REVIEW ARTICLE



A comparative study of bioelectrochemical systems with established anaerobic/aerobic processes

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Abstract

Biomass can be considered the most abundant source of renewable energy on this planet and also the most viable green alternative to the conventional energy sources. The review work encompasses the study of bioelectrochemical systems (BES) and various types of BES in usage and their multifarious applications, their mechanisms, and variations. In the past few decades, microbial fuel cells have made their presence felt wherein biomass energy can be converted to electrical energy. The study also dwells on the various challenges related to the conversion rates and yields. The work will also entail the various aspects associated with anaerobic and aerobic processes, technologies, their advantages and disadvantages, and some recently developed technologies like AnMBR. The pros and cons of all the technologies have been discussed in detail.

Keywords Bioelectrical systems \cdot MFC \cdot MEC \cdot Aerobic \cdot Anaerobic

1 Introduction

In the past few years, there has been an ever-growing need for new and renewable energy resources that is fueled due to the diminishing presence of fossil fuels. The annual global energy needs to stand today at more than 13 TW and are predicted to be around 23 TW by the year 2050 [1]. As the global needs keep on mounting every day with increasing demands from industry, agro, and municipal sectors, the degradation to the environmental setup is steadily mounting. Although the recent COVID pandemic has done some good in that direction as the world came to a standstill with most of these activities coming to a complete halt, once the things are restored, this degradation will escalate with a higher degree than before to make up for the industry losses. Keeping that in mind, exploring new, sustainable, and cost-effective renewable technologies is essential for creating a sustainable and long-lasting landscape that needs less dependency on fossil fuels and conventional energy sources. In the past 2 decades, bioelectrochemical systems (BESs)

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¹ Department of Chemistry, BITS Pilani K K Birla Goa Campus, Sancoale, Goa, India 403726 have shown a tremendous potential of emerging as a strong contender for valorizing a broad spectrum of gas and liquid waste streams. It is emerging slowly as a strong contender for wastewater treatment against conventional technologies like aerobic and anaerobic processes which are already wellestablished technologies with a large global footprint. The most commonly prevalent treatment technologies employed for sewage and industrial effluent in India are activated sludge, trickling filters, rotating biological contractors, upflow anaerobic sludge blanket process (UASB), and waste solubilization ponds. The current review focuses on shedding light on bioelectrochemical systems by discussing types and summarizing the electron transfer pathways. A comparative study was made between aerobic and anaerobic process for different parameters. Also, various aspects related to the aforementioned technologies in terms of design parameters, various types of BES in usage, their working principles, working, product formation and removal, wastewater treatment technologies, and some newly developed hybrid technologies like AnMBR were presented [2].

1.1 Introduction to BES

The conversion of waste into useful energy concurrently addresses the problems pertaining to environmental and energy crises. Fuel based on biomass is set to play a pivotal role in bringing down the CO_2 emissions significantly. The

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transformation of biomass into energy and fuel is usually initiated by either thermo-chemical or biochemical routes. Bioelectrochemical systems in this regard offer strategical promise by transforming organic waste/biomass into chemical/electrical products in MFCs (microbial fuel systems)/MECs (microbial electrolysis cells) via electrochemical reduction. The unique features of BESs such as operating under comparatively mild conditions and employing a large range of organic substances and usage of inexpensive metals outweigh the other benefits in the conventional fuel cells [3].

The importance of energy in propelling the global economy is well known owing to human reliance in their day-to-day lives. As per the literature [4], the average global power consumption is 13 TW. In a recent report, it was realized that energy usage greatly hampers economic activity [5]. Furthermore, to keep the global standards high, a quantum jump is needed for meeting the ever-growing demands of ramping populations across the globe. Nonetheless, on the other hand, depleting non-renewable energy resources implies poor chances for substantial improvement in energy supply. In the view of sustainable and eco-friendly generation of power, electrochemical energy is under extensive study in recent times [6]. Energy obtained from "negative-value" waste streams can not only aid in meeting the world's energy demands, but also in reducing the pollution. Moreover, the costs associated with it are cheap. Over several decades, anaerobic digestion has been widely regarded for CH₄ recovery from both solid and liquid waste streams. The fermentation of CH_4 has many benefits over aerobic treatments such as renewable energy production, lower energy expenses, reduced treatment of sludge, and lower disposal costs. Due to the commercial success of anaerobic technology, a huge number of full-scale plants are operative around the world [7]. In a similar line, dark fermentation also drew decent attention owing to its clean energy generation via H₂ fuel cells. However, the existing fermentation technologies could offer a maximum yield of 2-3 mol H₂ per mole of glucose as the organic matter remains stuck as VFA or alcohols and lower the energy production. Therefore, the process is more suitable for feedstock that contains carbohydrates like glucose.

Many reducing bacteria like *Shewanella oneidensis* and *Geobacter sulfurreducens* catalyze the transport of electrons from the anode (more commonly graphite), which acts as an electron acceptor [8]. As the cathode is connected to an external circuit, the electric power can be generated in the fuel cell by bacterial respiration [9].

