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Recent Advances in Bio-electrochemical System Analysis in Biorefineries

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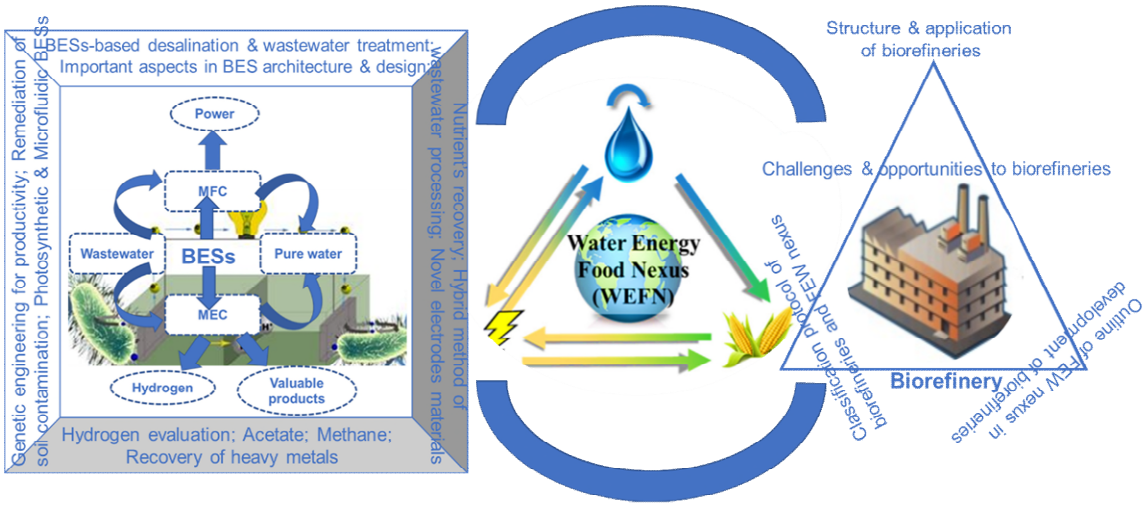
Abstract:

Concerns around acquiring the appropriate resources toward a growing world population have emphasized the significance of crucial connections between food, energy, and water devices, as described within the food-energy-water nexus theory. Advanced biorefineries provide second-generation biofuels and added-value chemicals through food products have affected these nexus sources. We combine various conversion technologies and expected options to look further for cost-effective technologies that maximize the value of resource use and reuse and minimize the amount of resource needed and environmental impacts. In this review article, our central focus is on structure and application, the outline of food-energy-water (FEW) nexus in biorefineries and bio-electrochemical system (BES) and looking into the energy-efficient and value-added product recovery. In addition, based on BES analysis for energy efficiency and valuable product recoveries such as hydrogen evaluation, acetate, recovery of heavy metals, nutrient's recovery has been discussed under this article. Additionally, we focused on wastewater processing methods, novel electrode materials used in BES, BESs-based desalination and wastewater treatment, recent BES architecture and designs, genetic engineering for enhanced productivity, and valuable materials production surfactants and hydrogen peroxide. Finally, we concluded the topic by discussing the remediation of soil contamination, photosynthetic & microfluidic BES systems, possibilities of employing CO_2, including prospects and challenges.

Keywords: Bio-electrochemical system; biorefinery; microbial fuel cells; environmental impacts; value-added products.

Graphical abstract:



1. Introduction:

Bioelectrochemical systems (BES) have been developed as niche expertise toward converting scrap rivulets and algae within useful power. Microbial fuel cells (MFCs) and microbial electrolysis cells (MECs) are two kinds of BES that generate power and H_2 sequentially by utilizing the organic matter under aqueous rivulets [1]. A few biomass components that make it suitable raw material, from renewable (low-carbon) chemical and energy generation, are recyclable CO_2, garbage valorization, and its usage as an available renewable energy source [3-6]. The evolution of distinct approaches, which conferred similar biorefineries, has been done in biorefineries' initial configuration. An additional component causing the development in bio- and solar plants commonly used and valorizing the CO_2 generated within biorefineries is to combine sustainable energy [7]. Zhang *et al.* [8] proposed biorefineries-based photosynthesis to generate vast volumes of compounds through H_2/power and CO_2 for next-generation.

A biorefinery is the ease of solid fuel's maintainable transformation within combined, practical and straightforward processing in varied commodities (such as chemicals, feed, pet supplies and energy goods) [9,10]. According to the types of raw material used (i.e., algae, organic waste, and lignocellulose), the conversion technology (biological, thermochemical) can be grouped into biorefineries. Different stages of complexity in biorefineries are Class I (different raw material single output), Class II (solitary raw material several outputs) and Class III (various raw materials including different outcomes). The food-energy-water (FEW) nexus approaches have not yet recognized the biorefinery model's synergies during the assessment of biorefinery operation for the different classes. The advanced biorefineries (Classes II and III) have encouraged the possibilities to discuss connection problems with stakeholders producing food, energy, and clean water sustainably while protecting the climate and ecosystems [11-14].

The energy recovery from a biochemical conversion method to originating liquid fuels, for example, ethanol of lignocellulosic solid fuel under a standard procedure, is approximately 53.5% [15] . The biomass's residual energy is carried out towards the atmosphere within the class of small-scale garbage heat, finishing below a decay of about 46.5% from the received biomass energy. The standard systems receive energy from

remaining organics, including byproducts, through flaming under an evaporator or separate them by wastewater processing. The wastewater treatment plant can produce biogas applied to fuel towards a thermochemical oil generation component. Besides the energy waste, a notable quantity of water has been allowed through dissipation and chimney gas discharge facing the atmosphere. Current literature has shown the significance of water recycling within a standard biorefinery method, especially during biochemical conversion [17-19].

As we know, MFCs and MECs can be employed in polluted water while producing valuable energy products such as electricity or H_2 [1,22-25]. The employment of these machinery has studied biodiesel production and metropolitan waste-water processing within food production [26]. Common contaminants in the emerging biorefinery of the water system involve sugar- and lignin-degeneration goods, acetate, fermentation derivatives, and remaining carbohydrates. The contaminants' transformation includes furfural, hydroxymethyl furfural, acetate, hydroxybenzaldehyde, hydroxy acetophenone, and vanillic acid toward electricity using MFCs technique [27]. Renovation of different sugars and starches toward power generation has been described by employing MFCs [28,29]. This initiates opportunities to construct method choices applying MFCs to improve energy by remaining organics in the biorefinery by allowing water recycling.

The continuing estimation of water and energy synergy under the food operation began during the 1980s. In the previous years, the essential breakthroughs impacting water-related energy (WrE) estimate within the food policy [30].

The various developments in MECs and MFCs have collected together and shown for energy production in **table 1**.

Table 1. Different types of integration developments of microbial electrolysis cells (MEC) and different types of machinery for energy production.

S. No.	Integration type	Electrode materials (Anode & Cathode)	Applied voltage	Electrolyte/Substrate	Current/power density	References
1	MECs	Graphite brush & Carbon cloth (CC)	0.8 V	Waste activated sludge	-	[31]
2	Constructed wetland (CW)-MFCs	Stainless steel (SS) mesh & charcoal	0.44 V	Swine and synthetic wastewater	0.07 A/m^3	[32]
3	MEC with MFC	Carbon brush & Silicon nanowires	-	Growth media	0.68 A/m^2	[33]
4	CW-MFCs	Graphite granules & graphite plate	0.08 V	Synthetic wastewater	0.16 A/m^3	[34]
5	MECs	Pt-catalyst & CC	0.8 V	Domestic wastewater	189 A/m^3	[35]

6	MEC with dye-sensitized solar cell	Carbon felt (CF) & Plain graphite	0.7 V	Growth media	-	[36]
7	MECs	Carbon fibers & CC	0.8 V	Domestic wastewater	158 A/m^3	[21]
8	MEC with MFC	Carbon paper & Pt. coated cathode paper	0.8V	Growth media	0.25 mA	[37]
9	MEC with hydrogen bioreactor (HBR)	Graphite plate	0.2-1.0 V	HBR effluent	-	[38]
10	MECs	Graphite fiber brush & CC holding Pt catalyst	0.5 V	Wastewater	1.15 A/m^3	[39]
11	MEC with forward osmosis (FO)	Carbon brush & Pt. incorporated CC	0.6-1.0 V	Synthetic wastewater	4.5 mA	[40]

12	MEC with FO	CF fixed upon perforated SS plate using Ag paste & Perforated titanium plate	0.7 V	Synthetic wastewater	3.34 A/m^2	[41]
13	MEC with anaerobic digester (AD)	CF & SS	0.4 V	AD effluent	1.3 mA	[42]
14	MEC with AD	Carbon brush & SS mesh	0.8 V	Sludge fermentation liquid	9.6 mA	[43]
15	MEC with AD	Carbon brush & Ti/RuO_2	0.8 V	Food and sewage sludge in changing ratios	Steady-state with applied voltage	[44]
16	MEC with AD	CF & SS mesh	0 mV	Raw pig slurry	2.01 ± 0.63 A/m^2	[45]
17	MEC with simultaneous desalination	CC & Pt. coated CC	0.55 V	Phosphate buffer solution (PBS)	1.4 A/m^2	[46]

18	MECs	Carbon paper & Carbon paper/Pt	0.5 V	Domestic wastewater	0.6 A/m^2	[47]
19	Dark fermentor (DrF)-MEC MFC	Carbon brush & Pt incorporated CC	0.33 to 0.47 V	DrF effluent	52 A/m^3	[48]
20	MEC with DrF	Carbon fibres with SS mesh & SS mesh	-0.4 V	Sugar beet extract in the diverse substrate to inoculum proportions	3.6 A/m^2	[49]
21	MECs	Graphite fiber brush & CC/Pt	0.5 V	Swine wastewater	106 A/m^3	[50]
22	MEC with DSSC	CF & Pt.-coated titanium plate	0.7 V	Growth media	0.30 A/m^2	[51]
23	MEC with HBR with spent wash effluent	Graphite plate	0.2- 0.6 V	HBR effluent	-	[52]
24	MECs	Graphite fiber brush	0.7 V	Industrial and food processing wastewater	2.1 A/m^2	[53]

		& CC/Pt				
25	MEC with upflow anaerobic sludge bed (UASB) reactor	Ti mesh with Ir-MMO coating & SS mesh	140-260 mW/LR	UASB effluent	-	[54]
26	MEC (multi anode) with DrF	Graphite felt & CC	0.8 V	Dark fermentation effluent	298 A/m^3	[55]
27	MECs	Graphite fiber brush & CC/Pt	0.9 V	Potato wastewater	-	[56]
28	MEC with biomass & pyrolysis effluent	CF & Pt-incorporated CC	0.96 V	Bio-oil aqueous phase	202 A/m^3	[20]
29	MECs	Graphite felt & Ni-based gas diffusion	1.0 V	Synthetic fermentation effluent	206 A/m^3	[57]

30	MEC with electrical voltage from the thermoelectric micro converter	Plain CF & Carbon paper with Pt	0.17 to 0.83 V	Acetate	0.28 to 1.10 A/m^2	[58]
31	MECs	Graphite fiber brush & SS mesh	0.9 V	Winery wastewater	7.4 A/m^3	[59]
32	MECs	Graphite fiber brush & Graphite fiber cloth/Pt	0.8 V	Milk, glycerol, starch	150 A/m^3	[60]

Hence, there is an urgent need for upgrading the BES for energy efficiency and value-added product recovery [61]. Researchers worldwide are actively striving to optimize the method, and various substitute biological systems have been examined [62]. Various kinds of BES have been used as energy recovery or energy-efficient systems to use high-strength wastewater. It is challenging to use low-energy results, such as contaminated water and food/feed products. In this review article, our primary focus is on the principal technical and non-technical challenges and opportunities, classification protocol of biorefineries and bio-electrochemical systems (BES) and looking into the energy-efficient and value-added product recovery. This article describes novel cathode and anode materials and catalysts, recent BES architecture and designs, genetic engineering for enhanced productivity, production of valuable materials including surfactants and hydrogen peroxide, simultaneous desalination and wastewater treatment, remediation of soil contamination, photosynthetic BES systems, microfluidic BES, an alternate approach integrating BES within biorefinery designs to enhance energy effectiveness, nutrients recovery, wastewater processing, possibilities of employing CO_2 and prospects for technical assistance with the challenges, future prospects with concluding remarks.

2. Structure and applications, the outline of FEW nexus of biorefinery and bio-electrochemical system

2.1. Structure and applications of biorefineries

A ‘biorefinery’ is a theoretical design towards a prospective biofuel generation system comprising fuels and valuable substances. The biorefinery concept strives to use solid fuel transformation, which has been used to purify fuel. Bioindustries would instantaneously generate biofuels along with bio-based substances, heat, and energy. Biorefineries would perform a cost-effective alternative at which bio-based compounds are sided commodities concerning liquid combustible [63,64]. Imminent biorefineries would be suitable to imitate the energy performance of new oil purifying by massive heat mixture and side creation improvement. As per the National Renewable Energy Laboratory (NERL), a biorefinery combines biomass regeneration methods and devices to generate energy, substances, and fuels. The international energy agency (IEA) bioenergy Task 42

has described a biorefinery as “the sustainable processing of biomass within a spectrum of commercial commodities and energy”. Therefore, a biorefinery may be a convenient method for manufacturing or many equipment types to transform biomass [65].

