TITLE:

Benchmarking of low environmental footprint biological processes for the treatment of industrial waste streams

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ABBREVIATIONS

Abbreviation	**Full Phrase**
AD	Anaerobic Digestion
AnMBR	Anaerobic Membrane Bioreactor
CAS	Conventional Activated Sludge
COD	Chemical Oxygen Demand
EGSB	Expanded Granular Sludge Bed
HRT	Hydraulics Retention Time
IFBR	Inverse Fluidized Bed Reactor
LCA	Life Cycle Assessment
OLR	Organic Loading Rate
SBR	Sequencing Batch Reactor
UASB	Upflow Anaerobic Sludge Blanket Reactor
UF	Ultrafiltration

ABSTRACT

Industrial wastewater contains complex and slowly biodegradable compounds which often renders the conventional activated systems (CAS) ineffective. The advanced anaerobic technologies for industrial wastewater are an alternative. This study reviews the different anaerobic configurations, the factors which impact on their final performance and how the operational and design parameters are combined in the most sustainable way. The anaerobic membrane bioreactor, the upflow anaerobic sludge blanket reactor, the expanded granular sludge bed, the anaerobic hybrid reactor, the inverse fluidized bed reactor are the principal anaerobic treatment schemes discussed in the current work. Their major advantages include the low energy requirements, the energy recovery in the form of methane and the capacity for effectively removing high organic loads. pH~7.0, operation in a mesophilic environment and a hydraulic retention time (HRT) long enough to permit the completion of the anaerobic digestion in economically accepted reactor volumes are conditions which optimize the anaerobic schemes' performance. The evaluation takes into consideration environmental aspects. The results of Life Cycle Assessment (LCA) on anaerobic technologies for industrial wastewater reveal their positive environmental effect in terms of greenhouse gases emissions. Methane (a greenhouse gas) is indeed produced during anaerobic treatment. However, it is converted to energy (heat, electricity) and is not emitted to the atmosphere. Thus, it does not contribute to the aggravation of the greenhouse effect.

KEYWORDS

Advanced anaerobic processes, industrial wastewater, anaerobic digestion, methane, sustainability

1. INTRODUCTION

Wastewater originating from industrial activities contains complex and slowly biodegradable organic compounds which are not easy to treat [1]. Thus, appropriate treatment of industrial wastewater is important in order to avoid phenomena such as eutrophication of surface waters, hypoxia and algal bloom which cause further pollution of the scarce clean water resources [2-5]. The design of the industrial wastewater treatment is challenging due to various factors that are related with the characteristics of the industrial streams, such as the high COD load, the different pH values depending on the wastewater origin and the salinity levels [6-7]. Anaerobic treatment has been implemented for the industrial influents by the use of configurations such as the anaerobic membrane bioreactors (AnMBRs), the upflow anaerobic sludge blanket reactors (UASB), the expanded granular sludge bed reactors (EGSB), the anaerobic hybrid (AH) reactor, the inverse fluidized bed reactor (IFBR). Moreover, this technology offers the possibility to produce biogas which is afterwards utilized for the production of electricity and energy [4-5, 7-11]. With the view to achieving sustainable performance, wastewater treatment plants should produce high-quality effluent satisfying the increasingly strict discharge legislation, expand their wastewater reuse and energy recovery potential (moving towards the concept of circular economy), have the capacity for upgrading and retrofitting energy-efficient and cost-effective technologies, decrease the investment costs and, generally, have a low overall environmental impact [2-3, 9, 12-13]. In terms of industrial wastewater treatment, the implementation of anaerobic technology (e.g. AnMBR, UASB etc.) increases the system efficiency so that it meets the standards for the treated effluent reuse or discharge. Nevertheless, the latter does not guarantee the desired low environmental footprint of the plant due to high total energy requirements which are not always outweighed by the biogas production [14-16]. The decision-making upon the most appropriate process/configuration depends on several parameters including the specific origin of each wastewater stream. This is due to the fact that several operational parameters (e.g. addition of chemicals, energy requirements etc.) are selected upon the influent origin; thus, it is important to make the most sustainable choice [17-18]. In this study, the emphasis is put on the anaerobic configurations. Our goal was firstly to investigate how the treatment of industrial streams in anaerobic schemes is influenced by factors such as the influent chemical oxygen demand (COD), the organic loading rate (OLR), the pH, the temperature, the hydraulic retention time (HRT) etc. and, secondly, how these are optimally combined towards a sustainable performance. Biogas production is also used as performance indicator of the examined anaerobic processes. Finally, the life cycle assessment of anaerobic industrial wastewater treatment is presented as a way to holistically evaluate the environmental impact resulting from the application of such technologies.

