This is the final draft of the contribution published as:

The publisher's version is available at:

Biofouling of membranes in microbial electrochemical technologies: Causes, characterization methods and mitigation strategies

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Abstract

The scope of the review is to discuss the current state of knowledge and lessons learned on biofouling of membrane separators being used for microbial electrochemical technologies (MET). It is illustrated what crucial membrane features have to be considered and how these affect the MET performance, paying particular attention to membrane biofouling. The complexity of the phenomena was demonstrated and thereby, it is shown that membrane qualities related to its surface and inherent material features significantly influence (and can be influenced by) the biofouling process. Applicable methods for assessment of membrane biofouling are highlighted, followed by the detailed literature evaluation. Finally, an outlook on e.g. possible mitigation strategies for membrane biofouling in MET is provided.

Keywords: membrane; biofouling; ion transport; mass transfer; microbial electrochemical technology; microbial fuel cell

1. Introduction

Microbial fuel cells (MFC) are among microbial electrochemical technologies (MET) that generate electrical energy from the biological decomposition of organic matter (Logan et al., 2006; Schröder et al., 2015; Zhang et al., 2016). MFC resemble classical chemical fuel cells (FC), for instance, fed with hydrogen and oxygen. In both types of electrochemical cells, at the anode fuel oxidation and at the cathode oxygen reduction take place. Both electrodes have to be connected via an external circuit in order to allow electron transfer and energy harvesting. Consequently, adequate passage of ions between anode and cathode is necessary to assure charge balancing (Santoro et al., 2017). Using membranes or other separators divides the electrochemical cell into an anode and a cathode half-cell and yields a two-chamber configuration (Du et al., 2007). In many cases, conventional membrane materials for proton exchange membrane (PEM) FC such as Nafion are employed in MFC, as well (Harnisch et al., 2008; Kokabian and Gude, 2015). Although there are similarities between FC and MFC, they are significantly different. The biggest difference is the catalyst in MFC, i.e. electrochemically active bacteria (EAB) that oxidize organic compounds and transfer the electrons directly or indirectly to the anode (Pant et al., 2010). Therefore, MFC compared to FC have to operate at different physical and chemical conditions, e.g. neutral pH or ambient temperature.

It seems evident that materials are not similarly suitable for MFC and FC. For instance, the above-mentioned membrane material, Nafion, had been previously exploited for FC (Kraytsberg and Ein-Eli, 2016; Peighambardoust et al., 2010) and was thereafter adopted for MFC (seen as a FC-derivative technology) (Harnisch et al., 2008; Rozendal et al., 2006). Nafion was considered for long time as the primary

reference material for two-chamber MFC (Bakonyi et al., 2018). However, the deployment of Nafion and other ion exchange membrane materials in MFC has revealed severe weaknesses, such as low proton selectivity, high gas and substrate crossover, high fabrication cost (Chae et al., 2014; Park et al., 2017). Furthermore, membrane fouling both in chemical and biological terms (biofouling) is one of the most critical issues, although its importance has not yet been sufficiently addressed in MFC (Choi et al., 2011; Ghasemi et al., 2013; Rahimnejad et al., 2014; Xu et al., 2012). The definition of fouling according to IUPAC is "loss of performance of a membrane due to the deposition of suspended or dissolved substances on its external surfaces, at its pore openings, or within its pores" (IUPAC, 1997). Nowadays, apart from MFCs, many other potential technologies derived from the MET platform are being under intense research such microbial electrolysis cell (Zhen et al., 2017) or microbial desalination cell (Kim and Logan, 2013), where membrane biofouling could be serious threat, as well.

Consequently, in this review, it will be discussed what membrane properties should be taken into account and how these can influence the efficiency of MET operation, with priority given to biofouling. Thereafter, methods for characterization of membrane biofouling are assessed. This is followed by critical assessment of recent developments on membranes for various MET. Finally, future considerations regarding possible mitigation strategies are presented. To our knowledge, this topic has not yet been specifically reviewed.

2. Role of membranes in microbial electrochemical technologies and the adverse effect of biofouling

In most cases, membrane separators applied in MET are chemically-synthetized from polymers (Bakonyi et al., 2018, Koók et al., 2019a). In addition to those, ceramics (Khalili et al., 2017; Pasternak et al., 2016; Yang et al., 2016a; Winfield et al., 2016) as well as (more affordable) materials fabricated with the aid of natural substances (Hernández-Flores et al., 2016; Kondaveeti et al., 2018; Winfield et al., 2014) are found as alternatives. Regardless of the material the membrane is made of, it has to fulfill several key-properties (Bakonyi et al., 2018; Daud et al., 2015; Yang et al., 2019) in terms of *mass transfer* between the electrodes, and *ionic conductivity* or low *membrane resistance* (that contributes to the total *internal cell resistance*). Even if a membrane shows advantageous initial properties, its stability in longer-terms remains of concern due to chemical as well as biological fouling, induced by the interaction of the membrane with certain foulants (Tan et al., 2017).

Chemical fouling: Fouling can be caused by chemicals (e.g. nutrients, minerals, salts) present in the liquid media (for MFC mostly on the anode facing side of the membrane). Among these, ionic species play a role in ensuring the good *electrolytic conductivity*, however, they can also have an adverse effect by occupying the oppositely charged functional groups of ion exchange membranes. In this case, the transport of ionic substances between the electrode compartments is hindered. This finally causes deterioration of the membrane performance. Additionally, multi-valent ions i.e. Mg^{2+} and Ca^{2+} and their occasional precipitation (e.g. $CaCO_3$, $Mg(OH)_2$) can cause serious operating issues in MET coupled with desalination and reverse electrodialysis (Mei and Tang, 2018; Ping et al., 2013; Vermaas et al., 2013;

Yang et al., 2019). For instance, divalent cations can form precipitates with naturally-occurring organic matter in water resources and thus contribute to the development of compact fouling layers on the membrane (Luo et al., 2012ab; Zhang et al., 2017b, 2018). Furthermore, they can enhance bio-flocculation, which is one of the key-mechanisms of membrane fouling. In essence, as explained by Kim and Jang (2006), multi-valent ions can bridge bacterial *extracellular polymeric substances* (EPS), resulting afterwards in the aggregation and stabilization of biopolymers as well as microbes.

Biological fouling can be defined as: fouling arising from biological processes (Guo et al., 2012). It has been widely emphasized that microorganisms can attach to the membrane surface to form a biofilm (Chae et al., 2008; Saeed et al., 2015). The biofilm layer can make the membrane substantially thicker and consequently, increase its resistance to mass transfer and ion transport (Sulonen et al., 2016). Both effects limit the operating efficiency of MET. Depending on the interactions between biofilm and membrane, the material may be impaired due to biological attacks, leading also to deterioration of mass- and charge transfer properties. In addition to membranes, the biofouling can hit hard on other architectural components too, such as cathodes (Oliot et al., 2016a).

