

Advanced technologies for the treatment of wastewaters from agro-processing industries and cogeneration of by-products: a case of slaughterhouse, dairy and beverage industries

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Abstract Agro-industrial wastewaters are known by high strength of organic pollutants that cause an adverse effect on the water bodies. Wastewater management becomes a major task, leads environmental regulations to be stricter worldwide. Increased disposal of untreated/partially treated industrial wastewaters are major environmental problems in Ethiopia. In Ethiopia, industries most commonly dispose their untreated wastewater straight into the nearby rivers. Somewhat, constructed wetlands are used by some industries for treatment of wastewaters. The objective of this review paper was to summarize the characteristics and recent research efforts done on anaerobic treatment of some selected agro-industrial wastewaters and innovative technologies used for cogeneration of byproducts. Many developed countries designed cost effective approaches for agro-industrial wastewater management. The full-scale anaerobic treatment system in China generates 40,000 m³ biogas daily for 20,000 households from agro-industrial wastes. Likewise, the Brewery, Addis Ababa, Ethiopia used full-scale anaerobic treatment technology and produce average methane yield of 487 Nm³/day. The estimated maximum methane production potential of Kera, Luna slaughterhouses, and Ada milk factory were 4.5599LCH₄, 0.1878LCH₄, and

0.9952LCH₄, respectively. These indicate that they can be potential sources of biogas production. Limitations of the brewery are burning of the produced energy and some quantified parameters being become above national standards while meat processing and dairy industries are discharging their wastewater without treatment into the rivers. We devised the brewery to use the produced energy properly and extend its treatment to achieve the national standards using integrated sequencing batch reactor. Similarly, slaughterhouse and dairy industries should install anaerobic–aerobic integrated treatment techniques.

Keywords Industrial wastewater · Anaerobic reactors · Anaerobic digestion · Ethiopia environmental protection authority · Wastewater management

Introduction

Rapid agro-industrial expansion in both developed and developing countries are major contributors of environmental pollution worldwide (Rajagopal et al. 2013). Increased industrial activities, particularly in developing countries led to pollution stress on surface water, due to the discharging of large quantities of wastewater without adequate treatment techniques. For example, among agro-industries, breweries are known to cause pollution by discharging effluents into receiving streams, ground water, rivers, and soil (Akpomie et al. 2014). Agro-industrial wastewater containing high organic matter content poses environmental problems (Jayathilakan et al. 2012). The main crucial environmental issues of the agro-industrial wastewater are total solids (TS), total nitrogen (TN), total phosphorus (TP), biochemical and

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chemical oxygen demand (BOD and COD), and pathogens (Akpomie et al. 2014). Up to date, the environmental protection issues have raised, which lead governments and environmental protection agencies to put strict environmental regulations that forced industries to achieve standard discharge limits. Among the variety of agro-industries, slaughterhouse, beverage, and dairy industries are commonly known by high organic pollutants in their wastewaters. To fulfill the regulations, industries begin to use sustainable technologies for adequate and comprehensive wastewater management. Environmentally friendly anaerobic biotechnologies have better treatment options than conventional aerobic technologies due to their cost effectiveness and economical benefit. For example, UASB reactors become viable for industrial wastewater in recent years in developed countries to reduce the negative environmental impact of discharging high organic content effluents (Mutombo 2004).

Anaerobic biotechnologies play a great role in the treatment of agro-industrial wastewaters. Agro-industrial wastewater organic pollutants are degraded by microbes under anaerobic conditions and finally, converted large organic compounds into end products of CO_2 and CH_4 . For example, China built 600 anaerobic reactors to treat brewery and other agro-industrial wastewaters. These anaerobic reactors had a holding capacity of 220,000 m^3 and produced biogas to 84,000 families for heating. From these, the largest anaerobic treatment system consisting of two 5,000 m^3 anaerobic reactors which produces 40,000 m^3 biogas daily for 20,000 households. Generally, anaerobic reactors had worldwide applications in Brazil, India, Mexico, Philippine, Taiwan, Israel, Chile, South Africa, Kenya, Malawi, Malaysia, etc. (Fang and Liu 2001). Accelerated water quality change due to industrial wastewater discharging with large quantities of nutrients and toxic substances into the environment become an issue problem in developing countries. It is estimated that 90% of wastewater in developing countries is still discharged to rivers and streams without any adequate treatment. Likewise, in Ethiopia, most of the factories have no wastewater treatment plants. In Ethiopia, industries most commonly dispose their untreated toxic wastewater simply into the nearby rivers, lakes, and streams. The effects of industrial activities on the environment in the country are becoming evident through the pollution of water bodies and human habitat in the major cities, rivers, and lakes (Angassa 2011). Therefore, the objective of this review paper was to summarize the characteristics of slaughterhouse, dairy, and brewery influents and the recent research efforts done on anaerobic treatment of slaughterhouse, dairy, and beverage agro-industrial wastewaters and innovative technologies used for cogeneration of byproducts and finally, to devise

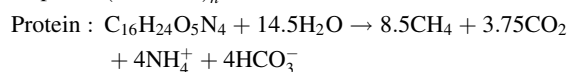
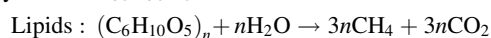
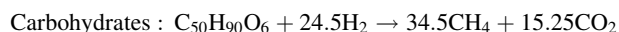
possible treatment mechanisms for agro-processing industries in Ethiopia. This review has done for a period of one semester (February–May, 2016) for the fulfilment of the course advanced wastewater treatment at Addis Ababa University.

Anaerobic digestion (AD)

Biogas production by AD of wastewater takes place with a combinational activity of diverse microbial populations. AD is initiated by the aid of bacteria that are responsible for the hydrolysis of high molecular weight organic substances. Subsequently, the products produced by hydrolysis further degraded to intermediate products such as volatile fatty acids (VFAs) (acidogens) and then to acetic acid, as well as CO_2 and H_2 (acetogens). The final step (methanogenesis) is accomplished by acetoclastic and hydrogenotrophic Archaea, which convert acetic acid or CO_2/H_2 into methane (Fig. 1) (Goswami et al. 2016). Methane formation in anaerobic digestion involves four different steps: hydrolysis, acidogenesis, acetogenesis, and methanogenesis (de Mes et al. 2003).

Hydrolysis

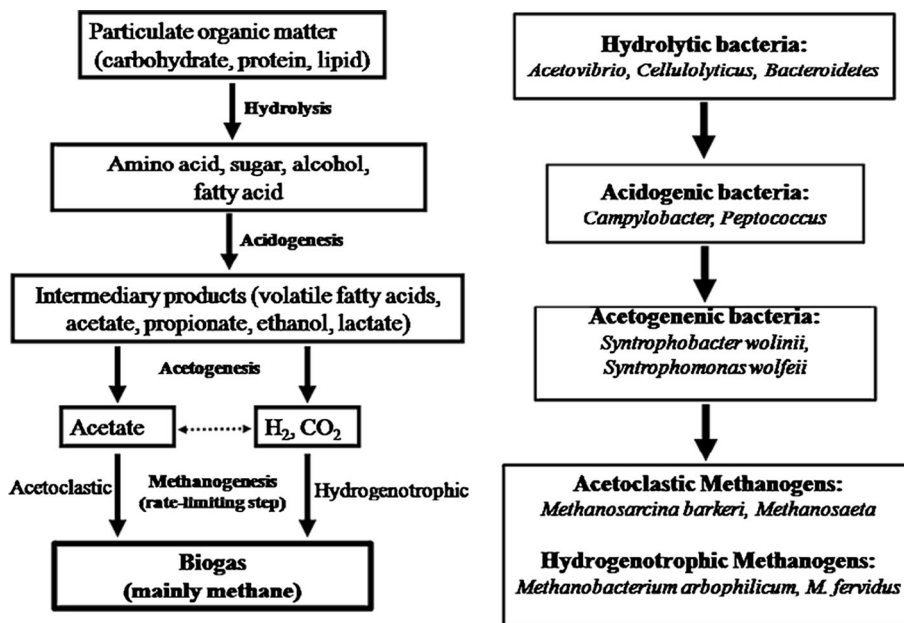
This is the first stage in anaerobic digestion process, involves the enzyme-mediated transformation of insoluble organic materials and higher molecular such as carbohydrates, lipids, and proteins into soluble organic materials, i.e., to compound of suitable use as source of energy for microorganisms (Adekunle and Okolie 2015). These organic compounds are degraded into simpler products in the presence of hydrolytic bacteria as follows (Leung and Wang 2016).



