Bioresource Technology xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Review

Fermentative hydrogen production in anaerobic membrane bioreactors: A review

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HIGHLIGHTS

- Anaerobic, integrated membrane bioreactors (AnMBRs) are reviewed.
- Specific AnMBR applications for biohydrogen production are discussed.
- Hydrogen generation possibilities and potentials in AnMBRs are critically evaluated.

ARTICLE INFO

Article history:
Received 6 December 2013
Received in revised form 16 January 2014
Accepted 20 January 2014
Available online xxxx

Keywords:
Biohydrogen
Bioreactor
Design
Membrane
Integrated system

ABSTRACT

Reactor design considerations are crucial aspects of dark fermentative hydrogen production. During the last decades, many types of reactors have been developed and used in order to drive biohydrogen technology towards practicality and economical-feasibility. In general, the ultimate aim is to improve the key features of the process, namely the H_2 yields and generation rates. Among the various configurations, the traditional, completely stirred tank reactors (CSTRs) are still the most routinely employed ones. However, due to their limitations, there is a progress to develop more reliable alternatives. One of the research directions points to systems combining membranes, which are called as anaerobic membrane bioreactors (AnMBR). The aim of this paper is to summarize and highlight the recent biohydrogen related work done on AnMBRs and moreover to evaluate their performances and potentials in comparison with their conventional CSTR counterparts.

1. Introduction

Hydrogen represents one of the highly attractive directions in alternative energy research (Winter, 2009). It is an environmentally gentle compound which can be formed by several biological ways including both the light-dependent and dark fermentative processes (Show et al., 2012). Nowadays, considering practicality aspects, the latter class seems more feasible and therefore not only receives high scientific attention in laboratories but also there is a remarkable, ongoing progress towards scaling-up. As a result, a couple of pilot plants have recently been established (La Licata et al., 2011; Lin et al., 2011) and demonstration as well as full-scale facilities may be expected (Guo et al., 2010). Although fermentative hydrogen production is undoubtedly promising and it is developing step by step to a level of real field applications, scientists need to spend additional efforts to enhance the overall process efficiency, preferentially by using waste materials (Sinha and Pandey, 2011). In particular, from the upstream point of view, further advancements are essential to attain better generation rates and yields so that hydrogen can be made more competitive with other energy carriers e.g. in economical terms (Hallenbeck and Ghosh, 2009). Nevertheless, it has been shown that the fate of biohydrogen is also dependent on the successfulness of the downstream technology which may contribute to the intensification of the production side (Bakonyi et al., 2013).

Hence, various biological and engineering approaches have been suggested with the aims mentioned, such as the construction of more sufficient and robust hydrogen producer microorganisms (metabolic- and genetic engineering), fermentation optimization and bioreactor design (Guo et al., 2010). All of these approaches possess high importance because strains require proper surroundings (e.g. pH, temperature, H_2 partial pressure, mass transfer, etc.) to express their advantageous properties (Wang and Wan, 2009). Moreover, since bioreactors are the places of the microbiological hydrogen conversion, their quality features such as type and configuration significantly affect the applications reliability. In the last decade, as a response to the demand for biosystems with upgraded hydrogen generation performance, several researchers have started to deal with the novel and innovative way of combining traditional hydrogen fermenters with membrane technology. Recently, our group comprehensively assessed the integration

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0960-8524/$ - see front matter © 2014 Published by Elsevier Ltd.
http://dx.doi.org/10.1016/j.biortech.2014.01.079

possibilities of membranes and bioreactors for biohydrogen recovery and enrichment in *gas separation membrane bioreactors* (Bakonyi et al., 2013) or in other words, in *hydrogen extractive membrane bioreactors* (Ramírez-Morales et al., 2013). This is one particular way to establish membrane-based systems for fermentative hydrogen technology. Another one is the design of anaerobic bioreactors employing membranes in the liquid phase, which are in the scope of the present paper. Although a couple of review papers have recently been published on anaerobic membranes bioreactors (AnMBR) (Lin et al.,2013; Ozgun et al., 2013; Singhania et al., 2012; Smith et al., 2012) and their potential for hydrogen production was enlightened (Gallucci et al., 2013; Jung et al., 2011), H_2 production in systems combining liquid filtration membranes has not specifically been addressed and evaluated so far.

