Third generation in bio-electrochemical system research – A systematic review on mechanisms for recovery of valuable by-products from wastewater

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ABSTRACT

Bio–electrochemical system (BES) mainly focused on bio–energy generation in the form of methane and bio–hydrogen while treating wastewater in anodic chamber. The potential of BES to produce intermittent energy and high-value derivatives has been immensely explored since last decade by adopting modified reaction kinetics. This review article deals with the mechanism of recovery of resources and by-products during redox reactions in BES. The BES offers flexible platform for both oxidation and reduction processes. Development of BES for product synthesis via bio-electrochemical pathway has greatly extended the new horizon in bioenergy research. Microbial fuel cell and microbial electrolysis cell, the major two variants of BES, are useful to convert the energy present in wastewater to recover resources like bio-electricity, hydrogen, nutrients, heavy metals, minerals and industrial chemicals. Thus, after improving the performance of BES, widening the scope for products recovery by developing better understanding of the process and with efforts to reduce its production cost, it can become a sustainable technology for treatment of wastewater with added advantage of recovery of resources and bio-energy generation.

1. Introduction

1.1. Energy status and importance of by-product recovery

The national energy policy drivers of any country are the energy security, energy growth and environmental protection. Being an indispensable part of human life, energy and water necessitate environmental protection. Increasing population and high rate of economic growth proportionately increases the environmental pollution as well. In developing countries pollution is exceeding with rapid industrialization and urbanization, leading to generation of enormous amount of solid waste and wastewaters; hence, a few technological suggestions are arising regarding its proper utilization as a potential source of energy and exploiting by-products recovery. Considering wastewater solely as a source, the energy potential contains in it could be five times more than the energy consumed to treat it [1].

The ecological impact associated with global energy crisis demands to recover the useful forms of energy by adopting more recent technologies. A rapidly developing technology of bio–electrochemical system (BES) can exploit the process of electrochemical conversion of organic matter to generate usable by-products, fuels and bio-electricity by microbial metabolic conversion [2]. BES offers a set of configurations that can convert chemical energy present in waste (oxidizable organic matter) into electricity or other valuable products. Studies on BES have been majorly focused on its high efficiency of energy conversion, microbes-anode interaction and up-scaling. Some specific application niches of bio-electrochemical technology (BET) over commercially applicable conventional anaerobic digestion (AD) processes are, (i) the ability of treating organic substrates even at lower chemical oxygen demand (COD) concentration in the wastewater and also at higher concentration of volatile fatty acids (VFAs), (ii) feasibility of operation at lower operating temperature (20 °C), (iii) reduced sludge production, hence possible reduction of operating cost associated with sludge handling and disposal, and (iv) reduced cost for aeration. Thus, a promising and sustainable technical solution can be provided by employing two major variants of BES: microbial fuel cell (MFC) and microbial electrolysis cell (MEC) for recovery of renewable energy with high yield and useful chemical by-products [3]. According to the mode
of application of BES, another two up-coming research approaches such as, enzymatic fuel cell (EFC) and microbial solar cell (MSC) are being developed and are getting popular [4].

To address to the issues of energy and water crisis, the novel approach of MFC can be exploited to treat wastewater along with simultaneous electricity generation using microbes as biocatalyst. Most of the MFC research has been focused on wastewater treatment and electricity generation. However, MFC can also offer a promising option for by-products recovery (heavy metals and redox chemicals) from wastewater [5,6], which needs to be explored more. In MEC system, due to the application of controlled external voltage to cathode, the reaction between proton and electron can lead to formation of hydrogen, methane, hydrogen peroxide and other high-value end products, having further potential to expand the MEC applications. Enzymatic fuel cell with immobilized enzymes on electrodes imposes higher catalytic oxidation of substrate. Specific enzymatic reaction imparts utilization of redox mediators, demonstrating better electron transfer efficiency in such fuel cell [7,8]. The aim of this article is to review the scope of different valuable by-products recovery through redox mechanisms, while treating wastewater in BES. A detailed description on recovery of few important but less discussed chemical by-products and the mode of their simultaneous production in BES has also been discussed in this paper. The processes are mainly focused to discuss the mode of chemical synthesis during biological conversion, fundamental and theoretical outlook of process parameters and value-addition by chemical recovery, which provide a significant knowledge contribution with effective solution to formulate more efficient wastewater treatment processes. Application niches, limitations and possible reactor modifications are also suggested to achieve higher yield of by-products and bio-energy generation.

