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Tricks and Tracks in Resource Recovery from Wastewater Using Bio-electrochemical Systems (BES): A Systematic Review on Recent Advancements and Future Directions

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Abstract

Rapid industrialization and ameliorated lifestyle have vividly contributed to the release of huge quantity of wastewater into the environment. On the other hand, wastewater is enriched with resources like nutrients, metals, and chemicals that possess greater economic value. As a result, resource recovery from wastewater promoted 'wastewater to wealth' notion, thereby fostering the circular economy approach. In the recent years, bio-electrochemical systems (BES) emerged as versatile technology for simultaneous wastewater treatment and resource recovery. While the technology offers numerous advantages, its widespread commercial

application has been hindered by challenges in scaling up, economical aspects, operational aspects, etc. Over the past few years, substantial efforts have been made to enhance the efficiency of electrode materials, choice of biocatalysts and design improvisations of BES. These improvements have significantly increased the performance efficiency of BES. Nevertheless, further enhancements are still necessary for BES to become economically viable. This review provides a comprehensive over view of recent developments in BES, with a particular focus on their resource recovery applications. The article covers fundamental concepts, various BES types, and the mechanisms underlying electron transfer, with a specific focus on their role in resource recovery from wastewater. Furthermore, the article delves into the challenges of scaling up BES for practical applications and provides in-depth insights into real-world applications of BES technology. The future potential of integrating phototrophic options into BES is also discussed to further enhance resource recovery and the production of value-added products.

Keywords: Bio-electrochemical systems, Circular economy, Resource recovery, Wastewater Valorization.

1. Introduction

Globally, accelerated industrialization, urbanization,and improved living standard have significantly contributed to the rising global demand for water. Consequently, the extensive utilization of water results in the generation of a substantial volume of wastewater, with a significant portion being discharged into the environment untreated. This poses a severe environmental threat [1,2]. Hence, it is imperative to employ an effective and efficient technology for wastewater treatment to protect the environment. This aligns with sustainable development goals and the promotion of circular economy and sustainability practices. Instead of viewing wastewater as a source of pollution, it should be recognized as a valuable resource. Wastewater contains valuable nutrients, energy, and potential value-added products. Therefore, effective wastewater treatment is essential for environmental protection, while resource recovery from wastewater further contributes to conservation, ultimately fostering circular and sustainable development. A shift in approach to wastewater management, emphasizing resource recovery, is crucial [3,4].

Several conventional wastewater treatment options are available, but greater sludge generation,

high energy consumption, and operational cost are the primary bottlenecks that limit their widespread application [5]. Therefore, addressing these concerns, and achieving a reduced environmental footprint and recovering valuable resources recovery become imperative. In this context, the utilization of sustainable technology and resource recovery from wastewater holds significant importance in achieving environmental protection. Bioelectrochemical systems (BES) are sustainable, unique, widely adopted, and promising systems. They demonstrate the capacity not only to effectively treat wastewater but also to offer promising opportunities for the valorization and recovery of resources, including energy, nutrients, and value-added products such as H_2 and CH_4, from wastewater [6].

BES systems are capable to transform the chemical energy stored in the wastewater to value added products by integrating microorganisms or biocatalysts with electrochemical processes achieving superior redox metabolism [7,8]. Generation of value added products from negative value wastewater using BES is a sustainable approach that simultaneously addresses wastewater management and resource recovery [9,10].

The BES process integrates various fields of study such as microbiology, bioelectrochemistry, environmental science, and material science. Microorganisms are typically employed in BES systems to catalyze either oxidation, reduction, or both types of reactions. As a result, the oxidation process happens at the anode while the reduction process takes place at the cathode, creating an electric potential that drives the electron flow within the system [11,12]. Various types of BES configurations have been reconnoitered; among them, Microbial fuel cell (MFC) is most employed to recover resources from wastewater. Similarly, other configurations include microbial electrolysis cell (MEC), microbial recovery cell (MRC), microbial desalination cell (MDC), microbial solar cell (MSC) and microbial electrosynthesis (MES). MFC is most widely used to recover electricity from wastewater, whereas in MEC, an external voltage is applied to augment the cathode potential thereby encourage generation of value-added products.

Likewise, MDC is used for water desalination and generation of electricity from plants and sediments. MSC and MFC share many similarities, but the former incorporates photosynthetic microorganisms in conjunction with electrochemically active bacteria to generate renewable electricity and other by-products like methane (CH_4) and hydrogen (H_2). MES is one of BES, in which organic molecules and CO_2 are transformed to value added products at cathode [13,14]. In this direction, the present review contributes to the state-of-the-art overview of BES in several key aspects such as (i) types of BES systems, (ii) mechanisms involved in electron

transfer for facilitating redox reactions, thereby enabling resource recovery from wastewater, (iii) Factors influencing the performance of BES. Additionally, this article highlights recent advancements in BES, particularly in terms of design and the selection of cost-effective materials for electrodes and catalysts, aimed at resource recovery. Furthermore, it addresses the challenges related to electrochemical, operational, and economic limitations when scaling up BES systems, as well as explores the practical applications of BES.

2. Types of Bio-electrochemical systems (BES)

BES is categorized into various subtypes, including electrohydrogenesis systems, electrogenesis systems, microbial electrosynthesis systems, and microbial desalination systems, based on the intended application, end-use, and system configuration. Overview of various categories of BES systems including type and description about each BES is explained in detail in the subsequent sections.

2.1 Microbial fuel cell (MFC)

MFCs harness electricity generation by employing electrochemically active bacteria to degrade the organic matter present in the wastewater [11]. The electrochemically active bacteria are referred to as exoelectrogens [15]. MFCs generally contain two parts, namely anode and cathode, and these two parts are separated by cation-exchange membrane (CEM) (Fig. 1). Organic substances in wastewater undergo oxidation by exoelectrogens, which develop as biofilm on the anode surface. The quantity of electricity generated by MFC depends on the capacity of exoelectrogens existing on anode, which eases the transfer of electrons generated during the oxidation of organic matter in the wastewater to anode. Various exoeletrogens include *Geobacter* and *Shewanella* shown ability as an electron transferring microbes. However, mixed cultures are more effective in generating stable and greater currents when compared with using pure cultures alone in MFC [16]. Additionally, during the degradation of compounds along with electrons, protons are also produced into the anolyte, while the organic compounds are transformed into CO_2. Additionally, the electrons produced in the anodic chamber are transferred to the cathodic chamber via an external circuit that includes a resistor, while protons move to the cathode side through a CEM to maintain electrical neutrality. The anodic reaction considering glucose as substrate and cathodic reaction in MFC is provided below.

Anode reaction: $$C_6H_{12}O_6 + 6H_2O \xrightarrow{exoelectrogens} CO_2 \uparrow + 24\,H^+ + 24\,e^- \quad (1)$$

Cathode reaction: $4\,H^+ + O_2 + 4\,e^- \rightarrow 2\,H_2O$ (2)

"Insert Fig. 1 here"

Several researchers employed MFC technology for simultaneous wastewater treatment and as well as to produce electricity. The major benefits of using MFC technology for wastewater treatment are (i) eco-friendly and sustainable technology (ii) direct conversion of chemical energy to electricity (iii) less quantity of sludge production after the treatment (iv) minimum energy requirement.

The electricity generation using MFC method depends on nature of substrate, electrode material, anode potential and chemistry of electrolyte plays an imperative role in regulating the microbial activity and electron transfer mechanisms [17]. Greater electrolyte conductivity aids for the superior performance of BES systems, but the conductivity should not exceed the tolerance limit of bacteria [18].

2.2 Microbial electrolysis cells (MEC)

MEC is one of the BES employed with an objective to generate H_2 gas (Fig. 2). MEC is similar to MFC uses microorganisms to transform the chemical energy exist in organic compounds of wastewater to electrical energy for concurrent treatment and resource recovery. Nevertheless, the divergence between MEC and MFC lies in the cathodic reactions and an external power is supplied to the electric circuit of MEC, which further drives the movement of electrons from anode to cathode and facilitates H_2 production at cathode (Equations 5 and 6). Furthermore, anaerobic conditions are maintained in the cathode chamber of MEC in contrary to MFC to ease the H_2 gas production. The anodic reactions of

MEC and MFC are same, while the cathodic reactions of MEC and MFC are different.

Anodic reactions: considering acetate as substrate

$CH_3COO^- + 4\,H_2O \rightarrow 2HCO_3^- + 9H^+ + 8e^-$ (3)

Or

$CH_3COO^- + H_2O \rightarrow 2CO_2 + 7H^+ + 8e^-$ (4)

Cathodic reactions:

$8H^+ + 8e^- \rightarrow 4\,H_2$ (5)

Or

$8\,H_2O + 8e^- \rightarrow 4\,H_2 + 8OH^-$ (6)

"Insert Fig. 2 here"

Various studies reported H_2 gas production using MEC are listed in Table 1. The electricity generated using MEC is higher than MFC, which is owing to supplementary power applied to overcome the barriers.

"Insert Table 1 here"

2.3 Microbial desalination cell (MDC)

MDC is a modified version of MFC. MDC uses the potential difference created between the anode and cathode (similar to MFC) to carryout desalination. MDC possess three compartments include anode, desalination and cathode chambers. Desalination chamber in the MDC is isolated from anode and cathode chambers using anion exchange membrane (AEM) towards anode and CEM towards cathode, respectively (Fig. 3). In the anode chamber of BES, microorganisms break down the organic compounds in wastewater and release both electrons and protons. These electrons are then transported to the cathode chamber through an external circuit, generating a potential difference between the anode and cathode. As a result, anions such as SO_4^{2-} and Cl^- are driven towards the anode in the desalination chamber through an AEM, while cations such as Na^+ and K^+ migrate towards the cathode through a CEM. Therefore, desalination occurs in the middle compartment. Cao et al. [27] illustrated the water desalination using MDC. The reaction occurs in the anode and cathode compartments of MDC are identical to MFC (Equations 1 and 2). Nonetheless, numerous reactions occur in the desalination compartment, where the permeability of membranes plays a vital role in allowing the ions that are possessing different charge as that of membrane, while the membrane inhibit the passage of ions that consists of same charge as that of it.

Insert Fig.3 here

Previous studies illustrates that desalination performance of 90% could achieved using MDC along with high energy production. On the other side, MDC consists of several disadvantages as well, which include greater salinity in anode and cathode chambers, which not only jeopardize the survival of anodic/cathodic bacteria but also inhibit the utilization of treated

water for further applications.

2.4 Microbial electrosynthesis (MES)

MES is a new-fangled type of BES and the process in MES is exactly opposite to that of MFC (Fig. 4). MES is an electrochemical process, utilizing biocatalytic activity of the microbes to harvest the electrons from organic substances present in wastewater to transform CO_2 and H_2O to economic value products. Therefore, in MES, by providing or withdrawing electrons from microbes triggers biochemical reactions (e.g., transform CO_2 to acetic acid). Hence, MES uses the power produced from anodic oxidation to generate value added products (CH_4, acetate etc.) in cathode [28]. Specifically, sludge is inoculated into the cathode chamber to promote the biofilm growth on cathode surface thereby encourage degradation of organic compounds present in wastewater at cathode. On the other side, oxygen is generated at the anode through catalysis of abiotic substances and biotic oxidization of pollutants. Majorly, MES system is used to produce value added products like bio alcohols, bio plastics, H_2, acetate, butyrate and CH_4 by utilizing cathodic biocatalysts to reduce terminal electron acceptor [29]. MES technique mainly depends on catalyzing capacity of biocatalyst and type of terminal electron acceptor involved in the process. The reactions occur at cathode and anode for acetate production using MES is provided below. However, reactions in MES depend on required value-added product need to be produced.