2. TECHNOLOGIES FOR THE BIOLOGICAL TREATMENT OF INDUSTRIAL WASTEWATER

This section is dedicated to technologies for the industrial wastewater treatment and reuse; the emphasis is put on schemes which stand as an alternative to the Conventional Activated Sludge (CAS) systems. The activated sludge process, although popular and globally applied, requires the use of chemicals and involves high capital, operational and maintenance costs [5]. The sequencing batch reactors (SBRs) are used for municipal as well as industrial wastewater treatment as an improved version of the CAS systems. They operate under a sequence of phases (filling, aeration, settling and decantation) within a single tank which functions both as an equalization tank and as a clarifier. In terms of industrial wastewater treatment, the SBRs produce a high-quality effluent with easy operation and low energy consumption [19-21]. An example for that is the lab-scale study of Jiang et al. [22] who implemented a SBR for the treatment of aniline-rich industry wastewater and observed a COD removal of 95.80%. In addition to the SBRs, anaerobic treatment has been put into practice for the effective treatment of industrial influents [5]. Anaerobic wastewater treatment is the process during which anaerobic microorganisms convert organic material into usable energy (in the form of methane) and an amount of biosolids [23]. It occurs either through attached-growth systems or suspended-growth systems. The main advantages of the attached-growth over the suspended-growth system are the simpler operation, the lower energy requirements, the absence of sludge bulking problems and the bigger resistance to system shocks [24]. In a suspended-growth configuration, a greater number of microorganisms can be retained compared to the attached-growth systems; therefore, a smaller tank volume is required [25]. More specifically, the main configurations for suspended-growth anaerobic wastewater treatment include: the anaerobic membrane bioreactor (AnMBR), the upflow anaerobic sludge blanket reactor (UASB), the expanded granular sludge bed (EGSB), the anaerobic hybrid (AH) reactor, the inverse fluidized bed reactor (IFBR) [26-31].

The anaerobic membrane bioreactor (AnMBR) couples the anaerobic suspended-growth bacteria biological process with membranes for solid-liquid separation, allowing the biomass immobilization. In some configurations, the membrane is placed on the side stream (external, cross-flow configuration) and a recirculation pump provides the required trans-membrane pressure within the membrane chamber. Thus, the cross-flow velocity constantly interrupts the development of a filtration cake onto the membrane. Alternatively, the membrane is submerged either directly in the AnMBR or in a separate chamber. These two configurations require no recirculation pump which reduces the energy consumption and the microorganism stress; the latter is due to the absence of the cross-flow effect and the lesser shear forces. However, the anaerobic conditions are less favorable for the filtration and more prone to fouling; the latter restricts the full-scale adoption of the process [7, 32]. Nevertheless, successful full-scale AnMBR implementations for the treatment of industrial wastewater do exist. The first full-scale AnMBR was installed in North America for the treatment of food industry wastewater with a design influent chemical oxygen demand (COD) of 39,000 mgL^{-1}. The average effluent COD was constantly significantly lower (210 mgL^{-1}). Furthermore, the operating expenses were gradually reduced because the system could progressively treat a higher biomass content and there was less need to dewater and dispose the dewater solids [33]. In smaller scales, Van Zyl et al. [34] measured a COD removal of 96.8% in a lab-scale AnMBR treating coal industrial wastewater and Zayen et al. [35] a COD removal of 90.7% in a pilot-scale AnMBR for landfill wastewater. The major drivers for the wider adoption of the AnMBR process include: low energy requirements, energy recovery in the form of methane, capacity for removing high organic load and low sludge production. On the other hand, the main barriers for the extensive application of AnMBRs are related with the operational cost for the membrane cleaning and replacement as well as with the energy required for the gas recirculation. Other disadvantages are the need for nutrient supplementation and the slow growth of the microorganisms involved [14, 16, 26, 36-38]. All in all, the benefits from biogas recovery can generally counterbalance the operating cost. For example, the energy requirements of a semi-industrial AnMBR plant treating wastewater with high sulfate concentration (105 mg SO_4-S L^{-1}) were minimized to 0.07 kWh m^{-3} at ambient temperature (17-33ºC) after the sludge retention time optimization [39]. Pretel et al. [39] consider the AnMBR treating high-sulfate influents in warm/hot climates capable of producing energy up to 0.11 kWh m^{-3}.