2 Types of BES

BESs are typically classified into two types: enzymatic fuel cells (EFC) and microbial fuel cells (MFC). A further sub-division of BES is seen into MFCs (MEC, microbial desalination cells (MDCs) and microbial solar cells (MSC)). The idea of MSC's was comprehensively demonstrated in a few reports, and readers are encouraged to go through it [10–12]. Nevertheless, employing BESs for simultaneous use in desalination and energy recovery was introduced only in recent times [13] and extended further by other groups [14, 15]. Stacked MDCs were also considered in this regard, where desalination and concentrated chambers are separated by compartmental anion exchange membranes (AEMs) and its cationic counterpart membrane (CEMs) [16]. In another study, operating a twin-desalination chambered MDC having an external resistance of 10 V (1.4 times that of one-desalination chambered MDC), a record TDR (total desalination rate) of approximately of 0.0252 g h^{-1} was achieved. Lately, the idea of the microbial electrochemical snorkel (MES) was started for treating the urban wastewaters [17]. In contrast to MFCs, an MES does not ensure diverting energy but maximizes the organic matter oxidation efficiency. Hence, an MES cannot directly generate current, but improves the efficiency of process treatment.

3 MFC

As stated before, MFCs transform chemical energy into electrical energy by catalytically breaking down the organic substrates. Usually, the organic oxidation occurs in the anode compartment, followed by which protons and electrons are produced. Later, the electrons are transported towards terminal electron acceptor (TEA) (via external circuit) for its reduction. On the other hand, protons are transported to the cathode via a membrane that bifurcates cathode and anode. TEAs such as nitrates, oxygen, and sulfate diffuse into the cell to accept electrons to form new products, which leaves the cell. For instance, the microorganisms act as catalyst to oxidize the substrate (and remove electrons) in the anode chamber, and electrons are then transported to cathode through the circuit. To catalyze the reduction reaction at cathode surface, either microorganism or Pt can be used; nevertheless, expensive materials are usually avoided. In the anodic chamber, the organic substance forms CO₂, which leaves the cell, and the protons from the same reaction diffuse into membrane and reach the anodic surface. The protons and TEAs such as O₂ (in the aerobic chamber) receive electrons from the cathodic surface and release clean water. Nonetheless, certain exoelectrogenic bacteria are capable to transport electrons exogenously to reduce TEA. These exoelectrogenic bacteria are responsible for generating power in an MFC system [18]. The scientific interest on MFCs has been increasingly high [19], owing to its safe and clean alternative approach treating wastewater, energy generation, and bioremediation [20, 21]. Many reviews have previously demonstrated the multifarious applications of MFCs to use a broad wide range of substrate materials [19]. Also, the power outputs of MFCs have been enhanced substantially during the last decade by modifying their design parameters and biocatalyst selections [22].

Unlike other bioprocesses, a major benefit with MFCs is the low loading rates [23]. Generally speaking, anaerobic takes in influent organic concentrations in a range of 20 000 mg COD/L or more before generating the net energy, whereas the aerobic processes operate below that [24]. With so much sophistication, as we witness in recent times, it is unlikely that MFCs will contribute to generate power (from organic wastes) and serve as a perpetual source of electricity. Nevertheless, they may be employed in a practical sense when high-energy liquid wastes like food processing and milk are considered to produce electricity.

3.1 Microbial electrolysis cell (MEC)

In MECs, H₂ production is achieved from acetate and other fermentation products by electro-hydrogenizes. Here, the bacteria are called exoelectrogens [25], oxidizing the substrate and generating electrons at the anode. Unlike MFC, the current generation is not possible in MECs as the cathode is anaerobic. Hence, a low small voltage is externally applied, thereby ensuring H_2 generation at the cathode by reducing H⁺ ions [26]. When the substrate is acetate, a voltage of around 0.2 V is needed for H_2 evolution [27]. The required voltage is significantly lower than what is required for hydrogen production by water electrolysis (1.8–2.0 V) [28]. Therefore, cathodic reactions occur without oxygen, while the anodic reaction is similar to that of MFCs. The working mechanisms and the advancements in the technology were previously demonstrated in few reports [26]. MECs also draw special attention due to its effectiveness for H₂ recovery from swine wastewater. However, the process requires an extended evaluation of limiting the generation of CH₄ and simultaneously improving the efficiency of organic matter conversion to power and also on enhancing the H_2 gas generation at cathode [28].

3.2 Enzymatic fuel cells (EFC)

EFCs utilize biofuels that are already present in nature such as sugars and alcohols [29]. EFCs possess higher power densities as compared to MFCs, but with poor lifetime and partial oxidation of fuel [30]. However, the usage of newer polymers that immobilizes and stabilizes the enzymes has been considered to enhance the life-time in recent times [31]. Further, as enzymes are very specific, they do not need the presence of a membrane separator. The usage of one enzyme (or enzyme cascades) ensures reaction pathways that are defined on the electrode surface and overcome the shortcomings in output performance of MFCs [32]. This may be referred to as the mass transfer resistance across the membrane cell (Fig. 1).

4 Electron transfer mechanism in BES

The electron transport pathway witnessed in BESs is similar to pathways studied for dissimilar metal-reducing microorganisms. Till date, three major plausible electron transport mechanisms were considered: (a) direct electron transfer (DET) with proteins on the surface of cells, (b) mediated electron transfer (MET) via using redox reactive molecules which transfer electrons to the surface of the electrode by a diffusion-limited process, and (c) electrically favorable appendages also called as bacterial or microbial nanowires [34]. Although these mechanisms are sufficient to draw appropriate conclusions, the electron transfer mechanism remained controversial [35]. The widely considered microorganisms in the MFCs are related to *Pseudomonas, Geobacter, Proteobactor, Shewanella*, and families.