Anodic reaction: $4H_2O \rightarrow 2O_2 + 8H^+ + 8e^-$ (7)

Cathodic reaction: for acetate is given below

$2CO_2 + 8H^+ + 8e^- + H_2O \rightarrow CH_3COOH + 2O_2$ (8)

"Insert Fig.4 here"

2.5 Microbial solar cells (MSC)

MSC works similar to the MFC, in which photoautotrophic microbes are employed to capture solar energy and this energy, will be utilized by electrochemically active bacteria for in situ generation of value-added products like H_2, methanol and CH_4 and electricity (Fig. 5). In MSC, primarily organic matter would be synthesized using photosynthesis under sunlight, which is further fed into anode compartment where it is oxidized by electrochemically active bacteria, thereby electrons are produced. Hence, the released electrons are transferred to cathode part through external circuit and further promote the reduction of oxygen and led to the formation of water. Wang et al. [30] reported the treatment of algal blooms in lakes

using MSC. The algal biomass provided by *Chlorella vulgaris* and *Microcystis aeruginosa* is utilized as substrate for concomitant wastewater treatment and electricity generation. As mentioned above, algal biomass produced in photo bioreactor after the anaerobic treatment can be used as a substrate in MFC [31]. Strik et al. [32] reported that power density of 14mW/m^2 could be achieved by using MSC with photobireactor consists of *Chlorella*. Improvement of efficiency of MSC is possible only through photobioreactor performance optimization; enhance chemical energy transfer from algae to anode and greater electrode surface area [33].

Insert Fig.5 here

2.6 Microbial recovery cell (MRC)

MRC is an advanced version of MDC, which is extensively employed to recover nutrients from the wastewater. An additional chamber is introduced in between anode and cathode chambers for concentrating the nutrients. This arrangement proves to be highly beneficial for nutrient recovery, thereby facilitating the generation of fertilizers. Sometimes separation of concentrated nutrients from the MRC is complicated. In such cases, utilization of biocompatible materials within MRC is favorable, which allows recycling of the recovered nutrients, thus it can be used as soil conditioner [13]. Schematic representation of MRC has been provided in Fig. 6.

"Insert Fig.6 here"

3. Electron transfer mechanisms involved in BES

3.1 Extracellular electron transfer

3.1.1 Electron transfer in microbial electrochemical system

BES particularly in MFCs and MECs, microbes itself act as a catalysts. In MFCs, during the degradation of organic substances, electrons are released. As noted by Jayashree et al. [6], in BES, the electrons generated are collected by the anode and transferred to the cathode via an external circuit, thus generating electricity. Conversely, in MECs, Yin et al. [34] have shown that electrons are released at the cathode and subsequently captured by microbes. An imperative prerequisite for occurrence of electrochemical reactions is smooth transfer of

electrons across the microbial cell membrane. Reactions occur on the electrode surface of various electrode materials exhibit different electrochemical behavior, thereby different mechanisms prevail for transfer of electrons between microbes and electrodes.

The occurrence of electron transfer in BES is mainly attributed due to 3 approaches. The approaches are (i) direct electron transfer with the aid of proteins on the surface of microbes (ii) electron transfer through mediators or electron shuttles (iii) electron transfer through e-pili. The three electron transfer mechanisms are showed in Fig. 7. Direct electron transfer takes place through outer membrane cytochrome of the microbe. Electron transfer mainly occurs through endogenous mediators or exogenous mediators. Likewise, appendages include microbial nanowires and e-pili are also vital for extracellular electron transfer by microbes [35]. As mentioned above, microbial nanowires and e-pili serve in extracellular electron transfer but slightly differ in terms of composition, structure, and origin [36,37]. Microbial nanowires are protein based conductive filaments produced by certain type of bacteria. The major proteins involved in the microbial nanowires are multiheme cytochromes. While e-pili are a specific type of pili found in certain type of bacteria. Furthermore, e-pili is composed of pilin proteins, which are electrically conductive in nature. Usually, microbial nanowires are straight and long filaments continuing from cell or form networks of interconnected filaments. Furthermore, some microbial nanowires also consist of branching structures or be associated with outer membrane vesicles. Whereas e-pili are thin, hair-like appendages extending from the bacterial cell surface. They form a network of conductive nanofibers, which interconnects with the neighbouring cells. The overall structure of e-pili is typically straight and can be comprised of multiple pilin subunits. Microbial nanowires are apparently yielded by specific bacteria as a means of extracellular electron transfer. However, e-pili are a specific type of pili found in selective electrogenic bacteria. These bacteria have evolved the ability to transfer electrons outside the cell using e-pili as conduits.

"Insert Fig.7 here"

Each electrogenic microbe group has its own electron conductive mechanism. For example, *Shewanella* microbe channels the direct transport of electrons to electrodes through extracellular mechanism using outer membrane cytochrome [38]. Similarly, *Geobacter*, another electrochemically active strain capable of generating e-pili with cell growth and embroil extracellular electron transfer between cells and electrodes [39]. Further, these

species require outer membrane cytochrome for electron capture. *G. sulfurreducens* microbes are not possessing electron transfer proteins like cytochrome, however able to transfer electrons proportionately because of amino acid sequence and structure of pilin protein, PilA [40]. Likewise, the microbial nanowires generated by *S. oneidensis* MR-1 are protein assemblages consists of both pilin and cytochrome protein [41].

As mentioned above, outer membrane cytochrome, e-pili and other appendages are vital constituents for electrochemically active microbe. Furthermore, growth of biofilm augments the extracellular electron transfer [42]. Existence of biofilm guarantees greater catalytic rate, power generation and long-distance electron transfer. Presently, researchers employed conductive porous materials to facilitate the growth of biofilm on the electrode surface, thus provide favorable environment for greater electricity generation [43]. Dumas et al. [44] illustrated that carbon felt possess greater porosity characteristics compared to stainless steel, but the conductivity of carbon felt is lower compared to stainless steel and results in lower electricity production.

On the other side, electrochemically inactive bacteria are lack of extracellular electron transfer mechanism. But they react with electrodes with addition of mediators. Usually, *Clostridium, Actinobacillus succinogenes* and *Escherichia coli* attain electron transfer in the presence of mediators. However, electrochemically inactive bacteria also capture electrons from electrode through intracellular metabolism [45].

3.1.2 Interspecies electron transfer

A startup period is essential to generate electricity through BES systems. During this period microbes particularly electrochemically active species are absorbed onto the electrode surface and form biofilm. Additionally, if the electrons are directly transferred to bacterium, they themselves acts as an electron donors rather than anode; thereby time required to generate value added products would be reduce considerably. Zheng et al. [46] illustrated that *Geobacter* and *Methanosaeta* together promoted CH_4 generation owing interspecies electron transfer mechanism. Further, interspecies electron transfer also strengthens the synergism between various microbes to generate value added products.

Conductive materials are commonly utilized to facilitate interspecies electron transfer and enhance co-culture fermentation within BES systems. Additionally, electron mediators may be employed to promote interspecies electron transfer and expand the synergy to different bacteria.

3.2 Intracellular electron transfer

The intracellular electron transfer (ETC) consists of carriers such as coenzyme Q,

oxidoreductases and cytochrome for carrying electrons and protons. Outer membrane cytochrome on the electrochemically active bacteria facilitates the electron transfer and stimulates the intracellular metabolism. *Geobacter* and *Shewanella* possess ability to transfer electrons through intracellular mechanism; thereby these species were commonly employed in MFCs. However, certain microbes have capacity to amend the electron transfer route depending upon the potential difference available within the system [47]. *Shewanella* microbe belongs to one such group of microbes follow bidirectional electron transfer with one intracellular electron transfer [48].

Electrochemically inactive bacteria require electron shuttles or mediators to interact with electrodes. Chemical based electron shuttles are available, which nurture higher diffusion rate and ensure bidirectional electron transfer between cell membrane and electrode [49]. However, the electron transfer efficiency through intracellular route by electrochemically inactive bacteria is ineffective when compared with electrochemically active species.

4. Factors influencing BES

The overall performance of BES depends on functionality of microorganisms and functional microorganisms present in the reactor. As a result, efficiency of microorganisms are impacted by environmental factors include pH, temperature, conductivity, moisture level, availability of amount of nutrients and oxygen and concentration of contaminants [50,51]. Based on the impact of above-mentioned parameters, performance enhancement measures could be employed to augment the overall efficiency of BES. Performance enhancement measures include adjustment of temperature, moisture and pH, external supply of nutrients (glucose, inorganic ions etc.), aeration at the cathode to increase oxygen level, promote greater electron transfer activity (doping of electrode with carbon fibre, activated carbon etc.). The above-mentioned measures foster the contaminant removal and as well as resource recovery using BES.

4.1 pH

pH particularly, the catholyte pH is one of the most key parameter influencing the performance of BES. The organic matter present in the anode region undergoes oxidation and generates electrons and protons. Later, generated electrons in the anode region are migrated to cathode region through an external circuit. Similarly, protons are transferred to cathode region with the help of salt bridge or proton exchange membrane (PEM) existed in the system. Further, protons and electrons moved to the cathode region would actively react

with oxygen and forms water [50]. However, salt bridge and PEM possess high internal resistance, which impedes the proton transport through it; thus this condition led to lower proton transport rate when compared to anodic output rate, consequently create a pH gradient among anode and cathode [52]. For instance, proton accretion takes place adjacent to anode, which advances the formation of acid – alkaline zone (i.e., pH variation) from anode to cathode in BES. As a result, activity and growth of microorganisms are greatly impacted, which ultimately suppress the performance of BES. Therefore, to overcome this adverse impact, appropriate pH maintenance is pivotal for microorganism survival [53]. For example, pH variation causes the disparity in charge carried by nucleic acids and proteins, thereby influencing the capability of microbial cells to absorb nutrients. Hence, identification of suitable pH for both degrading microorganisms and electrogenic microorganisms is imperative in BES.

Jadhav and Ghangrekar [54] illustrated the influence of pH on COD removal and coulombic efficiency using BES. The pH in the anode chamber was maintained at 5.5, 6.0, 6.5, 7.0 and 7.5 using phosphate buffer and the pH of the catholyte was kept ta 7.0. During the studies, greater COD removal and coulombic efficiency was attained at pH 6.5. These results indicate that anolyte pH is a significant factor and controls the production of electrons and protons in BES, which significantly impact the metabolic activity of the substrate specific microorganisms. Correspondingly, at higher pH (pH > 9) conditions, generation of protons is minimized in BES and is not favorable for generation and transmission of electrons [55]. According to Zhang et al. [50], pH has a significant impact on the formation of CH_4, as the methanogenesis process is highly sensitive to pH, impacting the activity and composition of microbes involved in CH_4 production. Low pH (i.e., 5.5) values and high pH (i.e., >8) values have adverse effects on methanogenic activity leading to reduced CH_4 generation. In contrast, a near neutral pH (6.2 to 7.5) is conducive to the activity of methanogens. Hence high production of CH_4 is observed at neutral pH.

pH also affects the speciation of heavy metal ions in the system; acidification of the anode chamber (i.e., lower pH) promotes the desorption of heavy metals, while alkalization (i.e., higher pH) favors the precipitation of cations and reduces electrical conductivity, thereby increasing internal resistance. In addition, the pH difference between the cathode and anode also influences the internal resistance, with a greater pH difference between the two chambers promoting proton transport through the PEM and reducing internal resistance [54].