The Upflow Anaerobic Sludge Blanket Reactor (UASB) is another suspended-growth system where the sludge granules grow in a tubular reactor [40]. It is the most frequent option for the anaerobic domestic wastewater treatment mainly in warm climates; high temperatures offer the appropriate conditions for the anaerobic degradation. The latter along with the simple operation, the good pathogen removal, the limited land requirements and the ability to treat high organic loads justify the wide UASB application in developing tropical countries [41-43]. There are successful UASB applications on industrial streams. For instance, the lab-scale UASB of Djalma Nunes Ferraz Junior et al. [44] treating industrial wastewater from ethanol production (COD removal=96.1±1.7%) and the lab-scale UASB of Sivakumar and Sekaran [45] treating dairy wastewater (COD removal=94.70%). Despite the positive aspects in the UASB use, a modified UASB version, the Expanded Granular Sludge Bed (EGSB) reactor, was developed in order to attain higher upflow velocities and loading rates [46]. The higher upflow velocity increases the fluidization of the granular sludge bed which, subsequently, improves the contact between the wastewater and the sludge [47]. For example, Petropoulos et al. [48] worked on a lab-scale EGSB treating winery wastewater and observed a COD removal≤96.0%. Another efficient scheme is the anaerobic hybrid (AH) reactor which couples the anaerobic filtration with the UASB concept and has been successfully applied for various industrial wastewaters such as wine industry wastewater (e.g. lab-scale study of Wahab et al. [49]: COD removal=94.0%) and brewery wastewater (e.g. lab-scale of Li et al. [50]: COD removal=92.0%) [29, 51]. Finally, since the beginning of the century, fluidized beds have been placed within the reactors in order to achieve shorter HRTs than the respective ones in UASB systems. The inverse fluidised bed reactors (IFBRs) offer the possibility of treating bigger wastewater volumes in a limited space because they provide increased specific surface area for the biomass; this is how the shorter HRTs are attained. The implemented floatable particles have a lower specific density than the liquid; thus, the particles are fluidized downwards. The produced biogas flows in the opposite direction than the liquid and this enhances the bed expansion. Thus, the fluidization velocities in this inverse system are lower than in the upflow ones, which leads to lower energy consumption [10, 27, 52]. Examples for the successful IFBR application are the lab-scale studies of Arnaiz et al. [52] for dairy wastewater and Alvarado-Lassman et al. [53] for brewery wastewater with COD removal≥90.0% in both.

On the whole, suspended-growth systems for anaerobic treatment (AnMBR, UASB, EGSB, IFBR etc.) are significantly successful in the cases of industrial influents and they perform with satisfying COD removal and energy recovery. The crucial point is to carefully select the design parameters and ensure their optimal combination so that the anaerobic digestion successfully occurs. Then, the cost related to oversizing and membrane cleaning is minimized.

3. PERFORMANCE OF ANAEROBIC TECHNOLOGIES FOR INDUSTRIAL WASTEWATER TREATMENT: HOW IS IT AFFECTED?

This section discusses how the performance of the examined anaerobic technologies for the treatment of industrial wastewater can be affected. Table 1 provides an overview of existing studies on the treatment of industrial streams by the implementation of the technologies mentioned in section 2**.** The goal is to identify how target parameters (e.g. OLR, pH, temperature, HRT) influence the performance of the system in terms of target contaminants removal.

Table 1: Effect of target parameters on the efficiency of alternative anaerobic systems for the treatment of various industrial streams.

