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Review

Sustainable Agro-Food Industrial Wastewater Treatment Using High Rate Anaerobic Process

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Abstract: This review article compiles the various advances made since 2008 in sustainable high-rate anaerobic technologies with emphasis on their performance enhancement when treating agro-food industrial wastewater. The review explores the generation and characteristics of different agro-food industrial wastewaters; the need for and the performance of high rate anaerobic reactors, such as an upflow anaerobic fixed bed reactor, an upflow anaerobic sludge blanket (UASB) reactor, hybrid systems *etc.*; operational challenges, mass transfer considerations, energy production estimation, toxicity, modeling, technology assessment and recommendations for successful operation.

Keywords: anaerobic digestion; agro-food wastewater; biogas; high-rate systems; sustainable wastewater treatment

1. Introduction

Agro-industries are major contributors to worldwide industrial pollution. Effluents from many agro-food industries are a hazard to the environment and require appropriate and a comprehensive management approach. Worldwide, environmental regulatory authorities are setting strict criteria for discharge of wastewaters from industries. As regulations become stricter, there is now a need to treat and utilize these wastes quickly and efficiently. With the tremendous pace of development of sustainable biotechnology, substantial research has been devoted recently to cope with wastes of ever increasing complexity generated by agro-industries. Anaerobic digestion is an environmentally friendly green biotechnology to treat agro-food industrial effluents. In addition, the carbon emission and, therefore, the carbon footprint of water utilities is an important issue nowadays. In this perspective, it is essential to consider the prospects for the reduction of the carbon footprint from small and large wastewater treatment plants. The use of anaerobic treatment processes rather than aerobic would accomplish this purpose, because no aeration is required and the biogas generated can be used within the plant. Anaerobic digestion is unique, as it reduces waste and produces energy in the form of methane. Not only does this technology have a positive net energy production, but the biogas produced can also replace fossil fuel; therefore, it has a direct positive effect on greenhouse gas reduction. Thus, the carbon-negative anaerobic digestion process is considered as a sustainable wastewater treatment technology, which also provides the best affordable (low-cost) process for public health and environmental protection, as well as resource recovery. The attractiveness of biogas technology for large scale applications has been limited, essentially, because of the slow rate and process instability of anaerobic digestion. The slow rate means large digester volumes (and consequently, greater costs and space requirements) and process instability means the lack of assurance for a steady energy supply. These two major disadvantages of conventional anaerobic processes have been overcome by high rate anaerobic reactors, which employ cell immobilization techniques, such as granules and biofilms. Thus, various reactor designs that employ various ways of retaining biomass within the reactor have been developed over the past two decades. The purpose of this article is to summarize the current status of the research on high rate anaerobic treatment of agro-food industrial wastewater and to provide strategies to overcome some of the operational problems.

2. Agro-Food Industrial Wastewaters

About 65%–70% of the organic pollutants released in the water bodies in India are from food and agro-product industries, such as distilleries, sugar factories, dairies, fruit canning, meat processing and pulp and paper mills [1]. Similarly, the pulp and paper industry is one of the most significant industries in Sweden, as well as many other countries around the world, and the products constitute important industrial trade in terms of value of production [2]. Wine production is one of the leading agro-food industries in Mediterranean countries, and it has also attained importance in other parts of the world, such as Australia, Chile, the United States, South Africa and China, with increasing influence on the economy of these countries [3]. The wine industry generates huge volumes of wastewater that are mainly originated from several washing operations, e.g., during crushing and pressing of the grapes, cleaning the fermentation tanks, containers, other equipment and surfaces. In addition to this, olive oil

industries have gained fundamental economic importance for many Mediterranean countries [4]. Malaysia presently accounts for 39% of world palm oil production and 44% of world exports [5]. Due to its surplus production, a huge amount of polluted wastewater, commonly referred to as palm oil mill effluent (POME) is generated. Fia *et al.* [6] reported that in coffee producing regions, such as Brazil, Vietnam and Colombia, the final effluent produced from this process has become a large environmental problem, creating the need for low cost technologies for the treatment of wastewater. Nieto *et al.* [7] determined the potential for methane production from six agro-food wastes (beverage waste, milled apple waste, milk waste, yogurt waste, fats and oils from dairy wastewater treatment and cattle manure). The wastewater generation varies from country to country. For instance, world wine production in 2011 was estimated to be about 270 million hectoliters, with the European Union producing 152 million hL (France with 50.2 million hL; Italy, with 40.3 million hL; Spain, with 35.4 million hL), whereas it was estimated to be 18.7, 15.5, 11.9, 10.6, 9.3 and 2.3 million hL for countries, such as the USA, Argentina, Australia, Chile, South Africa and New Zealand, respectively [8]. The annual worldwide production of olive oil is estimated to be about 1750 million metric tons, with Spain, Italy, Greece, Tunisia and Portugal being the major producers, and about 30 million cubic meters of oil mill wastes (OMW) are generated annually in the Mediterranean area during the seasonal extraction of olive oil [4,9].