5 Thermodynamics of BES

In a typical MFC, reduction and oxidation of electron acceptors and donors happen at cathode and anode, respectively [36]. The electron donor (which is acetate here) is oxidized to HCO₃⁻, and O₂ is reduced to H₂O [21]. The net cell voltage obtained was positive, and therefore, electricity is generated. On the other hand, the absence of O_2 in a microbial electrolysis cell resulted in the reduction of acceptors such as H^+ to form hydrogen, at a potential around -0.41 V vs SHE. The resulting cell voltage was around ca. -0.13 V, which makes the reaction non-spontaneous. Therefore, an external force or energy is required to drive the reaction. BES can work similarly to an MFC when electricity is recovered where external power is needed to improve the kinetics of the reaction. Due to the losses incurred, the output energy is very less, whereas the input energy required higher than the calculated theoretical value. Activation overpotential losses are usually attributed to catalysis that is not sufficiently perfect at the electrode.

6 Types of product of BES

6.1 Methane

During the inception of MECs, CH_4 production was not considered an option; however, lately, there is a paradigm shift in this regard [37]. Since H_2 production from acetate is thermodynamically not feasible at standard conditions, an extra voltage of around 0.14 V must be applied to the electrolysis



cell. Typically, a voltage of around 0.20 V is required to initiate the production of electricity [26]. Given that the electron donor does not contain any organic substances, the applied electrical energy is less than the specific energy content of the end product, thereby theoretically generating a positive energy balance in a MEC. The advantage of CH_4 is that its transportation is relatively easier. Moreover, the compression, transportation, and storage demand advanced techniques and readily be coupled with available equipment to achieve an enhanced performance [38]. Besides, the CH_4 producing MECs were regarded as energy-friendly effluent polishing step for digester effluents without any aeration expenses [39]. The synthesis of CH_4 by reducing CO_2 at biocathode is presented in a study using a pure culture of Methanobacterium palustre [38]. Despite the possibility of direct electron transfer to methanogens, there are not enough reports to make conclusive statements relating to it.

6.2 Ethanol

Biologically reducing acetate by using H_2 is a promising strategy to transform biomass waste into C_2H_5OH . Acetate reduction to C_2H_5OH with methyl viologen (MV) as a mediator was investigated in recent times [40]. The C_2H_5OH formation observed a CE value around ca. 49% and alongside ethanol, n-butyrate, H_2 , and the nonreversible reduced MV2 + generated at cathode. In the previous reports, the research groups illustrated the reduction of butyrate to butanol by employing hydrogen at low overall yields of alcohol [41]. When acetate is successfully converted to C_2H_5OH in the setup discussed before, butyrate formed might lead to butanol [21]. To further enhance the C_2H_5OH formation, the microorganism can be grown at cathode, thereby driving the reduction of acetate [40]. Also, considering the immobilization of methyl viologen on the electrode could bring desired results in this regard.

6.3 Hydrogen peroxide

The synthesis of H_2O_2 carried out using BES was first reported by coupling anode (oxidation) to the cathode (reduction) [42]. When an external voltage of around 0.5 V was applied, 1.9 kg $H_2O_2/m^3 day^{-1}$ was obtained at 83.1% efficiency of 1258[43]. Since maximum energy was drawn from acetate, the energy requirement was substantially reduced to almost half. Nevertheless, hydrogen peroxide was observed to very low ca. 0.13%, thereby making it tedious for the useful recovery.

6.4 Removal of recalcitrant compounds

Recently enhanced wastewater treatment in BES has been reported employing cathode [44]. The cathode ensures a larger pace from the physical aspect for carrying out the biological treatment and aids in the removal of those recalcitrant compounds that are not removed through oxidation. Usually, most of the recalcitrant compounds are removed by oxidation; some like nitrobenzene can be removed by reduction. Nitrogen can also be removed by cathodic reduction and was reported in BES [45]. This can be extended to nitrate, nitrite, ammonia, etc.

Hexavalent chromium, Cr(IV), can be reduced catalytically to less soluble, trivalent Cr, Cr(III), and less toxic avatar in an acidic environment [33] at the cathode. Air bubbling cathode MFC has also been employed for carrying out this process.

Since sulfur and sulfur compounds are usually seen to be present in wastewater and organic wastes, their conversion generates toxic, corrosive, and odorous sulfides [33] whose removal is essential. Sulfate removal can be carried out by employing MFCs by electrochemically oxidizing them at the anode which can then be used for the generation of power.