Reference	Scale/ Configuration	Industrial Wastewater Source	Temp. (°C)	pH	HRT or Cycle duration	OLR (kg CODm^{-3}d^{-1})	Influent COD (mgL^{-1})	COD Removal (%)	CH_4 production or other observation
[54]	Pilot-scale External-Crossflow UF AnMBR	Brewery	36±1	6.9-7.2	HRT=2.5-4.2d	28.5	80,000-90,000	97.0	• CH_4 content of biogas drops from 80.0% to 65.0% towards the end of the operation • CH_4 yield: 0.28 m^3 CH_4/kg COD removed
[55]	Lab-scale External-Crossflow UF AnMBR	Distillery	53-55	7.5-8.5	HRT=15d	2.06	22,600	97.0	• The biogas production rate steadily increases and is stabilized≈2.8Ld^{-1} • CH_4 content of biogas≈ 55.0%
[30]	Lab-scale External-submerged AnMBR	Bamboo industry	28-30	7.4-8.0	HRTs (d): • 2 (OLR=11.0 kg COD/m^3) • 5 (OLR=4.4 kg COD/m^3) • 10 (OLR=2.2 kg COD/m^3)	• 11.0 (HRT=2d) • 4.4 (HRT=5d) • 2.2 (HRT=10d)	22,000	• HRT from 5d to 10d: from 91.0% to 93.0% • HRT from 10d to 2d: from 93.0% to 80.0% • Final: 91.0%	• HRT≥5d: membrane fouling can be effectively controlled
[56]	Lab-scale UASB (Hollow centered packed bed)	Palm oil mill	55	6.8-8.0	HRT=2d (for the optimised set of operating parameters)	27.65 (for the optimised set of operating parameters)	32,580±9,500	91.8 (for the optimised set of operating parameters)	• CH_4 content of biogas≈ 60.0% • Max COD removal (=97.5%) with OLR=6.66 kg COD m^{-3}d^{-1}, HRT=5d and biogas with 65.6% of methane
[57]	Pilot-scale UASB	Sugar-processing	35	6.0-7.0	HRT=1d	13.8	128,400	87.0-95.0	• CH_4 content= 68.5%·at 13.8 kg-COD m^{-3} d^{-1}
[58]	Lab-scale EGSB	Brewery	20 and 15	6.8-7.2	HRT=18h	• 20°C: 9.7 • 15°C: 5.5	• 20°C: 7,300 • 15°C: 4,100 for 85.0 % removal efficiency • 15°C: 5,200 (only 73.0% removal efficiency)	• 20°C: 85.0 (for COD load 7,300 mg/L) • 15°C: 85.0 (for COD: 4,100 mg/L) ≠73.0 (for COD: 5,200 mg/L)	• From 20 to 15°C: proportion of *Methanosaeta* (acetate-utilizing methanogens) decreases from 60.0% to 49.3% • Reactor performance strongly influenced by temperature under psychrophilic conditions.
[59]	Pilot-scale EGSB	Coal gasification	35	7.0-7.5	HRT=4d	0.63	2,340-2500	65.0	• CH_4 production rate= 227.23 mL-CH_4 L^{-1} d^{-1} at 0.63 kg-COD m^{-3} d^{-1}

[20]	Lab-scale Anaerobic SBR	Palm oil mill	26-30	8.33-9.14	Cycle duration=22h (fill, react, settle, decant)	1.8-4.2	13,950-17,050	95.1-95.7	• Anaerobically digested palm oil mill effluent needs aerobic SBR post-treatment to meet the discharge limits
[29]	Lab-scale anaerobic hybrid (AH) reactor and SBR	Fruit-juice	26	7.5	• Single-stage AH: HRT=10.2h • Two AH reactors: HRT=20h • Two-stage AH followed by SBR: HRT=31h	• Single-stage AH: 11.8 • Two AH reactors: 5.9 • Two-stage AH followed by SBR: 5.3	4,980±1,706	• Single-stage AH: 42.0% • Two AH reactors: 67.4% • Two-stage AH followed by SBR: 99.0%	• The integrated system of two-stage AH reactors followed by a SBR produces an effluent which can be reused in agriculture.
[27]	Lab-scale IFBR	Pulp and Paper	36±1	7.5	• Continuous operation: HRT=3.5h • Batch operation: HRT=8h	20	1,000-8,000	• Continuous operation: 81.0% • Batch operation: 92.0% (with the progression of the batch cycles)	• Combined start-up strategy: continuous-batch operation • Continuous operation: 0.237 L-CH_4/g COD • Batch operation: 0.283 L-CH_4/g COD (with the progression of the batch cycles)
[10]	Lab-scale IFBR	Dairy	10	6.8-7.2	HRT=2d	0.5	1,000	69.0±10.0	• CH_4 production: 0.241L-CH_4 d^{-1} • Poor mixing in the reactor provokes poor hydrolysis of the substrate and, thus, low COD removal