The composition and concentration of different agro-food wastewaters vary from low (wash water from sugar mill or dairy effluents) to high strength substrates (cheese, winery and olive mill wastewaters), particularly in terms of organic matter, acids, proteins, aromatic compounds, available nutrients, *etc.* [1,3,10]. The main parameters of the agro-food industrial wastewater, such as total solids (TS), total nitrogen (TN), total phosphorus (TP) and biochemical and chemical oxygen demand (BOD and COD), respectively are given in Table 1.

Table 1. Characteristics of typical agro-food industrial wastewater.

Industry	TS (mg L ⁻¹)	TP (mg L ⁻¹)	TN (mg L ⁻¹)	BOD (mg L ⁻¹)	COD (mg L ⁻¹)	Reference
Food processing ^a	-	3	50	600–4,000	1,000–8,000	[11]
Palm oil mill	40	-	750	25	50	[12]
Sugar-beet processing	6100	2.7	10	-	6,600	[13]
Dairy	1,100–1,600	-	-	800–1,000	1,400–2,500	[14]
Corn milling	650	125	174	3,000	4,850	[15]
Potato chips	5,000	100	250	5,000	6,000	[16]
Baker's yeast	600	3	275	-	6,100	[17]
Winery	150–200	40–60	310–410	-	18,000–21,000	[1,3]
Dairy	250–2,750	-	10–90	650–6,250	400–15,200	[18]
Cheese dairy	1,600–3,900	60–100	400–700	-	23,000–4,0000	[1]
Olive mill	75,500	-	460	-	130,100	[19]
Cassava starch	830	90	525	6,300	10,500	[20]

Notes: ^a contains flour, soybean, tomato, pepper and salt. TS: total solids; TN: total nitrogen; TP: total phosphorus; BOD: biochemical oxygen demand; COD: chemical oxygen demand.

3. High Rate Anaerobic Reactors

High-rate anaerobic digesters receive increasing interest, due to their high loading capacity and low sludge production [21]. The commonly used high-rate anaerobic digesters include: anaerobic filters, upflow anaerobic sludge blanket (UASB) reactors, anaerobic baffled, fluidized beds, expanded granular sludge beds (EGSB), sequencing batch reactors and anaerobic hybrid/hybrid upflow anaerobic sludge blanket reactors [1,21].

Rajagopal *et al.* [22] developed high-rate upflow anaerobic filters (UAFs) packed with low-density polyethylene media for the treatment of wastewater discharged from various agro-food industries with different composition and COD concentrations *viz.* synthetically prepared low strength (~ 1.9 g COD L⁻¹), fruit canning (~ 10 g COD L⁻¹), winery (~ 20 g COD L⁻¹) and cheese-dairy (~ 30 g COD L⁻¹) wastewaters. High organic loading rates (OLRs) ($12\text{--}27$ g COD L⁻¹ d⁻¹) were reported in this study. Low-density polyethylene support (29 mm high; 30–35mm diameter; density: 0.93 kg m⁻³; specific area: 320 m² m⁻³) was able to retain between 0.7 and 1.6 g dried solids per support. This study concluded that the low-density polyethylene support is a good colonization matrix to increase the quantity of biomass in the reactor compared to conventional treatment systems.

In a similar study, Ganesh *et al.* [3] investigated the performance of upflow anaerobic fixed-bed reactors filled with low density supports of varying size and specific surface area for the treatment of winery wastewater. They found that efficiency of reactors increased with decrease in size and increase in specific surface area of the supports. A maximum OLR of 42 g L⁻¹ d⁻¹ with 80% COD removal efficiency was attained, when supports with the highest specific surface area were used. However, for long-term operation, clogging might occur in the reactors packed with small size supports.

Esparza *et al.* [23] reported that a pilot-scale upflow anaerobic sludge blanket (UASB) reactor treating cereal-processing wastewater at 17 °C with OLR 4–8 kg COD m⁻³ d⁻¹ and a hydraulic retention time (HRT) of 5.2 h removed 82%–92% of the COD. Shastry *et al.* [24] investigated the feasibility of a UASB reactor system as a pretreatment for hydrogenated vegetable oil wastewater. COD removal efficiency of 99%–80% at OLR varying in the range 1.3–10 g COD L⁻¹ d⁻¹ was obtained with a specific methane yield of 0.30–0.35 m³ CH₄ kg⁻¹ COD.

Won and Lau [25] operated an anaerobic sequencing batch reactor (ASBR) to investigate the effect of pH, HRT and OLR on biohydrogen production at 28 °C. For a carbon-rich substrate, a maximum hydrogen production rate and yield of 3 L H₂ L⁻¹ reactor d⁻¹ and 2.2 mol H₂ mol⁻¹ hexose, respectively, were achieved at pH 4.5, HRT 30 h and OLR 11.0 g L⁻¹ d⁻¹. A mesophilic anaerobic sequencing batch biofilm reactor (ASBBR) treating lipid-rich wastewater with OLR as much as 12.1 g COD L⁻¹ d⁻¹ was achieved with 90% COD removal efficiency [26].