The optimum pH conditions for BES systems depend on the purpose and the microorganisms employed, which can vary under different conditions. Alkaline anolyte pH (i.e., 9) is

advantageous for hydrogenogens for H_2 production in BES [55]. Since, at low pH, permeation of H^+ reduces and acidifies the anolyte. Thus, acidification of anolyte impedes microbial activity. Similarly, presence of high concentration of OH^- ions at pH > 10, neutralizes the H^+ ions in anolyte. Therefore, impacts the generation of H_2. Likewise, even for electricity production also neutral pH is recommended, since activity of electrogenic bacteria is enhanced [56]. As highlighted above, low pH in anolyte acidifies and arrests the microbial activity; high pH neutralizes H^+ ions and contributes to low electricity production using BES.

4.2 Temperature

Temperature is a crucial factor that affects the growth, activity, and distribution of microorganisms in BES. The optimal temperature range for enzyme activity, growth, and biofilm formation is typically between 35°C and 40°C, as this can promote substrate degradation rate and accommodate a diverse range of microorganisms [57]. Adelaja et al. [58] demonstrated the impact of temperature using MFC technology for degrading petroleum hydrocarbons and observed that 40°C is the optimum temperature for degradation of organics and as well for generating maximum power. Further it also witnessed that power generation is two times more at 40°C when compared with 30°C. Similarly, degradation rate at 50°C is reduced to one fourth of degradation rate at 40°C.

The impact of temperature on BES comprises various kinematic and thermodynamic principles owing to several complex reactions. Furthermore, temperature is not directly related with either electricity production or organic substance degradation by BES. For instance, greater temperatures can enhance thermodynamic activity of microorganisms, microbial reaction kinetics, and mass transfer efficiency. Similarly, higher temperatures also contribute for the growth of non- electrogenic microorganisms includes methanogens and fermentation bacteria. Hence, these methanogens and fermentation bacteria compete with electrogenic microorganisms and ultimately responsible for lower current density production in BES, but increasing COD removal efficiency [59]. On the other hand, lower temperatures hinder the growth of methanogens and enhance the H_2 production [58]. Lu et al. [60] investigated the impact of temperature variation on MEC efficiency and as well as on number of methanogenic microorganisms. As the temperature reduced from 30°C to 4 – 9°C, the number of methanogens also reduced from 91% to 68%, respectively. Depending upon the sensitivity of microorganisms to temperature, identifying suitable range could significantly contribute to attain satisfactory BES performance.

4.3 Substrate

Concentration and type of substrate plays a vital role in shaping the structure of

microorganisms and population in BES [61]. During the treatment of wastewater using BES, media consists of wide variety of complex substrates, in which degrading and electrogenic microbes are also integral part of the system. To explore the influence of substrate on microbial structure, researchers employed several substrates as carbon sources. In MFC, glucose, lactate and acetate were used as substrates. During the usage of glucose as a substrate, the growth of *Geobacter sulfurreducens* and *Bacteroidetes* were observed on anode surfaces. Additionally, *Firmicutes* species were also witnessed in MFC operated with glucose substrate. *Firmicutes* species plays an imperative role in breakdown of complex organic substances to simpler substances and oxygen scavenging [62]. Amelioration of *Geobacter* species were commonly observed in BES employed with acetate substrate [63].

Determining the microbial response to substrate changes is crucial to understand the impact of substrate on microorganisms in BES. BES employing simpler compounds like glucose as substrates foster the growth of exoelectrogens. Glucose is readily and effectively utilized by microbes, thus promoting the growth and microbial activity, which, in turn, contributes to the efficient nutrient recovery. On the other hand, when complex substrates are employed in BES, firstly microbes need to transform the complex substrates to simpler forms. This transformation process requires, energy and O_2, which ultimately affects substrate utilization and nutrient recovery. Therefore, BES enriched with simpler substrates like glucose exhibits better performance in terms of recovery of power, H_2, and other value-added products compared to BES systems utilizing complex substrates. However, non-electrogenic species also compete for this energy source, leading to lower coulombic efficiency. Similarly, substrate morphology and their bioavailability also influence the efficiency of BES. Dunaj et al. [64] investigated the performance of MFCs operated with agricultural soil and forest soil and attained approximately 17 times higher electricity production using agricultural soil. It has been demonstrated that agricultural soil has lower carbon content than forest soil; however, the quality of the available carbon is a key factor in achieving higher electricity production. Thus, the effectiveness of BES is directly related to the bioavailability of the substrate, which is inversely related to its complexity [65].

4.4 Reactor configurations

Reactor configurations include various components such as anode, cathode and PEM, which also influence the performance of BES either directly or indirectly. A conventional BES consists of anode chamber, cathode chamber separated by proton permeable material include PEM or salt bridge [39]. Microorganisms grow and reproduce in the anode chamber of MFCs by consuming organic matter and producing electrons. In order to ensure sufficient dissolved

oxygen as an electron acceptor, aeration is required in the cathode chamber or an external power supply is needed to reduce protons [66]. The practical applications of this configuration are limited due to the cost of PEM and the energy required for aeration. Moreover, introducing aeration in the cathode chamber can negatively affect the anaerobic environment in the anode chamber, thereby affecting the activity of microorganisms [67]. As a result of the limitations of the dual chamber system, there is a need for a single chamber system that does not rely on aeration. The single chamber system addresses this issue by directly supplying oxygen to the cathode, which prevents oxygen from diffusing into the anode. Additionally, the single chamber system has several advantages, including efficient use of space, cost-effectiveness, and significant potential for practical applications.

Functional microbes are attached to the anode as a primary component of BES. Therefore, the selection of anode material impacts both the quantity of microorganisms attached to it and the transfer of electrons from microbial cells to the electrode surface. Carbon-based materials have garnered significant attention among various materials due to their low cost and high electrical conductivity. Carbon cloth, graphite rods, carbon felt, and carbon paper are some of the frequently used carbon-based materials as anodes [68]. Each carbon-based material has its own electrochemical properties due to biocompatibility and specific surface area. For BES fed with glucose substrate, three types of anode materials are most commonly used include graphite foam, graphite rod and graphite felt. Among these graphite felt exhibited best performance, which is attributed due to low electrode internal resistance and greater surface area for growth of microbes [50]. Logan et al. [69] determined that graphite brushes with pore structure showed greater power generation when compared with carbon paper and possess potential for scale up of BES for practical applications. Low electron transfer is the major predominant factor controlling the performance of BES.

To enhance the electron transfer efficiency, modifications in the anode is imperative to augment the overall performance. Several ways are available for carrying the modifications in anode material. One such way is to introduce the positive charged functional groups on anode material thereby permitting more numbers of negatively charged bacterial cells to attach to it, thus amplifying the electron transfer efficiency. Cheng and Logan [70] noticed that carbon cloth anode modified with ammonia gas amplified the power density from 1.33 to 1.97 W/m^2. Similarly, Du et al. [71] noticed that anode modified with polydopamine attained greater COD removal and coulombic efficiency and is mainly ascribed to addition of amine groups. Recently researchers employed various nano materials for modifying anodes due to their excellent physical and chemical properties. Liang et al. [72] introduced powdered carbon

nano tubes in the anode region along with *G.subreducens* to form composite membrane. However, introduction of special materials and modifications inevitably contribute to attain greater BES efficiency by minimizing the cost.

4.5 Other factors

In addition to the above-mentioned parameters, electric field strengths, choice of cathode catalysts, electron mediators, and anaerobic conditions also plays a vital role in shaping microbial communities and reduction of organic substances through BES [73]. Electric fields with various strengths impact the migration of ions and exhibit stress on microorganisms. Similarly, each cathode catalyst has its own electro catalytic activity and redox potential, which impair harmful impact on microorganisms. External additions of mediators promote electron transfer from electrogenic bacteria to anode surface, but the toxicity of mediator influence the activity and function of microbes. Anaerobic conditions in BES have a significant impact on resource recovery. In such environments, where oxygen is absent or limited, microbial communities play a crucial role in the decomposition of organic matter, often leading to enhanced nutrient recovery and bioenergy generation. The absence of oxygen encourages the growth of anaerobic microorganisms, such as exoelectrogens, which can efficiently oxidize organic substrates. This anaerobic metabolism not only facilitates the recovery of valuable resources like H_2, CH_4, and other energy-rich compounds but also minimizes the release of greenhouse gases during the treatment of organic waste. Studies by Liu et al. [55] have highlighted the potential of anaerobic BES for resource recovery and their applications in sustainable wastewater treatment and bioenergy production. Overview of all the above-mentioned parameters influencing performance of BES is provided in Table 2.

"Insert Table 2 here"

5. Current application of BESs for treatment and resource recovery

BESs are widely deployed to recover various resources including energy, nutrients, metal, water, and other value-added products (H_2, CH_4, etc.,). The summary of application of BES for recovery of resources is provided in Fig. 8.

"Insert Fig.8 here"

5.1 Energy recovery

Organic substances present in the wastewater are utilized to engender electricity using BES, which minimizes the energy required to carry out the treatment. Furthermore, the power generated by BES does not require additional purification or polishing step in comparison with the energy produced during anaerobic digestion process. The electricity output from the BES is expressed as kWh/m^3 of wastewater treated or kWh/COD. Several parameters like inoculum, operational conditions and configuration of BES also influence the electricity generation. The presence of ammonium (NH_4^+) can negatively affect electricity generation by competing for electron donors/acceptors, which can ultimately lead to the inhibition of microbial function. In a study by Nam et al. [80], it was observed that an increase in NH_4^+ concentration from 500 to 4000 mg/L resulted in a reduction in power generation from 4.2 to 1.7 W/m^3 in MFC. Similarly, Kim et al. [81] also reported that the augment in the NH_4^+ concentration contributes for decreased power production. Furthermore, greater pH in the anolyte also minimizes the NH_4^+ concentration through hydrolyzation reaction (Equation 9)

$$NH_4^+ \leftrightarrow H^+ + NH_3(aq) \quad (9)$$

In addition, nitrogen related compounds impact the electrolyte pH by biological or chemical reactions. Nitrification releases H^+ ions in the cathode chamber and buffer the OH^- ions released through O_2 reduction, thereby pH elevation in the cathode reaction is impeded. Overall, the hydrolyzation reaction of NH_4^+/NH_3 acts as a proton shuttle between the anode and cathode compartments, which helps regulate the pH of the electrolyte. As mentioned above, nitrogenous compounds along with microbes compete for organic substances (i.e., electron donors) and O_2 (i.e., electron acceptor) [13]. Therefore, in this context carbon source is utilized by denitrifying microbes under greater NO_3^- concentration. As a result, the amount of organic substances available for the electrogens is minimized and ultimately contributes for the reduction of electricity. Additionally, this creates a competition between denitrifying microbes and cathode for O_2 during biological nitrification. Therefore, greater NH_4^+ concentration impedes the electricity generation [82]. Overview of various studies reported energy generation from wastewater is provided in Table 3.

