been proposed and developed. The first one is an eMBR which uses the membrane directly as the cathode and filtration module or applies the electrochemical processes as a pre-treatment in a separate chamber (Akamatsu et al., 2010; Chen et al., 2007; Liu et al., 2012b), while the second type, known as submerged membrane electro-bioreactor (SMEBR), applies the electric field between two electrodes placed inside the membrane bioreactor (Bani-Melhem and Elektorowicz, 2010; Giwa et al., 2015; Hasan et al., 2012).

The application of a direct current field to prevent membrane fouling in a membrane bioreactor was first investigated by Chen et al. (2007) who have designed a bioreactor divided into two compartments for separating the membrane assembly from the electric zone (Figure 4.3). In their

work, they observed that when electricity is applied, suspended solids and colloidal particles migrated away from the membrane surface. They attributed this to the electrophoresis mechanism and, thus, to the electrostatic repulsion between the negatively charged sludge surface and the electrically applied membrane which inhibited the deposition of these foulants and increased the membrane flux. The authors (Chen et al., 2007), indeed, found that appending an electric field from E=15 V/cm to 20 V/cm enhanced the membrane flux (Figure 4.3).

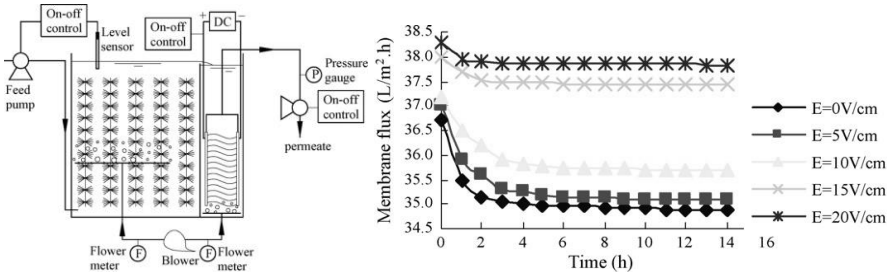

Figure 4.3 Experimental set up on the left and attenuation curves of membrane filtration flux over time on the right (Chen et al., 2007).

The electrocoagulation (EC) was applied as a pre-treatment to the submerged membrane bioreactor by Bani-Melhem and Smith (2012) for the treatment of grey wastewater. It involved an increase of the floc size of the sludge particles and an enhancement of the membrane filtration performance. Indeed, the EC combined with the MBR showed up to 13% reduction in membrane fouling compared to MBR without electrocoagulation. A removal of phosphate in the EC-MBR process was achieved while ammonia nitrogen was removed better in the conventional MBR.

Akamatsu et al. (2010) developed a fouling suppression system in MBRs which controls the motion of activated sludge by applying electric current only when the permeate flux has drastically declined due to membrane fouling. Platinum meshes were used as electrodes connected to the DC supply and were attached to both the upside and downside of the membrane module operating in crossflow mode (Figure 4.4). By switching on and off every 90 seconds, electric field strength of 6 V/cm facilitates detachment of negative activated sludge particles from the surface of the membrane, thus, significantly improved the average permeate flux (Figure 4.4).

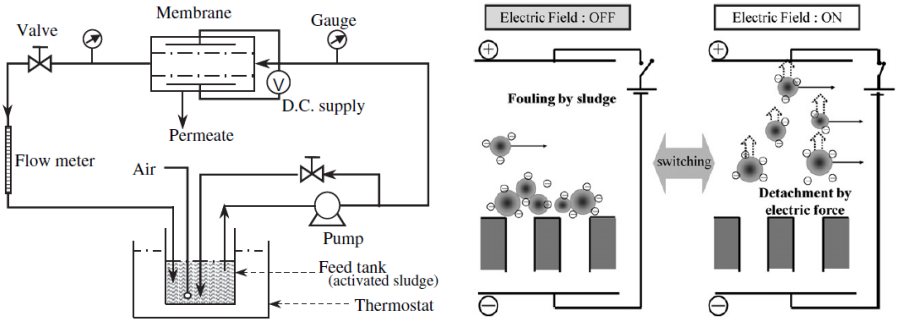

Figure 4.4 Experimental set up on the left and schematic illustration of the fouling suppression using an intermittent electric field on the right (Akamatsu et al., 2010).

Upon cost estimation, about half of the energy requirements were saved using this fouling suppression system. In another experiment, Akamatsu et al. (2012) developed a novel concept of a membrane-carbon cloth assembly for submerged MBRs by applying an electric field (4 min on/4 min off interval) directly on the membrane cathode made of carbon cloth. The results showed that the flux always recovered to the initial flux level whenever the intermittent electric field is applied.

A different configuration of the electrodes and membrane was applied by Liu et al. (2012a), inserting several copper wires inside the flat sheet membrane module and two stainless mesh anodes outside the membrane module in order to enhance the electrophoresis force and avoid the sludge deposition on the surface of the membrane. Two minute electric fields, 0.2 V and 0.4 V (0.036 V/cm and 0.073 V/cm), were applied using a low cost, micro-porous PP non-woven sheet and a polyester fabric filter cloth. For both membranes, application of either 0.2 V or 0.4 V electric field caused an increase in permeate flux, enhancement of microbial growth and activity, decrease of filtration resistance. The insert of the copper wires inside the membrane module allowed to operate with lower voltage gradient.

The integration of electrochemical, biological and membrane filtration processes into the same membrane bioreactor for fouling control and the improvement of the treatment efficiency was first studied at laboratory scale by Bani-Melhem and Elektorowicz (2010; 2011) and Elektorowicz et al. (2012). In the work of Bani-Melhem and Electorowicz (2010), the membrane module was placed at the centre of the bioreactor. Perforated iron mesh cathode and anode were placed

around the membrane module at a distance of 5.5 cm from each other which is enough to minimize the potential effect of an acidic/oxidation zone in microbial community and permit free air and flocs movement. The hybrid reactor is divided into two aerobic zones: zone 1, boarded between the external wall and the cathode is where biodegradation, electrocoagulation and electrosedimentation happen and zone 2, between cathode and membrane, is where membrane filtration and further biodegradation take place. The same authors in another study (Bani-Melhem and Elektorowicz, 2011), utilizing the same experimental set up and applying an intermittent direct current field of 1 V/cm with an operational mode of 15 min ON - 45 min OFF between two circular iron electrodes immersed around the membrane module, have found on average a 16.3% reduction in membrane fouling compared with the traditional submerged MBR (Figure 4.5) as well as an enhancement of COD and PO_4-P removal efficiency up to 96% and 98%, respectively.

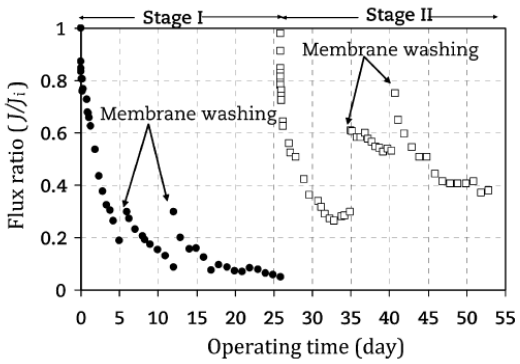

Figure 4.5 Enhancement of membrane filtration performance in the second stage after the application of the electric field (Bani-Melhem and Elektorowicz, 2011).

The authors attributed this increase of removal efficiencies to electrocoagulation process, which might involve electrochemical oxidation and adsorption by electrostatic attraction and physical entrapment. Conversely, ammonia nitrogen (NH_3-N) reduction through biological nitrification was reduced in the electro MBR operation, maybe due to greater sensitivity of nitrifying bacteria to the applied DC field and/or accumulation of iron in the electro-bioreactor, resulting in some inhibitory effects on the activity of nitrifying bacteria (Bani-Melhem and Elektorowicz, 2011). The study of Ibeid et al. (2013) analysed the

influence of a current field on the activated sludge properties using a series of batch electrokinetic bioreactors made up of aluminium anode and stainless steel cathode at different operating conditions (current density between 15 and 20 A/m^2 and electrical exposure modes 5'-ON/15' OFF and 5'-ON/20' OFF) in order to improve biological and membrane processes. Following the bench scale study, membrane fouling was assessed in a pilot scale SMEBR, which exhibited three times smaller membrane fouling rate than the MBR. Results showed that all runs exhibited lower SMP concentrations in the SMEBR than the MBR through electrocoagulation and other electrokinetic phenomena, resulting in a reduced membrane fouling rate. According to the authors (Ibeid et al., 2013), the removal of SMP made the sludge and subsequently the cake layer less viscous and cohesive, which allowed for better filtration of water. Simultaneously, the electroosmotic extraction of the tightly bound water from the suspended solids led to structural and morphological changes of activated sludge flocs and a reduction of membrane fouling.

Hasan et al. (2014), instead, have realized an electro membrane bioreactor at the pilot scale operated with an intermittent (5 min ON, 10 min OFF) current density of 12 A/m^2 analysing its performances during the start – up period and observing an enhancement of treatment removal efficiencies and a reduction of membrane fouling. The authors also observed a decrease of soluble EPS values and a reduction of zeta potential (ZP) magnitude (Figure 4.6) which is considered a significant membrane fouling factor. Large negative and positive zeta potentials indicate stable suspensions, which prevent the flocs' formation (Bani-Melhem and Elektorowicz, 2011). According to Hasan et al. (2014), Al^{3+} originating from the anode electrooxidation might have destabilized the soluble EPS and, thus, neutralized the negative charge. The electrocoagulation process also led to a reduction of ZP magnitude (from -26.2 to -14.2 mV) in the SMEBR indicating an enhancement of floc formation in the mixed liquor, an increase of particle size diameters (PSD) and, therefore, a reduction of membrane fouling.

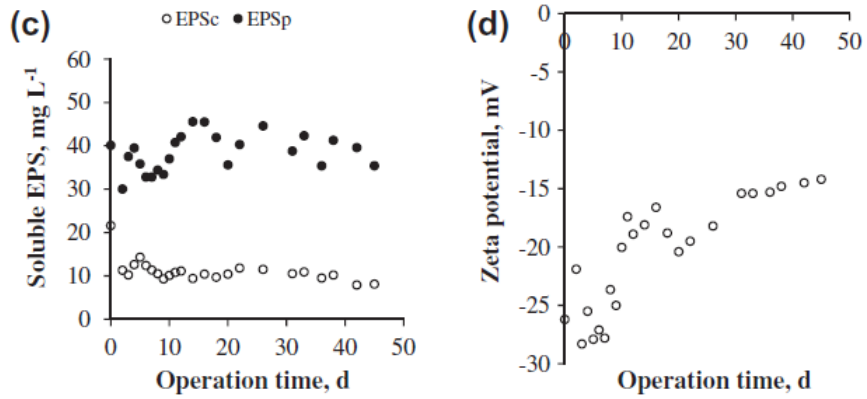

Figure 4.6 Soluble EPS on the left and zeta potential on the right in the pilot-scale SMEBR (Hasan et al., 2014).

In another study (Tafti et al., 2015), an alternating electric field was applied to two pairs of stainless steel plates installed as the electrodes inside the bioreactor, with current densities ranging from 5 to 23 A/m^2 under eight different electrical exposure modes, resulting in an improvement of activated sludge characteristics and effluent quality as well as in a lower membrane fouling. The results indicated that under the optimum condition with a current density of 12.5 A/m^2 and an exposure mode of 415 s OFF-185 s ON, the COD and phosphate removals were, respectively, 4% and 43% more compared to an unmodified MBR system (Tafti et al., 2015). The lowest value of specific oxygen uptake rate (SOUR) was observed by the authors in current densities higher than 20 A/m^2 due to MLVSS growth in the reactor and also inhibition of metabolism by nitrifying bacteria at such a high current.

The highest removal percentages of SMP was obtained at a current density of 5 A/m^2 and an exposure mode of 400 s OFF - 200 s ON, which were roughly 51% and 59% for proteins and polysaccharides, respectively. SMP was removed more efficiently due to ferric cations generated from the electrooxidation of anodes which neutralized the negatively charged particles. Proteins have a high density of negatively charged (Wilén et al., 2003), which react electrostatically with the cations to form stable flocs (Ramesh et al., 2006b).

Hua et al. (2015) investigated the impacts of electrocoagulation on sludge characteristics and fouling behaviour in an electro-MBR resulting in a fouling rate reduction of 7.8 fold, in an enhancement of sludge

compressibility and controlled growth of filamentous bacteria. Electric currents were applied at 15 min-ON/45 min-OFF to a pair of aluminum (Al) flat-plate electrodes with an effective area of 18 cm^2 with a current density ranging between 10 to 40 A/m^2. They reported that charge neutralization between negative charged sludge flocs and positive electro-generated coagulants during electro-coagulation would have absorbed and reduced soluble EPS. On the other hand, they suggested that bound EPS reduction can be attributed to the coexistence of electro-chemical oxidation, which may convert EPS into more biodegradable compounds that, then, can be reduced during aerobic treatment.

Hosseinzadeh et al. (2015) applied the electro membrane bioreactor as a pre-treatment of the reverse osmosis (RO) resulting in a removal of suspended solid of almost 100% and an improvement of COD removal of 4%. The hybrid reactor showed better settling characteristics, enhancing the dewaterability and filterability of the sludge.

In another study, Giwa and Hasan (2015) theoretically investigated the impact of operating conditions on the treatment performance observing that the removal of COD, TN and TP from the wastewater was favoured in the electro MBR unit by increasing the current density or HRT and decreasing the porosity of anode.

A low-voltage electro-membrane bioreactor (e-MBR) for fouling control was designed by Zhang et al. (2015) using stainless steel anodes and titanium sticks cathodes inserted into the flat sheet ceramic membrane (Fe-MBR). The electric field was applied intermittently for 2 min with a current of 0.1 A as soon as the suction was stopped and the corresponding voltage was on average 2.72 ± 0.13 V. Compared with another e-MBR with titanium anodes (Ti-MBR) and with one MBR without an electric field, the Fe-MBR had lower transmembrane pressure (TMP), less irreversible fouling and higher pollutant removals. Coagulation was not obvious because no significant changes were observed in either particle size or zeta potential. Strong positive correlation was obtained between fouling indexes and total organic carbon of soluble microbial products (SMPs), suggesting that the reduction of SMPs in the Fe-MBR could have led to the fouling depression due to the release of iron. The energy consumption estimation showed 10% more electricity was consumed to make TMP reduce by 30%, indicating the Fe-MBR would be promising in application.

These reported research studies, regarding the integration of electrochemical processes into membrane bioreactors, are newly developed, therefore, it is necessary to further assess the influence of these processes on activated sludge properties, membrane fouling formation and effluent wastewater quality especially in terms of nutrient removal. Indeed, although some previously studies have shown the enhancement of treatment efficiencies after the application of the electric field, the mechanisms of nutrient removal, in particular of ammonia compounds, inside the electro membrane bioreactor, have not been highlighted. Furthermore, no papers have been published regarding the influence of electrochemical processes on activated sludge flocs hydrophobicity and TEP concentration in a membrane bioreactor. In addition, considering the voltages applied, the possibility of recovery hydrogen from this system, operating as microbial electrolysis cell (MEC) and, thus, in anoxic or anaerobic conditions, has not investigated yet.

4.3.2 Combination of membrane bioreactors (MBR) with microbial fuel cells (MFCs)

The growth in demand and the shortage of water resources along with more stringent effluent regulations have given remarkable impetus to development of advanced technologies for wastewater treatment and reclamation. In this framework, membrane bioreactors (MBRs), which separate the effluent and activated sludge by filtration instead of sedimentation, are being increasingly applied in wastewater treatment and reuse due to their advantages over conventional activated sludge processes (CAS) (Tang et al., 2010; Zuthi et al., 2012). However, as a result of the interaction between sludge suspension and membrane system, membrane fouling decreases filtration performance, reduces flux or increases trans-membrane pressure (TMP) leading to frequent chemical/physical cleanings, supplying of excessive amount of air and high energy consumption (Z. Wang et al., 2012). Therefore, there is an urgent need to use an energy-efficient and environmental friendly technology for reducing fouling and offsetting this energy consumption (Li et al., 2014).

Despite the advantages associated with bio-electrochemical systems (BES) and their ability to harvest electrical energy in wastewater, further

treatments are needed before discharging or reusing the effluent of a BES. Therefore, the integration of membrane bioreactors into bioelectrochemical systems (BES) takes advantage of both processes in terms of wastewater treatment and energy recovery. The combined system aims to overcome the problem of high energy consumption of MBR and avoid dissolved methane that results in anaerobic MBR (Yuan and He, 2015).

Recently, different studies have reported about the combination of BES with MBRs (Ge et al., 2013; Ma et al., 2015; Tian et al., 2015). Ultrafiltration membrane (UF) can be immersed in a BES in an internal configuration or operated as an external module. In most of the studies, ultrafiltration (UF) membranes have been immersed in the MBR reactor as an internal configuration.

In the internal configuration, UF can be used as separator, operating as a ion exchange membrane, installed in the anode chamber of a MFC like an anaerobic MBR or in the cathode like an aerobic MBR (Yuan and He, 2015).

UF membrane was initially integrated in MFCs to investigate its feasibility as a separator between the anode and the cathode, resulting in lower current generation and Coulombic efficiency compared to ion exchange membranes (Kim et al., 2007). High rejection of total coliform (>97%) and a stable water flux of 14.1 LMH (L $m^{-2} h^{-1}$) were achieved in a MFC with UF membrane as a separator (Kim et al., 2013). The UF membrane can also be modified to reduce the electrical resistance without affecting ultrafiltration function. A conductive membrane was produced by coating multiwalled carbon nanotubes (MWCNTs) on a polyester nonwoven membrane base to form a membrane/biocathode assembly for MFC application achieving a turbidity <0.1 NTU and 91% of bacterial cells removed (Malaeb et al., 2013a). Using UF membranes as a separator can significantly lower the capital cost and enhance effluent quality (Yuan and He, 2015). However, their effects on the electrochemical process are not well understood and remain unclear (Kim et al., 2007).

Ge et al. (2013) installed hollow fiber UF membranes in the anode chamber of a tubular MFC, operating like an anaerobic membrane bioreactor and achieving almost 90% COD removal and an effluent turbidity <1 NTU when treating real wastewater from a primary effluent. The results observed by the authors have suggested that installing membranes within the anode compartment may not be an optimal

approach to integrate membranes with MFCs, due to the difficulty of membrane cleaning. Indeed, the results observed severe membrane fouling formation with a rapid TMP increase from zero to around 50 kPa in 15 days.

Therefore, in order to control fouling using aeration, UF membranes have been inserted in the cathode chamber of a MFC (Li and He, 2015; Ma et al., 2015; Tian et al., 2015). It was demonstrated an average current production of 1.9 ± 0.4 mA with a 50 Ω resistor and COD removal efficiency of 89.6 ± 3.7% over a period of about 40 days using the aeration tank of a MBR as the cathode chamber of a MFC (Y.-P. Wang et al., 2012) treating wastewater (Figure 4.7).

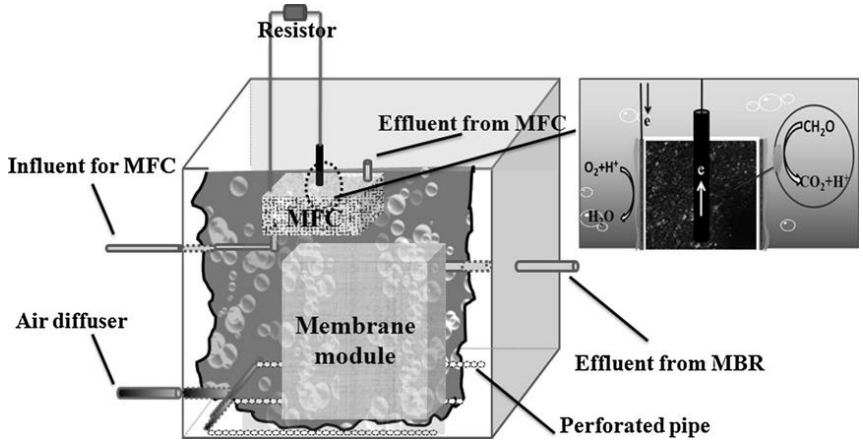

Figure 4.7 Experimental set up of the MBR-MFC combined system (Y.-P. Wang et al., 2012).

In this study, carbon felt was used as the cathode in order to allow biofilm development and for reducing the investment and operating cost, low-cost nylon mesh were adopted as the filter material (Figure 4.7). The preliminarily treated wastewater in MFC module then flew into the aeration tank of the MBR for further treatment. The MFC promised an energy offset to the overall treatment process (Y.-P. Wang et al., 2012).

In another study (Tian et al., 2015), an anaerobic chamber was submerged into the MBR to operate as the anodic chamber of the MFC (Figure 4.8).

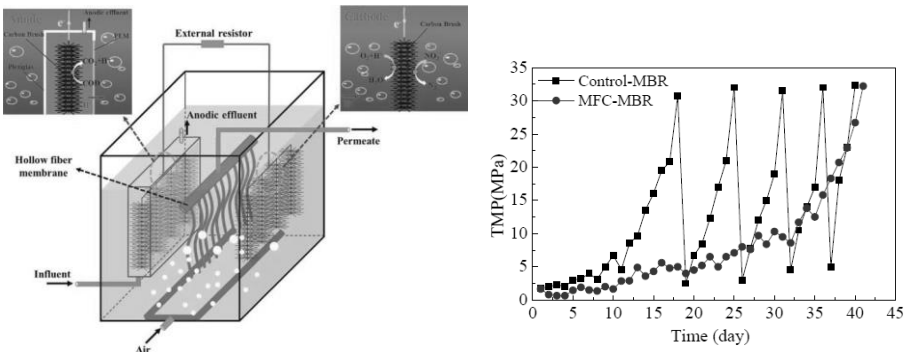

Figure 4.8 Scheme of the MBR-MFC on the left and profiles of TMP increases over time in the MFC–MBR and in the conventional MBR (Control-MBR) on the right (Tian et al., 2015).

The aeration tank of the MBR was directly used as the cathodic chamber, while the submerged carbon brushes opposite to the anodic chamber were utilized as the cathode of the MFC (Figure 4.8). The hollow fiber membrane module was placed between the anodic chamber and the cathode (Figure 4.8). The electric field between the two electrodes enhanced the microbial activity improving the wastewater treatment, preventing the negatively charged foulants from attaching on the membrane and modifying the sludge properties to mitigate membrane fouling (Tian et al., 2015). The authors, indeed, observed a membrane fouling reduction (Figure 4.8) with an increase of the dewaterability and filterability of the sludge due to the decrease of the less loosely bound extracellular polymeric substances (LB-EPS), filamentous bacteria and an increase of SMPp/SMPc ratio. Indeed, stimulated by the electricity, the sludge in the MFC–MBR had higher activity than that in the conventional MBR (Tian et al., 2015). Thus, more LB-EPS were released into the supernatant and degraded by the bacteria in the MFC–MBR, which might eventually lead to the reduction of LB-EPS (Tian et al., 2015). A maximum power density of 2.18 W/m^3 and an average voltage output of 0.15 V were achieved at an external resistance of 50 Ω (Tian et al., 2015). The Coulombic efficiency (CE) of the MFC–MBR was 1.9%. The authors attributed this low value to the fact that besides the electroactive bacteria oxidizing the COD to generate electricity, there were also some other bacteria sustained by alternative metabolisms without electricity generation in the anodic chamber, such as fermentation, methanogenesis and using alternate electron acceptors

(Tian et al., 2015, Logan et al., 2006). The removal efficiencies of COD, ammonia nitrogen and total nitrogen (TN) in the MFC–MBR were improved by 4.4%, 1.2% and 10.3%, respectively, due to sludge activity enhancement induced by the electric field.

Liu et al. (2014) studied the integration of MBR-MFC for electricity generation, fouling mitigation and artificial wastewater treatment. The anaerobic anode chamber and aerobic cathode chamber were separated by filter cloth (Liu et al., 2014). The flat sheet stainless steel mesh membrane modules were used as cathode and filtration unit. After anaerobic biological treatment, the water permeated through filter cloth into the aerobic cathode chamber was further treated under aerobic condition by active sludge. The final effluent was filtrated by membrane modules in aerobic cathode chamber (Liu et al., 2014).

The authors reported that the sludge properties and aeration in cathodic chamber were the main affecting factors on electricity generation. They observed that MFC successfully alleviated membrane fouling under closed circuit condition. Electrons generated in anaerobic chamber can be transferred to cathode membranes via an external circuit and the protons generated in anode zones would cross the separator to cathode chambers (Figure 4.9).

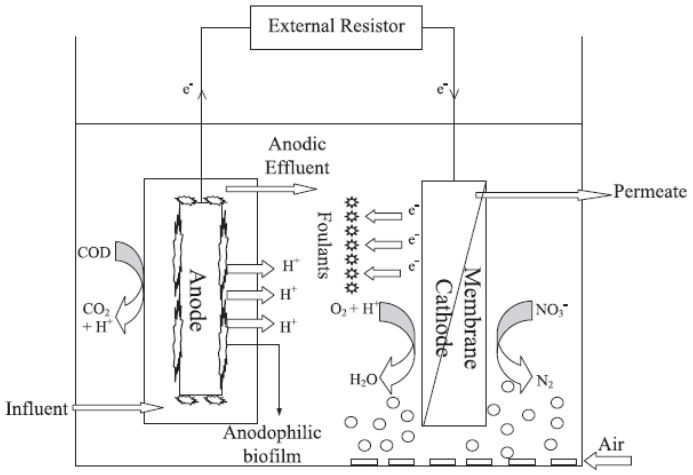

Figure 4.9 Schematic diagram of MFC-MBR and electric field mechanisms for membrane fouling mitigation (Liu et al., 2014; Neoh et al., 2016).

This led to an additional repulsion force to membrane foulants such as negatively charged sludge, organic matters and mitigated membrane fouling (Figure 4.9). This system was successful in the removal of offensive smell, total nitrogen, COD and turbidity after aerobic treatment and filtration from the synthetic wastewater, and similar to the sequential anaerobic–aerobic system (Neoh et al., 2016). With filter cloth separating the anode and cathode chambers, ~ 0.2 V cell potential was maintained under stable situation (Liu et al., 2014).

Li and He (2015) developed a combined system characterized by a tubular reactor, made of an anion exchange membrane. A carbon brush was installed in the anodic chamber as an anode electrode and carbon cloth, which wrapped the membrane tube, was used as cathode. Therefore, the cation exchange membrane (CEM) was replaced in the study by an anion exchange membrane (AEM) in order to enhance the removal of total inorganic nitrogen, through the combination of nitrification in the cathode, nitrate migration across the AEM driven by electricity generation and denitrification in the anode. The coupled system removed 56.9% of the total inorganic nitrogen, significantly higher than the 7.6% of the same system equipped with a CEM.

In another study, Zhou et al. (2015) developed a novel overflow-type electrochemical membrane bioreactor (EMBR) without ion exchange membrane which utilized electricity recovered by microbial fuel cell (MFC) for membrane fouling mitigation in membrane bioreactor (MBR). The reactor was constructed with anodic and cathodic chambers which were connected through an overflow channel with a width of 5 mm to allow the flow of anodic effluent to the cathodic chamber for further treatment. Anode was made of an "O ring" carbon felt and a stainless steel (SS) mesh was used as cathode. The maximum power density of 629 mW/m^3 or 7.18 mW/m^2 was obtained. The removal efficiencies of chemical oxygen demand, ammonia nitrogen and total nitrogen under appropriate ranges of hydraulic retention times (16.9–8.5 h) were 92.6 ± 5.4%, 96.5 ± 2.8% and 73.9 ± 9.7%, respectively. In comparison to a conventional MBR, five significant effects of the MFC integration on the sludge properties have been observed by the authors: including particle zeta potential decrease, particle size distribution macroaggregation, soluble microbial products and extracellular polymeric substances reduction and SMP_P/SMP_C ratio increase of 25.6%, leading to membrane fouling mitigation. The SMP concentration in the overflow-type EMBR was decreased due to the higher activity bacteria stimulated

by the presence of the electric filed (Zhou et al., 2015). Furthermore, the SMP_P/SMP_C ratio in the overflow type EMBR increased for the easier degradation of carbohydrate by bacteria (Zhou et al., 2015).
In this system realized by Ma et al. (2015), an anode chamber filled with carbon felts, two cathode chambers (anoxic zone) with suspended four brush cathodes of carbon fibers and an oxic zone were used (Figure 4.10).

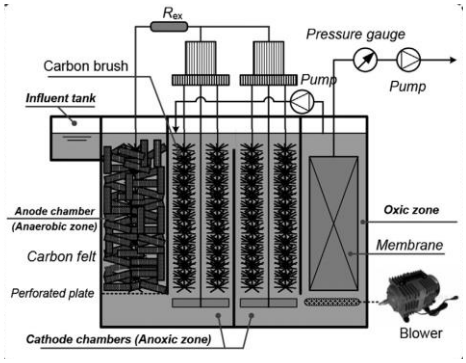

Figure 4.10 Illustration of MBR combined with the MFC (Ma et al., 2015).

Influent organic matter could act as electron donor in the anode chamber and, then, denitrification was driven on the cathodes. With the rebound of water temperatures over 15~20 °C, efficient redox reactions were achieved in the system, which subsequently resulted in sludge reduction (27.3% lower than the control MBR in terms of mgTSS/mgCOD) and membrane fouling alleviation. Biological maintenance metabolism was not enhanced due to the integration of exoelectrogenesis process (Ma et al., 2015). Therefore, the authors infer that the biomass reduction in the MBR combined with MFC should be mainly attributed to the source reduction of COD (Ma et al., 2015). Since a fraction of the influent organic matters were degraded and converted to bioelectricity with an average coulombic efficiency of 0.24% in the anode chamber (Figure 4.11), the following heterotrophic proliferation was restricted on available substrates (Ma et al., 2015).
Although fouling mitigation was reported in MFC combined with MBR in internal configuration, aeration requires a large amount of energy, which may be not economically feasible in large-scale practice (Yuan and He, 2015). Furthermore, the removal efficiency of total nitrogen was

generally low, since anaerobic denitrification was not effectively carried out in the aerobic cathode chamber (Yuan and He, 2015).