Shanmugam and Akunna [27] investigated the performance of a granular bed baffled reactor (GRABBR) for the treatment of low-strength wastewaters at increasing OLRs (up to 60 g COD L⁻¹ d⁻¹). They showed experimentally that GRABBR encouraged different stages of anaerobic digestion in separate vessels longitudinally across the reactor, and it had greater process stability at relatively short HRTs (1 h) with 86% methane in biogas. Bialek *et al.* [28] assessed the performance of two kinds of reactors (inverted fluidized bed (IFB) and expanded granular sludge bed (EGSB) reactors) treating simulated dairy wastewater. At 37 °C, they obtained more than 80% of COD and protein removals with an OLR of 167 mg COD L⁻¹ h⁻¹ and a HRT of 24 h.

Rajagopal *et al.* [29] proposed a modified UAF reactor design, called “hybrid upflow anaerobic sludge-filter bed (UASFB) reactor”, to overcome problems faced by fixed bed reactors, such as clogging, short circuiting and biomass washout. This configuration contains a sludge bed in the lower part of the reactor and a filter bed in the upper part. For the treatment of wine distillery vinasse (21.7 g COD L⁻¹) they achieved a high OLR (18 g COD L⁻¹ d⁻¹) at a short HRT (26 h), while maintaining high COD removal efficiencies of about 85%. However, an aerobic post-treatment is required to make the effluent fit for final disposal, especially in terms of nitrogen [3,14,22]. Table 2 summarizes the performance of anaerobic digesters for the treatment of various agro-food wastewaters in terms of design and applied operational conditions, process efficiency and energy characteristics.

Other Treatment Strategies to Enhance the Reactor Performance

Biogas production can be augmented by using ample lignocellulose materials *viz.* agricultural and forest residues [30,31]. However, the complex lignocellulose structure limits the accessibility of sugars in cellulose and hemicellulose. Consequently, a pretreatment is essential and several potential pretreatment techniques have been developed for lignocellulose material [32].

Nkemka and Murto [31] evaluated the biogas production in batch and UASB reactors from pilot-scale acid catalyzed steam-pretreated and enzymatic-hydrolysed wheat straw. They showed that the pre-treatment increased the methane yield [0.28 m³ kg⁻¹ volatile solids (VS) fed] by 57% compared to untreated straw. The treatment of straw hydrolysate with nutrient supplementation in a UASB reactor resulted in a high methane production rate (2.70 m³ m⁻³ d⁻¹) at an OLR of 10.4 g COD L⁻¹ d⁻¹ and with 94% COD reduction.

Badshah *et al.* [2] proved that the methanol condensate can be efficiently converted into biogas in a UASB reactor instead of methanol, with much of the smell of the feed eliminated. Bosco and Chiampo [33] reported polyhydroxyalkanoates (PHAs) (biodegradable plastic) production from milk whey and dairy wastewater activated sludge. They defined the suitable C/N ratio, the pre-treatments required to lower the protein content and the effect of pH correction.

Garcia *et al.* [34] investigated the effect of polyacrylamide (PAM) for the biomass retention in an UASB reactor treating liquid fraction of dairy manure at several organic loading rates. They have concluded that PAM addition enhanced sludge retention and reactor performance (with a total COD removal of 83% compared to 77% removal efficiencies for UASB without polymer addition).

In order to remove ammonia nitrogen, Yu *et al.* [35] attempted to enrich anammox bacteria in sequencing batch biofilm reactors (SBBRs) with different inoculations. The maximum total nitrogen loading rate of SBBR gradually reached 1.62 kg N m⁻³ d⁻¹, with a removal efficiency higher than 88%. Few researchers [36,37] reported that anammox bacteria have slow growth rate kinetics, and hence, they are vulnerable to external conditions, such as low temperature, high dissolved oxygen and some inhibitors. Although this technique faces some complications in full-scale applications, such as long start-up and instability, anammox is still an innovative technological development in reducing ammonia from wastewater [35,38].

Table 2. Performance of anaerobic digesters for the treatment of various agro-food wastewaters.

Substrate	Reactor type ^a	TCOD (g L ⁻¹)	pH	HRT (h)	OLR (g COD L ⁻¹ d ⁻¹)	TCOD removal (%)	SCOD removal (%)	VFA/alkalinity	Comments	Reference
Fruit canning	UAF	9–11.6	6–6.5	12	19	68	81	0.35	Specific sludge loading rate (SSLR): 0.56 g COD g ⁻¹ VSS d ⁻¹	[1]
Cheese dairy	UAF	23–40	6–6.5	40	17	71	82	0.6	SSLR: 0.63 g COD g ⁻¹ VSS d ⁻¹	
Winery wastewater	FBR	18–21	8–11	15–23	22–42	65–70	80	0.8	SSLR: 0.93–1.2 g COD g ⁻¹ VSS d ⁻¹	[3]
Dairy manure	UASB	16.5–20.4	7.4	36–48	9–12.7	76.5–83.4	-	-	- Methane yield: 0.296–0.312 L CH ₄ g ⁻¹ COD; - Higher values corresponded to UASB with polymer addition	[34]
Dairy wastewater	AF/BAF	1.8–2.4	6.6–8.4	18.2–38.6	0.66–0.72	98–99 (Overall)	-	-	- Recirculation ratio ranged 100%–300%; - Specific growth rate of the integrated biomass: 0.621–1.208 d ⁻¹	[39]
Distillery vinasse	UASFB	3.1–21.7	6–6.5	25–27	17.9–18.2	80–82	84–87	<0.4	SSLR: 0.43–0.47 g COD g ⁻¹ VS d ⁻¹	[29]
Food processing	JBILAFB	0.96–7.9	3.4–11.2	24	1.6–5.6	80	-	0.2–0.5	- Methane production: 0.414 m ³ L ⁻¹ reactor volume day ⁻¹ ; - Specific energy input for the anaerobic reactor: 0.12 kWh m ⁻³	[11]
Cassava starch wastewater	UMAR	10.5	4.5–4.92	6	10.2–40	77.5–92	-	-	- The optimum HRT was 6.0 h at influent COD of 4000 mg L ⁻¹ ; - Specific methanogenic activity: 0.31 and 0.73 g COD _{CH4} g ⁻¹ VSS d ⁻¹ for the first and second feed	[20]
Olive mill effluent	UMAR	5–48	~7	240–120	5–48	81–87	-	-	Maximum biogas production: 1.4 m ³ m ⁻³ d ⁻¹	[19]