1.2. Principle of BES

Application of BES is a novel approach based on electrochemical conversion processes, capable of converting the chemical energy stored in biodegradable organic materials by catalytic activity of microorganisms. BES consists of anodic (oxidative) and cathodic (reductive) half-cells to produce electricity or other chemically derived products (Fig. 1) by integrating the biochemical and electrochemical processes. Electrochemically active bacteria (EAB) catalyze the oxidation of organic electron donors in the anodic chamber and deliver electrons to the anode, which can be captured directly as bio-electricity. To maintain the electro-neutrality, protons (H+) generated during the catalytic conversion travels through cation exchange membrane from anodic chamber to cathodic chamber, where protons are utilized to produce value-added chemicals under imposed external potential. In the last two decades, BES has drawn significant attention of the researchers due to its promising applications in scientific fields such as renewable energy production, bioremediation, wastewater treatment [9] and other by-product recovery. In this direction, considerable amount of literature exists, suggesting its basic operations, architecture, applications [10,11], scale-up requirements [12], mode of electron transfer by anode-respiring bacteria [13,14] and their metabolism, energy losses [15,16], cathodic limitations [17,18] and critical comparison between BES and conventional anaerobic technologies [3,10,19]. Also, BET offers a new and transformative solution for integrated wastewater treatment processes leading to recovery of energy and resources, which provides a flexible platform for both oxidation of pollutants and reduction oriented methods for product recovery [20].

1.3. Advancement in BES research

In early 1911, Potter [21] discovered bacterial capability to oxidize the organic matter using an electron accepting anode. During first generation, the BES research was mainly focused on organic matter removal during wastewater treatment. Combination of hybrid approach of wastewater treatment processes using BES helped to enhance the treatment of wastewater. With advancement in multidisciplinary research, this technology was used to recover energy in the form of electricity, hydrogen and intermediate products, during second generation of BES research. One order of magnitude increment in power density from MFC was achieved with the help of modified electrode materials, application of novel catalysts, improved understanding of mechanisms and microbial electrogenic pathways for substrate oxidation and modifications in geometry of MFCs.

Recently, more emphasis has been given on resource and by-products recovery to increase the treatment competence of BES to match with the existing wastewater treatment processes during third generation of BES. The by-products and resources like heavy metals, nutrients, minerals, and industrial intermediate chemicals can be recovered during bacteria catalyzed redox reactions. Quite large number of research/review articles have been published to address the different aspects of BES such as electrode materials, materials used for components, substrates, microbes, pollutant removal, modelling aspects, etc. to enhance the performance of BES [22]; however, few articles (less than 1%) discussed the scope of by-products recovery from wastewater in BES [23,24] (Fig. 2). A promising and sustainable solution for recovery of useful chemical by-products with (or without) a provision to generate renewable energy in the form of electricity can be offered by BES. Dual purpose of BES i.e. energy generation and
bioremediation makes BES more attractive to the researchers. However, to make it more practical for real life application and positive energy gain, the recovery of by-products from wastewater should be focussed. Considering existing research gaps, this review emphasizes on recovery of useful chemical by-products from wastewater, which will be a major breakthrough in BES research to encourage its application. This article is an effort to contribute knowledge towards production of value-added and important chemical by-products, their mode of synthesis and recovery while treating wastewater in BES.

The recovery of by-products during bio-electrochemical reactions reduces additional energy requirement for individual by-product synthesis processes. The major technological breakthrough is the possibility to apply external voltage as the driving force in MEC during microbial electro-catalysis to accelerate the production of high value reduced chemicals such as methane, hydrogen gas, caustic soda or hydrogen peroxide at the cathode, at a much lower energy cost [25–27]. Higher market value of these reduced by-products in comparison with the cost of applied electrical potential to produce them makes BES technology economically more attractive. Subsequently, electricity-driven processes have also been applied and widely explored in the context of bioremediation and inorganic/resource recovery. Studies on life cycle assessment (LCA) or Cradle-to-gate analysis represents that the recovery of high value products from well-designed BES can provide significant environmental benefits [28]. Thus, BES has potential to offer a promising solution for recovery of products, other than bio-electricity, through different mechanisms as discussed here in details.

2. Production and recovery of high-value end-products from BES

2.1. Recovery of inorganic materials

2.1.1. Heavy metal recovery

Heavy metals present in industrial effluents pose a serious problem to the environment and public health, since many of these metals are toxic even at low concentrations. Physical, chemical, and biochemical technologies for heavy metals removal from wastewater have been developed, and further efforts have been made for its possible recovery. Such treatment processes can be made cost-effective and sustainable by facilitating metal recovery using BES. Moreover, BET has ability to remove and recover metals even when present at very low concentration in aqueous medium, making it an economically viable option than other alternative processes.