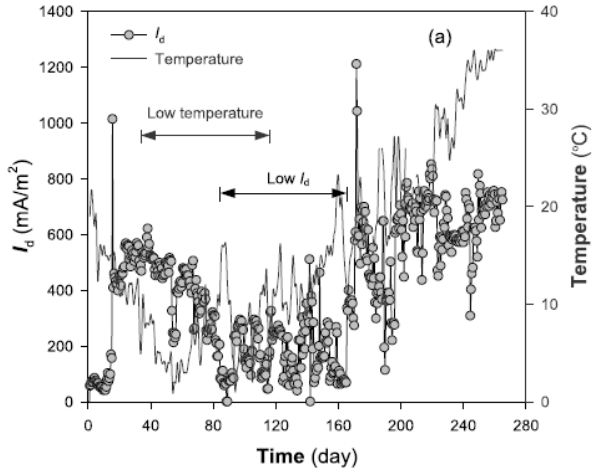

Figure 4.11 Variations of electricity generation over time (Ma et al., 2015).

BES can be also linked externally to MBR in order to improve the performance of one of the processes and the flexibility of the coupled system (Yuan and He, 2015). Su et al. (2013) applied a single-chamber air cathode MFC to treat the excess sludge from a conventional MBR, recycling the non-consumed sludge in the MFC to the MBR. The anodic compartment of the MFC directly used MBR sludge as anodic inoculum and substrate.

They achieved a sludge reduction 5.1% higher than the conventional MBR and a decrease equal to 22% of loosely bound extracellular polymeric substances with a mitigation of membrane fouling when the sludge was recycled to the MBR reactor. Indeed, the operation cycle in the combined system was found nearly twice as long as that in the conventional MBR (Su et al., 2013). Furthermore, in the combined system, the COD and ammonia treatment efficiencies were more than 90%. The average voltage and maximum power production of the MFC were 430 mV and 51 mWm^{-2}, respectively (Su et al., 2013).

The external configuration increases the flexibility of the coupled system allowing the management and operation of individual component without much influence on each other (Yuan and He, 2015). Indeed, membrane cleaning can be performed without influencing the

bioelectrochemical processes in BES (Yuan and He, 2015). However, capital cost of two separate units may be higher than the combined one in the internal configuration, and some mutual advantages such as oxygen and electricity-influenced anti fouling may not be shared as those with internal configuration (Yuan and He, 2015).

As highlighted, limited studies are available regarding the combination of MBR with MFC in an external configuration. Furthermore, the main electron transfer mechanism governing the anode electro-active biofilms in a MFC fed with activated sludge from a MBR has not been investigated yet.

5 MATERIALS AND METHODS

The experimental activity has been carried out at the Sanitary Environmental Engineering Division (SEED), Department of Civil Engineering of Salerno University (Italy) and at the Laboratory of Chemical and Environmental Engineering (LEQUIA) of the University of Girona (UdG) (Spain). Research activity has been conducted in four phases during the three years of the research program:

- **Phase I**: the first year (January - December 2013) of the Ph.D program, an electro membrane bioreactor plant has been designed and realized at laboratory scale at the Sanitary Environmental Engineering Division (SEED) of the University of Salerno;
- **Phase II**: in the second year (January - December 2014), the integration of electrochemical processes into membrane bioreactors (electro membrane bioreactor – eMBR) has been evaluated;
- **Phase III**: in the first semester of the third year (January - June 2015), the application of a microbial fuel cell (MFC), as a down-stream process for treating the excess sludge from a MBR pilot plant, has been investigated. This part of the experimental activity has been performed for three months (March – May 2015) at the Laboratory of Chemical and Environmental Engineering (LEQUIA) of the University of Girona;
- **Phase IV**: the last phase of the experimental activity has regarded the assessment of hydrogen production in the electro MBR operating in anoxic conditions like a microbial electrolysis cell (MEC) at the Sanitary Environmental Engineering Division (SEED).

In the following paragraphs, experimental setups, sampling and analytical methods for the electro membrane bioreactor (eMBR), the MFC combined with an MBR in an external configuration and electro MBR in anoxic conditions will be shown.

5.1 ELECTRO MEMBRANE BIOREACTOR

5.1.1 Experimental setup

A laboratory scale membrane bioreactor was designed with 13 L working volume, able to operate as a conventional membrane bioreactor or as an electro membrane bioreactor (Figure 5.1 and Figure 5.2).

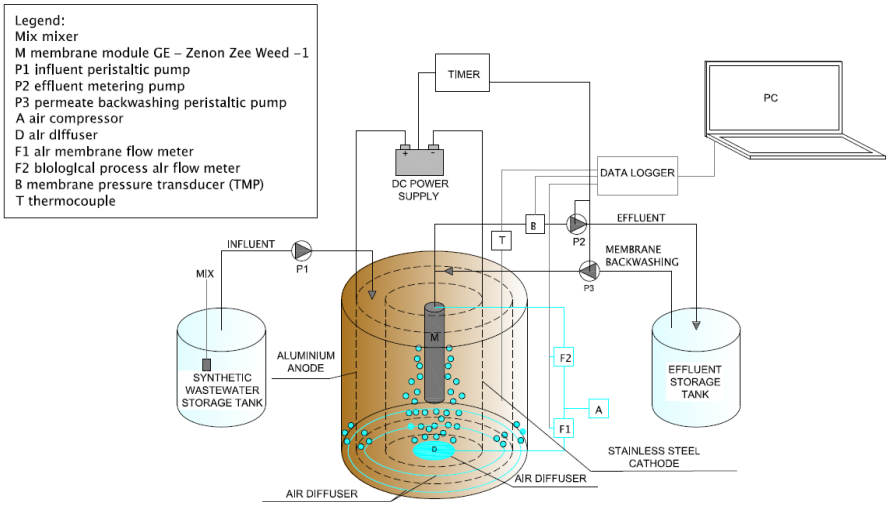

Figure 5.1 Experimental set-up of the electro MBR.

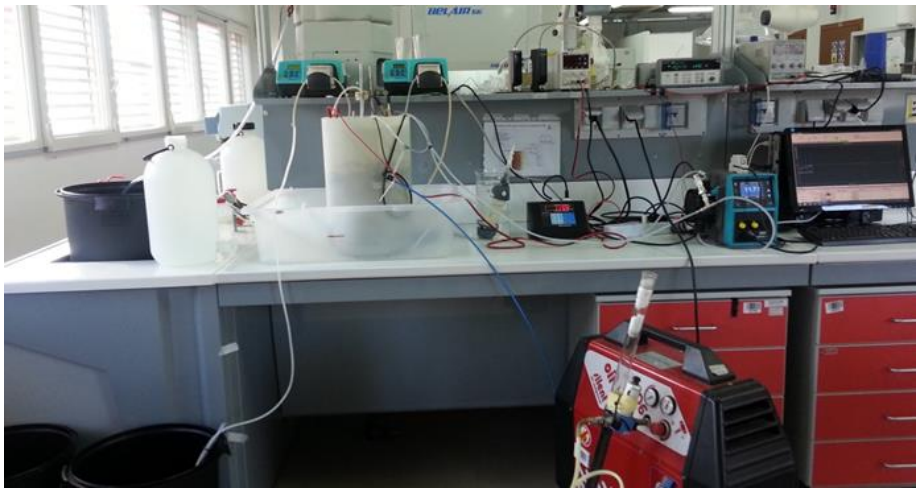

Figure 5.2 Image of the conventional/electro MBR realized at the Sanitary Environmental Engineering Division (SEED) of Salerno University.

The bioreactor was operated continuously fed with synthetic solution, simulating real municipal wastewater, whose composition is reported in Table 5.1. The feed tank was always stirred (IKA Eurostar 100) and an influent flow of 0.54 L h^{-1} was pumped (Watson Marlow 323U, Watson Marlow) to the bioreactor.

Table 5.1 Composition of synthetic wastewater (Li et al., 2013, 2005; Yang et al., 2002).

Compound	Concentration [mg L^{-1}]
$C_6H_{12}O_6$	200
$C_{12}H_{22}O_{11}$	200
Protein	68.33
$(NH_4)_2SO_4$	66.73
NH_4Cl	10.91
KH_2PO_4	4.43
K_2HPO_4	9.00
$MgSO_47H_2O$	21.00
$MnSO_4H_2O$	2.68
$NaHCO_3$	30.00
$CaCl_2\,6H_2O$	19.74
$FeCl_36H_2$	0.14

A submerged PVDF hollow fibre ultrafiltration membrane module ZeeWeed®-1 (ZW-1) (GE/Zenon Membrane Solution) with a nominal pore diameter of 0.04 μm and an effective membrane surface area of 0.047 m^2 was placed vertically in the centre of the bioreactor (Figure 5.3a).

When the bioreactor operated as an electro MBR, perforated cylindrical aluminium anode and stainless steel cathode were immersed around the membrane filtration module at a distance between them of 6 cm (Figure 5.3b-c).

They should, indeed, be placed at an appreciable distance in order to minimize the potential effect of an acidic/oxidation zone on microbial community and to avoid the damage of the membrane module.

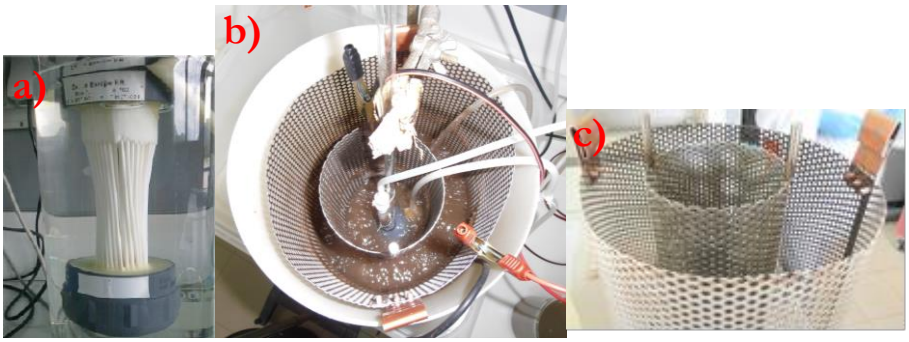

Figure 5.3 ZeeWeed®-1 membrane module (a), electrodes around the membrane module inside the bioreactor (b), electro cell (c).

The anode and cathode had a diameter of 24 cm and 12 cm, respectively (Figure 5.3b-c). The electrodes were connected to a digital DC power supply (CPX400, TTi, 0-60 V, 0-20 A) with an intermittent operation mode of 5 min ON and 20 min OFF by a programmable electronic controller (ChronTrol XT, Chrontrol US) (Figure 5.4).

Figure 5.4 DC power supply (a) and programmable electronic controller (b).

Two air diffusion systems were located below and around the membrane module for maintaining the aerobic conditions inside the reactor, providing good mixing of suspended sludge flocs and reducing fouling.
An inoculum of fresh activated sludge was taken as required from the secondary clarifier at the municipal wastewater treatment plant in Salerno (Italy).

5.1.2 Operating conditions

The reactor was operated at constant flow rate of 15 LMH, withdrawing the effluent via metering pump (qdos30, Watson-Marlow Pumps Group), with an hydraulic retention time (HRT) equal to 19 h and an organic loading rate (OLR) of 0.78 kgCOD/m^3d. A cyclic membrane operation mode consisted of production and backwashing periods of 14.5 min and 0.5 min, respectively, was applied.
The reactor was operated in three consecutive runs, each lasted for more than 30 days and repeated three times in order to validate the results: in the first it worked as a conventional submerged membrane bioreactor (MBR), in the second and in the third, electrochemical processes were integrated into the membrane bioreactor and two external voltage gradients of 1 V/cm (eMBR-1) and 3 V/cm (eMBR-3), respectively, were applied to the electrodes, through the DC power supply, with cycles of ON-OFF as previously reported.
The membrane module was removed at the end of the each run from the bioreactor and physically and chemically cleaned, with sodium hypochlorite according to manufacturer's prescriptions, in order to recovery the membrane permeability. Chemical cleaning was also performed during each run every time the transmembrane pressure (TMP) achieved an approximate value of 50 kPa. Therefore, each run was characterized by different cycles.
Sludge was not discharged during the operational period from the membrane bioreactor except for the necessary analysis and chemical cleaning of the membrane.

5.1.3 Sampling and analytical methods

Samples were collected from the feeding tank (P1), electro-membrane bioreactor (P2) and permeate about every 48 hours (P3) (Figure 5.5).

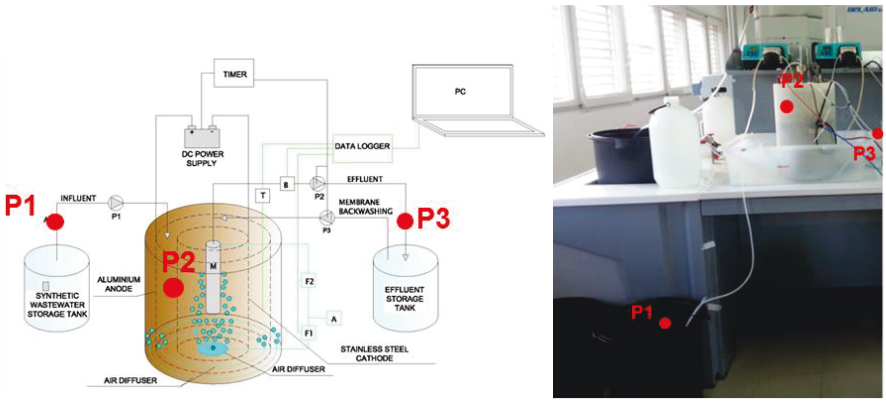

Figure 5.5 Sampling points for the different experimental runs.

The sampling plan and the analysis performed for the conventional MBR and the electro MBR, during the different runs of the experimental activity, are reported in the Table 5.2.

Table 5.2 Sampling plan and analysis performed during the experimental activity.

INFLUENT (P1)		REACTOR (P2)		PERMEATE (P3)	
PARAMETER	**FREQUENCY**	**PARAMETER**	**FREQUENCY**	**PARAMETER**	**FREQUENCY**
COD_S	Weekly	COD_t- COD_s - DOC	Three times a week	COD_S- DOC	Three times a week
BOD_5	Monthly	SSV-SST	Three times a week	BOD_5	Monthly
DOC	Weekly	NH_4^+, UV_{254}	Three times a week	DOC	Three times a week
NH_4^+, UV_{254}	Three times a week	PO_4^{3-}, NO_3^- , NO_2^-	Three times a week	NH_4^+, UV_{254}	Three times a week
PO_4^{3-}, NO_3^- , NO_2^-	Three times a week	SMP - EPS (proteine e carboidrati)- TEP, hydrophobicity	Three times a week	PO_4^{3-}, NO_3^- , NO_2^-	Three times a week
pH, O_2, T	Daily	Metals (only eMBR)	Start and end each run	pH, O_2, T	Daily
Redox potential		pH, T, O_2	Daily	Redox potential	Daily
Conductivity		Redox potential, conductivity	Daily	Conductivity	Daily

Organic substances and nutrients

The standard methods 5130, 4030, 4020 (APAT and CNR-IRSA, 2003) were utilized for analysing total and soluble chemical oxygen demand (tCOD, sCOD), ammonia nitrogen (NH_4-N), nitrate nitrogen (NO_3-N), nitrite nitrogen (NO_2-N) and orthophosphate (PO_4-P) in order to assess treatment performance. UV_{254} was measured using UV/VIS spectrometer (Lambda 25, PerkinElmer).

Biomass and operational parameters

The biomass present inside the reactor was evaluated analysing the mixed liquor total suspended solids (MLTSS) and mixed liquor volatile suspended solids (MLVSS) in agreement with standard method 2090 (APAT and CNR-IRSA, 2003).
Dissolved oxygen concentration (DO), pH, temperature, conductivity and redox potential (ORP) were measured every day using a multiparametric probe (Hanna Instruments, HI769828).

Metal evaluation

Aluminium concentration in the mixed liquor before and after each run, characterized by the application of the electric field, was analysed by inductively coupled plasma – optical emission spectroscopy (ICP-OES) previously digesting the samples according to standards methods 3010 and 3020 (APAT and CNR-IRSA, 2003). Regarding the solid samples present on the electrodes surface at the end of run eMBR-1 and eMBR-3, the aluminium content was determined digesting the samples according to the method US EPA 3051 and the resulting solution was analysed with the same previous instrument according to the method 3020 (APAT and CNR-IRSA, 2003).

Membrane fouling: transmembrane pressure (TMP)

The trans-membrane pressure (TMP) variation over time was measured continuously through a pressure transducer (PX409-0-15VI, Omega) connected to a datalogger (34972A LXI Data Acquisition/ Switch unit, Agilent) which recorded the data (Figure 5.6).
Membrane fouling formation was assessed in term of fouling rate evaluated for each cycle of a single run as trans-membrane pressure

(TMP) variation over time, ΔTMP/dt. This value has been also normalized for the cycle average content of MLVSS (gMLVSS/L) in order to make comparable the three runs (MBR, eMBR-1, eMBR-3) that worked with a slightly different concentrations of MLVSS.

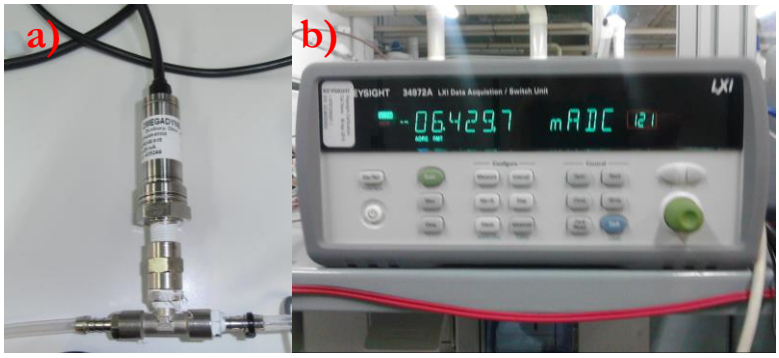

Figure 5.6 Pressure transducer (a), data logger (b).

Membrane fouling: extracellular polymeric substances (EPS) and soluble microbial products (SMP)

The bound EPS, soluble EPS or SMP were measured for evaluating the membrane fouling formation. Bound EPS (bEPS) and SMP were extracted from the sludge floc according to the heating method (Le-Clech et al., 2006; Morgan et al., 1990) modified. In particular, the sludge samples were centrifuged for 20 min at 5000 rpm (Centrifugette 4206, ALC). The supernatant was filtered by glass fiber filters with pores size of 1.2 μm (Whatman, Maidstone, UK) in order to measure the sEPS or SMP. The pellet obtained from centrifuge and resuspended with DI water was placed in the oven at 80 °C for 10 min. Then, it was centrifuged (Centrifugette 4206, ALC) for 20 min at 5000 rpm and the supernatant was collected for bEPS measurements by filtration through 1.2 μm glass fiber filters (Whatman, Maidstone, UK). SMP and bEPS were characterized by their relative content of protein (SMPp - bEPSp) and carbohydrate (SMPc - bEPSc), measured by photometric methods according to Frølund et al. (1995) and DuBois et al. (1956), respectively, using bovine serum albumin (BSA) (Sigma, USA) and D-glucose (Sigma, USA) as the standards.
Carbohydrates were determined adding 1 mL of extracted EPS or SMP in a test tube along with 1 mL of phenol (5% w/w) following by 5 mL of

sulphuric acid (95.5%). After 20 minutes, the absorbance was read at 480 nm with the spectrophotometer (Lambda 25, PerkinElmer), using the blank as reference.
For the protein measurement, five reagents were prepared: R1 143 mM NaOH and 270 mM Na_2CO_3; R2 57mM $CuSO_4$; R3 124 mM Na_2-tartrate; R4 Mixture of reagents R1, R2 and R3 in proportion 100: 1: 1 and R5: Folin reagent diluted 1:2 with distilled water.
0,5 mL of the extracted EPS or SMP samples were mixed with 0,7 mL of R4 in a test tube and left at room temperature for 10 minutes. After that, 0,1 mL of R5 was added and after 45 minutes the absorbance was read at 750 nm with the spectrophotometer (Lambda 25, PerkinElmer), using the blank as reference.
The concentrations of bEPS and SMP were then normalized for the content of MLVSS.

Membrane fouling: Transparent exopolymer particles (TEP)

TEP concentrations were measured spectrophotometrically using alcian blue, a cationic dye which binds to acidic mucopolysaccharides basing on the protocol developed by De la Torre et al. (2008) modified and using Xanthan gum for the calibration (Figure 5.7a). In particular, the mixed liquor samples were filtered by filter papers (Schleicher and Schuell / Whatman, black ribbon Ø 90 mm, Germany). The filtered samples were then mixing with 0.5 mL of 0.055% alcian blue solution and 4.5 mL of 0.2 mol/L acetate buffer solution (pH 4) in a flask (De la Torre et al., 2008).
The flask was then stirred for 1 min and centrifuged at 5000 rpm (Centrifugette 4206, ALC) for 30 min. After that, the TEP reacted with the alcian blue solution yielding a low solubility dye–TEP complex, the concentration of the alcian blue in excess was determined by reading the absorbance at 602 nm (Lambda 25, PerkinElmer) (De la Torre et al., 2008), using distilled water as reference. The concentrations of TEP were then normalized for the content of MLVSS.

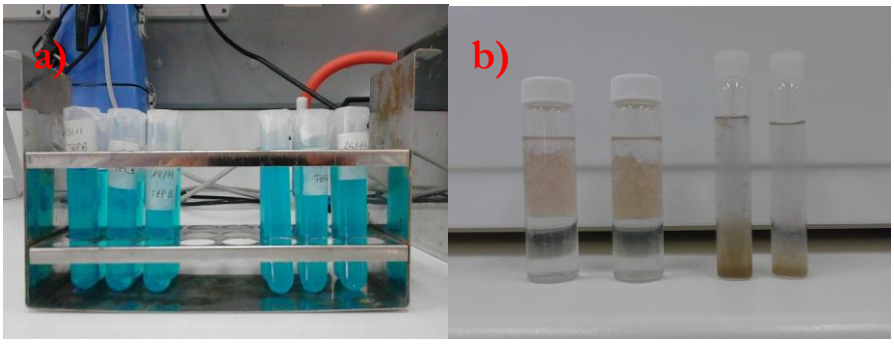

Figure 5.7 TEP analysis with alcian blu dye (a), hydrophobicity analysis with hexan extraction (b).

Membrane fouling: relative hydrophobicity (RH)

Hydrophobicity is the tendency of the mud flakes to repel water. The relative hydrophobicity, expressed as percentage of hydrophobic sludge, was measured using the protocol described by Rosenberg et al. (1980) with hexane extraction (Figure 5.7b).
In particular, 50 mL of mixed liquor, previously diluted to 1 g L^{-1} SST, was centrifuged at 5000 rpm (Centrifugette 4206, ALC) for 5 minutes, separating the supernatant without dropping the mud and, then, refilling the tube up to the previous volume with milli-Q water and mixing until the clay was resuspended. The process was repeated twice. Subsequently, 10 mL of sample was put in four test tubes and 10 mL of hexane was added in two of these test tubes.
The other two tubes were not filled with hexane (blank). The four tubes were, then, mixed for 15 minutes at a stirrer rotational. After 15 minutes, the content was left decanting for 5 minutes. After 5 minutes, the absorbance of the aqueous phase was read at 650 nm. The relative hydrophobicity value was calculated with the following equation:

$$RHx\,(\%) = \left(1 - \frac{Ai}{Ab}\right) * 100 \qquad (36)$$

Where

- RHx: relative hydrophobicity;
- Ai: values of the absorbance of the samples with hexane;

- Ab: values of the absorbance of the blank (without hexane).

5.2 MICROBIAL FUEL CELL AS A DOWN-STREAM PROCESS FOR THE TREATMENT OF MBR SLUDGE

5.2.1 Experimental setup

A three-neck 0.5 L round-bottom flask (MFC) was operated potentiostatic controlled with a three-electrode arrangement and without a proton exchange membrane between the cathode and the anode in order to avoid its clogging due to the high solids content of the fed sludge (Figure 5.8). Two carbon clothes (3 x 3 mm, NuVant's ELATs LT2400W, FuelCellsEtc, USA) electrically connected through titanium wires to two graphite rods (250 x 5 mm, Mersen Iberica, Spain) were used as working - and counter- electrodes, respectively (Figure 5.9). The anode as working electrode and the cathode as counter electrode were placed at lateral necks while the Ag/AgCl reference electrode (0.197 V vs. SHE, model RE-5B BASi, United Kingdom) (Figure 5.9) was placed at the central neck (Figure 5.8). The working electrode is the electrode where a given electrochemical reaction takes place and is studied, the oxidation at the anode. In the three electrode system, its potential is controlled versus the reference electrode which is a non-polarizable electrode with a fixed potential.
The counter electrode allows that the reaction at the working electrode takes place with a reverse reaction, the reduction at the cathode. The electrodes were previously washed in 1 M HCl and 1 M NaOH to remove possible metal and organic contamination (Bond and Lovley, 2003). The same set-up without the reference electrode and in Open Circuit Voltage (OCV-MFC) was performed as control test. The systems were in a thermostatically controlled room at 22 ± 1 °C and at atmospheric pressure.

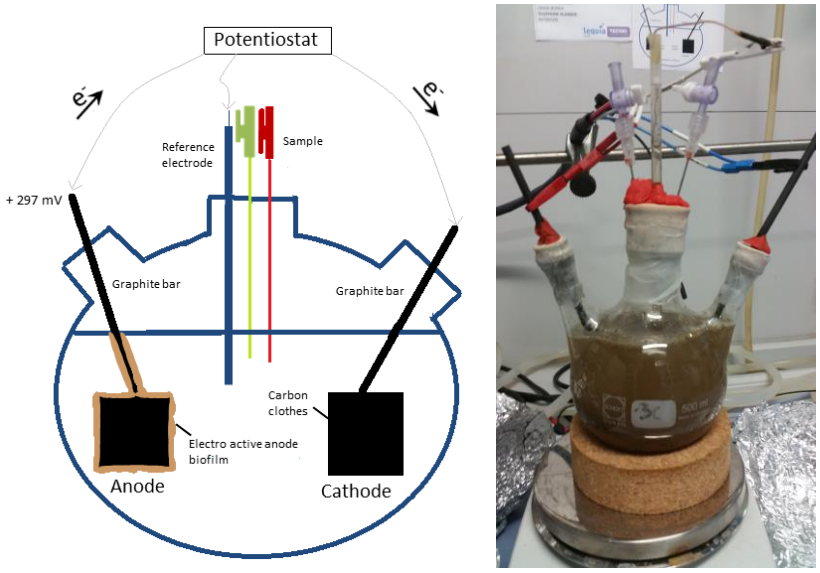

Figure 5.8 Experimental set-up and image of the three-neck round-bottom flask MFC realized at Lequia-University of Girona.

Figure 5.9 Working and counter electrodes with carbon clothes and graphite bar on the left and Ag/AgCl reference electrode on the right.

5.2.2 Start up and operating conditions

At the start of the experiments, the round-bottom flasks were fed with acetate containing medium in order to grow an electroactive biofilm. The synthetic medium was prepared with deionized water sparged with nitrogen and it contained 0.410 gL^{-1} of CH_3COONa as organic electron donor, 0.1 g L^{-1} of NH_4Cl, 0.5 g L^{-1} of NaCl, 0.1 g L^{-1} of $MgSO_4 \cdot 7H_2O$,0.015 g L^{-1} $CaCl_2 \cdot 2H_2O$, 10 mM of PBS and 1.0 ml L^{-1} of trace elements (concentration per litre: 1 mg EDTA ,1 mg $FeSO_4 \cdot 7H_2O$,

146 mg L^{-1} $ZnSO_4 \cdot 7H_2O$,100 mgL^{-1} $MnCl_2 \cdot 4H_2O$,6 mg L^{-1} H_3BO_3,130 mg L^{-1} $CaCl_2 \cdot 6H_2O$, 2 mg L^{-1} $CuCl_2 \cdot 2H_2O$,24 mgL^{-1} $NiCl_2 \cdot 6H_2O$, 36 mg L^{-1} $Na_2Mo_4 \cdot 2H_2O$, 238 mg L^{-1} $CoCl_2 \cdot 6H_2O$). The reactors were inoculated per 0.5 L of synthetic medium with a mixture of 0.025 L of aerobic activated sludge from a pilot MBR reactor treating synthetic wastewater, 0.015 L of anode effluent from a parent MFC treating swine manure and 0.015 L of cathode effluent from a denitrifying MEC treating nitrate contaminated groundwater. Once inoculated and during all the experiments, the anode (working electrode) potential of the potentiostatic controlled round-bottom flask was polarized chronoamperometrically at +100 mV vs. Ag/AgCl (+297 mV vs. SHE at 25ºC) (Figure 5.10). The current production in A over time was monitored with a potentiostat (model VSP, Bio-logic, France) with the chronoamperometry technique (Figure 5.10).

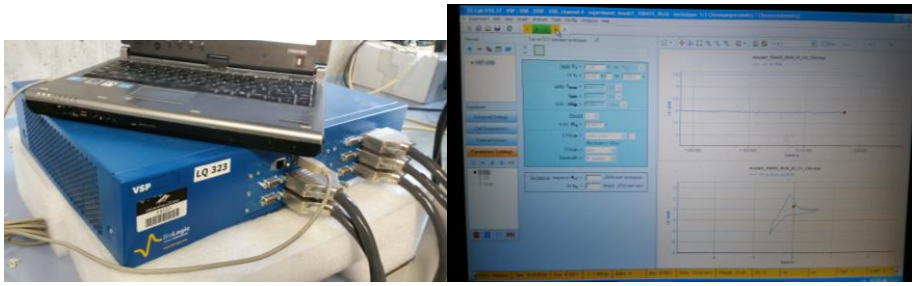

Figure 5.10 Potentiostat on the left (model VSP, BioLogic, France), scan window of the EC Lab software with chronoamperometry and cyclic voltammetry graphs on the right.