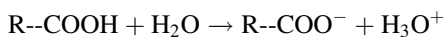
Acidogenesis

It is the second phase of anaerobic digestion. Most of the microbes involved in hydrolysis step are also involved in fermentation. Further degradation of hydrolysis products is carried out by the genera microbes such as *Enterobacterium*, *Acetobacterium*, and *Eubacterium* into short chain organic acids such as VFAs (acetic, propionic acid, butyric acid, succinic acid, lactic acid, etc.), alcohols, ammonia (from amino acids), carbon dioxide, and hydrogen. Within

Fig. 1 Mechanisms of biogas production



these various fermentation reactions, the monomers produced in the hydrolytic phase are taken up by various acid forming bacteria (acidogens). In general, acidogens are relatively fast growing microorganism (Adekunle and Okolie 2015). The only chemically relevant functional group of VFAs, the carboxylic group makes these compounds acidic in nature. This functional group dissociates in water solutions following (Prochazka 2008):

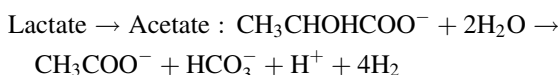
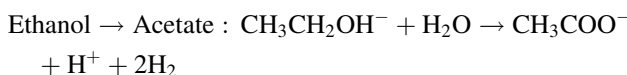
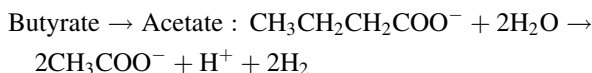
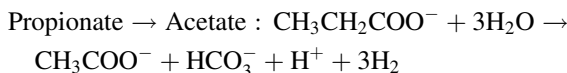


where R—represents hydrogen (for formic acid) or aliphatic hydrocarbon skeleton for other VFAs.

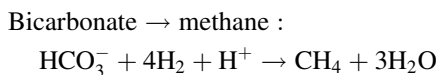
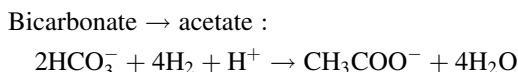
Acetogenesis

In this step, acid producing bacteria convert intermediate products of acidogenic processes into simpler forms (Yimer and Sahu 2014). Substrates for acetogenesis consist of various fatty acids, alcohols, some amino acids, and aromatics. In addition to hydrogen gas, these compounds primarily form acetate and carbon dioxide. *Syntrophomonas*, *Syntrophus*, *Clostridium*, and *Syntrobacter* are examples of genera in which there are numerous organisms that can perform acetogenesis (Goswami et al. 2016). Some important oxidation–reduction reactions in AD that convert products of fermentative bacteria into acetate, hydrogen, and methane are shown in the following equations (Chernicharo 2007):

Oxidation reaction (electron donors)



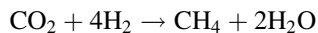
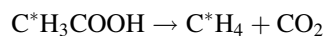
Reduction reaction (electron acceptor)



Methanogenesis

This is a last phase of AD. In this phase, the production of CH₄ and CO₂ from intermediate products is formed under strictly anaerobic conditions via group of methanogenic bacteria. In this stage, methane is formed by two main basic reaction mechanisms. The first step is cleavage of acetic acid in the absence of oxygen, means that cleave methyl group of the acetic acid into methane and carbon dioxide while in the second step, reduction of carbon dioxide occurs through oxidation of the carboxylic group into carbon dioxide due to the role of hydrogenotrophic

methanogenic organisms and aceticlastic methanogenic organisms (Chernicharo 2007).



Agro-industrial anaerobic biotechnologies

Technology selection eventually depends upon agro-industrial wastewater characteristics and on the required effluent quality levels, with regard to the cost, operation, and performance efficiency. Effluent quality control is objectively aimed for public health protection (e.g., for recreation, irrigation, and water supply), prevention of eutrophication, preventing toxic compounds from entering the water and food chains, and promotion of water for reuse (Veenstra et al. 1997).

Anaerobic filter (AF)

Called packed bed, is the earliest and simplest types of design, typically consists of a tall reactor filled with media, in which biomass is retained on the attachment of a biofilm to the solid or stationary carrier material for entrapment of sludge particles and formation of very well settling sludge aggregates (Fig. 2a). The organisms are growing either on the attached media or in a suspended form, within the interstices of the media. The wastewater to be treated is usually passed upward through the filter, and exits through a gas syphon (Marchaim 2016).

Anaerobic baffled reactor (ABR)

ABR is a simple rectangular tank, with physical dimensions similar to a septic tank, and is divided into different equal compartments, by means of partitions from the roof and bottom of the tank (Fig. 2b). The liquid flow alternately upward and downward between the partitions, and on its upward passage the waste flows through an anaerobic sludge blanket. Hence, the waste is in an intimate contact with active biomass. This reactor appears to be able to treat high solids contents, and hence may be an alternative to AF (Marchaim 2016).

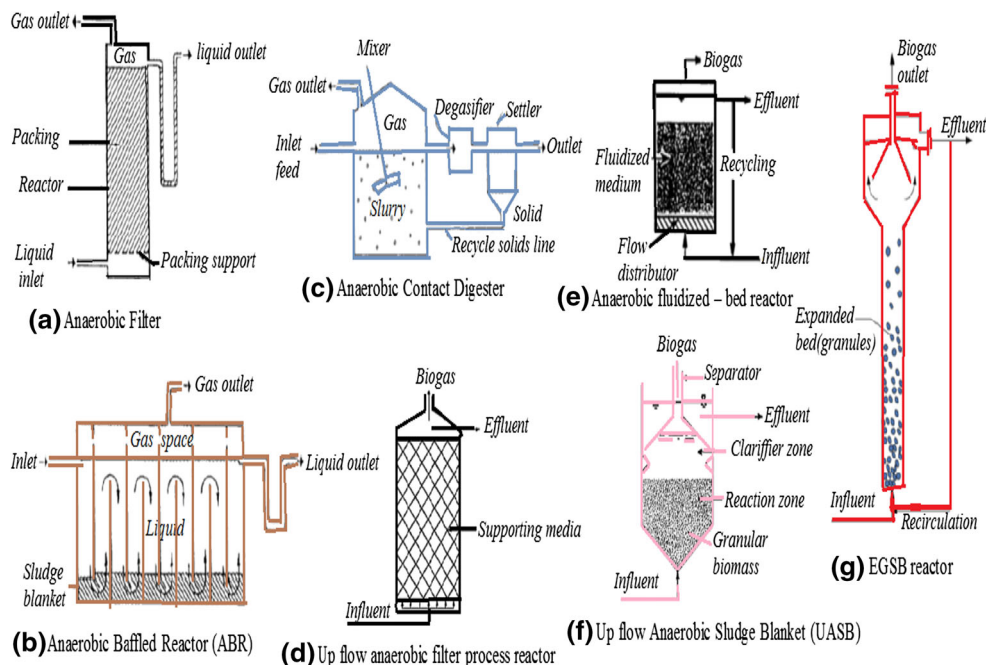
Anaerobic contact process (AC)

Modern AC systems (Fig. 2c) are very effective for relative highly suspended solids. An alternative way of sludge retention was found by applying inert support material into the bioreactor on which the anaerobic organisms can adhere. Even so, AC effluents require a subsequent treatment step in order to comply with effluent restrictions (Lier et al. 2015).