Therefore, this work attempts to overview the progress on the anaerobic membrane bioreactors used in the fermentative hydrogen technology. Firstly, the main features of conventional, anaerobic membrane bioreactors are presented. Thereafter, several main process considerations (retention time, nutrient loading, membrane related issues) affecting the performance of *anaerobic hydrogen producing membrane bioreactors* (AnHPMBR) are discussed. Finally, the feasibility of AnMBRs for biological hydrogen generation in comparison to the traditional CSTRs will be evaluated.

2. General features of AnMBR systems

AnMBRs have been used for a long time in different fields, mostly in waste water treatment for process intensification purposes even at full-scale plants (Judd, 2008).

Integrated systems assisted by membranes – being either aerobic or anaerobic and regardless the purpose of use – can be distinguished as external loop (Fig. 1A) and submerged (Fig. 1B) bioreactors (Yang et al., 2006). In the former case, as indicated in Fig. 1A, the liquid filtration membrane module is linked to the reactor from outside and handles the circulating fermentation broth. In the latter solution, as demonstrated in Fig. 1B, the membrane module is sunk in the liquid phase of the reactor vessel or sometimes immersed in a separate tank.

Both types of bioreactors have their own advantages and disadvantages. Basically, the external loop arrangement is recognized with a higher operation energy demand but cleaning and replacement of the membrane is easier to perform. On the other hand, submerged membrane bioreactors are less energy intense but require larger membrane surface area to ensure sufficiently high permeate fluxes in comparison to their external loop counterparts (Lin et al., 2013). As foreshadowed in Figs. 1B and 2, AnMBRs can be operated in bubble coarse mode when headspace gases are recycled to the bottom of the reactor through diffusers or spargers. On one hand, it can help mixing and gas bubbles contacting the membrane surface may contribute to reduce the developing cake layer. On the other hand, continuous gas flushing can improve the liquid to gaseous phase mass transfer rate so that dissolved gases are more efficiently removed. Theoretically, it is desirable in the case of dark fermentative hydrogen production since the catalytic activity of hydrogenase enzymes can be sensitive to increasing H_2 concentrations in the aqueous phase (Bakonyi et al., 2013; Hallenbeck, 2009; Nath and Das, 2004; Ramírez-Morales et al., 2013).

Taking into account the possible reactor configurations, membranes are most commonly joined to completely stirred tanks. However, there are some alternative solutions such as certain kinds of upflow- and granular sludge bioreactors (Ozgun et al., 2013). From the viewpoint of the membrane, it can be noticed that membranes made of several commercial polymers e.g. PE, PP, PVDF, etc. are preferentially applied due to process economical reasons. These materials are often built into flat sheet and tubular modules. Furthermore, the hollow fiber configuration is also favorable because of its high packing density (Santos and Judd, 2010).

In general, based on the experiences with anaerobic membrane bioreactors their implementation could appear to be prosperous but it is important to note their limits and drawbacks. It is a common observation that in integrated systems – combining