With a potentiostat either the potential or the current of an electrode can be controlled in order to study the electrochemical response of the electrode at that specific condition (Logan et al., 2006). The reactors were operated in fed-batch mode for four different fed-batch cycles in which the acetate-exhausted medium was replaced for fresh medium containing, in the last two cycles, the double amount of the initial acetate concentration. After these fed batch cycles, the anode biofilm was grown and visible on the electrode (Figure 5.11).

Figure 5.11 Image of the electro active biofilm developed at the end of the start-up phase.

Therefore, the medium in the reactors was replaced with aerobic activated sludge of a pilot MBR reactor treating real wastewater. The activated sludge sparged with nitrogen was fed in batch for four different cycles characterized by a total suspended solids (TSS) content of 1 g L^{-1}, 2 g L^{-1}, 6 g L^{-1} and 10 g L^{-1}, respectively.

5.2.3 Analytical methods

Liquid and gas analysis

The liquid analysis was carried out on the samples taken at the start and the end of each feeding cycle. The concentration of acetate and other VFA was measured with an Agilent 7890A gas chromatograph (GC) equipped with a DB-FFAP column and a flame ionisation detector (FID). Total COD (tCOD) and soluble COD (sCOD) were analysed on the sludge samples according to the recommendations of the American Public Health Association (APHA) (APHA, 2005). Conductivity and pH were measured with a pH and EC meters (pH-meter basic 20^{+}, EC-Meter BASIC 30^{+}, Crison Instruments, Spain).
The produced gas was sampled with a glass syringe during the start-up. The composition of the gas phase was analysed in a second channel of

the GC equipped with an HP-Molesieve column and a thermal conductivity detector (TCD) to detect H_2, O_2, N_2, CH_4, CO, and CO_2.

Sludge characterization

The sludge characterization was performed by analysing the samples at the start and the end of each feeding cycle after the start-up period. The mixed liquor total suspended solids (MLTSS) and volatile suspended solids (MLVSS) content was measured according to the standard methods of the American Public Health Association (APHA) (APHA, 2005). The bound extracellular polymeric particles (EPS) were separated from the soluble fraction of the EPS or soluble microbial products (SMP) trough filtration of the mixed liquor with folded filter paper. The filtered part was filtered again by 0.45µm cellulose acetate filters in order to obtain the SMP. The EPS, present in the retained part, were extracted through a cationic exchange resin according to the method described by Frølund et al. (1996) (Figure 5.12c). Then, EPS and SMP were analysed for their relative content of protein (EPSp, SMPp) (Frølund et al., 1995) and carbohydrate (EPSc, SMPc) (DuBois et al., 1956). The relative hydrophobicity, expressed as percentage of hydrophobic sludge, was measured using the protocol described by Rosenberg et al. (1980), reported in the paragraph 5.1.3. The capillarity suction time (CST) (Triton electronics Ltd., type 304 B) was used to investigate the dewaterability of the sludge (Scholz, 2005) (Figure 5.12a) and a sludge filterability test was also performed by means of the paper filtration test method and measuring in mL of the filtrate collected passing by a folded filter paper in 5 min of an initial 50 mL activated sludge sample (Kubota, 2004) (Figure 5.12b).

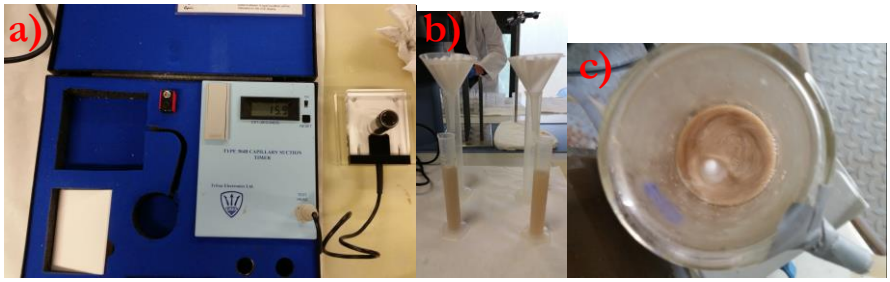

Figure 5.12 Capillary suction time (a) and filterability (b) test, EPS extraction (c).

Bioelectrochemical measurements

Cyclic voltammetry (CV) analysis was performed under turnover conditions (presence of organic substrate) and non-turnover conditions (absence of organic substrate) at different stages (Figure 5.10).
Cyclic voltammetry is a tool used in electrochemistry to study and characterize the electron transfer interactions between microorganisms or microbial biofilms and microbial fuel cell anodes (Fricke et al., 2008). In the voltammetry tests, the potential of the working electrode (anode or cathode) is varied at a certain scan rate (expressed in V s-1) and the current production is recorded (Logan et al., 2006). The cyclic voltammograms, at different stages of biofilm formation and substrate availability (and thus different stages of current generation), can provide valuable information on the electron transfer mechanism (Fricke et al., 2008).
The scan window of the CV was from 600 to -600 mV. In every CV, three cycles were performed at a scan rate of 1 $mV \cdot s^{-1}$ with the same three electrode configurations and using the last one to do the calculations. The data extracted from the CVs were analysed using the free-software SOAS software (Fourmond et al., 2009) in order to perform derivatives and identify the oxidation and reduction peaks. The mid-point potential (E_m) of redox couples was calculated as the mean value of the oxidative and reductive potential and referred vs. SHE.
The Coulombic Efficiency (CE) was determined according to the methodology described by Logan et al. (2006). The Coulombic efficiency is the ratio of total Coulombs actually transferred to the anode from the substrate, to maximum possible Coulombs if all substrate removal produced current (Logan et al., 2006). The total Coulombs obtained is determined by integrating the current over time (Logan et al., 2006):

$$\epsilon_{Cb} = \frac{M \int_0^{t_b} I \, dt}{Fbv_{An}\Delta COD} \qquad (37)$$

Where M=32, the molecular weight of oxygen, F is Faraday's constant, b = 4 is the number of electrons exchanged per mole of oxygen, v_{An} is the

volume of liquid in the anode compartment, and ΔCOD is the change in COD over time *th* of the bacth cycle.

5.3 ELECTRO MEMBRANE BIOREACTOR AT ANOXIC CONDITIONS

5.3.1 Experimental setup and analytical methods

In the last experimental phase, the electro membrane bioreactor, realized at the Sanitary Environmental Engineering Division of Salerno University, was closed along with the aeration inside the reactor itself for around three hours, in order to operate as microbial electrolysis cell (MEC) and easily detect the hydrogen production at the cathode side due to the electric field applied. The reactor in anoxic conditions is shown in Figure 5.13.
The hydrogen produced was accumulated on the headspace of the reactor. The tests were conducted with the electric field ON and OFF in order to evaluate the hydrogen production due to the electrochemical process without the contribution of the anaerobic digestion. At the end of the test, the hydrogen produced was aspirated with a Dräger gas detector pump and analysed with a colorimetric tube for hydrogen determination (Kitagawa precision gas detector tubes) passing previously in an activated carbon filter (Figure 5.14).
The colorimetric tube had a measurement range of 0.05%-0.8%, assuming a coloration from green to blue in presence of the gas.

Figure 5.13 Experimental set-up of the electro MBR at anoxic conditions at SEED – University of Salerno.

Figure 5.14 Dräger gas detector pump on the left, colorimetric tube for hydrogen determination (Kitagawa precision gas detector tubes) on the right.

The percentage of gas detected was converted in ppm and this gas concentration was, then, transformed into mg/L, using the the ideal gas law (P=1atm; T=298K):

$$H_2[mg/L] = \frac{H_2[ppm] \cdot M_H \cdot P}{R \cdot T \cdot 1000(\mu g/mg)} \quad (38)$$

Where:

- M_H is the molecular mass of hydrogen gas equal to 2.106 g mol^{-1};
- R is the universal gas constant equal to 0.08205 $\frac{L \cdot atm}{mol \cdot K}$;
- P is the pressure equal to 1 atm;
- T is the temperature equal to 298.15 K.

The total mass of hydrogen produced in mg was then calculated multiplying the volume of the headspace V_h for the hydrogen concentration H_2 in mg/L. The volumetric hydrogen production rate was assessed dividing the hydrogen mass for the time that the electric field was open. This hydrogen production rate was also normalized for the content of VSS.

6 RESULTS AND DISCUSSION

The present chapter shows results and discussion related to the last three experimental phases. In particular, the results illustrated concern the integration of electrochemical processes into a membrane bioreactor through the application of an electric field (electro MBR), the combination of a microbial fuel cell with a MBR as a downstream processes for the treatment of activated sludge from a membrane bioreactor and the electro MBR operating at anoxic conditions, like a microbial electrolysis cell (MEC), in order to evaluate the hydrogen production rate.

6.1 ELECTRO MEMBRANE BIOREACTOR

The influence of the electric field, applied to a membrane bioreactor, on the overall treatment performance and membrane fouling formation, in terms of fouling rate, sludge hydrophobicity and membrane fouling precursors (bEPS, sEPS or SMP and TEP), has been investigated at the different voltage gradients applied. The results observed, compared with those of a conventional membrane bioreactor, are reported in the following.

6.1.1 Removal of organic substances

When a direct current field is applied to a membrane bioreactor different electrochemical mechanisms occur such as electrocoagulation, electrooxidation, electroosmosis and electrophoresis, which influence the sludge properties in the bioreactor and, thus, the removal performances.
The total COD removal efficiencies were almost constant during the whole experimental period since the conventional membrane bioreactor (MBR) already showed high removal values (Table 6.1). Tafti et al. (2015) and Hosseinzadeh et al. (2015) also found only a 4% increase of COD removal respect to the unmodified MBR system.

It should be taken into account that, in the experimental runs performed, the influent wastewater was essentially constituted by soluble COD and, thus, rapidly biodegradable.
The values of soluble COD in the reactor decreased from 56 ± 20 mg/L in the conventional MBR to 47.8 ± 3.9 mg/L in the eMBR-1 and 27.3± 8.8 mg/L in the eMBR-3 with a simultaneously reduction of tCOD values observed. Therefore, electrochemical oxidation and electrocoagulation processes caused by the applied electric field increased the biodegradability of organic substances and the removal of organic matter resulting in lower values of sCOD in eMBR-1 and eMBR-3.
Regard to the UV_{254} removal, it was improved of around 30% by the application of the two different electric fields of 1 V/cm (eMBR-1) and 3 V/cm (eMBR-3), as shown in Table 6.1, respect to the conventional membrane bioreactor (MBR).

Table 6.1 Characteristics of the influent, effluent and average pollutant removal efficiencies with standard deviations observed in the conventional membrane bioreactor (MBR) and in the electro membrane bioreactor at the different voltage gradients applied (eMBR-1, eMBR-3).

		Experimental runs and applied voltage gradient [V/cm]		
		MBR	**eMBR-1**	**eMBR-3**
		0	1	3
COD	Influent [mg/L]	589 ± 41	522±20	557.45±39
	Effluent [mg/L]	11.88 ± 4.12	13.1 ± 4.3	9.82 ± 4.3
	Removal [%]	97.9 ± 0.68	97.5 ± 0.82	98.2 ± 0.7
UV_{254}	Influent [mg/L]	0.13±0.06	0.14±0.05	0.09±0.04
	Effluent [mg/L]	0.07±0.05	0.04±0.03	0.02±0.01
	Removal [%]	46.3±26	80.1±18	84.7±11
NH_4-N	Influent [mg/L]	29.9 ± 6.0	24.7 ± 3.8	27.9 ± 5.1
	Effluent [mg/L]	17.8 ± 5.4	11.0 ± 2.3	8.5 ± 4.7
	Removal [%]	42.4 ± 15.8	52.9 ± 12.9	69.3 ± 16.4
PO_4-P	Influent [mg/L]	11.7 ± 1.2	8.7 ± 2.8	7.2 ± 1.4
	Effluent [mg/L]	7.9 ± 1.9	0.5 ± 0.09	0.3 ± 0.09
	Removal [%]	33.0 ± 23.6	93.4 ± 7.3	96.1± 5.4

Therefore, this further demonstrates the enhancement of organic matter removal due to the electrochemical processes applied which are able to

coagulate the colloidal organic particles, also those with a high molecular weight, and oxidize electrically the organic substances according to Tafti et al. (2015).

6.1.2 Nutrient removal

The application of electrochemical processes inside the membrane bioreactor, as it can be seen in Figure 6.1, led to a significant variation of operational parameters with a decrease of redox potential and dissolved oxygen values when the electric field was ON. In this latter case, the reductive reactions at the cathode side have consumed the dissolved oxygen which acted as an electron acceptor, generating anoxic conditions in the bioreactor, according to the following reaction:

$$O_2 + 4\,H^+ + 4\,e^- \rightarrow 2\,H_2O \qquad (32)$$

This is in compliance with the decrease of redox potential from typical values of aerobic conditions (100 – 300 mV) to anoxic conditions values (around 0 mV). This variation of the operation parameters was first highlighted in this experimental study.

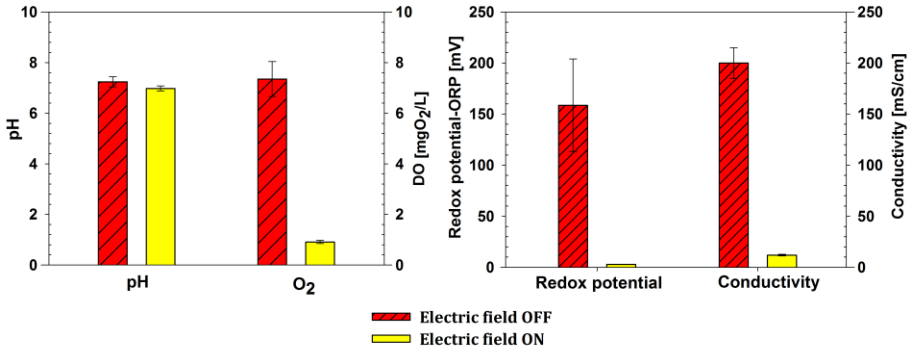

Figure 6.1 Values of membrane bioreactor operational parameters in absence of electric field (MBR) and in presence of electric field (eMBR-3).

The alternation of anoxic and aerobic conditions in the eMBR-1 and eMBR-3 have enhanced the performance of the nitrification process and allowed, beyond it, the denitrification as well. Indeed, in comparison to the conventional membrane bioreactor (MBR), the removal efficiency of the ammonia nitrogen (NH_4-N) was increased by 11% and 27% on

average, respectively in the eMBR-1 and eMBR-3, when electrochemical processes were applied to the membrane bioreactor (Table 6.1). Furthermore, the average nitrate nitrogen concentrations in the effluent were found equal to 0.32±0.10 mg/L and 0.18±0.15 mg/L in the eMBR-1 and eMBR-3, respectively, compared to 18.70±9.0 mg/L in the MBR (Figure 6.2). This shows that the applied electric field led to an almost complete removal of the ammonia compounds due to the denitrification process (Figure 6.2).

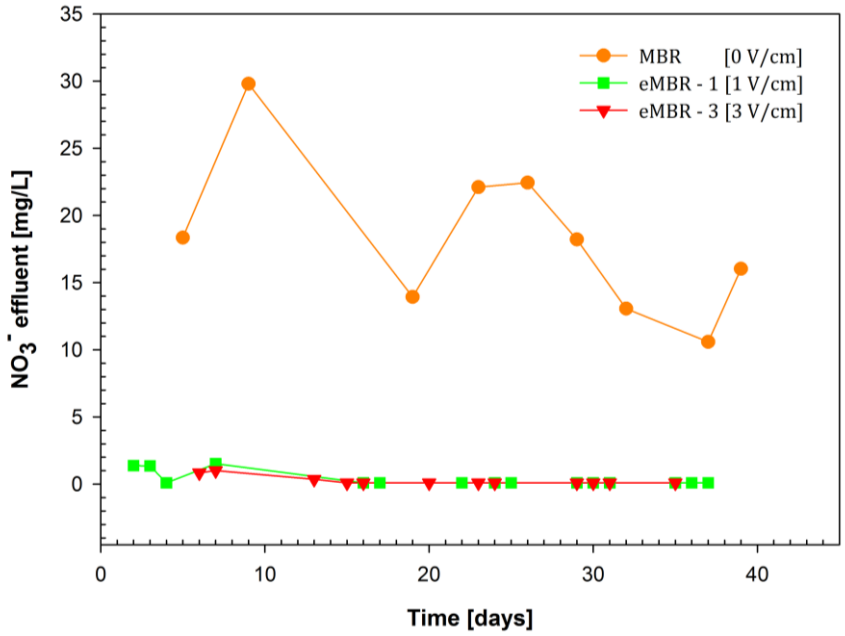

Figure 6.2 Nitrate nitrogen concentrations observed in the effluent of the membrane bioreactor over time.

These results are in agreement with the study of Ibeid et al. (2015) who highlighted the potentiality of the electro membrane bioreactor of achieving a complete nitrification of ammonium and denitrification of nitrate if the loading of ammonium is lower than the nitrification capacity of the reactor. However, the mechanisms of nutrients removal have not been highlighted. Conversely, previous studies (Bani-Melhem and Elektorowicz, 2011; Bani-Melhem and Smith, 2012) observed that the nitrification of ammonia nitrogen was reduced due to the sensitivity of microbial community to the electric field. Hence, the anoxic

conditions generated in the second (eMBR-1) and third run (eMBR-3), when the electric field was ON (Figure 6.1), first verified in this experimental study, have favoured the reduction of nitrate to nitrogen gas, consuming organic carbon as an electron donor.
There is also the possibility of autotrophic reductions of nitrate and nitrite via hydrogenotrophic denitrification.
At the voltage gradients applied, the formation of the hydrogen gas could have occurred at the cathode side according to the following reaction (Aouni et al., 2009):
At the cathode (reaction 20):

$$3H_2O + 3e^- \rightarrow (3/2)H_{2(g)} + 3OH^-_{(aq)} \quad (20)$$

Hence, the overall reaction of nitrate reduction in presence of the hydrogen gas could have happened as follows (Kurt et al., 1987; Lee et al., 2010):

$$NO_3^- + 2.5\ H_2 \rightarrow 0.5N_2 + 2H_2O + OH^- \quad (39)$$

The integration of electrochemical processes into membrane bioreactor also caused a significant enhancement of phosphorus removal which was increased, compared with the MBR, by 61% and 63% after the application of the 1 V/cm (eMBR-1) and 3 V/cm (eMBR-3) voltage gradients (Table 6.1).
This improvement results from electrocoagulation and precipitation of $AlPO_4$ and $Al(OH)_3$ (Attour et al., 2014). Indeed, electrolytic reactions at electrode surfaces, formation of coagulants in the aqueous phase and adsorption of soluble or colloidal pollutants on coagulants occur during electrocoagulation (Aouni et al., 2009).
The oxidation of the aluminum anode forms amorphous $Al(OH)_{3(s)}$ "sweep flocs" with a large surface areas which is beneficial for trapping of colloidal particles and a rapid adsorption of soluble organic compounds (Bayramoglu et al., 2004) and soluble phosphorus, according beyond to the reaction (18) also to the following reactions (Aouni et al., 2009):

- At the anode (reaction 19):

$$Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^- \quad (19)$$

- In the solution (reaction 21):

$$Al^{3+}_{(aq)} + 3H_2O \rightarrow Al(OH)_{3\,(s)} + 3H^+_{(aq)} \quad (21)$$

Furthermore, insoluble phosphorous can react with the aluminium ions released from the aluminium electrode formed hard to dissolve precipitate of $AlPO_4$ in presence of PO^{3-}_4 ions (Kim et al., 2010) that can float or precipitate in the membrane bioreactor as follows:

$$Al^{3+}_{(aq)} + PO^{3-}_{4\,(aq)} \rightarrow AlPO_{4\,(s)} \quad (40)$$

These processes reflect the superior phosphorus removal efficiency especially at the highest value of electric field applied (eMBR-3) (Table 6.1). Bani-Melhem and Elektorowicz (2011) also found an enhancement of PO_4-P removal efficiency up to 98% in an electro MBR.

6.1.3 Impact of electrochemical processes on sludge characteristics

A reduction of sludge conductivity was observed when the electric field was applied to membrane bioreactor (Figure 6.1). Electrolytic oxidation of the aluminum anode releases Al^{3+} ions and generates in situ charged species of aluminum hydroxides, destabilizing the charged colloids and soluble solutes in the suspension (Hasan et al., 2012) and resulting in a lower sludge conductivity (Giwa et al., 2015; Tafti et al., 2015).
The dissolution of Al^{3+} ions in the mixed liquor was demonstrated by the increase of aluminium dose in the eMBR-1 and eMBR-3 after the application of the electric field considering that the initial values were negligible (Figure 6.3).
The Al dosage was also determined by weighing the anode electrode before and after each run and these values, reported in the Figure 6.3, were higher than the measured values due to the deposition of high quantity of aluminium in the biomass and mineralized organic substances found attached on the anode electrode at the end of each run (Figure 6.4).

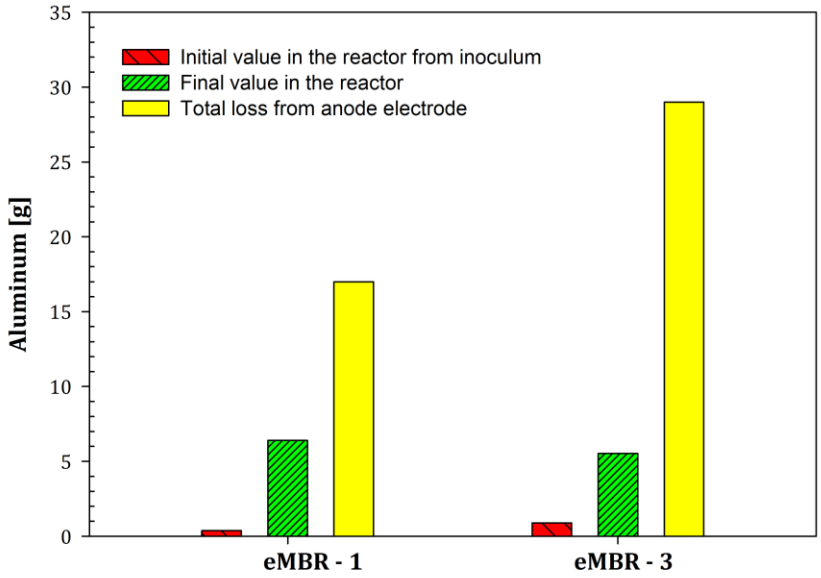

Figure 6.3 Aluminium balance in eMBR processes.

Figure 6.4 Biomass found attached on the anode electrode at the end of the second run (eMBR-1) and at the end of the third run (eMBR-3).

Figure 6.5 shows the aluminium anode electrode at the start of the experimental runs and at the end of the second (eMBR-1) and third run (eMBR-3) after that the biomass was removed from it.

Figure 6.5 Aluminium anode at the start of the experimental runs (a), at the end of the second run (eMBR-1) and of the third run (eMBR-3).

Electrocoagulation and charge neutralization of charged particles allowed them to band together and form larger flocs. The production of larger flocs could reduce the retention of water among these flocs increasing hydrophobicity (Deng et al., 2015). Indeed, the values of relative hydrophobicity increased from 45.1±1.36 % in the conventional MBR to 71.7 ± 6.0% in the eMBR-3.

Since membranes typically used in membrane bioreactors are hydrophilic in order to improve their water permeability, low hydrophobicity of sludge flocs is expected to produce high fouling due to stronger interactions with the membrane surface (Van den Broeck et al., 2011). Hydrophobic particles interact less with the hydrophilic membrane, enhance bioflocculation and reduce floc deterioration (Le-Clech et al., 2006; Van den Broeck et al., 2011), improving membrane performance. Indeed, as it can be seen in the following section, higher values of relative hydrophobicity corresponded to lower fouling rates in eMBR-1 and, in particular, in eMBR-3.

Regarding the biomass, the reactor worked with a content of MLVSS equal to 4216±452 mg/L in the MBR, 4262 ± 869 mg/L in eMBR-1 and 3918±1030 mg/L in eMBR-3. MLVSS/MLTSS ratios remained almost constant in the MBR while showed a decreasing trend over time in the eMBR-1 and eMBR-3, as reported also in previous work (Hua et al., 2015), due to the dissolution and accumulation of inorganic Al^{3+} inside the bioreactor for electrooxidation and of aluminium hydroxide for electrocoagulation process (Figure 6.6).

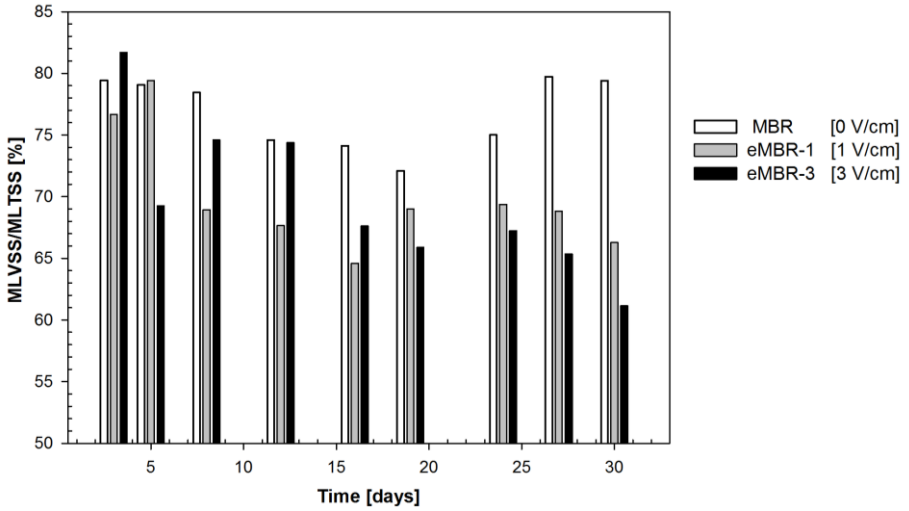

Figure 6.6 Trend of the ratio MLVSS/MLTSS in the membrane bioreactor over time for the three experimental runs.

6.1.4 Membrane fouling formation

Under constant flux operating mode, membrane fouling can be determined by the rise of TMP over time. The increase of TMP is one of the most important indicators of membrane fouling since it is directly related to membrane fouling resistance. The TMP variation over time was monitored during the three experimental runs (MBR, eMBR-1, eMBR-3). The three TMP profiles obtained during the membrane filtration at a constant flux of 15 LMH are reported in Figure 6.7.
The frequency of chemical cleaning, calculated as the numbers of chemical cleaning performed divided by the overall filtration time, was considered as a factor of comparison in terms of fouling tendency.

As it can be seen in the Figure 6.7, the TMP increased more quickly in the MBR respect to the eMBR-1 and, in particular, to the eMBR-3.
The conventional membrane bioreactor (MBR) showed an average frequency of chemical cleaning equal to 0.166 cleaning/d, whereas an average frequency of 0.125 cleaning/d and 0.058 cleaning/d was observed in the eMBR-1 and eMBR-3, respectively (Table 6.2).
Hence, the frequency of chemical cleaning respect to the MBR was reduced by 24.7% in the eMBR-1 and by 65.0% in the eMBR-3 (Table 6.2). The application of electrochemical processes in the last two experimental runs (e-MBR-1, eMBR-3) to the membrane bioreactor allowed to extend the time between chemical cleaning and, therefore, the filtration cycles.
These results are consistent with those found regarding the membrane fouling rates. Indeed, the average membrane fouling rates were lower in the eMBR-1 and the eMBR-3 than those of the conventional MBR (Table 6.2). In particular, there was a reduction of the average membrane fouling rate of 15.9% in the eMBR-1 and of 54.3 % in the eMBR-3, respect to the MBR without electrochemical processes applied, characterized by an avarage membrane fouling rate equal to 8.08 kPa/d (Table 6.2). With regard to normalized membrane fouling rates, these percentage reductions increased up to 18.2% and 32.9%, in the eMBR-1 and eMBR-3, respectively, respect to the MBR.
Bani-Melhem and Elektorowicz (2011) found a lower membrane fouling reduction (16%) in a submerged electro membrane bioreactor operated at laboratory scale with a DC field operational mode of 15 min ON and 45 min OFF and voltage gradient of 1 V cm^{-1}. Whereas, Zhang et al. (2015) observed in an electro membrane bioreactor, with stainless steel mesh as the anode and under an intermittent voltage of 2.72 V and current of 0.1 A, a 30% reduction of the membrane fouling rate compared to the conventional MBR.
The improvement of membrane filtration noticed in the present experimental study is due to the different electrochemical processes that are involved when an electric field is applied to a membrane bioreactor. The increase of particle diameter due to electrocoagulation minimizes membrane fouling (Shen et al., 2015).