2.1.1. Challenges and opportunities to biorefineries

There are several scientific and non-scientific holes in biorefinery that should be affected by industrialization. Current technological limitations, including energy yields, are connected to by-product, price, and issues during accumulation and stocking the substance produced. This is mainly for yearly or different crops that need to be accumulated quickly during the autumn. Several scientific non-technical challenges correlated with increasing energy crops involve nutrients plus the power of insects and sickness [66,67].

The main non-technical challenges are the applications upon the worth of soil (food, energy, home usage, business, classifications being fields of natural elegance, particular scientific concern), along with the ecological impacts of vast regions of monoculture [68,69]. On the other side, the extensive application of vegetable oils can create additional critical challenges and need in developing nations.

There are some scientific limitations in making biomass-ignited plants in a specific order. The volume and producing ability of biomass factories are significantly lower than the current natural-gas-fired turbine operations. On the residential scale, the output is about 50 MW; beyond that point, the accessibility and price of producing fuel become important [70]. The main non-practical barriers to advancing in more extensive operations are commercial, or few nations follow preparation circumstances and public view. A definite diagnosis cannot be executed among current, useful biomass energy plants and more traditional contaminating furnace projects[72,73]. From the commercial point of view, the application of crops without aid is too costly to provide, whichever bioethanol or biodiesel is at a cost contentious, including untaxed fuel. In contrast, techniques toward employing cost-effective lignocellulosic substances have not been completed [74-77].

2.1.2. Classification protocol of biorefineries and the FEW nexus

A classification approach toward biorefinery operations concentrating upon profitable ideas or might suit attention in the coming years to produce high volumes of transportable biofuels. The primary purpose of this classification method in biorefinery operation may be to classify the resulting four principal characteristics (arranged in order of significance): platforms, products, feedstock and processes. A biorefinery system is a transformation pathway of raw materials into outputs through platforms and processes. The platforms are intermediating via the final goods are obtained. They are the essential characteristic in defining the kind of biorefinery [78].

These also serve appropriate possibilities to promote complete operations, which convert nexus provocations within integrative possibilities. Such a complete operations strategy should include the FEW nexus as a structure for improving biomass utilization sustainability. The following points, such as biomass ingredients and extricate food segments within raw material, energy, and water, combine to develop environmental and utility chain stages. The remaining consumption, including wastewater processing by restoring nutrients, is restored toward food and biomass feed material improvement with water to reuse and recover and combined effect among FEW nexus elements with biomass utility chains [30]. Critical problems correlated by biorefineries, including the FEW nodes with the whole quantity chain, should be analyzed similarly [81].

2.2. Outline of food-energy-water (FEW) nexus in biorefineries

Kibler *et al.* [82] suggested the food trash impacts the FEW nexus through two consistent tools; mutually are operated by human performance and decision-creation. First, within both generation and waste administration aspects, food waste consequences toward the FEW nexus. Second, preferences constituted food acquiring, using, control, and joint determination forming on the societal level concerning food composition and food waste administration (such as landfilling *vs* AD) [83]. Entirely food delivered needs sources and energy, water manure, herbicides/pesticides, land, and employment, whether employed or misused. Water and energy are applied instantly into the food product when water and

energy are required to spraying water for ship food, or produce chemical manures and pesticides/herbicides. **Fig. 1** displays the design of the FEW nexus models [84].

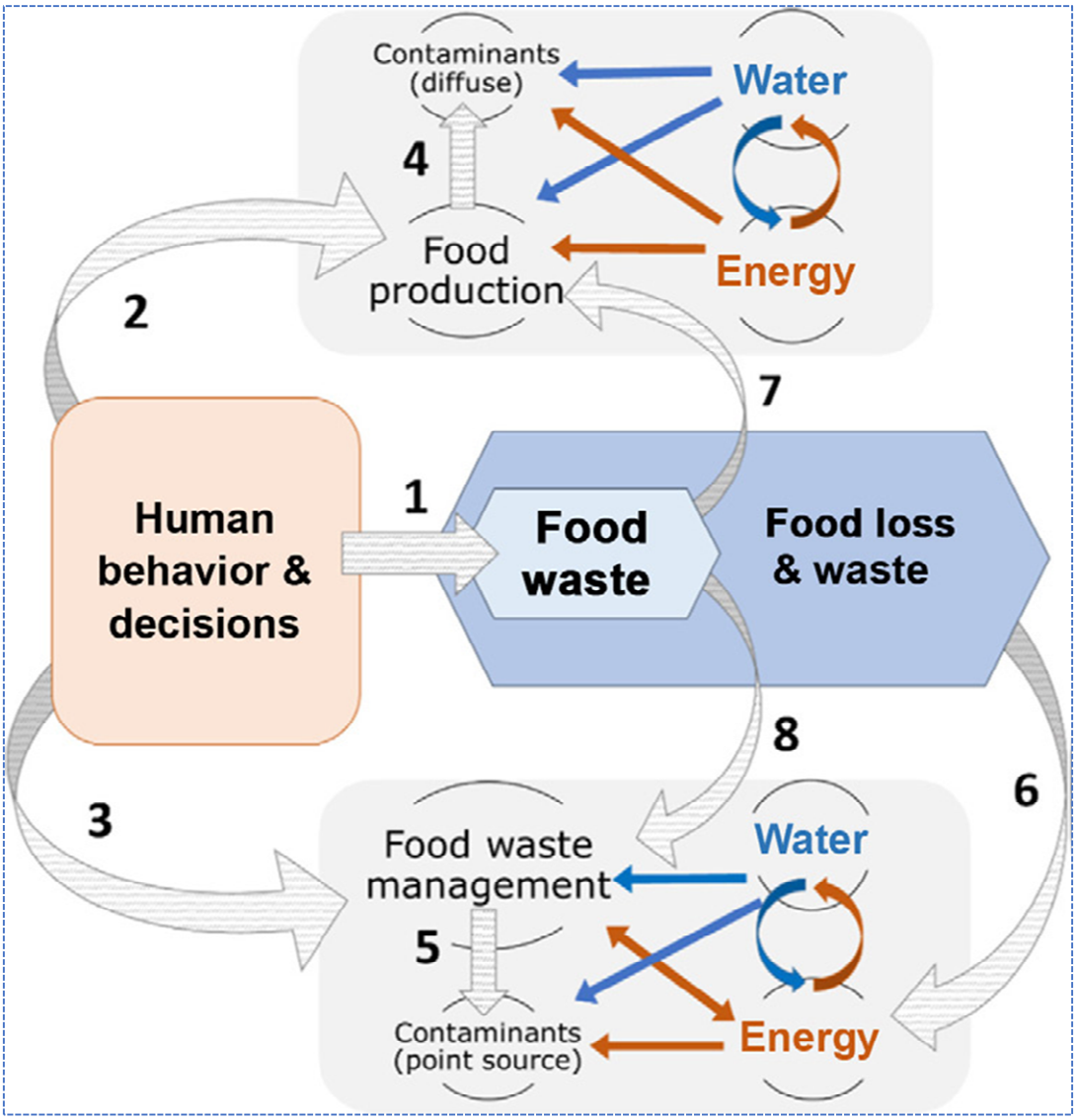


Fig. 1. FEW nexus in food construction and waste organization stages. Reprinted with permission from Ref. [84].

The FEW nexus of biorefineries shows the numerous designs contingent upon the biomass and methods. However, entirely biorefineries will affect water, energy sources and food stores. **Fig. 2** summarizes synergies of current biorefineries that primarily practice for food crops, such as corn, and wheat, to biofuels production [11].

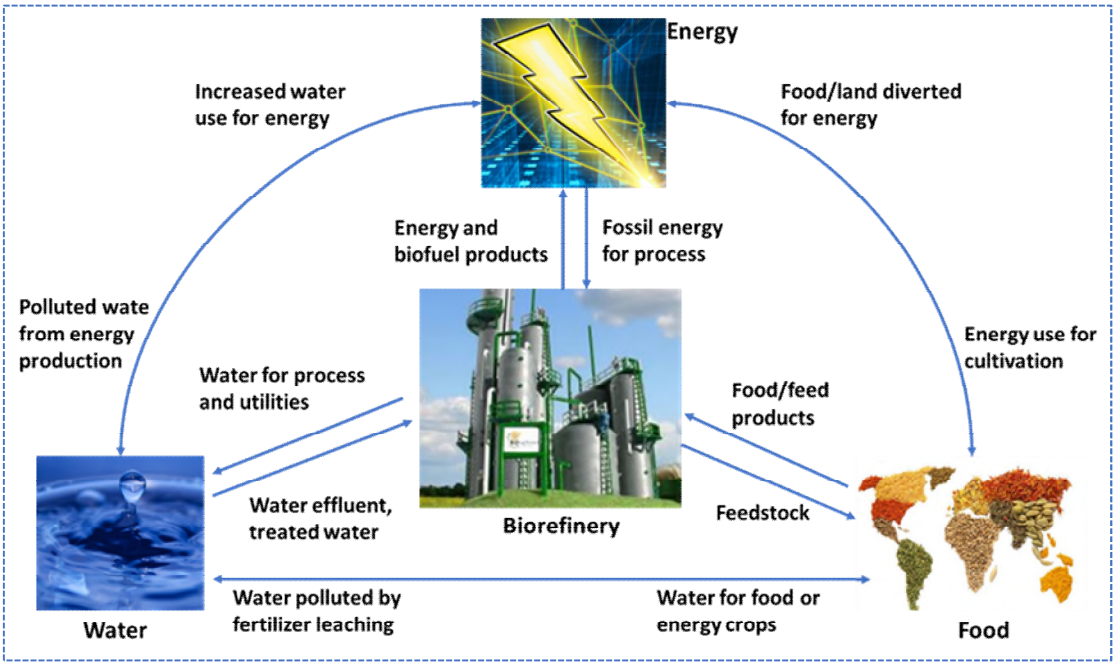


Fig. 2. FEW nexus relations about existing biorefineries that largely practice for food crops or first-generation raw materials. Reprinted with permission from Ref. [11].

Moreover, ineffective energy practice in biorefineries would drive improved water control to cooling services, building an energy-water node problem.

2.2.1. Prospects by FEW nexus in development of biorefinery

To understand the nexus hurdles, the current biorefineries should be developed in combined conveniences for allowing on-site energy production by sewage [88], crop utilization, alteration of supplies and food components at the outline step [89]. However, the demand for isolating biomass parts for effective adaptation within multiple outcomes generates sufficient complexity and range to mass and energy combination. Moreover, biorefineries may guide closing stock circles and annular economy [90,91] used for practical administration of consumption in combined effect including food, energy and water policies.

A further extensive review of the potential toward life cycle assessment (LCA), deep investigation and mathematical software design to fix nexus effects has been exhibited subsequently [94]. Several investigations have been done on the three elements of the FEW

nexus into an optimization structure [95]. The nexus has been overly stressed within analysis progress across the preceding decade as a device to drive organizations towards a green market and usually better source protection. Instead, the FEW nexus has been emphasized toward its potential to examine the interdependencies among sources at various ranges, given as an antidote to conventional “siloed” techniques [96]. Hence, there is a requirement to produce devices, that may find innovative clarifications by approaching nexus problems, supply trade-offs, and analyzing nexus integration possibilities.

2.2.2. Biorefineries and various losses

An essential part of biomass power is wasted in heat through chimney gases, water vaporization, and atmospheric heat while the previous choice is practiced. The waste-water approach may produce biogas applied to fuel a reservoir or a component in thermochemical fuel generation. As well as the energy waste, a considerable water volume is also dropped through vaporization and chimney gas discharge to the atmosphere. Current literature has shown the significance of water reprocessing in a conventional biorefinery method, especially in the biochemical regeneration method [97]. Therefore, method options, including the potential to enhance the process's energy effectiveness and reuse water, are required. MFCs and MECs are possible technologies for employing polluted water while producing valuable energy into electricity or hydrogen sequentially [98]. Alteration of different sugars and carbohydrates toward power utilizing MFCs has been described [99,100]. It will unlock the opportunities for the growth of method alternatives employing MFC/MECs to improve energy by remaining organics into the biorefinery while allowing water recycling.

2.2.3. Connection between FEW nexus, biorefineries, BESs

Here, the question is raised: what will be a relation between FEW nexus, biorefineries, and BESs? Therefore, process options, including the possibilities to develop the method's energy performance and convert water, are required. The streams' capability to generate energy and H_2 described the synergy among biorefineries and BES. Combining BES technology in the biorefinery process may be notable for improving energy enhancement through biomass. It will drive advanced energy effectiveness, reduce surplus streams generated within the biorefinery, and reduce greenhouse gas ejections. These factors may

provide development into the sustainability of biorefinery methods. Several investigations have described the evaluation of sustainability parameters concerning BES technology.

In an introductory study of FEW synergies, biorefineries can provide first-generation bio-oils that can be applied as reservoirs. Bio oils give just 4% of worldwide carrying fuels. Hence, the production makes 3% of global water use. They practice land and products that could fill 30% of the community, allowing food scarcity. Using the constant Yellow River's yearly water exudation, 5-10% of developed land requires being distracted to give biorefinery raw material to reach China's bio-oil destination [85]. These facts show the influence of regularly examining the nexus synergies of bioindustries to circumvent negative results and scale supply trade-offs. The weak energy-food interfaces have been extensively discussed that present biorefineries participate obliquely towards increasing food with increasing animal supplies [86]. Synergies among the energy method derive using natural gas and power to drive biorefining methods, including reducing the life cycle energy releases carbon equilibrium [87]. This indicates an improvement to fossil sources that bioenergy, including bio-oils, to restore, an irony that needs to be evaded or reduced.