Actually, the mass- and charge transfer in MET with membranes is mainly governed by (i) diffusion (due to concentration differences in the two compartments) and (ii) migration, induced by the electric field (Hedbavna et al., 2016; Luo et al., 2018; Sleutels et al. 2017). For instance, Harnisch et al. (2009a) did modelling of ion transfer across ion exchange membranes in MET. The ion fluxes associated with diffusion and migration terms were evaluated based on the 1-D form of Nernst-Planck equation, whereas the mass transfer via convection was neglected. Nevertheless, in

case of MET combined with membrane processes, e.g. reverse electrodialysis or forward osmosis, convective flow could be relatively more substantial and taken into account. For the above reasons, it is needed to pay attention to biofouling issues in MET and understand what factors influence this process. Here it has to be noted that, numerous aspects of (bio)fouling mechanisms described for membrane processes such as membrane bioreactors (MBRs), may be analogous for MET, too (Yuan and He, 2015) especially in cases when MET are coupled with MBRs (Cheng et al., 2018). In MBRs, important fouling mechanisms originate from adhesion/deposition and subsequent rise of mass transport resistance (e.g. leading to increased filtration resistance). As for adhesion/deposition process, interfacial interactions between foulants and the membrane can be decisive (Teng et al., 2018a, 2019; Qu et al., 2018). Further mechanisms linked to mechanisms driven by the electrochemical potential (linked to foulant/cake layer filtration) also play a role in the build-up of filtration resistance (Chen et al., 2016a; Teng et al., 2018b; Zhang et al., 2013). Interestingly on the biofouling aspect, as reviewed by Jia et al. (2016), the integration of electrochemical cell with MFC-biosensor could be a promising way to monitor biofouling potential of resources such as seawater based on the availability of assimilable organic carbon (Quek et al., 2015).

3. Background and mechanism on membrane biofouling in MET

3.1.   Membrane-associated aspects

Biofouling is caused by biofilm growth on the membrane surface. This, however, is affected by certain membrane properties, such as its physical structure,

particularly the *surface morphology.* From this viewpoint, *roughness of membrane surface* is a notable parameter to deal with. As summarized by Williams (2014), this membrane feature is linked to the measure of surface texture and signifies to what extent the membrane surface deviates from an ideally smooth one. In fact, surface roughness will largely influence how the membrane behaves under given environmental circumstances and basically, with the increment of surface roughness, more space (area) becomes potentially available for microbes to invade and colonize the membrane (Zhong et al., 2012). This situation represents a bigger threat for the occurrence of biofouling and subsequently, membranes with smoother surface characteristics should be preferred for MET. This is supported by the conclusions of relevant literature reports, saying that membrane separators with more uniform, flat surface topology are expected to be more resistant to the development of biofilms (Dhar and Lee, 2013). Besides that, the *porosity and pore size* of the membrane can also matter. It is known from literature that on the top of non-porous membranes, porous micro- or ultrafiltration ones could be employed in MET. It should be taken into account that higher porosity – meaning larger pore volume compared to the total volume of the membrane (Smolders and Franken, 1989) – and larger pore size may provoke more intense biofilm formation. As a matter of fact, pores could be obvious places for microorganisms to settle and reproduce themselves, leading to clogging (Lim et al., 2012). Certainly, pores can be plugged not only by microorganisms but also by penetration and accumulation of organic/inorganic substances found in the compartments.

Moreover, among membrane qualities, the *wettability* also deserves attention. Wettability refers to the hydrophilicity (or hydrophobicity) of the material, which is a function of its chemical composition and describes the affinity to water. Obviously,

hydrophilic membrane separators reflect a better potential to withstand biofouling, as explained by the findings of research studies. As a matter of fact, according to Elangovan and Dharmalingam (2016), microbes and biological macromolecules, e.g. EPS ascribed to their relatively hydrophobic features, have less preference to make connections with hydrophilic membrane surfaces (in comparison with hydrophobic ones). This can be attributed to the lack of thermodynamic benefit originating from low interfacial energy between the cells/components and the membrane surface. Besides that, as deduced by Kim et al. (2014), the adhesion of hydrophobic foulants to the hydrophilic membrane surface can be suppressed thanks to existing steric hindrances. For the record, hydrophilic membranes tend to have a lower ohmic resistance (Oliot et al., 2016b).

In addition to the already evaluated membrane properties, the role of membrane *surface charge* needs to be outlined as it is also a factor that influences the interaction of membranes and (bio)fouling agents (Zinadini et al., 2017). As reported, highly negative surface charges are considered advantageous to counteract biofouling (Kim et al., 2014). The key reason seems to be the electrostatic repulsion force evolving between the biological cells (carrying in general an overall negative charge) and the negatively charged membrane surface.

3.2. Microbiology-related considerations

Apart from the inherent membrane traits assessed in Section 3.1., a range of microbiology-associated factors also governs biofouling. First, EPS can be identified as organic foulant (Lin et al., 2014). As it was outlined by researchers such as Miskan et al. (2016) and Nguyen et al. (2012), EPS – acting as biological glue (Flemming

and Wingender, 2001; Flemming, 2016) – promote the arrangement of microbes into aggregates and in that way, take part in the formation of biofilms. Hence, the determined amounts/concentrations of EPS on the membrane can be seen as indicators for biofouling. Alternatively, indirect measurement of the *microbial activity* on the membrane surface such as dehydrogenase activity (DA) (Reddy et al., 2010) gives indications concerning the severity of biofouling. As biofilm formation is a consequence of microbiological growth, methods directly quantifying the *cell number* (Heidrich et al., 2016) or the *protein mass* could be applied (Qiao et al., 2017). Here, it should be underlined that the growth of microorganisms depends on the environmental conditions such as the actual redox potentials in the system. Actually, membranes can be described by quite distinct *mass transport properties* especially the diffusion coefficients (D) of ions and other chemicals, e.g. *oxygen diffusion* (D_o), which is directly proportional to the membrane thickness and the oxygen mass transfer (Chae et al., 2008; Kim et al., 2007). Therefore, membranes demonstrating lower D_o could be more suitable for MFC in order to maintain anaerobic conditions in the anodic compartment and preserve EAB, e.g. *Geobacter* sp. (Logan and Regan, 2006; Kim et al., 2015). In other words, the use of such membrane separators should therefore enhance the electrochemical performance of the whole MFC (Bakonyi et al., 2018; Koók et al., 2017a). Apart from the case of EAB, it is reasonable to assume that the extent of oxygen transfer through the membrane affects microorganisms growing on the membrane surface (Kokko et al., 2018). Accordingly, a membrane with higher dissolved oxygen flux can select more aerobic microorganisms on the membrane (Leong et al., 2013). Thus, advanced molecular biological tools to analyze microbial community structures can be helpful to investigate what microorganisms are attached on membranes of MET (Kouzuma et al., 2018; Saratale et al., 2017ab).