3.1 COD removal efficiency, OLR and pH

The origin of the industrial effluent plays an important role in the efficiency of the examined anaerobic processes for the achievement of satisfying COD removal and energy recovery. The type of the industrial process affects the characteristics of the produced wastewater; it determines the COD and nutrients level, the pH and the concentration of other pollutants [4]. In 1983, Speece [60] had already underlined that there was no controversy over the suitability of anaerobic wastewater treatment for the industrial wastewaters. According to Speece [60], the emphasis was on the rate/degree of industrial wastewater degradability to methane given that the industrial influents composition can be detrimental to the methanogenic activity. Rajeshwari et al. [47] underlined the need to design/modify an existing reactor based on the influent characteristics in order to achieve, amongst others (e.g. biogas production), the desired COD removal. For instance, Najafpour et al. [61] claimed that the start-up period (2-4 months) required within a UASB is long and suggested the use of an AH reactor as an alternative for the successful palm oil mill treatment; the AH rector had a start-up period of 26 days and accelerated the anaerobic granulation. In the case of distillery wastewater, Rajeshwari et al. [47] recommended the application of a UASB along with aerobic post-treatment in order to meet the desired COD discharge levels.

Table 1 summarizes the results of studies which deal with the treatment of different industrial wastewater streams characterized by different COD levels. Thus, the range of the initial COD concentration can vary from 1,000 mg/L in the study of Bialek et al. [10] (dairy wastewater treated in a lab-scale IFBR) to 80,000-90,000 mg/L in the study of Anderson et al. [54] (brewery wastewater treated in a pilot-scale AnMBR) and 128,400 mg/L in the study of Kim et al. [57] (sugar-processing wastewater treated in a pilot-scale UASB). The results of the studies reported in Table 1 reveal that the application of suitable anaerobic processes can lead in high COD concentration removal. Anderson et al. [54] and Kim et al. [57] observed that the COD was removed by 97.0% and 87.0-95.0% respectively, whereas in the case of the significantly less loaded influent of Bialek et al. [10] the COD removal was only 69.0±10.0%. Anderson et al. [54] noted that the increase of the mixed liquor volatile suspended solids (8.0→50.0 kgm^{-3}) had no negative effect on the COD removal efficiency after ensuring the maintenance and recirculation of the digester sludge under good physical conditions (heating, mixing etc.); the methanogenic bacteria, however, were negatively affected leading to the decrease of the methane content of the biogas from 80.0% to 65.0% towards the end of the operation. Kim et al. [57] positively correlated the composition of the active bacterial and archaeal communities (84.0% of *Lactococcus* and 80.0% of *Methanosaeta*, respectively) with the methane production and the organic loading rate (4.01 L-CH_4 at 13.8 kg-COD m^{-3} d^{-1}). They optimized the operation by investigating in advance the response of the active UASB microbial community to different OLRs [57]. Bialek et al. [10] explained their results through the poor mixing in the implemented IFBR, which subsequently, induced a poor hydrolysis of the substrate. The COD removal efficiency in Table 1 was higher than 80.0% for all the examined processes and initial COD loads. It can be deduced that, after optimizing the conditions which enhance the methanogenic activity, the anaerobic process (with or without the use of pre/post-treatment depending on the wastewater stream and the configuration) can be a good option for industrial effluents characterized by high level of organic content.

