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Anaerobic membrane bioreactors—a mini review with emphasis on industrial wastewater treatment: applications, limitations and perspectives

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ABSTRACT

Anaerobic membrane bioreactors (AnMBRs) are increasingly being used in industrial wastewater treatment as the technology represents a cost-effective alternative to that based on aerobic processes. Not only AnMBRs are highly efficient in reducing chemical oxygen demand but the organic matter removed is transformed into a useful energy source—biogas. AnMBRs produce effluent that is free of solids and pathogens and rich in nutrients, while occupying a small footprint. As the membrane retains biomass, AnMBRs enhance performance when dealing with inhibitory or toxic substrates, typical of industrial wastewaters. Some drawbacks remain, however, including membrane fouling and its associated effects as well as poor efficiency at lower temperature (AnMBRs are usually operated at mesophilic or thermophilic conditions). Further research is needed on lowering hydraulic retention time, removal of nutrients, removal of specific micro-pollutants, establishing quantitative mass and energy/economic balances and inclusion of efficient dissolved methane recovery. In this mini review, the applications, limitations and perspectives of AnMBRs are summarized and evaluated with an emphasis on industrial wastewater treatment. Moreover, the AnMBR is compared with other wastewater treatment technologies presently available.

Keywords: Anaerobic membrane bioreactor; Industrial wastewater; Membrane fouling; Methane recovery

1. Introduction

Treatment of industrial wastewaters is usually difficult mainly due to rapid changes in their composition; high chemical oxygen demand (COD), pH, salinity, etc; and presence of synthetic or natural substances that inhibit or are toxic toward the activated sludge micro-organisms [1]. Presence of inhibiting or toxic substances can lead to a decrease in biological activity, which in turn will result in lowered system

removal performance, negatively affecting final effluent quality [2,3].

In general, anaerobic treatment technology has been proven over the long term, having been successfully applied in the treatment of a range of industrial and processing wastewaters for more than a century [4].

Anaerobic wastewater treatment offers a number of advantages, including high organic matter removal efficiency, low excess sludge production, stable operation and production of energy in the form of biogas [5].

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In combination with membrane separation, high effluent quality is achieved, with no total solids or bacteria in the effluent. Anaerobic membrane bioreactors (AnMBRs) combine the advantages of anaerobic treatment with membrane separation, making it an attractive approach for the treatment of a broad spectrum of wastewaters [3,6]. Due to their high operation stability, AnMBRs are suitable for treating wastewaters under extreme conditions, including high salinity, high suspended solids content or poor biomass granulation. As a result, AnMBRs are currently of great interest to both researchers and the industrial community, with many laboratory- and pilot-scale studies being undertaken, especially as regards the wide range of industrial wastewaters needing treatment [7,8]. The remarkable increase in interest in AnMBR is reflected in the number of peer-reviewed publications related to AnMBR and industrial/municipal wastewater treatment over the past 15 years found in Scopus (Fig. 1(a)-keyword "AnMBR", Fig. 1(b)—"AnMBR" plus "industrial wastewater", and "municipal wastewater").

Here, we present a mini review, based on a comprehensive literature survey of the current applications, limitations and perspectives for AnMBRs as regards industrial wastewater treatment. In addition, we present a summary of AnMBR, including system configurations and membrane materials, and discuss the advantages and disadvantages in comparison with other wastewater treatment technologies presently available. Finally, we address future perspectives and the needs for further research.

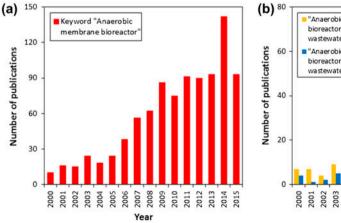
2. Fundamentals of AnMBR

2.1. Reactor configuration

As the membrane used in AnMBRs acts as a total barrier to micro-organisms, it can be located in either of two places in AnMBR system, resulting in two basic AnMBR configurations: pressure-driven cross-flow with external membrane (side-stream; Fig. 2(a)) and vacuum-driven, with the membrane submerged directly in the anaerobic reactor (Fig. 2(b)). A further configuration combines external placement of the membrane, which is submerged in a separate chamber and vacuum-driven operation (Fig. 2(c)).

2.1.1. Side-stream configuration

In the side-stream configuration, the recirculation pump ensures required trans-membrane pressure in the membrane chamber (Fig. 2(a)). As a result, crossflow velocity permanently disrupts formation of a filtration cake on the membrane's surface. While this process consumes energy, any remaining energy can be used to mix the suspension in the anaerobic reactor. The cross-flow velocity along the membrane's surface is typically kept within a range of 2-4 m s⁻¹, in order to achieve optimum operational efficiency as regards filtration cake removal and energy demand [9]. Of importance here is the disintegration of larger sludge agglomerates and flocs due to high shear forces, which leads to a decrease in biomass particle size. Subsequent release of soluble microbiological products can result in more rapid fouling and,



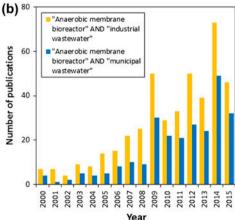


Fig. 1. Number of publication over the past 15 years (Scopus) using the key phrases; (a) "AnMBR" only, and (b) "AnMBR" in combination with "industrial wastewater" and "municipal wastewater". The number of publications in 2015 is shown only till September.