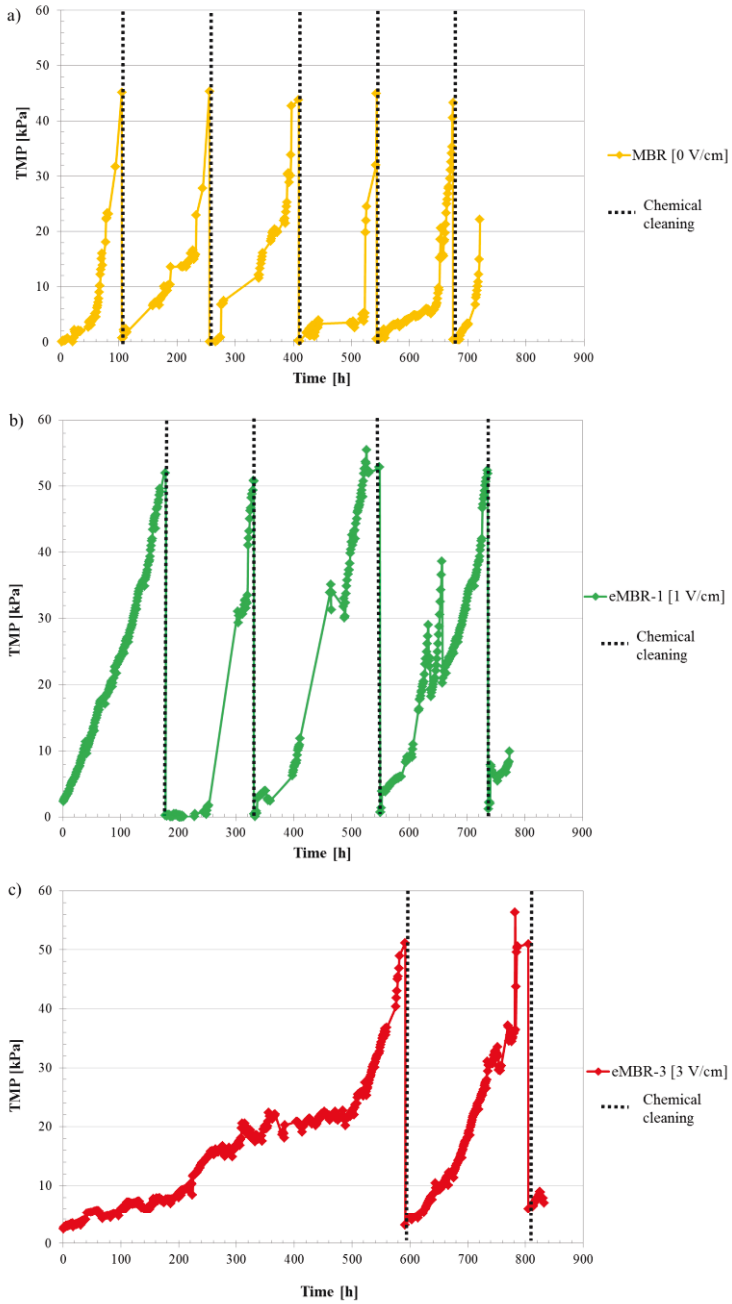

Figure 6.7 TMP rise-up over time in the three experimental runs: a) MBR – Conventional MBR at 0 V/cm, b) eMBR-1 - Electro membrane bioreactor at 1 V/cm, c) eMBR-3 - Electro membrane bioreactor at 3 V/cm.

Therefore, the flocs formed by EC could be easily removed by the filtration since they are relatively large, contain less bound water and are more stable (Khandegar and Saroha, 2013). Furthermore, the application of the electric field can bring the removal of bound water from the microbial flocs electrical double layer due to electroosmosis mechanism, thus increasing sludge dewaterability by decreasing the specific resistance to filtration (Ibeid et al., 2013). The electroosmosis mechanism was witnessed by the increase of hydrophobicity values in eMBR-1 and eMBR-3.

Table 6.2 Frequency of chemical cleaning and membrane fouling rates at the different voltage gradients applied to the electro membrane bioreactor.

RUN	Voltage gradient applied [V/cm]	Frequency of chemical cleaning [cleaning/d]	Fouling rate ΔTMP/ dt [kPa/d]	Fouling rate normalized ΔTMP/ (dt x C_{MLVSS}) [kPa/(d x g MLVSS/L)]
MBR	0	0.166	8.08	1.92
eMBR-1	1	0.125	6.80	1.57
eMBR-3	3	0.058	3.69	1.29

Electrophoresis, the movement of charged colloids toward the oppositely charged electrode at which they deposit, is another electrochemical mechanism responsible for the reduction of membrane fouling. The surface of activated sludge is generally negatively charged (Lee, 2003; Liao et al., 2001). This means that it may be possible to control the motion of activated sludge by applying an external electric field, thus controlling membrane fouling (Akamatsu et al., 2010). Indeed, the negative charged activated sludge particles were attracted from the anode which was positive charged moving away from the membrane module located inside the cathode which was negative charged as shown in Figure 6.8 and Figure 6.9. Indeed, the cathode at the end of the second (eMBR-1) and third run (eMBR-3) (Figure 6.8a) showed less biomass attached on it respect to anode due to electrophoresis mechanism (Figure 6.8 b-c). At the same way, the membrane module at the end of the first run (MBR) exhibited a higher fouling than that showed at the end of the second (eMBR-1) and third run (eMBR-3) as visible in the Figure 6.9.

Figure 6.8 Pictures of the cathode at the end of the second (eMBR-1) and third (eMBR-3) run (a), anode at the end of the second run (eMBR-1) (b) and of the third run (eMBR-3) (c).

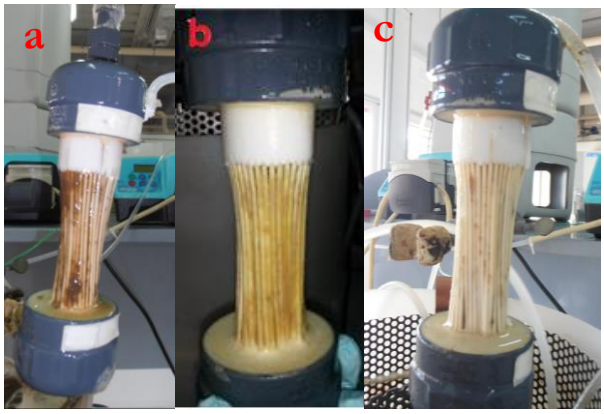

Figure 6.9 Pictures of the membrane module at the end of the first run (MBR) (a), of the second run (eMBR-1) (b) and of the third run (eMBR-3) (c).

Therefore, in the electro membrane bioreactor different electrochemical processes could occur that are expected to limit membrane fouling.
Since the membrane fouling is directly related to membrane fouling precursors (SMP, EPS, TEP) (de la Torre et al., 2010; Drews et al., 2008; Lin et al., 2014), they were investigated, as reported in the following paragraph, in order to understand their influence on membrane fouling

formation and, thus, on reduction of membrane fouling rates found in the results observed for the eMBR-1 and eMBR-3.

6.1.5 Impact of electrochemical processes on membrane fouling precursors

The biomass in a membrane bioreactor is characterized by different amounts of particulate, colloidal and dissolved fractions which are responsible for membrane fouling (Drews, 2010). In particular, as reported in the third chapter, extracellular polymeric substances (EPSs) are currently assumed to be the main origin of membrane fouling in membrane bioreactors (Drews et al., 2008). Generally, polysaccharides and proteins are considered as the major fractions that contribute to fouling. Thus, the determination of bEPS or SMP concentrations is based almost exclusively on polysaccharides and proteins measurements (Drews, 2010).
The gel structure of bEPS and SMP makes them able to block the membrane pores, reducing the filtration and constituting a possible nutrient for biofilm formation (Rosenberger et al., 2005).
Regarding the TEP, they are very sticky substances that exhibit the characteristics of gels and are considered as the acid fraction of polysaccharides (Passow, 2002).
In the experimental activity, a decrease of avarage SMPp normalized concentration in the mixed liquor equal to 44.0% and 60.4% was found in the eMBR-1 and eMBR-3, respectively, after the application of the voltage gradients respect to the conventional MBR (Table 6.3). Whereas, SMPc showed a significant reduction of 74.2% only in the eMBR-3 characterized by the highest electric field applied (3 V/cm) (Table 6.3). The same behavior was observed for the average bound EPSp normalized concentration in the mixed liquor which decreased by 76.8% and 83.3% in the eMBR-1 and eMBR-3, respectively, compared to the MBR (Table 6.3).
While, a reduction of bound EPSc equal to 63.5% was found only in the eMBR-3. Furthermore, the results also pointed out that TEPs, whose behavior in an electro MBR was firstly investigated in the present study, were able to be removed in the mixed liquor by electrochemical processes. In particular, a substantial reduction equal to 71.75% and 75.78% was found respect to the conventional MBR after the application of 1V/cm (eMBR-1) and 3 V/cm (eMBR-3) (Table 6.3), respectively.

EPSs carry ionizable functional groups such as carboxyl, phosphoric and hydroxyl groups which render them negatively charged at near neutral pH (Lin et al., 2014). Hence, aluminum hydroxides positive charged formed at the anode side due to the electrolytic oxidation of the aluminum anode destabilized and neutralized the negative charged EPS, the charged colloids and soluble solutes in the suspension (Le-Clech et al., 2006). These hydroxide precipitates adsorbed suspended particles, colloids and soluble organics leading to a substantial reduction of membrane fouling precursors (SMP, EPS, TEP) and, thus, of the membrane fouling. Hua et al. (2015), indeed, reported that charge neutralization between negative charged sludge flocs and positive electro-generated coagulants during electro-coagulation can absorb and reduce soluble EPS. On the other hand, they suggested that bound EPS reduction can be attributed to the coexistence of electro-chemical oxidation, which may convert EPS into more biodegradable compounds that, then, can be reduced during aerobic treatment.

Table 6.3 Average concentrations with standard deviations of bEPS, SMP and TEP found in the mixed liquor after the application of the different voltage gradients.

	Experimental runs and applied voltage gradient [V/cm]		
	MBR	**eMBR-1**	**eMBR-3**
	0	1	3
bEPSp [mg/g VSS]	32.75±12.9	7.61±2.6	5.45±3.4
bEPSc [mg/g VSS]	6.5±3.1	9.50±3.6	2.37±1.4
SMPp [mg/g VSS]	12.52 ±5.6	7.00 ± 3.1	4.96 ± 2.0
SMPc [mg/g VSS]	8.99±4.7	9.28±2.6	2.31±1.4
TEP [mg/g VSS]	12.64± 7.4	3.57±2.7	3.06±0.9

Indeed, water electrolysis and oxidation on anode surface could have generated hydroxyl radicals (Wang et al., 2004), species that provide a high oxidation potential, able to mineralize polysaccharides and proteins also in bound form, making SMP, bEPS and TEP more biodegradable products that have been then biologically degraded.

The different behaviour observed between proteins and carbohydrates in the second run (eMBR-1), characterized by the lowest electric field applied, could be due to the fact that the proteins have high density of negatively charged (Wilén et al., 2003), which react electrostatically with the cations to form stable flocs (Ramesh et al., 2006b).
Lower concentrations of the precursors denoted less foulants in the mixed liquor and, therefore, less potential to cause membrane fouling. Indeed, the results observed are consistent with the decrease of the membrane fouling rate (Figure 6.10).

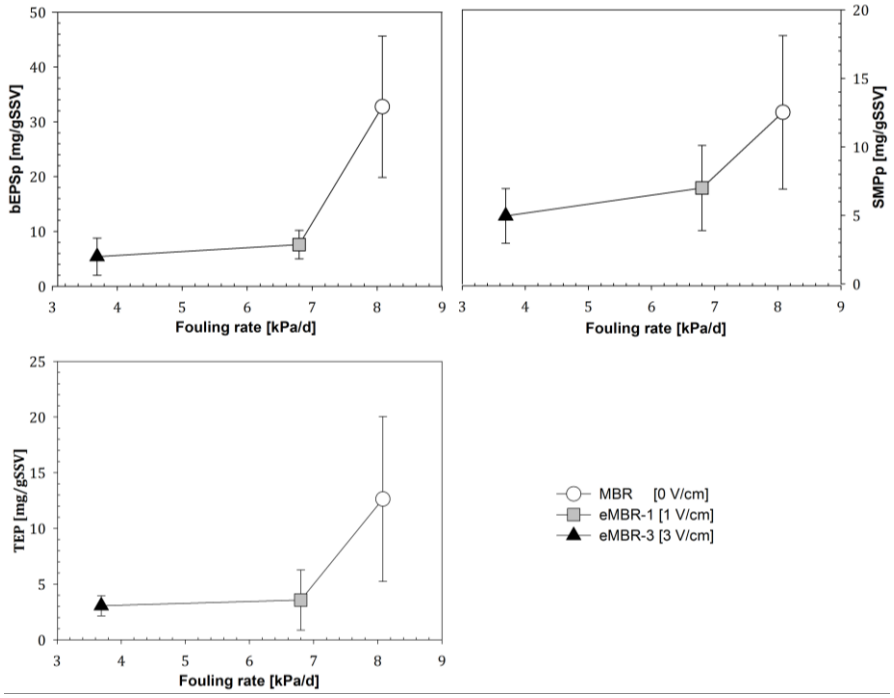

Figure 6.10 Average concentrations of TEP, bEPSp, SMPp with standard deviations related to the membrane fouling rates observed in the conventional membrane bioreactor (MBR) and in the electro membrane bioreactor at the different voltage gradients applied (eMBR-1, eMBR-3).

The removal of bEPS, SMP and TEP observed after the application of the two DC fields corresponded to a substantial reduction of membrane fouling rates (Figure 6.10). Therefore, the removal of the membrane fouling precursors enhanced the filterability of the mixed liquor making the sludge less viscous and reducing the membrane fouling rate.

6.2 TREATMENT OF MBR SLUDGE WITH A MICROBIAL FUEL CELL IN AN EXTERNAL CONFIGURATION

The results regarding the combination of a MBR with a MFC as a down-stream process are reported in the following. A MFC was fed in batch with activated sludge from a membrane bioreactor under different influent total suspended solids (TSS) content. The influence of bioelectrochemical processes on concentration of organic matter, sludge content and properties, in particular, on main parameters that affect fouling in membrane bioreactors were investigated. Furthermore, the electrochemical characterization of the system was also undertaken in order to evaluate the current production and the anode electron transfer mechanism. Indeed, the main electron transfer mechanism governing the anode electro-active biofilms in a MFC, in an external configuration and fed with activated sludge from a MBR characterized by different solids concentrations, has not been investigated yet.

6.2.1 BES start-up

Development of an electro-active anodic microbial biofilm

The anodic biofilm was grown feeding in batch the system with acetate-containing medium according to previous studies (Pous et al., 2016), after inoculating it with aerobic activated sludge of a pilot MBR and anode and cathode effluent of a MFC and a denitrifying MEC, respectively. In the Figure 6.11, the chronoamperometric (CA) biofilm growth on working anode electrode was shown at an applied potential of +297 mV (vs. SHE) with acetate as the electron donor. The acetate concentration was doubled respect to the initial concentration in the third and fourth fed batch cycle and was equal to 0.600 g L^{-1} in order to allow the biofilm growth to begin and, therefore, to develop a mature anodic biofilm able to oxidize acetate. The low current production during the first days of operation was also due to the time needed to microorganisms to establish. The current density, calculated normalizing the current production (A) for the anode area, started to increase, indeed, after the second fed batch cycle achieving a maximum value at around the 20^{th} day of the start-up period. The decrease in the current at the end of the start-up period was caused by substrate exhaustion. A coulombic

efficiency (CE) of 40.4% was observed in the last fed batch cycle (Table 6.4).

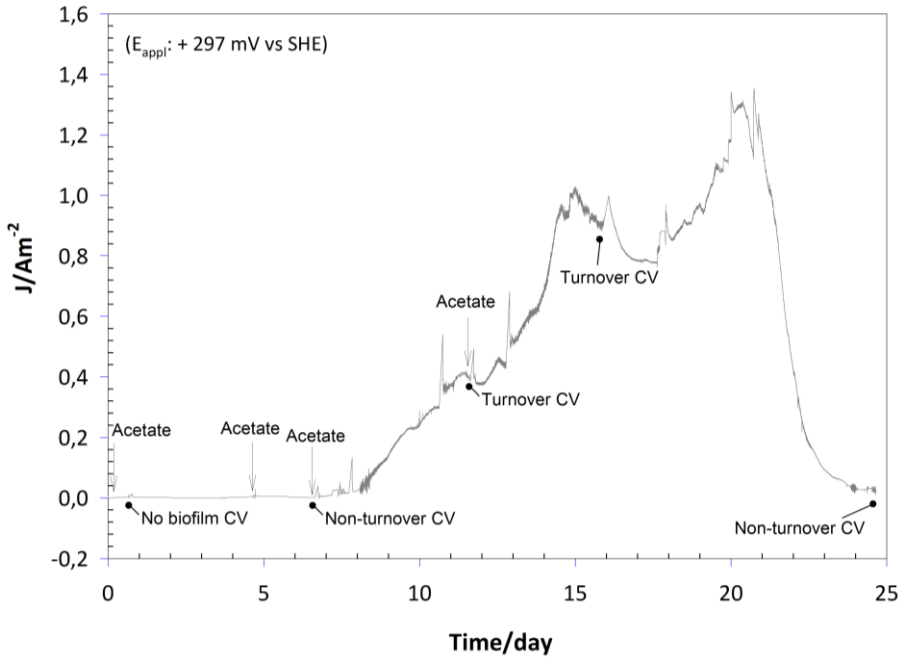

Figure 6.11 Chronoamperometry graph of biofilm formation at the anode side during the start-up period. Vertical arrows indicate tha addition of acetate.

CV analyses of anodic microbial biofilm

In order to study the anodic biofilms behaviour and the anodic electron transfer processes, cyclic voltammetry tests were done in presence (turnover) and absence of substrate (non-turnover) and compared to the CV of the bare graphite – carbon anode electrode immersed in the growth media. Representative CVs for the different conditions are reported in Figure 6.12.

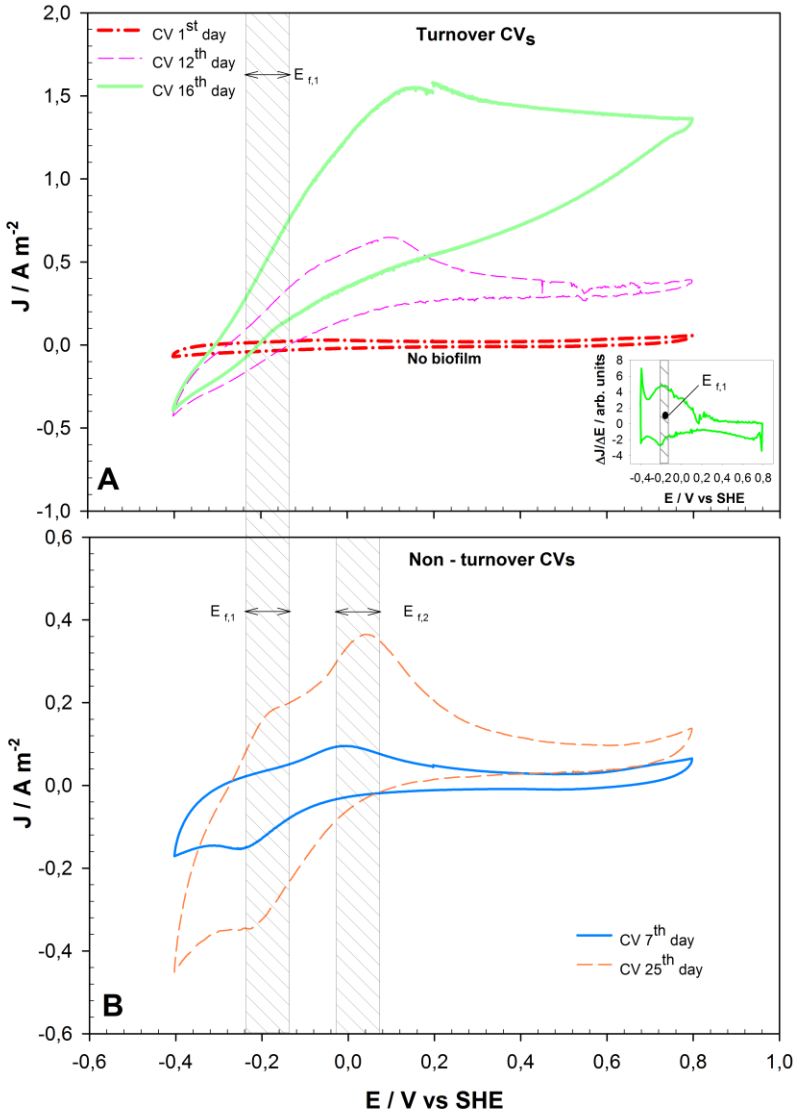

Figure 6.12 Representative cyclic voltammograms of the biofilm during the start-up period. A) Anodic CVs under turnover conditions with the inset of the first derivative of the CV at 16th day and B) Anodic CVs under non turnover CV.

The control CV of the bare electrode did not show an appreciable signal. This confirms the development and firmly attachment of a mature

biofilm on the anode electrode pointed out by the turnover and non-turnover CV signals. Representative CVs under turnover conditions also exhibited a sigmoidal shape typically observed in biofilm characterized by anode-respiring bacteria (ARB) able to generate high currents and thick biofilms with a direct electron transfer (DET) mechanism via outer membrane cytochromes (Carmona-Martínez et al., 2013; H. J. Kim et al., 2002).

The turnover CVs revealed one inflection point, reflected by one maximum in the CV first derivative curve (reported in Figure 6.12), and, thus, one main redox couple at a formal potential $E_{f,1}$ equal to -0.164 ± 0.025 V vs. SHE (Table 6.4).

The electrochemical behaviour of biofilm was also characterized at substrate depletion and non-turnover CVs are reported in Figure 6.12. Under this condition a redox couple with a formal potential of -0.163 ± 0.060 V vs. SHE was observed (Table 6.4). This could indicate that the electron transfer mechanism involved was the same in turnover and non-turnover conditions. This formal potential was similar to the value (-175±05 mV vs. SHE) observed by Pous et al. (2016) who developed a mature anodic electro active biofilm using activated sludge as inoculum and acetate as electron donator and identified a biofilm predominantly composed by Geobacter sp. Fricke et al. (2008) also found in their system inoculated with Geobacter sulfurreducens a redox couple characterized by a formal potential of - 376 mV vs. Ag/AgCl (-179 mV vs. SHE).

Table 6.4 Electrochemical characterization of the MFC in the start-up phase and during the four batch cycles with MBR sludge.

Cycle	CE [%]	Condition	$E_{f,1}$ [V vs. SHE]	$E_{f,2}$ [V vs. SHE]
Start- up phase	40.4	Turnover	-0.164 ± 0.025	-
		Non turnover	-0.163 ± 0.060	0.036
1st sludge cycle (1 gTSS L^{-1})	6.5	Turnover	-0.211 ± 0.040	-0.009 ± 0.054
2nd sludge cycle (2 gTSS L^{-1})	1.9			
3rd sludge cycle (6 gTSS L^{-1})	12.9			
4th sludge cycle (10 gTSS L^{-1})	17.9			

Therefore, it could be inferred, according to previous work, the values of formal potential observed and CVs shapes, that the biofilm grown on the anode electrode in the present experiment belonged to the Geobacteraceae family.
An oxidation peak at 0.036 V ($E_{f,2}$) was also found in last CV under non turnover conditions, as shown in Figure 6.12, indicating a possible parallel and competing electron transfer mechanism via a similar membrane associated species (Fricke et al., 2008).

6.2.2 Sludge degradation

After the start-up phase and the development of an electro active anodic biofilm, the microbial fuel cells were fed with MBR sludge from a pilot MBR plant. Figure 6.13 shows the degradation of the sewage sludge under the four batch cycles characterized by a different content of the influent TSS (Table 6.5). Compared to the control experiment with an open circuit MFC (OCV – MFC), which was considered as a typical anaerobic digestion test, the tCOD removal rates in MFCs were significantly higher, achieving a maximum removal equal to 44% in the last batch cycle.

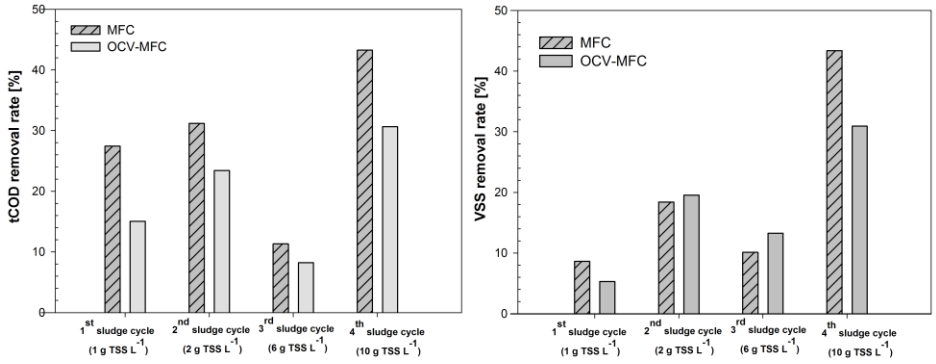

Figure 6.13 MBR sludge degradation in the MFC and in the control open circuit voltage MFC (OCV-MFC) under the four different batch cycles.

Jiang et al. (2011) also found that the MFC fed with raw sludge degraded 7.9% more tCOD compared to conventional anaerobic digestion tests. Z. Wang et al. (2013) also reported an increase of tCOD removal in the MFC respect to the control test. In the OCV-MFC, the organic matter in

the sludge has been oxidized by anaerobic bacteria. In the MFC, anode-respiring bacteria (ARB), developed during the start -up phase, hydrolysed the organic substances into soluble organic matter. Indeed, as reported in Table 6.5, the sCOD content of the sludge increased respect to the influent values, due to the hydrolysis process, in both MFC and OCV-MFC. However, OCV-MFC showed higher sCOD effluent values than MFC, since in the last soluble generated organics have been readily utilized by ARB for producing electricity.

Table 6.5 COD concentrations in the MFC and in OCV-MFC at the different sludge batch cycles.

Cycle	tCOD influent [mg L^{-1}] MFC/ OCV-MFC	tCOD effluent [mg L^{-1}]		sCOD influent [mg L^{-1}] MFC/ OCV-MFC	sCOD effluent [mg L^{-1}]	
		MFC	OCV-MFC		MFC	OCV-MFC
1st sludge cycle (1 gTSS L^{-1})	1064±68	772±23	904±21	23,53±3.2	66±7.3	84±6.3
2nd sludge cycle (2 gTSS L^{-1})	2290±70	1576±36	1754±28	47,06±4.1	63±8.6	83±5.1
3rd sludge cycle (6 gTSS L^{-1})	6140±52	5445±54	5636±63	47,76±4.3	124±7.5	459±9.4
4th sludge cycle (10 gTSS L^{-1})	12182±88	6912±67	8448±89	47,76±4.5	773±9.1	748±8.9

According to Jang et al. (2011), the MFC can be considered as an enhanced sludge digester with additional pathways for substrate hydrolysis and degradation.

Regarding the biomass, MFC generally showed higher reduction of VSS content compared to OCV-MFC with a maximum removal of 43% exhibited in the last cycle (Figure 6.13). The biomass reduction in the MFC could be mainly attributed to the source reduction of COD, since the influent organic matter was degraded and converted to electricity limiting the following heterotrophic proliferation on available substrates (Ma et al., 2015). Furthermore, the transport of electrons through the external circuit could deprive the biomass of electrons needed for cell synthesis and, thus, resulting in overall reduced biomass production (Gajaraj and Hu, 2014). Therefore, the production of electricity and the

consequent reduction of VSS content enhance the sludge stabilization in a MFC.

6.2.3 Electrochemical characterization

Electricity generation

Following an acclimation period of around 25 days, the MBR sludge was fed into the MFC and the OCV-MFC for four batch cycles characterized, as reported in Table 6.5, by a different content of TSS and tCOD. The MFC showed electricity production with a relatively good performance (Figure 6.14). In particular, the current density reached a maximum at around 2.0 A m^{-2} during the fourth cycle since it was characterized by higher influent content of TSS and tCOD (Table 6.5) than the previous cycles.

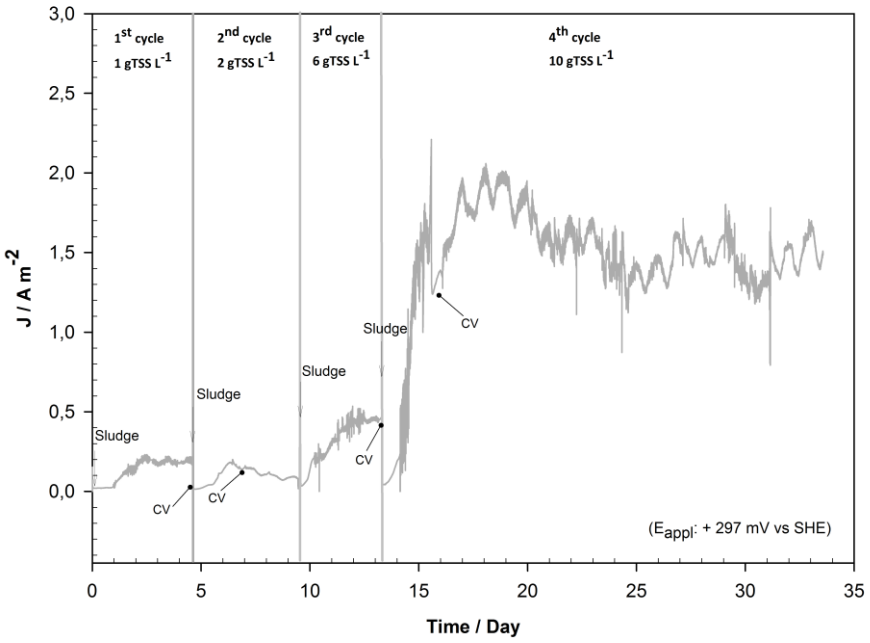

Figure 6.14 Chronoamperometry graph of the MBR sludge in the MFC at the different sludge cycles. Vertical arrows indicate addition of sludge.