Given the variety of effluents and corresponding COD loads presented in Table 1, the OLRs differed from study to study within a range of 0.5 kg COD $m^{-3}d^{-1}$ [10] to 28.5 kg COD $m^{-3}d^{-1}$ [54]. Lower OLRs are accompanied with higher COD removal efficiencies. The latter was demonstrated in the study of Wang et al. [30] (lab-scale AnMBR treating bamboo industry wastewater: 80.0% removal efficiency at OLR=11.0 kg COD $m^{-3}d^{-1}$ and 93.0% at OLR=2.2 kg COD $m^{-3}d^{-1}$) as well as in the work of Poh and Chong [56] (lab-scale UASB for the treatment of palm oil mill wastewater: 91.8% removal efficiency at OLR= 27.65 kg COD $m^{-3}d^{-1}$ instead of 97.5% removal efficiency at OLR=6.66 kg COD $m^{-3}d^{-1}$). Although higher OLRs accelerate granulation, they also disturb the balance between acidogenic and methanogenic populations leading to a poor reactor performance [56, 62]. For this reason, it is essential to apply an optimal OLR which does not sacrifice the effluent quality over the methane yield.

The anaerobic digestion strongly depends on the pH [63]. pH shocks (pH > 9.0) in a system applying anaerobic process coupled with membranes resulted in less biogas production and poor membrane performance, since anaerobic digestion takes place at a pH range from 6.5-8.5 and, ideally, at a pH between 7.0 and 8.0 [16, 64-66]. The optimal pH for the methanogenic bacteria is 6.8-7.2; if the pH drops to more acid values the acidogenic bacteria activity prevails over the methanogens. As a consequence, acid zones are formed inside the reactors and the methane production is reduced [67]. Moreover, the pH shocks lead to dispersion of the sludge flocs. Small-sized particles (e.g. colloids) exist in the sludge suspension and get placed onto the membrane surface. As a results, increasing membrane fouling occurs [65]. Considering the above, the fact that the pH is maintained around 7.0 in the majority of studies listed in Table 1 seems coherent. Nevertheless, the pH stabilization requires the addition of chemicals, especially in the case of industrial streams which are characterized by low pH [16]. Consequently, the need for the pH neutralization increases the overall operational cost and the environmental footprint of the applied process. The high COD removal efficiencies in Table 1 consist a preliminary indication of the efficiency of the examined anaerobic schemes as an alternative or supplement to the CAS systems in the domain of industrial wastewater treatment (at least at lab-scale as the majority of the studies in Table 1). An example for the successful combination of anaerobic and CAS technology is the pilot-scale study of Wu et al. [68] where a 3-stage system of a catalytic-ceramic-filter anaerobic reactor followed by an UASB and, finally, at the last stage, by an activated sludge reactor achieved an overall 98.0% COD removal efficiency while treating monensin production wastewater. All things considered, the decision-making on the combination of target factors (e.g. OLR, pH etc.) is crucial for the sustainable operation of the examined anaerobic processes in industrial wastewater treatment. Firstly, it can be concluded that the use of chemicals for the adjustment of the influent pH at ~7.0 must be optimized in order to reduce the environmental impact and the cost of the process. Secondly, high COD removal efficiency can be obtained when the process operates at low OLR.

3.2 Temperature

Higher temperatures are considered to be favourable for methane production, but disadvantageous for the immobilization of the anaerobic biomass. Thus, in industrial wastewater influents which possibly have remarkably high temperatures (e.g. 90.0ºC), pre-cooling is needed for mesophilic (20.0-42.0ºC)/thermophilic anaerobic treatment (42.0-75.0ºC) [16, 23, 47]. Anaerobic treatment under mesophilic conditions results in satisfactory biogas production and moderate energy requirements for the pre-cooling of the influent. The majority of the studies included in Table 1 apply the anaerobic process at mesophilic environment. The effect of low temperature in the process performance is examined by Bialek et al. [10] using a psychrophilic (10.0ºC) lab-scale IFBR for dairy wastewater and by Xing et al. [58] who examined the application of a lab-scale EGSB at 20.0 ºC and 15.0ºC for the treatment of brewery wastewater. Bialek et al. [10] applied psychrophilic conditions in order to investigate the efficiency of the anaerobic treatment in northern countries where the yearly average temperature is below 15.0ºC. Xing et al. [58] observed that by lowering the temperature from 20.0ºC to 15.oºC the proportion of *Methanosaeta* (acetate-utilizing methanogens) decreased from 60.0% to 49.3%, which subsequently resulted in a reduced methane production. The COD removal efficiency was also affected; at 20.0^{o}C, the COD removal was 85.0% (for a COD load of 7,300 mgL^{-1}), whereas at 15.0^{o}C the COD removal was 85.0% (for a lower COD load of 4,100 mgL^{-1}) and only 73.0% (for a slightly increased COD load of 5,200 mgL^{-1}) (Xing *et al.*, 2009). It is demonstrated that comparable removal efficiencies can be attained at lower temperatures through the application of a lower COD load. The application of mesophilic conditions in anaerobic treatment is recommended for process sustainability or, equivalently, the optimal combination of the following: optimal conditions for the occurrence of the anaerobic digestion, sufficient COD removal and satisfying methane production. If the anaerobic process takes place at a mesophilic instead of a psychrophilic environment, the possible additional cost for the pre-cooling of the influent (in case it happens to have a temperature >42.0ºC) is reduced. Thus, the energy recovery (in the form of methane) is not outweighed by the pre-cooling energy requirements.