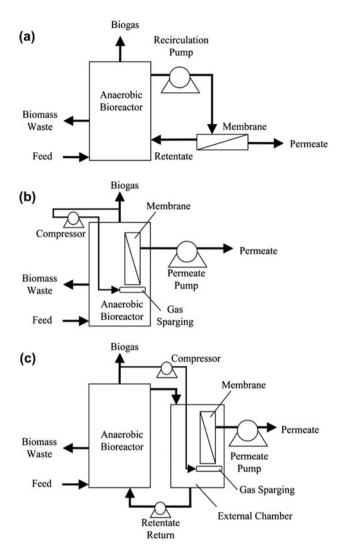


Fig. 2. AnMBR configurations: (a) side-stream (external, cross-flow) configuration—pressure-driven membrane, (b) submerged configuration with membrane immersed directly in the reactor—vacuum-driven membrane, and (c) submerged configuration with membrane in separate chamber—vacuum-driven membrane (figure adopted from Ref. [4]).

especially, membrane clogging [10,11]. Indeed, clogging of membrane pores is a well known and serious issue associated with membrane fouling [12,13]. Fouled membranes require chemical cleaning and this is more easily accomplished when using the sidestream configuration as the membrane is more accessible and can be cleaned without interrupting system operation, unlike submerged membranes that are immersed directly into the anaerobic reactor [14,15]. For the same reason, membrane inspection or replacement is also much easier.

2.1.2. Submerged membrane

The advantage of submerging the membrane directly in the anaerobic reactor lies in the absence of a recirculation pump in the membrane compartment (Fig. 2(b)). As a result, energy consumption is lower than in the side-stream configuration. Furthermore, the absence of a recirculation pump means that there is no cross-flow effect and shear forces are lowered, resulting in less micro-organism stress [14]. Disruption of filtration cake formation on the membrane's surface, along with anaerobic reactor mixing is typically ensured using the produced biogas or an external stirrer. Mixing with biogas, however, can lead to operational problems, especially during AnMBR start-up or when toxic compounds occur in the feed. In such situations, activity of the anaerobic consortia can be inhibited, reducing biogas production to levels too low to ensure adequate mixing in the anaerobic reactor. A mechanical stirrer is commonly installed into the reactor in order to avoid such a situation [16]. Compared with the side-stream configuration, mixing with either biogas or a mechanical stirrer is less efficient in removing filtration cake from the membrane's surface, meaning that membranes become fouled quicker [17]. As mentioned above, chemical cleaning of submerged membranes is difficult as AnMBR operation has to be interrupted and the membrane removed before cleaning [15]. Finally, a larger membrane surface area with submerged membranes is required to achieve the same hydraulic performance as achieved with the side-stream configuration [18].

2.2. Membrane materials and modules used in AnMBR

In general, membrane materials can be divided into three basic categories: polymer, ceramic and metallic. Polymer membranes have the advantage of lower cost compared to ceramic or metallic membranes; hence they are favoured for a broad range of different applications, with ceramic or metallic membranes being used for specialized applications. The polymer membranes used in AnMBRs are typically based on polyvinylidene difluoride (PVDF), polyethersulfone (PES) [19], polyethylene (PE) [20], polypropylene (PP) [21] or polysulfone (PSF) [22]. Polymer membranes do have drawbacks, however, including lower permeability and reduced stability toward chemical cleaning compared with ceramic or metallic membranes [23].

From an operational point of view, ceramic membranes are a more suitable option for AnMBRs than polymer membranes. Under anaerobic conditions, membrane fouling tends to be more pronounced than

in aerobic MBRs [24]; meaning that more concentrated chemicals, higher temperatures and/or longer exposure is required in order to recover membrane permeability. Since ceramic membranes have outstanding chemical and thermal stability, as well as increased resistance to corrosion and abrasion [3], they can be cleaned more effectively compared to polymer membranes [25]. Although metallic membranes exhibit higher hydraulic performance, easier permeability recovery after fouling, improved stability, greater tolerance to oxidation and high temperatures than polymer membranes, they are expensive, hence used only in specific applications [3,24].

Based on the conducted literature survey, most AnMBRs currently use PVDF microfiltration or ultrafiltration membranes (Table 1). Only Xie et al. have tested a flat-sheet dynamic membrane in AnMBR treating the landfill leachate [26]. Unlike the microfiltration or ultrafiltration membranes, the characteristics and performance of dynamic membranes is determined especially by concentration, type, shape, molecular weight of solution being filtered as well as hydrodynamic conditions along the membrane [12].

Hollow-fibre membrane modules tend to be the most commonly used in current AnMBRs (Table 1) likely due to their high packing density and cost efficiency, followed by flat-sheet membrane modules, which show good stability and are easily cleaned or replaced when defective [27]. Despite having a low fouling tendency, due to high cross-flow velocities, and being easy to clean or replace [3], tubular membrane modules are rarely used nowadays as having low packing density and high dead volume [28,29]. Full overview about membrane characteristics used in current AnMBRs is shown in Table 1.