This could facilitate the understanding of plausible cross-effects, in particular membrane properties and underlying microbial consortia. In addition to oxygen transport, following the transfer of ions- and protons could also provide complementary information to evaluate the membrane behavior and its change over time (Bakonyi et al., 2018).

Thus, studying the impacts of various membrane separators in MET could be suggested to better elaborate how much the actual type of membrane affects the system behavior both in electrochemical and microbiological terms (Sotres et al., 2015). Feasible techniques possibly used for this purpose will be interpreted in the following section.

4. Methods for the evaluation of membrane biofouling in microbial electrochemical technologies

This section introduces methods that could be used to investigate membrane properties, particularly those that are considered to influence its biofouling resistivity/sensitivity (as detailed in Sections 2 and 3). These parameters could be helpful to make implications regarding the expected behavior of membranes, e.g. for a preliminary ranking of the materials. The comparative assessment of new and used membranes, based on these factors, can assist the explanation of biofouling phenomena and its effects on MET performance.

4.1. Methods for assessing membrane surface morphology, roughness, pore size, porosity, wettability

The *surface typology/morphology* of a given membrane can be studied by scanning electron microscopy (SEM). Visualization at different points of cell operation could reveal the existence of biofouling layer on the membrane surface (Miskan et al., 2016). In addition, SEM may show the difference in the extent of *surface roughness* for various virgin membranes (Ghasemi et al., 2016). Further technologies for membrane surface image analysis, with different topological resolution, are the use of non-contact profilometer in the (sub)mm-scale (Elangovan and Dharmalingam, 2016, 2017; Prabhu and Sangeetha, 2014; Venkatesan and Dharmalingam, 2015a) and Atomic Force Microscopy (AFM) for nm-scale (Ghasemi et al., 2012; Leong et al., 2015; Lim et al., 2012; Mokhtarian et al., 2013; Rahimnejad et al., 2012; Zinadini et al., 2017).

Other intrinsic traits of a membrane separator for MET, such as mean and maximum pore size could be measured by filtration velocity and bubble point methods, while porosity can be examined with gravimetric methods, as demonstrated by Huang et al. (2017). As mentioned earlier, membrane wettability is an important factor to influence biofouling. It reflects the ability of a liquid to wet a surface (Gugliuzza, 2015) and can be associated with the surface tension. To characterize these measures, the contact angle between a liquid droplet and a solid surface could be used. This will express whether the solid material – here the membrane – is rather hydrophilic or hydrophobic (Huang et al., 2017; Jebur et al., 2018) and can be gained using a goniometer (Kim et al., 2014).

4.2. Methods for assessing membrane surface charge, ion exchange capacity, water uptake, thickness

The *surface charge* of a membrane can be determined by the surface zeta potential, which can be extracted from electro-kinetic experiments (Hurwitz et al., 2010).

Actually, zeta potential measurements may derive from electrophoretic light scattering (ELS) method, as reported by Kim et al. (2014), who characterized the surface charge for a set of ultrafiltration membranes in MFC. The *ion exchange capacity* (IEC), as substantial attribute of (ion exchange) membrane separators is commonly examined with titration techniques (Hwang and Ohya, 1998; Venkatesan and Dharmalingam, 2015b; Xu et al., 2012). In the work of Xu et al. (2012), IEC for membranes was gained by Eq. 1.

$$IEC = (A \times B) \, M^{-1} \tag{1}$$

where IEC is given in the unit of mmol g^{-1}, A and B denote the added titrant volume (dm^3) and its molar concentration (mmol dm^{-3}), respectively, while M designates the dry weight of the membrane sample (g).

The *membrane thickness* (L), does affect the membrane resistance in a considerable manner. One approach to determine and monitor this parameter in MET was presented by Miskan et al. (2016), who observed the change of membrane samples in different periods of MFC operation (2, 4 and 6 months) by SEM and evaluated how L was varied. Apart from visualization-based methods, the membrane thickness is obtainable by using micrometer screw gage, as reported by Wang et al.

(2015). The *water uptake* characteristic of a particular membrane material is also a significant feature. The amount of water absorbed by a membrane separator in the course of MET operation can result in swelling, consequently, increasing the thickness and hence the membrane resistance. Moreover, membrane swelling is an important issue in a membrane electrode assembly (MEA) MET because it may lead to serious performance deterioration by delaminating electrode from the MEA (Chae et al., 2014). Water uptake also influences proton conductivity of the membrane, since water molecules can participate in conveying them across the membrane if it is properly hydrated (Daud et al., 2019). Therefore, the water uptake property should be a subject of interest and could be calculated from immersion method, which considers the weight of membrane before and after hydration (Venkatesan and Dharmalingam, 2015b).

4.3. Methods for assessing the membrane resistance

Technical solutions to determine the (ohmic) membrane resistance are based on electrochemical impedance measurements (EIS). Mostly, EIS is done with a potentiostat equipped with a frequency response analyzer. In this case the impedance is examined by applying a constant voltage perturbation signal, typically with an amplitude of ±10 mV over a defined frequency range, e.g. between 100 Hz and 1MHz (Elangovan and Dharmalingam, 2016) or 10 kHz to 100 mHz (Zhang et al., 2009). The impedance Z is determined by measuring the phase shift and the ratio of the amplitude difference (modulus |Z|) between perturbation (voltage) and relaxation (current) signal. Alternatively to potentiostat, Choi et al. (2011) applied an

LCR meter to examine the ohmic resistance of membranes, based on voltage perturbation measurements.

As described by Zhang et al. (2009), EIS can be used to reveal the ohmic resistance of the electrolyte in microbial fuel cells assembled (i) with and (ii) without membrane separator (as solid electrolyte). From the differences of those two values, membrane resistance could be reported (Zhang et al., 2009). **Fig. 1** shows an exemplary Nyquist Plot for illustration. Apart from that, two-electrode measurements are widely used for determining the solid + liquid electrolyte resistance, when the anode is used as working, while the cathode plays the role of both the reference and counter electrodes (Wei et al. 2013). By analyzing the obtained EIS plots, the total internal resistance can be separated to solid + liquid electrolyte, charge transfer and diffusion resistance components (Nam et al. 2010).

4.4. Proton conductivity of membranes

The efficient charge balancing (ion and proton transfer) of the membrane is one of the most essential requirements to achieve good operational performance in MET (Bakonyi et al., 2018). In real applications, the widely used PEMs are not ideally selective to proton as they allow the passage of various ions at the same time. Related to this, it was shown that the transport of H^+ in MFC plays a minor role at this charge balancing process, because of their significantly (4 - 5 orders of magnitude) lower concentration compared to other ions in the systems (Rozendal et al., 2006; Zhao et al., 2006). Although, once the amount of cations in the cathode chamber is high enough, transport of protons becomes energetically more favorable (Sleutels et al., 2017). In case of the occurrence of membrane biofouling, meaning that the

movement of ions and protons is getting physically obstructed, the membrane can lose some of its attractiveness (Kim et al., 2016). Therefore, the ion and proton conductivity of a particular membrane is a quality that is worthy to be monitored.