Indeed, the hydrolyses of particulate COD into soluble COD in MFC, validated by the increase of sludge sCOD (Table 6.5), allowed the bacteria to take up the sCOD and converted it into electricity. The current produced corroborated the development of an established electro-active anodic biofilm.
As shown in Table 6.4, the coulombic efficiency (CE) of the system increased from the first cycle to the last one, except for the second cycle, according to the increase of electricity production, although the MFC did not exhibit high CE values. Gajaraj et al. (2014) and Su et al. (2013) also found low value of coulombic efficiency in an integrated MFC-MBR and feeding the MFC with MBR sludge, respectively. These low CE values could be attributed to the fact that, beyond electro-active anodic biofilm able to oxidize organic matter producing electricity, there were also other microorganisms with alternative metabolisms without electricity generation such as fermentation, methanogenesis (Logan et al., 2006; Tian et al., 2015). Furthermore, there could be other factors that decreased the CE such as the presence, beyond the anode, of other terminal electron acceptors for example oxygen and nitrate, which are used preferably when present, or over potentials and ohmic losses which hinder the flow of electrons through the electrodes (Gajaraj et al., 2014).
The MFC produced, at the fourth sludge cycle, a maximum voltage outputs of 100 mV which corresponds to a power density of 0.2 W m^{-2}, considering the maximum current density reached in the same cycle.
Even with the low Coulombic efficiencies reached, the relatively high voltage output obtained suggests that the MFC could achieve efficient recovery of electric energy from MBR sludge.

Cyclic voltammograms

According to CV curves (Figure 6.15), the last cycle showed higher electrochemical activities than previous one. The results of CV analysis are consistent with chronoamperometry graphs. Indeed, the electrochemical activity increased with the increase of the influent content of TSS and tCOD. Therefore, the MFC performance is markedly influenced by the sludge features. As for the chronoamperometry graph, only the second cycle, characterized by an influent content of TSS equal to 2 g L^{-1}, showed a different behaviour in terms of electricity production (CA) and electrochemical activity (CV).

According to Xiao et al. (2011), this may be due to that the hydrolysis rate of insoluble matters was slower than the consumption rate of soluble organic matters and the exoelectrogenic bacteria needed to adapt to the new conditions. This was also reflected by the lower value of CE in the second cycle (Table 6.4).

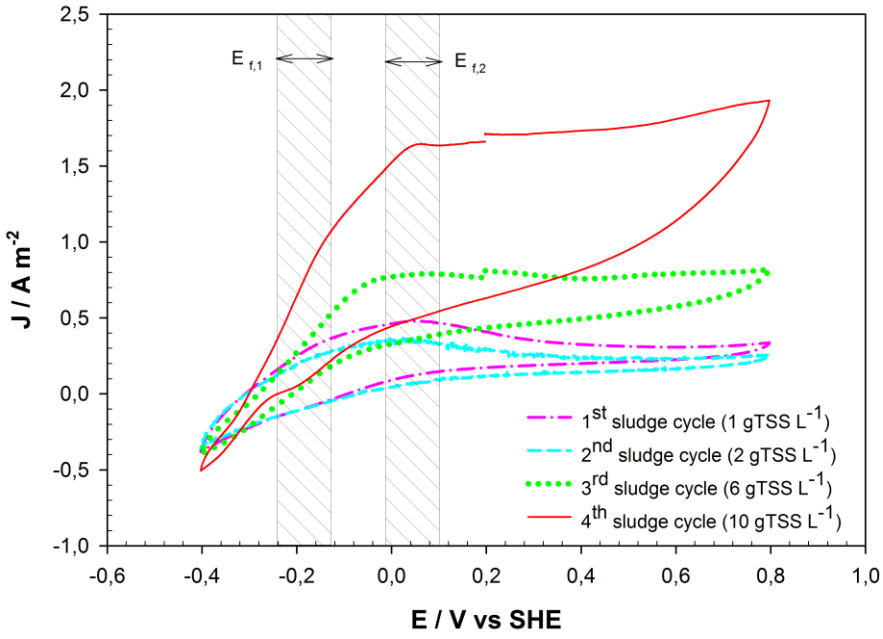

Figure 6.15 Representative cyclic voltammograms of the biofilm during the four sludge cycles.

The CV spectra (Figure 6.15) showed a characteristic sigmoid shape indicating an electrically active biofilms enriched on the anode. The CVs revealed an inflection point, reflected by a maximum in the CV first derivative curves and, thus, a main redox couple at a formal potential $E_{f,1}$ equal to -0.211 ± 0.040 vs. SHE (Table 6.4).
This could indicate that, from an electrochemical perspective, a similar direct electron transfer (DET) mechanism, via outer membrane cytochromes, should be involved during the start- up phase and the batch sludge cycles with no significant shift of the formal potentials for acetate and sludge oxidation.

Furthermore, according to previous observations and the formal potential, biofilms on the anode could belong to the Geobacteraceae family. Another redox couple, as shown in Figure 6.15, at a formal potential $E_{f,2}$ equal to -0.009 ± 0,054 vs. SHE (Table 6.4) was also found in the CVs indicating, as for the start-up phase, a possible parallel and competing electron transfer mechanism via a similar membrane associated species (Fricke et al., 2008).

6.2.4 Sludge characteristics

Hydrophobicity, capillary suction time and filterability

Hydrophobicity is usually considered as the tendency of non-polar molecules to form aggregates in order to decrease their surface of contact with water molecules (Meyer et al., 2006). As shown in Figure 6.16, the relative hydrophobicity of the MBR sludge increased after the treatment in the MFC and OCV-MFC.

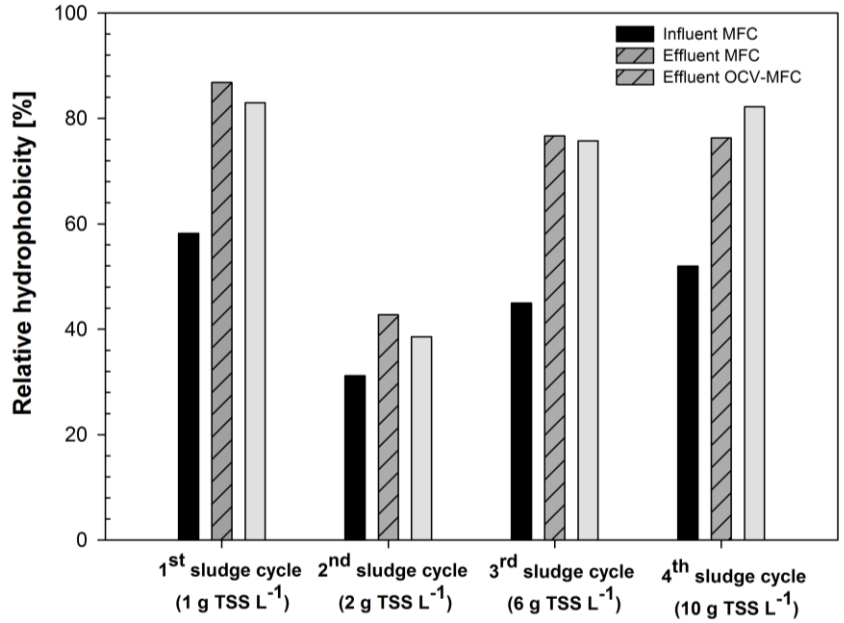

Figure 6.16 Relative hydrophobicity of the sludge before and after the treatment in the MFC and in the OCV-MFC.

In particular, the MFC generally exhibited higher values than the control test. The decrease of flocs hydrophobicity is typically assumed to cause higher fouling in MBR due to flocs deterioration, low flocculation propensity and stronger interactions with the generally hydrophilic membrane (Drews, 2010). Therefore, the recirculation of the sludge treated in the MFC to the membrane bioreactor might limit membrane fouling increasing the flocs hydrophobicity.

The capillary suction time (CST) was evaluated in order to determine the dewaterability of the MBR sludge before and after the treatment in the MFC and OCV-MFC. Sludge filterability was also performed. A decrease in the sludge filterability (Table 6.6), except for the last cycle, and an increase in CST (Table 6.6) were observed when comparing to the influent values in the MFC and OCV-MFC.

The filterability and dewaterability of anaerobic MBR (AnMBR) sludge were found worse than aerobic MBR sludge due to different floc and EPS structure under aerobic and anaerobic conditions (Dereli et al., 2014). Therefore, in the MFCs the anaerobic conditions may have led to a change of sludge structure which in turn has decreased the sludge filterability and dewaterability. However, Su et al. (2013), feeding a MFC with MBR sludge and recirculating it to the MBR after the treatment, found in the combined MBR system better filterability and dewaterability.

Table 6.6 Capillary suction time (CST) and sludge filterability in the MFC and in OCV-MFC at the different sludge batch cycles.

Cycle	CST influent [s L gTSS $^{-1}$] MFC/ OCV-MFC	CST effluent [s L gTSS $^{-1}$]		Influent filterability [mL gTSS^{-1} L^{-1}] MFC/ OCV-MFC	Effluent filterability [mL gTSS^{-1} L^{-1}]	
		MFC	OCV-MFC		MFC	OCV-MFC
1st sludge cycle (1 gTSS L^{-1})	11.38±0.41	12.31±4.67	17.82±0.44	44.08±0.65	34.35±0.61	46.11±0.73
2nd sludge cycle (2 gTSS L^{-1})	9.66±2.6	19.75±1.58	18.33±0.92	19.57±0.53	19.40±1.27	18.89±1.23
3rd sludge cycle (6 gTSS L^{-1})	14.20±0.39	28.07±1.43	22.7±2.19	4.58±0.11	3.55±0.13	3.14±0.67
4th sludge cycle (10 gTSS L^{-1})	10.28±0.8	43.46±1.8	23.76±12.44	2.95±0.1	4.18±0.1	3.91±0.10

Therefore, further studies are needed to understand if the recirculation of sludge to the MBR could improve the sludge characteristics.

Fouling precursors

As shown in Figure 6.17a, a removal of EPSp and SMPc respect to the influent values was found after the treatment in the MFC and OCV-MFC, except for the last cycle characterized by the higher content of influent TSS and which exhibited different values also for the previous reported sludge filterability.

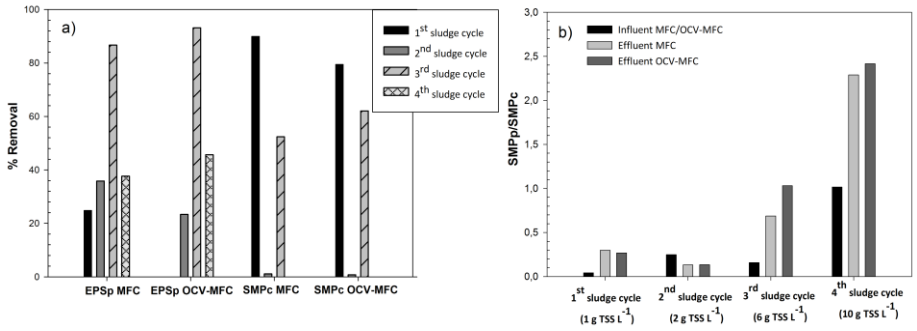

Figure 6.17 EPS protein (EPSp) and SMP carbohydrate (SMPc) removal (a) and SMPp and SMPc ratio (b) in the MFC and OCV-MFC in the four batch cycles (data non reported in figure a corresponded to no removal of EPSp and SMPc in that cycle).

EPSc and SMPp showed a different behaviour with an increase or decrease of the values, depending on the cycle considered, maybe due to the integration of anaerobic digestion and electricity generation (Table 6.7 and Table 6.8)

After all, stimulated by the electricity, the sludge in the MFC had higher activity (Tian et al., 2015) and the insoluble EPSp could have been hydrolysed into simple macromolecules that then have been used by bacteria as sources of carbon and energy for metabolic activity (Sheng et al., 2010). The hydrolysis of EPSp maybe originated the release of SMPp with the consequent increase of its concentration in some cycles.

The carbohydrates can be more easier degraded by bacteria than the proteins (Zhang and Bishop, 2003).

Table 6.7 EPSc and EPSp concentrations found in the influent and effluent of MFC and OCV-MFC in the different batch cycles.

Cycle	EPSc influent [mg gVSS^{-1}] MFC/ OCV-MFC	EPSc effluent [mg gVSS^{-1}]		EPSp influent [mg gVSS^{-1}] MFC/ OCV-MFC	EPSp effluent [mg gVSS^{-1}]	
		MFC	OCV-MFC		MFC	OCV-MFC
1st sludge cycle (1 gTSS L-1)	13,15	15,50	7,82	2,67	2,01	3,08
2nd sludge cycle (2 gTSS L-1)	4,23	11,15	8,47	2,08	1,33	1,59
3rd sludge cycle (6 gTSS L-1)	2,46	2,00	2,26	0,93	0,12	0,06
4th sludge cycle (10 gTSS L-1)	1,13	1,60	1,96	0,94	0,58	0,51

Table 6.8 SMPc and SMPp concentrations found in the influent and effluent of MFC and OCV-MFC in the different batch cycles.

Cycle	SMPc influent [mg gVSS-1] MFC/OCV-MFC	SMPc effluent [mg gVSS^{-1}]		SMPp influent [mg gVSS^{-1}] MFC/OCV-MFC	SMPp effluent [mg gVSS^{-1}]	
		MFC	OCV-MFC		MFC	OCV-MFC
1st sludge cycle (1 gTSS L-1)	91,28	9,19	18,78	3,78	2,73	5,04
2nd sludge cycle (2 gTSS L-1)	11,32	11,20	11,24	2,80	1,47	1,51
3rd sludge cycle (6 gTSS L-1)	6,06	2,88	2,30	0,95	1,98	2,37
4th sludge cycle (10 gTSS L-1)	0,80	4,16	2,50	0,81	9,52	6,05

This has led to the decrease of carbohydrate in SMP which, along with the release of SMPp, contributed to the increase, except for the second cycle, of the SMPp/SMPc ratio in the MFC and OCV-MFC (Figure 6.17b). Tian et al. (2015) and Zhou et al. (2015) also found an increase of SMPp/SMPc ratio of 29% and 25.6%, respectively, in MFCs integrated into MBRs. It was reported that the higher ratio of SMPp/SMPc induced less irreversible membrane fouling (Yao et al., 2011). In addition, Sun et al. (2013), combining a MBR with a MFC as an external configuration, found a release of SMPs in the MFC and, at the same time, the proteins and the carbohydrates produced were degraded when the sludge was returned to the MBR. Therefore, the increase of SMPp/SMPc ratio and the reduction of EPSp and SMPc observed are

expected to be beneficial for membrane fouling abatement in the case that the sludge, treated in the MFC, is recycled to the MBR tank.

6.3 HYDROGEN PRODUCTION IN THE ELECTRO MEMBRANE BIOREACTOR AT ANOXIC CONDITIONS

The hydrogen production in the electro bioreactor was evaluated at anoxic condition in four different experimental tests applying the electric field and closing the reactor and the aeration inside for around three hours. This was done in order to easily determine the hydrogen production at the cathode side and, at the same time, work as a microbial electrolysis cell (MEC), avoiding the presence of oxygen as electron acceptor. Indeed, experiments have shown that 0.25V has to be applied in a MEC in order to reach reasonable current densities and rates of hydrogen (Logan, 2008) in comparison to the theoretical minimum voltage of 1.23 V required for water electrolysis (Rozendal et al., 2007). In the experimental tests performed, a voltage of 18 V was applied. When the electric field was OFF, no hydrogen production was detected in the system while, when the electric field was ON, the hydrogen productions, showed in Figure 6.18 and reported in Table 6.9, were observed.

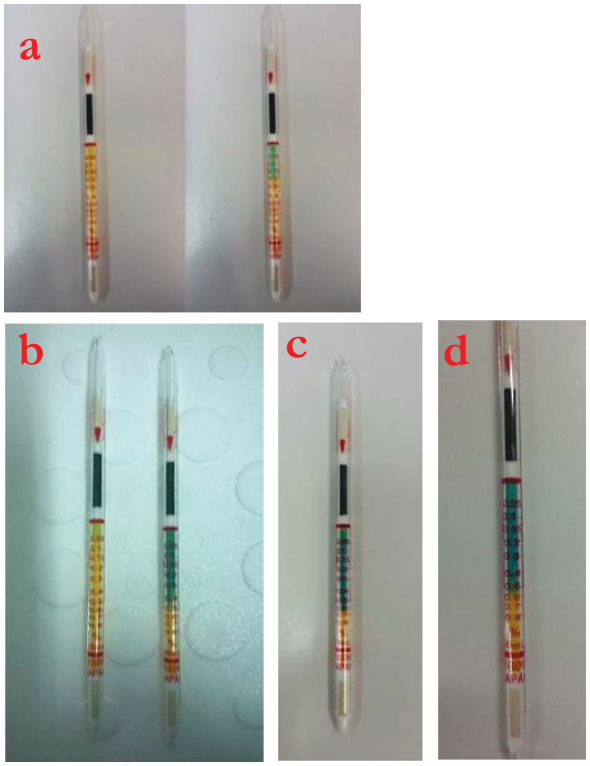

Figure 6.18 Hydrogen detected with the colorimetric tubes: first test before and after the measurement (a), second test before and after the measurement (b), third test after the measurement (c) and fourth test after the measurement (d).

Table 6.9 Hydrogen concentrations detected in the different tests.

Test	Time from the activation of the eMBR [days]	H_2 [%]	H_2 [mg/L]	Headspace volume [L]	H_2 [mg]
Test 1	14	0.2	0.16	14.78	2.44
Test 2	28	0.4	0.33	13.55	4.47
Test 3	35	0.6	0.49	14.78	7.31
Test 4	42	0.7	0.58	14.78	8.53

The volumetric hydrogen production rates, reported in Table 6.10, were calculated dividing the mass of hydrogen produced for the liquid volume of the reactor and the activation time of the electric field (35 minutes),

since it was assessed that, without the electric field, hydrogen was not produced. The volumetric hydrogen production rates were normalized for the content of VSS present in the reactor (Table 6.10).

Table 6.10 Volumetric and normalized hydrogen production rates.

Test	Time from the activation of the eMBR [days]	Volumetric hydrogen production rate	VSS	Normalized hydrogen production rate
		[mg(H_2)/m^3 min]	[g/L]	[µg(H_2)/gVSS min]
Test 1	14	5.14	3.16	1.62
Test 2	28	8.64	4.421	1.95
Test 3	35	15.42	7.63	2.02
Test 4	42	17.99	6.14	2.93

The hydrogen production observed was due to the reduction at the cathode side of protons, developed after the oxidation reactions taken place at the anode, and to the reduction of water according to the following reactions:

$$3H_2O + 3e^- \rightarrow (3/2)H_{2(g)} + 3OH^-_{(aq)} \quad (20)$$

$$2H^+ + 2e^- \rightarrow H_2\ (g) \quad (35)$$

It can be seen (Table 6.10) that the hydrogen production rate increased over time due to the development of a more stabilized electro active biofilm.

6.3.1 Energy considerations

The need to replace depleting oil reserves and slow the impact of global warming through the reduction of CO_2 emissions has given the increasingly rise of "clean fuels" (Gomez et al., 2011). H_2 can be considered a clean fuel, since it presents a high energy yield (142.35 kJg^{-1}) and it is water the exclusive product obtained from its combustion (Das and Veziroglu, 2001; Gómez et al., 2011). Considering the maximum hydrogen volumetric production rate reached in the last test, the energy produced was 0.043 kJ m^{-3} s^{-1}.

The electric voltage applied for achieving this production was 18 ± 0.005 V with an average current intensity of 0.5 ± 0.06 A. The electric power applied is equal to:

$$P = V\,I \qquad (41)$$

Where V is the voltage applied in V and I is the current intensity in A circulating in the system between the two electrodes. The energy consumed per second of applied electric field and per volume of the reactor is 0.7 kJ m^{-3} s^{-1}. Therefore, the energy produced per unit of time and reactor volume is lower than the electric energy required for the process.

However, a more complete energy balance and cost analysis should be made, taking into account other energy consumptions and operational costs. The energy consumptions, indeed, are not limited to the application of the electric field but also involve the operation of the pumps for the influent wastewater, the permeate extraction and the backwashing and the aeration of the system. Other costs concern the chemical cleaning of the membrane module. As previously showed, the application of the electric field leads to a significant reduction of membrane fouling increasing the period of filtration cycles. This means that it is possible to reduce the operational costs through the decrease of the number of backwashing and chemical cleaning of the membrane module. Thus, the energy produced in form of hydrogen and the energy saving due to the fouling reduction might offset the energy consumption for the application of the electric field or might produce an energy surplus with a positive net balance. Without considering that the decrease of membrane fouling increases the membrane lifespan and, thus, reducing the cost for the replacement of the membrane modules.

An overall energy balance and costs analysis of the system studied have not been performed due to the laboratory scale of the reactor which could have given results not plausible or applicable to full scale plants.

7 CONCLUSIONS AND FUTURE PERSPECTIVES

Membrane bioreactors (MBRs) are recognized worldwide as a promising technology for wastewater treatment and reuse due to their advantages over conventional wastewater treatments. MBR systems, indeed, combining membrane filtration with biological degradation, incur a smaller footprint and reactor volume, higher and more stable effluent quality as a consequence of membrane filtration, less sludge production and lower sensitivity to contaminant peaks (Melin et al., 2006). Despite these advantages, maintaining membrane permeability and preventing membrane fouling are major problems in operation of membrane bioreactors (Judd, 2011).

The traditional methods for fouling mitigation, such as physical and chemical cleaning, increase energy demand and operating costs as well as reduce the membrane lifespan. Therefore, over the last years a significant amount of advanced strategies for reducing membrane fouling and offsetting this energy consumption has emerged.

Recent studies have proven that the integration of electrochemical and bioelectrochemical processes into membrane bioreactors represents an alternative technological approach for membrane fouling control and the enhancement of treatment efficiencies.

The integration of electrochemical processes into membrane bioreactors involves the application of a direct current field inside the membrane bioreactors or as pre-treatment to the MBR.

Bioelectrochemical systems, such as microbial fuel cell (MFC) and microbial electrolysis cell (MEC), are a new and promising approach for simultaneously treating wastewater while generating electricity or hydrogen gas due to the oxidation of organic matter by exoelectrogenic bacteria. Since further treatments are needed before discharging or reusing the effluent of a BES, the combination of membrane bioreactors with bioelectrochemical systems (BES) takes advantage of both processes in terms of wastewater treatment and energy recovery.

The experimental research activity developed in present study aimed to control fouling in membrane bioreactors and enhance the performance of the treatment. In order to reach these objectives, electrochemical processes have been integrated into a MBR (electro MBR/eMBR), applying two intermittent voltage gradients (1 V/cm and 3 V/cm) between two electrodes placed inside the bioreactor around the membrane module. Furthermore, a microbial fuel cell (MFC) was applied as a down-stream process for the treatment of the excess sludge from a MBR pilot plant.

An additional objective was the assessment of the energy production in these combined systems in terms of electricity for the MFC and of hydrogen for the electro MBR working at anoxic conditions, in order to operate as a microbial electrolysis cell (MEC).

Regarding the electro MBR, the results observed demonstrated that the integration of electrochemical processes into a membrane bioreactor leads to improve the overall performance of the treatment in terms of effluent quality and membrane filtration.

The total COD removal was almost constant during the experimental period while the values of sCOD in the reactor decreased after the application of the electric fields due to electrochemical oxidation and electrocoagulation processes. Indeed, UV_{254} removal efficiency was also improved of around 30% in the eMBR-1 and eMBR-3. The dissolution of aluminium ions at the anode side due to electrocoagulation processes allowed to remove 93.4% and 96.1% of orthophosphate, at 1 V/cm and 3 V/cm voltage gradients applied respectively, compared to only 33.0% reduction by the conventional MBR. The study has first showed that the application of DC fields allowed the alternation of anoxic and aerobic conditions in the bioreactor, due to the reduction of oxygen at the cathode side, resulting in an improvement of the NH_4^+-N removal efficiency up to 69.3% in the eMBR-3 characterized by the highest electric field applied (3V/cm). In particular, the electrochemical processes led to an almost complete removal of ammonia compounds, allowing beyond the nitrification of the influent wastewater also the denitrification of the nitrate.

Furthermore, the different electrochemical mechanisms involved in the membrane bioreactor were able to improve membrane filtration performance. Indeed, the filtration cycles were extended with a reduction of the frequency of chemical cleaning. The membrane fouling rate was reduced by 15.9% at 1 V/cm voltage gradient applied (eMBR-1) and

54.3% at 3 V/cm (eMBR-3) respect to the MBR. The reduction of membrane fouling rates corresponded to an increase of relative sludge hydrophobicity up to 71.7% in the eMBR-3 and a removal of membrane fouling precursors (bEPS, SMP, TEP), demonstrating the positive impact of electrochemical processes on these compounds and, thus, on membrane fouling formation. In particular, the average TEP normalized concentration in the mixed liquor, first investigated in the present study, decreased by 71.8% and 75.8% in the eMBR-1 and eMBR-3, respectively, compared to the conventional MBR. Therefore, the study highlights the potential applicability of TEP as a new membrane fouling indicator which is easily to determine respect to conventional parameters.

Closing the reactor and working at anoxic conditions, hydrogen production was detected in the electro MBR due to the reduction of protons and water at the cathode side with a maximum volumetric production rate of around 18 mg(H_2) $m^{-3}min^{-1}$ which corresponds to an energy production of 0.043 kJ m^{-3} s^{-1}. Hence, the study shows that the advantages of the combination of these processes are not limited to the improvement of the treatment efficiencies and membrane filtration performance but also involve the possibility of producing energy from wastewater which could be used for lessening the input of external energy in the combined system.

Regarding the combination of a MFC with a MBR reactor in an external configuration, a potentiostatic controlled microbial fuel cell (MFC), fed in batch with activated sludge from a membrane bioreactor at different influent solid content, was compared with an open circuit voltage microbial fuel cell (OCV-MFC), operated as a control test. The results observed demonstrated that, compared to the OCV-MFC, the MFC was able to degrade more effectively the organic matter present in the sludge and stabilize it through the reduction of COD and VSS content, with a maximum removal of 44% and 43%, respectively. The hydrolyses of particulate COD into soluble COD in MFC allowed the bacteria to use this in order to produce electricity, achieving a maximum current density of 2.0 A m^{-2} and voltage output of 100 mV. The current produced and the electrochemical characterization corroborated the development of an established and thick electro - active anodic biofilm. Voltammetric analyses revealed a direct electron transfer (DET) mechanism via outer membrane cytochromes with sludge oxidation at a formal potential of -0.211 ± 0.040 V vs. SHE. The MFC also showed a modification of the

sludge properties, with an increase of the capillary suction time and reduction of the sludge filterability. Furthermore, an increase of sludge hydrophobicity and a reduction of EPSp and SMPc along with SMPp/SMPc ratio increase were observed in the MFCs, which could be an effective strategy for membrane fouling mitigation if the treated sludge is recycled to the MBR reactor.

The results obtained suggest that using a MFC as a down-stream process for treating MBR excess sludge is a viable option since it could simultaneously reduce and degrade sludge, produce electricity and modify sludge properties, influencing membrane fouling parameters.

Although the results observed suggest the feasibility of the combination of electrochemical and bioelectrochemical processes with membrane bioreactors, further studies should be focused on:

- the treatment in the electro MBR of real wastewater characterized by more recalcitrant organic substances in order to see the influence of electrochemical processes on the biodegradability and, thus, the removal of these compounds;
- the maximization of the hydrogen production rate, working for example at anaerobic conditions like a microbial electrolysis cell (MEC) in order to avoid the presence of oxygen;
- the combination of the electro MBR and the MFC as a down-stream process for the treatment of the electro MBR sludge. The sludge treated could be recycled to the electro MBR in order to assess the influence on membrane fouling;
- detailed analysis in terms of costs and energy balance of the combined system at pilot scale;
- scale up of the combined system using the electricity produced in the MFC along with the hydrogen generated in the electro MBR as part of the energy input required.

REFERENCES

Aelterman, P., Rabaey, K., Pham, H.T., Boon, N., Verstraete, W., 2006. Continuous Electricity Generation at High Voltages and Currents Using Stacked Microbial Fuel Cells. Environ. Sci. Technol. 40, 3388–3394. doi:10.1021/es0525511

Ahmed, Z., Cho, J., Lim, B.-R., Song, K.-G., Ahn, K.-H., 2007. Effects of sludge retention time on membrane fouling and microbial community structure in a membrane bioreactor. J. Membr. Sci. 287, 211–218. doi:10.1016/j.memsci.2006.10.036

Akamatsu, K., Lu, W., Sugawara, T., Nakao, S., 2010. Development of a novel fouling suppression system in membrane bioreactors using an intermittent electric field. Water Res. 44, 825–830. doi:10.1016/j.watres.2009.10.026

Akamatsu, K., Yoshida, Y., Suzaki, T., Sakai, Y., Nagamoto, H., Nakao, S.I., 2012. Development of a membrane-carbon cloth assembly for submerged membrane bioreactors to apply an intermittent electric field for fouling suppression. Sep. Purif. Technol. 88, 202–207. doi:10.1016/j.seppur.2011.12.031

Alldredge, A.L., Passow, U., Logan, B.E., 1993. The abundance and significance of a class of large, transparent organic particles in the ocean. Deep Sea Res. Part Oceanogr. Res. Pap. 40, 1131–1140. doi:10.1016/0967-0637(93)90129-Q

Aouni, A., Fersi, C., Ben Sik Ali, M., Dhahbi, M., 2009. Treatment of textile wastewater by a hybrid electrocoagulation/nanofiltration process. J. Hazard. Mater. 168, 868–874. doi:10.1016/j.jhazmat.2009.02.112

APAT and CNR-IRSA, 2003. Metodi analitici per le acque. Manuali e Linee Guida 29/2003.

APHA, 2005. Standard Methods for the Examination of Water and Wastewater, 19th ed. Washington DC, USA.