2.3. Bio-electrochemical system

BES is a suitable substitute approach associated with other traditional wastewater operation and bioenergy conversion or reproduction processes. In the last few years, BES prepares more fascination owing to the energy yield from wastewater with the metabolism of microbes. This method can work as a feasible approach toward clean energy production linked to more useful bioremediation. BES has been examined for its possible applications in several fields, particularly wastewater processing, including synchronous reproduction of bioenergy and biopolymers [101,102]. BES is an innovative method based on electrochemical alteration methods, able to transform the biological energy deposited in recyclable organic substances with the catalytic performance of microbes. BES involves oxidative and reductive half-cells to generate power or other chemically obtained outcomes (**Fig. 3a**) by combining the bio- and electrochemical methods.

The derivatives and sources such as heavy alloys, nutrients, ores, and transitional manufacturing chemicals may be retrieved through microorganisms catalyzed redox effects. A relatively massive quantity of analysis studies has been issued to discuss the

various features of BES. For example, electrode substances, materials employed for segments, supports, microbes, contaminant extraction, modelling perspectives, etc., to improve the activity of BES [103], though, some manuscripts (around 1%) addressed the extent of by-products improvement by wastewater in BES [104,105]. BES and its applications in energy generation (**Fig. 3b**) [106].

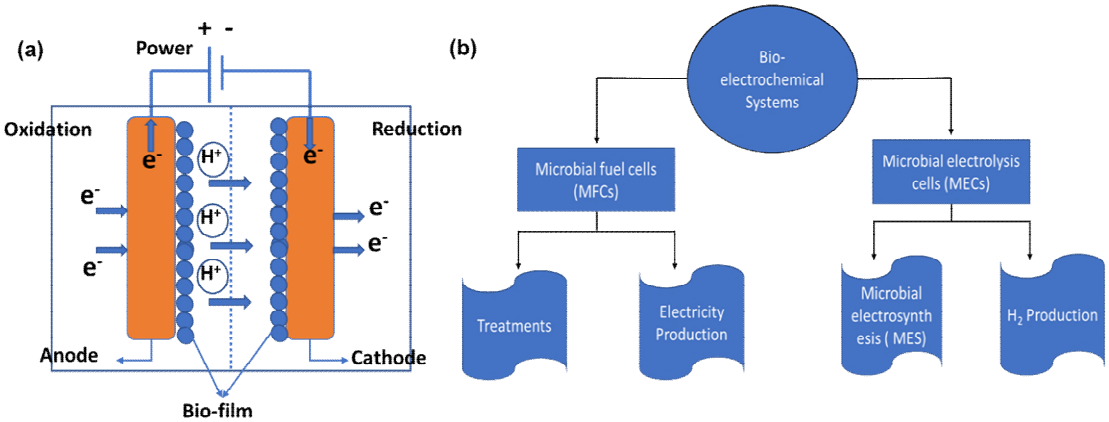


Fig. 3. (a) Schematic diagram of a bio-electrochemical system and (b) The BESs and used in energy generation[106].

The dual objective of BES for energy production and the bioremediation approach is more appealing for scientists. BES gives an encouraging and sustainable clarification towards restoring valuable synthetic derivatives in the presence (or absence) of a plan to produce renewable energy in the term of power. However, to deliver it more useful for real-world purpose and actual energy accumulation, the restoration of derivatives by wastewater should be concentrated.

2.3.1. Types of bio-electrochemical systems:

BES may be categorized reliant against the form of works: MFC, microbial electrosynthesis (MES), MEC, microbial desalination cell (MDC) and microbial solar cell (MSC). Generally, in each BES, the electroactive bio-sheet at anode oxidizes the organic material to produce energy. However, at the cathode, various products, for example, hydrogen generation and precious chemicals, may be obtained depending on the model of BES [107]. The appropriate kind of BES, including explicit classifications, are analyzed following in the next segments. The primary laws of MFC and MEC operations are

described in the following part. A description of cell studies is listed under the research examining MEC and MFC cells created, including an anode, a cathode, electrolyte, and an electrical loop[108].

2.3.1.1. Microbial fuel cells:

MFCs tackle power by the microbial oxidation for biological material employing a solid electrode as an electron receiver [109]. The cathode electrode's surface in MFCs promotes microbial adjunct, including oxidation of organics and producing electrons that assign together towards the cathode cell through an outer circuit comprising a surface charge. Electroneutrality is approved via ions transportation within an ion penetrable mechanism or a membrane if power is generated inside the system. M.C. Potter described the first of such practices in 1911, which attained the highest voltage of 0.3-0.5 V. Generation of bioelectricity in MFC is immediately reliant on the volume of exoelectrogens (microbes producing power) instant at the cathode side, which promote the transmission of electrons by the mitigate support toward the anode. Oxidation of complex organic material into wastewater needs distinct microbial inhabitants. Many bacterial varieties have been observed as capable of generating electrical current. The current progress in MFC as a biosensor has the potential for immediate and real-world intensive care of water conditions, making more substantial fascination. MFC improved with electrochemically effective microbes has been employed as biochemical oxygen demand (BOD) and toxic memory biosensor [110]. Here, the power generation was recognized to rise during the pollute range progress. Furthermore, [111] specified that MFC would be applied for detecting food scraps. This can be suitable for quick evidence and characteristics of microbes within food products.

2.3.1.2. Microbial electrolysis cells:

MECs is an encouraging process concerned with biorefinery for trash to outcome regeneration [112]. Apparent power used at the power circuit of BES makes electrons as positive to the anode electrode also promotes the H_2 production on the cathode surface [113]. Opposite from the MFCs, the cathode of MECs works below anaerobic

circumstances that promote H_2 generation. However, the anoxic conditions in the MECs and the high concentrations of H_2 composition may also increase CH_4 generation once CO_2 and methanogens are possible. Some of the approaches to alleviate CH4 generation involve:

- the aeration of the cathode assembly among groups
- decreasing the pH
- performance on low detention times
- providing a heat stupor upon the inoculum
- combining chemicals that hinder the extension of methanogens.

Hydrogen generation under MECs, according to their arrangements and the supports employed. Advanced electric currents are naturally perceived into MECs while associated with MFCs, owing to the different employed potential supporting the cathode restrictions [114]. Another separate MFC can give the energy needed for the MEC process as a power reservoir [48]. The high hydraulic detention time was agreeable for CH_4 generation within MEC and cost-effective.

MECs are innovative technologies that may produce H_2 gas by low-grade supports, for example, organic trash. A standard MEC is comprised of an anode and a cathode divided through an ion-exchange membrane, including the broad scope of purposes of MECs (**Fig. 4**) [115,116]. The electrochemically activated microorganisms oxidize organic material and alteration electrons toward the anode terminal to extracellular inhalation through membrane-connected cytochromes, shuttle particles and/or electroactive pili [117]. MECs, as an anaerobic method, generates slight scrap residue and are repellent to atmosphere changes than the standard activated residue method, highlighting the sustainability of H_2 generation and wastewater processing. During the prior several years intensively investigated on lab-scale MECs [116,118], industrial-scale MECs have displayed the following: the probability of H_2 generation by residential and metropolitan wastewater [119].

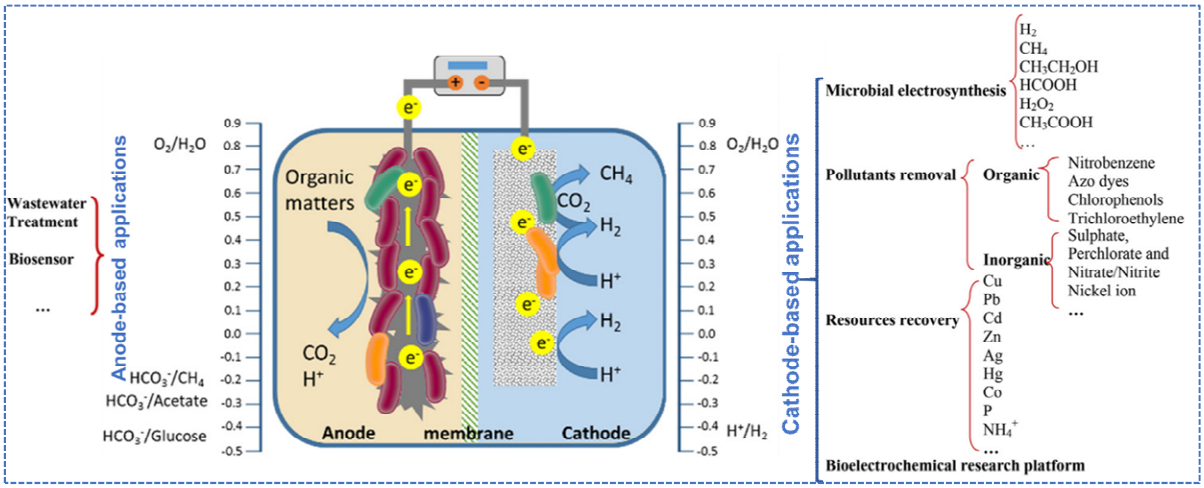


Fig. 4. Representation of a MEC, including an anode and cathode-based applications. The redox potentials are shown as V vs. NHE on pH 7. Reprinted with permission from Ref. [115,116].

3. BES analysis for energy efficiency and value-added product recovery

3.1. Hydrogen evaluations

In addition, the energy effectiveness increases the potential by applying a low-temperature MEC result; the production of H_2 can also increase the energy products by the method. The H_2 can be employed to produce high-octane fluid oils or the generation of more significant valuable compounds. The quantity of H_2 which a MEC focus can provide to several constituents with the chemical oxygen mandate of the method rivulet, flow rate, biodegradability about the biological material, and competence of catalytic H_2 generation reactions [120]. A protocol for ascertaining rates of possible H_2 generation with used-water rivulets was published recently. It can be applied to evaluate H_2 generation by several stillage rivulets, with those cellulosic and ethanol manufacturing methods [122].

A lignocellulosic biorefinery employing 2000 tons of maize Stover/day as supplies have a technical latent to produce 7200 m^3/hr of H_2, depends upon the opinion of 50% regeneration performance and a biodegradability aspect of about 0.5. The biodegradability aspect relates to the highest organic matter segment, which may be diminished with bacteria. The assessment involves H_2, which produced with the sugar-degradation goods, e.g., furfural, HMF, besides the lignin-degradation goods, for example, phenolic aldehydes, ketones, alcohols, plus acids, as well as acetate and remaining sugars. The technique to

obtain energy by these particles within the electricity mode through an MFC was described latterly [123,124]. The anode microbial reactant acts as the primary function of material division, electron and proton generation interfaced among the H_2 generating electrochemical reactant at the cathode surface and the required overpotential (i.e., a MEC). So, H_2 generation by these streams applying a MEC is achievable [125].

Wastewaters by industries, farms, and municipal roots include large quantities of decayed organic material that are an inherent source for chemical and fuel generation [126,127]. Biological processing techniques are recognized for the generation of energy by used water. Methanogenic anaerobic absorption has previously been applied globally to the generation of biogas. H_2 generation by wastewater with acetogenic agitation is a different process of utilizing wastewater [128,129]. Though lowering products and thermodynamic constraints into microbial metabolism are under the agitation method. BESs suggest a substitute technology to improve the H_2 product at a comparatively low electric energy supply compared to traditional water electro-oxidation (**Fig. 5)**. This technology is also called bioelectrohydrogenesis [130].

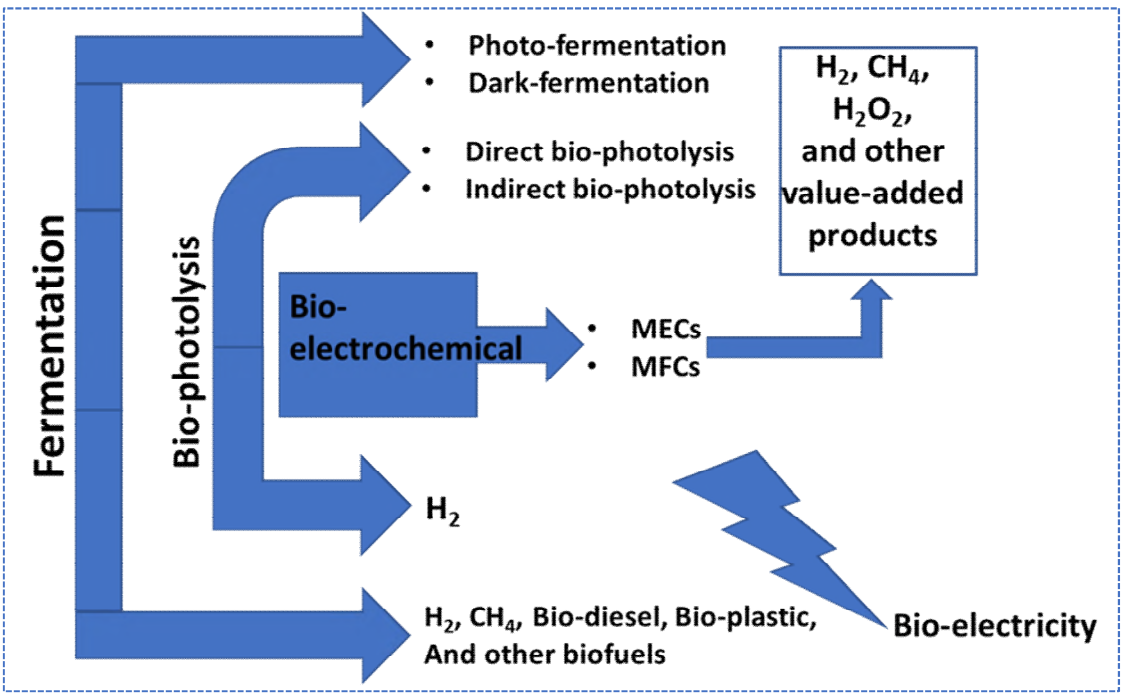


Fig. 5. Representation of the biological paths toward clean and sustainable H_2 generation. Reprinted with permission from Ref. [129].