7 Biological treatment process (anaerobic/ aerobic)

The treatment of municipal waste and wastewater from industries at an appropriate level is very important to protect the environment and public health. Generally, aerobic biological processes such as activated sludge and the variants of it are employed to mitigate biodegradable COD that are present in the wastewater. Despite the abovementioned processes outweighs chemical-physical processes on the grounds of cost factor and sustainability, the energy requirements are too high for aeration. Hence, it is essential to shift the direction towards reducing the energy requirements by considering the energy recovery solutions. In this regard, anaerobic processes were regarded for treating industrial wastewater as one of the alternatives for the aerobic process. The advantage of the former comes with no requirement for aeration. In an effort to develop further, the anaerobic process was coupled with a microalgae reactor. In this integrated system, carbon dioxide generated from anaerobic processes was consumed by microalgae in the photobioreactor to promote their growth. The microalgae are later separated and dried before using them for various processes such as conversion to bio-diesel, bio-ethanol, maximization of energy production, and carbon dioxide eradication from wastewater. Coupling of the microalgae growth with the anaerobic reactor gives it an innovative twist wherein bioelectricity generation occurs due to incorporation of membrane within the cells, thereby not only generating bioelectricity but also biogas generation. When all the important factors are considered, the shift towards the innovative process of anaerobic digestion process (from traditional active sludge) can always result in substantial energy reduction. Figure 2 depicts the comparison between the conventional activated sludge and an innovative anaerobic digestion process.

7.1 Wastewater treatment technologies

The aerobic biodegradation of COD is the widely considered biological process for wastewater remediation (such as the active sludge process). Usually, the aerobic process records higher efficiency for biodegradation when compared to its anaerobic counterpart; however, greater energy requirements limit its widespread use. Importantly, the anaerobic process is very much suitable for converting waste organics into energy (up to 3516 kWh for every ton of COD), and the absence of energy utilization attributed to aeration is another added advantage. Low biomass generation, maintenance, and decreased endogenous decay during starvation are among other benefits with anaerobic digestion [46]. The sludge generated in the anaerobic digestion processes is abundant in minerals, hence may be employed as a fertilizer. Nevertheless, the process also suffers from some flaws such as low COD removal efficiency and slowness in comparison to the aerobic digestion process. These drawbacks of AD are compensated to a large extent by using longer values of the solids residence time than the aerobic processes. Notably, anaerobic digestion offers decent compensation in terms of providing longer residence times for solids, thereby having an overall lead over the aerobic process. A comprehensive comparative study between aerobic and anaerobic processes was shown in Table 1. As the investigation involves energy production from wastewater, the discussion is made accordingly and hence dedicated more to the anaerobic process.

Table 2 depicts the detailed study of various anaerobic digesters. As stated above, despite there are clear-cut benefits, the anaerobic process fails in reaching the required quality for reuse; hence, further treatment is mandatory to meet the acceptable quality standards. In this regard, the strategic integration of anaerobic reaction with membrane filtration could serve the purpose without requiring any aerobic post-treatment. This coupling of the anaerobic reactor and membrane filtration (low-pressure ultra-micro filtration membrane) is known as anaerobic membrane bioreactor (AnMBR). In this system, the wastewater is filtered, and the volatile suspended solids (VSS) are retained. The resultant slurry comes in the compressed and biodegradable form contributing to a reduction in reactor volume.

AnMBR is capable of remediating high COD, TDS wastewater samples, which is key in decreasing the pretreatment demands. The pre-treatment requirements are Fig. 2 Schemes for wastewater treatment: a conventional aerobic activated sludge process; b innovative anaerobic process followed by photobioreactor (PBR) for microalgae production, discussed in this paper [2]



 Table 1 Comparison of anaerobic and aerobic treatment [47]

Parameter	Anaerobic	Aerobic
Energy requirement	Low	High
Degree of treatment	Moderate	High
Sludge	Low	High
Organic removal efficiency	High	High
Bioenergy and nutrient recovery	Yes	No
Process stability	Low	High
Start-up time	2 to 4 months	2 to 4 weeks
Nutrient requirements	Low	High for certain industry wastes
Biogas production	Yes	Low

usually high in conventional digesters. Typically, this can reach close to 94–99% COD removal and a methane generation of 0.25–0.35 $m^3 kg^{-1}$ COD [48]. Additionally, it can be coupled to existing anaerobic digesters with less complexities and enhance the working and quality of effluent. Employing a membrane in an anaerobic digester could substantially improve the SRT and reduce the HRT, thereby decreasing the reactor size also. Table 3 depicts the parametric study for biogas generation from different sources.

The combined effect of anaerobic reactors coupled with membrane decreases the overall required energy. Numerous studies highlighted the benefits of this synergetic effect over traditional aerobic processes for wastewater treatment [54]. In a few reports, PVDF micro-/ultrafiltration was believed to be widely employed; however, the only exception was employing a flat sheet dynamic membrane [55]. In contrast to the former, the performance of the latter was greatly controlled by the molecular weight of the solution and its concentration and shape. A lot of reports have demonstrated full-scale aerobic MBR studies [56]; nevertheless, as of now, only one investigation has been performed on AnMBR; in whose case, wastewater was retained [57]. High SRT, a strength of AnMBRs, ensures

Table 2	Comparison	between t	he types	of anaerobic	digesters	[2]
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Reactor	Feed	COD removal	Organic loading rate (kg COD/m ³ -d) COD/(md)	Hydraulic retention time (d)	Methane produc- tion (m ³ /kg of COD)
Anaerobic membrane bioreactor	Brewery	99%	Above 30	2.5 to 4.2	0.28
	Distillery	97%	1.5	15	0.26
	Municipal Wastewater	94%	0.4–0.9	0.67-1.5	0.24
UASB reactor	Wastewater	90% COD	2-3.6	3.91	0.22
Fixed film reactor	Domestic Wastewater	64–78%	1.6	4–6	0.152
Hybrid reactor	Vinasses	69% COD removal	17.05	7.5	0.263
Expanded bed reactor	Domestic Wastewater	89% COD removal	4.4		0.22