Up flow anaerobic filter process (UAF)

UAF is the most significant high-rate anaerobic treatment reactor developed in Netherlands. This type of bioreactor contains a medium, i.e., a microbial support (Fig. 2d). Granulated microorganisms exist either in suspension or

Fig. 2 Some high rate Anaerobic reactor



attached forms within the medium; hence, a high-density microbial population is retained in the reactor and creating a hybridization of microbial adhesion. To avoid short-circuiting flow through the packed column, a distributor is fitted at the bottom to provide a homogeneous up flow of wastewater. At the top, treated waste water and the biogas produced are separated by a free board (Goswami et al. 2016).

Anaerobic fluidized-bed (AFB) reactor

In this reactor, the medium to which the microbes adhere is fluidized within the reactor (Fig. 2e). Anaerobic microbes grow on the surface of the medium, expanding the apparent volume of the medium, that is, why its name designated as an expanded bed reactor. In this reactor, the bacterial attachment is either in non-fixed or mobile carrier particles, which consist of fine sand, quartzite, alumina, granular activated carbon, etc. In AFB reactor, good mass transfer results from less clogging and less short-circuiting due to the occurrence of large pores through bed expansion, and high specific surface area of the carriers due to their small size. Due to these, FB reactors are highly efficient. However, long-term stable operation appears to be problematic (Lier et al. 2015).

Up flow anaerobic sludge blanket (UASB)

One of the most distinguished anaerobic treatment process technology, developed in Netherlands. Successful construction of a UASB process is capable of pay for self-granulation of anaerobic microbes. The distinguished characteristics are the presence of active biomass at the bottom of the reactor operating on suspended growth system. In this bioreactor, wastewater flows in upward directions through sludge bed and sludge blanket and is degraded by anaerobic microorganisms. The produced gas is then separated by a gas–liquid separator and the clarified liquid is discharged over a weir, while the granular sludge naturally settles at the bottom (Fig. 2f) (Amoatey and Bani 2011).

Expanded granular sludge bed (EGSB) reactor

EGSB reactor (Fig. 2g) is the family of UASB reactors. It has been objectively developed to improve the substrate–biomass contact within the treatment system by means of expanding the sludge bed with a high up flow liquid velocity (>4 m/h) which intensifies hydraulic mixing and results in better performance and stability than the UASB.

The high up flow liquid velocity in the reactor is achieved through the application of a high effluent recirculation rate. As a result of high velocity, granular sludge bed will be in an expanded or fluidized state in the higher regions of the bed which results an excellent contact between the wastewater and the sludge. Compared to UASB reactors, higher organic loading rates can be accommodated in EGSB systems. Consequently, the gas production is also higher (Chan et al. 2009).

AD of agro-industrial wastewaters

Meat industry

Meat processing activities use large amount of water for hygienic reasons and produce large amount of wastewater at the end. The existence of large number of suspended solids in wastewater generates odor, a major environmental problem associated with this slaughter wastewater. Slaughterhouse wastewaters are characterized by the presence of high concentration of animal's blood, bleeding out, skinning, cleaning of animal bodies, cleaning of rooms, etc., have high organic content of suspended solids, and high concentration of nutrients (Sunder and Satyanarayan 2013). Wastewater discharge without proper treatment from slaughterhouses has been recognized to contaminate water bodies (Seif and Moursy 2001). Researchers have given attentions for slaughterhouse wastewater to reduce its environmental impact using anaerobic treatment methods. The sequencing batch reactor (SBR) treatment showed that better removal efficiency of pollutants from slaughterhouse wastewaters (Table 1) (Kundu et al. 2013). Anaerobic digestion (AD) treatments such as anaerobic contact (AC), up flow anaerobic sludge blanket (UASB), and anaerobic filter (AF) reactors are used for slaughterhouse wastewater treatment. However, the high-rate anaerobic reactors like UASB treatment systems are less popular for slaughterhouse wastewater treatments due to high fat and suspended matters accumulation in the influent which affects the performance efficiency of the treatment systems. This indicates that a pre-treatment steps necessary for removal of fats and suspended solids in order to use UASB reactor as a slaughterhouse wastewater treatment. Table 2 summarizes the different anaerobic reactor performance efficiency for the treatment of slaughterhouse wastewater (Kundu et al. 2013).

Anaerobic treatment reactors effluents contain high nutrient and low COD and does not fulfill the wastewater standard limits. Sequencing Batch Reactor (SBR) systems are efficient to remove nutrients from one single reactor combining anaerobic and aerobic stages that used in slaughterhouse wastewater treatment. Last column under

Table 1 Characteristics of the slaughterhouses and removal efficiency of SBR (Kundu et al. 2013)

Parameter	Influent concentration	Effluent concentration	Removal efficiency (%) ^a
pH	8.0–8.5 (8.3)	7.5–8.5 (7.7)	–
TSS (mg/L)	10,120–14,225 (12,566)	2055–2540 (2315)	81.6
COD (mg/L)	6185–6840 (6501)	830–1045 (936)	85.6
BOD5 at 20 °C (mg/L)	3000–3500 (3262)	210–525 (242)	92.6
TKN (mg/L)	1050–1200 (1136)	305–525 (434)	61.8
NH ₄ ⁺ -N (mg/L)	650–735 (697)	95–525 (141)	79.8

() = average values

^a Calculated using: removal efficiency (%) = $\frac{(C_i - C_e) \times 100}{C_i}$, where C_i influent concentration and C_e effluent concentration of pollutants**Table 2** Treatment systems for slaughterhouse wastewater

Type of reactor	Organic loading rate (OLR) (KgCOD/m ³ /day)	Removal efficiency (%)	Reference
UASB	1–1.65	COD = 90	Ruiz et al. (1997)
ASBR	2.07–4.9	COD = 96	Massé and Masse (2000)
MBSBR	1.18–2.3	COD = 80–96	Sombatsompop et al. (2011)
FBSBR	0.5–1.5	COD = 90–96	Rahimi et al. (2011)
HUASB	19	COD = 80–92	Rajakumar et al. (2012)
AF	2.3	COD = 85	Aspasia and Anastassios (2012)
AC	3	COD = 85	Aspasia and Anastassios (2012)
SBR	0.55–0.925	COD = 97–99, TN = 97–99 TP = 84–94 with 48 days HRT	Min (2013)

ASBR anaerobic sequencing batch reactor, MBSBR moving bed sequencing batch reactor, HUASB hybrid up flow anaerobic sludge blanket reactor, FBSBR fixed bed sequencing batch reactor

Table 2 summarizes secondary treatment of slaughterhouse wastewater (Min 2013).