"Insert Table 3 here"

5.2 Nutrient and metal recovery

Application of BES especially MFCs are not only limited to electricity production and

treatment but also employed to recover value added products like acetate, H_2 etc., at cathode [88]. In addition, MFCs are also employed to recover nutrients and metals from effluents that are rich in metals like wastewaters from mining and metallurgical processes and leachates. Thus, the recovered nutrients and metals could be used for various industrial applications and ultimately contribute to promote sustainable utilization of resources [11].

Recovery of metals through BES systems are classified into four different categories. In the first category, metals include Cu, Fe and Ag possesses greater redox potential compared to anode, thereby directly reduced on the cathode surface [89,90]. This is effective and favorable approach owing to no input energy requirement [91]. Whereas in second category, metals such as Cd, Pb and Ni consist of redox potentials, however these redox potentials are lower than anode potentials. Consequently, additional power supply is imperative to initiate the electron movement from anode to cathode. Remarkably, complete reduction of these metals can be achieved by supplying sufficient external power. However, the amount of power required for metal reduction through BES is significantly lower than traditional electrolysis, as BES provides some of the energy needed to reduce metal ions. The third category involves the use of specialized microorganisms on the biocathode to reduce targeted metals on the cathode [92]. In this approach, the cathode potential is adjusted in such a way that the metals present in catholyte could be adsorbed onto the biofilm and further reduced by microbial species during microbial respiration. Fourth category engrosses external power supply and biocathode to expedite metal reduction with lower potential and to promote the flow of electrons from anode to cathode to achieve metal adsorption on cathode surface. Furthermore, biocathode does not permit the desorption of metal after the removal of imposed potential. Ter Heijne et al. [93] revealed that acetate oxidation at anode using BES systems expedite the reduction of copper electrochemically at cathode. However, bipolar membrane was employed for both electricity production and copper reduction in the process. Further, it is also observed that reduced copper was coated on the electrode. Similarly, Zhang et al. [94] recovered chromium and vanadium using dual chambered MFC along with bioelectricity production. During the process, 970 mW/m^2 of power generation was accomplished along with V^{5+} and Cr^{6+}. Despite of this, double chambered BES configuration is most preferred for metal recovery owing to the fact that wastewater rich in organics and metals can be fed in anode and cathode compartment respectively. Additionally, nutrient recovery especially NH_4^+ recovery was also accomplished using MFCs. NH_4^+ recovery through BES occurs in four steps. In the first step, NH_4^+ transportation takes place from anode to cathode through CEM.

After that accretion of NH_4^+ in catholyte and high localised pH condition prevailed at the cathode is conducive for conversion of NH_4^+ to NH_3. In the final step volatile NH_3 is adsorbed by utilizing acid solutions and then transform it into valuable products. As mentioned above the transportation of NH_4^+ is mainly due to diffusion because of concentration gradients and power – driven movement. H_2SO_4 is the most commonly used acid to adsorb volatile NH_3, thus formation of ammonium sulphate takes place. Additionally, ammonium sulphate has a wide variety of applications in food, agricultural and fertilizer industry [95]. Kuntke et al. [96] illustrated the recovery of NH_4^+ from urine using MFC and attained NH_4^+ recovery of 3.29 g-N/d. m^2.

On the other side, phosphate (PO_4^{3-}) recovery is commonly accomplished through BES using chemical precipitation takes place at the cathode as a result of high pH owing to cathode reduction [95]. Particularly, in single chambered BES, formation of PO_4^{3-} related precipitates (in combination with NH_4^+) occur on the cathode surface. Cusick and Logan [97] employed single chambered BES to recover PO43- in the form of struvite and attained a yield of 0.3–0.9 g/m^2.h on cathode surface. During the process, raise of localized pH in catholyte is imperative and conducive for PO_4^{3-} recovery in BES. However, the major drawback of single chambered BES is both anode and cathode possess same electrolyte, as a result elevation of pH near cathode surface is challenging, which ultimately influence the recovery of PO_4^{3-}. Therefore, double chambered or multi chambered BES gained widespread attention. Ye et al. [98] employed dual chambered MFC to recover nutrients from domestic wastewater. At the end of treatment, approximately 80% of PO_4^{3-} and NH_4^+ were recovered as struvite.

5.3 Water recovery

Water recovery through BES could be accomplished by assimilating BES with membrane filtration techniques. Among the various membrane filtration techniques, forward osmosis (FO) membrane technique is most feasible to integrate with BES owing to low energy requirement and less membrane fouling [99]. In FO technique, osmatic pressure drives the water to transport from feed side to draw side. However, assimilation of FO with BES can be performed in two ways namely external and internal. In external way of integration, membrane is connected externally. Whereas, in internal integration, membrane itself acts as a separator for cathode and anode chambers. Qin et al. [100] demonstrated the external integration of FO with BES to treat leachate and achieve simultaneous recovery of NH_4^+ and water. As a result, 65% of NH_4^+ was recovered and 51% of water recovery was obtained. Li et al. [101] demonstrated the integration of ultrafiltration membrane technique with BES.

In this study, authors installed ultrafiltration membrane in the cathode compartment and achieved 90% COD removal and turbidity less than 2 NTU. Likewise, MDC with low internal resistance is most widely utilized to recover fresh water from saline water. The major advantage of using low internal resistance in MDC is that it nurtures the current density; thereby promote the ionic movement even though the voltage kept as constant [13].

5.4 Chemical recovery

5.4.1 Methane (CH_4)

Anaerobic digestion has been considered as a promising and in practice technique to generate CH_4 from organic substrates. However, considering sustainability aspect, reutilization of CO_2 liberated from different biological process could be assimilated to generate greater quantity of CH_4 by electrosynthesis assisted by microbes. Electrosynthesis assisted by microbes employed to produce CH_4 also termed as electromethanogenisis. The major advantages of electromethanogenis are low operating temperatures and greater CH_4 yield when compared to anaerobic digestion process [102]. Clauwaert and Verstraete [103] illustrated the CH_4 production through BES by single chambered configuration and attained 0.87 L /L. day of CH_4 production at a COD loading rate of 4.13 kg/m^3. Hence, BES especially MEC has been considered as a promising technology for CH_4 production and as well as for treatment of wastewater. Sasaki et al. [104] depicted the appropriateness of membrane less configured BES for CH_4 production and concluded that this approach is efficient for generating CH_4. Furthermore, multi electrode configurations of MECs also effective for H_2 production and with time the conversion of H_2 to CH_4 were attained effectively [105]. Villano et al. [106] employed mixed culture of methanogens as biocatalysts to generate CH_4 from CO_2. Lu et al. [107] illustrated the production of CH_4 using MEC. During the process H_2 released within MEC is utilized by hydrogenotrophic methanogens.

5.4.2 Acetate

Among different BES, MES uses to fix CO_2 present in various compounds including chemicals and fuels especially liquid in nature through reduction reactions. MES technology majorly employed to store the electrical energy in C – C bond of value added chemicals. At first, Nevin et al. [108] described the usage of acetogen *Sporomusa ovata* species to directly absorb the electrons released from graphite cathode to reduce CO_2 and produce acetate. However, the electron recovery by these microbial species is approximately 85% greater than that of electrons transfer at cathodes. Other microbial species such as *Sporomusa sphaeroides, Clostridium aceticum* and *Sporomusa silvacetica* has shown potential for conversion of CO_2 to

acetate. Marshall et al. [109] exemplified that to attain greater production of acetate by reducing CO_2, it is advisable to use mixed microbial cultures rather than employing pure cultures alone. Likewise, Jiang et al. [110] employed biotic cathode that consists of mixed microbial cultures that accepts electrons from anode chamber and generate H_2 abiotically by fixing CO_2 to acetate.

Despite all the above-mentioned circumstances, the conditions is the MES must be maintained in such a way that it promote the optimal metabolism of biocatalyst existed in biocathode. Additionally, cathodic or external potential need to be applied to overcome the potential barrier of biological reaction, thereby ultimately contributes for efficient reduction reaction in MES. The homo-acetogenic group of microorganisms is efficient in converting CO_2 to acetate, which is a critical intermediate compound in biochemical production. Additionally, several other factors, such as reactor design, electrode material, and mediators, also play a significant role in the overall performance of the process.

5.4.3 Hydrogen (H_2)

Wastewaters released from various sources include agricultural, municipal and industrial are rich in organic content, which is viable source and sustainable approach for recovery of fuel and chemicals [11]. Several techniques especially biological methods are used to recover energy from wastewaters. Methanogenic anaerobic digestion and acetogenic fermentation is commonly employed to recover resources like biogas and H_2 from wastewaters. However, lower yield and microbial metabolism are the major shortcomings of fermentation approach. BESs are potential alternative techniques to generate H_2 with low energy input in comparison with traditional techniques like electrolysis. In BES, particularly MEC is a promising approach to generate significant quantity of H_2 [111].

In recent years, H_2 is considered as a potential alternative to fossil fuels and widely utilized as fuel and chemical for various applications. Furthermore, for a particular value of COD the H_2 production is nearly 7 times greater than CH_4 production [112]. To generate H_2 from MEC, different organic material including waste and non-fermentable substances could be used as substrates. At anode, microbes particularly exoelectrogens oxidize the organic matter (e.g., acetate) and release electrons, protons and CO_2. Later, these electrons were transferred to the anode by electrochemical interaction between exoelectrogens and anode followed by conveyance to the cathode chamber through an external circuit. Subsequently, electrons combine with protons in the cathode chamber and produce H_2 gas. Protons released in the anode chamber are transported to the cathode chamber through CEM to maintain charge

neutrality. An applied voltage of 0.2V is essential for H_2 production, which is lower when compared to the voltage (i.e 1.6 V) required for traditional electrolysis. The reactions take place at anode and cathode chamber with acetate as a substrate has been given in Equations 3 and 5. Therefore, concomitantly both clean energy (i.e., H_2) production and wastewater treatment in MEC is an effective, economically viable and sustainable approach. Several researchers performed MEC studies to generate H_2 using MEC. H_2 formation reaction (Equation 5) occurs at slow rate on carbon-based cathode materials and requires overpotential. Hence, to minimize these potentials researchers employed Ni and stainless-steel based materials for H_2 generation in MEC. Jeremiasse et al. [113] Illustrated that enhancing the surface area of the electrode is an efficient strategy to produce greater quantity of H_2. Furthermore, it also noticed that among the metals, Pt and Ni possess high H_2 production.