3. Comparison with other technologies and advantages of AnMBR

Many industrial wastewaters contain high concentrations of biodegradable organic matter, making them suitable as feed for anaerobic treatment. Some commonly used anaerobic technologies, such as up-flow anaerobic sludge beds (UASBs), hybrid UASBs, anaerobic filters, expanded granular sludge beds or internal circulation reactors can achieve high organic matter removal efficiencies with such wastewaters, often reaching over 90%. At the same time, the organic matter is transformed into biogas. Effluents from these reactors, however, often contain organic matter and suspended solids [39]. Speece, for example, recorded suspended solids at more than 1 g L⁻¹ in effluent from a UASB [40]. Moreover, the biomass characteristics

(mainly granulation properties) can easily be affected in such systems, with biomass subsequently washed out during operational problems, e.g. when toxic compounds occur in the treated wastewater or during fast system overloading [41,42]. Due to the membrane, AnMBRs are capable to fade concentration and hydraulic peaks unlike conventional anaerobic technologies and thus tolerate fluctuations in organic loading [1]. The membrane ensures that biomass is separated from the effluent; hence this technology shows great promise for the treatment of those wastewaters that negatively impact granular biomass in high-rate anaerobic reactors [3,6].

A number of studies have already confirmed high operational stability, high treatment efficiency and stable biogas production in AnMBRs under extreme conditions, e.g. [3,6]. In addition to separation of suspended solids, AnMBRs are also capable of retaining bacteria and pathogens from effluent and at low energy consumption levels [43]. As the effluent from AnMBR contains nutrients, such as nitrogen and phosphorus, and displays a higher COD than effluents from aerobic MBRs [44], it can be reused for non-potable purposes, especially for irrigation or process waters (depending on required final water quality) [38,45,46]. When effluent is discharged into water bodies, its post-treatment can be needed in order to comply with local standard discharge limits.

AnMBR effluent quality tends not to be affected by changes in biomass settling or granulation properties, unlike that from other anaerobic treatment technologies. Finally, fast system operation recovery is achieved due to the complete retention of biomass by the membrane. According to Tao et al. [47] and van Lier [48], the membrane represents a total barrier to the slow-growing micro-organisms that can remove specific pollutants from industrial wastewaters as they accumulate in the system, regardless of hydraulic retention time (HRT). Tao et al., for example, increased the activity of slow-growing Anammox micro-organisms by 19 times through their retention by a membrane [47].

AnMBRs offer other significant operational advantages in addition to those associated with the membrane. For example, as no oxygen is needed for biotransformation of organic matter, total energy consumption is reduced. Further, the treatment of organic matter produces biogas as a useful end product. Biogas, a renewable energy source, is usually combusted to produce electricity and heat. The heat is then used to ensure appropriate temperatures for anaerobic digestion processes in the reactor. Note, however, that most studies to date have been undertaken under mesophilic (35–37°C) conditions and there is a general

Table 1
Membrane characteristics, including permeabilities (calculated based on presented data) in recent laboratory-scale (L), pilot-plant scale (P) and full-scale (F) AnMBRs; En.—external (side-stream) set-up; In.—internal (submerged) set-up; UF—ultrafiltration, MF—microfiltration, HF—hollow-fibre, FS—flat sheet

Scale	Set- up	Wastewater source	Permeability (LHM bar ⁻¹)	Membrane	Module	Material	Supplier	Refs.
L	Ex.	Bamboo industry	97–14	UF	HF	PVDF	_	[30]
P	In.	Slaughterhouse (side A)	625–50	UF	HF; ZW-10	PVDF	Zenon	[31]
P	In.	Slaughterhouse (side B)	40–8	UF	HF; ZW-10	PVDF	Zenon	[31]
L ^a	In.	Molasses	92	UF	FS	Chlorinated PE	Kubota	[32]
Γ_p	In.	Molasses	96	UF	FS	Chlorinated PE	Kubota	[32]
P^{c}	Ex.	Liquid dairy manure	62	UF	Tubular	PVDF	X-flow	[29]
P^d	Ex.	Liquid dairy manure	10	UF	Tubular	PVDF	X-flow	[29]
L	In.	Landfill leachate	1,200-15	Dynamic	_	_	_	[26]
L	Ex.	Pharmaceutical industry	400–13	ÚF	HF	PVDF	GE-LS1	[33]
L^{e}	Ex.	Pharmaceutical industry	500-13	UF	HF	PVDF	GE-LS1	[33]
L	Ex.	Debris leachate	7–2	UF	HF	PVDF	Norit-X flow	[34]
L	Ex.	Lipid rich corn-to- ethanol thin stillage	-	UF	Tubular	PVDF	Pentair X-Flow	[28]
P	In.	Food industry (oil and grease content)	37	MF	HF	PVDF	Micronet R	[7]
F	In.	Food industry (salad dressings)	417–42	MF	FS	-	Kubota	[35]
L	In.	Food industry	200–114	MF	FS	Chlorinated PE	Kubota	[36]
L	In.	Food industry (sugarcane vinasse)	50–10	MF	HF	Polyetherimide	Pam Membranas Seletivas	[37]
P	In.	Food industry (snacks)	30–7	UF	HF	PVDF	Porous Fibre Spain	[5]
P	In.	Municipal wastewater	40	UF	FS	PES	Microdyn-Nadir	[38]

^aNon-vibrating AnMBR.

lack of studies conducted under thermophilic temperature (only study by Qiao et al. [36]), despite improved filtration due to better sludge rheological properties [49] and the possibility to operate under higher organic loading rates under such conditions [50]. This lack of studies with thermophilic temperature is probably due to the risk of deterioration in performance associated with accumulation of volatile fatty acids, resulting in the inhibition of microbial activity [51]. Furthermore, Meabe et al. noted increased membrane fouling and only slightly higher biogas production under thermophilic conditions compared to mesophilic temperature [49].