Notes: ^a UAF: upflow anaerobic filter; FBR: anaerobic fixed bed reactor; UASB: upflow anaerobic sludge blanket reactor; AF/BAF: integrated anaerobic/aerobic filter system; UASFB: hybrid upflow anaerobic sludge-filter bed reactor; JBILAFB: full-scale jet biogas internal loop anaerobic fluidized bed; UMAR: upflow multistage anaerobic reactor; TCOD: total chemical oxygen demand; HRT: hydraulic retention time; OLR: organic loading rates; SCOD: soluble chemical oxygen demand; VFA: volatile fatty acids; VSS: volatile suspended solids; VS: volatile solids.

4. Specific Design and Operational Considerations

Within the high rate anaerobic treatment technologies, the immobilization of the microorganisms in the fixed bed reactors and the formation of the granules in UASB have been recognized as the two most frequently used anaerobic techniques to reduce the HRT during the anaerobic digestion of wastewater having low organic matter concentration [1,21]. The upflow fixed bed and UASB reactors are discussed in the subsequent sections.

4.1. Upflow Fixed Bed Reactors

The upflow fixed bed reactors or upflow anaerobic filter (UAF) is one of the earlier designs, and its characteristics are well defined [3,22,40]. The UAF is a relatively simple technology; and in engineering terms, it is not as complex as fluidized bed reactors, and in biological terms, it does not require the formation of a granular sludge, a prerequisite for the UASB reactor, which is usually very difficult to maintain. Also, fixed-film processes are inherently stable and resistant to organic and hydraulic shock loading conditions [6]. Since there is no provision made for intentional wastage of excess biomass from the filters similar to UASB reactors, clogging occurs with continued operation [1].

To accommodate the accumulation of non-attached biomass without plugging of the bed, the early designs of low voidage, rock-packed reactors have largely been replaced by systems that incorporate synthetic packing materials [6,41]. The microorganisms' immobilization on surfaces of synthetic carrier material is an increasingly used strategy to enhance biological treatment. The preferable features of the immobilized cells in comparison to the non-immobilized counterparts includes lower sensitivity to toxic loads, greater catalytic stability, longer microbial residence time, more tolerance to oligotrophic conditions and lower biomass washout risk [42,43].

Nikolaeva *et al.* [40] used waste tire rubber and zeolite as microorganism immobilization supports; Fia *et al.* [6] used blast furnace cinders, polyurethane foam and crushed stone as the supporting materials with porosities of 53%, 95% and 48%, respectively. Other materials that have been utilized for the adhesion of biomass included brick ballasts [44], Raschig rings (1.2 cm diameter \times 1.2 cm) [45], low and high-density polyethylene media [3,22,35,41], polypropylene pall rings [46], non-woven disks [47], porous polyurethane foam [48] and modified porphyritic andesite (WRS) as ammonium adsorbent and bed material [49]. Rajagopal [1] suggested the unclogging procedures with fluidization by gas re-circulation or using liquid, which can be applied whenever clogging occurs. Such a problem can also be overcome by using UAF filled (80% or lower by volume) with low-density floating media [22]. Recently, biofilm reactors have also attracted more attention, especially for treatment of wastewaters containing bio-recalcitrant, inhibitory and toxic compounds [50,51]. However, there is a necessity of (i) post-treatment to reach the discharge standards for organic matter, nutrients (e.g., NH_4^+ , PO_4^{3-} , S^2) and pathogens; and (ii) purification of biogas [22,52].

4.2. UASB Reactors

The chief characteristics of a UASB reactor that makes it the established high-rate anaerobic digester worldwide (particularly in tropical countries) is the availability of granular or flocculent sludge, allowing it to achieve high organic matter (COD) removal efficiencies without the need of a

support material [21,34,52,53]; the natural turbulence caused by the rising gas bubbles enhances the reactor content mixing and provides efficient wastewater and biomass contact. Therefore, mechanical mixing is not required, thus significantly reducing the energy demand and its associated cost.