Hydrogen is widely accepted equally for chemical and fuel, into different industrial methods, for example, updating fossil fuels including immersing oils, so H_2 has anomalous related to CH_4. H_2 generation by wastewater is seven times higher than CH_4 generated by the equivalent quantity of wastewater toward the COD source. H_2 generation during MEC can be prepared by several organic origins, including waste substances in addition to non-fermentable substrates [1]. Microbes oxidize organic composites naturally, acetate and produce CO_2, electrons, and protons on a MEC cathodic probe. Besides an outside potential, the electrons move toward the anodic probe at which it joins with protons to produce H_2 gas (**Eqs. (1) and (2))** [2]. Toward charge impartiality, the protons transfer from cathodic to anodic electrode into the suspension. In tradition, a potential of >0.2 V is needed for H_2 generation in MEC, which is smaller than the standard potential (>1.6 V) expected toward water electro-oxidation. A membrane divides the cathodic and anodic probe assembly to evade the complexity of the support and output. The reactions which arise within a MEC by acetate as support is as below.

$$At\ anode: \quad CH_3COO^- + 4H_2O \rightarrow 2HCO_3^- + 8e^- + 9H^+ \rightarrow \quad (1)$$

$$At\ cathode: \ 8H^+ + 8e^- \rightarrow 4H_2 \ \ or\ 8H_2O + 8e^- \rightarrow 4H_2 + 8OH^- \rightarrow \quad (2)$$

H_2 production on the negative probe happens after overwhelming the endothermic limit of 0.414 V versus SHE using a low exterior potential variation of 0.14 V toward the MEC. The oxidation reaction brought out with the cathodic probe germs may provide the residual over potential (0.279 V) [132]. Simultaneously wastewater processing and H_2 generation in MEC is an effective way to produce reliable energy.

There are numerous benefits of composing H_2 *vs* CH_4 with the organics already within the biorefinery method water rivulet. These involve a great interest due to the high cost of H_2, the capability to apply instantly for upgrading biorefinery outcomes, such as F-T liquids, possible to work as oil into fuel cells, and as an essential substance toward the regeneration of different biorefinery intermediates to valuable commodities [133]. Updating F-T liquids toward significant octane or big decane oils will be a crucial move to generate renewable shipping fuels. While the application of CH_4 to improving F-T liquids is probable [134], the further moves into such a method than that of MECs can drive to more expensive and

economical overall energy competence. Application of H_2 being a fuel under PEM also different fuel cells can similarly occur toward higher energy regeneration competencies related to the practice of CH_4 under elevated heat fuel cells or into turbines, etc. [135].

Several methods into biorefineries may help from onsite H_2 accessibility. The three fractions-cellulose, hemicelluloses, and lignin of each stock tree may apply H_2 generation of other higher-value results [125]. . Sorbitol is an initial element of various goods, with vitamin C, alkyd resins, and surfactants [138]. The hydrogenation procedure from d-glucose into d-sorbitol. *Fructose* is a different output produced by glucose through glucose, applying high pressure plus temperature circumstances under the appearance of H_2. Its application into food and pharmaceutical products may be transformed within hydroxymethyl furfural (HMF) plus levulinic acid, which are valuable initial substances toward several manufacturing chemicals. H_2 is utilized in many of these methods for turning HMF plus levulinic acid within furan and levulinate byproducts. The reproduction of succinic acid by glucose is at its approach toward speculation. Subjunction of the support glucose, including H_2, has been given to improve succinic acid produces suggestively [139].

3.2. Acetate

MES used a different way to set CO_2 within multi-carbon aggregates, for example, liquid oils or chemicals with current-ambitious reduction reactions. This treatment is recognized as a technology toward the warehouse of electrical energy into the C-C bond of valuable compounds [140]. Additionally, it showed the first evidence of MES applying the acetogen Sporomusa ovata, which could allow atoms immediately received by a graphite cathode toward the mitigation of CO_2 to generate acetate and low amounts of 2-oxobutyrate. Electron curing in certain goods was additional substantial than 85% of the electrons carried on the cathodes. The subsequent investigations showed the method of CO_2 mitigation employing MES through a more comprehensive array of microorganisms [141]. The product yield (or yield performance) of inorganic nutrients and organic substances are arranged within **Table 2** [103].

Table 2: Relative yield also energy productivity of biochemical complexes. Reprinted with permission from Ref. [103].

Elements	**Reactor/technique**	**Subtraction productivity**	**Energy/current detention efficacy**
CH_4	CO_2 - CH_4 into BES (at-0.65V E_c vs. SHE)	0.005±0.002 m mol/day	
	MEC with electromethanogenesis (at -0.7V E_c vs. Ag/Agcl)	80%	90%
	MEC (on -0.55V E_c vs. SHE)	0.006 $m^3/(m^3/day)$	51.3%
H_2	Bio-catalyzed electrolysis (used potential: 0.5 V)	0.02 $m^3/ (m^3$ day)	53 ± 3.5%
	Bio-catalyzed electrolysis (on -0.7 V EC vs. SHE)	0.63 $m^3/(m^3$ day)	49%
H_2O_2	BES (used potential: 0.5 V)	1.9 ± 0.2 $kg/(m^3day)$	83.1 ± 4.8%
Ethanol	BES (on -0.7 V EC vs. SHE)	13.5 ± 0.7 mM	74.6 ± 6%
Triglycerides	Smooth dish electrochemical cell (on -0.9 V EC vs. SHE)	Caproate: 739 mg/L Caprylate: 36 mg/L	26%

The MES method's circumstances need to be designed to provide the ideal metabolism of biocatalyst already on the biocathode. A proper electrode electron receiver could be possible toward the cathodic reaction. A strong cathodic reaction employed the cathodic or used voltage, which discloses the thermodynamic boundary of a biological response within MES. Homo-acetogenic microorganisms may effectively change CO_2 into acetate, a primary central particle to the generation of biochemicals [142]. Thermodynamically, the reduction of CO_2 into acetate needs 280 mV vs SHE cathodic voltage. Following applied circumstances, a significantly below voltage is needed to succeed the latent wounds due to the microbial energy acceptance, including mass and charge transmission resistances associated with a bio-electrochemical operation. Aside from the primary determinants, many other fundamental issues, such as probe substances, reactor configuration, and media in electron transfer, control the complete process performance [143].

Nevin *et al.* [140] described the probability of converting CO_2 to acetate through acetogenic microorganism *Sporomusa ovata* electrons carried instantly of a graphite probe. It was observed that *S. ovata* biofilms at the graphite cathode facet absorbed electrons of the terminal and turned CO_2 into acetate and little volumes of 2-oxobutyrate. These outcomes apprehended 85 % of provided electrons. An engaging and unique path introduced the idea of MEC, which might transform solar energy into precious organic commodities more efficiently compared to conventional methods. The relevant tools, base opinion, and method perception are still on the route as entirely different processing. Rabaey and Rozendal [144] explained the policies, hurdles and possibilities of MECs, provided an essential detail of illustration on this exciting and unique system on the nexus of microbiology and electrochemistry. Currently, the MES technology is opening; hence, modern research focuses on building new ideas.

3.3. Methane

A membrane-less MEC would generate pure energy, including methane (CH_4) as the final major commodity. CH_4 is usually identified within the MECs at the time of H_2 generation due to methanogens' extension. The CH_4 generation through MECs is different from inoculum, support and container arrangement [145]. The presence of methanogens is stunning within H_2 generating MECs, as it reduces the H_2 product. Various approaches

have been utilized to hinder the completion of methanogens during MECs. Though the maximum of the techniques is inefficient or energy accelerated. Somewhat of restraint of methanogens, the direct product of CH_4 within MECs includes numerous benefits than that of conventional anaerobic digestion (AD) techniques.

Methane production by AD of organic supports had primarily been used, which is acknowledged as a renewable method. However, to develop the CH_4 production method [146], reprocessing the CO_2 produced by different biological methods may generate higher CH_4 by MES. Microbial electrosynthesis of CH_4, also identified as electro-methanogenesis, may move at lower heat compared to AD. The importance of electro-methanogenesis by MEC is that the organic material existing within wastewater may be employed and at a similar time, the CH_4 product is obtained. This method gives more benefits than conventional methanogenesis regarding greater CH_4 yield and application of the wastes emitted by AD methods [50,31].

Wang *et al.* [147] examined the CH_4 and H_2 generation during MEC; H_2 gas was recognized in the last of the first cycle. The reactors were later run across various batch cycles covering the next month to secure durable and steady performance before conducting H_2 generation experiments (**Fig. 6(a)**). In contradiction to BES, lumazine did not affect CH_4 generation. The lumazine direct CH_4 generation into mixed-culture MECs on an input of 0-1144 μM (**Fig. 6(b)**). **Fig. 6(c)** confers a standard CH_4 product into the anode and cathode assembly below anodic methanogens restrained circumstances following a BES dose. Acetate was not identified within the cathode, and a BES dose in the cathode assembly did not decrease the level of CH_4 generation. It shows that CH_4 composition under the cathode is essentially a hydrogenotrophic methanogen-linked method, including acetoclastic methanogens' minimum participation. Remarkably, CH_4 was yet composed on the cathode. In contrast, the cathode chamber was autoclaved to reduce the biogenic movement near 120 ^oC concerning 20 min as an abiotic controller experiment. However, its capacity was comparatively small associated with the unautoclaved cathode (**Fig. 6(d)**). Therefore, a different pathway for cathodic CH_4 product is also assumed [145].

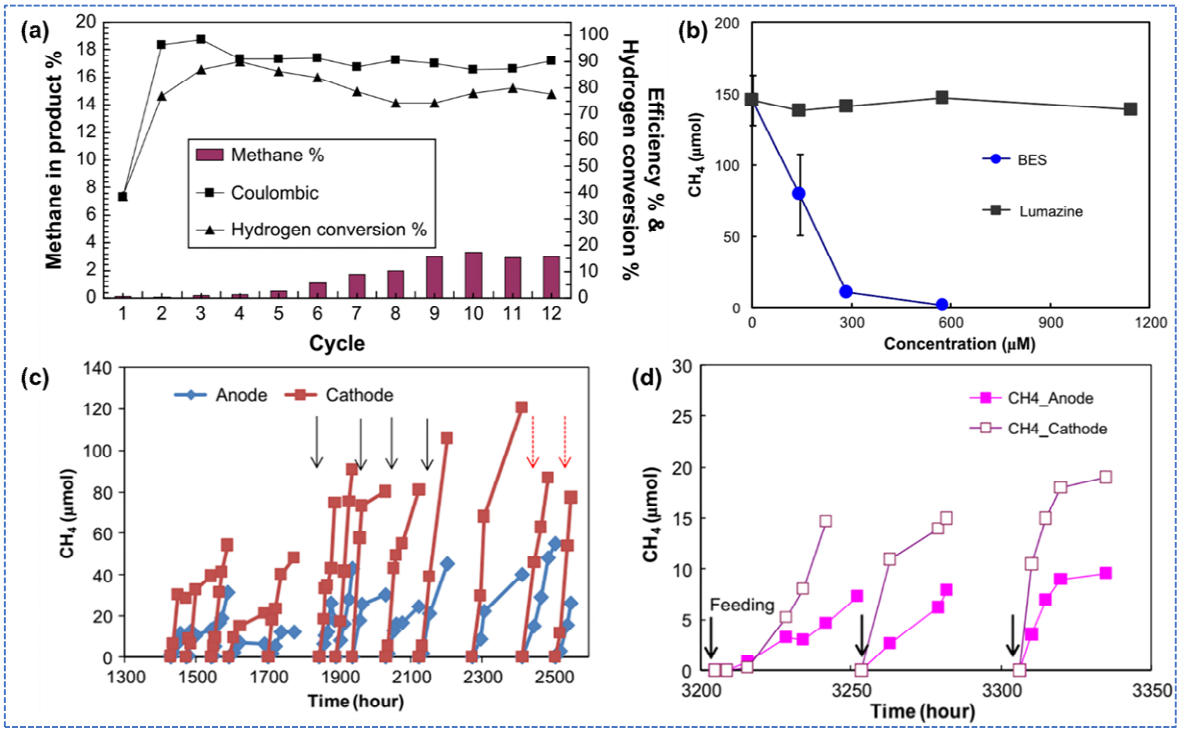


Fig. 6(a) CH_4 generation and H_2 conversion performance into a separate container MEC on 0.7 V. Reprinted with permission from Ref. [147]. (b) CH_4 generation as a function of methanogen inhibitor combinations (about 2.86 µM acetate at 0.5 V). (c) CH_4 composition under the anode and cathode while methanogen-contained process including the BES dose within anode (about 2.86 µM acetate). The arrows show chemical doses in the cathode: solid for BES of 286 µM; dashed toward lumazine about 286 µM. (d) Abiotic CH_4 composition, including an autoclaved cathode chamber, happened as the anodic methanogen-contained process. Reprinted with permission from Ref. [145].