For instance, specific ionic conductivity measurements can be performed by experimental arrangement following Eq. 2 (Xu et al., 2012):

$$\sigma = L \ (R \times S)^{-1} \tag{2}$$

where σ, L, R and S are assigned for the conductivity (S cm^{-1}), the distance between the electrodes (cm), the membrane resistance (Ω) and the area of the membrane (cm^2), respectively.

4.5. Mass transport properties

4.5.1. Proton mass transfer

It is important to complement the characterization of a membrane with proton mass transfer properties, since these are significantly related to the pH-splitting phenomena. The pH-splitting does refer to the accumulation of protons in the anode chamber and hydroxides in the cathode chamber, as charge balancing ion transfer is realized by other ions than H$^+$/ OH$^-$ (Li et al., 2011; Sleutels et al., 2017). In order to describe H$^+$ mass transfer, the methodology detailed by Zhang et al. (2009) seems to be applicable. In brief, the tests should be carried out in an abiotic, dual-chambered cell with a pH sensor installed into one side to be able to record the pattern of pH

changes between the two compartments adjusted to different initial pH values, as described by Eq. 3.

$$k_H = -\frac{V}{2At} \cdot \ln \left[\frac{(C_{1,0} + C_{2,0} - 2 \cdot C_2)}{C_{1,0} - C_{2,0}} \right] \qquad (3)$$

where V is the liquid volume, A is the membrane surface area, $C_{1,0}$ and $C_{2,0}$ are the initial proton concentrations in the chambers with neutral and elevated pH (considered as cathode and anode chambers, respectively), while C_2 is the proton concentration in the anode solution at time t. After multiplying k_H with the membrane thickness, the proton diffusion coefficient of a particular membrane can be displayed (Bakonyi et al., 2018). Alternative to Eq. 3., the so-called transport number (or transference number) can be derived (Harnisch et al., 2008), which shows the "the part of the current that is transported through the electrolyte due to the motion of the ionic species" according to Oliot et al. (2016b). Such an approach was applied by Park et al. (2017) to characterize the proton transport through membrane in two-chambered bioelectrochemical reactors.

4.5.2. Bulk ions and substrates

The characterization of ions that also contribute to the electro-neutralizing charge transfer can be done by calculating their mass transfer coefficients ($k_{I/S}$) based on the ion concentration in the compartment with high ion activity ($C_{S,0}$) and in the receiving compartment with low ion activity (C_S), according to Eq. 4 (Xu et al., 2012).

$$k_{I/S} = -\frac{V}{2At} \ln \left[\frac{(c_{S,0} - 2c_S)}{c_{S,0}} \right] \tag{4}$$

This method can be used for quantifying the mass transfer of any ionic species present in the system. In two-chamber MFC where EAB are present and fed in the anode compartment, the transfer of (biodegradable) substrate from the anode to the cathode compartment because of concentration differences will result in loss and therefore, in a decreasing activity of the EAB in the anode half-cell. Substrate leakage may promote microbiological proliferation and hence, the contamination of the cathode-side by biological agents, leading to increased biofouling on the cathode-facing surface of the membrane and the cathode electrode too, as well as mixed potential formation and internal currents (Harnisch et al., 2009b). Analogously, this applies to MET where EAB are located at the cathode (systems with biocathode) and materials are lost to the anode side across the membrane. For instance, Ping et al. (2013) investigated microbial desalination cells (containing a pair of AEM and CEM as well as seawater in between those) during long-time operation (8 months). It was found that in addition to deposited particles, some amount of microbes could be even found attached to the CEM's cathode-facing side (tap-water catholyte), as well, while the middle-chamber facing side of the CEM was also biofouled, and even the presence of fungi could be observed. Meanwhile, the anode was strongly biofouled. Hence, it is a possible scenario that biofouling also occurs on the membrane surface that is not in direct contact with the EAB- and substrate-rich compartment.

4.5.3. Oxygen mass transfer

The capability of a membrane to transport oxygen affects the dissolved oxygen concentration in the anode chamber of a MFC (Mohamed et al., 2016). Therefore, membranes being more permeable to (dissolved) oxygen will promote the growth of aerobic strains on its surface. These types of bacteria, in general, can be attributed with shorter duplication time and greater biomass yield in comparison with less oxygen-tolerant/more anaerobic ones. Hence, it might be assumed that membranes leading to larger oxygen fluxes (from the aerated cathode to the non-aerated anode) are more prone to biofouling and accumulate more biomass on the surface.

To determine the oxygen mass transfer coefficient (k_O) of a separator, the procedures suggested by Kim et al. (2007) and Chae et al. (2008) could be followed. Basically, k_O is produced by experimental data fitted into Eq. 5.

$$k_O = -\frac{V}{At}\ln\left[\frac{(C_0-C)}{C_0}\right] \tag{5}$$

where V is the liquid volume, A is the membrane surface area, C_0 and C are the dissolved oxygen concentrations (i) in the oxygen saturated cathode half-cell and (ii) in the anode chamber at time t, respectively. Afterwards, by combining membrane thickness (L) with k_O (Eq. 6), the oxygen diffusion coefficient is obtained.

$$D_O = k_O L \tag{6}$$

4.6. Membrane biofouling characterization

4.6.1. Chemical composition

Various authors, for example Miskan et al. (2016), Mohamed et al. (2016), Kondaveeti et al. (2018) and Xu et al. (2012) communicated that Fourier-Transform Infrared Spectroscopy (FT-IR) can be used to follow the biofouling process in MET. Analyzing the FT-IR spectra can help to (i) evaluate some of the main biopolymers in the biofouling layer (Miskan et al., 2016), (ii) reveal the potential modifications of membrane's chemical structure (Mohamed et al., 2016) and (iii) describe the characteristics of contaminants found on the membrane surface (Kondaveeti et al., 2018) or in other words, characterize the fouling layer (Xu et al., 2012). Moreover, Energy Dispersive X-ray spectrometry (EDX) is a measurement technology to get insight regarding the microscopic structure and inorganic elemental composition of a membrane, e.g. its cation content after use in MET (Choi et al., 2011; Rozendal et al., 2006; Xu et al., 2012).