Developed countries, like USA and Australia, extensively used anaerobic lagoons for treating their slaughterhouse wastewater due to its low operational and maintenance costs and high efficiency in reducing polluting charges. However, anaerobic lagoons cause odor problems and emission of methane, major contributors to greenhouse gas with a heat-trapping capacity of 20 to 30 times to that of carbon dioxide. But now, sophisticated anaerobic reactors were developed in Europe and Asia to increase treatment efficiency. Among these, a high-rate anaerobic contact (AC) reactor was applied in full scale in UK for treating slaughterhouse wastewater. The reactor showed that a 90% BOD5 reduction with an OLR ranges from 0.12 to 0.28 kg/m³/day. Another modern high-rate anaerobic reactor called AF, which has a good bacteria retention capacity through adhesion of biomass to a fixed or floating inert material called filter. AF was installed in full-scale in Germany and has OLRs between 3 and 10 kg/m³/day with HRTs between 21 and 27 h showed a COD reduction ranges from 70 to 90% (Massé and Masse 2000). Research

study carried on the slaughterhouse revealed that slaughterhouse wastewater is potential to generate methane because of the degree of organic materials available in it (Table 3) (Olvera and Lopez-Lopez 2012).

Likewise, the increasing demand of meat in Ethiopia leads further expansions of slaughterhouses in the country. These expansions of slaughterhouses result a large number of wastewaters. For example, Kera and Luna slaughterhouses in Addis Ababa and Modjo, respectively, consume large amount of water resources for removal of hide from animals and discharge their wastewater into their neighboring rivers, i.e., Akaki and Modjo rivers without adequate treatment and causes eutrophication of the rivers. The physicochemical characteristics of both Kera and Luna slaughterhouse wastewater at Addis Ababa and Modjo, respectively, were summarized in Table 4. To reduce eutrophication of rivers of the receiving environments, some slaughterhouse has started to use lagoons, e.g., Luna slaughterhouse at Modjo as wastewater treatment, while untreated effluent of Kera is discharging without treatment (Mulu and Aynalem 2015). The conventional treatment of

Table 3 Potential of slaughterhouse wastewater for production of methane (Olvera and Lopez-Lopez 2012)

Wastewater	Reactor type	HRT (day)	OLR (KgCOD/m ³ /day)	Temperature (°C)	Yield of CH ₄ (m ³ /KgCOD)
Slaughterhouse	AF	0.6–0.3	3.7–16.5	25	0.41
Slaughterhouse	CSTR	20–30	0.2–0.3	37	0.45

CSTR continuously stirred tank reactor

Table 4 Kera and Luna slaughterhouse wastewater characteristics (Mulu and Aynalem 2015; EEPA 2009)

Parameters	Kera influent concentration	Luna influent concentration	Luna effluent concentration ^a	Removal efficiency (%) ^b	EEPA standard
pH	7.3	7.25	6.81	–	6–9
TSS (mg/L)	3835.5	1111	125.7	88.7	80 mg/L
COD (mg/L)	11,546.6	4752.67	431.7	90.9	250 mg/L
BOD5 (mg/L)	3980	2110	177	91.6	80 mg/L

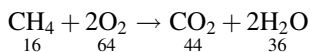
^a Wastewater treated with lagoons

^b Calculated using: removal efficiency (%) = $\frac{(C_i - C_e) \times 100}{C_i}$

lagoons treatment system for Luna slaughterhouse does not achieved the EEPA standard limits.

Estimation of theoretical maximum methane production potential considering degraded COD

The biochemical methane potential of a waste is related to the concentration of organics (COD) that exists in it and the efficiency of the treatment plant. The maximum theoretical yield of methane is 0.35m³CH₄/KgCOD. This calculation is done assuming all COD contents in anaerobic process are converted to methane, and determining the COD equivalence of methane. This is done by calculating the amount of oxygen required to completely oxidize 1 mol of CH₄ at STP (standard temperature and pressure) conditions. The balanced reaction is (Mang 2016):



The COD of methane is 64 grams O₂/16 g of CH₄. The complete metabolism of 1 kg of COD will produce 0.25 kg of methane. This is equivalent to 15.6 mol, which is obtained by dividing 250 g/16 g/mol. The volume of 1 mol of gas is 22.4 L. The total volume of gas produced is:

$$\text{Volume} = \frac{22.4\text{L} \times 15.6 \text{ moles}}{\text{mole}} = 349 \text{ L} = 0.35 \text{ m}^3$$

If a simple calculation using the above equation is done, the Kera raw wastewater will have a maximum methane production potential (MP) of:

$$\begin{aligned} \text{MP} &= \frac{11546.6 \text{ mg} \times 0.35 \text{ m}^3 \text{ of methane}}{1 \text{ KgCOD}} \\ &\times \left(\frac{1 \text{ Kg}}{1,000,000 \text{ mg}} \right) \\ &= 0.0040413 \text{ m}^3 \text{ methane} \end{aligned}$$

Similarly, the Luna meat processing wastewater has also a maximum methane production potential of:

$$\begin{aligned} \text{MP} &= \frac{4752.67 \text{ mg} \times 0.35 \text{ m}^3 \text{ of methane}}{1 \text{ KgCOD}} \\ &\times \left(\frac{1 \text{ Kg}}{1,000,000 \text{ mg}} \right) \\ &= 0.0016634345 \text{ m}^3 \text{ methane} \end{aligned}$$

Another technique of estimating the production of methane from degraded COD value in the reactor at STP is using (Chernicharo 2007):

$$V(\text{methane}) = \frac{\text{COD}}{K(t)}$$

where, V (methane) = Volume of methane produced (L), COD = load of COD converted into methane (g), K (t) = correction factor (gCOD/L), determined as

$$K(t) = \frac{P \times K}{R \times (273 + T)}$$

where, P = atmospheric pressure (1 atm.), K = COD corresponding to 1 mol of CH₄ (64 g), R = gas constant (0.08206 atm. L/mol. K), T = operational temperature (25 °C).

For Kera slaughterhouse wastewater, COD = 11546.6 mg, V_{CH_4} is:

$$V_{CH_4} = \frac{COD}{K(t)} = \frac{COD}{P \times \frac{K}{R \times (273+T)}} = \frac{11546.6 \text{ mg}}{1 \text{ atm.} \times \frac{64 \text{ g/mol}}{\left(0.08206 \text{ atm.} \frac{\text{L}}{\text{mol.K}}\right)^{(273+25)K}}} = 4.5599 \text{ L}$$

For Luna slaughterhouse wastewater, COD = 475.67 mg, V_{CH_4} is:

$$V_{CH_4} = \frac{COD}{K(t)} = \frac{COD}{P \times \frac{K}{R \times (273+T)}} = \frac{475.67 \text{ mg}}{1 \text{ atm.} \times \frac{64 \text{ g/mol}}{\left(0.08206 \text{ atm.} \frac{\text{L}}{\text{mol.K}}\right)^{(273+25)K}}} = 0.1878 \text{ L}$$

The above simple calculations indicate that both Kera and Luna meat processing factories have the potential organic matter content in their raw wastewater that is able to generate biogas.

Dairy industry

The improper treatment systems of cheese dairies become a series environmental problem due to their high organic matter content. However, wastewaters coming from cheese dairies are one of another most important industrial pollutants as an alternative energy resources rather than a pollutant through appropriate treatment systems, due to their high content of COD and BOD (Najafpour et al. 2008). Anaerobic treatment of cheese factories effluents is more preferable than conventional methods for production of biogas. Cheese whey (CW) is a protein rich byproduct of cheese industry. It contains highly biodegradable organic matter (Demirel et al. 2000). However, its chemical composition depends on the quality and composition of milk and its production techniques, i.e., amount of yeast and acid used for fermentation and coagulation, respectively. CW is composed of a high strength organic pollutant COD and BOD5 values ranges from 60,000–100, 000 to 40,000–60,000, respectively (Aspasia and Anastassios 2012).