While significantly lower operational costs are expected under psychrophilic conditions, only a limited number of studies have been conducted under such conditions [33,34,37,38]. Martinez-Sosa et al. also operated an AnMBR pilot-plant at 20°C; however, the operational period lasted for only 21 d, whereupon the temperature was increased to 35°C [38]. Moreover, the municipal wastewaters treated in this pilot-plant AnMBR were unlike those in the previously mentioned studies.

Operational costs in AnMBR plants are significantly reduced as no oxygen is needed, and a large fraction of the electricity and heating required to

^bVibrating AnMBR.

^cSingle membrane AnMBR.

^dMulti-membrane AnMBR.

^eAnaerobic bio-entrapped MBR.

operate the plant can be covered by the biogas produced. The degree to which such costs are covered will depend on biomass production [52]. Total AnMBR costs for treatment of Kraft mill effluent, for example, were significantly lower than those using aerobic treatment [53]. As a result, the largest percentage of both operational and capital costs during AnMBR operation is attributable to the membrane itself and to factors associated with membrane fouling [3]. Membrane fouling, which decreases flux, is considered the main disadvantage preventing widespread application and faster commercialization of membrane technology in the field of wastewater treatment [54,55]. Hence, membrane fouling, flux decrease and membrane life time, along with cross-flow pumping or gas scouring of the membrane, all have to be calculated into the total operational costs directly associated with use of the membrane. In part because of this, AnMBRs are usually operated at lower fluxes than aerobic MBRs [3,23].

Excess sludge production in AnMBR is lower than in aerobic MBRs [56]; compared to aerobic MBRs up to 20 times [57], thereby further decreasing operational costs. Lastly, AnMBRs also have the advantage of a shorter start-up period compared to UASB reactors, whereas the start-up period for UASB reactors can take several months [58], both Hu and Stuckey [59] and Lin et al. [52] have reported start-up times of only 6 and 12 d, respectively, for AnMBRs.

When compared with the other technologies used in wastewater treatment, e.g. activated sludge process, advanced oxidation processes (AOPs) and biofilm filtration, AnMBRs tend to be less expensive than AOPs and more efficient than either activated sludge systems [1] or biofilm/biofiltration when treating industrial wastewaters under extreme conditions, e.g. high suspended solids content, high salinity, presence of fat and oil or other inhibiting compounds [60].

4. Disadvantages and limitations of AnMBR

While AnMBRs display a number of advantages over "conventional" systems, several problems still remain. As in aerobic MBRs, the most serious drawback in AnMBRs is the membrane fouling [3,12]. Foulwhich results in decreased hydraulic performance, has limited the widespread application of membrane technology [23,61]. Membrane fouling is a complex problem that is affected by a range of factors, including operational conditions, influent characteristics, membrane and biomass properties and their mutual combination [10,12,62,63]. As a result, a wide range of issues related to membrane fouling have been the subject of intensive study. Membrane fouling is

mainly caused by deposition and accumulation of micro-organisms, colloids, solutes and cell debris on or inside the membrane [12,23]. Precipitation of inorganic compounds, mainly struvite (MgNH₄PO₄; magnesium ammonium phosphate), has also been identified as important part of irreversible fouling on membranes in AnMBRs [64]. Other inorganic salts as potassium struvite (K2NH4PO4) and calcium carbonate (CaCO₃) have been also identified in the fouling layer [49,65,66]. Both membrane properties and operational parameters can play a significant role in the rate at which inorganic compounds are precipitated. Meabe et al. [49], for example, reported that fouling by struvite increased at higher operating temperatures (55°C, compared to 35°C) due to increased ammonia nitrogen concentrations.

The filtration cake that is formed on the membrane in AnMBRs is usually harder to remove than that in an aerobic MBR, meaning that a more strict cleaning protocol, using more concentrated chemicals, higher temperatures and/or longer exposure times needs to be applied to remove deposition on membrane in AnMBR. While moderate concentration (from 200 to 500 mg L⁻¹) of NaOCl is typically used in aerobic MBRs [23], for example Ramos et al. applied NaOCl solution having concentration of up to 2,000 mg L⁻¹ for 18 h to remove the filtration cake that formed in AnMBR pilot-plant [67]. Similarly, also Cho et al. used NaOCl around concentration of 5,000 mg L⁻¹ introducing this solution in anoxic/anaerobic MBR pilot-plant [68]. Despite the importance of this issue, there is a general lack of publications dealing with membrane fouling in AnMBR, especially under pilot- or full-scale conditions.

5. Operational costs of AnMBR

Costs associated with the membrane are an important issue limiting widespread application of AnMBR. Although membrane costs have decreased significantly over recent years [23], capital costs of membrane and particularly operational costs associated with filtration process still represent one of the main disadvantages of membrane bioreactors in general. For example, according to Pretel et al. up to 85–90% of the power requirements in AnMBR is related to filtration process and membrane fouling mitigation [69]. Most energy is consumed by membrane tank biogas recycling blower or membrane tank sludge feeding pump representing up to 75% of the total energy demand in AnMBR [69].