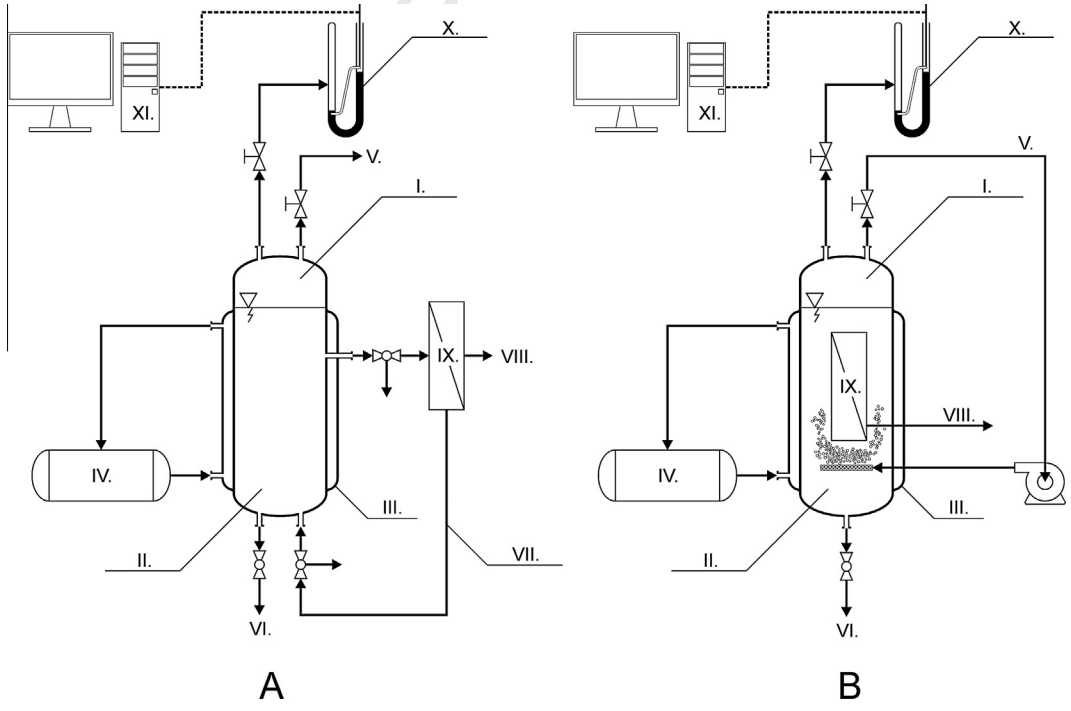

Fig. 1. External loop (A) and submerged (B) anaerobic membrane bioreactors I – Headspace, II – Fermentation media, III – Double-wall water jacket, IV – Temperature control, V – Gas sampling/recycling, VI – Spent media, VII – Retentate stream, VIII – Permeate stream, IX – Membrane module, X – Gas meter, XI – Data acquisition (PC).

Please cite this article in press as: Bakonyi, P., et al. Fermentative hydrogen production in anaerobic membrane bioreactors: A review. Bioresour. Technol. (2014), http://dx.doi.org/10.1016/j.biortech.2014.01.079

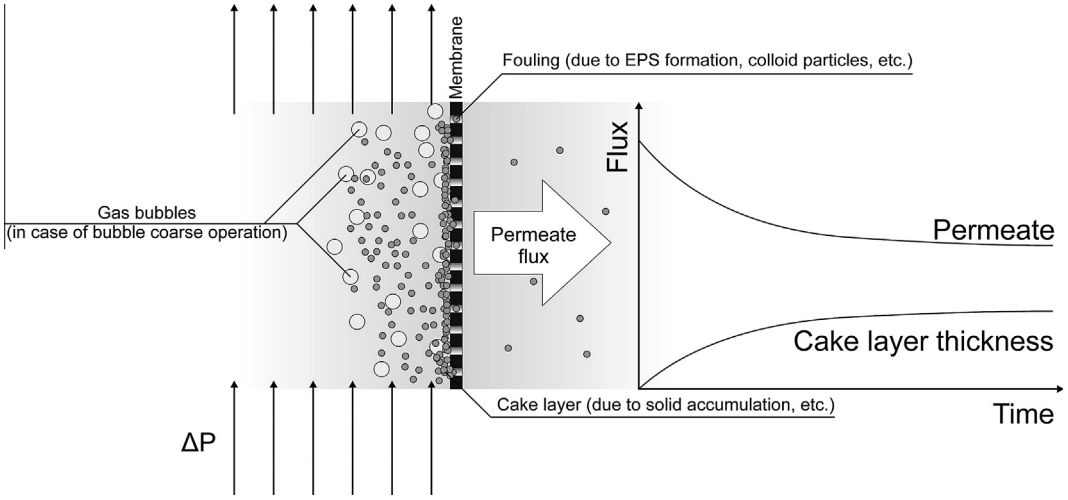

Fig. 2. Cake formation during cross-flow filtration in anaerobic membrane bioreactors.

liquid/solid separation membranes and bioreactors – fouling is a potential threat (Gallucci et al., 2013; Lin et al., 2013). If occurs, it is accompanied by an increased membrane resistance and hence it lowers the most important trait, the flux of the membrane (Fig. 2) and may cause operational failures (e.g. shortened membrane lifetime). Thus, fouling inherently affects the process economy and should be restricted as much as possible. The overall resistance of the membrane (R_o) – expressed by Eq. (1) – is a product of various terms such as the inherent membrane resistance (R_m), the resistance of the cake layer (R_c), the resistance caused by pore plugging (R_p) and the resistance associated with biological activity referring to biofouling (R_b) e.g. biofilm formation.