Further, the bioelectrochemical CH_4 products applying a different container shape into MEC mode [148], employing conventional graphite as an electrode. Processing of AD effluents within a separate container MEC and CH_4 generation has prospected as a viable technology toward effective scrap processing. Sasaki et al. [149] concentrated on applying a membrane-free form in a practical voltage 0.395 (vs SHE) in neutral pH and showed effective CH_4 generation. It was mentioned that the controlling methanogens at the anode probe were different from those developed under command reactors without electrochemical reactions. Villano *et al.* [150] practiced different methanogenic cultures as cathodic biocatalysts into a dual compartment arrangement CH_4 by CO_2 on different employed cathode voltage -0.65 V to -1.0 V (vs SHE).

During the scalability comparisons toward MEC, including multi-probe arrangements toward H_2 generation employing acetate as support [151], published that the methanogenesis rates improved continuously over time. Furthermore, after 16 days of running, the method presented a small H_2 product rather than a consequent CH_4 generation, including better substrate reduction performance, revealing that electro-methanogenesis became the practical method on the biocathode while working with wastes shady agitation and AD methods.

3.4. Recovery of heavy metals

BESs are rising as a new technology floor toward removing and recovering metal ions by metallurgical scraps, method rivulets, and wastewaters. Biodegradation of organic material through electroactive biofilms on the anode has been favourably linked to the cathodic reduction concerning metal ions. Heavy metals existing within industrial effluents model a severe obstacle to the climate and public fitness as several of these minerals are poisonous on lower densities. Physical, chemical, and biochemical types of machinery towards heavy metals extraction from drainage water has been formed and works assigned for its potential restoration. Such processing methods can be offered economical and renewable by promoting metal restoration utilizing BES [152]. Furthermore, BES can extract and collect metals when being on actual low frequency in an aqueous means, delivering a cost-effective feasible opportunity compared to other substitute methods. Some investigations exhibited retrieval of metals through lower redox potential, for example, Ni^{2+}($E^{0\prime}$=0.250 V), Pb^{2+}($E^{0\prime}$=0.130 V), Cd^{2+}($E^{0\prime}$=0.400 V) and Zn^{2+}($E^{0\prime}$=0.762 V), via applying biotic anode and abiotic cathode below the impact of outer energy origin to drive the migration of atoms by anode to the cathode front. Furthermore, the more leading reduction of chromium and different transition elements may be accomplished following microbial metabolism on bio-cathode, including the absence of poised voltage [153].

Metals existing into trash brooks should be collected to reduce their warning to the atmosphere and reuse limited sources. For example, numerous metal cations, such as Cu^{2+} and Hg^{2+}, have been examined as electron gainers on the cathode of MFCs [154,155].

These alloys may be retrieved into MFCs including, further power generation, as they usually have excellent conversion potential (for example, 0.34 V toward Cu^{2+}) [156]. Unfortunately, though, to these metal ions, including lower mitigation voltages, restoration may not be accomplished during MFCs in the absence of additional energy accumulation. Nevertheless, considering MECs possess numerous benefits, such as low energy necessary than that of the standard electrochemical method, this could be a substitute for energy-effective metal restoration.

The bioelectrochemical recovery of heavy metals (such as; Cu, Pb, Cd, and Zn) of a blended solution into 2 M HCl was provided out under four test periods for recovering the elements in the direction of reducing conversion voltage. At the cathode surface, the metal ion arrays are displayed within **Fig. 7(a)**. Through periods 1, 2, 3 and 4, Cu^{2+}, Pb^{2+}, Cd^{2+}, and Zn^{2+} were dismissed of the catholyte. The input potential needed to collect the metals into the bioelectrochemical reactor enhanced, including reducing cathode voltage (negative cell potential indicates electrical power input under **Fig. 7(b)**. The nutrient mechanism TOC absorption and pH declined at the anode surface due to acetate oxidation and charge immigration (**Fig. 7(c)**). During period 3, about 230 h, the test was discontinued for four days. The new nutrient medium supplied while again started over the anode, which describes the rise in TOC absorption and pH recognized. While periods 1-3, the anode voltage was constant among -0.25 and -0.17 V (**Fig. 7(d)**) [156].

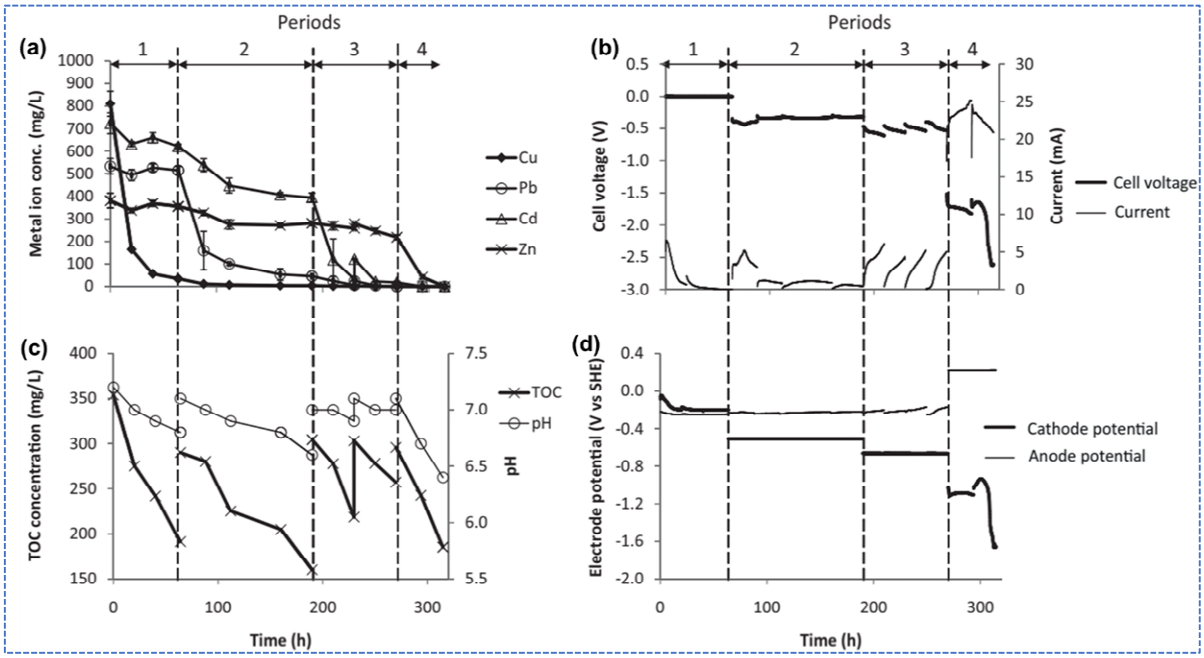


Fig. 7. (a) Metal ions concentrations near the catholyte, (b) cell potential and current, (c) TOC absorption and pH within the anolyte, and (d) cathode and anode voltage while the examination toward the restoration of metals by a various solution catholyte. Reprinted with permission from Ref. [156].

3.5. Nutrient's recovery

Nutrient's administration is an essential responsibility of wastewater processing, and the elimination of nutrients is normally compared among significant energy/financial prices. The nutrient extraction and rehabilitation by urine and pig drainage water may be brought out with choosing biological methods under BES [157-159]. Urine may be recognized as an absolute fuel (origin of C, P, N, and K) toward power generation within MFC. Therefore, the potential energy and NH_3 retrieval by urine applying a BES was investigated [160,161]. NH_4 revival in MFC was achieved by managing urine near the anodic container. The following consumption attended movement of NH_4^+ by dispersion to the cathodic container. The higher current density of 3.6 A/m^2 including the pointedly advanced improvement of NH_4^+ near 61% in MFC, was summarized into a microbial electrochemical cell below power-ambitious immigration [162]. The modern MFC promoted ammonium improvement theory is presented in **Fig. 8(a),** and **Fig. 8(b)** displays the test structure's design.

Blázquez *et al.* [163] published a unique method for handling high potency sulphate wastewater with bio-electrochemical methods. The advancement of bio-cathode including autotrophic sulphate reduction bacteria (SRB) and sulphide oxidizing bacteria (SOB), drives metal sulphur restoration through the infectious metabolic method. By employing H_2 as an electron contributor, the conversion of sulphate with SRB was perceived inside the cathodic container assembling H_2S [164], completing sulphate conversion rate of about 388 mg. $S\text{-}SO_4^{2-}$/(l. day). Additionally, H_2O was scattered in the anodic container to provide O_2, which moved to the cathodic cell by anion transfer film and gave attention to SOB to catalyze the H_2S oxidation to generate elemental sulphur collected at the cathode exterior.

3.6. Hybrid method of wastewater processing for effective co-product retrieval

By improving BES investigation, numerous readings appeared by combining wastewater processing, including BES, to improve the effluent feature and retrieve the most accessible energy instant toward the wastewater. The outcomes, for example, bio-H_2, bio-CH_4, power, bio-fertilizer, caustic soda, H_2O_2, etc. were developed through the combined performance of composite BES. H_2 and CH_4 generation when such integrated process executes the composite practice more engaging and effective [165]. **Fig. 8. (c & d)** A sediment microbial fuel cell (SMFC) including microbial anode and cathode gives energy toward the power control operation [166] and representing the sensor device for estimating subsurface microbial movement through the current generation by subsurface probes [167], correspondingly.

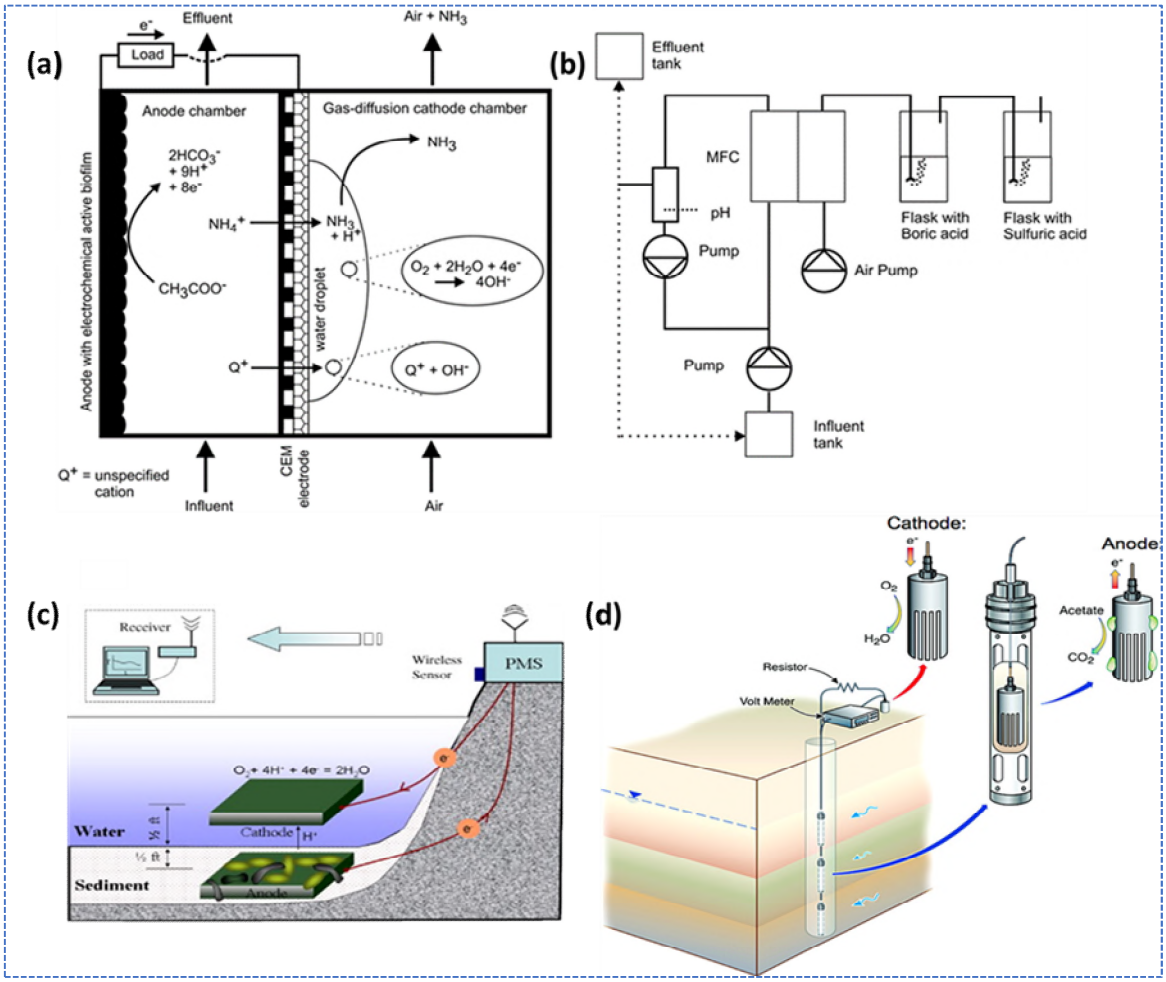


Fig. 8. (a) Schematic illustration of the methods included within the NH4 retrieval employing an MFC; (b) Schematic illustration of the laboratory structure for NH4 retrieval utilizing an MFC. Reprinted with permission from Ref. [160]. (c) An SMFC, including microbial anode and cathode, gives energy toward the power management system (PMS). Reprinted with permission from Ref. [166]. (d) The sensor device for estimating subsurface microbial performance through the current product from subsurface probes. Reprinted with permission from Ref. [167].