Generally, dairy industries generate strong wastewaters characterized by high BOD and COD concentrations. (Demirel et al. 2005). One phase anaerobic digestion process involves degradation of organic matters by microorganisms in the absence of oxygen and leads to biogas, mixture of carbon dioxide and methane and biomass formation. Some research studies indicate that 90% CW of hydrolyzed organic matter is converted into biogas at the methanogenesis stage. It is also assessed that one liter of CW can produce 45 L of

biogas containing 55% methane and 80% of COD removal. For individual liter of CW, 20 L of CH_4 can be produced, equivalent to 700 Btu of energy production. Another pilot scale research studies done on biogas production systems using different reactors from CW are summarized in Table 5 (Aspasia and Anastassios 2012).

Two-phase anaerobic treatment is particularly suitable for wastewaters that contain high concentrations of organic matters, such as dairy wastewaters. Numerous research studies carried on the anaerobic acidogenesis of dairy wastewaters indicate better treatment efficiencies were achieved on dairy effluents, namely cheese, fresh milk, and milk powder/butter factories, using a small-scale mesophilic two-phase system. For example, for the cheese factory wastewater, at organic loading rate (OLR) of 2.82 KgCOD/m³/day, 97% COD removal was achieved, while at OLR of 2.44 KgCOD/m³/day, 94% COD removal was obtained for the fresh milk effluent. For the powder milk/butter factory with an OLR of 0.97 KgCOD/m³/day, 91% COD removal was achieved. Table 6 shows the summary of data for two-phase anaerobic dairy wastewater treatment practices (Demirel et al. 2005).

Dairy factories in developing countries like Ethiopia show an increasing in numbers. These factories discharge their wastewater into the environment and leads to contamination of the surroundings. For example, Ada milk factory found in Bishoftu town has had a problem since the beginning of its establishment due to the discharging of its odorous wastewater which contains organic matter, suspended solids, nitrogen, and phosphorous causing serious health problems to animals and human beings. The dairy factory effluent commonly contains milk, byproducts of processing operations, cleaning products and various additives that may be used in the factory. According to Solomon Ali pilot study report on dairy wastewater treatment of the Ada milk factory, effluents showed a decline in the concentrations of some pollutants (Table 7). These few declines of pollutants were achieved mainly using a horizontal surface flow constructed wetlands (HSFCW). These treatment systems are most commonly used in developing countries due to their low cost and easy maintenance for treating industrial wastewaters but not effective in removing organic pollutants (Ali 2013).

This pilot study for the milk factory effluents indicates that the removal efficiencies of constructed wetland system except ammonia, shown in Table 7 brackets are very low with many other environmental effects such as increasing odor problems and greenhouse gas emissions when compared to anaerobic treatment systems. Therefore, this agro-industrial factory should use anaerobic treatment methods for better removal likewise the cheese whey treatment above. Following the simple calculation done for predicting the maximum methane potential yield of Kera and



Table 5 Cheese whey treatment systems using anaerobic reactors

Wastewater	Reactor	pH	HRT	OLR	Temperature	Biogas/CH ₄ yield	COD-removal (%)	References
CW	UASB	7.18	5	5.96	33	9.57LCH ₄ /L feed/day	98	Yan et al. 1989
CW	UFFLR	6.7	5	14	35	5.6 m ³ /m ³ /day	95	Wildenauer and Winter 1985
CW	FBR	4.3	0.4	77	35	0.39 m ³ /KgCOD	90	Boening and Larsen 1982
CW	AHR	7–8	0.75	13.3	20	0.69 (CH ₄ yield)	80	McHugh et al. 2006
CW	TSMAMD	7.9–8.5	4	19.78	37	0.70 (CH ₄ yield)	98.5	Yilmazer and Yenigün 1999
CW	UAFFR	–	2	35	37	0.72 (CH ₄ yield)	81	Patel et al. 1995
CW	UASFF	–	2	25	36	3.75L/day	97.5	Saddoud et al. 2007
CW	CSTR	–	4	–	–	0.55 m ³ /KgCOD	95	Najafpour et al. 2008

UFFLR up flow fixed film loop reactor, AHR anaerobic hybrid reactor, UAFFR up flow anaerobic fixed film reactor, TSMAMD two stage mixed anaerobic membrane digester, UASFF up flow anaerobic sludge fixed film

Table 6 Two-phase anaerobic treatment of dairy wastewater in small-scale

Type of Waste	Reactor type	HRT	OLR	Temperature	COD removal	Reference
Milk bottling plant	CSTR + UF	2 day	–	35 °C	90%	Cohen et al. 1994
Skimmed milk	CSTR + UF	2 day	–	20 °C	95%	Anderson et al. 1994
Milk and cream bottling plant	CSTR + UF	2 day	5KgCOD/m ³ /day	33–36 °C	90–95%	Jeyaseelan and Matsuo 1995
Synthetic cheese whey	CSTR + UF	2 day	–	35 °C	95%	Ince 1998

Table 7 Characteristics of dairy wastewater (Ali 2013)

Parameters	Influent concentration	Effluent concentration	EEPA standard
COD (mg/L)	2520	359 (85.7%)	250 mg/L
BOD5 (mg/L)	506	241 (52.3%)	60 mg/L
TSS (mg/L)	318	265 (17.1%)	50 mg/L
VSS (mg/L)	200	156 (22%)	–
NH ₃ -N (mg/L)	4.35	0.152 (96.5%)	15 mg/L
PO ₄ ³⁻ -P (mg/L)	5.3	3.64 (31.3%)	–
pH	5.7	7.4	6–9

Luna meat processing waste waters, the Ada milk factory has also the maximum methane potential of:

$$MP = \frac{2520 \text{ mg} \times 0.35 \text{ m}^3 \text{ of methane}}{1 \text{ KgCOD}} \times \left(\frac{1 \text{ Kg}}{1,000,000 \text{ mg}} \right) = 0.001 \text{ m}^3 \text{ methane}$$

OR

$$V_{CH_4} = \frac{COD}{K(t)} = \frac{COD}{P \times \frac{K}{R \times (273+T)}} = \frac{2520 \text{ mg}}{1 \text{ atm.} \times \frac{64 \text{ g/mol}}{\left(0.08206 \text{ atm} \cdot \frac{\text{L}}{\text{mol} \cdot \text{K}}\right) (273+25)K}} = 0.9952 \text{ L}$$

Therefore, this physicochemical characterization study for the milk factory influent COD value indicates that the

Ada milk agro-industrial factory wastewater can be an alternative renewable energy source. Therefore, the factory should adopt to use anaerobic treatment method.

Brewery industry

Brewery is one the huge amount of water consuming agro-industrial sector. The brewery effluent quality depends on various different processes that take place within the brewery, particularly in the raw material handling, wort preparation, fermentation, filtration, CIP, packaging, etc. Organic compounds found in the brewery effluent are mainly consist of sugars, soluble starch, ethanol, volatile fatty acids, etc., and generally, easily biodegradable. The characteristics of some relevant brewery physicochemical environmental parameter are COD ranges from 2000 to

6000 mg/L, BOD ranges from 1200 to 3600 mg/L, nitrogen ranges from 25 to 80 mg/L, and phosphorus ranges from 10 to 50 mg/L (Driessen and Vereijken 2003).