4.6.2. Quantification of EPS

As noted above, EPS play a key-role in the membrane biofouling process. EPS, in accordance with Jiang et al. (2010), can cover a range of constituents, in particular high molecular-weight polymers, e.g. saccharides and proteins. Therefore, the carbohydrate and protein portions of EPS are distinguished and analyzed separately. Determination of EPS on the membrane requires their extraction first (Kim et al., 2014). Thereafter, carbohydrates can be quantified by phenol/sulfuric-acid method, while proteins can be measured for example via the Lowry method based on

bovine serum albumin (BSA) standard or other ready-made test kits i.e. micro BCA protein assay (Jiang et al., 2010; Kim et al., 2014).

4.6.3. Evaluation of the microbial community

Biofouling is a consequence of biofilm formation on the membrane, which can be depicted as a mass of microorganisms in an adhered, consistent structure. For instance, Heidrich et al. (2016) underlined that methods for quantification of selected microbes include (i) quantitative polymerase chain reaction (qPCR) as well as (ii) fluorescence in situ hybridization (FISH). In addition, Kim et al. (2014) did total cell counting in MFC with Confocal Laser Scanning Microscopy (CLSM) and DAPI (4'6-diamidino-2-phenylindole) staining. CLSM could also be applied to study biofilm structure (Xu et al., 2012), for instance, living and dead cells in anode biofilms of microbial electrochemical devices (Sun et al., 2015).

Biomass/cell quantity can be related with the total protein content, e.g. in samples drawn from a surface of a membrane. As reported by Qiao et al. (2017), the procedure to determine proteins can rely on the colorimetric Bradford Protein Assay and the Lowry method (Xu et al., 2012).

To enrich the information about biofilms on membranes in MET, it is also worthy to address *who they are*. For instance, works of Zhi et al. (2014) and Saratale et al. (2017ab) provide details of the microbiological and molecular biological tools for studying microbial communities, particularly species abundance and population dynamics. For imaging and analyzing microbes and their properties, the use of (laser-based) flow-cytometry technique can be a feasible approach. Mainly, it can characterize samples (wastewaters, electrode-surface biofilms) in the aspects of

physiological heterogeneity and population dynamics (Harnisch et al., 2011). It evaluates the microbial community structures and activity (both qualitatively and quantitatively) in using almost real-time. The summary of the mentioned methods for (bio)fouled membrane as well as fouling layer characterization is provided in form of **Fig. 2**.

5. Biofouling experiences with membrane separators

Biofouling normally occurs on the side of the membrane that is in touch with the compartment containing the biological catalysts. Accordingly, research strategies should focus on the (i) development of new materials and/or (ii) the improvement of existing ones to withstand against such effects thanks to better surface properties. Particular examples are listed in **Table 1**. Accordingly, one plausible direction could be seen in the preparation of organic-inorganic combined materials. As concluded by Venkatesan and Dharmalingam (2015b), hydrophilic inorganic composite particles, e.g. TiO_2 incorporated in PEM could be useful to improve resistance of the membranes against biofouling. In their study (Venkatesan and Dharmalingam, 2015b), it was observed that sulfonated poly-ether-ether-ketone (SPEEK) membranes made with TiO_2 metal oxide (7.5 %) enhanced the hydrophilic feature of the resulting membrane and consequently, reduced the adhesion of bacteria to its surface. This was confirmed by counting the *E. coli* cells (used as indicator for biofouling) on the membranes. SPEEK – TiO_2 membranes showed an order of magnitude lower *E. coli* absorption than simple SPEEK or Nafion membranes. The hybrid membranes also exhibited less significant cation transfer and in that way, were considered to decrease the threat of salt precipitation, which is also advantageous

from a biofouling aspect (Venkatesan and Dharmalingam, 2015b). Interestingly, for SPEEK membranes, Ghasemi et al. (2016) found that the degree of sulfonation (DS) may have an influence on the type of fouling that the membrane suffers from. It seemed from SEM image analysis that lower DS (20.8 %) caused mineral, while higher DS (63.6 %) rather microbiological fouling. However, Lim et al. (2012) experienced certain adverse effect of mixing SPEEK (3 %) with poly(ether sulfone) (PES) due to higher surface roughness, which has made this material to be a potential target for microbial adhesion and consecutive biofilm formation.

As a new attempt to substitute expensive fluorine-based Nafion membranes, sulfonated hydrocarbon-based ion-conducting polymers have been actively studied. Leveraged by such characteristics, Chae et al. (2014) developed sulfonated polyether ether ketone (SPEEK)-based composite PEM with polyimide nanofiber supporter. Although SPEEK exhibits higher proton exchange capacity than Nafion, it has several physically instability (e.g. high swelling, dimensional change). This problem was solved by embedding the polyimide nanofiber in the center of SPEEK as a supporting structure to reinforce the dimensional stability (Chae et al., 2014). In addition to SPEEK, sulfonated poly(arylene ether sulfone) (SPAES) has been considered as an efficient hydrocarbon-based proton-conducting block copolymer (Park et al., 2017). These SPEEK- and SPAES composite PEMs exhibited an improved proton selectivity while excluding other competing cations (Ca^{2+}, Mg^{2+}, NH_4^+, etc.), and less substrate crossover through PEM as well. Such enhanced performance was attributed to a well-defined microstructure that has narrow, branched, tortuous ion-conducting hydrophilic channels, compared to that of Nafion. These reduced crossovers for both substrate and divalent cations can lead to conditions that are more favorable to mitigate biofouling.

Another approach was demonstrated by Choi et al. (2013), who fabricated membrane separators from nonwowen fabric and poly[2,5-benzimidazole] (ABPBI). It turned out from the experiments that in comparison with Nafion, the nonwoven fabric-based material showed better resistance against biofouling in an MFC for a period of more than 300 days.

Furthermore, Kim et al. (2014) have revealed that coverage of ultrafiltration membrane (UF) by polydopamine led to substantial increase of biofouling resistance. The authors showed that the reason was primarily linked to the alteration of membrane surface charge, resulting in the increment of electrostatic repulsion forces between the membrane surface and the bacteria. Similarly, beneficial impact ascribed to enhanced electrostatic repulsion forces was reported by Huang et al. (2017) employing a conductive flat microfiltration membrane comprising of polyvinylidene fluoride, N-methyl- 2-pyrrolidone, polyvinyl pyrrolidone and reduced graphene oxide (RGO) on stainless steel mesh base. In addition, the authors noted the advantage of membrane's more hydrophilic nature, which had contributed to the biofouling mitigation as well (Huang et al., 2017).

In another work by Angioni et al. (2016), the modification of Nafion polymer turned also out to be efficient for improving the membrane material and reduce biofouling in MFC. As it was elaborated, the silica-based, functionalized fillers added to Nafion helped to achieve more negative membrane surface charges and hence the composite membranes were more successful to tackle the biofouling phenomena in MFC. Mokhtarian et al. (2013) demonstrated that the proper combination of Nafion with polyaniline could actually decrease the surface roughness of the membranes attained and accordingly, this material was more resistive to biofouling due to the less available surface area for bacterial attachment.