Overall, there have been very few studies that have calculated the costs associated with operating AnMBRs, particularly with those that treat industrial wastewaters. One example, Ferrer et al. reported capital and operational expenditure for an AnMBR treating both sulphate rich and low-sulphate municipal wastewaters [70]. These authors reported a clear dependency between increasing mixed liquor suspended solids (MLSS) concentration and membrane scouring, use of chemical reagents and operational costs. The optimum MLSS concentration for this AnMBR was found at 12 g L⁻¹, with an associated specific energy demand of 0.22 kW h m⁻³ of treated wastewater during operation with no energy (biogas) recovery. When the biogas was re-used, the final specific energy demand dropped to 0.14 kW h m⁻³ [70]. Similarly, Pretel et al. reported the energy requirements of AnMBR treating sulphate-rich urban wastewater [69]. They stated the specific energy demand in the range of 0.11-0.49 kW h m⁻³ (depending on various operational and filtration scenarios) when biogas was captured. Enhance in the energy balance of the AnMBR may be also achieved through capturing both the biogas methane and the methane dissolved in the effluent, or operating AnMBR at high ambient temperature and/or high solids retention times (SRT) [69].

Compared to aerobic MBR, for instance Gabarrón et al. reported values for total specific energy demand in a full-scale aerobic MBR reaching 1.54 kW h m⁻³ for flat-sheet membrane and 1.12 kW h m⁻³ for hollow-fibre membrane [71]. Even after implementation of their energy-saving strategies involving mainly optimization of both biological aeration and membrane air-scouring, the specific energy demand reached 1.12 kW h m⁻³ and 0.71 kW h m⁻³, respectively, regardless of similar yearly averaged hydraulic loads [71].

Martin et al. evaluated both the aerobic and anaerobic MBRs and stated the total specific energy demand about 2 kW h m⁻³ for aerobic MBR with complete sludge retention, while in AnMBR the energy demand ranged from 0.03 to 5.7 kW h m⁻³ [72]. The highest energy demand was observed as a result of increased gas demand for intense membrane fouling control.

Another example reporting on AnMBR operational costs is study by Smith et al. [73]. These authors compared, based on the results of process modelling and system analyses, AnMBR with other technologies involving high-rate activated sludge, conventional activated sludge and aerobic MBR, all coupled with anaerobic digestions. It was found that AnMBR has the potential to recover more energy for medium and high strength domestic wastewaters compared with evaluated technologies [73]. The energy recovery, however, strongly depends on composition and

temperature of the wastewater, operational conditions or pre-treatment processes [69,74].

previously mentioned, permeabilities AnMBRs are usually lower than those in aerobic MBRs [3,23]. While permeabilities in aerobic MBRs are typically about 200 LHM bar⁻¹ and more [23], as can be seen from Table 1, the common permeabilities were within the range from 10 to 150 LHM bar⁻¹ in current AnMBRs. The highest initial permeability reached 1,200 LHM bar⁻¹, however, it was observed for dynamic membrane that is characterized by high hydraulic performance. Also the initial permeability of 400 and 500 LHM bar⁻¹ for ultrafiltration membrane reported by Ng et al. was caused by significantly lower MLSS concentration reaching about 7.2 and $1.7 \mathrm{~g~L}^{-1}$, respectively, when compared with other reported studies (Table 2) [33]. Lowered hydraulic performance of AnMBR together with membrane fouling has to be, therefore, taken into account when calculating the total cost balance.

6. AnMBR application in industrial wastewater treatment

According to Skouteris et al., there had been very few scientific studies based around pilot-scale AnMBRs until 2012 [75,76], most studies being conducted under laboratory conditions with laboratory-scale apparatus [50]. Many of the laboratory-scale studies (and some of the pilot-scale studies) have been conducted on AnMBRs fed with synthetic wastewater [21], which is usually used to verify laboratory-scale AnMBR performance or test new reactor/system concepts [4].

To date, AnMBR pilot-plants have been used for the treatment of different wastewaters with a high content of organic matter, such as that from food processing and industrial use (e.g. [51,77]), the pulp and paper industry [52,78-80], textile production [81,82] and polymer synthesis [83]. Most recently, laboratoryand pilot-scale AnMBR plants have been used to treat different food processing wastewater, e.g. from slaughterhouses [31], molasses production [32], dairy manure [29], pharmaceutical production [33] and landfill leachate [26]. While a number of full-scale aerobic MBR studies have been conducted on municipal or industrial wastewaters [23,84-86], there has only been one study to date reporting on a full-scale AnMBR installation for industrial wastewater treatment ([35]; Table 2). This full-scale AnMBR is employed to treat wastewaters originating from salad dressings production. Overview about basic technological parameters of current AnMBRs is summarized in Table 2.