Argüello, M.A., Álvarez, S., Riera, F.A., Álvarez, R., 2003. Enzymatic cleaning of inorganic ultrafiltration membranes used for whey

protein fractionation. J. Membr. Sci. 216, 121–134. doi:10.1016/S0376-7388(03)00064-4

Arruda Fatibello, S.H.., Henriques Vieira, A.A., Fatibello-Filho, O., 2004. A rapid spectrophotometric method for the determination of transparent exopolymer particles (TEP) in freshwater. Talanta 62, 81–85. doi:10.1016/S0039-9140(03)00417-X

Attour, A., Touati, M., Tlili, M., Ben Amor, M., Lapicque, F., Leclerc, J.-P., 2014. Influence of operating parameters on phosphate removal from water by electrocoagulation using aluminum electrodes. Sep. Purif. Technol. 123, 124–129. doi:10.1016/j.seppur.2013.12.030

Bacchin, P., Aimar, P., Field, R.W., 2006. Critical and sustainable fluxes: Theory, experiments and applications. J. Membr. Sci. 281, 42–69. doi:10.1016/j.memsci.2006.04.014

Bani-Melhem, K., Elektorowicz, M., 2011. Performance of the submerged membrane electro-bioreactor (SMEBR) with iron electrodes for wastewater treatment and fouling reduction. J. Membr. Sci. 379, 434–439. doi:10.1016/j.memsci.2011.06.017

Bani-Melhem, K., Elektorowicz, M., 2010. Development of a Novel Submerged Membrane Electro-Bioreactor (SMEBR): Performance for Fouling Reduction. Environ. Sci. Technol. 44, 3298–3304. doi:10.1021/es902145g

Bani-Melhem, K., Smith, E., 2012. Grey water treatment by a continuous process of an electrocoagulation unit and a submerged membrane bioreactor system. Chem. Eng. J. 198-199, 201–210. doi:10.1016/j.cej.2012.05.065

Bard, A.J., Faulkner, L.R., 2000. Electrochemical Methods: Fundamentals and Applications. Wiley.

Bar-Zeev, E., Berman-Frank, I., Girshevitz, O., Berman, T., 2012. Revised paradigm of aquatic biofilm formation facilitated by microgel transparent exopolymer particles. Proc. Natl. Acad. Sci. 109, 9119–9124. doi:10.1073/pnas.1203708109

Bar-Zeev, E., Berman-Frank, I., Liberman, B., Rahav, E., Passow, U., Berman, T., 2009a. Transparent exopolymer particles: Potential agents for organic fouling and biofilm formation in desalination and water treatment plants. Desalination Water Treat. 3, 136–142.

Bayramoglu, M., Kobya, M., Can, O.T., Sozbir, M., 2004. Operating cost analysis of electrocoagulation of textile dye wastewater. Sep. Purif. Technol. 37, 117–125. doi:10.1016/j.seppur.2003.09.002

Beier, S.P., Guerra, M., Garde, A., Jonsson, G., 2006. Dynamic microfiltration with a vibrating hollow fiber membrane module: Filtration of yeast suspensions. J. Membr. Sci. 281, 281–287. doi:10.1016/j.memsci.2006.03.051

Bentzen, T.R., Ratkovich, N., Madsen, S., Jensen, J.C., Bak, S.N., Rasmussen, M.R., 2012. Analytical and numerical modelling of Newtonian and non-Newtonian liquid in a rotational cross-flow MBR. Water Sci. Technol. J. Int. Assoc. Water Pollut. Res. 66, 2318–2327. doi:10.2166/wst.2012.443

Berman, T., 2010. Biofouling: TEP–a major challenge for water filtration. Filtr. Sep. 47, 20–22.

Berman, T., Holenberg, M., 2005. Don't fall foul of biofilm through high TEP levels. Filtr. Sep. 42, 30–32.

Bilad, M.R., Mezohegyi, G., Declerck, P., Vankelecom, I.F.J., 2012. Novel magnetically induced membrane vibration (MMV) for fouling control in membrane bioreactors. Water Res. 46, 63–72. doi:10.1016/j.watres.2011.10.026

Boero, V.J., Bowers, A.R., Eckenfelder Jr, W.W., 1996. Molecular weight distribution of soluble microbial products in biological systems. Water Sci. Technol., Water Quality International '96 Part 3: Modelling of Activated Sludge Processes; Microorganisms in Activated Sludge and Biofilm Processes; Anareobic Biological Treatment; BiofoulingSelected Proceedings of the 18th Biennial Conference of the International Association on Water Quality 34, 241–248. doi:10.1016/0273-1223(96)00651-8

Bond, D.R., Lovley, D.R., 2003. Electricity production by Geobacter sulfurreducens attached to electrodes. Appl. Environ. Microbiol. 69, 1548–1555.

Brepols, C., Drensla, K., Janot, A., Trimborn, M., Engelhardt, N., 2008. Strategies for chemical cleaning in large scale membrane bioreactors. Water Sci. Technol. J. Int. Assoc. Water Pollut. Res. 57, 457–463. doi:10.2166/wst.2008.112

Brillas, E., Garcia-Segura, S., Skoumal, M., Arias, C., 2010. Electrochemical incineration of diclofenac in neutral aqueous medium by anodic oxidation using Pt and boron-doped diamond

anodes. Chemosphere 79, 605–612. doi:10.1016/j.chemosphere.2010.03.004

Brookes, A., Jefferson, B., Guglielmi, G., Judd, S.J., 2006. Sustainable Flux Fouling in a Membrane Bioreactor: Impact of Flux and MLSS. Sep. Sci. Technol. 41, 1279–1291. doi:10.1080/01496390600634509

Brookes, A., Jefferson, B., Le-Clech, P., Judd, S., 2003. Fouling of membrane bioreactors during treatment of produced water, in: Proceedings of the International Membrane Science and Technology Conference (IMSTEC), Sydney, Australia. pp. 10–14.

Call, D.F., Merrill, M.D., Logan, B.E., 2009. High Surface Area Stainless Steel Brushes as Cathodes in Microbial Electrolysis Cells. Environ. Sci. Technol. 43, 2179–2183. doi:10.1021/es803074x

Cañizares, P., Martínez, L., Paz, R., Sáez, C., Lobato, J., Rodrigo, M.A., 2006. Treatment of Fenton-refractory olive oil mill wastes by electrochemical oxidation with boron-doped diamond anodes. J. Chem. Technol. Biotechnol. 81, 1331–1337. doi:10.1002/jctb.1428

Carmona-Martínez, A.A., Pierra, M., Trably, E., Bernet, N., 2013. High current density via direct electron transfer by the halophilic anode respiring bacterium Geoalkalibacter subterraneus. Phys. Chem. Chem. Phys. 15, 19699. doi:10.1039/c3cp54045f

Chae, S.-R., Wang, S., Hendren, Z.D., Wiesner, M.R., Watanabe, Y., Gunsch, C.K., 2009. Effects of fullerene nanoparticles on Escherichia coli K12 respiratory activity in aqueous suspension and potential use for membrane biofouling control. J. Membr. Sci. 329, 68–74. doi:10.1016/j.memsci.2008.12.023

Chang, I.-S., Kim, S.-N., 2005. Wastewater treatment using membrane filtration—effect of biosolids concentration on cake resistance. Process Biochem. 40, 1307–1314. doi:10.1016/j.procbio.2004.06.019

Chang, I.-S., Le Clech, P., Jefferson, B., Judd, S., 2002. Membrane Fouling in Membrane Bioreactors for Wastewater Treatment. J. Environ. Eng. 128, 1018–1029. doi:10.1061/(ASCE)0733-9372(2002)128:11(1018)

CHANG, I.S., LEE, C.H., AHN, K.H., 1999. Membrane Filtration Characteristics in Membrane-Coupled Activated Sludge System:

The Effect of Floc Structure on Membrane Fouling. Sep. Sci. Technol. 34, 1743–1758. doi:10.1081/SS-100100736

Chaudhuri, S.K., Lovley, D.R., 2003. Electricity generation by direct oxidation of glucose in mediatorless microbial fuel cells. Nat. Biotechnol. 21, 1229–1232. doi:10.1038/nbt867

Chen, D., Columbia, M., 2011. Enzymatic control of alginate fouling of dead-end MF and UF ceramic membranes. J. Membr. Sci. 381, 118–125. doi:10.1016/j.memsci.2011.07.033

Chen, G., 2004. Electrochemical technologies in wastewater treatment. Sep. Purif. Technol. 38, 11–41. doi:10.1016/j.seppur.2003.10.006

Chen, J.-P., Yang, C.-Z., Zhou, J.-H., Wang, X.-Y., 2007. Study of the influence of the electric field on membrane flux of a new type of membrane bioreactor. Chem. Eng. J. 128, 177–180. doi:10.1016/j.cej.2006.10.010

Chen, V., Fane, A.G., Madaeni, S., Wenten, I.G., 1997. Particle deposition during membrane filtration of colloids: transition between concentration polarization and cake formation. J. Membr. Sci. 125, 109–122. doi:10.1016/S0376-7388(96)00187-1

Cho, B.D., Fane, A.G., 2002. Fouling transients in nominally sub-critical flux operation of a membrane bioreactor. J. Membr. Sci. 209, 391–403. doi:10.1016/S0376-7388(02)00321-6

Choi, H., Zhang, K., Dionysiou, D.D., Oerther, D.B., Sorial, G.A., 2005. Effect of permeate flux and tangential flow on membrane fouling for wastewater treatment. Sep. Purif. Technol. 45, 68–78. doi:10.1016/j.seppur.2005.02.010

Cho, J., Song, K.-G., Hyup Lee, S., Ahn, K.-H., 2005. Sequencing anoxic/anaerobic membrane bioreactor (SAM) pilot plant for advanced wastewater treatment. Desalination, Membranes in Drinking and Industrial Water Production 178, 219–225. doi:10.1016/j.desal.2004.12.018

Choo, K.-H., Lee, C.-H., 1998. Hydrodynamic behavior of anaerobic biosolids during crossflow filtration in the membrane anaerobic bioreactor. Water Res. 32, 3387–3397. doi:10.1016/S0043-1354(98)00103-1

Çiçek, N., Franco, J.P., Suidan, M.T., Urbain, V., Manem, J., 1999. Characterization and Comparison of a Membrane Bioreactor and a Conventional Activated-Sludge System in the Treatment of Wastewater Containing High-Molecular-Weight Compounds. Water Environ. Res. 71, 64–70.

Costa, A.R., de Pinho, M.N., Elimelech, M., 2006. Mechanisms of colloidal natural organic matter fouling in ultrafiltration. J. Membr. Sci. 281, 716–725. doi:10.1016/j.memsci.2006.04.044

Cui, Z.F., Chang, S., Fane, A.G., 2003. The use of gas bubbling to enhance membrane processes. J. Membr. Sci. 221, 1–35. doi:10.1016/S0376-7388(03)00246-1

Daneshvar, N., Ashassi Sorkhabi, H., Kasiri, M.B., 2004. Decolorization of dye solution containing Acid Red 14 by electrocoagulation with a comparative investigation of different electrode connections. J. Hazard. Mater. 112, 55–62. doi:10.1016/j.jhazmat.2004.03.021

Das, D., Veziroğlu, T.N., 2001. Hydrogen production by biological processes: a survey of literature. Int. J. Hydrog. Energy 26, 13–28. doi:10.1016/S0360-3199(00)00058-6

DeCarolis, J.F., Adham, S., 2007. Performance Investigation of Membrane Bioreactor Systems During Municipal Wastewater Reclamation. Water Environ. Res. 79, 2536–2550. doi:10.2175/106143007X212184

Decarolis, J., Hong, S., Taylor, J., 2001. Fouling behavior of a pilot scale inside-out hollow fiber UF membrane during dead-end filtration of tertiary wastewater. J. Membr. Sci. 191, 165–178. doi:10.1016/S0376-7388(01)00455-0

Defrance, L., Jaffrin, M.Y., 1999. Reversibility of fouling formed in activated sludge filtration. J. Membr. Sci. 157, 73–84. doi:10.1016/S0376-7388(98)00356-1

de la Torre, T., Iversen, V., Stüber, J., Drews, A., Lesjean, B., Kraume, M., 2010. Searching for a universal fouling indicator for membrane bioreactors. Desalination Water Treat. 18, 264–269. doi:10.5004/dwt.2010.1783

De la Torre, T., Lesjean, B., Drews, A., Kraume, M., 2008. Monitoring of transparent exopolymer particles (TEP) in a membrane bioreactor (MBR) and correlation with other fouling indicators. Water Sci Technol 58, 1903–1909.

Deng, L., Guo, W., Ngo, H.H., Zuthi, M.F.R., Zhang, J., Liang, S., Li, J., Wang, J., Zhang, X., 2015. Membrane fouling reduction and improvement of sludge characteristics by bioflocculant addition in submerged membrane bioreactor. Sep. Purif. Technol. 156, 450–458. doi:10.1016/j.seppur.2015.10.034

Dereli, R.K., Grelot, A., Heffernan, B., van der Zee, F.P., van Lier, J.B., 2014. Implications of changes in solids retention time on long term evolution of sludge filterability in anaerobic membrane bioreactors treating high strength industrial wastewater. Water Res. 59, 11–22. doi:10.1016/j.watres.2014.03.073

Diez, V., Ramos, C., Cabezas, J.L., 2012. Treating wastewater with high oil and grease content using an Anaerobic Membrane Bioreactor (AnMBR). Filtration and cleaning assays. Water Sci. Technol. 65, 1847–1853. doi:10.2166/wst.2012.852

Drews, A., 2010. Membrane fouling in membrane bioreactors—Characterisation, contradictions, cause and cures. J. Membr. Sci. 363, 1–28. doi:10.1016/j.memsci.2010.06.046

Drews, A., Kraume, M., 2005. Process Improvement by Application of Membrane Bioreactors. Chem. Eng. Res. Des. 83, 276–284. doi:10.1205/cherd.04259

Drews, A., Lee, C.-H., Kraume, M., 2006. Membrane fouling - a review on the role of EPS. Desalination, Euromembrane 2006 Euromembrane 2006 200, 186–188. doi:10.1016/j.desal.2006.03.290

Drews, A., Vocks, M., Bracklow, U., Iversen, V., Kraume, M., 2008. Does fouling in MBRs depend on SMP? Desalination 231, 141–149. doi:10.1016/j.desal.2007.11.042

DuBois, M., Gilles, K.A., Hamilton, J.K., Rebers, P.A., Smith, F., 1956. Colorimetric Method for Determination of Sugars and Related Substances. Anal. Chem. 28, 350–356. doi:10.1021/ac60111a017

Ein-Mozaffari Farhad, M.M., 2009. An Overview of the Integration of Advanced Oxidation Technologies And Other Processes For Water And Wastewater Treatment. Int. J. Eng. 3.

Elabbas, S., Ouazzani, N., Mandi, L., Berrekhis, F., Perdicakis, M., Pontvianne, S., Pons, M., Lapicque, F., Leclerc, J., 2015. Treatment of highly concentrated tannery wastewater using electrocoagulation: Influence of the quality of aluminium used for the electrode. J. Hazard. Mater. 1–9. doi:10.1016/j.jhazmat.2015.12.067

Elektorowicz, M., Oleszkiewcz, J., Bani-Melhem, K., 2012. Wastewater treatment system and method. US8147700 B2.

Emamjomeh, M.M., Sivakumar, M., 2009. Review of pollutants removed by electrocoagulation and electrocoagulation/flotation processes.

J. Environ. Manage. 90, 1663–1679. doi:10.1016/j.jenvman.2008.12.011

Escapa, A., Mateos, R., Martínez, E.J., Blanes, J., 2016. Microbial electrolysis cells: An emerging technology for wastewater treatment and energy recovery. From laboratory to pilot plant and beyond. Renew. Sustain. Energy Rev. 55, 942–956. doi:10.1016/j.rser.2015.11.029

Esplugas, S., Contreras, S., Ollis, D.F., 2004. Engineering aspects of the integration of chemical and biological oxidation: simple mechanistic models for the oxidation treatment. J. Environ. Eng. 130, 967–974.

Evenblij, H., Geilvoet, S., van der Graaf, J.H.J.M., van der Roest, H.F., 2005. Filtration characterisation for assessing MBR performance: three cases compared. Desalination, Membranes in Drinking and Industrial Water Production 178, 115–124. doi:10.1016/j.desal.2005.02.005

Fan, F., Zhou, H., Husain, H., 2006. Identification of wastewater sludge characteristics to predict critical flux for membrane bioreactor processes. Water Res. 40, 205–212. doi:10.1016/j.watres.2005.10.037

Fan, X., Urbain, V., Qian, Y., Manem, J., 1996. Nitrification and mass balance with a membrane bioreactor for municipal wastewater treatment. Water Sci. Technol. U. K.

Feng, L., 2013. Advanced Oxidation Processes for the Removal of Residual Non-Steroidal Anti- Inflammatory Pharmaceuticals From 233.

Feng, Y., Wang, X., Logan, B.E., Lee, H., 2008. Brewery wastewater treatment using air-cathode microbial fuel cells. Appl. Microbiol. Biotechnol. 78, 873–880. doi:10.1007/s00253-008-1360-2

Ferri, V., Ferro, S., Martínez-Huitle, C.A., De Battisti, A., 2009. Electrokinetic extraction of surfactants and heavy metals from sewage sludge. Electrochimica Acta 54, 2108–2118. doi:10.1016/j.electacta.2008.08.048

Field, R.W., Wu, D., Howell, J.A., Gupta, B.B., 1995. Critical flux concept for microfiltration fouling. J. Membr. Sci. 100, 259–272. doi:10.1016/0376-7388(94)00265-Z

Flemming, H.C., Wingender, J., 2001. Relevance of microbial extracellular polymeric substances (EPSs)--Part I: Structural and

ecological aspects. Water Sci. Technol. J. Int. Assoc. Water Pollut. Res. 43, 1–8.

Fouad, Y.O., 2014. Separation of cottonseed oil from oil–water emulsions using electrocoagulation technique. Alex. Eng. J. 53, 199–204. doi:10.1016/j.aej.2013.10.005

Fourmond, V., Hoke, K., Heering, H.A., Baffert, C., Leroux, F., Bertrand, P., Léger, C., 2009. SOAS: A free program to analyze electrochemical data and other one-dimensional signals. Bioelectrochemistry 76, 141–147. doi:10.1016/j.bioelechem.2009.02.010

Fricke, K., Harnisch, F., Schröder, U., 2008. On the use of cyclic voltammetry for the study of anodic electron transfer in microbial fuel cells. Energy Environ. Sci. 1, 144. doi:10.1039/b802363h

Frølund, B., Griebe, T., Nielsen, P.H., 1995. Enzymatic activity in the activated-sludge floc matrix. Appl. Microbiol. Biotechnol. 43, 755–761.

Frølund, B., Palmgren, R., Keiding, K., Nielsen, P.H., 1996. Extraction of extracellular polymers from activated sludge using a cation exchange resin. Water Res. 30, 1749–1758. doi:10.1016/0043-1354(95)00323-1

Gabarrón, S., Gómez, M., Monclús, H., Rodríguez-Roda, I., Comas, J., 2013. Ragging phenomenon characterisation and impact in a full-scale MBR. Water Sci. Technol. J. Int. Assoc. Water Pollut. Res. 67, 810–816. doi:10.2166/wst.2012.633

Gajaraj, S., Hu, Z., 2014. Integration of microbial fuel cell techniques into activated sludge wastewater treatment processes to improve nitrogen removal and reduce sludge production. Chemosphere 117, 151–157. doi:10.1016/j.chemosphere.2014.06.013

Gander, M., Jefferson, B., Judd, S., 2000. Aerobic MBRs for domestic wastewater treatment: a review with cost considerations. Sep. Purif. Technol. 18, 119–130.

Ganzenko, O., Huguenot, D., van Hullebusch, E.D., Esposito, G., Oturan, M.A., 2014. Electrochemical advanced oxidation and biological processes for wastewater treatment: a review of the combined approaches. Environ. Sci. Pollut. Res. 21, 8493–8524. doi:10.1007/s11356-014-2770-6

Gao, J., Luo, Q.S., Zhu, J., Zhang, C.B., Li, B.Z., 2013. Effects of electrokinetic treatment of contaminated sludge on migration

and transformation of Cd, Ni and Zn in various bonding states. Chemosphere 93, 2869–2876. doi:10.1016/j.chemosphere.2013.08.079

Gatsios, E., Hahladakis, J.N., Gidarakos, E., 2015. Optimization of electrocoagulation (EC) process for the purification of a real industrial wastewater from toxic metals. J. Environ. Manage. 154, 117–127. doi:10.1016/j.jenvman.2015.02.018

Geng, Z., Hall, E.R., 2007. A comparative study of fouling-related properties of sludge from conventional and membrane enhanced biological phosphorus removal processes. Water Res. 41, 4329–4338. doi:10.1016/j.watres.2007.07.007

Germain, E., Stephenson, T., 2005. Biomass Characteristics, Aeration and Oxygen Transfer in Membrane Bioreactors: Their Interrelations Explained by a Review of Aerobic Biological Processes. Rev. Environ. Sci. Biotechnol. 4, 223–233. doi:10.1007/s11157-005-2097-3

Ge, Z., Ping, Q., He, Z., 2013. Hollow-fiber membrane bioelectrochemical reactor for domestic wastewater treatment: Hollow-fiber Membrane Bioelectrochemical Reactors. J. Chem. Technol. Biotechnol. 88, 1584–1590. doi:10.1002/jctb.4009

Ghanbari, F., Moradi, M., 2015. A comparative study of electrocoagulation, electrochemical Fenton, electro-Fenton and peroxi-coagulation for decolorization of real textile wastewater: Electrical energy consumption and biodegradability improvement. J. Environ. Chem. Eng. 3, 499–506. doi:10.1016/j.jece.2014.12.018

Giwa, A., Ahmed, I., Hasan, S.W., 2015. Enhanced sludge properties and distribution study of sludge components in electrically-enhanced membrane bioreactor. J. Environ. Manage. 159, 78–85. doi:10.1016/j.jenvman.2015.05.035

Giwa, A., Hasan, S.W., 2015. Theoretical investigation of the influence of operating conditions on the treatment performance of an electrically-induced membrane bioreactor. J. Water Process Eng. 6, 72–82. doi:10.1016/j.jwpe.2015.03.004

Glendinning, S., Lamont-Black, J., Jones, C.J.F.P., 2007. Treatment of sewage sludge using electrokinetic geosynthetics. J. Hazard. Mater. 139, 491–499. doi:10.1016/j.jhazmat.2006.02.046

Gómez, X., Fernández, C., Fierro, J., Sánchez, M.E., Escapa, A., Morán, A., 2011. Hydrogen production: Two stage processes for waste

degradation. Bioresour. Technol., Special Issue : Biofuels-III: Biohydrogen 102, 8621–8627. doi:10.1016/j.biortech.2011.03.055

Grelier, P., Rosenberger, S., Tazi-Pain, A., 2006. Influence of sludge retention time on membrane bioreactor hydraulic performance. Desalination, International Congress on Membranes and Membrane ProcessesInternational Congress on Membranes and Membrane Processes 192, 10–17. doi:10.1016/j.desal.2005.04.131

Günder, B., Krauth, K., 1998. Replacement of secondary clarification by membrane separation — Results with plate and hollow fibre modules. Water Sci. Technol., Water Quality International '98Selected Proceedings of the 19th Biennial Conference of the International Association on Water Quality 38, 383–393. doi:10.1016/S0273-1223(98)00537-X

Hasan, S.W., Elektorowicz, M., Oleszkiewicz, J.A., 2014. Start-up period investigation of pilot-scale submerged membrane electro-bioreactor (SMEBR) treating raw municipal wastewater. Chemosphere 97, 71–77. doi:10.1016/j.chemosphere.2013.11.009

Hasan, S.W., Elektorowicz, M., Oleszkiewicz, J.A., 2012. Correlations between trans-membrane pressure (TMP) and sludge properties in submerged membrane electro-bioreactor (SMEBR) and conventional membrane bioreactor (MBR). Bioresour. Technol. 120, 199–205. doi:10.1016/j.biortech.2012.06.043

Heidrich, E.S., Dolfing, J., Scott, K., Edwards, S.R., Jones, C., Curtis, T.P., 2012. Production of hydrogen from domestic wastewater in a pilot-scale microbial electrolysis cell. Appl. Microbiol. Biotechnol. 97, 6979–6989. doi:10.1007/s00253-012-4456-7

Heilmann, J., Logan, B.E., 2006. Production of electricity from proteins using a microbial fuel cell. Water Environ. Res. Res. Publ. Water Environ. Fed. 78, 531–537.

He, Y., Xu, P., Li, C., Zhang, B., 2005. High-concentration food wastewater treatment by an anaerobic membrane bioreactor. Water Res. 39, 4110–4118. doi:10.1016/j.watres.2005.07.030

Holbrook, R.D., Higgins, M.J., Murthy, S.N., Fonseca, A.D., Fleischer, E.J., Daigger, G.T., Grizzard, T.J., Love, N.G., Novak, J.T., 2004. Effect of alum addition on the performance of submerged

membranes for wastewater treatment. Water Environ. Res. Res. Publ. Water Environ. Fed. 76, 2699–2702.

Hong, H., Peng, W., Zhang, M., Chen, J., He, Y., Wang, F., Weng, X., Yu, H., Lin, H., 2013. Thermodynamic analysis of membrane fouling in a submerged membrane bioreactor and its implications. Bioresour. Technol. 146, 7–14. doi:10.1016/j.biortech.2013.07.040

Hong, S.P., Bae, T.H., Tak, T.M., Hong, S., Randall, A., 2002. Fouling control in activated sludge submerged hollow fiber membrane bioreactors. Desalination 143, 219–228. doi:10.1016/S0011-9164(02)00260-6

Hosseinzadeh, M., Bidhendi, G.N., Torabian, A., Mehrdadi, N., Pourabdullah, M., 2015. A new flat sheet membrane bioreactor hybrid system for advanced treatment of effluent, reverse osmosis pretreatment and fouling mitigation. Bioresour. Technol. 192, 177–184. doi:10.1016/j.biortech.2015.05.066

Hua, L.-C., Huang, C., Su, Y.-C., Nguyen, T.-N.-P., Chen, P.-C., 2015. Effects of electro-coagulation on fouling mitigation and sludge characteristics in a coagulation-assisted membrane bioreactor. J. Membr. Sci. 495, 29–36. doi:10.1016/j.memsci.2015.07.062

Huang, L., Logan, B.E., 2008. Electricity generation and treatment of paper recycling wastewater using a microbial fuel cell. Appl. Microbiol. Biotechnol. 80, 349–355. doi:10.1007/s00253-008-1546-7

Huang, X., Wei, C.-H., Yu, K.-C., 2008. Mechanism of membrane fouling control by suspended carriers in a submerged membrane bioreactor. J. Membr. Sci. 309, 7–16. doi:10.1016/j.memsci.2007.09.069

Huang, Y.-X., Liu, X.-W., Sun, X.-F., Sheng, G.-P., Zhang, Y.-Y., Yan, G.-M., Wang, S.-G., Xu, A.-W., Yu, H.-Q., 2011. A new cathodic electrode deposit with palladium nanoparticles for cost-effective hydrogen production in a microbial electrolysis cell. Int. J. Hydrog. Energy 36, 2773–2776. doi:10.1016/j.ijhydene.2010.11.114

Hu, H., Fan, Y., Liu, H., 2008. Hydrogen production using single-chamber membrane-free microbial electrolysis cells. Water Res. 42, 4172–4178. doi:10.1016/j.watres.2008.06.015

Hwang, K.-J., Chan, C.-S., Tung, K.-L., 2009. Effect of backwash on the performance of submerged membrane filtration. J. Membr. Sci. 330, 349–356. doi:10.1016/j.memsci.2009.01.012

Ibeid, S., Elektorowicz, M., Oleszkiewcz, J., 2015. Processes and apparatuses for removal of carbon, phosphorus and nitrogen. US20150001094 A1.

Ibeid, S., Elektorowicz, M., Oleszkiewicz, J.A., 2013. Modification of activated sludge properties caused by application of continuous and intermittent current. Water Res. 47, 903–910. doi:10.1016/j.watres.2012.11.020

Itokawa, H., Thiemig, C., Pinnekamp, J., 2008. Design and operating experiences of municipal MBRs in Europe. Water Sci. Technol. 58, 2319–2327. doi:10.2166/wst.2008.581

Itonaga, T., Kimura, K., Watanabe, Y., 2004. Influence of suspension viscosity and colloidal particles on permeability of membrane used in membrane bioreactor (MBR). Water Sci. Technol. J. Int. Assoc. Water Pollut. Res. 50, 301–309.

Ivanovic, I., Leiknes, T., 2008. Impact of aeration rates on particle colloidal fraction in the biofilm membrane bioreactor (BF-MBR). Desalination, Selected Papers Presented at the 4th International IWA Conference on Membranes for Water and Wastewater Treatment, 15-17 May 2007, Harrogate, UK. Guest Edited by Simon Judd; and Papers Presented at the International Workshop on Membranes and Solid-Liquid Separation Processes, 11 July 2007, INSA, Toulouse, France. Guest edited by Saravanamuthu Vigneswaran and Jaya Kandasamy 231, 182–190. doi:10.1016/j.desal.2007.11.046

Jamal Khan, S., Visvanathan, C., Jegatheesan, V., 2012. Effect of powdered activated carbon (PAC) and cationic polymer on biofouling mitigation in hybrid MBRs. Bioresour. Technol., Special issue on the Challenges in Environmental Science and Engineering 113, 165–168. doi:10.1016/j.biortech.2011.12.107

Jang, N., Ren, X., Choi, K., Kim, I.S., 2006. Comparison of membrane biofouling in nitrification and denitrification for the membrane bioreactor (MBR). Water Sci. Technol. J. Int. Assoc. Water Pollut. Res. 53, 43–49.

Jefferson, B., Brookes, A., Le Clech, P., Judd, S.J., 2004. Methods for understanding organic fouling in MBRs. Water Sci. Technol. J. Int. Assoc. Water Pollut. Res. 49, 237–244.