$$R_o = R_m + R_c + R_p + R_b \quad (1)$$

The sustainability of membrane performance is dependent on a few factors related to the operational circumstances (e.g. shear rate on the membrane surface, operational flux, separation temperature, hydraulic- and solid retention times, etc.), membrane characteristics (e.g. pore diameter – usually 0.2–1 μm, hydrophobicity) and the qualities of the media to be filtrated (e.g. composition, microbial community structure, solid particulate size) (Calderón et al., 2011; Gao et al., 2010, 2011; Liao et al., 2006; Lin et al., 2010; Meng et al., 2009; Ozgun et al., 2013; Singhania et al., 2012; Smith et al., 2012; Szentgyörgyi and Bélafi-Bakó, 2010; Wijekoon et al., 2011).

In case the membrane usability reaches an insufficient level due to the reasons mentioned above, users can turn to various on physical, chemical or enzymatic techniques in order to suppress fouling. The physical ones comprise backwashing, membrane relaxing (Le-Clech et al., 2006) and recently vibration through exposure to ultrasonic irradiation receives noticeable research interest (Sui et al., 2008; Wen et al., 2008). However, these approaches have limited effectiveness and in many cases the troubleshooting of fouling demands more drastic methods such as adding chemicals which encompass bases e.g. NaClO, NaOH and acids e.g. citric-, hydrochloric-, nitric or other agents such as EDTA or ozone (Lin et al., 2013; Sun et al., 2011b). Although these processes are mature and routinely used to recover membrane performance, they might damage the membrane itself (Drews, 2010) and hence alternative biological direction, namely the enzymatic treatment has been proposed by a couple of investigators (Allie et al., 2003; Maartens et al., 2002; te Poele and van der Graaf, 2005).

Furthermore, the external addition of so-called flux enhancers (e.g. poly-aluminum chloride, powdered activated carbon) is also a realistic option to hinder permeability decrease (Aun Ng et al., 2013; Ozgun et al., 2013).

3. Biohydrogen production in anaerobic membrane bioreactors

3.1. The effect of solid- and hydraulic retention times in AnHPMBRs

Hydrogen bioproduction by continuous cultures is frequently carried out in well-mixed vessels in which proliferation of microorganisms is determined by the dilution rate applied, presenting a potential risk for biomass washout (Li and Fang, 2007; Show et al., 2008). Therefore, decoupling hydraulic- (HRT) and solid/biomass retention times (SRT) in anaerobic, hydrogen producing bioreactors (Table 1) possesses several benefits.

Preserving cells in continuous bioreactors can be accomplished in several alternative ways such as the immobilization and recycling of the suspended cells. However, the former may suffer from mass transfer limitations due to the slow diffusion rate of substrates through biofilms or carrier matrices (e.g. alginate beads) that represent an apparent limitation during the process. Nevertheless, retraining cells in a suspended form may help to avoid diffusion limitations. Nowadays, such cell-retention devices ensuring a sufficiently long SRT are attractively designed by using membranes and refer to *anaerobic hydrogen producing membrane bioreactors*.

Previously, tt has been well demonstrated that maintaining longer SRT and shorter HRT might improve the bioH_2 generation efficiency (Hafez et al., 2009). This is because in such systems a more substantial population of active H_2 producer strains can be provided and it expectedly results in a higher biogas turnout and substrate conversion (Jung et al., 2011;Melin et al., 2006) especially when poorly soluble and slowly biodegradable raw materials are the targets of the fermentation (Meabe et al., 2013).

Although it seems that independent solid- and hydraulic retention times are key process variables for a more promising hydrogen production their values should carefully be chosen since it is possible that an immoderate solid retention time decreases the hydrogen formation capacity. Moreover, in general, the levels of HRT and SRT were demonstrated to have an adverse effect on hydrogen yield and volumetric productivity, meaning that peak values may occur under distinct operational (retention time) conditions (Lee et al., 2007; 2010; Kim et al., 2011). Besides, the impacts of SRT could be correlated with the formation of extracellular polymeric substances (EPS), as well. The release of EPS is usually more intense at elevated SRTs and the accumulation of such metabolic side-

Table 1
Performances of anaerobic membrane bioreactors employed for hydrogen fermentation.