Table 2
Overview of technological parameters used in recent AnMBRs; TS—total solids, TSS—total suspended solids, VS—volatile solids, VSS—volatile suspended solids, MLSS—mixed liquor suspended solids

Scale	Set-up	Wastewater source	Solids (g L ⁻¹)	HRT (d)	SRT (d)	Temp. (℃)	Refs.
L	Ex.	Bamboo industry	8.0-14.0 (VSS)	2–10	_	28–30	[30]
P	In.	Slaughterhouse (side A)	26.1 (TS)	2–7	50-1,000	37	[31]
P	In.	Slaughterhouse (side B)	17.0-40.2 (TS)	4–7	50	37	[31]
L	In.	Molasses (concentrated)	18.7 (TSS)	26	1,535	34	[32]
L	In.	Molasses (diluted)	10.0 (TSS)	5.3	1,535	34	[32]
P	Ex.	Liquid dairy manure (phase 1)	54.0 (VS)	19 (10–35)	19 (10–35)	Room	[29]
P	Ex.	Liquid dairy manure (phase 2)	28.0 (VS)	12	24	Room	[29]
L	In.	Landfill leachate	16.9 (VSS)	2.5	125	37	[26]
L	Ex.	Pharmaceutical industry	6.0-8.4 (MLSS)	21.3-42.6	700	27	[33]
L^{a}	Ex.	Pharmaceutical industry	$1.2-2.1 + 11.0^{b}$ (MLSS)	21.3-42.6	700	27	[33]
L	Ex.	Debris leachate	6.0-7.0 (MLSS)	15.5	_	23	[34]
L	Ex.	Lipid rich corn-to-ethanol thin stillage	15.2-24.9 (VSS)	10.1	20; 30; 50	37	[28]
P	In.	Food industry (oil and grease content)	11.4 (VSS)	_	_	36	[7]
F	In.	Food industry (salad dressings)	20.0-45.0 (MLSS)	_	_	33	[35]
L	In.	Food industry	75.0 (MLSS)	20-70	20-100	57	[36]
L	In.	Food industry (sugarcane vinasse)	20.0 (MLVSS)	_	_	19–27	[37]
P	In.	Food industry (snacks industry)	18.0 (VS)	_	_	30–36	[5]
P	In.	Municipal wastewater	15.0-20.0 (TSS)	-	-	35/20	[38]

^aAnaerobic bio-entrapped MBR.

One of the main operational advantages of an AnMBR is the possibility of operating the reactor at higher SRT compared to conventional digestion technology. In general, high SRTs ensure high COD removal efficiency [28]. Further, high SRTs also help micro-organisms to adapt to the different compounds present in industrial wastewaters, many of which can be difficult to biodegrade, e.g. those in pharmaceutical wastewaters [33], saline wastewaters [32] or both in combination [87]. Dereli et al. [6], Ismail et al. [88] and Lefebvre and Moletta [89] have all reported high salt concentrations as one of the most serious limiting factors for anaerobic systems due to their inhibitory/toxic effects on non-adapted biomass. Following biomass adaptation, however, AnMBRs are capable of achieving very high COD removal efficiencies when fed with otherwise poorly biodegradable wastewater [31,55,90].

As can be seen from Table 3, the lowest COD removal efficiencies were found for liquid dairy manure, with levels reaching around 40% [29]. Note, however, that liquid dairy manure had a COD concentration more than twice that of other feeds (see summary in Table 3), with only molasses wastewater and lipid-rich corn-to-ethanol thin stillage having higher COD concentrations (110.9 and 72.2 g L⁻¹, respectively). Even then, however, removal efficiencies reached 94.4% and >99%, respectively, despite the AnMBR treating the lipid-rich corn-to-ethanol thin

stillage being operated under a lower HRT and a comparable SRT with that for treating liquid dairy manure [28,32]. The AnMBR treating the molasses wastewater was operated at a higher HRT (26 d) and a significantly higher SRT (1,535 d) than the SRT operational maximum of 50 d in AnMBR used for the lipid-rich corn-to-ethanol thin stillage or 35 d for liquid dairy manure.

Biological activity decreases with a decline in temperature and, in anaerobic systems, this results in an associated decrease in COD removal efficiency [91]. As a result, the majority of current studies have been carried out under mesophilic temperatures, e.g. [26,31,32]. Thermophilic temperatures have been applied very rarely (Table 2), with just Qiao et al. used such temperature for the treatment of food industry wastewater [36]. Psychrophilic (or ambient) conditions, on the other hand, have frequently been applied in cases of low-strength wastewater [33,92,93], domestic wastewater [38,75,94] or under higher ambient climate [33,95].

7. The future of AnMBRs and further research needed

It is generally accepted that the quantity of industrial wastewaters of extreme composition will increase in the future. Consequently, increase in the application

^bBiomass concentration attached on carriers.

Table 3
Influent and effluent characteristics, including COD removal efficiency, in recent AnMBRs