5.4.4 Other chemicals

In the recent years, recovery of value-added products other than CH_4, acetate and H_2 using BES has been emphasized [11]. Valuable products include hydrogen peroxide (H_2O_2) and caustic soda is recovered by supplying extra potential in BES, which subsequently contributed to augmenting the overall treatment efficiency. Nancharaiah et al. [114] corroborated the recovery of H_2O_2 through valorization of grey and black water. Furthermore, fuels such as methanol and butyrate are also recovered using BES. Methanol production through BES is less energy intensive and sustainable when compared with methanol produced using electrosynthesis approach. Using BES especially MES, Bajracharya et al. [115] described the microbial reduction of CO_2 and during the process H_2 released at the cathode acts as a mediator for this reduction. Additionally, Li et al. [116] demonstrated the formic acid production from CO_2 through biochemical reactions followed by isobutanol production from it by engineered *Ralstonia eutropha*. The conversion of glycerol to 1,3−propanediol has been uccessfully achieved by leveraging the innovative BES technology [117]. MDC technique has been effectively employed to recover HCl and NaOH using bipolar membrane [118]. Venkatamohan et al. [119] demonstrated the synthesis of polyhydroxyalkanoates in the cathode chamber under abundant accessibility of nutrients and carbon.

6. Advancements in BES

In the early 20th century, researchers identified the ability of microorganisms to oxidize the organic substances present in wastewater. Hence, research is primarily focused on elimination of organic substances during wastewater treatment. Over time, there has been a significant shift

in research emphasis towards a more holistic approach, combining various treatment techniques with BES to achieve more effective wastewater treatment. With multidisciplinary advancements, the research focus has evolved towards resource recovery in the form of power, nutrients, metals, H_2, CH_4 and other value-added products. Recent progress in BES research has led to superior power generation through application of novel and modified electrode materials, novel catalysts and better understanding of pathways and mechanisms involved in oxidation of organic substances [3]. In the contemporary context, there is a strong emphasis on the recovery of resources and value-added products to enhance the overall efficiency of BES, aligning it with existing treatment techniques. The remarkable potential for resource and value-added product recovery in BES is facilitated by microbe-catalyzed redox reactions, making it a versatile technique that simultaneously promotes sustainable resource recovery and the valorization of wastewater. Furthermore, life cycle assessment and cradle- to grave analysis provide insight into environmental benefits obtained by deploying well designed BES technology through resource recovery [11]. This evolving research landscape underscores the growing importance of BES not only in wastewater treatment but also in the sustainable utilization of resources, contributing to a more environmentally friendly and efficient approach to water management.

7. BES as sensors

Recently BES is effectively employed for analyzing water quality. Furthermore, BESs based biosensors are developed for sensing toxic compounds and estimation of BOD in water. BESs are potential technologies for monitoring on-site and off- site water quality. Further, the sensors developed using BES methods are economical when compared to the sensors developed based on conventional methods, since inexpensive carbon-based materials are employed for development. Biosensors developed using BES; organic matter oxidation from influent is estimated based on growth of bacteria on anode and liberate electrons, which ultimately contributes for power generation in BES. The quantity of electrons released and power production is proportional to metabolic activity of biofilm [120]. Any hindrance in the metabolic activity of microbes is significantly inferred as variation in power quantity.

The presence of toxic compounds in the influent greatly impacts the activity of microbes particularly exoelectrogens, which can be measured through variation in power generation. Therefore, variation in power production is directly related to disruption of activity of biofilm, while other operating parameters include pH and temperature kept constant [11,121]. Furthermore, BESs are highly sensitive to different substances present in the influent. Hence,

these systems can be used as biosensors for detecting toxic compounds and BOD in the influent has been illustrated in the subsequent sections.

7.1 Sensors for toxic compounds

Application of BES particularly MFC are employed for sensing toxic compounds. Variation of electric current is majorly due to the presence of toxic compounds such as heavy metals (i.e., Hg and Pb) and organophosporous pesticides (i.e., Diazinon) in the influent. As mentioned above, the activity of microbes and substrate utilization rate are directly connected to power generation. Reduction in the power output under the exposure to toxin, when the remaining operating parameters maintained as constant is regarded as toxic inhibition. Furthermore, influence of toxic compounds on exoelectrogens has been observed through polarization curves. Greater concentration of contaminant results in lower power output for various values of potentials [122]. Overview of sensors based on BES for detecting toxic compounds has been provided in Table 4. Moreover, these sensors are effective for detecting the toxic compounds of concentration lower than 1 ppm. Recent developments occurred in BES based sensors results in economical water quality monitoring. Utilization of acid/base resistant microbes during manufacturing of sensors is most efficient for industrial wastewater applications [123].

Insert Table 4 here

7.2 Sensors for BOD

BOD is the most generally used parameter to indicate the organic matter contamination in water. Based on the concentration of organic matter present in the influent electric charge is developed in BES. Hence electric charge developed is in good correlation with the concentration of organic matter. Therefore, BES has been employed as BOD sensors [129,130]. Chang et al. [129] monitored the BOD of water by employing BES particularly MFC technology through electric current generated during the process. Furthermore, MFC as BOD sensor can be effectively utilized for span of 5 years with lower maintenance [129]. Overview of characteristics of MFCs employed as BOD sensor is summarized in Table 5. Further, for effective BOD detection, MFC employed with mixed cultures are advisable for long term stability and allow the microorganisms to acclimatize to the wide range of substrates.

“Insert Table 5 here”

8. Challenges for scaling up of bio-electrical systems

8.1 Limitations in real scale implementations

The primary objective for developing BES is to alleviate the intensive energy utilization during aerobic treatment and recovery of metals at low concentrations. Several researchers worked towards enhancing the practical suitability and long-term utilization of BES by conducting studies from laboratory scale and semi – pilot scale to pilot-scale [133]. Most of the research studies reported that a maximum power density of 10 to 25A/m^2 was attainable under controlled operating parameters using BES particularly MFC, which corroborating the insupportable quantity of power for operating small electrical devices. As a result, the greatest bottlenecks for BES technique are to illustrate its techno-economic feasibility for real field applications and global utility. Furthermore, greater capital cost (i.e., CAPEX) and operating cost (i.e., OPEX) is also limiting factor for deploying BES for practical applications.

The overall performance of BES approach depends on governing parameters include pH, substrate concentration and composition, electrode material, surface area of electrode, reactor configuration and loading rate [134]. Understanding the causes and impacts of these factors is imperative to accomplish a strategy that contributes to augment the overall performance of BES. Furthermore, optimal operating conditions resulted from laboratory studies cannot be translated linearly during scale up, which greatly impact the economics. Therefore, a brief note on importance of each factor associated with scale up and remedial measures has been demonstrated in the subsequent sections.

8.2 Limitations in electrochemical aspects

8.2.1 Electrodes

Electrodes play a crucial role in bioelectrochemical reactions by providing active sites for exoelectrogens during biofilm formation and acting as an interface for electron transfer between microorganisms and the electrode surface. In the scientific literature, numerous carbon and metal-based materials with varying compositions and sizes have been utilized as electrodes. Even through metal-based electrodes results in generation of great quantity of power, their application is limited owing to the costs associated with these materials during the scale up of BES. Therefore, utilization of such type of materials as electrodes needs to be omitted during scale up to cut down the costs. Subsequently, carbon and metal-based anode electrode materials are susceptible to corrosion [135]. Similarly, Al, Cu and brass based anode materials are toxic for microbial growth; hence usage of these materials is not feasible. Studies carried out with durable and robust composite materials as anodes exhibited enhanced

efficiency [134]. Besides the above-mentioned key considerations, biocompatibility is also another key component that decides the fate of microbial growth and electron transfer between exoelectrogens and surface of electrode.

8.2.2 Reactor design

Design and construction of reactor are considered as primary elements during the initial stages of pilot scale BES. The type of material used for construction plays a vital role in determining the efficiency of BES. Volume of reactor is also another governing factor that impacts the costs and membrane bio fouling during scale up of BES. Large sized BES pilot plants scaled from laboratory studies failed to achieve the power that they delivered during laboratory study. Some of the reasons for not attaining the power output are spacing of electrodes and arrangement of electrodes. Recent literature suggests that going with large surface area electrodes (anode and cathode) is considered as a fruitful option to attain desired power output especially during up scaling. Hsu et al. [136] reported that mere increasing the anode and cathode surface area linearly does not contribute to attain greater power density. Cheng and Logan [137] depicted that increasing the cathode surface area nearly twice that of anode surface area contributes to attain 62% more power. Nevertheless, when the same approach is applied for the anode, the power attained was only 12% more. Thus, these results indicate that cathode electrode surface area is the governing factor for power output in pilot scale BES.

8.3 Limitations in operational factor aspects

8.3.1 Lag period

Startup or lag period is the critical factor need to be considered particularly for large scale applications of BES. Generally, lag period varies from days to months. Furthermore, based on literature the values of lag period vary from 60 to 103 days. Reactor configuration, inoculum and type of substrate crucially effect the lag period in BES. Along with these factors, other factors like pH also influences the biofilm growth and startup period in BES [134]. Therefore, to minimize the lag period, bio augmentation is the most effective and efficient way for quick start and reduce the lag period in BES. Similarly, utilization of inoculum acclimatized to the similar conditions or employing inoculum from existing treatment plants accommodated to the same substrate is the favorable condition for quick start of BES. Additional measures to minimize the startup period include adding substrates to the wastewater that promote the growth and metabolic activity of exoelectrogens, as demonstrated by Liu et al. [138]. Additionally, maintaining the appropriate conductivity levels in the anolyte can significantly hinder the growth of non-exoelectrogens and help reduce the lag period,

particularly during scale-up, as shown by Wang et al. [139].

8.3.2 Loading rate

Loadings particularly both sludge loading rate (SLR) and organic loading rate (OLR) influence the effectiveness of BES. These factors dictate the quantity of microbes required to degrade organic substances and capacity of reactor per volume respectively [140]. Numerous studies have demonstrated that the efficiency of BES is directly affected by SLR and OLR, which are directly proportional to the amount of power generated and organic matter degradation [141]. Especially during scale up, the loss of energy is significant even for lower loading values. Hence, determination of optimum values for SLR and OLR is vital for scale up thereby, maximum power production and organic matter removal could be attained.

8.4 Limitations in Economical aspects

BES is a self-sustaining along with concomitant waste minimization technique; however, their scale -up for practical applications is limited owing to economic considerations. Cost comparison of BES with conventional treatment provides broad view of techno economic aspects. Supplementary advantages of employing BES over other treatment technologies are low biomass generation, no energy requirement for aeration and feasible energy recovery.

BES systems are economically viable, however long-term application considering the cost is distant from veracity. The major impediments are fabrication and material costs for BES, electrodes, usage of exquisite metals for manufacturing electrodes, CEM/ separators etc., are few major components contributing for heightened cost [142,143]. Among the electrode materials particularly cathode material alone contributes for 75% of CAPEX. Therefore, impregnation of cathode with other materials like stainless steel and Ni is most preferred to attain greater power densities (23–36 W/m^3). As mentioned above CEM/separator is another component that augments the overall cost. Utilization of CEM/separator in large scale applications is conducive to ensure less electrode spacing, which ultimately results in reducing the reactor volume. Hence, single chambered BES offers less CAPEX than dual chambered BES, paucity of CEM/separator makes to compromise on electricity output [135]. Furthermore, existence of CEM/separator curtails short circuiting and provides a choice to accommodate both the electrodes (anode and cathode) very closely. Furthermore, utilization economic materials as separators have been investigated by several researchers, however their long-term application, stability and efficiency need to be determined for large scale applications [135]. BES is still evolving technologies and the costs associated with these methods are enormous, therefore developments in techno-economic aspect are needed to be considered to overcome the economic blockade.