Inoculum	Substrate	Retention time		H_2 generation performance (highest values)		Reference
		Hydraulic	Solid/Biomass	Yield	Productivity	
Heat-treated soil inocula	Glucose	3.3–5	3.3–48 h	N.S.	9.2 L H_2/L-d	Oh et al. (2004)
Acid-treated, acclimated sludge	3 Hexoses	1–4 h	N.S.	39 L H_2/mol glucose	66 L H_2/L-d*	Lee et al. (2007)
Heat-treated sludge	Glucose	9 h	450 d	N.S.	2.5 L H_2/L-d	Lee et al. (2008)
Screened anaerobic digester sludge	Glucose	8 h	24 h	40.2 L H_2/mol glucose	4.5 L H_2/L-d	Shen et al. (2009)
Heat-treated sludge	Glucose	9 h	12.5 h	35.4 L H_2/mol glucose	5.9 L H_2/L-d	Lee et al. (2009a)
Heat-treated, acclimated sludge	Glucose	N.S.	90 d	19.5 L H_2/mol glucose	2.5 L H_2/L-d	Lee et al. (2009b)
Heat-treated, acclimated sludge	Glucose	9 h	2–90 d	27 L H_2/mol glucose	5.8 L H_2/L-d	Lee et al. (2010)
Acclimated sludge	Glucose	8 h	24 h	N.S.	4.4 L H_2/L-d	Shen et al. (2010)
Heat-treated sludge	TPW	2–8 h	N.S.	42.4 L H_2/mol hexose**	19.8 L H_2/L-d	Kim et al. (2011)

N.S.: not specified; TPW: Tofu processing waste; *: on fructose; **: hexose added.

products within the reactor may be accountable for the inhibition of H_2 evolution (Lee et al., 2010).

Nevertheless, the literature is not consistent regarding the optimal set of SRT. For example, one study found the 90 days long SRT already unfavorable (Lee et al., 2010), meanwhile another AnHPMBR with extreme solid rejection time as long as 450 days was possible to run without observing any undesired performance loss in terms of hydrogen generation (Lee et al., 2008). These results imply a need for the system- or case-specific determination of the most proper SRT similarly to the case of HRT which is another indicator that allows elucidating the behavior of an AnHPMBR. For instance, varying the HRT can change the nutrients loading rate and thus it likely alters the utilization efficiency of substrates fed and concomitantly the achievable bioreactor performance, as well (Lee et al., 2007; Oh et al., 2004).

Furthermore, alterations in SRT may lead to a remarkable shift in the microbial diversity which in turn is able to directly and completely divert the reactor behavior to a new state being perhaps accompanied by a different biohydrogen production pattern (Oh et al., 2004). This can be attributed to the fact that extended biomass residence time can not only accelerate the proliferation of H_2 evolving bacteria but also that of the competitive and hydrogen-consuming microbes (e.g. methanogenes, homoacetogenes, etc.), or in other words, the population composition can change due to the appearance of new, dominant organisms. Nevertheless, to be straightforward, none of the relevant works in the literature reported on appearing methanogenic activity, not even when high SRT values were maintained. Therefore, addressing the microbial community aging along with SRT deviation can be an interesting object of future investigations.

It is to conclude that though membrane bioreactors are quite frequently employed e.g. for the purpose of biological wastewater treatment as stated above, their applicability in the field of biohydrogen has not reached such dimensions up to now. Hence, these applications should grow to a wider recognition.

3.2. Effect of nutrient loading in AnHPMBRs

The availability of nutrients comprising carbon sources and other substances such as mineral salts is a crucial issue not only in standard free cell- but also in membrane-coupled bioreactors. The first group usually takes the role of substrates that are bioconverted into molecular hydrogen gas.

The hydrogen formation biosystems in AnMBRs design are constructed with the aim of improving the generation efficiency as compared to CSTRs both in terms of H_2 yields and production rates under versatile circumstances e.g. operated with various substrate loading rates. However, the relevant studies on this subject did not provide definitive answers so far whether the deployment of AnHPMBRs could lead to prominent hydrogen formation capacities when testing with different organic loading rates (OLR). In fact, some authors communicated declined H_2 yields and mostly lower H_2 evolution rates in AnMBR mode (Shen et al., 2009). In contrast, other report justified the excellence of AnHPMBR operation over a wide range of organic matter loadings although it showed certain substrate specific dependency (Lee et al., 2007). Additionally, it has been found that a gradually increased OLR (from 4 to 22 g COD/L-d) could aid the H_2 production but the excessively high levels (30 g COD/L-d) caused a noticeable (20%) depression in the gas generation performance (Shen et al., 2010).