Nevertheless, there are still unresolved issues in the anaerobic treatment technology. One of the major drawbacks of these reactors has been the requirement of a long solids retention time, which is not associated with the increasing volume of sludge produced from industrial and human activities [21]. Garcia *et al.* [34] listed various factors affecting granulation and, then, efficiency in UASB reactors *viz.* composition and concentration of organic matter in wastewater to be treated, operating temperature, pH, high ammonia nitrogen concentrations, presence of polyvalent cations, hydrodynamic conditions, inoculated seed and the production of exo-cellular polymeric substances by anaerobic bacteria. Rajagopal *et al.* [29] mentioned that with poor sedimentation characteristics in high loaded anaerobic reactors with suspended solids, the active biomass can be washed out from the reactor with the effluent, causing digester instability. Other drawbacks have been the long start-up period, flotation and disintegration of granular sludge, sludge bulking, deterioration of performance at low temperatures, high sulfate concentration, impure biogas and insufficient removal of organic matters, pathogens and nutrients in the final effluent, thereby failing to comply with the local standards for discharge or reuse [39,52,54,55].

4.3. Integrated Approach: Modified Configurations and Combined Systems

The researchers have been trying to find out new technologies to enhance the performance of anaerobic digesters, especially on the effluent quality, start up and biogas purification, in order to develop a global sustainable wastewater treatment technology. Rajagopal *et al.* [29] proposed the hybrid upflow anaerobic sludge-filter bed (UASFB) reactors, in which the filter bed is located above the sludge bed zone, to reduce the risk of biomass washout from the reactor, especially at high loading rates. This configuration also improved the hydrodynamics characteristics by minimizing the clogging and short circuiting problems inside the reactors.

Lim and Fox [39] developed an anaerobic/aerobic filter (AF/BAF) system for the treatment of dairy wastewater, primarily to remove organic matter and nitrogen simultaneously. The influent was blended with recirculated effluent (100%–300%) to allow for pre-denitrification in the AF, followed by nitrification in the BAF. The average COD removal efficiency was 79.8%–86.8% in the AF, and the average total nitrogen removal efficiency was 50.5%–80.8% in the AF/BAF system. They have concluded that linear velocity was a critical parameter to determine sloughing of biomass in the AF.

Huang *et al.* [56] studied the mesophilic two-phase anaerobic system for the treatment of maize ethanol wastewater, particularly in terms of start-up, cultivation and the morphology of mature granular sludge in an improved methanogenic UASB reactor. By gradually increasing volumetric loading rate and regulating internal circulation, the UASB reactor developed bigger size granules (more than 1.3 mm), and hence, a quick start-up was achieved. They observed that the microfloras of mature methanogenic granular sludge were mainly *Brevibacterium* and filamentous bacteria.

A three-phase separator configuration increased the COD removal by 20%, biogas yield by 29% and decreased biomass wash out by 25% in an UASB treating fruit canning wastewater [57]. An intermittent feeding strategy at an OLR of 4.8 g COD L⁻¹ d⁻¹ of olive mill wastewater applied to an

inverted anaerobic sludge blanket (IASB) reactor improved long chain fatty acids mineralization, prevented biomass washout and yielded $1.4 \text{ m}^3 \text{ CH}_4 \text{ m}^{-3} \text{ d}^{-1}$ [19]. Diez *et al.* [58] reported that an anaerobic membrane bioreactor (AnMBR) removed 97% of the COD of oil and greasy wastewater (COD of 22 g L^{-1}) at an OLR of $5.1 \text{ kg COD m}^{-3} \text{ d}^{-1}$. Kim *et al.* [59] implemented a high-rate two-phase system (OLR = $6.5 \text{ g COD L}^{-1} \text{ d}^{-1}$) of an anaerobic sequencing batch reactor (ASBR) and an upflow anaerobic sludge blanket (UASB) reactor in series to treat synthetic dairy wastewater treatment. The overall lipid and COD removals were about 80%.

A three-stage configuration of a pre-acidification tank and sequential upflow anaerobic sludge bed reactors (UASBRs) at OLRs of $2.8\text{--}7 \text{ g COD L}^{-1} \text{ d}^{-1}$ has been used to treat raw cheese whey with an effluent recycling achieved COD removal of 50%–92% and fat removal of 63%–89% [60]. An upflow anaerobic packed bed (UAPB) reactor filled with seashell treated cheese whey at OLRs of 1.6 to $9.9 \text{ g COD L}^{-1} \text{ d}^{-1}$, and HRTs of 6–24 h at $25 \text{ }^\circ\text{C}$ removed 95% of COD [61].

In order to upgrade the quality of anaerobically treated effluent to a level recommended for irrigation, Yasar and Tabinda [62] integrated the UASB reactor with UV and AOPs (advanced oxidation processes) (Ozone, $\text{H}_2\text{O}_2/\text{UV}$, Fenton and photo-Fenton) primarily for complete color and COD removal and disinfection of pathogens.