BES process reflected efficient wastewater processing separate from power production. Improved substrate (COD) decrease was recognized near-contemporary appearance and TDS extraction. COD elimination response ranged within 33.33% and 72.84% while the MFC process. According to energy production, the carbon part of wastewater worked as an electron contributor during the metabolic method occurring in substrate degeneration. A good decrease in COD identifies the valuable niche of diverse microflora in managing still wastewater.

Around 29.5% increase in substrate reduction was seen owing to the combination of probes in the dark-fermentation method (MFC operation; producing bioelectricity) related toward the dark-fermentation method (biofilm reactor without probe arrangement; producing biohydrogen) [168]. Distillery wastewater revealed higher substrate reduction performance related to composing synthetic and chemical wastewater assessed below comparable working situations in the same MFC arrangement. Improvement in substrate degeneration was published under MFC (dual container) while composite chemical sewer water processing on the developed substrate storing position as opposed to the traditional anaerobic processing method [169]. The perceived advancement in substrate degeneration through MFC performance may be associated with the bio-electrochemical catalyzed aspects as described: (a) direct anodic oxidation (DAO) wherever the contaminants are adsorbed at the anode exterior and become degenerated through the anodic electron substitution reactions [170]; (b) Indirect oxidation (IO) negotiated with the oxidants similar to chlorine dioxide, hypochlorite, hydroxyl fanatics, ozone, and H_2O_2 produced electrochemically at the anode exterior oxidizes the organic material.

3.7. The novel cathode and anode materials used in BES

An electrode is a compact electric material that provides the electric flow within BESs. The electrodes in BESs are classified in anode and cathode, including particular attention presented when selecting a substance as electrodes toward BESs. A few of these constituents such as good conductivity, improved mass transference, and high surface area. The activity of BESs depends upon the electrode substance. Metals prototype toward the anode comprises carbon and its components [172].

Substances fit toward the cathode comprise Pt black and graphite [173]. Pt covered electrodes usually are used owing to their effectiveness and perfection during the production of electricity. Notwithstanding the high price of Pt materials, this is the best-known reactant toward oxygen reduction reactions (ORR). However, inadequate oxygen conversion happens among Pt-free cathodes. Therefore, various electron acceptors rather than O_2 were employed within BESs to overwhelm the weak ORR, for example, potassium ferricyanide [174], permanganate [175], and sodium hypochlorite [176]. Biocathode is a

different approach that utilises the aerobic biofilm on the cathode exterior as an electron gainer [177]. During MEC, Pt is also the most suitable material for hydrogen evolution reactions (HER). However, owing to its vast price and easy poising, its use in these operations is insufficient. Distinct Pt-free synergists were studied in MEC toward HER, for example, stainless steel, nickel compounds, including tungsten carbide [178,179]. Likewise, biocathode is recommended to be utilized within MEC toward HER. Though, the biocathode influences the cleanliness of H_2 generated owing to the increasing methanogenesis bacteria [180].

3.8. BESs based desalination and wastewater treatment

Based upon the prior primary composition of the BESs depended on desalination, different arrangements, while depends upon the MFC or MEC, will be included within the next part.

3.8.1. MFC based desalination cells (MDCs)

A microbial desalination cell (MDC) is a BES that yields comparable characteristics by an MFC [181]. These Desalination cells based upon the electric driving power produced from the microbial metabolism within the anode assembly, which animates ion departure by the desalination container to both electrodes [182]. Several investigations have been brought out on the MDC utilized acetate, including phosphate buffer as an anolyte. As a result, the MDC gained higher activity, greater power density, higher COD discharge, and higher coulombic efficiency. This notable development within the cell performance was correlated toward the advancement of the conduction of the sewer water through the ions, stabilization of the pH on the anode, and the difference of the anode microbial arrangement [183,184].

3.8.2. MEC based desalination cells (MEDCs)

MEC is an example of the BESs employed towards new wastewater processing and biohydrogen generation implementing a minute voltage between the anode and the cathode

assembly. The microbial electrolysis desalination cell (MEDC) was a newly expanded technology by merging the MDC and MEC rather than the MFC arrangement as the desalination performance of the MDC is restricted with the varied voltages generated through the exoelectrogenic microbes [25]. Microbial electrochemical technologies (MET) dependent upon MFC or MEC (**Fig. 9(a)**) allow a chance to treat wastewater by the concomitant regeneration of power biologically. Within MFCs or MECs, microorganisms, including extracellular electron transfer (EET) ability, transport the electrons produced through the oxidation of organics during wastewater towards the anode [185].

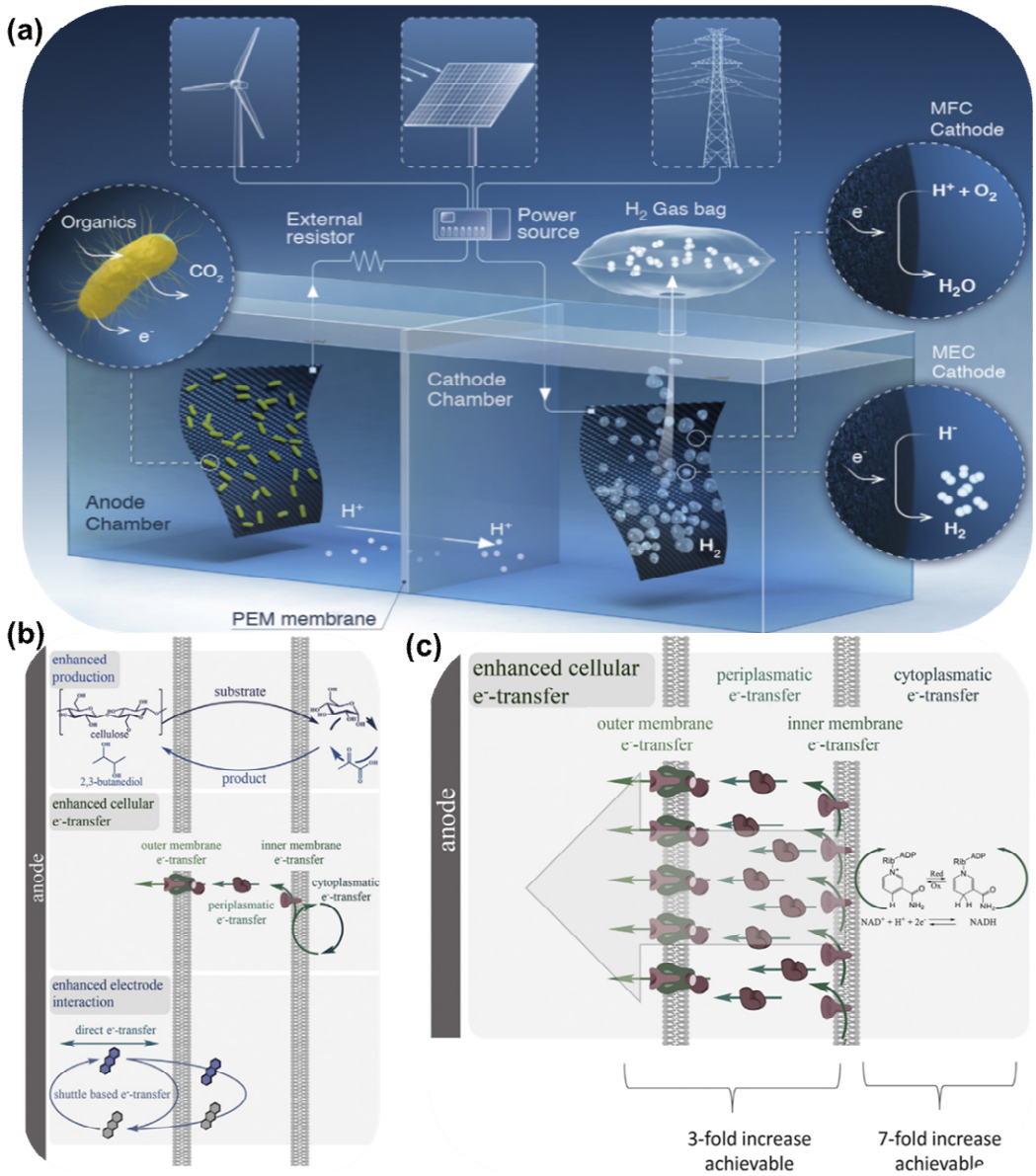


Fig. 9. (a) Schematic illustration of the various arrangements of METs toward wastewater procedure, including the restoration of energy. Reprinted with permission from Ref. [185]. (b) Various policies to improve the applications of microorganisms within BES. (c) Design the central way toward EET, including a tailored cytochrome channel and manufacturing the intracellular particle equipment. Recent research linking the design policies would drive over a 10-times increment in current value. Reprinted with permission from Ref. [186].

3.9. Important aspects in BES architecture and designs

Despite the layout and structure of the MFCs, the specific ingredients, e.g., separator, electrode substances, inoculum, and wastewater, are the final part of the production. Therefore, during the previous years, an extensive investigation has surfaced dealing with the growth of the peculiar parts to obtain this technology fit toward employment within the area. There is also an inadequate expanse to get a few novel progressions into the membrane and electrode substances these days. The membrane separators, or ion exchange layers, are a crucial ingredient of MFCs, which should have different vital resources, e.g., high ion exchangeability, durability into an intense atmosphere, and impermeability of the mass flux of oxygen and basic materials. Membranes are also the initial condition of biofouling improvement upon the cathode exterior. Hence, antifouling layers are further fit within MFCs [187].

Likewise, electrodes would maintain a large surface area, durability, biocompatibility, and electric performance. Most importantly, both electrode and separators would be economical to guarantee their practical purpose within industrial MFCs. Therefore, the maximum of the novel study turns throughout the construction of cost-effective substances.

3.10. Genetic engineering for enhanced productivity in BES

As we know, BESs may be utilized to produce valuable compounds, bioelectricity, wastewater processing, and biosensing, among others. Transforming a substrate toward the required output through generating current within a BES can be separated within various modules. To enhance the complete performance of the biocatalyst, the generative architecture of the smallest one of these modules should be examined. Within **Fig. 9(b)**, the four central modules are displayed. A facile-utilized path to improve extracellular inhalation is to concentrate upon intracellular destinations that interfere with electron alteration (i) by the cytoplasm toward the menaquinone equipment, (ii) by the menaquinone pool toward the periplasm, (iii) via the periplasm and (iv) via the exterior layer.

Other strategies try to develop potency by optimizing microorganism-electrode synergy. It may either be transferred with enhancing straight or shuttle-based electron transfer.

Immediate electron alteration can be enhanced by optimizing the organisms' biofilm production capabilities. In contrast, the shuttle-based particle transference is usually enhanced with growing the number of convenient shuttle composites. While in another side, through manufacturing, the intracellular electron supplies a seven-time increment within the current value that appears to be possible. While there seem to be no apparent causes of why the two consequences would not be combinable, the purpose of the central cytochrome way toward EET and the progress in intracellular releasable particles may start to a 10-times advancement within the current value (**Fig. 9 (c)**) [186].

3.11. Production of valuable materials in BESs

Hydrogen peroxide (H_2O_2) is a multifaceted, eco-friendly, oxidizing solid compound, including various modern uses. This is affirmed that BES is a promising technology for H_2O_2 biosynthesis, such as MFC and MEC usually. Currently, the BESs are developed of pure electricity production toward the reductive composition of an energy-rich substance, for example, H_2O_2 within MECs. The idea of MECs was introduced in 2005 by the essential characteristic of applying an outer voltage over the MFC potential to produce H_2 gas on the cathode by the proton conversion. A comparable policy, two-electron ORR toward H_2O_2 production, was primarily identified in 2009 within the cathodic container [188].

Electrodes that may generate H_2O_2 are supposed flawed for MFC uses because of not maximum power production. Although, it should provide an industrial compound into a green integration, especially during joined electrochemical methods [189]. It extensively knows that the anode voltage based upon the respiratory enzymes' potential to produce power toward the cell from the oxidation of the organic material. Generally, MECs need the potential produced from support oxidation on the anode to be supported, including an external power amount; to succeed the thermodynamic limitation and/or force the cathodic H_2O_2 production, extraordinary speeds initiated the creation of anolyte distinct from MFCs [190].

The current development within bioelectrochemistry of BESs and electro-biotechnology revealed a necessary combination of composites that significantly provide performance and capability: surface-active tools and surfactants. Lately, crucial scientific observation has been adjusted to replace the chemically manufactured surfactants with biosurfactants that microorganisms may present within various bioreactors. However, biosurfactant functionalities in existing systems have yet not been completely known. Models of the essential functions of biosurfactants cover: improving the exterior area and bioavailability of hydrophobic supports, adjusting the addition, the impartiality of microorganisms to the facades, joining within *quorum sensing* devices, merging of heavy elements, and antimicrobial performance. The functions discussed up can consequently have a significant influence on the BES execution [191].