Moreover, the degradation efficiency of substrate introduced to the bioreactor was shown to be considerably influenced by the SRT applied, indicating that a sufficiently prolonged solid retention may be a key factor for a better microbiological uptake and organic matter transformation (Lee et al., 2010). Furthermore, Shen et al. (2010) investigated the impact of OLR on the features (concentration, mean diameter) of colloidal organic matter (polysaccharides and proteins) in AnHPMBRs, however, no clear correlations were identified between the factors.

As indicated at the beginning of this section, minor elements present in the broth can strongly affect the successfulness of the hydrogen fermentation in AnMBRs, depending on their concentrations. Accordingly, the iron level of the media is designated as an important variable since it can either improve or suppress the process. It is explained by the fact that most H_2-evolver enzymes are characterized with Fe-content in their active core/site. Thereby, sustainable H_2 production in AnHPMBRs needs proper iron supplementation (Lee et al., 2009a) so that Fe can be utilized as a building element of hydrogenases. However, Fe should not be supplied above a certain tolerable concentration otherwise strains get overloaded and subsequently poisoned that easily leads to reduced hydrogen formation efficiency.

Though several conclusions could be drawn concerning the impact of nutrient loading in AnHPMBRs, further research seems essential with various, currently untested and preferentially complex materials in order to increase the knowledge about the substrate quality- and quantity-dependent behavior of fermentative biohydrogen systems employing membranes.

3.3. The issue of membrane fouling in AnHPMBRs

The microbiological processes themselves can have a notable impact on the overall performance of membranes applied in AnHPMBRs (Table 2) which is a consequence of the metabolic product release of the strains present.

In this regard, the formation of EPS such as proteins, polysaccharides, etc. and biopolymer clusters can increase fermentation liquor viscosity and promote biofilm formation on the surface of the

Table 2
Specific characteristics of anaerobic membrane bioreactors used for fermentative hydrogen production.

Type of AnMBR	Membrane					Reference
	Configuration	Surface area (m^2)/Pore size (μm)	Material	Type of membrane	Supplier	
External-loop	Tubular	0.0055/0.2–0.8	Ceramic	Membralox®	US Filter Co.	Oh et al. (2004)
External-loop	Hollow-fiber	0.1/0.2	PP	MicroDyn MD020CP2 N	Mycrodyn-Nadir GmbH	Lee et al. (2007)
Submerged	Plate-flame	0.1/0.45	PE	Microfiltration	Kubota Co.	Lee et al.(2008)
Submerged	Hollow-fiber	0.047/0.04	PVDF	ZeeWeed® ultrafiltration module	GE Water and Process Technologies	Shen et al. (2009, 2010)
Submerged	Plate-flame	0.1/0.45	PE	Microfiltration	Kubota Co.	Lee et al. (2009a)
Submerged	Plate-flame	0.1/0.45	PE	Microfiltration	Kubota Co.	Lee et al. (2009b)
Submerged	Plate-flame	0.1/0.45	PE	Microfiltration	Kubota Co.	Lee et al. (2010)
External-loop	Hollow-fiber	0.025/N.S.	N.S.	Microfiltration	N.S.	Kim et al. (2011)

N.S.: not specified.

membrane. Consequently, it may lead to (bio)fouling with a concurrent increase in membrane transport resistance and thereby an unsteady operation (Choi et al., 2005; Choo and Lee; 1996; Ramesh et al., 2006; Sun et al., 2008, 2011a; Wang and Li, 2008).

On the other hand, EPS could also express a particularly advantageous effect since they play a main role in the granulation of the microorganisms (Hung et al., 2011), which may govern the hydrogen producing biosystem towards better stability and a more viable performance.