Jeison, D., van, L., 2007. Cake formation and consolidation: Main factors governing the applicable flux in anaerobic submerged membrane bioreactors (AnSMBR) treating acidified wastewaters. Sep. Purif. Technol. 56, 71–78. doi:10.1016/j.seppur.2007.01.022

Jeremiasse, A.W., Hamelers, H.V.M., Buisman, C.J.N., 2010. Microbial electrolysis cell with a microbial biocathode. Bioelectrochemistry, From fundamentals to microbial power plants: Electrochemically Active Biofilms 78, 39–43. doi:10.1016/j.bioelechem.2009.05.005

Jiang, J., Zhao, Q., Wei, L., Wang, K., Lee, D.-J., 2011. Degradation and characteristic changes of organic matter in sewage sludge using microbial fuel cell with ultrasound pretreatment. Bioresour. Technol. 102, 272–277. doi:10.1016/j.biortech.2010.04.066

Jiang, T., Kennedy, M.D., Guinzbourg, B.F., Vanrolleghem, P.A., Schippers, J.C., 2005. Optimising the operation of a MBR pilot plant by quantitative analysis of the membrane fouling mechanism. Water Sci. Technol. J. Int. Assoc. Water Pollut. Res. 51, 19–25.

Ji, J., Qiu, J., Wai, N., Wong, F.-S., Li, Y., 2010. Influence of organic and inorganic flocculants on physical–chemical properties of biomass and membrane-fouling rate. Water Res. 44, 1627–1635. doi:10.1016/j.watres.2009.11.013

Ji, L., Zhou, J., 2006. Influence of aeration on microbial polymers and membrane fouling in submerged membrane bioreactors. J. Membr. Sci. 276, 168–177. doi:10.1016/j.memsci.2005.09.045

Jinsong, Z., Chuan, C.H., Jiti, Z., Fane, A.G., 2006. Effect of Sludge Retention Time on Membrane Bio-Fouling Intensity in a Submerged Membrane Bioreactor. Sep. Sci. Technol. 41, 1313–1329. doi:10.1080/01496390600683647

Jorand, F., Zartarian, F., Thomas, F., Block, J.C., Bottero, J.Y., Villemin, G., Urbain, V., Manem, J., 1995. Chemical and structural (2D) linkage between bacteria within activated sludge flocs. Water Res. 29, 1639–1647. doi:10.1016/0043-1354(94)00350-G

Juang, R.-S., Lin, K.-H., 2004. Flux recovery in the ultrafiltration of suspended solutions with ultrasound. J. Membr. Sci. 243, 115–124. doi:10.1016/j.memsci.2004.06.013

Judd, S., 2011. The MBR Book: Principles and Applications of Membrane Bioreactors for Water and Wastewater Treatment. Elsevier.

Kang, I.-J., Lee, C.-H., Kim, K.-J., 2003. Characteristics of microfiltration membranes in a membrane coupled sequencing batch reactor system. Water Res. 37, 1192–1197. doi:10.1016/S0043-1354(02)00534-1

Kang, S., Hoek, E.M.V., Choi, H., Shin, H., 2006. Effect of Membrane Surface Properties During the Fast Evaluation of Cell Attachment. Sep. Sci. Technol. 41, 1475–1487. doi:10.1080/01496390600634673

Keerthi, Vinduja, V., Balasubramanian, N., 2013. Electrocoagulation-integrated hybrid membrane processes for the treatment of tannery wastewater. Environ. Sci. Pollut. Res. 20, 7441–7449. doi:10.1007/s11356-013-1766-y

Khandegar, V., Saroha, A.K., 2013. Electrocoagulation for the treatment of textile industry effluent – A review. J. Environ. Manage. 128, 949–963. doi:10.1016/j.jenvman.2013.06.043

Khor, S.L., Sun, D.D., Liu, Y., Leckie, J.O., 2007. Biofouling development and rejection enhancement in long SRT MF membrane bioreactor. Process Biochem. 42, 1641–1648. doi:10.1016/j.procbio.2007.09.009

Kim, H.-G., Jang, H.-N., Kim, H.-M., Lee, D.-S., Chung, T.-H., 2010. Effect of an electro phosphorous removal process on phosphorous removal and membrane permeability in a pilot-scale MBR. Desalination 250, 629–633. doi:10.1016/j.desal.2009.09.038

Kim, H.J., Park, H.S., Hyun, M.S., Chang, I.S., Kim, M., Kim, B.H., 2002. A mediator-less microbial fuel cell using a metal reducing bacterium, Shewanella putrefaciens. Enzyme Microb. Technol. 30, 145–152.

Kim, H.Y., Yeon, K.-M., Lee, C.-H., Lee, S., Swaminathan, T., 2006. Biofilm Structure and Extracellular Polymeric Substances in Low and High Dissolved Oxygen Membrane Bioreactors. Sep. Sci. Technol. 41, 1213–1230. doi:10.1080/01496390600632354

Kim, I.S., Jang, N., 2006. The effect of calcium on the membrane biofouling in the membrane bioreactor (MBR). Water Res. 40, 2756–2764. doi:10.1016/j.watres.2006.03.036

Kim, J., DiGiano, F.A., 2006. A two-fiber, bench-scale test of ultrafiltration (UF) for investigation of fouling rate and characteristics. J. Membr. Sci. 271, 196–204. doi:10.1016/j.memsci.2005.07.027

Kim, J., Kim, K., Ye, H., Lee, E., Shin, C., McCarty, P.L., Bae, J., 2011. Anaerobic fluidized bed membrane bioreactor for wastewater treatment. Environ. Sci. Technol. 45, 576–581. doi:10.1021/es1027103

Kim, J.R., Cheng, S., Oh, S.-E., Logan, B.E., 2007. Power Generation Using Different Cation, Anion, and Ultrafiltration Membranes in Microbial Fuel Cells. Environ. Sci. Technol. 41, 1004–1009. doi:10.1021/es062202m

Kim, K.-Y., Chae, K.-J., Choi, M.-J., Yang, E.-T., Hwang, M.H., Kim, I.S., 2013. High-quality effluent and electricity production from non-CEM based flow-through type microbial fuel cell. Chem. Eng. J. 218, 19–23. doi:10.1016/j.cej.2012.12.018

Kim, S.O., Moon, S.H., Kim, K.W., Yun, S.T., 2002. Pilot scale study on the ex situ electrokinetic removal of heavy metals from municipal wastewater sludges. Water Res. 36, 4765–4774. doi:10.1016/S0043-1354(02)00141-0

Kimura, K., Watanabe, Y., Ohkuma, N., 2000. Filtration resistance and efficient cleaning methods of the membrane with fixed nitrifiers. Water Res. 34, 2895–2904. doi:10.1016/S0043-1354(00)00040-3

Kobya, M., Demirbas, E., 2015. Evaluations of operating parameters on treatment of can manufacturing wastewater by electrocoagulation. J. Water Process Eng. 8, 64–74. doi:10.1016/j.jwpe.2015.09.006

Kobya, M., Gebologlu, U., Ulu, F., Oncel, S., Demirbas, E., 2011. Removal of arsenic from drinking water by the electrocoagulation using Fe and Al electrodes. Electrochimica Acta 56, 5060–5070. doi:10.1016/j.electacta.2011.03.086

Kraume, M., Wedi, D., Schaller, J., Iversen, V., Drews, A., 2009. Fouling in MBR: What use are lab investigations for full scale operation? Desalination 236, 94–103. doi:10.1016/j.desal.2007.10.055

Kubota, 2004. Instruction Manual for Submerged Membrane Unit (Type LF). English version prepared on 13 December 2004 (KE-04-004-01). K. Corporation, Tokyo, Japan.

Kuokkanen, V., Kuokkanen, T., R??m??, J., Lassi, U., Roininen, J., 2015. Removal of phosphate from wastewaters for further utilization using electrocoagulation with hybrid electrodes - Techno-economic studies. J. Water Process Eng. 8, e50–e57. doi:10.1016/j.jwpe.2014.11.008

Kurt, M., Dunn, I.J., Bourne, J.R., 1987. Biological denitrification of drinking water using autotrophic organisms with H(2) in a fluidized-bed biofilm reactor. Biotechnol. Bioeng. 29, 493–501. doi:10.1002/bit.260290414

Laspidou, C.S., Rittmann, B.E., 2002. A unified theory for extracellular polymeric substances, soluble microbial products, and active and inert biomass. Water Res. 36, 2711–2720. doi:10.1016/S0043-1354(01)00413-4

Le-Clech, P., Chen, V., Fane, T.A.G., 2006. Fouling in membrane bioreactors used in wastewater treatment. J. Membr. Sci. 284, 17–53. doi:10.1016/j.memsci.2006.08.019

Le Clech, P., Jefferson, B., Chang, I.S., Judd, S.J., 2003. Critical flux determination by the flux-step method in a submerged membrane bioreactor. J. Membr. Sci. 227, 81–93. doi:10.1016/j.memsci.2003.07.021

Le-Clech, P., Jefferson, B., Judd, S.J., 2005. A comparison of submerged and sidestream tubular membrane bioreactor configurations. Desalination 173, 113–122. doi:10.1016/j.desal.2004.08.029

Le-Clech, P., Jefferson, B., Judd, S.J., 2003. Impact of aeration, solids concentration and membrane characteristics on the hydraulic performance of a membrane bioreactor. J. Membr. Sci. 218, 117–129. doi:10.1016/S0376-7388(03)00164-9

Lee, J.W., Lee, K.H., Park, K.Y., Maeng, S.K., 2010. Hydrogenotrophic denitrification in a packed bed reactor: Effects of hydrogen-to-water flow rate ratio. Bioresour. Technol. 101, 3940–3946. doi:10.1016/j.biortech.2010.01.022

Lee, K.R., Yeom, I.T., 2007. Evaluation of a membrane bioreactor system coupled with sludge pretreatment for aerobic sludge digestion. Environ. Technol. 28, 723–730. doi:10.1080/09593332808618837

Lee, W., Kang, S., Shin, H., 2003. Sludge characteristics and their contribution to microfiltration in submerged membrane bioreactors. J. Membr. Sci. 216, 217–227. doi:10.1016/S0376-7388(03)00073-5

Lesjean, B., Huisjes, E.H., 2008. Survey of the European MBR market: trends and perspectives. Desalination, Selected Papers Presented at the 4th International IWA Conference on Membranes for Water and Wastewater Treatment, 15-17 May 2007, Harrogate, UK. Guest Edited by Simon Judd; and Papers Presented at the

International Workshop on Membranes and Solid-Liquid Separation Processes, 11 July 2007, INSA, Toulouse, France. Guest edited by Saravanamuthu Vigneswaran and Jaya Kandasamy 231, 71–81. doi:10.1016/j.desal.2007.10.022

Lesjean, B., Rosenberger, S., Laabs, C., Jekel, M., Gnirss, R., Amy, G., 2005. Correlation between membrane fouling and soluble/colloidal organic substances in membrane bioreactors for municipal wastewater treatment. Water Sci. Technol. J. Int. Assoc. Water Pollut. Res. 51, 1–8.

Leyva-Díaz, J.C., Martín-Pascual, J., Muñío, M.M., González-López, J., Hontoria, E., Poyatos, J.M., 2014. Comparative kinetics of hybrid and pure moving bed reactor-membrane bioreactors. Ecol. Eng. 70, 227–234. doi:10.1016/j.ecoleng.2014.05.017

Liao, B.Q., Allen, D.G., Droppo, I.G., Leppard, G.G., Liss, S.N., 2001. Surface properties of sludge and their role in bioflocculation and settleability. Water Res. 35, 339–350.

Li, J., He, Z., 2015. Optimizing the performance of a membrane bio-electrochemical reactor using an anion exchange membrane for wastewater treatment. Env. Sci Water Res Technol 1, 355–362. doi:10.1039/C5EW00001G

Li, J., Zhang, X., Cheng, F., Liu, Y., 2013. New insights into membrane fouling in submerged MBR under sub-critical flux condition. Bioresour. Technol. 137, 404–408. doi:10.1016/j.biortech.2013.03.158

Lim, A.L., Bai, R., 2003. Membrane fouling and cleaning in microfiltration of activated sludge wastewater. J. Membr. Sci. 216, 279–290. doi:10.1016/S0376-7388(03)00083-8

Lin, H., Peng, W., Zhang, M., Chen, J., Hong, H., Zhang, Y., 2013. A review on anaerobic membrane bioreactors: Applications, membrane fouling and future perspectives. Desalination 314, 169–188. doi:10.1016/j.desal.2013.01.019

Lin, H., Wang, F., Ding, L., Hong, H., Chen, J., Lu, X., 2011. Enhanced performance of a submerged membrane bioreactor with powdered activated carbon addition for municipal secondary effluent treatment. J. Hazard. Mater. 192, 1509–1514. doi:10.1016/j.jhazmat.2011.06.071

Lin, H., Zhang, M., Wang, F., Meng, F., Liao, B.-Q., Hong, H., Chen, J., Gao, W., 2014. A critical review of extracellular polymeric substances (EPSs) in membrane bioreactors: Characteristics,

roles in membrane fouling and control strategies. J. Membr. Sci. 460, 110–125. doi:10.1016/j.memsci.2014.02.034

Liu, H., Cheng, S., Logan, B.E., 2005. Production of Electricity from Acetate or Butyrate Using a Single-Chamber Microbial Fuel Cell. Environ. Sci. Technol. 39, 658–662. doi:10.1021/es048927c

Liu, H., Logan, B.E., 2004. Electricity Generation Using an Air-Cathode Single Chamber Microbial Fuel Cell in the Presence and Absence of a Proton Exchange Membrane. Environ. Sci. Technol. 38, 4040–4046. doi:10.1021/es0499344

Liu, J., Liu, L., Gao, B., Yang, F., 2013. Integration of bio-electrochemical cell in membrane bioreactor for membrane cathode fouling reduction through electricity generation. J. Membr. Sci. 430, 196–202. doi:10.1016/j.memsci.2012.11.046

Liu, J., Liu, L., Gao, B., Yang, F., Crittenden, J., Ren, N., 2014. Integration of microbial fuel cell with independent membrane cathode bioreactor for power generation, membrane fouling mitigation and wastewater treatment. Int. J. Hydrog. Energy 39, 17865–17872. doi:10.1016/j.ijhydene.2014.08.123

Liu, L., Liu, J., Gao, B., Yang, F., 2012a. Minute electric field reduced membrane fouling and improved performance of membrane bioreactor. Sep. Purif. Technol. 86, 106–112. doi:10.1016/j.seppur.2011.10.030

Liu, L., Liu, J., Gao, B., Yang, F., Chellam, S., 2012b. Fouling reductions in a membrane bioreactor using an intermittent electric field and cathodic membrane modified by vapor phase polymerized pyrrole. J. Membr. Sci. 394-395, 202–208. doi:10.1016/j.memsci.2011.12.042

Liu, R., Huang, X., Wang, C., Chen, L., Qian, Y., 2000. Study on hydraulic characteristics in a submerged membrane bioreactor process. Process Biochem. 36, 249–254. doi:10.1016/S0032-9592(00)00210-7

Li, X., Gao, F., Hua, Z., Du, G., Chen, J., 2005. Treatment of synthetic wastewater by a novel MBR with granular sludge developed for controlling membrane fouling. Sep. Purif. Technol. 46, 19–25. doi:10.1016/j.seppur.2005.04.003

Li, Y., Liu, L., Liu, J., Yang, F., Ren, N., 2014. PPy/AQS (9, 10-anthraquinone-2-sulfonic acid) and PPy/ARS (Alizarin Red's) modified stainless steel mesh as cathode membrane in an

integrated MBR/MFC system. Desalination 349, 94–101. doi:10.1016/j.desal.2014.06.027

Logan, B.E., 2008. Microbial Fuel Cells. John Wiley & Sons.

Logan, B.E., 2004. Extracting hydrogen and electricity from renewable resources. Environ. Sci. Technol. 38, 160A–167A.

Logan, B.E., Hamelers, B., Rozendal, R., Schröder, U., Keller, J., Freguia, S., Aelterman, P., Verstraete, W., Rabaey, K., 2006. Microbial Fuel Cells: Methodology and Technology †. Environ. Sci. Technol. 40, 5181–5192. doi:10.1021/es0605016

Logan, B.E., Murano, C., Scott, K., Gray, N.D., Head, I.M., 2005. Electricity generation from cysteine in a microbial fuel cell. Water Res. 39, 942–952. doi:10.1016/j.watres.2004.11.019

Lu, N., Zhou, S., Zhuang, L., Zhang, J., Ni, J., 2009. Electricity generation from starch processing wastewater using microbial fuel cell technology. Biochem. Eng. J. 43, 246–251. doi:10.1016/j.bej.2008.10.005

Lyko, S., Wintgens, T., Al-Halbouni, D., Baumgarten, S., Tacke, D., Drensla, K., Janot, A., Dott, W., Pinnekamp, J., Melin, T., 2008. Long-term monitoring of a full-scale municipal membrane bioreactor—Characterisation of foulants and operational performance. J. Membr. Sci., A special Issue on Membrane Reactors & Bioreactors 317, 78–87. doi:10.1016/j.memsci.2007.07.008

Maartens, A., Swart, P., Jacobs, E.P., 1996. An enzymatic approach to the cleaning of ultrafiltration membranes fouled in abattoir effluent. J. Membr. Sci. 119, 9–16. doi:10.1016/0376-7388(96)00015-4

Mahmoud, A., Olivier, J., Vaxelaire, J., Hoadley, A.F.A., 2011. Electro-dewatering of wastewater sludge: Influence of the operating conditions and their interactions effects. Water Res. 45, 2795–2810. doi:10.1016/j.watres.2011.02.029

Mahmoud, A., Olivier, J., Vaxelaire, J., Hoadley, A.F.A., 2010. Electrical field: A historical review of its application and contributions in wastewater sludge dewatering. Water Res. 44, 2381–2407. doi:10.1016/j.watres.2010.01.033

Ma, J., Wang, Z., He, D., Li, Y., Wu, Z., 2015. Long-term investigation of a novel electrochemical membrane bioreactor for low-strength municipal wastewater treatment. Water Res. 78, 98–110. doi:10.1016/j.watres.2015.03.033

Ma, J., Wang, Z., Yang, Y., Mei, X., Wu, Z., 2013. Correlating microbial community structure and composition with aeration intensity in submerged membrane bioreactors by 454 high-throughput pyrosequencing. Water Res. 47, 859–869. doi:10.1016/j.watres.2012.11.013

Malaeb, L., Katuri, K.P., Logan, B.E., Maab, H., Nunes, S.P., Saikaly, P.E., 2013a. A Hybrid Microbial Fuel Cell Membrane Bioreactor with a Conductive Ultrafiltration Membrane Biocathode for Wastewater Treatment. Environ. Sci. Technol. 47, 11821–11828. doi:10.1021/es4030113

Malaeb, L., Le-Clech, P., Vrouwenvelder, J.S., Ayoub, G.M., Saikaly, P.E., 2013b. Do biological-based strategies hold promise to biofouling control in MBRs? Water Res. 47, 5447–5463. doi:10.1016/j.watres.2013.06.033

Manuel, M.-F., Neburchilov, V., Wang, H., Guiot, S.R., Tartakovsky, B., 2010. Hydrogen production in a microbial electrolysis cell with nickel-based gas diffusion cathodes. J. Power Sources 195, 5514–5519. doi:10.1016/j.jpowsour.2010.03.061

Martínez-Huitle, C.A., Brillas, E., 2009. Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: A general review. Appl. Catal. B Environ. 87, 105–145. doi:10.1016/j.apcatb.2008.09.017

Martínez-Huitle, C.A., Ferro, S., 2006. Electrochemical oxidation of organic pollutants for the wastewater treatment: direct and indirect processes. Chem. Soc. Rev. 35, 1324–1340. doi:10.1039/B517632H

Martinez-Sosa, D., Helmreich, B., Netter, T., Paris, S., Bischof, F., Horn, H., 2011. Pilot-scale anaerobic submerged membrane bioreactor (AnSMBR) treating municipal wastewater: the fouling phenomenon and long-term operation. Water Sci. Technol. 64, 1804–1811. doi:10.2166/wst.2011.745

Massé, A., Spérandio, M., Cabassud, C., 2006. Comparison of sludge characteristics and performance of a submerged membrane bioreactor and an activated sludge process at high solids retention time. Water Res. 40, 2405–2415. doi:10.1016/j.watres.2006.04.015

Melin, T., Jefferson, B., Bixio, D., Thoeye, C., De Wilde, W., De Koning, J., van der Graaf, J., Wintgens, T., 2006. Membrane bioreactor

technology for wastewater treatment and reuse. Desalination 187, 271–282. doi:10.1016/j.desal.2005.04.086

Meng, F., Chae, S.-R., Drews, A., Kraume, M., Shin, H.-S., Yang, F., 2009. Recent advances in membrane bioreactors (MBRs): Membrane fouling and membrane material. Water Res. 43, 1489–1512. doi:10.1016/j.watres.2008.12.044

Meng, F., Shi, B., Yang, F., Zhang, H., 2007. Effect of hydraulic retention time on membrane fouling and biomass characteristics in submerged membrane bioreactors. Bioprocess Biosyst. Eng. 30, 359–367. doi:10.1007/s00449-007-0132-1

Meng, F., Yang, F., 2007. Fouling mechanisms of deflocculated sludge, normal sludge, and bulking sludge in membrane bioreactor. J. Membr. Sci. 305, 48–56. doi:10.1016/j.memsci.2007.07.038

Meng, S., Rzechowicz, M., Winters, H., Fane, A.G., Liu, Y., 2013. Transparent exopolymer particles (TEP) and their potential effect on membrane biofouling. Appl. Microbiol. Biotechnol. 97, 5705–5710. doi:10.1007/s00253-013-4979-6

Merzouk, B., Gourich, B., Sekki, A., Madani, K., Vial, C., Barkaoui, M., 2009. Studies on the decolorization of textile dye wastewater by continuous electrocoagulation process. Chem. Eng. J. 149, 207–214. doi:10.1016/j.cej.2008.10.018

Meyer, E.E., Rosenberg, K.J., Israelachvili, J., 2006. Recent progress in understanding hydrophobic interactions. Proc. Natl. Acad. Sci. 103, 15739–15746. doi:10.1073/pnas.0606422103

Min, B., Cheng, S., Logan, B.E., 2005. Electricity generation using membrane and salt bridge microbial fuel cells. Water Res. 39, 1675–1686. doi:10.1016/j.watres.2005.02.002

Mishima, I., Nakajima, J., 2009. Control of membrane fouling in membrane bioreactor process by coagulant addition. Water Sci. Technol. 59, 1255–1262. doi:10.2166/wst.2009.090

Miyoshi, T., Tsuyuhara, T., Ogyu, R., Kimura, K., Watanabe, Y., 2009. Seasonal variation in membrane fouling in membrane bioreactors (MBRs) treating municipal wastewater. Water Res. 43, 5109–5118. doi:10.1016/j.watres.2009.08.035

Mollah, M.Y.A., Morkovsky, P., Gomes, J.A.G., Kesmez, M., Parga, J., Cocke, D.L., 2004. Fundamentals, present and future perspectives of electrocoagulation. J. Hazard. Mater. 114, 199–210. doi:10.1016/j.jhazmat.2004.08.009

Mollah, M.Y.A., Schennach, R., Parga, J.R., Cocke, D.L., 2001. Electrocoagulation (EC) — science and applications. J. Hazard. Mater. 84, 29–41. doi:10.1016/S0304-3894(01)00176-5

Morgan, J.W., Forster, C.F., Evison, L., 1990. A comparative study of the nature of biopolymers extracted from anaerobic and activated sludges. Water Res. 24, 743–750. doi:10.1016/0043-1354(90)90030-A

Mouli, P.C., Mohan, S.V., Reddy, S.J., 2004. Electrochemical processes for the remediation of wastewater and contaminated soil: Emerging technology. J. Sci. Ind. Res. 63, 11–19.

Muñoz-Aguado, M.J., Wiley, D.E., Fane, A.G., 1996. Enzymatic and detergent cleaning of a polysulfone ultrafiltration membrane fouled with BSA and whey. J. Membr. Sci. 117, 175–187. doi:10.1016/0376-7388(96)00066-X

Munoz, L.D., Erable, B., Etcheverry, L., Riess, J., Basséguy, R., Bergel, A., 2010. Combining phosphate species and stainless steel cathode to enhance hydrogen evolution in microbial electrolysis cell (MEC). Electrochem. Commun. 12, 183–186. doi:10.1016/j.elecom.2009.11.017

Muthukumaran, S., Yang, K., Seuren, A., Kentish, S., Ashokkumar, M., Stevens, G.W., Grieser, F., 2004. The use of ultrasonic cleaning for ultrafiltration membranes in the dairy industry. Sep. Purif. Technol., Selected Papers from the 9th APPChE Conference, September 2002 , Christchurch, New Zealand 39, 99–107. doi:10.1016/j.seppur.2003.12.013

Naddeo, V., Belgiorno, V., Borea, L., Secondes, M.F.N., Ballesteros, F., 2015a. Control of fouling formation in membrane ultrafiltration by ultrasound irradiation. Environ. Technol. 36, 1299–1307. doi:10.1080/09593330.2014.985731

Naddeo, V., Borea, L., Belgiorno, V., 2015b. Sonochemical control of fouling formation in membrane ultrafiltration of wastewater: Effect of ultrasonic frequency. J. Water Process Eng. 8, e92–e97. doi:10.1016/j.jwpe.2014.12.005

Nagaoka, H., Kurosaka, M., Shibata, N., Kobayashi, M., 2006. Effect of bubble flow velocity on drag-force and shear stress working on submerged hollow fibre membrane. Water Sci. Technol. 54, 185–192. doi:10.2166/wst.2006.818

Neoh, C.H., Noor, Z.Z., Mutamim, N.S.A., Lim, C.K., 2016. Green technology in wastewater treatment technologies: Integration of

membrane bioreactor with various wastewater treatment systems. Chem. Eng. J. 283, 582–594. doi:10.1016/j.cej.2015.07.060

Ng, H.Y., Tan, T.W., Ong, S.L., 2006. Membrane fouling of submerged membrane bioreactors: impact of mean cell residence time and the contributing factors. Environ. Sci. Technol. 40, 2706–2713.

Odendaal, P.E., Wiesner, M.R., Ph D., Mallevialle, J., 1996. Water Treatment Membrane Processes: American Water Works Association Research Foundation : Lyonnaise Des Eaus : Water Research Commission of South Africa. Mcgraw-Hill, New York.

Oh, S., Logan, B.E., 2005. Hydrogen and electricity production from a food processing wastewater using fermentation and microbial fuel cell technologies. Water Res. 39, 4673–4682. doi:10.1016/j.watres.2005.09.019

Oller, I., Malato, S., Sánchez-Pérez, J.A., 2011. Combination of Advanced Oxidation Processes and biological treatments for wastewater decontamination—A review. Sci. Total Environ. 409, 4141–4166. doi:10.1016/j.scitotenv.2010.08.061

Oturan, N., Brillas, E., Oturan, M.A., 2011. Unprecedented total mineralization of atrazine and cyanuric acid by anodic oxidation and electro-Fenton with a boron-doped diamond anode. Environ. Chem. Lett. 10, 165–170. doi:10.1007/s10311-011-0337-z

Park, J.-S., Yeon, K.-M., Lee, C.-H., 2005. Hydrodynamics and microbial physiology affecting performance of a new MBR, membrane-coupled high-performance compact reactor. Desalination 172, 181–188. doi:10.1016/j.desal.2004.07.035

Passow, U., 2002. Transparent exopolymer particles (TEP) in aquatic environments. Prog. Oceanogr. 55, 287–333. doi:10.1016/S0079-6611(02)00138-6

Perez, L.S., Rodriguez, O.M., Reyna, S., L., S.-S.J., A., Q.M., R., B.E., 2015. Oil refinery wastewater treatment using coupled electrocoagulation and fixed films biological processes. Phys Chem Earth (Submitted. doi:http://dx.doi.org/10.1016/j.pce.2015.10.018

Petrus, H.B., Li, H., Chen, V., Norazman, N., 2008. Enzymatic cleaning of ultrafiltration membranes fouled by protein mixture solutions. J. Membr. Sci. 325, 783–792. doi:10.1016/j.memsci.2008.09.004

Pham, T.H., Rabaey, K., Aelterman, P., Clauwaert, P., De Schamphelaire, L., Boon, N., Verstraete, W., 2006. Microbial Fuel Cells in

Relation to Conventional Anaerobic Digestion Technology. Eng. Life Sci. 6, 285–292. doi:10.1002/elsc.200620121

Pous, N., Carmona-Martínez, A.A., Vilajeliu-Pons, A., Fiset, E., Bañeras, L., Trably, E., Balaguer, M.D., Colprim, J., Bernet, N., Puig, S., 2016. Bidirectional microbial electron transfer: Switching an acetate oxidizing biofilm to nitrate reducing conditions. Biosens. Bioelectron. 75, 352–358. doi:10.1016/j.bios.2015.08.035

Poxon, T.L., Darby, J.L., 1997. Extracellular polyanions in digested sludge: Measurement and relationship to sludge dewaterability. Water Res. 31, 749–758. doi:10.1016/S0043-1354(96)00319-3

Prieske, H., Böhm, L., Drews, A., Kraume, M., 2010. Optimised hydrodynamics for membrane bioreactors with immersed flat sheet membrane modules. Desalination Water Treat. 18, 270–276. doi:10.5004/dwt.2010.1784

Prip Beier, S., Jonsson, G., 2009. A vibrating membrane bioreactor (VMBR): Macromolecular transmission—influence of extracellular polymeric substances. Chem. Eng. Sci. 64, 1436–1444. doi:10.1016/j.ces.2008.12.008

Puig, S., Serra, M., Vilar-Sanz, A., Cabré, M., Bañeras, L., Colprim, J., Balaguer, M.D., 2011. Autotrophic nitrite removal in the cathode of microbial fuel cells. Bioresour. Technol. 102, 4462–4467. doi:10.1016/j.biortech.2010.12.100

Qin, J.-J., Kekre, K.A., Oo, M.H., Tao, G., Lay, C.L., Lew, C.H., Cornelissen, E.R., Ruiken, C.J., 2010. Preliminary study of osmotic membrane bioreactor: effects of draw solution on water flux and air scouring on fouling. Water Sci. Technol. 62, 1353–1360. doi:10.2166/wst.2010.426

Quan, X., Cheng, Z., Chen, B., Zhu, X., 2013. Electrochemical oxidation of recalcitrant organic compounds in biologically treated municipal solid waste leachate in a flow reactor. J. Environ. Sci. 25, 2023–2030. doi:10.1016/S1001-0742(12)60253-8

Rabaey, K., Boon, N., Höfte, M., Verstraete, W., 2005a. Microbial Phenazine Production Enhances Electron Transfer in Biofuel Cells. Environ. Sci. Technol. 39, 3401–3408. doi:10.1021/es048563o

Rabaey, K., Boon, N., Siciliano, S.D., Verhaege, M., Verstraete, W., 2004. Biofuel Cells Select for Microbial Consortia That Self-Mediate Electron Transfer. Appl. Environ. Microbiol. 70, 5373–5382. doi:10.1128/AEM.70.9.5373-5382.2004

Rabaey, K., Clauwaert, P., Aelterman, P., Verstraete, W., 2005b. Tubular Microbial Fuel Cells for Efficient Electricity Generation. Environ. Sci. Technol. 39, 8077–8082. doi:10.1021/es050986i

Rabaey, K., Lissens, G., Siciliano, S.D., Verstraete, W., 2003. A microbial fuel cell capable of converting glucose to electricity at high rate and efficiency. Biotechnol. Lett. 25, 1531–1535.