3.3 HRT

Long HRTs are usually applied during anaerobic treatment of industrial effluents in order to ensure that the substrate hydrolysis and the methanogenesis are given enough time to occur [16]. This is in accordance with Wang et al. [30] who observed a decrease of the COD removal (from 93.0% to 80.0%) with a HRT decrease from 10 to 2 days. Moreover, a COD removal of 97.0% was achieved in the AnMBR of Choo and Lee [55] treating distillery wastewater at a HRT equal to 15 days. Tawfik and El-Kamah [29] applied a lab-scale integrated system of a two-stage AH reactor followed by an SBR for the treatment of fruit-juice industry wastewater. COD removal was 99.0% after the application of a HRT of 31h for the whole system [29]. Shorter HRTs lead to a shorter contact time between the sludge and the substrate and, consequently, to a poorer system performance; a significant amount of biomass does not settle and is washed out without appropriate treatment [30]. On the other hand, the need to decrease the overall cost and operate in smaller reactor volumes pushes towards the application of lower HRTs [69]. Taking into consideration that the anaerobic treatment tanks are characterized by a high concentration of suspended solids, an insufficient HRT increases the accumulation of soluble microbial components onto the membrane, which subsequently aggravates membrane fouling [30, 37]. The latter was one of the main drivers of the study of Wang et al. [30] who tested the effect of different HRTs (2, 5 and 10 d) on the membrane fouling in their lab-scale AnMBR for a bamboo industry stream; minimum HRT (≥ 5 days) was required for an effective control of the membrane fouling. This last observation reveals the need to discover the optimal effective HRT for each configuration. Firstly, an optimal HRT is long enough to ensure the efficient substrate degradation and the limited accumulation of solubles onto the membrane. In addition, it is short enough to require economically acceptable reactor volumes for its application.

3.4 Biogas production

One of the major advantages in the anaerobic wastewater treatment is the recovery of biogas which usually has the following composition: 70.0-90.0% of methane (CH_4), 3.0-15.0% of carbon dioxide (CO_2) and 0.0-15.0% of nitrogen (N_2) [16]. Biogas with more than 60.0% of methane is desired in order to avoid further treatment before using it for digester heating, electricity generation and fuel production [16, 56]. Lower methane yields can be explained by the high methane solubility especially in lower temperatures, such as 15.0ºC [16, 70]; this justifies the decreased methanogenic activity in the study of Xing et al. [58] (lab-scale EGSB treating brewery wastewater). Higher temperatures generally benefit the methane generation [16]. For example, Kim et al. [57] obtained a production of 4.01L-CH_4 d^{-1} under mesophilic conditions (35.0°C), whereas Bialek et al. [10] found lower production (i.e. 0.241L-CH_4 d^{-1}) in a psychrophilic environment (10.0°C). In addition, pH constitutes an inhibitory parameter for the methane generation if it is below 6.0 or above 8.5; the optimal pH ranges between 7.0 and 8.0 [16, 64]. The majority of the studies in Table 1 apply pH around 7.0 in order to eliminate the effect of this parameter in biogas production. Finally, Poh and Chong [56] concluded in the following interesting observation in their study (thermophilic environment: 55°C and pH~7.0): the most efficient methane production (biogas with 65.6% of methane) along with a COD removal of 97.5% occurred by applying OLR=6.66 kg COD $m^{-3}d^{-1}$ and HRT=5d. However, another combination of parameters with a higher OLR and a lower HRT (OLR=27.65 kg and HRT=2d) was found to be the optimal; it resulted in satisfying methane content (57.4%) and COD removal (91.8%) while demanding lower reactor volume due to the lower applied HRT [56]. It can be concluded that the anaerobic process sustainability requires the maximal methane generation under the optimal combination of parameters such as the OLR and the HRT. In this way the operational cost (e.g. reactor volume) will not prevail over the gain from the energy recovery.