As specified in Section 3.1., the intensity of EPS formation is likely a function of the SRT applied. Therefore, the extent of capturing suspended solids inside the bioreactor, or in other words, the accumulated concentration of certain substances (covering cell-mass, as well) is denoted as a potential factor influencing the membrane's usability. It is because (colloidal) compounds as well as microorganisms can be deposited and adhered on the membrane surface that potentially cuts down the achievable permeate flux in AnHPMBRs (Shen et al., 2010). Upon the sedimentation of living cells onto the membrane interface, biofilm may start to develop and increase the risk of biofouling. (Habimana et al., 2014). Similarly to microbes, EPS are typically neither allowed to pass through the liquid filtration membrane unit and may be bound to the phase barrier surface, inducing severe biofouling. Moreover, it has been elucidated that EPS – because of their pendant functional groups – can likely form complexes with metal cations and/or other ligands present in the fermentation broth. As it has turned out, this phenomenon may not only influence micronutrient availability but also depress permeate flux in membrane-based biohydrogen production reactors (Lee et al., 2008). Apart from the concentration of EPS, suspended organic matter and bacterial cell mass, membrane permeate flux in AnHPMBRs reflects a dependency on parameters such as transmembrane pressure, cross-flow velocity and membrane pore diameter (Oh et al., 2004).

Consequently, membrane durability in AnMBRs is apparently determined by two main groups of variables associated with (1) biological phenomena e.g. EPS release, cell–surface interactions and (2) membrane operation.

However, membrane fouling may take place regardless the membrane operational conditions in AnHPMBRs and occasional regeneration e.g. regular backwashing should be applied to control the phenomena (Oh et al., 2004).

Although anaerobic hydrogen producing membrane bioreactors can suffer from membrane fouling (Lee et al., 2010) e.g. as a result of EPS accumulation, cake formation, high solid (colloidal particle) content, biological growth (biofilm development on the membrane surface) it does not inevitably happen according to the experiences. A couple of literature reports state that it was possible to run the H_2 generation bioreactor for a long time without any membrane-related operational failures (Kim et al., 2011; Lee et al., 2007). This is of significance because each membrane is contributed with cost- and lifetime factors which substantially determine the (larger-scale) feasibility of AnMBRs for biohydrogen generation.

Nevertheless, the phenomenon of membrane fouling in AnHPMBRs deserves a more particular evaluation. Basically, in continuous bioreactors, the SRT/HRT ratio defines a so-called concentration factor for the solid compounds in the broth. As can be seen in Table 1, the relevant studies employed quite distinct SRT/HRT ranging from low and moderate (Oh et al., 2004; Lee et al., 2009a, 2010; Shen et al., 2009) to extremely high values (Lee et al., 2008, 2010). Basically, increasing the SRT/HRT factor yields higher metabolite and suspended solid concentrations under steady-state bioreactor conditions, moreover, it causes the reduction of the permeate fluxes. It is attributable to the fact that during membrane (micro)filtration the streams containing more substances are more difficult to be filtrated (Lee et al., 2008; Oh et al., 2004) since the composition of the media significantly determines the filtration performance.

As a summary, separate HRT and SRT values in AnHPMBRs should be set to obtain a higher biomass density, however it may lead to undesired alterations in membrane effluent fluxes. In case of intolerably decreased liquid permeation, intermittent backwash and relaxing of the membrane may help to recover the performance though these techniques were found to be effective only for relatively short-terms (Lee et al., 2008; Oh et al., 2004). Another way to reclaim decent filtration rate is increasing the driving force (transmembrane pressure difference) of the process. Although enhancing the pressure ratio between the primary and secondary sides of the membrane module sounds quite logical to sustain the intended permeate fluxes, such strategy may lead to undesired consequences in membrane usability. This can be made clear by taking into account the contributions of various factors to the overall membrane resistance (see Eq. (1)). At the beginning of the AnMBR operation when the concentration of solids in the fermentation liquor is relatively lower, suspended solids and colloids start to accumulate on the membrane surface and the developing cake- and gel layer resistances are dominant (Lee et al., 2008). Depending on their thickness, these depositions obstruct the movement of the flowing liquid across the membrane and therefore flux may gradually decline (Fig. 2). At that point if a higher transmembrane pressure gradient is adjusted in order to fix the permeation properties, substances from the surface of the membrane penetrate deep into the pores inherently causing plugging. The occurrence of pore blockage as a result of cake compression is to avoid since it may reflect an even more pronounced impact on fouling as compared to the external layers resistance and from this state of the membrane

it is rather complicated to recover the filtration performance (Oh et al., 2004). Therefore, manipulating the driving force with the aim of regaining membrane unit efficiency is advised only with care and membranes should be regenerated by alternative methods in order to avoid pore clogging.