Table 3 Comparison of parameters for biogas production in AnMBRs from different sources

Wastewater	Brewery	Food industry	Kraft evaporator condensate	Sewage	Landfill	Coal industry	Distillery
COD (gL ⁻¹)	80–90	-	10	-	41	19.1	22.6
Temperature (°C)	35–37	24–35	36–38	24-35	37	37	53-55
Organic loading rate (kg COD/(m ³ d)	Above 30	0.4–11	22.5	0.4–11	6.27	Up to 25	1.5
HRT (day)	2.5-4.2		-	-	7	1.3	15
MLSS concentration (gL ⁻¹)	Up to 51	16–22	8-12	16-22	-	36	-
COD (removal)	99.00%	60–95%	93–99%	60–95%	90.70%	96.80%	97%
Methane(m ³ /kg COD)	0.28	-	0.25	-	0.18	-	0.26
References	[49]	[49]	[50]	[51]	[52]	[51]	[53]

higher COD removal besides helping the microorganisms to adapt in bizarre environments like saline waters and pharmaceutical wastewaters [56].

The salt content on non-adapted biomass limits the efficiency of anaerobic systems, due to the former's toxic effect on the latter. Due to the inverse proportionality of efficiency with temperature, numerous reports displayed results in mesophilic conditions [58, 59]. Nevertheless, a study was reported in thermophilic conditions for treating the wastewaters obtained from the food industry [60]. Other reports concluded ambient conditions work best for low strength [61] and domestic wastewaters [62]. When the water is complex and contains larger particulate chunks, high operating temperatures can result in consequential problems. Operating the system below 20 °C is difficult in those situations; nevertheless, some studies have been undertaken at simulated conditions [61]. In a similar context, the same group performed studies at15, 12, 9, 6, and 3 °C and observed a substantial decrease in COD [63]. This reduction leads to better performance using membrane biofilm. Also, the reusability tests were performed at psychrophilic conditions, and the results suggested a higher efficiency of submerged AnMBR over conventional AnMBR.

7.2 Aerobic treatment processes

Processes that employ aerobic methods to remediate wastewater are activated sludge process (ASP), rotating biological contactors (RBC), aerated lagoons, and trickling filters, and ASP is the most widely used treatment process for eliminating organic substances. The advantages of the process are it can be operated in isolated facilities like hotels, hospitals, and small communities. Besides, it comes with other advantages such as high resistance to organic and hydraulic shock loads with a range of loading rates. Also, the process ensures a decrease in BOD, COD, and pathogen levels up to 99% [64]. Further, high nutrient removal is possible. ASPs can be altered to reach specific desired discharge limits depending on the demands. ASP is a self-sustaining process with manageable mechanical work.

ASPs demand high electric power, capital, and importantly; operating expenses is a major constraint. Another constraint is lack of availability of all the materials, demanding experience in designing, unique construction, and high maintenance. Moreover, the process is vulnerable to complex biological and chemical problems and requires posttreatment on the completion of the process [64].

RBC is an aerobic fixed film biological treatment that could operate with minimal power, nonetheless, displays

high stability ascribed to its shock resistance [65, 66]. Despite consuming a low amount of energy, RBC requires an uninterrupted power supply for its operation. RBC demands high maintenance costs and skilled technical labor, and the contact media are usually not accessible at local markets [65].

Trickling filter is an attached growth process that demands a small land area with capabilities of operating for a large range of organic loadings. The nitrification process of organic waste is very potent in this process. Here, high capital expenses, the need for the design expertise, high maintenance costs, and uninterrupted power and water supply are among the limitations. Moreover, the unavailability of parts and clogging makes tricking filter difficult to use.

An aerated lagoon is a suspended-growth biological treatment process with a large earthen lagoon or basin. It is provided with mechanical aerators to mimic the aerobic environment and also to avoid settling of the suspended biomass. Aerated lagoons are inexpensive, demanding low energy, low maintenance, and simplicity in operation are some important attributes. In addition to this, it is capable of handling intermittent usage and shock loadings relatively better than other considered systems, thereby making it the best choice for resorts, and other seasonal properties. Aerated lagoon demands large land areas and hence can prove to be expensive if land is available at a premium in the place of interest. However, aerated lagoons are not so efficient in cold climatic conditions, thereby demanding large HRT. The aerated lagoons that are not well-maintained host insects, and they always underperform while removing heavy metals from wastewater. Furthermore, the system contains algae and requires constant attention and polishing to reach the discharge limits, which increases the maintenance cost.

7.3 Anaerobic treatment process

Anaerobic digestion is a 4-step tortuous method where initially nutrients are broken down to simpler organic substances, followed by conversion to acids and acetates and finally to end products such as methane and carbon dioxide (Fig. 3). The four steps include hydrolysis, acidogenesis, acetogenesis, and methanogenesis in order. The main reason behind the breaking down of nutrients to simpler organic compounds is to promote digestion. In the first step, polymeric molecules such as carbohydrates, lipids, and proteins are hydrolyzed by the extracellular hydrolases that are released from microbes [67]. The carbohydrates, proteins, lipids, and starch are hydrolyzed by cellulose, proteinase, lipase, and amylase to glucose and cellobiose, amino acids, fatty acids and glycerol, and glucose, respectively [68]. The simpler molecules from step one are further broken down into carbonic acids, alcohols, hydrogen, carbon dioxide, and ammonia in the acidogenesis step. As the performance largely depends on pH, an optimum pH (ca. 6.5) was maintained to obtain higher yields of methane [69].