Direct reduction of metals having redox potential (vs. SHE) higher than the potential of biotic anode to impose thermodynamically favourable reaction kinetics was studied, where the electrons generated in anode are directly consumed by abiotic metal cathode such as Cu(II) (E° = 0.337 V), Fe(III) (E° = 0.770 V), Au(III) (E° = 1.001 V), V(V) (E° = 0.991 V), Cr(VI) (E° = 1.330 V), Ag(I) (E° = 0.799 V) and Hg(II) (E° = 0.911 V) without external power supply [29]. Few studies showed recovery of metals with lower redox potential, such as Ni(II) (E° = 0.250 V), Pb(II) (E° = 0.130 V), Cd(II) (E° = 0.400 V) and Zn(II) (E° = 0.762 V), by using biotic anode and abiotic cathode under the influence of external power source to force the movement of electrons from anode to cathode side (Table 1). Higher reduction rate of chromium and other transition metals can be achieved under the assistance of microbial metabolism at biocathode with or without poised potential [30].

A sustainable self-driven MFC-MEC based treatment has been studied for recovering Cr(III), Cu(II) and Cd(II), when their initial feed concentration was fixed to 5 mg/L, which showed complete recovery in MEC with simultaneous bioelectricity generation in MFC [31]. For heavy metals removal from fly ash leachate, Tao et al. [32] designed a hybrid system of BES and electrolysis reactors in which Cu (II) was recovered in the form of Cu2O during cathodic reduction (Eq. (1)); whereas, Zn and Pb were recovered during electrolysis (Eqs. (2) and (3)) and found a respective removal of Zn, Cu and Pb as 95.4%, 98.5% and 98.1% at 25 °C.

\[
\begin{align*}
\text{Cu}^{2+} + 2e^- & \rightarrow \text{Cu} (E^0 = 0.337 \text{V}) ... \quad (1) \\
\text{Zn}^{2+} + 2e^- & \rightarrow \text{Zn} (E^0 = -0.762 \text{V}) ... \quad (2) \\
\text{Pb}^{2+} + 2e^- & \rightarrow \text{Pb} (E^0 = -0.130 \text{V}) ... \quad (3)
\end{align*}
\]

Moreover, the metal assimilation and dissimilation mainly depends on interactions between microbes and metals in BES. Hence, the novel approach of BES can provide solution for effective metal recovery through redox reactions.

2.1.2. Iron oxide recovery

Iron oxide compounds, recovered from red-mine mud, have been found to be an inexpensive and effective option as catalysts for fuel cell applications [33–35]. The novel approach of MFC was used to treat wastewater (acid mine drainage, AMD) along with simultaneous electricity generation, using microbes as biocatalyst. A dual-chamber MEC was developed to concurrently produce H2 and recover heavy metals like Cu2+, Ni2+, and Fe3+ from AMD with single and mixed metal present in the solution [34]. Cheng et al. [36] developed a chemical fuel cell for treatment of AMD containing Fe2+ ions in the anodic chamber, and demonstrated considerable power generation of 290 mW/m² (7.2 W/m³) under a thermodynamically favourable condition along with successful metal recovery (Fe2+ to Fe3+) (Eq. (4)). During oxidation in fuel cell, ferrous iron present in AMD was completely removed to insoluble ferric iron, forming a precipitate at the bottom of the anodic chamber as well as on surface of the anode. Around 99% iron removal with Coulombic efficiency of 19% at pH of 7.9 during treatment of AMD in cathodic chamber of MFC has also been obtained by Lefebvre et al. [37].

\[
\begin{align*}
\text{Fe}^{2+} + 3\text{H}_2\text{O} & \rightarrow \text{Fe(OH)}_3 + 3\text{H}^+ + e^- \quad (E^0 = 0.130 \text{V}) \quad \Delta G^0 = -27.15 \text{kJ/mol} ... \quad (4)
\end{align*}
\]