Anaerobic filter process was largely applied in pilot and full-scale form for the treatment of brewery wastewater. In the 1983, a large number of various configured attached growth anaerobic filter systems have been commercially installed at food processing plants, cheese plants, and brewery plants. The effectiveness of AF for treating brewery wastewater was carried out initially with loading rate of 10KgCOD/m³/day to setting number 1 on the effluent pump at mesophilic conditions (i.e., 35 °C) and showed COD reduction of 85%. After, its rate was maintained for approximately 5 weeks, the average biogas production was 0.4 m³/day and COD reduction was 81%. The loading rate was then increased to setting number 2 on the influent pump, and as shown in Table 8, the HRT was dropped from 23 to approximately 5 days, for an average of 562 L of influent per day. This corresponds to a loading rate of 1.27KgCOD/m³/day, indicates COD reduction of 85% and gas production of 1.42 m³ biogas containing over 75% methane. This indicates that increasing loading rates can result in even higher performance by the digester, possibly due to the higher bacterial populations in the digester over time (Williams et al. 1999).

Several studies showed that application of anaerobic digestion processes are successful to treat brewery wastewater. Another laboratory scale of anaerobic digestion processes indicates that brewery solid and wastewaters in combination together are also a good alternative for cogeneration of renewable energy. Anaerobic co-digestion is an advanced technology that takes advantage of complementary substrates to increase the methane yield of those substrates of brewery wastes. Brewery wastes (BW) is first used as co-substrate and co-digested with its solid wastes in batch mode at mesophilic conditions and finally achieved the maximum methane production of 287 LCH₄/KgCOD. The highest biochemical methane potential was obtained with hot trub, i.e., 251 LCH₄/KgCOD with higher methane production rate of 1.08 per day, which indicates its high biodegradability while the biodegradation of the spent grain and combination of T + SG samples were almost similar in their biochemical methane potential,

methane yield, and methane production rate (Costa et al. 2013).

In Ethiopia, most breweries industries release their wastewater into the environment. For example, St. George brewery, Addis Ababa, Ethiopia, the brewery produced approximately 107.7 thousand hectoliter (hL) beer and about 7.5 million hL total wastewater annually. This amount of wastewater was discharged into the water bodies previously and may cause Akaki river pollution. However, St. George Brewery installed the modern treatment plant (full-scale UASB) with re-aeration system in recently for better treatment of its waste. The waste water treatment system consists of a preliminary treatment unit, influent tank pit, equalization tank, UASB reactor, and a re-aeration treatment unit (Fig. 3). UASB operation is successfully carried out in the reactor at retention time of 6 h with loading capacity of 700 m³ in the presence of well-settling (granular) sludge in which the wastewater moved in the upward direction through a sludge blanket composed of biologically formed granules. The system was constructed from concrete and can treat 2000 hL water per day. The total time the wastewater spent in the treatment system is 17.5 h (Bula 2014).

The treatment process, first collected wastewater from different processing units of the brewery is passed through a fine screen in order to remove coarse material. Influent from fine screen goes to equalization tank, which buffer the influent wastewater with retention time of 8 h. This retention time is very useful to obtain sufficient hydraulic peak shaving and relief out of peaks in pH and organic loading and for partial hydrolysis of complex organic compounds to sugars, amino acids, and fatty acids. pH correction is done with NaOH or HCl additions and recycle of the anaerobic effluent at the pH correction tank. The pH correction tank is covered and off-gas is extracted and treated in the bio-filtration system. Then actual biological treatment of wastewater takes place in the UASB reactor. In this phase, the liquid flows in upward direction and mixed with settled biomass and treated wastewater flows through the re-aeration tank, remove odorous compounds and convert sulfides to sulfur and sulfate before discharged. At the top of the UASB-reactor, Lamella separator is installed for separation of the treated wastewater, biogas,

Table 8 AF performance in treatment of brewery wastewater at pilot scale (Williams et al. 1999)

Pump setting	Influent COD (mg/L)	Effluent COD (mg/L)	Influent pH	Effluent pH	HRT (day)	OLR (KgCOD/m ³ day)	Biogas (m ³ /day)
1	4757	896	7.41	7.18	23	0.20	0.40 (76.58%)
2	5859	855	7.44	7.17	4.6	1.27	1.42 (75.40%)
3	6050	800	6.31	7.10	2.2	2.79	2.83 (74.4%)

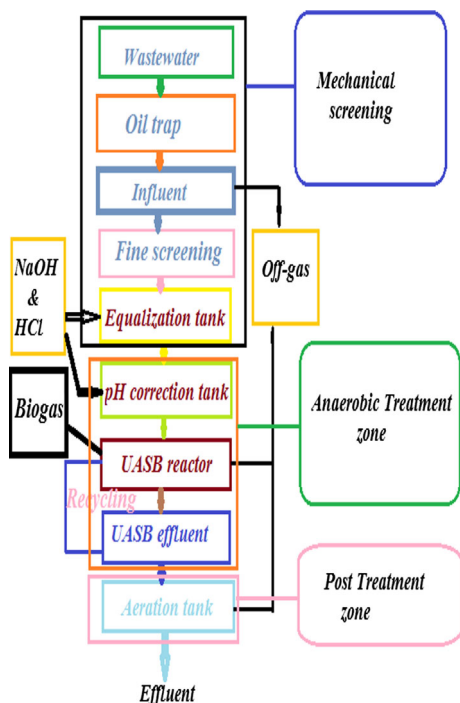


Fig. 3 St. George brewery wastewater treatment plant

and sludge. The produced CH₄ (487 Nm³/day) is burning by flare while CO₂ used for internal circulation for carbonation (Bula 2014). In over all, the treatment plant has low performance efficiency in removal of mainly nutrients (TN and TP) including TSS, BOD5 (Table 9). This may be due to the low understanding of the process and implementation of the technology. For further removal of these pollutants in order to achieve the Ethiopia Environmental Protection Authority (EEPA) standards, the St. George

brewery factory should extend its treatment using sequencing batch reactor. In general, for better removal of both organic matter and nutrients from brewery wastewater, SBR is very useful as post-treatment shown in Table 4, because of its high removal efficiencies for both organics and nutrients (Min 2013; Panbic 1996; Zhan et al. 2008). Based on the removal efficiency of the SBR from literature, a possible extended design treatment options for brewery wastewater is illustrated in Fig. 4.

Integrated anaerobic–aerobic bioreactors

Anaerobic–aerobic FFB reactor

The combination of two fixed-film bioreactors (FFB) is illustrated in Fig. 5a, with arranged media, the first anaerobic and the second aerobic, connected in series with recirculation for treatment of wastewater.