Few products in the process are indirectly transformed into CH_4 in methanogens. The reactant transforms to acetate intermediates, and the conversion step is termed as acetogenesis [69], and H_2 is an important part of this reaction as the conversion is indirectly proportional to the partial pressure of H_2 . In the final step, methane is produced by anaerobic digestion. Methanogens and obligate anaerobes physiologically couple together and form as bacteria that



produce CH_4 anaerobically. Acetate and H_2/CO_2 are major substrates, while formate, CH_3OH , methylamines, and carbon monoxide occur in minor concentrations. The final step or methanogenesis a key step in the overall process as it is rate-controlling [70]. Hydrolysis of nutrients is the slow step for the complex organic substrate. Owing to toxic products, the process fails and results in kinetic stress [71]. In a similar line, few reports claim methanogenesis the RDS for easily biodegradable substrates [72].

7.4 Mechanical pre-treatment

The coarser particles in the wastewater would have a negative impact by reducing the tank value; as they settle at the bottom. In this regard, size reduction is necessary, and mechanical pre-treatment performed in mills breaks down the cellular surface and enhances the surface area. Also, the viscosity in digesters is substantially decreased with a reduction in particle size. Usually, higher viscosity poses a problem to efficient mixing. However, the limitation of mechanical pre-treatment processes must be regarded when stone or metals present in the substrate may contribute to damaging of the mills and cause more economic losses.

7.5 Chemical pre-treatment

Chemical pre-treatment employs the acids and bases to dissolve the substrate particles, which sometimes also include thermal pre-treatment. Alkali pre-treatment causes swelling of lignocelluloses and partial lignin solubilization, and the most widely employed alkali is lime or sodium hydroxide (NaOH). The treatments displayed promising results in terms of yields; however, the shortcomings in terms of salt build-up, practicality, and enhanced pH outweigh their other benefits. This leads to ammonium-ammonia balance and hampers the methane formation [73]. Usually, the expensiveness of alkalis avoids pre-treatment technology, and oxidative pre-treatment can act as the best alternative in this regard as H₂O₂ or O₃ also results in swelling of lignocellulose. Moreover, the biogas generation was observed to be more than twice with H₂O₂ and ammonium pre-treatment. The one possible limiting factor for this may be the high cost factor due to usage of the materials involved.

7.6 Thermal pre-treatment

Increasing the temperature reduces the viscosity of sludge and also triggers the pathogen removal, thereby improving the dewaterability. Solubilization is the most important step in organic substance remediation from wastewater [74, 75]; however, operating at temperatures may have altered the chemical bonds and lead to agglomeration of particles [76]. In this regard, studies were performed in two regimes: (a) low temperature and (b) high temperature.

7.7 Thermal pre-treatment at lower temperatures

Low-temperature regimes operate in the temperature range of 60 to 100 °C. A substantial increase of 80% COD solubilization was obtained at pH ca.10 and temperature above 80 °C. Pre-treating the substrate at 60 °C, 80 °C, and 100 °C for 30 min enhanced the protein solubility from 2 to 12, 20, and 18% of the total protein, respectively [77]. Climent et al. [75] obtained 68.6% increase in biogas generation by pre-treatment at 70 °C for 9 min; however, few challenges are also present. For instance, reduction in dewateringability after undergoing thermal pre-treatment [78].

7.8 Thermal pre-treatment at higher temperatures

In the high-temperature regime, the operable temperature range is around 120–170 °C. Generally, in that temperature range, solubilization is favored and the extent of protein exposure is significantly improved, which results in higher biodegradability. To this end, many reports also claimed an increment in biogas production with temperature. The soluble carbohydrate content rises until 130 °C and then diminishes with a further increase in temperature [79]. Haug et al. [69] demonstrated an enhanced biogas production at 175 °C. Perez-Elvira et al. [80] concluded that enhancement in biogas generation is attributed to thermal treatment at 170 °C (for half an hour). Nevertheless, the high temperature (above 150 °C) promotes complex substrates which are difficult to degrade, thereby hindering the generation of biogas.

8 Membrane for the wastewater treatment

The biological membrane present in AnMBR is the key component due to which high membrane area, turbulence on the feed side, controlling energy requirements are completely ensured. Filter cartridge, spiral wound, and flat sheet are some of the commonly used module configurations in AnMBRs.

8.1 Membrane configuration

The two popularly considered membranes include submerged and side stream membranes, where the former is vacuum driven and the latter is driven by pressure [69].

8.2 The submerged membrane filtration

Here, the filter is submerged in the mixed liquor, either on the inner or outer side of setting up and has been extensively employed in the aerobic membrane processes. The setup demands less driving energy as compared to side stream setup due to lower operational trans-membrane pressure (TMP) and lower volumetric flow rates at low cross flow velocities. Usually, the CFV is lesser than 0.6 m/s with TMP around 21–103 kPa [81].