Apart from these, authors such as Chen et al. (2012) and Tao et al. (2015) emphasized that polyvinyl alcohol (PVA) is sufficiently hydrophilic, relatively easy to be film casted, cost effective, environmentally gentle and therefore, assumed to increase biofouling resistance of membranes. Moreover, Hou et al. (2014) explained that PVA membranes can be made proton conductive by attaching negatively charged functional groups into its structure. Results in MFCs operated with PVA-based membrane separators have been published by Khilari et al. (2013) and Zhang et al. (2017a). The authors added graphene oxide (GO) to the polymer matrix comprising of PVA and silicotungstic acid. By optimizing the membrane recipe, the power production in MFCs could be significantly enhanced and at the same time, biofouling was suppressed. Zhang et al. (2017a) also mentioned certain self-cleaning effect of membranes prepared with PVA, polyvinylidene fluoride and cotton fabric (referred originally as PVAc-g-PVDF coated cotton fabric), which may have contributed to the anti-biofouling property of the material in microbial fuel cell.

As for experiences with various kinds of membrane-equipped MET, results from osmotic MFCs can be highlighted. This system combines the benefits of MFCs (in terms of electricity production) and the osmotic pressure-driven water purification technologies reported data for fouling (mostly inorganic, but containing biopolymers as well) in osmotic MFCs equipped with forward osmosis membranes (FO) (Zhang et al., 2011; Zhu et al., 2016). Actually, it was found that fouling – in addition that water flux across the fouled membrane was close to zero – promoted the power generation efficiency of osmotic MFC compared to the outcomes of pristine membranes. At a first glance, this could be quite unexpected considering the usual feedback related to biofouling in MET. Nevertheless, it has been turned out by measuring the flux of charge carriers across the membrane that fouling enhanced the ion diffusion and ion

exchange mechanisms, resulting in accelerated flux of protons and ions (Zhu et al. 2016).

Yang et al. (2016b) also communicated that the water flux via cellulose acetate-based FO membrane was decreased by 50 %. In the same study, it was demonstrated that the use of silver nanoparticle – polydopamine coating (to modify the FO membrane) was effective to retard biofouling. The mechanism was explained by the anti-microbial effect of silver and the negatively-charged, hydrophilic environment of the membrane caused by polydopamine (Yang et al., 2016b). It is worth to mention that although the surface roughness of the modified FO membrane was considered theoretically more favorable for cell attachment, it seemed to be diminished by the surface charge, hydrophilicity and anti-microbial effect of the silver nanoparticles. In accordance with the conclusion of the authors two particular questions should be addressed: (i) the effectiveness of anti-microbial effect related with the silver content of the membrane in long term studies and (ii) the stability of silver-containing FO membrane such as silver loss during application. The positive influence of Ag content in membranes towards better anti-(bio)fouling was also reported by Zhang et al. (2019) in an electrically-assisted membrane filtration process. In the context of such membranes, the release of silver nanoparticles (SiNP) from membranes could be a concern since this may affect EAB. Though the exact mechanism behind the anti-microbial action of SiNP is not yet clarified, proposed theories were outlined by Prabhu and Poulose (2012).

6. Outlook on possible approaches to mitigate membrane biofouling in microbial electrochemical technologies

Although in some applications such as microbial recycling cells the deposition of salt and biofouling in microporous layers are viewed as advantages (Goglio et al., 2019), membrane biofouling in MET represents mostly a remarkable issue for long-term, efficient system performance (Aryal et al., 2018; Chen et al., 2016b; Liu et al., 2017). Therefore, the used membranes have to be engineered towards more convincing anti-fouling characteristics. In summary, to increase the chance of counteracting membrane biofouling in MET, membrane separators should have (i) smoother surface, (ii) negative surface charge (to aid electrostatic repulsion force), (iii) advantageous inner structure (in terms of the presence/absence of pores and their size/volume) and (iv) hydrophilic character (as implied in **Fig. 3**). Certainly, the efficiency of a membrane from a biofouling-resistance viewpoint will be determined together by these inner qualities of the material. To make a confidential ranking among different membranes, experiments will be required under identical experimental settings in MET.

In order to create membranes – typically made of polymer materials that are the most widespread in MET (Bakonyi et al., 2018) – with better potential to overcome biofouling, Leong et al. (2013) have introduced some possible directions to improve anti-microbial as well as anti-adhesion routes. These include mean specific chemical modifications to reduce bacterial proliferation or to suppress the attachment of foulants to the membrane surface, respectively (Leong et al., 2013).

So far, as evaluated in **Section 5**, several research strategies have been communicated to make membranes in MET more effective against biofouling. These

attempts resulted in (i) the use of hydrocarbon-based ion conducting materials prepared with SPEEK and SPAES (Venkatesan and Dharmalingam, 2015b; Ghasemi et al., 2016; Lim et al., 2012; Chae et al., 2014; Park et al., 2017), (ii) the modification of Nafion (Angioni et al., 2016; Mokhtarian et al., 2013), (iii) the support of cheap material with ion-specific conductor (Choi et al., 2013; Chae et a., 2014), (iv) the improvement of micro- and ultrafiltration membranes (Huang et al., 2017; Kim et al., 2014) and (v) the fabrication of membranes containing silver nanoparticles (Yang et al., 2016b).

Although these approaches are highly promising and show how membranes have been upgraded to diminish biologically-induced fouling in MET, establishment of further concepts can be suggested to broaden this field and provide more options for anti-fouling membrane construction. To facilitate this progress, lessons and experiences with biofouling from other membrane-related areas might be taken into account. An interesting and quite new approach is the deployment of ionic liquid-containing membranes (**Fig. 4**). It has been proved that certain supported ionic liquid membranes (prepared with imidazolium and methyl trioctylammonium cations and with $[PF_6]^-$, $[BF_4]^-$, $[Cl]^-$ and $[NTf_2]^-$ anions, by using polyamide supporting layer) (ILMs) were applicable in MFCs to substitute Nafion PEM (Hernández-Fernández et al. 2015; Koók et al., 2017ab, 2019b). On that matter, Jebur et al. (2018) found notable anti-microbial effect of imidazolium cation-based hydrophilic (with $[Cl]^-$ and $[Br]^-$ anions) and hydrophobic (with $[NTf_2]^-$ anion) ILMs using PTFE supporting layer and various test microorganisms. Hence, proper selection of ionic liquids and their use may be a feasible way to fabricate membranes with adequate antimicrobial properties. Accordingly, more work is encouraged in this topic to get more information about the feasibility of ILM in MET.