Scale	Source of wastewater	Influent (g L ⁻¹)	Effluent (g L ⁻¹)	COD rem. (%)	Refs.
L	Bamboo industry	COD 21.4; NH ₄ -N 0.398	COD 1.5; NH ₄ -N 0.36	85–90	[30]
P	Slaughterhouse (side A)	COD 5.92; NH ₄ -N 0.024; TP 0.019	COD 0.07; NH ₄ -N 0.17; TP 0.014	95	[31]
P	Slaughterhouse (side B)	COD 10.6; NH ₄ -N 0.059; TP 0.036	COD 0.18; NH ₄ -N 0.29; TP 0.025	95	[31]
L	Molasses (concentrated)	COD 110.9; TKN 12.0	COD 10.7	94	[32]
L	Molasses (diluted)	COD 14.5; TKN 1.10	COD 0.5	93	[32]
P	Liquid dairy manure (phase 1)	COD 53.7	_	41	[29]
P	Liquid dairy manure (phase 2)	COD 41.8	_	42	[29]
L	Landfill leachate	COD 13.0; NH ₄ -N 3.2	COD 4.91	62	[26]
L	Pharmaceutical industry	COD 15.4; TN 1.42; PO ₄ ³⁻ -P 0.17	COD 8.77	43	[33]
L^{a}	Pharmaceutical industry	COD 15.4; TN 1.42; $PO_4^{\overline{3}}$ -P 0.17	COD 8.23	47	[33]
L	Debris leachate	SO_4^{2-} 0.5–0.75	SO ₄ ²⁻ 0.05–0.5, Ca ²⁺ 0.2–0.5	$80 (SO_4^{2-})$	[34]
L	Lipid rich corn-to-ethanol thin stillage	COD 72.2; SO_4^{2-} 0.95	COD 0.47	>99	[28]
P	Food industry (high oil and grease content)	COD 7.9–22.8; BOD ₅ 4.9–10.3; TKN 0.08–0.38; PO ₄ ³ –P 0.06–0.16	COD 0.18-0.3	97	[7]
F	Food industry (salad dressings)	COD 39.0; BOD ₅ 18.0	COD 0.21; BOD 0.02	99	[35]
L	Food industry	_	COD 2.0-15.0	67	[36]
L	Food industry (sugarcane vinasse)	COD 17.7	COD 0.49	96	[37]
P	Food industry (snacks industry)	COD 11.0; BOD ₅ 7.3; N 0.2, P 0.04	COD 1.7	75	[5]
P	Municipal wastewater	COD 0.4	COD 0.08	90	[38]

^aAnaerobic bio-entrapped MBR.

of more modern and efficient treatment technologies, such as AnMBR is expected, especially considering the current focus on sustainable production and reduction of carbon footprints. AnMBRs are especially important as regards this latter point due to their ability to produce energy in the form of biogas. As a result, AnMBRs are likely to be applied much more under full-scale operating conditions in the future and over a much broader industrial spectrum [48].

To date, AnMBRs have been applied much more intensively for industrial wastewaters (Fig. 1(b)), with only limited full-scale applications for municipal wastewater treatment. While this is possibly due in part to the relative novelty of the technology, limitations associated with membrane fouling are also an important issue limiting more widespread application [1]. Significant effort needs to be put into rectifying this issue, therefore, before AnMBRs are more widely accepted. Below, several possible ways of improving membrane performance and reducing fouling, and research needs are discussed.

7.1. Operational conditions

Numerous studies have been undertaken on the impacts associated with changing operational parameters and membrane fouling (see e.g. review by Meng et al. [12]). As an example, one method for reducing the concentration of extracellular polymer substances, and thus reducing membrane fouling, is to increase SRT and HRT. It should be noted, however, that membrane fouling mechanism in AnMBRs may be similar to those of aerobic MBRs but the nature of the foulants is different [23]. Precipitation of inorganic salts and struvite in AnMBR, for example, tends to harden the fouling cake, rapidly increasing the rate of fouling [96]. Further studies are also required on the addition of coagulants as a means of reducing membrane fouling, both in anaerobic and aerobic systems.

There is also scope for optimizing reactor and/or membrane chamber design and improving the gas scouring process as a means of permanently reducing membrane fouling.

7.2. Membrane surface modification

Despite significant progress in the development of membrane materials over recent decades, membranes still account for a significant part of reactor capital costs (and, to a certain extent, operational costs), mainly due to fouling and the limited lifetime of present membranes. Hence, efforts are still needed on minimizing membrane fouling, for example through modifying commercial membrane surfaces and/or developing new membrane materials, such as the low-cost filters (Section 7.3) or dynamic and self-assembly membranes (Section 7.4).

Minimization of membrane fouling can be achieved through modification of the membrane's surface. A number of such modification techniques, such as the use of nanotechnology [97] or the preparation of new membrane types with additional surface properties, have been developed and tested to date. Generally speaking, these methods are all based on altering chemical or physical interaction with the membrane's surface, resulting in an increase in hydrophilic surface character [63], i.e. reducing hydrophobic interactions between the membrane's surface and microorganisms or compounds present in suspension [98]. As a direct result, foulants deposited on the membrane are also more readily removed during cleaning.

Chemical modification methods, as for example covalent bonding or "self-assembly" method produce a thin film on the membrane's surface, e.g. [99,100]. A range of compounds have been used for these techniques, including silver and silver nanoparticles, polyethylene oxide, polyvinyl alcohol, zirconium compounds and magnesium or titanium oxide, all of which confer additional properties to the membrane's surface [97,101–103]. Physical modification techniques include, for example, plasmatic membrane surface modification using nitrogen, air [104] or ammonia and carbon dioxide [105,106]. Ultra-violet light and gamma irradiation have also been used physically to alter the surface properties of membranes [107,108]. The main drawback of such high-energy methods, however, is the significant increase in final membrane production costs [101].

7.3. Application of low-cost and alternative membrane materials

Use of low-cost and/or alternative membrane materials not only results in capital savings but can also reduce the operational costs of the membrane unit itself [109]. Several studies have examined the use of alternative membrane materials [109–111], the findings of which indicate no significant loss in effluent quality

compared to that produced using polymer or ceramic membranes. Seo et al., for example, reported COD removal efficiencies of up to 91% in an anaerobic/aerobic bioreactor coupled with a non-woven module [110]. Likewise, Zhi-Guo et al. reported a negligible difference in effluent quality in a non-woven membrane system compared to that using a polymer hollow-fibre membrane [111]. Most of the materials used, to date, however, have been tested under laboratory-scale conditions or in aerobic MBRs. There is a need, therefore, for studies assessing the performance of such materials in pilot- or full-scale AnMBRs.