8.3 The side stream membrane filtration

In side stream membranes, the biological membrane is present outside the reactor and aids in screening the suspended particles with cylindrical hollow fiber cartridge modules. Here, the advantages that come with membrane fouling can be avoided by manipulating the liquid crossflow, hence producing the required shear on the membrane. Strohwald and Ross [82] operated a cross flow velocity of 1.5 m/s to prevent side stream membrane fouling as higher cross flow velocities aid in increased turbulence and shear. In this regard, the CFV was around 1–5 m/s, and the TMP was set in the range of 207–690 kPa. The setup roughly bear suspended particles in the range of 0.1 to 0.4 μ m in size [81].

8.4 Membrane fouling mechanism and control

Employing a membrane below the critical flux generates high shear stress across the membrane and decreases the rate of fouling. To maintain the flux at the critical point, the velocity gradient must be kept high; however, it must be maintained constant as altering the process parameters is challenging. Another possibility is gas sparging, which is better than the former in reducing the fouling.

8.4.1 Biofouling

Sludge cake formation, pore clogging, and adsorption of extracellular polymeric substances are 3 different pathways for biofouling [83]. Pore clogging occurs due to cell debris and particles of colloids [84]. The particles settle in the pores, thereby reducing the surface area for filtration. The sludge cake formation takes place if the shear stress at the membrane is not adequate to remove the solids [85]. When the shear stress at the membrane is not sufficient in process of removing solids, sludge cake is formed, which eventually resists slurry flow. As a consequence, mixed liquor suspended solids (MLSS) are more at the membrane surface rather than in the bulk phase [83].

8.4.2 Organic and inorganic fouling

The accumulation of organic and biopolymeric substances such as polysaccharides and proteins result in organic fouling [86]. Usually, organic loading at large rates promotes residual CODs and lower membrane fluxes [87], whereas inorganic fouling can be reasoned due to accumulated inorganic colloids on the pore surfaces and membranes. Further, there are two different ways by which inorganic fouling occurs; they are biological and chemical precipitation where the former is triggered by captured negative functional groups. Inorganic fouling is likely to happen as compared to organic or biofouling [86]. Some of the known inorganic fouling agents are struvite (MgNH₄PO₄·6H₂O) [69] found in urinary wastes, K₂NH₄PO₄, CaCO₃ [88].

8.4.3 Control measures for fouling

- 1. Organic fouling can be diminished by controlling the levels of EPS absorption/accumulation. Also, running the reactor with higher SRT and decreasing the exposure of COD concentration can aid in reducing the organic fouling rate.
- 2. Activate carbon and zeolites adsorb organic substance and decrease the fouling; nonetheless, they are not practical for full-scale operations.
- 3. Operating a membrane lower than critical flux by maintaining a higher velocity gradient or gas sparging as discussed earlier.
- Cleaning the membranes with chemicals such as HCl, H₂SO₄, NaOH, and NaOCl; these chemicals dissolve the organic fouling on the membranes.
- 5. To avoid cake polarization, a high shear rate can be applied, and a suspended solid concentration lesser than 50 g/L also works best as suggested elsewhere [88].

9 Coupling of anaerobic processes and microalgae cultivation

Since the effluent from anaerobic membranes is high on soluble biodegradable particles, the cultivation of microalgae following digester can be an effective solution to meet the disposal standards. Microalgae are unicellular photoautotrophic/photoheterotrophic microorganisms, such as simple plants and leaves, which thrive on photosynthesis [89]. Previously, this strategy was employed and showed encouraging results [90, 91]. In another report, it was suggested that microalgae boosted the biofuel yield (80,000 L/acre/year) against other plant sources [92].

9.1 Photobioreactors

Photobioreactor (PBR) is a biological reactor that grows phototrophic microorganisms by the consumption of light and nutrients. The microalgae growth is influenced by various aspects; for instance, its yield depends on light availability, nutrients, CO_2 , culture density, the extent of mixing of the nutrients and CO_2 , and the PBR operating conditions—temperature, pH, and H_2O flow rate. Efforts have been made in the past few years by several groups [91, 92] to improve all the above parameters in the view of increasing algal yields. For instance, a specially designed tubular system ensured uniform irradiation over the total volume of cultivated culture. In a similar context, different PBRs such as the flat plate PBR, bubble column PBR [93], vertical column PBR, the tubular PBR, and the airlift column PBR [94] were employed to enhance its performance. The pros and cons involved in different types of PBR and productivity and operating parameters in various types of PBR are tabulated in Table 4 and 5, respectively.

10 Bioelectrochemical systems applications

Inspired by BES, many microbial electrochemical techniques have been considered to synthesize value-added products [104]. Microbial biobased and electrochemical approaches use microbial cells for the transformation of dissolved carbon dioxide into products such as methane (with *Methanococcus maripaludis*) [105] and acetate production (with *Sporomusa ovata*) [106]. Electro fermentation is another potential technique, where the electron transport in anodic EF or cathodic EF can control the ORP and the NADC/NADH ratio, thereby altering the intracellular metabolism [107]. Photosynthetic MFCs is one of those strategies that can decent attraction in recent times, which considers integrating photosynthesis and electricity production and ensures sustainability [108]. In this regard, the microbes play a key role in harvesting the complexes and convert solar power to chemical energy [109]. Interestingly, this integration has opened new avenues and possibilities for renewable and sustainable bioenergy generation.