However, it is presumable for most strategies aiming to overcome biofouling that they are unable to ensure full success over longer time. In other words, adhesion and accumulation of biofoulants on the membrane are only a question of time and therefore, it may rather be the question how to increase the lifetime of membranes in MET. For instance, Kim et al. (2014) studied polydopamine coated ultrafiltration membranes in microbial fuel cells and showed that longer-term suppression of biofouling in such systems was rather unlikely. Thus, apart from the development of new, high-performance membranes, attention could also be paid to end-of-pipe solutions e.g. membrane cleaning. Though the specific topic of membrane cleaning for MET is currently underdeveloped, approaches demonstrated in membrane bioreactors (Lin et al. 2013; Wang et al., 2014) may be adapted to two-chambered MET to recover (bio)fouled membranes. This step may need case specific optimization according to the actual material properties in order to find a procedure that does not attack the chemical structure of the membrane but at the same time, is effective enough to play its part in membrane regeneration (Aslam et al., 2018). However, if cleaning is proven insufficient, then from time to time, membrane replacement is inevitable, adding an extra cost to the process (Ho et al., 2017).

Under any conditions, the assessment of MET operation in the light of relationships between the actual membrane type and the microbial community growing on it can be important to manage the biofouling problem Sánchez (2018).

7. **Conclusions**

We have illustrated that membrane biofouling is a crucial issue in MET. It was overviewed what membrane properties (e.g. mechanical stability or mass transfer)

are influenced by biofouling phenomena. Conversely, we deduced how certain membrane features (mainly surface morphology, charge, structure and hydrophilicity) affect the formation of biofouling layers. Accordingly, two-sided approach – considering the interrelation of membrane properties and biofouling – was suggested to address its complexity. Biofouling monitoring methods (in terms of fouling layer chemical composition, microbial community) were presented and possible directions in membrane development (such as the promising employment of ionic liquids) to counteract biofouling were demonstrated.

Acknowledgement

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Energy 125, 427-438.

Table 1 – Biofouling experiences with membranes/separators applied in MET.

Type of MET	Membrane/Separator	Inoculum	Assessment of membrane biofouling	Reason behind biofouling mitigation effect	Reference
MFC	SPEEK/TiO$_2$ composite	*E. coli*	The number of cells on membrane surface was evaluated by hemocytometer-method	The addition of TiO$_2$ to SPEEK polymer enhanced the hydrophilicity of the material	Venkatesan and Dharmalingam (2015b)
MFC	SPEEK with various degree of sulfonation	Anaerobic Sludge	The membranes were examined by SEM	Lower degree of polymer sulfonation seemed to influence positivetly the membrane resistivity against biofouling	Ghasemi et al. (2016)
MFC	SPEEK/PES composite	Anaerobic Sludge	The membranes were observed by SEM	Polymers with smaller pore size, lower porosity and smoother surface are favorable to deal with biofouling.	Lim et al. (2012)
MFC	Non-woven fabric filter (NWF)	Wastewater Sludge	NWF was studied by SEM	NWF was not effective to withstand biofouling (>300 days), but still maintained ion transport in its fouled form thanks to existing microscale interstitial access paths	Choi et al. (2013)

50

MFC	Polydopamine coated UF-M	Anaerobic Sludge	EPS concentrations and total cell numbers were determined from the membranes	PD-coated UF-M can more effectively retain EPSs and bacterial cells because of increased hydrophilicity- and more negative surface charge	Choi et al. (2013)
MFC	conductive, flat microfiltration membrane (PVDF/NMP/PVP/RGO)	Effluent of established-MFC	The biofouling layer attached to the membrane was observed by confocal laser scanning microscopy (CLSM)	Reduced membrane biofuling was observed as a result of enhanced hydrophilicity and greater electrostatic repulsion forces	Huang et al. (2017)
MFC	Nafion modified with silica-based, organically-functionalized mesostructured fillers	Wastewater Sludge	The membranes were analyzed by SEM	Higher electrostatic repulsion forces led to decreased membrane biofuling	Angioni et al. (2016)
MFC	Nafion/PANI composite	Anaerobic Sludge	The membranes were subjected to SEM	Smoother membrane surface was accompanied by weaker biofouling compared to plain Nafion	Mokhtarian et al. (2013)
MFC	PVAc-g-PVDF-coated cotton fabric	Anaerobic Sludge	MFC with various membranes were assessed based on power generation	"Self-cleaning" property of PVAc-g-PVDF-coated cotton fabric maintained the pores unblocked and thus, defended the membrane from biofouling	Zhang et al. (2017)

51

| Osmotic MFC | Silver nanoparticle-polydopamine coated forward osmosis membrane | Anaerobic Sludge | Total direct cell count as well as EPS analysis on the fouled membrane surfaces were performed | Mitigated membrane biofouling was associated with the antibacterial impact of silver nanoparticles (+ enhanced hydrophilicity) | Yang et al. (2016b) |

3

Fig. 1 – Exemplary Nyquist plot of an electrode immersed in an electrolyte (R||C

Element + electrolyte resistance) with R_{pol}: polarization resistance, C_{dl}: double layer

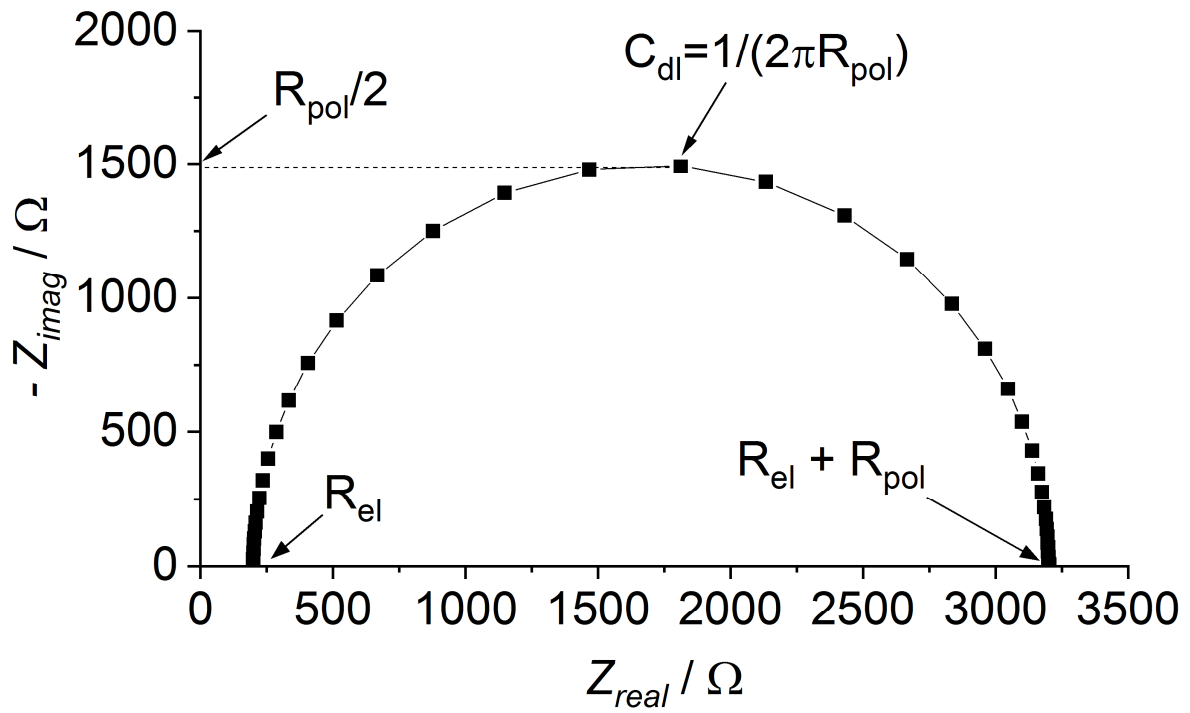capacity, R_{el}: electrolyte resistance, adapted from Hamann et al. (2007)