9. Future perspectives

BESs are potential and versatile technologies majorly deployed to convert chemical energy to electrical energy using microorganisms. In spite of that economic and technical challenges limit the wider application of BESs at commercial level. To minimize the cost, finding inexpensive and efficient materials as electrodes is essential, further complete knowledge and expertise in the fields of microbiology, electrochemistry and bio electrochemistry is imperative to accomplish best outcome from BES. Furthermore, among the various BES systems, MES is the recent form of BES developed for fuel generation. Moreover, to attain efficient outcome from MES technology, better understanding of multidisciplinary concepts is imperative as mentioned above and are at the level of infancy. Generally, the performance of biological processes depends on activity of microbes, substrate utilization and redox reactions occur during the process. Likewise, the overall efficiency of electrochemical processes depends on cathode and anode potentials, conductivity of catholyte and anolyte and charge transferetc. Subsequently, BES are combination of both biological and electrochemical processes, thereby the parameters influencing and the process limitations are complex in nature.

The major technical challenges associated with the BESs are greater columbic efficiencies and drop of over potentials. Scale up of BES at industrial level is great challenge and is the limiting step for widespread implementation of BES at commercial scale. Further, the favorable results obtained during lab scale BES studies must be reproducible in nature, which makes the BES technology cost-effective and eco-friendly viable. Furthermore, mixed culture microbes act as an effective biocatalyst over pure cultured microbes, especially for treating wastewater. Nonetheless, the electron transfer efficiency and the mechanisms (Intracellular or extracellular) involved depend on the selection of biocatalyst. The choice of terminal electron acceptor also depends on the type of biocatalyst existed during the process.

Further very limited studies are present on recovery and reuse of metals with BES during the treatment of wastewater. On the other hand, separation of metal precipitates formed during the process is also a great challenge, particularly when the biofilms are intact with the electrodes. Therefore, for effective separation of metals application of physical and chemical methods like solvent extraction are preferred, despite increase in the overall cost. Further research on competition between metals is imperative for effective recovery of metals. For the recovery of nutrients using BES, further research is necessary to study the interaction among cathode and nutrients, which impact the recovery efficiency. Thus, characterization of end

product obtained after the recovery using BES is essential for better understanding of mechanism of recovery through BES. In addition, studies on resource recovery using BES have been reported with synthetic wastewater at laboratory scale. Even through lab scale studies designate the viability of BES, studies at pilot scale and industrial scale are more plausible. Pilot and industrial scale investigations are more conducive to ascertain hurdles, which ultimately contributes for performance improvement.

Conclusions

Resource recovery from wastewater is a catalyst for sustainable development and a circular economy approach. Among the most versatile and promising technologies for simultaneous treatment and resource recovery are BES, which encompass the reclamation of energy, nutrient, metal, water, and chemicals such as CH_4, acetate and H_2. Laboratory and bench scale studies have already demonstrated the feasibility of BES for resource recovery. Recent advancements in BES have bolstered oxidation and reduction reactions, enabling simultaneous resource recovery and wastewater valorization. However, the volume of wastewater treated using BES at laboratory scale remains inadequate for industrial implementation. Therefore, further research is imperative to scale up BES technology for resource recovery at industrial scales. Moreover, incorporating phototrophic options, advancing the design from laboratory to pilot scale, developing cost effective electrode materials, and economically viable catalysts for promoting bacterial growth are vital steps to make BES more accessible for commercial applications. In summary, the comprehensive utilization of BES technology for resource recovery from wastewater serves as a cornerstone for promoting sustainable development.

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List of Tables with Captions

Table 1: Summary of studies employed MEC for H_2 production using mixed culture

BES configuration	Anode material	Cathode material	H_2 production ($m^3/m^3.day$)	H_2 recovery Efficiency (%)	Reference
Single chamber	PANI/MWCNT modified carbon cloth biocathode	-	0.67	42	[19]
Dual chamber	Autotrophic bioanode	Graphite plate	9.2 $L/m^2.d$	39.4	[20]
H - type	Graphite fiber fresh	Stainless steel mesh	2.84	75	[21]
Dual chamber	Graphite fiber brush	Pt coated graphite fiber cloth	0.94	91	[22]
MEC cassettes - 6	Carbon felt – 2 in each cassette	Stainless steel wool	0.006	48.7	[23]
Dual chamber	Autotrophic bioanode	Plain carbon cloth	376.5 $mmol/m^2.d$	70	[24]
Dual chamber	Autotrophic bioanode	Graphite granules	2.5	2.5	[25]
Dual chamber with anion-exchange membrane (AEM)	Carbon felt	-	-	90	[26]

Table 2: Summary of factors influencing the efficiency of BES

Source	Inoculum	Functional period (days)	Configuration of BES	pH	Temperature (°C)	Power density (mW/m^2)	Efficiency (%)	Reference
Wastewater	Activated sludge	7	Dual chamber	5.8 - 6	29	-	94	[6]
Wastewater	Anaerobically digested sludge	60	Dual chamber	7	20	0.6	85	[58]
Soil	-	135	Single chamber	8.7	30	35	15	[74]
Soil	-	65	Single chamber	7.9	30	43	26	[75]
Wastewater	Petroleum acclimated	155	Dual chamber	6.3	15 - 22	6.5	93	[76]
Wastewater	Anaerobic sludge	4	Dual chamber	7	30	163.8 ± 3.4	100	[77]
Wastewater	Diesel contaminated groundwater	21	Dual chamber	7	30	31	82	[78]
Wastewater	-	300	96 MFC modules	8	28	30	75	[79]

Table 3: Overview of energy generation from wastewater

S. No	Type of wastewater	Configuration of BES	Mode of operation	COD removal efficiency (%)	Energy recovery (kWh/m^3)	Reference
1.	Domestic	Single compartment	Continuous	77	1.7×10^{-2}	[79]
2.	Leachate	Dual compartment	Continuous	86	6.6×10^{-2}	[83]
3.	Brewery	Single compartment	Continuous	88	9.7×10^{-2}	[84]
4.	Leachate	Dual compartment	Continuous	89	-	[85]
5.	Municipal	Dual compartment	Continuous	85	2.1×10^{-2}	[86]
6.	Synthetic	Single compartment	Continuous	87	1.4×10^{-2}	[87]

Table 4: Overview of BES sensors for detecting toxic substances

S.No	Toxic substance	Concentration of toxic substance	Detection time (min)	Type of inoculum	Reference
1.	Cu^{2+}	5 – 7 mg/L	20	Domestic wastewater	[124]
2.	Cd^{2+}	1 – 50 µg/L	15	Mixed culture	[120]
3.	Cr^{6+}	5 – 20 mg/L	-	Mixed culture	[125]
4.	Ni	10 mg/L	30	Mixed culture	[126]
5.	Cr^{6+}	1- 8 mg/L	5	Mixed culture	[127]
6.	Formaldehyde	10 – 1000 mg/L	80	*Shewanella oneidensis*	[128]

Table 5: Overview of BES sensors for detecting BOD

S.No	BOD range (mg/L)	Detection time (min)	Type of inoculum	References
1.	3 - 164	2.8 – 8.7	Mixed culture	[120]
2.	23 - 100	60	Mixed culture	[129]
3.	0 – 60	2	Mixed culture	[131]
4.	10 - 250	40	Mixed culture	[132]

List of Figure with Captions

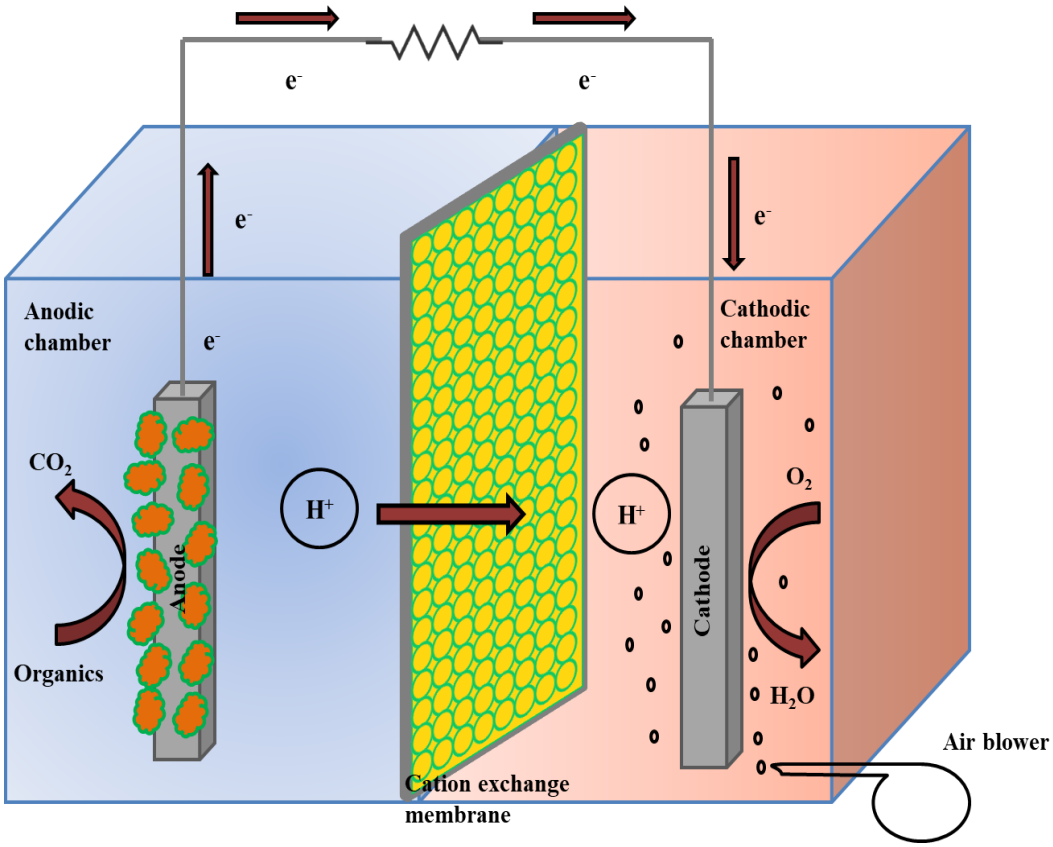

e-
e-
e-
e-
Anodic chamber
e-
Cathodic chamber
CO2
H+
H+
O2
Anode
Cathode
Organics
H2O
Air blower
Cation exchange membrane