3.4. Reactor design considerations for biohydrogen production: CSTR vs. AnMBR – which way to go?

The critical assessment of the relevant, available studies implies that AnMBRs are able to compete with CSTRs and both applications can be taken into account as feasible reactor configurations for fermentative hydrogen bioproduction but perhaps for different purposes. Accordingly, it would appear that a CSTR may be slightly better in cases when enhanced biohydrogen yields and/or specific hydrogen production rates are targeted (Lee et al., 2009b; Shen et al., 2009), meanwhile the alternative design of AnMBR presumably allows achieving relatively increased volumetric hydrogen production rates (Lee et al., 2007). However, in some reports, the overall hydrogen evolution performance of AnMBR fairly exceeds that of the CSTR under steady-state operation (Kim et al., 2011; Lee et al., 2008). Furthermore, AnMBRs may provide a more robust and consistent operating possibility.

Nevertheless, the selection between the two competing systems should be made case-specifically since one process may fit better for one particular project, while the other application can be more feasible for other purposes.

Moreover, it is important that not only H_2 yields and production rates as apparent key factors are to be considered when performing a throughout evaluation on the systems but some additional features, such as downstream aspects as well. This is because an overall, multi-aspect analysis of the intended process is able to change the suitability of the different reactor concepts and consequently, increase/decrease the relative attractiveness of CSTR and AnMBR. For example, even though biohydrogen yields are not always as high as in other continuous, free-cell applications, realizing an AnMBR can bring some advantages such as high quality effluent so that there would be no need of any complementary equipment (e.g. sedimentation tank) to recycle cells or to treat the spent media. Bioreactors aided with micro- or ultrafiltration membranes are able to ensure a relatively clean effluent e.g. in terms of solid organic matter and bacteriological parameters (Jeong et al., 2010). Hence, it reduces the need and the cost of any post-fermentation processes.

However, an extensive development of the field is required to establish conclusions on more solid grounds due to the limited number of studies employing AnMBRs for biohydrogen production.

To facilitate the progress in AnHPMBR research, some suggestions may be given for their design, as follows: First of all, the hydrogen producing inocula is of high importance. According to Table 1, heat- or acid pretreated anaerobic populations would appear to be feasible. Furthermore, it seems beneficial to get the inoculum acclimated to a certain substrate in common bioreactors (e.g. in continuously stirred vessels) before integrating the system with a membrane module and switching to AnMBR mode. The shifting time of MBR operation should be at the point when the washout of the whole cell biocatalysts becomes a potential threat in the conventional membrane-less fermenter ensuring equal hydraulic- and solid retention times. During AnMBR mode, the SRT/HRT ratio is a critical process variable for hydrogen production performance. The preliminary results obtained in the reactor lacking the membrane could be used as a benchmark for the ones attained in AnMBR configuration. As for the membranes, microfiltration units (Table 2) seems applicable but a proper operational concept is needed to restrict the chance of bioreactor failures e.g. due to fouling. This claims the adequate choice of the concentration factor (SRT/HRT ratio) and the permeate flux regeneration technique.

4. Conclusion

The present review on anaerobic membrane bioreactors – despite the limited number of relevant papers – indicates that these integrated systems are attractive for biohydrogen production and can be considered as alternative solutions to the most common CSTR applications. However, more research dedication is needed for the further development of the field e.g. to get a better understanding about the interrelationship of bioreactors and *t* coupled membranes, which is a key factor to achieve better performances and a more predictable, controllable and long-term, steady-state operation.

Acknowledgements

This work was supported by the European Union and financed by the European Social Fund in the frame of the TAMOP-4.2.2/A-11/1/KONV-2012-0071 project and the János Bolyai Research Scholarship of the Hungarian Academy of Sciences.

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Please cite this article in press as: Bakonyi, P., et al. Fermentative hydrogen production in anaerobic membrane bioreactors: A review. Bioresour. Technol. (2014), http://dx.doi.org/10.1016/j.biortech.2014.01.079