2.1.3. Elemental selenium recovery

Selenium is a mineral found in soil, water and some foods. MFC can convert significantly high concentration of dissolved selenium in selenate (Se(VI), SeO4²⁻) and selenide (Se(IV), SeO3²⁻) form, present in wastewater streams of glass manufacturing and electronic industrial effluents, to its elemental form Se(0) [38,39]. Microbial reduction of soluble selenium oxy-anions into insoluble elemental selenium is a key process exploited in the biological treatment of wastewater contaminated with selenium. Lee et al. [40] reported that facultative anaerobic Shewanella sp., well known for their capability to generate electricity in MFCs, were able to utilize selenite as the sole electron acceptor during their respiration under anaerobic conditions. This theory resulted in reduction of selenite from wastewater and deposition of bright red nano-sized spherical particles of elemental Se (Eq. (5)) over the anode as well as the water facing side of the cathode in an air-cathode MFC, demonstrating around 99% of selenite reduction [36].

\[
\begin{align*}
\text{Se}^4+ (\text{aq.}) + 4e^- & \rightarrow \text{Se}^0 (E^0 = 0.41 \text{V}) ... \quad (5)
\end{align*}
\]
processing facility. Bioremediation of uranium has also been suggested by converting toxic soluble U(VI) to insoluble U(IV), which was precipitated as UO2 onto the surface of cathode during electrochemical reduction (U(VI)/U(IV), Ecathode=-0.042 V) [42]. Thus, BES can also be utilized as a bioremediation system for soluble radioactive material recovery from contaminated water.

2.2. Nutrients recovery

Nutrient removal from wastewater has become a key challenge for many of the treatment processes. The nutrient removal and recovery from urine and swine wastewater can be carried out by adopting biological approaches in BES [5,43–46]. Urine can be considered as an ideal fuel (source of C, P, N, and K) for electricity production in MFC. The potential energy and ammonia recovery from urine using a BES was explored by Kutke et al. [47] and Ieroupolos et al. [48]. Ammonia recovery in MFC was done by treating urine in the anodic chamber and migration of ammonium ions by diffusion towards cathodic chamber was followed by subsequent absorption [47]. Higher current density of 3.6 A/m² and significantly improved recovery of NH4+ ions by 61% in MFC was reported in a microbial electrochemical cell under electricity-driven migration [49].

Swine wastewater is rich in phosphate and thus, its treatment is a crucial issue. Struvite (NH4MgPO4·6H2O) precipitation on the cathode surface and phosphate recovery up to 27% with phosphate removal efficiency of 70 – 82% was reported in BES [50,51]. Recovery of orthophosphate (600 mg/l) as fertilizer from digested sewage sludge was carried out along with generation of bio-electricity in MFC by the metabolic activity of Escherichia coli [52]. Hence, application of BES for ammonium and phosphate recovery with simultaneous energy production from urine and swine wastewater is possible.

A novel approach for treating high strength sulphate wastewater by bio-electrochemical processes has been reported by Blázquez et al. [53]; where, the enrichment of bio-cathode with autotrophic sulphate reducing bacteria (SRB) and sulphide oxidizing bacteria (SOB) leads to recovery of elemental sulphur during the bacterial metabolic process. By utilizing in-situ generated H2 as electron donor, the reduction of sulphate by SRB was observed in the cathodic chamber producing H2S [54], achieving sulphate reduction rate of 388 mg L−1 day−1. Also, water was dissociated in anodic chamber to produce oxygen, which travelled to cathodic chamber through anion exchange membrane and provide aid to SOB for catalysing the H2S oxidation to produce elemental sulphur which gets deposited on the cathode surface.

2.3. Production of algal biomass

Algal biomass generated during photosynthetic activities of algae can be used as a direct source of organic matter for electricity generation in MFC and production of bio-fuels [5,55]. Photoautotrophic microorganisms tend to produce organic compounds by using CO2 as a carbon source during carbon capture and storage process in microbial solar cell. Furthermore, the photosynthesis process could be encouraged in the cathodic chamber to supply oxygen for cathodic reduction and production of algal biomass as a by-product. The recovered algal biomass can effectively serve as a substrate in photo-bio-electrochemical cells, after different pre-treatments with heat, microwave, ultrasonic waves, acidic and alkaline chemicals, and even with the residue separated after extraction of algal oil [56]. Possibility of algal biomass recovery was previously reported by using microbial carbon capture cells, where sequestration of carbon dioxide can be achieved by sparging the produced anodic CO2 gas into catholyte, containing Chlorella vulgaris algae, forming a bio-cathode [57,60]. Furthermore, algal biomass of marine algae Chaetoceros sp. has the potential to inhibit the growth of methanogens present in the mixed inoculum and also it can be utilized as a substrate for anodic oxidation in MFC [58].