3.12. Remediation of soil contamination by BESs

Effective non-invasive methods are required to observe the remedy manner of polluted clays. Hydrocarbon poisoning owing to unexpected spills and vessel leakages describes a warning over the atmosphere. Several design explications have been used to improve the remedy technique among the natural attenuation of the contaminants. Lately, BESs were produced and examined towards the remedy of polluted hydrocarbon clays. While the remediation method, the BES presents an atmosphere toward electrochemically active bacteria (EAB) for catalyzing the oxidation of natural electron contributors, such as hydrocarbon poisoning, and convey the electrons on the electrode [192].

In this regard, Ren *et al.* [193] composed a life-size execution of column-kind BESs as in situ clay bioremediation could base upon the length by the anode where biodegradation remains to be improved, that is the radius of impact (ROI). **Fig. 10 (a)** shows the image of column-kind BES into a polluted soil remediation analysis. Two column-kind BESs were assembled as exhibited within **Fig. 10 (b)**, including one BES comprising a graphite granule anode (GGA) and the additional a biochar anode (BCA). The clay pH raised to 0.13 in the initial 5 days on a circular length of 1 cm by the anodes of every BES **(Fig. 10 (c))**. It is associated with the adsorption of ions and H+ via the anode bodies, accorded by a 17-37% reduction in electrical conductivity (EC). On days 5 to 25, the pH slowly reduced

near 0.22 on each sampling period, probably due to organic acid production by hydrocarbon metabolism. However, the organic acids could be quickly absorbed, following into pH rebound. It was recognized under the research that a pH rebound around 0.13 at day 45. As a result, the soil EC improved around the anodes of all BES but reduced by length. Ions immigration inspired by water destruction on the cathodes to electrode modules may cause this conductivity pattern [194].

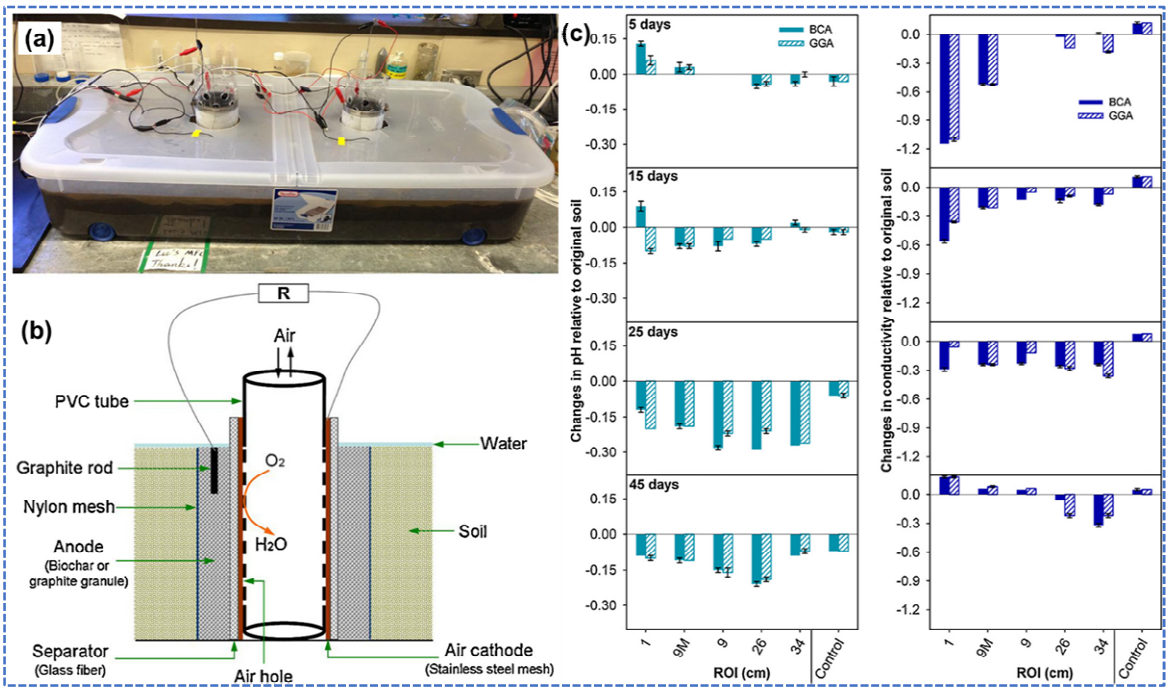


Fig. 10. (a) The image of column-kind BES within polluted soil remediation analysis, and (b) diagram of the column-kind BES configuration. (c) Variations into soil pH and EC during the BES- and control reactors. Reprinted with permission from Ref. [193].

3.13. Photosynthetic BESs

The scope of BES investigation covers a broad area of developing technologies that employ bacteria to catalyze anodic and/or cathodic responses in a fuel cell structure and has developed dramatically. Although most BESs use organic supports as a fuel reservoir (*such as* MFCs), numerous declarations are fueled with light steam. BESs applying different photosynthetic biocatalysts develop a comparatively latest method that is inadequately represented within the classification. Earlier, it may be separated within photosynthetic

microbial fuel cells (PMFCs; **Fig. 11 (a)**) and bio photovoltaic cells (BPVs; **Fig. 11 (b)**). Each kind of tool utilize an electron-generating phototroph on the anode; though, the final root of those electrons is separate. PMFCs are colonized with anaerobic chemoautotrophic bacteria that uses biochemical fuel being the initial electron origin and produce electric flows into a light-dependent style [195]. Different from traditional MFCs, P-MFCs may produce power regularly during plant development and may be utilized within any field used toward crop products without injuring the plants. However, the purpose of these regularities upon an extensive range has displayed significant hurdles up to now. It is initially owing to commercialization; further, low energy ability while associated with other operations [197].

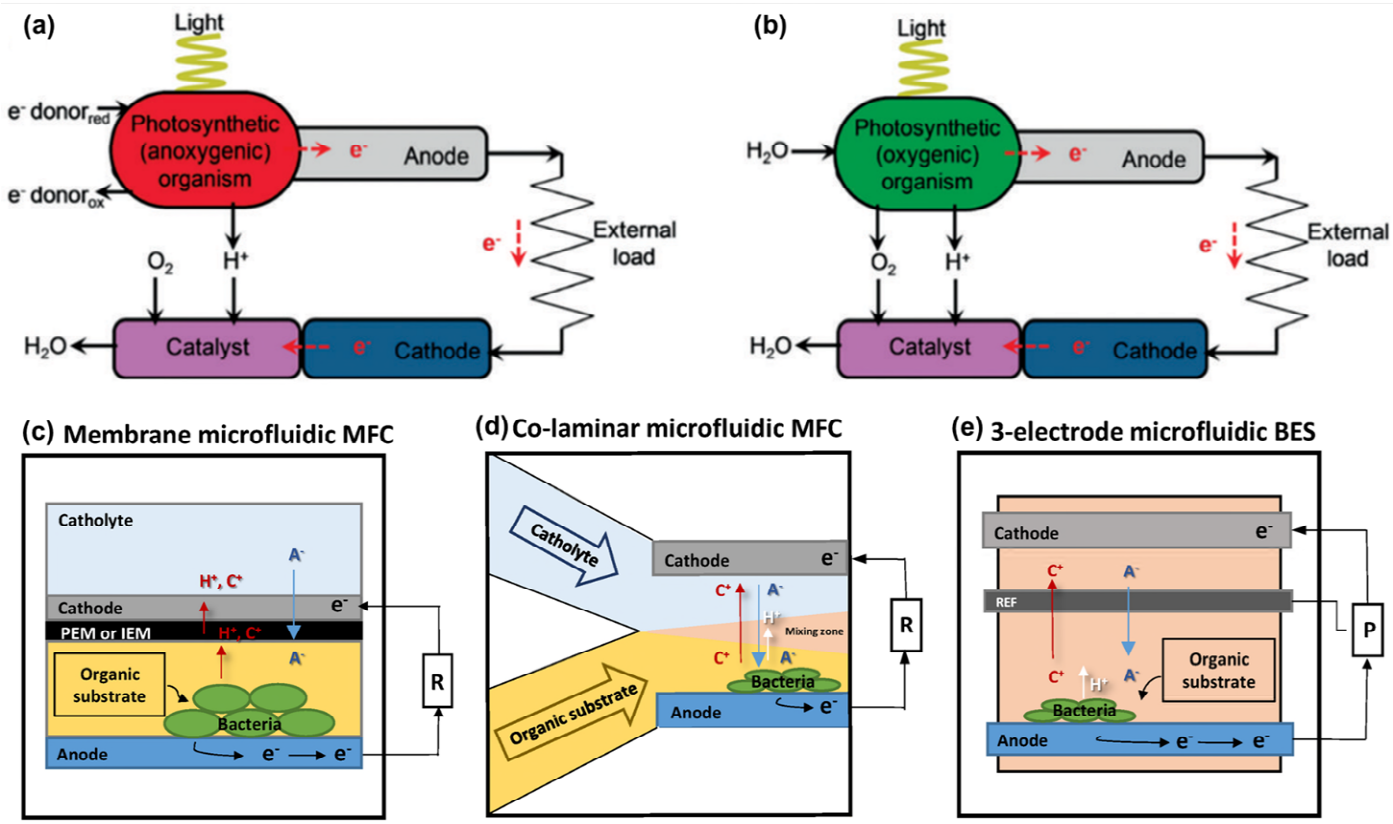


Fig. 11. Graphic illustrations of **(a)** P-MFCs and **(b)** cellular bio photovoltaic cells. Reprinted with permission from Ref. [195]. Exhibition of the three kinds of microfluidic BES. (**c**) low-range membrane MFC, (**d**) co-laminar electrode microfluidic, (**e**) BES is incorporating an added reference electrode. Reprinted with permission from Ref. [198].

3.14. Microfluidic BES

Since the last previous years, microfluidic devices have significantly improved, explain the primary area of bacterial EET and introduce innovative optimization approaches for improving and designing the latest BES systems. Microfluidics will undoubtedly remain to give to various interesting decisive fields of analysis. While studying microfluidics to promote the research and development of the BES area, this is essential to concentrate upon the powers that microfluidics systems maintain.

Within a standard MFC, electroactive microbes (**Fig. 11 (c)** treat the anode. The microbes oxidize natural substrates into the electrolyte and contribute electrons on the anode exterior immediately or lengthily. The electrons are transported toward the cathode via an outer shield; whither an abiotically catalyzed reaction electrochemically diminishes oxidants. A proton exchange membrane (PEM) or, more widely, an ionic exchange membrane (IEM) divides the two assemblies for preventing the mixing of their solution, during ions with protons may yet be switched within them. The arrangement is identical during a membrane microfluidic MFC; besides this, the electrodes are usually provided immediately, including microfabrication systems, to meet the microreactor system's range. As two identical channels could provide the cathodic and the anodic electrolytes to be introduced individually during a co-laminar microfluidic MFC, the fluid flow dynamics could limit the two electrolytes by mixing (**Fig. 11 (d)**). The appearance of a reference electrode determines the three-electrode microfluidic BES apparatus to normalize the effects noted by the working electrode (**Fig. 11 (e)**). Such a practice provides secure data to be received and electrochemical reaction kinetics reported separately at anodes and cathodes. Up to now, just rare classes of three-electrode arrangements have been developed within microfluidic BESs [198].

4. Possibilities for employing CO_2 in bio-factories

There are several different opportunities (as explained earlier) to usage CO_2 in biofactories to produce added-value compounds [199]. Mainly, the utilization of CO_2 is not triggered with the object toward reducing the greenhouse gas (GHG) emissions but through the opportunity to have substitute methods, outcomes by distinct features, or to utilize carbon causes on economic value. Generally, the purpose of these methods is not to combine sustainable energy inside the biobased product series. The product of succinic acid by glucose plus CO_2 with biotechnological methods [200]; are operating at the pilot/demo range composition of bio-succinic acid ($C_4H_6O_4$). $C_4H_6O_4$ may be hydrogenated into butanediol/tetrahydrofuran. The applicability of succinic acid is supposed to improve shortly, including plasticizers, polyurethanes, bioplastics, and chemical intermediates.

The generation concerning acetone by CO_2 plus H_2 with enzymatic ways (Evonik method); acetone, mutually including NH_3, CH_4, and CH_3OH are feedstocks to the Evonik method for generating methyl methacrylate (MMA) by acetone cyanohydrin [201]. So, in this section, the generic approach to producing 100 % fossil-fuel-free MMA has been discussed. Unlike $C_4H_6O_4$, the reaction and the whole generation of “renewable” MMA are yet far away from applicability. The composition of valuable compounds by the reaction of CO_2 [202] and a few of the biorefineries' derivatives are explained by Alper and Yuksel [203]. An enormous number of inorganics, organics, and metal reactants have been produced to different chemical transformations of CO_2. The accomplishments above the preceding five years are especially remarkable. The construction of cyclic carbonates (CCs) or polycarbonates, epoxides and carboxylation effects by CO_2, mitigation of CO_2, including another exciting reaction, have also been produced and examined broadly (**Fig. 12**) [204].