5. Mass Transfer Considerations

Rajagopal [1] described that substrate mass transfer into biomass occurs most rapidly when the bio-particle surface-to-volume ratio is high. According to that research, the suspended growth anaerobic processes generate relatively small bio-particles with optimal surface-to-volume ratios. Fixed film or attached growth reactors are often considered to be susceptible to bio-film surface area limitations. In this respect, Chen *et al.* [63] concluded that the bed expansion ratio of a super-high rate anaerobic bioreactor correlated positively with superficial gas and liquid velocities, while maximum bed sludge content and maximum bed contact time between sludge and liquid correlated negatively. Ganesh *et al.* [3] addressed the effect of media design on treatment performance and stated that physical parameters, like the type of media, its size and shape, affect the performance of waste treatment. Chen *et al.* [64] modeled the dynamic behavior and concentration distribution of granular sludge in a super-high-rate spiral anaerobic bioreactor (SSAB) and found that these two parameters depend on the ecological environment of microbial communities and substrate degradation efficiency along the bed's height. The sludge transport efficiency of up-moving biogas in SSAB is less than that in a UASB reactor. Yang *et al.* [65] analyzed the mass transfer in tubular membrane anaerobic bioreactors operated under gas-lift two-phase flow using fluid dynamic modeling. They found that the results with water were in contrast to those with sludge. The sludge filterability strongly influences the transmembrane pressure, and there is a difference between the mass transfer capacity at the noses and the tails of the gas bubbles. Feng *et al.* [66] reported a rapid-mass transfer in a fluidized bed reactor using brick particles as carrier materials; at increasing OLRs from 7.37 to $18.52 \text{ kg COD m}^{-3} \text{ d}^{-1}$ and HRT of 8 h, COD removals between 65% and 75% was obtained. To minimize non-idealities in reactor hydraulics, most anaerobic reactor designs utilize proprietary systems for enhancing process mixing. Anaerobic contact systems rely on mechanical or gas recirculation systems that must be properly sized for the specific application [1].

6. Energy Production Estimation

The production of a useful and valuable product during agro-food wastewater treatment, such as hydrogen and/or methane, could help to lower treatment costs [1,67]. Using a single-chamber microbial electrolysis cell with a graphite-fiber brush anode, Wagner *et al.* [67] generated hydrogen gas at the rate of 0.9–1.0 m³ m⁻³day⁻¹ using a full-strength or diluted swine wastewater. Under the best conditions, the specific hydrogen production rate of 270 mL H₂ g⁻¹ MLVSS d⁻¹ (or 3310 mL H₂ L⁻¹ d⁻¹) and a hydrogen yield of 172 mL H₂ g⁻¹ COD removed were obtained for the treatment of alcohol distillery wastewater containing high potassium and sulfate in an anaerobic sequencing batch reactor [68].

Nieto *et al.* [7] obtained methane yields ranging from 202 to 549 mL CH₄·gVS_{fed}⁻¹ at standard temperature and pressure (STP) from six wastes (beverage waste, milled apple waste, milk waste, yogurt waste, fats and oils (F&O) from dairy wastewater treatment, F&O and cattle manure). They reported that methane content in biogas ranged from 58% to 76%. Rajagopal *et al.* [69] developed a process combining anaerobic digestion and anoxic/oxic treatment to treat swine wastewater and obtained 5.9 Nm³ of CH₄ m⁻³ of slurry added. In another study, Labatut *et al.* [70] observed that co-digestion of dairy manure with easily-degradable substrates increases the specific methane yields when compared to manure-only. For instance, co-digestion of dairy manure with used oil (ratio: 75:25 on volatile solids basis) produced more methane yield (361 Nm³ ton⁻¹VS_{added}) than dairy manure with cheese whey (ratio: 75:25 on VS basis; methane yield: 252 Nm³ ton⁻¹VS_{added}). Ogejo and Li [71] obtained a biogas yield ranging from 0.072 to 0.8 m³ g⁻¹ VS (methane content ranging from 56% to 70%) by co-digesting flushed dairy manure and turkey processing wastewater. The biogas produced was enough to run a 50 kW generator to produce electricity for about 5.5 and 9 h for the 1:1 and 1:2 feed mixtures. In addition to the electricity to be produced, other possible revenues, such as carbon credits, renewable energy credits, green tags for electricity, putting a value to the environmental benefits of anaerobic digestion or subsidies from grants or other incentives programs to make the system economically viable should be considered. On average, 18.5–40 kg of VS added in to the anaerobic digestion system can produce a biogas yield of 10 ± 5 m³, when 65% VS removal is achieved [72]. This indicates a daily electricity generation of 12.5–33.6 kWh from biogas, on the assumption that the generator efficiency is 35%–50%. In addition, a daily heat energy profit of 17.8–46.5 kWh from biogas can be estimated. One cubic meter of biogas obtained while co-digesting dairy manure and animal fat is equivalent to 20 MJ of heat energy [73]. When used as fuel for a co-generator, 1 m³ of biogas can produce 1.7 kWh of electricity and 7.7 MJ of heat. In addition to co-digestion, Esposito *et al.* [74] suggested several pre-treatment techniques that can be applied to increase further the biogas production, such as mechanical comminution, solid–liquid separation, bacterial hydrolysis and alkaline addition at high temperature, ensilage, alkaline, ultrasonic and thermal pre-treatments.