Fig. 1

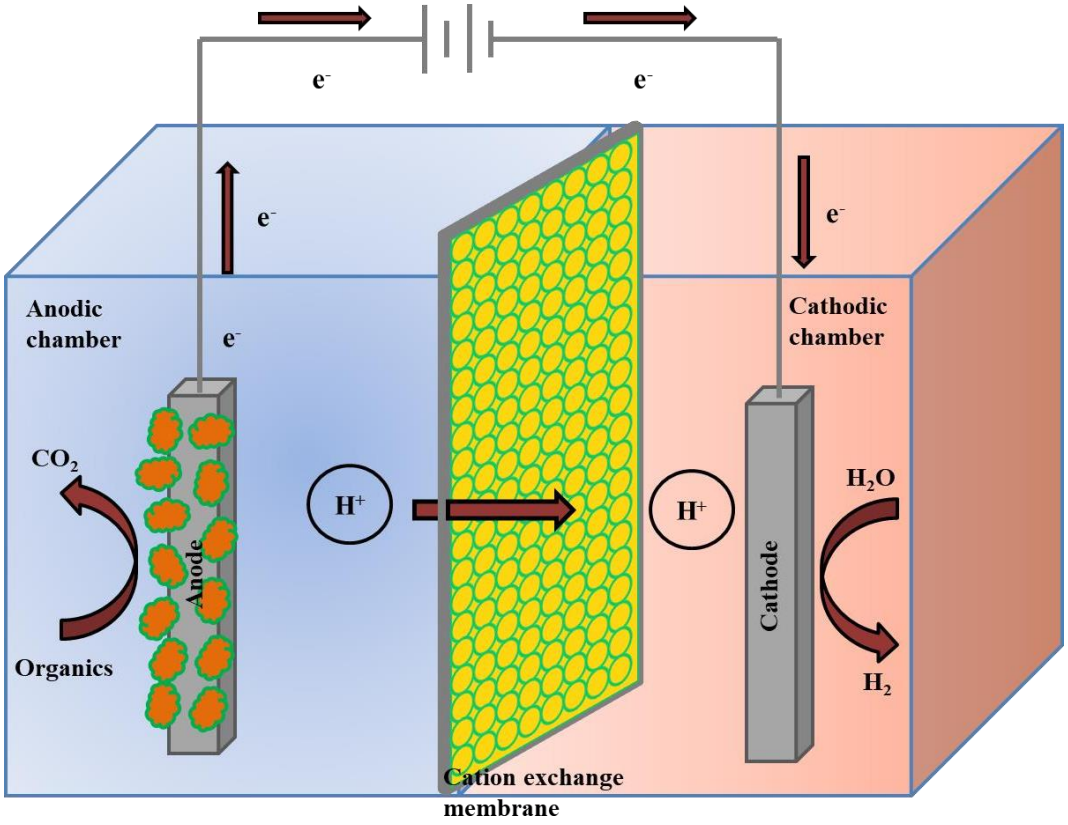

e⁻
e⁻
e⁻
e⁻
e⁻
Anodic chamber
Cathodic chamber
CO2
Organics
Anode
H+
H+
Cathode
H2O
H2
Cation exchange membrane

Fig. 2

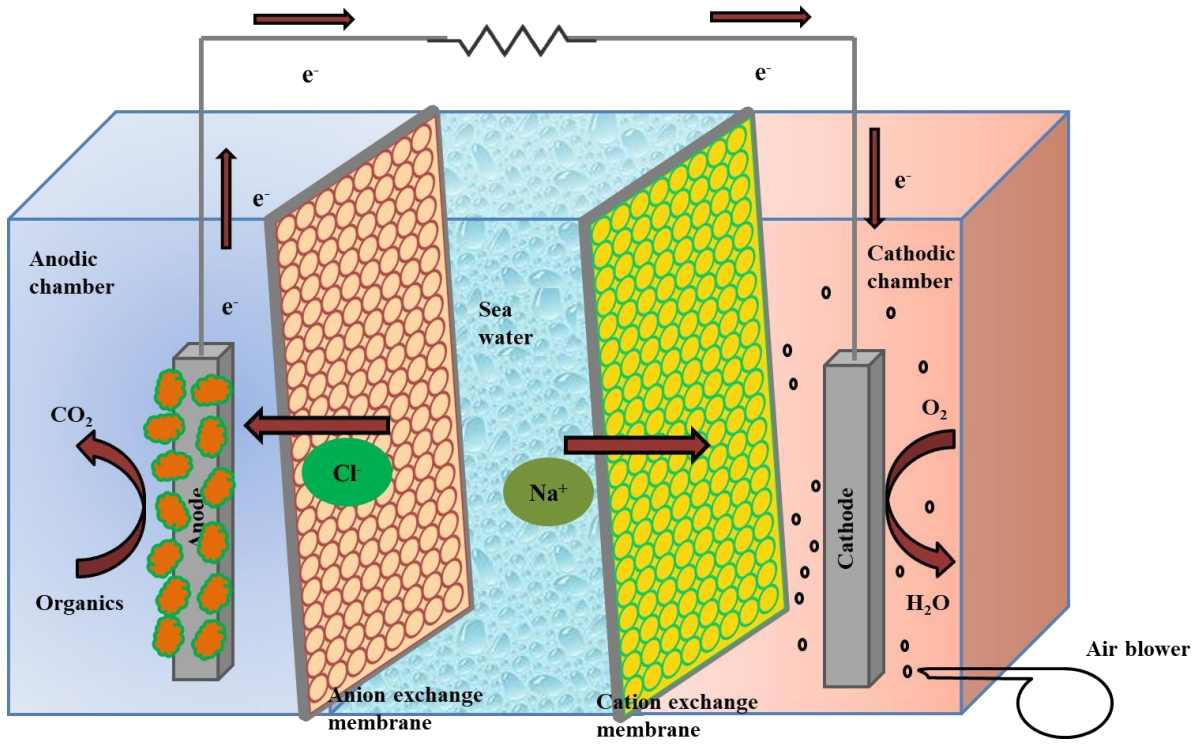

e-
e-
e-
e-
e-
Anodic chamber
Sea water
Cathodic chamber
CO2
Organics
Anode
Cl-
Na+
Cathode
O2
H2O
Air blower
Anion exchange membrane
Cation exchange membrane

Fig. 3

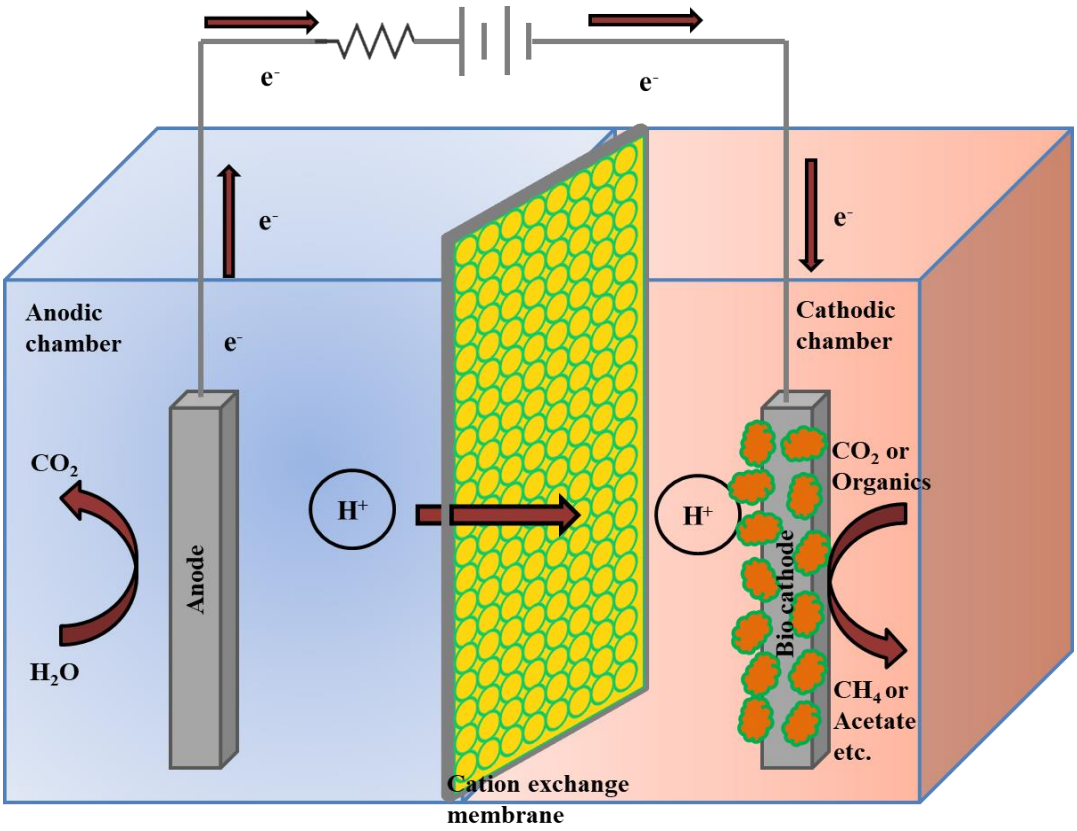

e⁻
e⁻
e⁻
e⁻
e⁻
Anodic chamber
Cathodic chamber
CO2
H2O
Anode
H+
H+
CO2 or Organics
Bio cathode
CH4 or Acetate etc.
Cation exchange membrane

Fig. 4

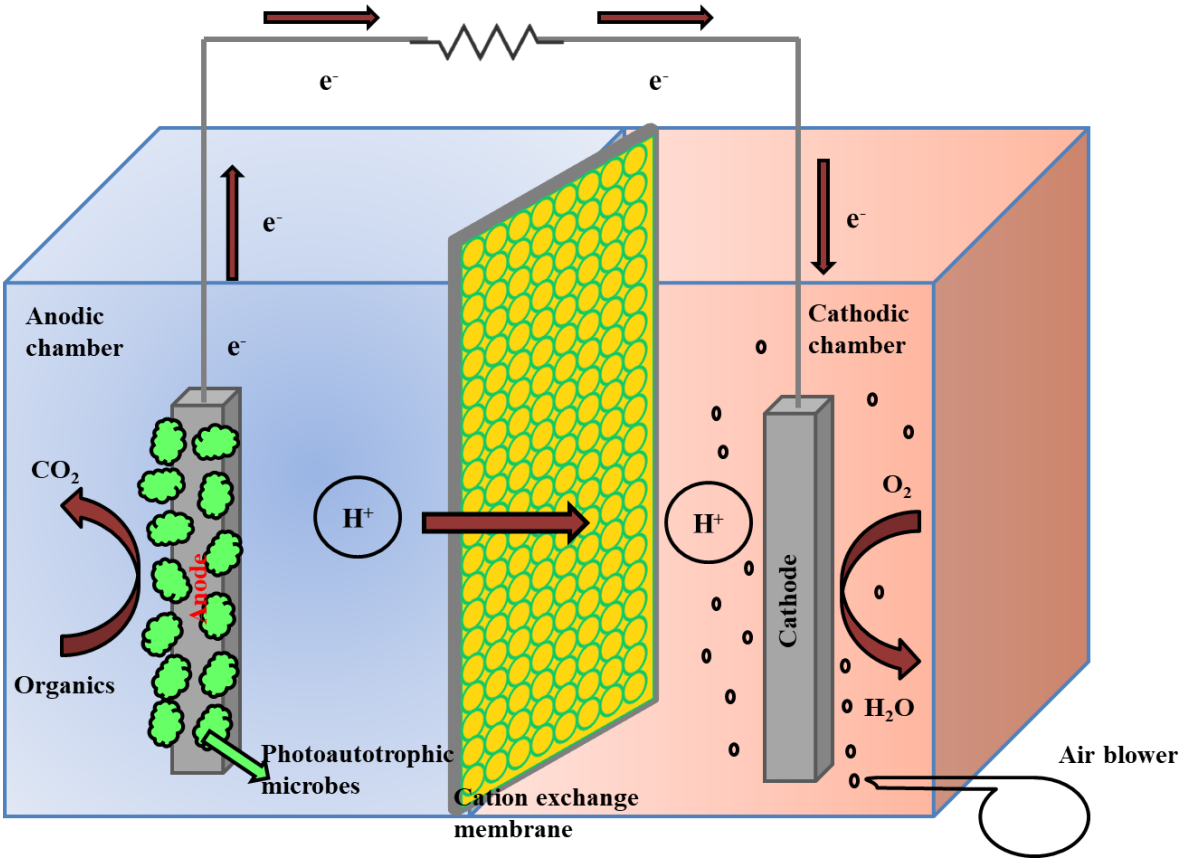

e⁻
e⁻
e⁻
e⁻
e⁻
Anodic chamber
Cathodic chamber
CO2
H+
H+
O2
Anode
Cathode
Organics
H2O
Photoautotrophic microbes
Cation exchange membrane
Air blower