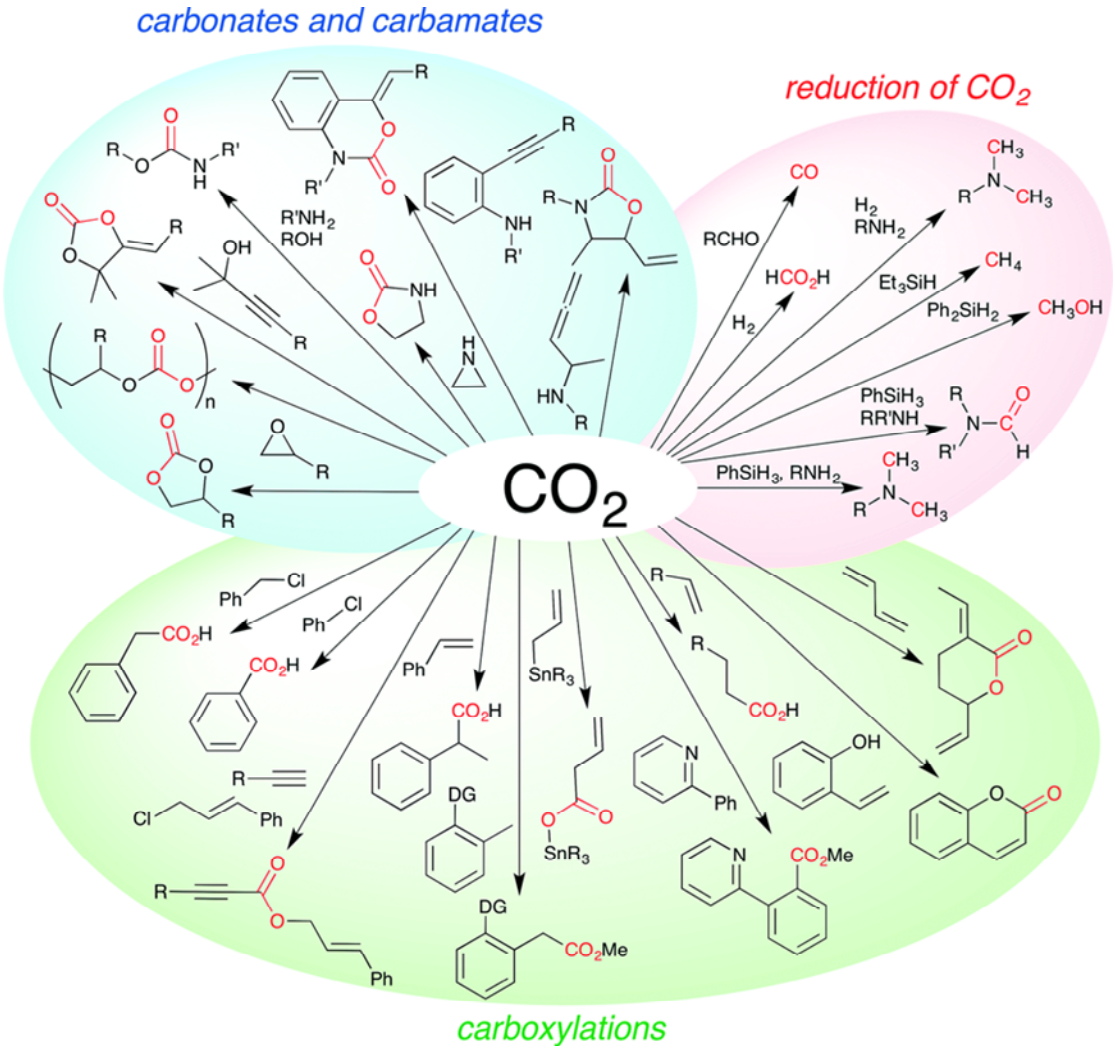


Fig. 12. Illustrations of the chemical fascination of CO_2. Reprinted with permission from Ref. [204].

Though the carboxylation reaction's application to make a broad class of compounds is identified, less data is possible for the uninterrupted usage of derivatives by biobased products originating from activated materials.

4.1. The amalgamation of cyclical carbonates by CO_2 and epoxides

CCs have been extensively utilized essentially (i) feedstocks toward polycarbonates, (ii) electrolytes into Li-ion dependent batteries, (iii) aprotic polar solutions, and (iv) fuel preservatives. While CCs have been integrated with the phosgene process, this approach has disadvantages, such as applying highly poisonous gas (phosgene), the production of

HCl (derivative) and wastewater comprising dichloromethane. While the phosgene process may create economical CCs at a wide range, the construction of environmentally favorable practices is needed, for example, the catalytic approach employing CO_2 and epoxides below moderate forms (**Fig. 13a**). **Fig. 13(b)** shows the metalloporphyrin networks of active reactants. A co-catalyst can be essential toward the nucleophilic ring-opening concerning the epoxide. Following the pioneering investigations by numerous metalloporphyrin compounds, for example, Co [207-209], or Sn [210] as a metal focus, have been established.

4.2. Carboxylation by CO_2

Besides the ring-opening effects of epoxides, including CO_2, considerable work has been done to promote catalytic transformations of CO_2 within other valuable aggregates. Tsuji *et al.* [211] produced the nickel-catalyzed carboxylation of aryl and alkenyl chlorides, including CO_2 and reaction tool at ambient condition (**Fig. 13 (c & d)**). This unique catalytic method is beneficial for aryl bromides, tosylates, including triflates. Mn0 degrades the Ni (II) compound toward Ni (0) kinds against proceeding. The following oxidative summation of aryl chloride provides a Ni (II) transitional. Ni (II) is later degraded with the Mn (0)/Et_4NI method to provide a Ni (I) standard. This electron donor Ni (I) sorts reacts by CO_2 to provide the carboxylatonickel transitional, which is demoted by Mn (0) to provide the similar Mn carboxylate, including the restoration of the Ni (0) synergist.

4.3. Reduction of CO_2

The conversion of CO_2 may generate CO, HCOOH, CH_3OH, CH_4, and so on. Newly, catalytic conversions of CO_2 have been investigated vigorously. Zhang and Gu obtained the N-heterocyclic carbene (NHC) conversion of CO_2 to CO utilizing aromatic aldehydes as reductants (**Fig. 13(e)**) [212]. It has presumed that carbonate and/or anhydride could be recovered by the reaction among cinnamaldehyde and imidazolium-carboxylate (NHC-CO_2), and then indeed, CO_2 acted being an oxidant. An active rotation path is given in **figure 13(f)**. (i) NHC responds by CO_2 for producing NHC-CO_2. (ii) The carboxylate strikes the formyl assembly, creating a potential transitional. (iii) Deprotonation effects within the NHC-CO network and a carboxylate salt through the C-O chain breaking. (iv) The NHC-CO compound discharges CO by the restoration of the NHC.

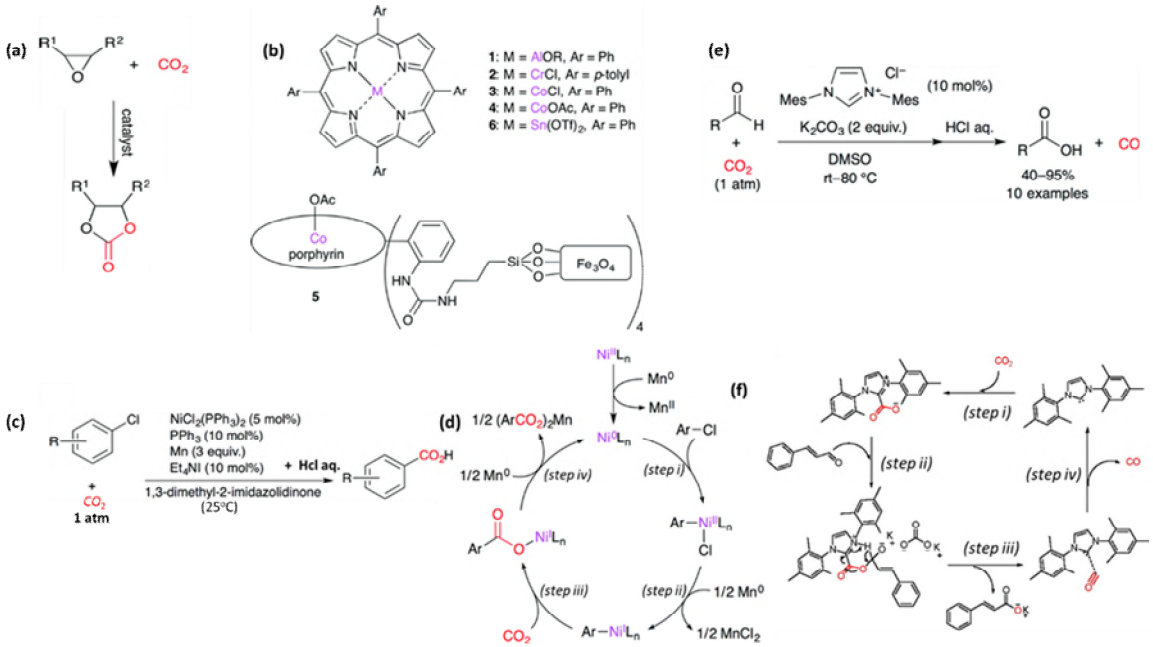


Fig. 13. (a) The combination of CCs by epoxides and CO_2. (b) Metalloporphyrin catalysts 1-6. Reprinted with permission from Ref. [204]. (c) Nickel-catalyzed carboxylation and (d) reasonable reaction pathways. Reprinted with permission from Ref. [211]. (e) The NHC-catalyzed and (f) reaction mechanism reduction of CO_2. Reprinted with permission from Ref. [212].

These cases provide a sight of the various opportunities possible to combine the consumption of CO_2 in biofactories, including the option that depends upon the particular business objectives to the biofactory.

5. Challenges and future prospects

Though several efforts have been made, MEC has not reached practical purpose, essentially examining the lab range. Furthermore, few other different technologies of this hybrid method (e.g., phosphate extraction based-high scale-initiated residue method) are also not implemented in the real world. Therefore, comparing up this combination way would be necessary. It needs to enhance this hybrid system's capacity and processing capability to a full-scale level and allowing proper energy restoration. Consequently, the most critical hurdle towards an experimental condition is how to optimize the practice size and concurrently support the fulfilment of every individual. MECs that can perform

essential roles within this hybrid method encounter some particular restrictions in full-scale utilization:

1. A long-distance within electrodes and pH inclination could drive to high intrinsic resistances during a large-range reactor.
2. High initial prices of charge electrodes and membrane substances also restrict its use.
3. There is still a complete understanding of microbiology into MECs, including fermentative bacteria, exoelectrogens and biocathode microorganisms.

With additional scheming MEC reactors, producing new substances, profoundly generous and appropriating command above microbiology is required to discuss these difficulties.

Since the previous decade, the investigation and advancement within ecological electrochemistry, the functionality for microbial electrochemical skills has grown intensely by adapted and enhanced production. Also, BES confers the ability to retrieve additional essential outcomes (H_2, power, etc.), for example, heavy metals, nutrients, manufactured substances, and volatile fuels. As explained in this review article, BES offers attractive possibilities for resource improvement; however, few biotechnological issues and commercial difficulties are still resolved. It may be executed on a wide range and acknowledged as an appealing option for the currently used water processing approaches.

The undesirable energy scale of existing used water processing operations may be modified if BES is employed to improve the energy by organic carbon, including phototrophic techniques, are executed toward nutrients and additional derivatives recovery [213]. Depending on the LCA research [214,215], MFC's performance must be developed with higher energy build as a commercially practical and competing solution similar to presenting anaerobic processing techniques. This mainly needs consideration in producing the cost-effective and active electrode materials to stimulate the O_2 conversion reaction at the cathode toward overcoming the cathodic overpotential to sustain advanced current densities.

After including the current scenario into biorefineries and possibly current patterns (e.g., olefin and standard/functional compound composition), the opportunities to combine CO_2 utilization in the bioeconomy were introduced to mark the options, also by evidence concerning the cost-effectiveness of a solar energy alliance. Lastly, the possibilities for applying CO_2 in biofactories plus the openings for technical cooperation were discussed. There is such a growing prospect for biobased generation, by innovative possibilities allowed through the combined utilization of CO_2 and renewable energy to drive sustainable, including economical carbon bioeconomy. Some machinery must be extended to facilitate the prospect and authoritative guidance, and purposes should understand the opportunities given. However, this is a clear way to support replacing fossil fuels to generate a low-carbon community.

6. Conclusion

BESs have been extensively studied towards electrical energy regeneration, bioremediation, the conventional compound composition, including newly, to valuable resource improvement. However, the recognition of the multi-disciplinary features associated with MES techniques yet on its start. Sustainability problems of biorefineries employing first-generation raw material observed the point of synergy among other regularities (for example, food and water composition). This review focused on BES analysis for energy efficiency and valuable product recoveries such as hydrogen evaluation, acetate, recovery of heavy metals, and nutrient recovery. Further, wastewater processing method, novel electrodes materials used in BES, BESs-based desalination and wastewater treatment, recent BES architecture and designs, genetic engineering for enhanced productivity, production of valuable materials have been discussed. Additionally, we have focused on surfactant and hydrogen peroxide, remediation of soil contamination and photosynthetic & microfluidic BES systems. Some other factors to mitigate the CO_2 towards the value-added products also discussed the advantages of H_2 compared to the other derivates.

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