Anaerobic (UBF)–aerobic (MBR) reactor

Anaerobic up flow bed filter (UBF) is a combined hybrid reactor of anaerobic UASB and anaerobic FFB (Fig. 5b). The bottom part of the UBF reactor is the UASB, in which granular sludge is developed. With the presence of stationary packing material, the upper part of the UBF serves as a FFB. The greater advantage of the UBF is its capacity to eliminate the problems of clogging and biomass washout which are commonly encountered in anaerobic FFB’s and UASB’s, respectively. Aerobic membrane bioreactors (MBR) combine membrane filtration with biodegradation processes, and separates solid–liquid through sieving. In a MBR, solid materials, biomass, pathogenic bacteria, and

Table 9 Average value of brewery wastewater parameters before and after treatment (Bula 2014; EEPA 2009)

Parameters	Raw wastewater	Influent tank effluent	Equalization tank effluent	UASB + Aeration effluent	EEPA standard
Characteristics of brewery					
pH	9.9	9.9	8.7	7.8	6–9
COD (mg/L)	2676	2534	2480	209 (92.2%)	250 mg/L
BOD5 (mg/L)	1505	1480	1413	79 (94.7%)	60 mg/L
TSS (mg/L)	686	551	397	87 (87.3%)	50 mg/L
TN (mg/L)	39	38.3	37.5	34.6 (11.3%)	40 mg/L
NH ₄ -N (mg/L)	16.5	15.6	15.2	14 (15.1%)	20 mg/L
NO ₃ -N (mg/L)	7.8	7.3	6.0	4.3 (44.9%)	–
S ²⁻ (mg/L)	0.24	0.29	0.37	0.04 (83.3%)	–
TP (mg/L)	57.3	57.0	55.1	52.0 (9.25%)	5 mg/L
PO ₄ ³⁻ (mg/L)	58.45	57.95	56.7	54.0 (6.61%)	–

() = Removal efficiency of integrated UASB–aeration systems

Fig. 4 Extended possible brewery wastewater treatment

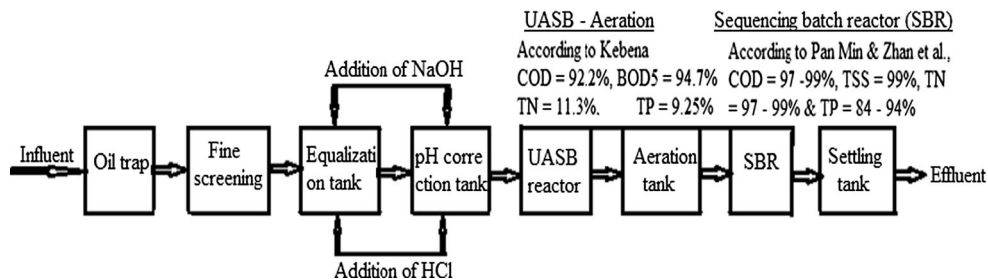
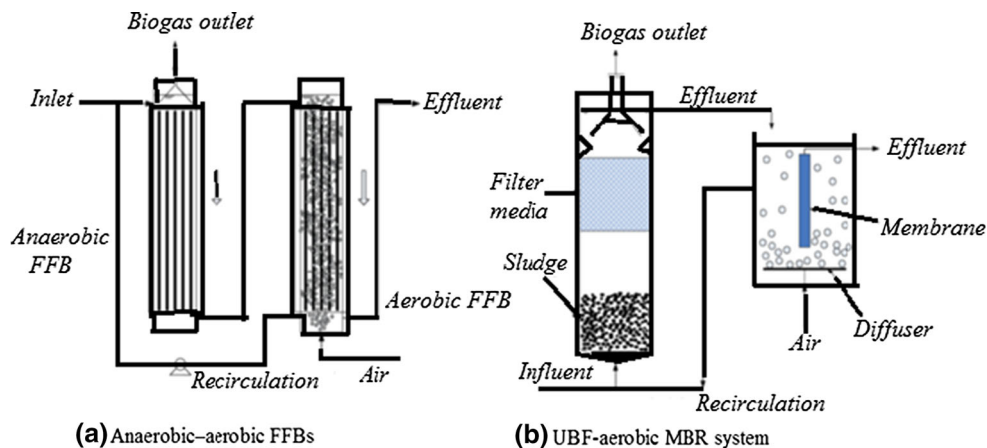


Fig. 5 Integrated anaerobic–aerobic reactor



macromolecules are retained while allowing water and smaller solution species to pass through the membrane and produce a very high quality effluent. The membrane-retained aqueous and particulate-based enzymes which are otherwise lost in the conventional sedimentation–clarification step are also able to improve the metabolic rate in the MBR (Chan et al. 2009).

Integrated anaerobic–aerobic bioreactors are a promising technology employed in industrial wastewater treatment to attain further emission reduction left from former treatment plant. In the recent years, high-rate integrated anaerobic–aerobic bioreactors are increasingly employed for high organic strength industrial wastewaters treatment. These bioreactors control environmental problems caused by high organic waste discharging through degradation of constituents by consortium of microorganism. In comparison with conventional wastewater treatment methods, anaerobic treatment is highly applicable for waste treatment based on the concept of recovery of valuable byproduct for utilization while aerobic biological methods are commonly used in the treatment of organic wastewaters for achieving high degree of treatment efficiency. Some anaerobic-integrated treatment systems efficiencies are summarized in Table 10 (Chan et al. 2009).

Despite the great advantages presented by anaerobic reactors, for example UASB, the quality of the treated effluents does not comply the discharge standard limits. The high strength industrial effluents produced by dairies,

slaughterhouses, and breweries usually require a post-treatment. The UASB–CW integration indicates the following abatement efficiencies with regard to BOD5 (92.9%), COD (79.2%), SS (94%), and fecal coliforms (98.8%) were achieved compared with single UASB treatment efficiencies shown in Fig. 6 (Raboni et al. 2014). Other post-treatment techniques (Fig. 7) aid to minimize UASB effluent quality problems are polishing pond (PP) works by maintaining wastes in ponds, constructed wetland systems using vegetation covers allowing to overland flow and dewatering the sludge, down flow hanging sponge (DHS) through providing a large surface area to accommodate microbial growth on a sponge cubes, because of oxygen supply through it naturally in the downstream way without external supply. Another method is duck weed pond (DP) uses aquatic macrophytes to recover the nutrient and transform them into easily harvested protein-rich byproducts. Last column of Table 10 indicates the treatment Performance of various Integrated UASB Post-treatment systems (Khan et al. 2016).

Some factors affecting anaerobic digestion

pH (potential hydrogen)

Due to the formation of different intermediates, anaerobic reactions are highly dependent on pH value, particularly for



Table 10 Anaerobic–aerobic high-rate reactors

Type of reactor	Type of wastewater	Influent COD (mg/L)	OLR (KgCOD/m ³ /day)	Anaerobic COD removal	Aerobic COD removal	Total HRT	References
2UASB + CSTR	food	5400–20,000	4.3–16	58–79%	85–89%	5.75 day	Agdag and Sponza 2005
RBC + FFB	cheese whey	37,400–65,700	5.2–14.1	46.3–62.6%	93–95%	–	Lo and Liao 1989
FFB + FFB	slaughterhouse	400–1600	0.39	–	–	4.7–7.3 day	Del Pozo and Diez 2003

Integration	BOD	COD	TSS	NH ₄ -N	TN	TP	Fecal coliforms (FC)
Characteristics of effluent (mg/L, except FC (MPN/100 mL))_(Khan et al. 2016)							
UASB + PP	24 (92%)	108 (79%)	18 (96%)	20 (50%)	25 (55%)	–	5.8 × 10 ² (99.999%)
UASB – DP	14 (96%)	49 (93%)	32 (91%)	0.41 (98%)	4.4 (85%)	1.1 (78%)	4.0 × 10 ³ (99.998%)
UASB + DHS	9 (96%)	46 (91%)	17 (93%)	18 (28%)	28 (40%)	–	3.4 × 10 ⁴ (99.95%)