7. Toxicity

Sodium toxicity is a common problem causing inhibition of anaerobic digestion. Digesters treating highly concentrated wastes, such as food and concentrated animal manure, are likely to suffer from partial

or complete inhibition of methane-producing consortia, including methanogens [75,76]. Zhao *et al.* [10] confirmed that organofluorine compounds, such as 4-fluorophenol (p-FP), 4-fluorobenzoic acid (p-FB) and 4-fluoroaniline (p-FA), have a potential toxicity on methanogenesis and biodegradability. Procházka *et al.* [77] described that high ammonia nitrogen concentration (especially the unionized form) (4.0 g L^{-1}) would inhibit methane production, while low ammonia nitrogen concentration (0.5 g L^{-1}) could cause low methane yield, loss of biomass (as VSS) and loss of the acetoclastic methanogenic activity. Chen *et al.* [78] indicated that certain ions, such as Na^+ , Ca^{2+} and Mg^{2+} , were found to be antagonistic to ammonia inhibition, a phenomenon in which the toxicity of one ion is decreased by the presence of other ion(s). At high concentrations, potassium, light metals ions (Na, K, Mg, Ca and Al) and other salts can also interrupt cell function [78].

Toxicity Control Strategies

Vyrides *et al.* [79] indicated that glycine-betaine (GB), an organic compound, can cause antagonism against sodium toxicity. However, using GB to decrease sodium toxicity in commercial scale anaerobic digesters would be too costly [75]. Suwannopadol *et al.* [75] described that when grass clippings were added at the onset of anaerobic digestion of acetate containing a sodium concentration of $7.8 \text{ g Na}^+ \text{ L}^{-1}$, a total methane production of about $8 \text{ L CH}_4 \text{ L}^{-1}$ was obtained, whereas no methane was produced in the absence of grass leaves. Another way of tackling the sodium salts problem is by allowing the anaerobic sludge to acclimate to high sodium concentrations [80], but this technique requires time for the methanogens to adapt to the saline conditions, which in turn, results in a prolonged period before the anaerobic reactor can achieve its full-loading capacity. Zhao *et al.* [10] concluded that adsorption was the main removal mechanism for the three F-substituent aromatics, such as 4-fluorophenol (p-FP), 4-fluorobenzoic acid (p-FB) and 4-fluoroaniline (p-FA). To overcome ammonia toxicity, many strategies have been suggested: chemical precipitation, pH and temperature control [78]; use of carbon fiber textiles [81]; acclimation of methanogenic consortia to high ammonia levels [82]; and ammonia stripping and adjustment of the C:N ratio of feedstock [83]. Uludag-Demirer *et al.* [84] and Wang *et al.* [49] described the physical, chemical and biological methods, such as addition of ammonium-selective adsorbent, ammonium removal by forming struvite precipitation or a biological anoxic/oxic (A/O) process. Among these methods, ammonium removal by adding ammonium-selective adsorbents could be the most attractive and practical, because of its easier operation and economic impact, and the ammonium-saturated adsorbents can be further used as nitrogen fertilizer [49].

8. Modeling Advances

Various kinetic equations reported for anaerobic processes [3,85] generally relied on Monod's equation. Monod's equation is based on the growth rate and the substrate utilization rate during biodegradation. Wong *et al.* [86] determined the biological kinetic constants for a laboratory anaerobic bench scale reactors (ABSR) treating palm oil mill effluent. The investigation showed that the growth yield (Y_G), specific biomass decay (b), maximum specific biomass growth rate (μ_{\max}), saturation constant (K_s) and critical retention time (θ_c) were in the range of $0.990 \text{ g VSS g}^{-1} \text{ COD}_{\text{removed}} \text{ d}^{-1}$, 0.024 d^{-1} , 0.524 d^{-1} , $203.433 \text{ g COD L}^{-1}$ and 1.908 d , respectively.

Fuzzato *et al.* [26] used simplified first-order kinetics for modeling a mesophilic anaerobic sequencing batch biofilm reactor (ASBBR) treating lipid-rich wastewater. Nikolaeva *et al.* [40] also observed that a first-order kinetic model described the experimental results obtained for the upflow fixed bed digesters treating dairy manure well. In addition, they also concluded that the first-order model was adequate for assessing the effect of HRT on the removal efficiency and methane production. Ganesh *et al.* [3] used a modified Stover-Kincannon kinetic model to predict the performance of anaerobic fixed bed reactors treating winery wastewater. In a similar study, Rajagopal *et al.* [87] applied bio-kinetic models, such as the modified Stover-Kincannon and second-order kinetic models for the upflow anaerobic filters treating high strength fruit canning and cheese dairy wastewaters. Fia *et al.* [6] also used the modified Stover-Kincannon and second-order kinetic models for the experimental data obtained from the upflow anaerobic fixed bed reactors treating coffee bean processing wastewater. Abdurahman *et al.* [85] employed kinetic equations from Monod, Contois and Chen and Hashimoto to describe the kinetics of palm oil mill effluent (POME) treatment in a membrane anaerobic system (MAS) at organic loading rates ranging from 1 to 11 kg COD m⁻³ d⁻¹. Kaewsuk *et al.* [88] conducted a pilot scale experiment to investigate the performance of the membrane sequencing batch reactor (MSBR) treating dairy wastewater and checked the suitability of the kinetics for an engineering design. The kinetic coefficients K_s , k , k_d , Y and m were found to be 174-mg COD L⁻¹, 7.42 d⁻¹, 0.1383 d⁻¹, 0.2281 d⁻¹ and 1.69 d⁻¹, respectively.