4. ENVIRONMENTAL ASSESSMENT

It is essential that an anaerobic configuration is effective from both a technological and an environmental perspective. Thus, there is a need to assess the overall environmental performance of an anaerobic scheme throughout its operation by taking into account the environmental impact of every stage involved. For this reason, Life Cycle Assessment (LCA) is conducted [71]. In order for an LCA to be highly holistic, it is important that it considers the biggest possible number of representative environmental indicators for each process. In the case of anaerobic industrial wastewater treatment, the LCA vectors can be related to energy and resource requirements, sources of greenhouse gases emissions, toxicological data, technical costs etc. [71-73]. Georgiopoulou et al. [74] applied LCA to evaluate the potential environmental and economic impact of five different biological technologies for dairy wastewater treatment. They compared the following: activated sludge, high-rate and extended aeration (a modified activated sludge process for influents with high organic and nitrogen load), predenitrification (activated sludge process with an anoxic reactor before the aeration basin), aerated lagoon (an earthen basin used as an aerobic reactor) and anaerobic digestion (a UASB reactor). They found that the anaerobic digestion was the most environmentally friendly option since it presented the lowest greenhouse gases emissions and energy requirements [74]. Foley et al. [75] examined the environmental impact of three industrial wastewater treatment options (i.e. full-scale data from anaerobic treatment with biogas generation, pilot-scale data for microbial fuel cell treatment with direct electricity generation and lab-scale data for microbial electrolysis cell with hydrogen peroxide production) through a LCA. They observed that the negative environmental impacts were related to electricity consumption and transportation/disposal of biosolids in all the examined processes. The anaerobic digestion demonstrated a more environmentally friendly performance than the microbial fuel cell treatment in terms of resource requirements and greenhouse gases generation. The microbial electrolysis cell with hydrogen peroxide production had the biggest positive impact amongst all the three technologies mainly due to the production of chemicals (hydrogen peroxide); however, it was noted that the limited scale (lab-scale) of the data concerning its operation was likely to have led to the underestimation of its negative environmental impacts [75]. O'Connor et al. [76] aimed at evaluating and comparing the environmental performance of different configurations for the pulp and paper effluent treatment based on the following six processes: primary clarification, dissolved air flotation (primary treatment), aerobic activated sludge, UASB (secondary/biological treatment), ultrafiltration and reverse osmosis (tertiary/membrane treatment). They found no single configuration which was optimal in terms of greenhouse gases emissions, water recovery, freshwater aquatic ecotoxicity and eutrophication discharge impact reduction. Nevertheless, the LCA indicated that the pre-treatment of the activated sludge in the UASB resulted in significant reduction of the freshwater aquatic ecotoxicity and the eutrophication discharge impact [76]. It was not feasible to concentrate different LCA studies on anaerobic industrial wastewater treatment under comparable conditions. Thus, a robust critical analysis amongst the cited LCA studies is difficult. However, it is indicated that the anaerobic technology is promising in terms on greenhouse gases emissions mitigation. The latter is possible if we consider that during the anaerobic digestion methane, which is a greenhouse gas, is produced and is later used for heating purposes, electricity and fuels production etc. instead of being emitted to the atmosphere.

5. CONCLUSIONS

The anaerobic technologies for wastewater treatment can effectively treat the industrial streams and produce biogas under conditions which promote the anaerobic digestion and the methanogenic activity. The latter is accomplished through the combination of a pH~7.0, a mesophilic environment and a minimal HRT which ensures the efficient substrate degradation under economically acceptable reactor volumes. In that case, the efficient treatment is achieved together with energy recovery without high operational/maintenance costs and negative environmental impacts. Especially in terms of greenhouse gases emissions mitigation, the anaerobic technologies for industrial wastewater treatment can be beneficial; the produced methane (greenhouse gas) is converted to energy and is not emitted to the atmosphere,

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