Radjenović, J., Matošić, M., Mijatović, I., Petrović, M., Barceló, D., 2008. Membrane Bioreactor (MBR) as an Advanced Wastewater Treatment Technology, in: Barceló, D., Petrovic, M. (Eds.), Emerging Contaminants from Industrial and Municipal Waste. Springer Berlin Heidelberg, Berlin, Heidelberg, pp. 37–101.

Raffin, M., Germain, E., Judd, S.J., 2012. Influence of backwashing, flux and temperature on microfiltration for wastewater reuse. Sep. Purif. Technol. 96, 147–153. doi:10.1016/j.seppur.2012.05.030

Ramesh, A., Lee, D.J., Lai, J.Y., 2006a. Membrane biofouling by extracellular polymeric substances or soluble microbial products from membrane bioreactor sludge. Appl. Microbiol. Biotechnol. 74, 699–707. doi:10.1007/s00253-006-0706-x

Ramesh, A., Lee, D.J., Wang, M.L., Hsu, J.P., Juang, R.S., Hwang, K.J., Liu, J.C., Tseng, S.J., 2006b. Biofouling in Membrane Bioreactor. Sep. Sci. Technol. 41, 1345–1370. doi:10.1080/01496390600633782

Ratkovich, N., Chan, C.C.V., Berube, P.R., Nopens, I., 2009. Experimental study and CFD modelling of a two-phase slug flow for an airlift tubular membrane. Chem. Eng. Sci. 64, 3576–3584. doi:10.1016/j.ces.2009.04.048

Resosudarmo, A., Ye, Y., Le-Clech, P., Chen, V., 2013. Analysis of UF membrane fouling mechanisms caused by organic interactions in seawater. Water Res. 47, 911–921. doi:10.1016/j.watres.2012.11.024

Rodrigo, M.A., Cañizares, P., Lobato, J., Paz, R., Sáez, C., Linares, J.J., 2007. Production of electricity from the treatment of urban waste water using a microbial fuel cell. J. Power Sources, CONAPPICE 2006Selected Papers Presented at the 2nd National Congress on Fuel Cells (CONAPPICE 2006), Madrid, Spain, 18-20 October 2006. 169, 198–204. doi:10.1016/j.jpowsour.2007.01.054

Rosales, E., Pazos, M., Sanromán, M.A., 2012. Advances in the Electro-Fenton Process for Remediation of Recalcitrant Organic

Compounds. Chem. Eng. Technol. 35, 609–617. doi:10.1002/ceat.201100321

Rosenberger, S., Evenblij, H., Tepoele, S., Wintgens, T., Laabs, C., 2005. The importance of liquid phase analyses to understand fouling in membrane assisted activated sludge processes—six case studies of different European research groups. J. Membr. Sci. 263, 113–126. doi:10.1016/j.memsci.2005.04.010

Rosenberger, S., Helmus, F.P., Krause, S., Bareth, A., Meyer-Blumenroth, U., 2011. Principles of an enhanced MBR-process with mechanical cleaning. Water Sci. Technol. J. Int. Assoc. Water Pollut. Res. 64, 1951–1958. doi:10.2166/wst.2011.765

Rosenberger, S., Kraume, M., 2003. Filterability of activated sludge in membrane bioreactors. Desalination 151, 195–200. doi:10.1016/S0011-9164(02)00998-0

Rosenberger, S., Laabs, C., Lesjean, B., Gnirss, R., Amy, G., Jekel, M., Schrotter, J.-C., 2006. Impact of colloidal and soluble organic material on membrane performance in membrane bioreactors for municipal wastewater treatment. Water Res. 40, 710–720. doi:10.1016/j.watres.2005.11.028

Rosenberg, M., Gutnick, D., Rosenberg, E., 1980. Adherence of bacteria to hydrocarbons: A simple method for measuring cell-surface hydrophobicity. FEMS Microbiol. Lett. 9, 29–33. doi:10.1111/j.1574-6968.1980.tb05599.x

Rozendal, R.A., Hamelers, H.V.M., Molenkamp, R.J., Buisman, C.J.N., 2007. Performance of single chamber biocatalyzed electrolysis with different types of ion exchange membranes. Water Res. 41, 1984–1994. doi:10.1016/j.watres.2007.01.019

Rozendal, R.A., Jeremiasse, A.W., Hamelers, H.V.M., Buisman, C.J.N., 2008. Hydrogen Production with a Microbial Biocathode. Environ. Sci. Technol. 42, 629–634. doi:10.1021/es071720+

Sadeddin, K., Naser, A., Firas, A., 2011. Removal of turbidity and suspended solids by electro-coagulation to improve feed water quality of reverse osmosis plant. Desalination 268, 204–207. doi:10.1016/j.desal.2010.10.027

Santos, A., Judd, S., 2010. The Commercial Status of Membrane Bioreactors for Municipal Wastewater. Sep. Sci. Technol. 45, 850–857. doi:10.1080/01496391003662337

Satyawali, Y., Balakrishnan, M., 2009. Effect of PAC addition on sludge properties in an MBR treating high strength wastewater. Water Res. 43, 1577–1588. doi:10.1016/j.watres.2009.01.003

Scholz, M., 2005. Review of Recent Trends in Capillary Suction Time (CST) Dewaterability Testing Research. Ind. Eng. Chem. Res. 44, 8157–8163. doi:10.1021/ie058011u

Scholz, W.H., 1993. Processes for industrial production of hydrogen and associated environmental effects. Gas Sep. Purif. 7, 131–139. doi:10.1016/0950-4214(93)80001-D

Selembo, P.A., Merrill, M.D., Logan, B.E., 2009. The use of stainless steel and nickel alloys as low-cost cathodes in microbial electrolysis cells. J. Power Sources 190, 271–278. doi:10.1016/j.jpowsour.2008.12.144

Sharma, M., Bajracharya, S., Gildemyn, S., Patil, S.A., Alvarez-Gallego, Y., Pant, D., Rabaey, K., Dominguez-Benetton, X., 2014. A critical revisit of the key parameters used to describe microbial electrochemical systems. Electrochimica Acta 140, 191–208. doi:10.1016/j.electacta.2014.02.111

Sheng, G.-P., Yu, H.-Q., Li, X.-Y., 2010. Extracellular polymeric substances (EPS) of microbial aggregates in biological wastewater treatment systems: A review. Biotechnol. Adv. 28, 882–894. doi:10.1016/j.biotechadv.2010.08.001

Shen, L., Lei, Q., Chen, J.-R., Hong, H.-C., He, Y.-M., Lin, H.-J., 2015. Membrane fouling in a submerged membrane bioreactor: Impacts of floc size. Chem. Eng. J. 269, 328–334. doi:10.1016/j.cej.2015.02.002

Smith, P.J., Vigneswaran, S., Ngo, H.H., Ben-Aim, R., Nguyen, H., 2006. A new approach to backwash initiation in membrane systems. J. Membr. Sci. 278, 381–389. doi:10.1016/j.memsci.2005.11.024

Smith, P.J., Vigneswaran, S., Ngo, H.H., Ben-Aim, R., Nguyen, H., 2005. Design of a generic control system for optimising back flush durations in a submerged membrane hybrid reactor. J. Membr. Sci. 255, 99–106. doi:10.1016/j.memsci.2005.01.026

Sofia, A., Ng, W.J., Ong, S.L., 2004. Engineering design approaches for minimum fouling in submerged MBR. Desalination 160, 67–74. doi:10.1016/S0011-9164(04)90018-5

Song, K.-G., Kim, Y., Ahn, K.-H., 2008. Effect of coagulant addition on membrane fouling and nutrient removal in a submerged membrane bioreactor. Desalination, European Desalination

Society and Center for Research and Technology Hellas (CERTH), Sani Resort 22 –25 April 2007, Halkidiki, GreeceEuropean Desalination Society and Center for Research and Technology Hellas (CERTH), Sani Resort 221, 467–474. doi:10.1016/j.desal.2007.01.107

Sopaj, F., 2013. Study of the influence of electrode material in the application of electrochemical advanced oxidation processes to removal of pharmaceutical pollutants from water.

Spettmann, D., Eppmann, S., Flemming, H.C., Wingender, J., 2007. Simultaneous visualisation of biofouling, organic and inorganic particle fouling on separation membranes. Water Sci. Technol. J. Int. Assoc. Water Pollut. Res. 55, 207–210.

Stephenson, T., Brindle, K., Judd, S., Jefferson, B., 2000. Membrane Bioreactors for Wastewater Treatment. Intl Water Assn, London, UK.

Sui, P., Wen, X., Huang, X., 2008. Feasibility of employing ultrasound for on-line membrane fouling control in an anaerobic membrane bioreactor. Desalination 219, 203–213. doi:10.1016/j.desal.2007.02.034

Su, X., Tian, Y., Li, H., Wang, C., 2013a. New insights into membrane fouling based on characterization of cake sludge and bulk sludge: An especial attention to sludge aggregation. Bioresour. Technol. 128, 586–592. doi:10.1016/j.biortech.2012.11.005

Su, X., Tian, Y., Sun, Z., Lu, Y., Li, Z., 2013b. Performance of a combined system of microbial fuel cell and membrane bioreactor: Wastewater treatment, sludge reduction, energy recovery and membrane fouling. Biosens. Bioelectron. 49, 92–98. doi:10.1016/j.bios.2013.04.005

Tafti, A.D., Seyyed Mirzaii, S.M., Andalibi, M.R., Vossoughi, M., 2015. Optimized coupling of an intermittent DC electric field with a membrane bioreactor for enhanced effluent quality and hindered membrane fouling. Sep. Purif. Technol. 152, 7–13. doi:10.1016/j.seppur.2015.07.004

Tang, S., Wang, Z., Wu, Z., Zhou, Q., 2010. Role of dissolved organic matters (DOM) in membrane fouling of membrane bioreactors for municipal wastewater treatment. J. Hazard. Mater. 178, 377–384. doi:10.1016/j.jhazmat.2010.01.090

Tardieu, E., Grasmick, A., Geaugey, V., Manem, J., 1999. Influence of hydrodynamics on fouling velocity in a recirculated MBR for

wastewater treatment. J. Membr. Sci. 156, 131–140. doi:10.1016/S0376-7388(98)00343-3

Tarnacki, K., Lyko, S., Wintgens, T., Melin, T., Natau, F., 2005. Impact of extra-cellular polymeric substances on the filterability of activated sludge in membrane bioreactors for landfill leachate treatment. Desalination, Membranes in Drinking and Industrial Water Production 179, 181–190. doi:10.1016/j.desal.2004.11.066

Tenca, A., Cusick, R.D., Schievano, A., Oberti, R., Logan, B.E., 2013. Evaluation of low cost cathode materials for treatment of industrial and food processing wastewater using microbial electrolysis cells. Int. J. Hydrog. Energy 38, 1859–1865. doi:10.1016/j.ijhydene.2012.11.103

Tian, Y., Li, H., Li, L., Su, X., Lu, Y., Zuo, W., Zhang, J., 2015. In-situ integration of microbial fuel cell with hollow-fiber membrane bioreactor for wastewater treatment and membrane fouling mitigation. Biosens. Bioelectron. 64, 189–195. doi:10.1016/j.bios.2014.08.070

Trussell, R.S., Merlo, R.P., Hermanowicz, S.W., Jenkins, D., 2006. The effect of organic loading on process performance and membrane fouling in a submerged membrane bioreactor treating municipal wastewater. Water Res. 40, 2675–2683. doi:10.1016/j.watres.2006.04.020

Tsioptsias, C., Petridis, D., Athanasakis, N., Lemonidis, I., Deligiannis, A., Samaras, P., 2015. Post-treatment of molasses wastewater by electrocoagulation and process optimization through response surface analysis. J. Environ. Manage. 164, 104–13. doi:10.1016/j.jenvman.2015.09.007

Urtiaga, A., Rueda, A., Anglada, Á., Ortiz, I., 2009. Integrated treatment of landfill leachates including electrooxidation at pilot plant scale. J. Hazard. Mater. 166, 1530–1534. doi:10.1016/j.jhazmat.2008.11.037

Van den Broeck, R., Krzeminski, P., Van Dierdonck, J., Gins, G., Lousada-Ferreira, M., Van Impe, J.F.M., van der Graaf, J.H.J.M., Smets, I.Y., van Lier, J.B., 2011. Activated sludge characteristics affecting sludge filterability in municipal and industrial MBRs: Unraveling correlations using multi-component regression analysis. J. Membr. Sci. 378, 330–338. doi:10.1016/j.memsci.2011.05.010

Van Nevel, S., Hennebel, T., De Beuf, K., Du Laing, G., Verstraete, W., Boon, N., 2012. Transparent exopolymer particle removal in different drinking water production centers. Water Res. 46, 3603–3611. doi:10.1016/j.watres.2012.04.002

Villacorte, L.O., Kennedy, M.D., Amy, G.L., Schippers, J.C., 2009. The fate of Transparent Exopolymer Particles (TEP) in integrated membrane systems: Removal through pre-treatment processes and deposition on reverse osmosis membranes. Water Res. 43, 5039–5052. doi:10.1016/j.watres.2009.08.030

Visvanathan, C., Yang, B.-S., Muttamara, S., Maythanukhraw, R., 1997. Application of air backflushing technique in membrane bioreactor. Water Sci. Technol., Water Quality Conservation in AsiaSelected Proceedings of Asian Waterqual '97, the 6th IAWQ Asia-Pacific Regional Conference 36, 259–266. doi:10.1016/S0273-1223(97)00727-0

Wang, A., Qu, J., Liu, H., Ge, J., 2004. Degradation of azo dye Acid Red 14 in aqueous solution by electrokinetic and electrooxidation process. Chemosphere 55, 1189–1196. doi:10.1016/j.chemosphere.2004.01.024

Wang, J.Y., Zhang, D.S., Stabnikova, O., Tay, J.H., 2005. Evaluation of electrokinetic removal of heavy metals from sewage sludge. J. Hazard. Mater. 124, 139–146. doi:10.1016/j.jhazmat.2005.04.036

Wang, Q., Wang, Z., Zhu, C., Mei, X., Wu, Z., 2013. Assessment of SMP fouling by foulant–membrane interaction energy analysis. J. Membr. Sci. 446, 154–163. doi:10.1016/j.memsci.2013.06.011

Wang, Y.-P., Liu, X.-W., Li, W.-W., Li, F., Wang, Y.-K., Sheng, G.-P., Zeng, R.J., Yu, H.-Q., 2012. A microbial fuel cell–membrane bioreactor integrated system for cost-effective wastewater treatment. Appl. Energy 98, 230–235. doi:10.1016/j.apenergy.2012.03.029

Wang, Z., Ma, J., Tang, C.Y., Kimura, K., Wang, Q., Han, X., 2014. Membrane cleaning in membrane bioreactors: A review. J. Membr. Sci. 468, 276–307. doi:10.1016/j.memsci.2014.05.060

Wang, Z., Ma, J., Xu, Y., Yu, H., Wu, Z., 2013. Power production from different types of sewage sludge using microbial fuel cells: A comparative study with energetic and microbiological perspectives. J. Power Sources 235, 280–288. doi:10.1016/j.jpowsour.2013.02.033

Wang, Z., Mei, X., Wu, Z., Ye, S., Yang, D., 2012. Effects of biopolymer discharge from MBR mixture on sludge characteristics and membrane fouling. Chem. Eng. J. 193-194, 77–87. doi:10.1016/j.cej.2012.04.019

Wang, Z., Wu, Z., 2009. A Review of Membrane Fouling in MBRs: Characteristics and Role of Sludge Cake Formed on Membrane Surfaces. Sep. Sci. Technol. 44, 3571–3596. doi:10.1080/01496390903182578

Wang, Z., Wu, Z., Tang, S., 2009. Extracellular polymeric substances (EPS) properties and their effects on membrane fouling in a submerged membrane bioreactor. Water Res. 43, 2504–2512. doi:10.1016/j.watres.2009.02.026

Wang, Z., Wu, Z., Yin, X., Tian, L., 2008. Membrane fouling in a submerged membrane bioreactor (MBR) under sub-critical flux operation: Membrane foulant and gel layer characterization. J. Membr. Sci. 325, 238–244. doi:10.1016/j.memsci.2008.07.035

Wen, C., Huang, X., Qian, Y., 1999. Domestic wastewater treatment using an anaerobic bioreactor coupled with membrane filtration. Process Biochem. 35, 335–340. doi:10.1016/S0032-9592(99)00076-X

Weng, C.H., Lin, Y.T., Yuan, C., Lin, Y.H., 2013. Dewatering of bio-sludge from industrial wastewater plant using an electrokinetic-assisted process: Effects of electrical gradient. Sep. Purif. Technol. 117, 35–40. doi:10.1016/j.seppur.2013.06.013

Wicaksana, F., Fane, A.G., Chen, V., 2006. Fibre movement induced by bubbling using submerged hollow fibre membranes. J. Membr. Sci. 271, 186–195. doi:10.1016/j.memsci.2005.07.024

Wilén, B.M., Jin, B., Lant, P., 2003. Relationship between flocculation of activated sludge and composition of extracellular polymeric substances. Water Sci. Technol. J. Int. Assoc. Water Pollut. Res. 47, 95–103.

Wingender, J., Neu, T.R., Flemming, H.-C. (Eds.), 1999. Microbial Extracellular Polymeric Substances. Springer Berlin Heidelberg, Berlin, Heidelberg.

Wisniewski, C., Grasmick, A., 1998. Floc size distribution in a membrane bioreactor and consequences for membrane fouling. Colloids Surf. Physicochem. Eng. Asp. 138, 403–411. doi:10.1016/S0927-7757(96)03898-8

Wu, B., Kitade, T., Chong, T.H., Uemura, T., Fane, A.G., 2012. Role of initially formed cake layers on limiting membrane fouling in membrane bioreactors. Bioresour. Technol. 118, 589–593. doi:10.1016/j.biortech.2012.05.016

Wu, G., Cui, L., Xu, Y., 2008. A novel submerged rotating membrane bioreactor and reversible membrane fouling control. Desalination 228, 255–262. doi:10.1016/j.desal.2007.10.014

Wu, J., Chen, F., Huang, X., Geng, W., Wen, X., 2006. Using inorganic coagulants to control membrane fouling in a submerged membrane bioreactor. Desalination 197, 124–136. doi:10.1016/j.desal.2005.11.026

Wu, J., Le-Clech, P., Stuetz, R.M., Fane, A.G., Chen, V., 2008. Effects of relaxation and backwashing conditions on fouling in membrane bioreactor. J. Membr. Sci. 324, 26–32. doi:10.1016/j.memsci.2008.06.057

Xia, L., Law, A.W.-K., Fane, A.G., 2013. Hydrodynamic effects of air sparging on hollow fiber membranes in a bubble column reactor. Water Res. 47, 3762–3772. doi:10.1016/j.watres.2013.04.042

Xiao, B., Yang, F., Liu, J., 2011. Enhancing simultaneous electricity production and reduction of sewage sludge in two-chamber MFC by aerobic sludge digestion and sludge pretreatments. J. Hazard. Mater. 189, 444–449. doi:10.1016/j.jhazmat.2011.02.058

Xiao, L., Wen, Z., Ci, S., Chen, J., He, Z., 2012. Carbon/iron-based nanorod catalysts for hydrogen production in microbial electrolysis cells. Nano Energy 1, 751–756. doi:10.1016/j.nanoen.2012.06.002

Yamamoto, K., Hiasa, M., Mahmood, T., Matsuo, T., 1988. DIRECT SOLID-LIQUID SEPARATION USING HOLLOW FIBER MEMBRANE IN AN ACTIVATED SLUDGE AERATION TANK, in: LIJKLEMA, L., IMHOFF, K.R., IVES, K.J., JENKINS, D., LUDWIG, R.G., SUZUKI, M., TOERIEN, D.F., WHEATLAND, A.B., MILBURN, A., IZOD, E.J. (Eds.), Water Pollution Research and Control Brighton. Pergamon, pp. 43–54.

Yamanoi, I., Kageyama, K., 2010. Evaluation of bubble flow properties between flat sheet membranes in membrane bioreactor. J. Membr. Sci. 360, 102–108. doi:10.1016/j.memsci.2010.05.006

Yamato, N., Kimura, K., Miyoshi, T., Watanabe, Y., 2006. Difference in membrane fouling in membrane bioreactors (MBRs) caused by

membrane polymer materials. J. Membr. Sci. 280, 911–919. doi:10.1016/j.memsci.2006.03.009

Yang, J. (Jeanne), Frost, R.L., Yuan, Y., 2009. Synthesis and characterization of chromium doped boehmite nanofibres. Thermochim. Acta 483, 29–35. doi:10.1016/j.tca.2008.10.024

Yang, P.Y., Cao, K., Kim, S.J., 2002. Entrapped Mixed Microbial Cell Process for Combined Secondary and Tertiary Wastewater Treatment. Water Environ. Res. 74, 226–234.

Yang, Q., Chen, J., Zhang, F., 2006. Membrane fouling control in a submerged membrane bioreactor with porous, flexible suspended carriers. Desalination, Selected paper from the 10th Aachen Membrane Colloquium10th Aachen Membrane Colloquium 189, 292–302. doi:10.1016/j.desal.2005.07.011

Yao, M., Ladewig, B., Zhang, K., 2011. Identification of the change of soluble microbial products on membrane fouling in membrane bioreactor (MBR). Desalination 278, 126–131. doi:10.1016/j.desal.2011.05.012

Yeo, A., Fane, A.G., 2005. Performance of individual fibers in a submerged hollow fiber bundle. Water Sci. Technol. J. Int. Assoc. Water Pollut. Res. 51, 165–172.

Yeon, K.-M., Cheong, W.-S., Oh, H.-S., Lee, W.-N., Hwang, B.-K., Lee, C.-H., Beyenal, H., Lewandowski, Z., 2009. Quorum Sensing: A New Biofouling Control Paradigm in a Membrane Bioreactor for Advanced Wastewater Treatment. Environ. Sci. Technol. 43, 380–385. doi:10.1021/es8019275

Yigit, N.O., Harman, I., Civelekoglu, G., Koseoglu, H., Cicek, N., Kitis, M., 2008. Membrane fouling in a pilot-scale submerged membrane bioreactor operated under various conditions. Desalination, Selected Papers Presented at the 4th International IWA Conference on Membranes for Water and Wastewater Treatment, 15-17 May 2007, Harrogate, UK. Guest Edited by Simon Judd; and Papers Presented at the International Workshop on Membranes and Solid-Liquid Separation Processes, 11 July 2007, INSA, Toulouse, France. Guest edited by Saravanamuthu Vigneswaran and Jaya Kandasamy 231, 124–132. doi:10.1016/j.desal.2007.11.041

Yi, X.S., Zhao, Z.W., Shi, W.X., Duan, Y.S., Sun, N., Ma, C., Xie, Y.Z., 2013. Organic pollutants variation and antifouling enhancement with attapulgite clay addition in MBR treating micro-polluted

surface water. Chem. Eng. J. 223, 891–898. doi:10.1016/j.cej.2013.02.110

You, H.S., Huang, C.P., Pan, J.R., Chang, S.C., 2006. Behavior of Membrane Scaling During Crossflow Filtration in the Anaerobic MBR System. Sep. Sci. Technol. 41, 1265–1278. doi:10.1080/01496390600632487

You, H.S., Tseng, C.C., Peng, M.J., Chang, S.H., Chen, Y.C., Peng, S.H., 2005. A novel application of an anaerobic membrane process in wastewater treatment. Water Sci. Technol. J. Int. Assoc. Water Pollut. Res. 51, 45–50.

Yuan, C., Weng, C.H., 2003. Sludge dewatering by electrokinetic technique: Effect of processing time and potential gradient. Adv. Environ. Res. 7, 727–732. doi:10.1016/S1093-0191(02)00030-8

Yuan, H., He, Z., 2015. Integrating membrane filtration into bioelectrochemical systems as next generation energy-efficient wastewater treatment technologies for water reclamation: A review. Bioresour. Technol. 195, 202–209. doi:10.1016/j.biortech.2015.05.058

Yu, C.-H., Fang, L.-C., Lateef, S.K., Wu, C.-H., Lin, C.-F., 2010. Enzymatic treatment for controlling irreversible membrane fouling in cross-flow humic acid-fed ultrafiltration. J. Hazard. Mater. 177, 1153–1158. doi:10.1016/j.jhazmat.2010.01.022

Yu, H., Wang, Z., Wang, Q., Wu, Z., Ma, J., 2013. Disintegration and acidification of MBR sludge under alkaline conditions. Chem. Eng. J. 231, 206–213. doi:10.1016/j.cej.2013.07.012

Yu, H.-Y., Hu, M.-X., Xu, Z.-K., Wang, J.-L., Wang, S.-Y., 2005. Surface modification of polypropylene microporous membranes to improve their antifouling property in MBR: NH3 plasma treatment. Sep. Purif. Technol. 45, 8–15. doi:10.1016/j.seppur.2005.01.012

Yuniarto, A., Noor, Z.Z., Ujang, Z., Olsson, G., Aris, A., Hadibarata, T., 2013. Bio-fouling reducers for improving the performance of an aerobic submerged membrane bioreactor treating palm oil mill effluent. Desalination 316, 146–153. doi:10.1016/j.desal.2013.02.002

Zhang, J., Chua, H.C., Zhou, J., Fane, A.G., 2006. Factors affecting the membrane performance in submerged membrane bioreactors. J. Membr. Sci. 284, 54–66. doi:10.1016/j.memsci.2006.06.022

Zhang, J., Loong, W.L.C., Chou, S., Tang, C., Wang, R., Fane, A.G., 2012. Membrane biofouling and scaling in forward osmosis membrane bioreactor. J. Membr. Sci. 403–404, 8–14. doi:10.1016/j.memsci.2012.01.032

Zhang, J., Satti, A., Chen, X., Xiao, K., Sun, J., Yan, X., Liang, P., Zhang, X., Huang, X., 2015. Low-voltage electric field applied into MBR for fouling suppression: Performance and mechanisms. Chem. Eng. J. 273, 223–230. doi:10.1016/j.cej.2015.03.044

Zhang, X., Bishop, P.L., 2003. Biodegradability of biofilm extracellular polymeric substances. Chemosphere 50, 63–69. doi:10.1016/S0045-6535(02)00319-3

Zhang, Y., Merrill, M.D., Logan, B.E., 2010. The use and optimization of stainless steel mesh cathodes in microbial electrolysis cells. Int. J. Hydrog. Energy, VIII symposium of the Mexican Hydrogen Society 35, 12020–12028. doi:10.1016/j.ijhydene.2010.08.064

Zhao, F., Harnisch, F., Schröder, U., Scholz, F., Bogdanoff, P., Herrmann, I., 2005. Application of pyrolysed iron(II) phthalocyanine and CoTMPP based oxygen reduction catalysts as cathode materials in microbial fuel cells. Electrochem. Commun. 7, 1405–1410. doi:10.1016/j.elecom.2005.09.032

Zhong, Z., Xing, W., Liu, X., Jin, W., Xu, N., 2007. Fouling and regeneration of ceramic membranes used in recovering titanium silicalite-1 catalysts. J. Membr. Sci. 301, 67–75. doi:10.1016/j.memsci.2007.05.036

Zhou, G., Zhou, Y., Zhou, G., Lu, L., Wan, X., Shi, H., 2015. Assessment of a novel overflow-type electrochemical membrane bioreactor (EMBR) for wastewater treatment, energy recovery and membrane fouling mitigation. Bioresour. Technol. 196, 648–655. doi:10.1016/j.biortech.2015.08.032

Zsirai, T., Buzatu, P., Aerts, P., Judd, S., 2012. Efficacy of relaxation, backflushing, chemical cleaning and clogging removal for an immersed hollow fibre membrane bioreactor. Water Res. 46, 4499–4507. doi:10.1016/j.watres.2012.05.004

Zuriaga-Agustí, E., Bes-Piá, A., Mendoza-Roca, J.A., Alonso-Molina, J.L., 2013. Influence of extraction methods on proteins and carbohydrates analysis from MBR activated sludge flocs in view of improving EPS determination. Sep. Purif. Technol. 112, 1–10. doi:10.1016/j.seppur.2013.03.048

Zuthi, M.F.R., Ngo, H.H., Guo, W.S., 2012. Modelling bioprocesses and membrane fouling in membrane bioreactor (MBR): A review towards finding an integrated model framework. Bioresour. Technol. 122, 119–129. doi:10.1016/j.biortech.2012.04.090