10   **Fig. 2** – Summary of membrane and fouling layer characterization methods.
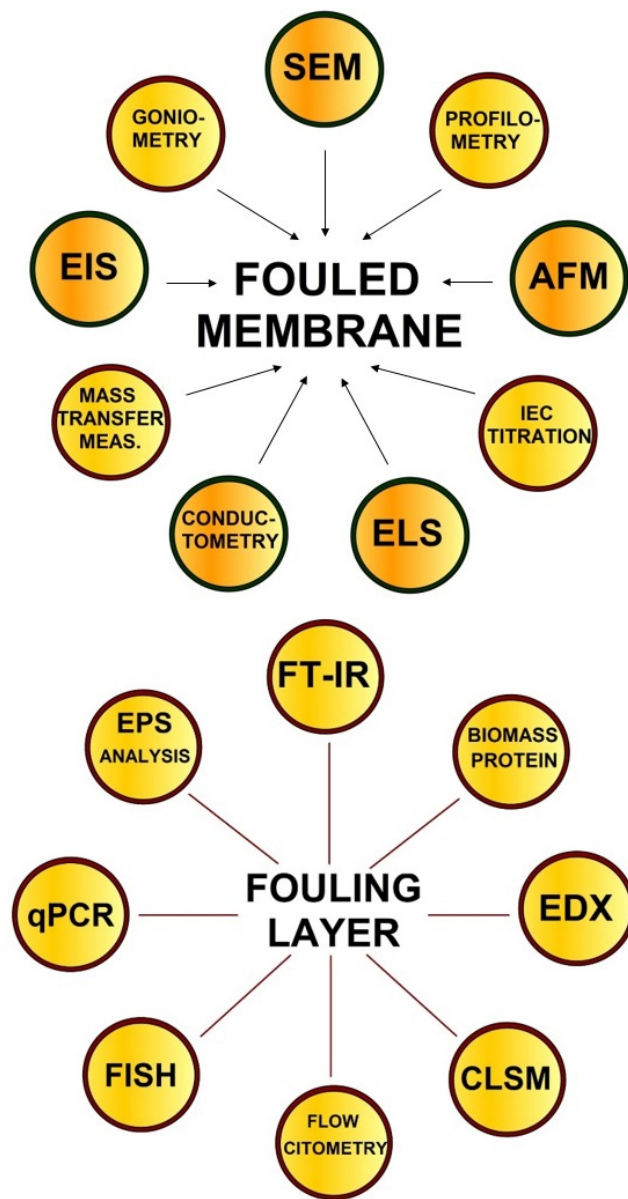
11

12

13

Fig. 3 – The formation process of chemical and biofouling highlighting the main causes and effects, and the crucial membrane features affecting the resistance of the membrane against fouling.
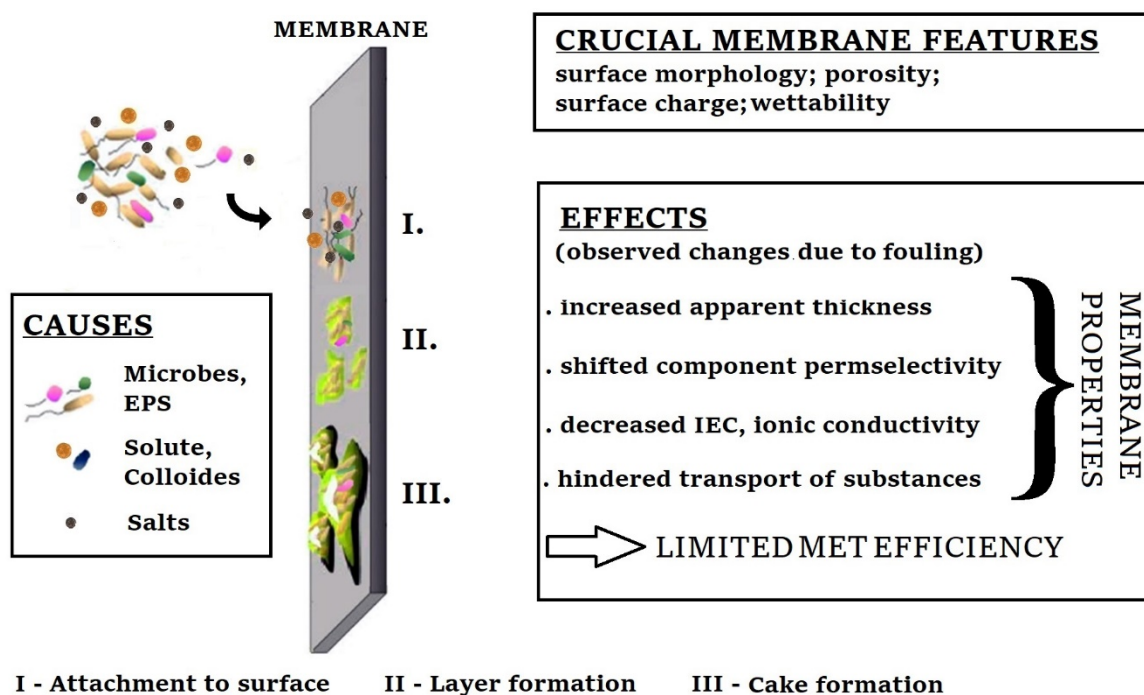

MEMBRANE

CRUCIAL MEMBRANE FEATURES
surface morphology; porosity;
surface charge; wettability

I.

II.

III.

CAUSES

Microbes, EPS

Solute, Colloides

Salts

EFFECTS
(observed changes due to fouling)

. increased apparent thickness

. shifted component permselectivity

. decreased IEC, ionic conductivity

. hindered transport of substances

} MEMBRANE PROPERTIES

⟹ LIMITED MET EFFICIENCY

I - Attachment to surface   II - Layer formation   III - Cake formation

20   **Fig. 4** – Scheme of the structure of supported ionic liquid membranes (SILM).

21

ions
protons

pore filled with
ionic liquid

supporting
membrane phase

supported liquid membrane
prepared with ionic liquid

22

23