Fig. 5

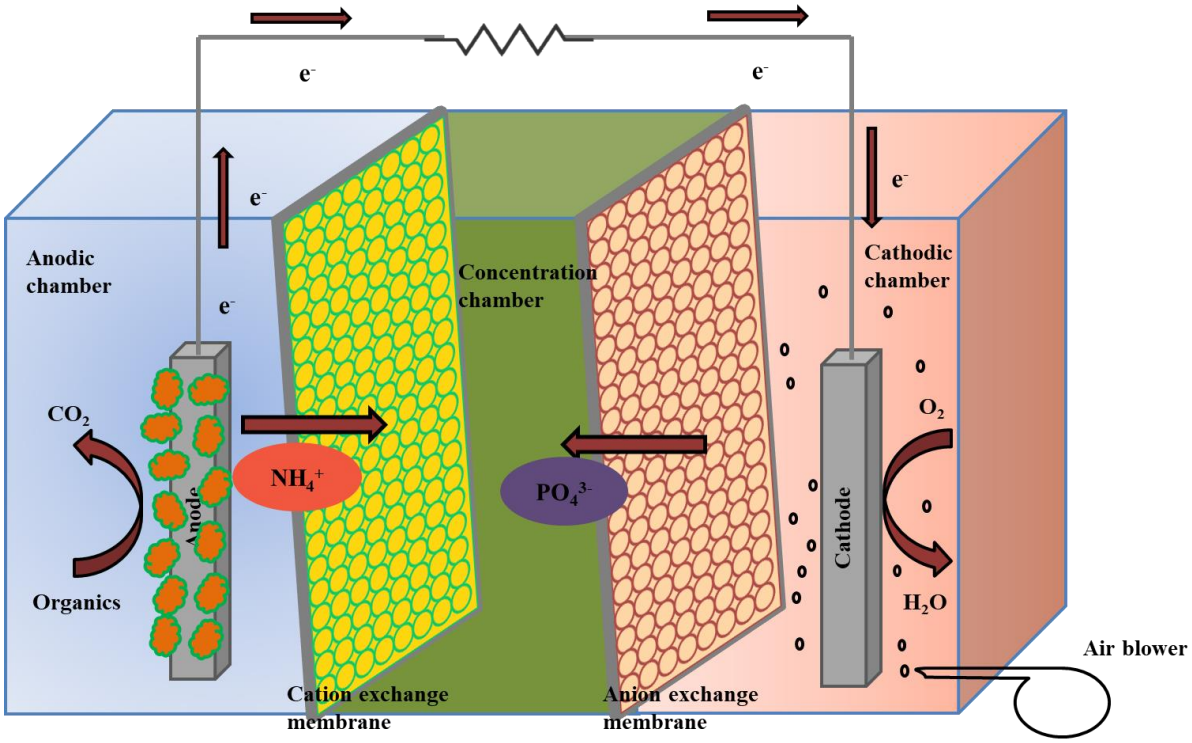
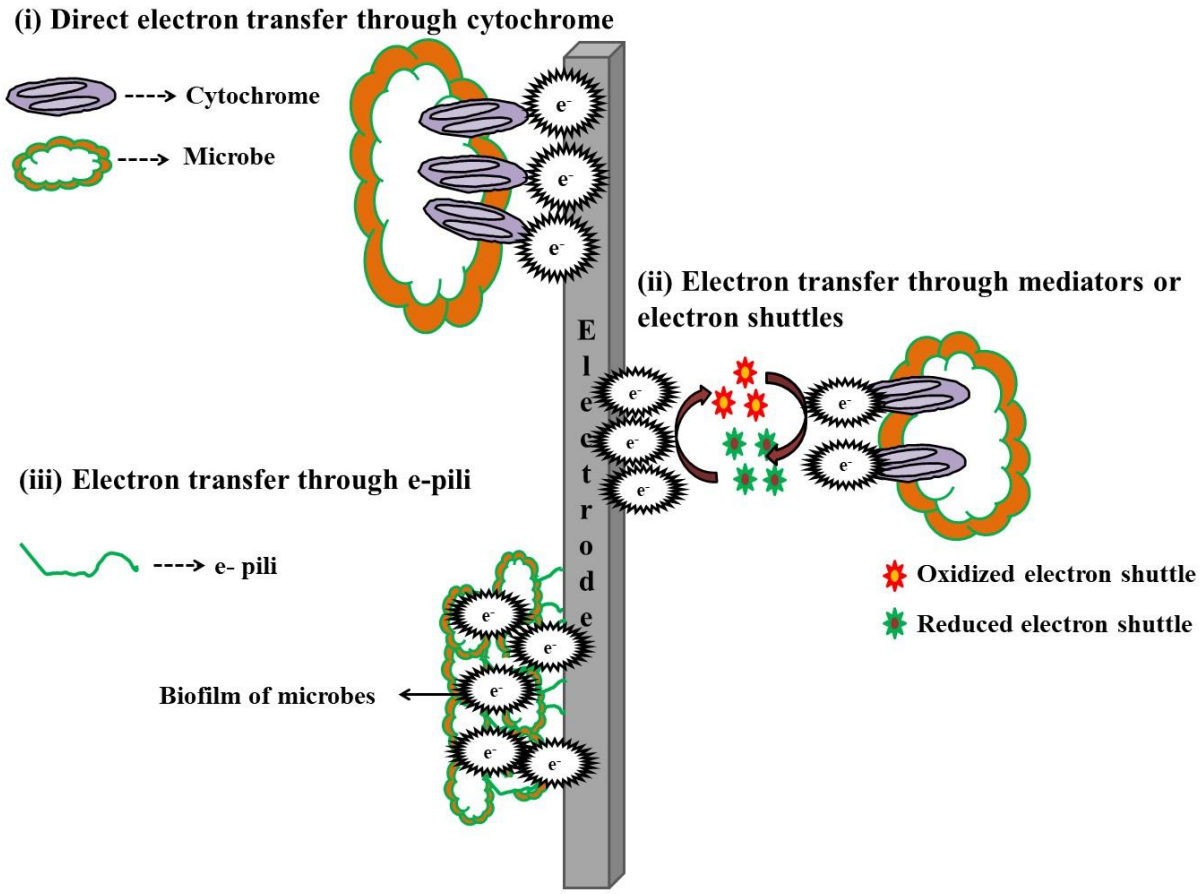

e⁻
e⁻
e⁻
e⁻
e⁻
Anodic chamber
Concentration chamber
Cathodic chamber
CO2
Organics
Anode
NH4+
PO4 3-
Cathode
O2
H2O
Air blower
Cation exchange membrane
Anion exchange membrane

Fig. 6


(i) Direct electron transfer through cytochrome
----> Cytochrome
----> Microbe
e-
e-
e-
(ii) Electron transfer through mediators or electron shuttles
e-
e-
e-
e-
e-
Electrode
(iii) Electron transfer through e-pili
----> e- pili
Biofilm of microbes
e-
e-
e-
e-
e-
Oxidized electron shuttle
Reduced electron shuttle

1

2

3 **Fig. 7**

4

5

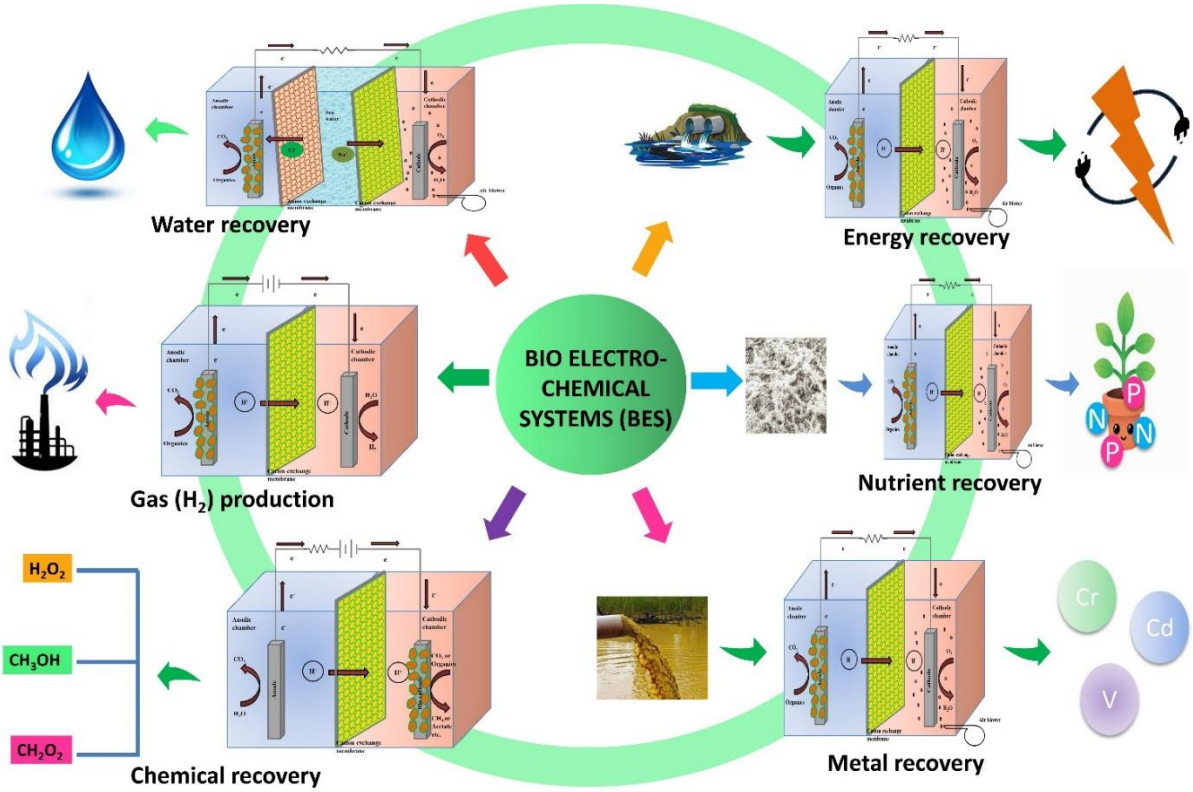

BIO ELECTRO-CHEMICAL SYSTEMS (BES)
Water recovery
Energy recovery
Gas (H_2) production
Nutrient recovery
Chemical recovery
Metal recovery
H_2O_2
CH_3OH
CH_2O_2
Cr
Cd
V
P
N
P
N

Fig. 8