11 Future prospects and conclusion

Over the past decade, bioelectrical systems (BESs) have emerged as a strong contender for wastewater treatment technologies including brackish, pharmaceutical wastewater and desalination against existing conventional

Table 4 Benefits and shortcomings in various types of PBRs [91]

PBR type Advantages		Limitations		
Tubular	 Large illumination surface area Suitable for outdoor cultures Good biomass productivities Paletical accompanies 	 Requires large land area Some degree of wall growth Gradients of pH throughout 		
Flat plate	 4. Relatively economical 1. Good for immobilization of algae 2. Easy to clean up 3. Large illumination surface area 4. Suitable for outdoor cultures 5. Good light path 	 Fouling Scale up requires support materials and many compartments Problems controlling culture temperature Possibility of hydrodynamic stress Some degree of wall growth 		
Vertical column 1. High mass transfer 2. Good mixing with low shear stress 3. Reduced photo inhibition & oxidation 4. Readily tempered		 Small illumination surface area Construction requires sophisticated materials Shear stress build up to algal cultures 		

Table 5Comparison ofproductivity and operatingparameters for different typesof PBRs

PBRs	Volume (L)	Volume (L) Photosynthetic strain		Reference	
Airlift tubular	200	Porphyridium cruentum	1.50	[95]	
Airlift tubular	200	Phaeodactylum tricornutum	1.20	[<mark>96</mark>]	
Airlift tubular	200	Phaeodactylum tricornutum	1.90	[95]	
Inclined tubular	6.0	Chlorella sorokiniana	1.47	[97]	
Undular row tubular	11	Arthrospira platensis	2.70	[<mark>98</mark>]	
Outdoor helical tubular	75	Phaeodactylum tricornutum	1.40	[<mark>99</mark>]	
Parallel tubular (AGM)	25,000	Haematococcus pluvialis	0.05	[100]	
Bubble column	55	Haematococcus pluvialis	0.06	[101]	
Flat plate	440	Nannochloropsis sp.	0.27	[<mark>91</mark>]	
Tubular	5.5	Spirulina platensis	0.42	[102]	
Tubular	146	Arthrospira	1.15	[103]	

technologies like aerobic and anaerobic. The BESs score over the other analogous technologies owing to its capability of operating under mild conditions, employing commercially available inexpensive components and making use of wide range of organic substances thereby scoring over the conventional fuel cells [3].

The anaerobic technologies are usually brought into use for treating wastewater with a higher organic load, typically in the order of COD > 4000 mg/L, whereas aerobic is generally used for treating relatively lower strength of wastewater in the order of 1000 mg/L. The anaerobic technologies generate CO₂, methane, and other biomass by breaking down the organic impurities in absence of oxygen. Bacterial biomass and oxygen are employed in aerobic treatment to assimilate organic matter and other pollutants like carbon dioxide, phosphorus, nitrogen into water, and other biomass.

Although aerobic has certain distinct advantages over anaerobic in terms of less odor, higher nutrient removal efficacy, etc., it also suffers from some serious drawbacks like the high cost of maintenance and being energy-intensive, thereby making it a not so attractive option. The anaerobic process requires much less maintenance, less energy intensive, and less biomass production as compared to its aerobic counterpart. It has also the added advantage of generating sludge that can be used as fertilizer due to the presence of high mineral elements. The actual applicability of aerobic vs anaerobic completely depends upon the specific output which is unique for each process treatment plant, loading rate. Anaerobic scores on more fronts as it can be coupled in conjunction with microalgae reactors employing photobioreactors. Recently [110] greywater treatment has been carried out using anaerobic/aerobic UASB with a fair degree of success.

Recent studies [111] have shown that mesophilic conditions are more favorable for VFA production as compared to thermophilic using bovine manure as inoculum. Wei and Guo [112] showed that for psychrophilic conditions, longer biogas fermentation time, lower VFA accumulation, and higher peak methane content were observed as compared to mesophilic conditions; however, the production of the biogas was almost similar for both.

To conclude, it can be said that over the past few years, BES has shown significant potential as a rapidly emerging technology for valorizing a variety of liquid and gaseous waste streams and proving to be strong contender against several well-established conventional approaches for treatment of wastewater. Recent advancements in the field of catalyst development, separation processes, and hybrid technologies like plant microbial fuel cells (PMFCs) with a higher greener impact have given tremendous boost to consider BES as an attractive and viable alternative for not only wastewater treatment but also for bioelectricity generation in the future. Abbreviations TW: Terawatts; BES: Bioelectrochemical systems; AnMBR: Anaerobic membrane bioreactor; MFC: Microbial fuel cell; MEC: Microbial electrolytic cell; VFA: Volatile fatty acids; EFC: Enzymatic fuel cell; MDC: Microbial desalination cell; MSC: Microbial solar cell; AEM: Anionic exchange membrane; CEM: Cationic exchange membrane; TDR: total desalination rate; TEA: Terminal electron acceptor; DET: direct electron transfer; COD: Chemical oxygen demand; TDS: total dissolved solids; PVDF: Polyvinylidene difluoride; HRT: Hydraulic retention time; CFV: Cross flow velocities

Author contribution Prof. Ranjan Dey: Conceptualization, methodology, data curation, and writing-original draft preparation.

Prof. Saroj Sundar Baral: Visualization, investigation, data curation, writing-original draft preparation.

Dr. Dileep Maarisetty: Investigation, data curation, and writingreviewing and editing.

Declarations

Competing interests The authors declare no competing interests.

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