7.4. Dynamic and self-assembly membranes

Dynamic membranes appear to be a promising approach for solving problems associated with high membrane cost, rapid membrane fouling and low membrane flux as such membranes exhibit low cost with high permeation at low transmembrane pressure [112]. Moreover, dynamic membranes can also improve the effluent quality [112–114].

Dynamic membranes (pre-coated or self-forming) are formed by the settling of fine organic or inorganic particles, present in a filtered suspension, onto a support material (typically a highly porous support). The pre-coated membranes are formed by solution with specific compounds over the surface of porous materials, while the self-forming membranes are composed of components in the solution to be filtered, for example, activated sludge [12]. The performance of dynamic membrane, therefore, depends upon various characteristics and process conditions used, with resulting differences in cake density and cake characteristics, playing a key role in the membrane's permeability. Creation of dynamic membranes, however, differs both between AnMBRs and aerobic MBR system [109,113].

Dynamic membranes can produce effluent of a very high quality; however, effluent characteristics depend very much on the ambient conditions close to the membrane. Hence, dynamic membranes have to be kept under optimal conditions throughout their operation. Since the pore size of such membranes is highly variable, retention of some particles and compounds can be poorer than when using polymer or ceramic membranes. In addition, effluent quality can fluctuate over time due to changes in operational conditions [112]. On the other hand, if permeate quality is not the main criterion, its worse quality can be balanced by the higher hydraulic performance of dynamic membranes (or new membrane materials), together with lowered operational costs. Furthermore,

effluents from anaerobic systems typically undergo a further post-treatment step in order to improve their quality prior to release into the receiving water body.

While searching the literature database for this mini review, only few studies [26,113] could be found regarding use of a dynamic membrane in an AnMBR and, as with the studies focused on low cost and alternative membrane materials, this was performed under laboratory-scale conditions only. Hence, there is a clear need for further studies regarding conditions in the dynamic membrane's active layer and on identifying the optimal operational conditions to ensure middle- to long-term operation of such membranes under pilot- or full-scale conditions.

7.5. Further research needs

In addition to the suggestions made in the sections above, there is a need for detailed studies on membrane fouling in relation to additives such as powder activated carbon, "flux enhancers" or nanomaterials, preferably in pilot- or full-scale AnMBR installations. Such studies could also provide new insights into the AnMBR fouling process itself.

A significant part of AnMBR operational costs (and/or biogas production) goes to keeping the anaerobic reactor at its optimal running temperature (typically around 37°C). Such costs could be reduced if AnMBRs could be run at lower (ambient) temperatures. In undertaking such research, however, careful attention needs to be paid towards lowered activity of anaerobic micro-organisms, particularly as regards hydrolysis [115] and higher suspension viscosities, which lead to lowered hydraulic performance. Furthermore, methane is more soluble under lower temperatures, resulting in significant losses in the effluent. As such, research is needed into improving methane recovery from effluent.

In recent years, there has been an increasing trend towards reuse of wastewater; therefore, dangerous micro-pollutants have to be removed prior to the wastewater reuse. Evidence for the removal efficiency of such dangerous micro-pollutants as phenolic compounds, phthalates and estrogens under anaerobic conditions has been contradictory to date, however, with some studies showing higher removal efficiency than conventional activated sludge systems (e.g. [116]) and others not (e.g. [117]). Furthermore, there is a lack of knowledge on the fate and biodegradation pathways of many micro-pollutants using AnMBR. Both of these issues require urgent studies, especially, taking into account great potential of AnMBR for water reuse. Option of water reuse, together with favourable energy balance predisposes the AnMBRs for coupling

with other wastewater treatment technologies or their integration into so-called "smart waste-handling systems". This fact makes AnMBRs especially attractive for modern water treatment practice.

8. Conclusions

AnMBRs have attracted a lot of attention recently as a possible answer to the increasing need for water reuse, as a means of obtaining renewable energy and reducing greenhouse gas emissions. AnMBRs display numerous advantages over "conventional" technology, particularly as regards treatment of toxic and concentrated wastewaters and for covering the gap between high-rate anaerobic systems and conventional digesters. Despite this, there has been only one full-scale installation (salad dressings wastewater), most studies to date being performed at laboratory- (treating wastewaters from pharmacy and food industry, bamboo and molasses treatment, or landfill and debris leachates) or pilot-scale conditions (treating wastewaters from slaughterhouse, liquid dairy manure or food industry). In part, this is because a number of important issues need to be solved prior to widespread fullscale uptake. Future research efforts, therefore, need to focus on the most critical problems, such as better understanding of membrane fouling and the restriction of fouling through new approaches.

In this respect, detailed evaluation of new membrane materials, such as the low cost, dynamic or self-assembly membranes under anaerobic conditions still needs to be undertaken.

There is also an urgent need to investigate effluent post-treatment, methane recovery from effluent and clarification of micro-pollutant removal pathways. Before full-scale adaptation of AnMBR technology can take place, complete energy and economic balances are also needed.

Only when these major issues have been addressed, AnMBR is likely to reach its full potential as a more "environmentally friendly" and cost-effective alternative to conventional industrial wastewater treatment technology.

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