() = Removal efficiency of integrated treatment systems

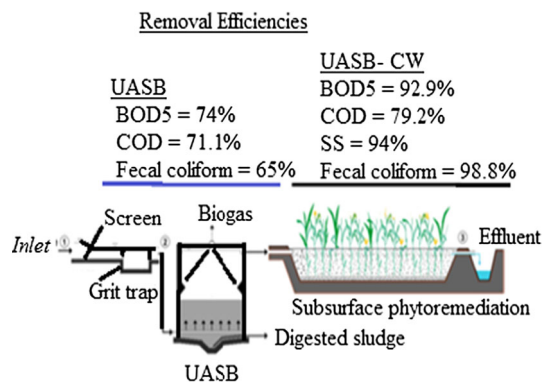
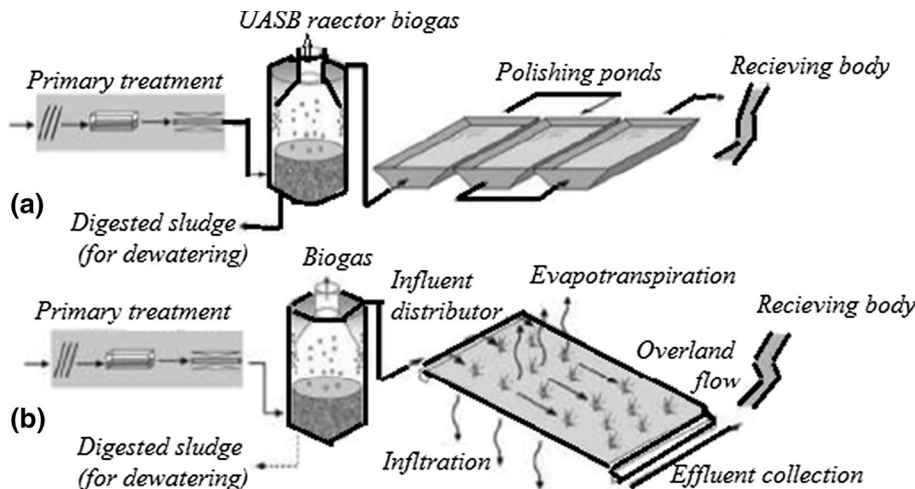


Fig. 6 UASB–CW integrated treatment plant

methane producing bacterial ranging between 6.8 and 7.2. While, acid forming bacteria are desirable to a more acidic condition. So, the pH of anaerobic system should be maintained between the methanogenic limits to avoid the

Fig. 7 a UASB—polishing ponds and **b** UASB—constructed wetland treatment system Source: Chernicharo (2007)



predominance of the acid forming bacteria which may cause volatile acid accumulation. Therefore, microbial groups involved in each phase require different pH conditions for optimum growth. To achieve this, it is essential to provide buffering agents like sodium bicarbonate to neutralize any eventual VFAs accumulation. Because, NaHCO₃ is useful for supplementing the alkalinity, which shifts the equilibrium to the desired condition without disturbing the microbial population (Saleh and Mahmood 2004).

Temperature

AD occurs under a variety of temperatures depending on the species of microorganisms employed. In general, controlled anaerobic digestion is subdivided into three temperature ranges, psychrophilic (10–20 °C), mesophilic

(20–40 °C), and thermophilic (50–60 °C). The structures of the active microbial communities at each temperature optima are quite different. For example, bacterial growth and conversion of organic materials is slower under psychrophilic conditions. The rate of methane production increases as temperature increases until maximum mesophilic temperature ranges, 35–37 °C, because in this temperature ranges mesophilic microorganisms are actively involved. In general, biogas production yield depends on the choice of optimal temperature conditions for microorganism activity. In general, most conventional anaerobic digestion processes occur under mesophilic temperatures. Because, this operation conditions are more stable and requires less energy input compared to operations under thermophilic conditions, and results in a higher degree of digestion (de Mes et al. 2003). The maximum (i.e., thermophilic) and minimum (psychrophilic) temperatures explain the limits of the temperature ranges for microbial optimal growth rate. The optimum temperature ranges are suitable conditions for maximum microbial growth rate. While the microbial growth becomes typically low below the optimal temperature levels and in some extent, it increases its growth exponentially at higher temperatures but some while microbial growth become restricted (Fig. 8; Chernicharo 2007).

C/N ratio

Unbalanced C/N ratio is one of a limiting factor of anaerobic digestion. Substrates with high C/N ratios, such as paper and most crop residues will be deficient in nitrogen, which is an essential nutrient for microbial cell growth. Thus, anaerobic digestion of very high C/N ratios may be limited by nitrogen availability. In the case of substrates with low C/N ratios, such as some animal manure, toxic ammonia buildup may become a problem. To overcome deficiencies in either carbon or nitrogen, co-

digestion of low C/N materials with high C/N materials has been proven an effective solution (Martin-Ryals 2012).

Nutrients

Nutrient at optimal levels are important for microorganisms for cellular building blocks and ensures that the cells are able to synthesize enzymes and co-factors responsible for driving metabolic activities. These include macronutrients such as nitrogen, phosphorous and sulfur, vitamins and trace elements (iron, nickel, magnesium, selenium, copper, cobalt). Even though, nutrients are required in very low amounts, lack of them causes significant effect on growth of microbes (Kock 2015).

Organic loading rate (OLRs)

Organic loading rate is defined as the number of volatile solids or chemical oxygen demand fed to the system per unit volume per time. Higher OLRs can allow for smaller reactor volumes thereby reducing the associated capital cost. However, at high OLRs there is a danger in overloading of the reactor, especially during reactor start-up. At higher OLRs, retention times must be long enough such that the microorganisms have enough time to sufficiently degrade the material. Thus, there is a balance between OLR and HRT that must be determined in order to optimize digestion efficiency and reactor volume (Martin-Ryals 2012). Hydraulic retention time (HRT) can be defined as the amount of time that waste remains in the digester and in contact with the biomass. For easily biodegradable compounds such as sugar, the HRT is low whereas more complex compounds need longer HRTs. HRT values influences the rate and extent of methane generation and is one of the most significant factors affecting the transformation of volatile substrates into gaseous products (Kock 2015).

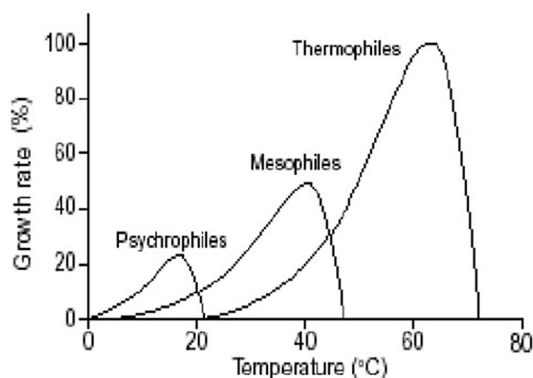


Fig. 8 Temperature effect on the relative growth rate of psychrophilic, mesophilic, and thermophilic methanogens

Conclusion

- Anaerobic reactors are efficient waste treatment technologies that harness natural anaerobic decomposition to treat wastewaters and generate biogas, widely used as a source of renewable energy. However, anaerobic digestion can be affected by pH, temperature, excess nutrients, organic loading rate, HRT, and others.
- Dairy, slaughterhouse, and brewery influents are increasingly being recognized as an important resource to produce value added products.
- The theoretical maximum methane production potential calculation from the COD value of Kera and Luna slaughterhouse and Ada milk factory influents indicates

that they are potential source for cogeneration of byproducts. Therefore, the EEPA should enforce these agro-industrial sectors to install integrated anaerobic–aerobic treatment technologies.

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