Recently, there has been a move by the International Water Association's (IWA) Task Group for Mathematical Modeling of Anaerobic Digestion Processes to develop a common model called Anaerobic Digestion Model No. 1 (ADM1) that can be used by researchers and practitioners [89,90]. Lee *et al.* [91] examined the application of the ADM1 for mathematical modeling of anaerobic process using a lab-scale temperature-phased anaerobic digestion (TPAD) process. Sensitivity analysis showed that $k_{m,process}$ (maximum specific uptake rate) and $K_{S,process}$ (half saturation value) had high sensitivities to model components. They have concluded that simulation with estimated parameters showed good agreement with experimental results in the case of methane production, uptake of acetate, soluble (SCOD) and total chemical oxygen demand (TCOD). The structure and properties of a microbial community may be influenced by process operation and, in their turn, also determine the reactor functioning. In order to adequately describe these phenomena, Ramirez *et al.* [89] emphasized that mathematical models need to consider the underlying microbial diversity. In order to demonstrate this contribution, they have extended the ADM1 to describe microbial diversity between organisms of the same functional group. Boubaker and Ridha [92] used the ADM1 model to simulate the mesophilic anaerobic co-digestion of olive mill wastewater (OMW) with olive mill solid waste (OMSW). The results indicated that the ADM1 model could simulate with good accuracy: gas flows, methane and carbon-dioxide contents, pH and total volatile fatty acids (TVFA) concentrations of effluents for various feed concentrations digested at different HRTs and especially at HRTs of 36 and 24 days. Furthermore, effluent alkalinity and ammonium nitrogen were also successfully predicted.

9. Technology Assessments

Onsite industrial wastewater anaerobic treatment requires systems with a significant capital cost and incur increasing expenses for successful long-term operation, control and maintenance. Farhan [93]

evaluated a high-rate digestion system for brewery wastewater technically and economically. The technical evaluating criteria consist of, among commonly used engineering design criteria, such as hydraulic and organic loading rates, wastewater characteristics and layout and space requirements, factors that reflect the dynamics of technology development. The abilities of the anaerobic high rate bioreactors to meet the regulatory requirements reliably with flexibility for future upgrading are some of the technical evaluating factors [93]. The energy savings and renewable energy credits are among the economical assessment criteria [93].

Gebrezgabher *et al.* [94] analyzed the economic performance of anaerobic digestion of a biogas plant using the net present value (NPV) and internal rate of return (IRR). They conclude that the uncertainty of the increasingly tightened regulations regarding the effluent of anaerobic treatment, the quality and value of the digestate and the high investment and operating costs limit the on-farm applications of anaerobic digestion of agro wastes.

10. Summary and Conclusions

A critical analysis of the literature reveals that there is a strong possibility and need to enhance the performance of high rate anaerobic biogas reactors. This technique has many advantages over other conventional methods. However, the challenges associated with the digester operation at lower HRT and higher OLR need to be addressed, which include biomass washout, clogging, short-circuiting, process inhibitions, poor final effluent and biogas quality. Different materials (polyethylene, polypropylene pall rings, polyurethane foam, carbon felt and waste tire rubber) had been tried as packing material in the anaerobic fixed bed reactors, depending upon their availability and other specifications, such as material properties, cost, *etc.* These packing materials would help to reduce hydraulic retention time, which in turn lessens the required volume of the reactor, and ultimately, the cost could be reduced. The practical aspects of using pure microbial film as magnifying microbial layers should be looked into. In the case of UASB reactors, the following important aspects should be looked into: (i) enhancing the start-up and granulation in UASB reactors; (ii) coupling with post-treatment unit to overcome the temperature constraint; and (iii) improving the removal efficiencies of the organic matter, nutrients and pathogens in the final effluent.

When talking about toxicity, there are many soluble organic and inorganic materials that can be either stimulatory or inhibitory. A good example of this is the effect of ammonia nitrogen on the anaerobic digestion process. When potential inhibitory materials are slowly increased within the environment, many biological organisms can rearrange their metabolic resources, thus overcoming the metabolic block produced by the normally inhibitory material. Under shock load conditions, sufficient time is not available for this rearrangement to take place. Finally, there is the possibility of antagonism and synergism effects of using different organic wastes as co-substrates. Antagonism is defined as a reduction of the toxic effect of one substance by the presence of another. Synergism is defined as an increase in the toxic effect of one substance by the presence of another. This is an important consideration when designing for potential cation toxicity. Additional research efforts are essential to get more insight about the stable performance of the digesters against various process inhibitors, such as ammonia, sodium, sulfur, *etc.* While lessening the economic losses, vigilant substrate management and early detection of inhibitions are critical.

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