3. Recovery of intermittent bio-chemical compounds from BES

3.1. Industrial chemicals/gases

Principally, MFC operation is targeted to harvest maximum energy in the form of electricity; however, the major fraction of energy is lost because of generation of methane and hydrogen gas. Performance of microbial bio-cathode was evaluated for the recovery of methane by reduction of carbon dioxide in cathodic chamber of MEC, using a pure culture of Methanobacterium palustre. It demonstrated higher rate of methane generation up to 0.055 mol/(gVSS. day) and electron capture efficiency (over 80%) by hydrogenophilic methanogenic culture. Methane was produced via both abiotically produced hydrogen gas (i.e. hydrogenophilic methanogenesis) by direct extracellular electron transfer and also during biological fermentation of organic matter [59]. The major incidences of methane production in MECs have been reported using hydrogen gas produced during the process by hydrogennotrophic methanogenesis. The CO2 generated during acetoclastic methanogenesis is used by hydrogenotrophic methanogens to produce methane (CH4) gas. The gases like H2, CO2, CO were recovered from wastewater using combination of MFC-MEC system and can be utilized further for industrial applications [60,61].

An emerging BET for cost effective production of hydrogen peroxide (H2O2), an important industrial chemical, and simultaneous co-products generation valorised the grey water and black water treatment [29,62,63]. Production of H2O2 along with electricity in MFC is a theoretically feasible process over a cell voltage of 0.58 V; however, the production rate is significantly lower. Moreover, when a voltage of 0.5 V (vs. SHE) was imposed, H2O2 was shown to be
recovered at the rate of 1.9 ± 0.2 kg H2O2/m3 day from acetate with 83.1 ± 4.8% of cathodic reduction efficiency of oxygen in MEC [64]. The reduction reaction was facilitated by providing thermodynamically favourable conditions to support the redox potential for overall reaction.

Lower cathodic overpotential and higher cathodic recovery for bio-catalytic reduction of CO2 to fuel gas CH4 can be facilitated either by direct or indirect extracellular electron transfer (EET), as discussed by Eerten-Jansen et al. [65]. The direct pathway of EET (ECat = −0.24 V vs. SHE) was found to be more energy-efficient process in MEC than MFC. At a cathode potential of −0.55 V vs. SHE, Cheng et al. [66] found the rate of methane recovery as 0.006 m3/(m3 day) in a methane producing MEC using acetate based synthetic wastewater (COD of 1 kg/m3) as an electron donor in anodic chamber. A similar study of bio-catalyzed electrolysis as a novel biological H2 production process demonstrated an approximate hydrogen generation of 0.02 m3/(m3 day) in cathodic chamber at an applied voltage of 0.5 V, when acetate was fed in the anodic chamber [67,68].

The urea bioreactor electrochemical system in combination with a forward osmosis subsystem removed more than 80% of organic carbons and recovered approximately 86% of the urea to ammonia (Eq. (7)) [69]. A granulated activated carbon (GAC) urease bioreactor was used to recover urea from human urine and to convert it to ammonia. In the bioreactor, the urea reacts with immobilized urease to form ammonia and carbolic acid (Eqs. (6) and (7)). The produced ammonia was injected to an electrochemical cell to generate direct electrical energy. Electrochemical cell was capable to oxidize ammonia molecules to produce molecular nitrogen and water (Eq. (7)), along with generation of six electrons during conversion of every two ammonia molecules.

Enzymatic hydrolysis (with urease) of recovered urea:

$$\text{CO(NH}_2\text{)}_2 + 2 \text{H}_2\text{O} \rightarrow 2\text{NH}_3 + \text{H}_2\text{CO}_3$$  

Oxidation of ammonia:

$$2\text{NH}_3 + 6\text{OH}^- \rightarrow N_2 + 6 \text{H}_2\text{O} + 6e^-$$  

3.2. Ethanol recovery

Beyond the general lignocellulose-to-ethanol pathway, a novel method of bio-electrochemical conversion of waste biomass to liquid ethanol fuel by biological acetate reduction with hydrogen and bio-cathode as an electron donor has been previously investigated by researchers [70–72]. A recent study with dual chambered MEC, equipped with three electrode system, a working electrode (WE – cathode), a reference electrode (RE) and a counter electrode (CE – anode), was configured and operated at constant cathode potential of −0.55 V vs. SHE (Fig. 4); whereas, the anodic reactions prevailed with the oxidation potentials of ferro-ferricyanide redox couple (Eqs. (8)–(10)). In the presence of mixed consortia, specific electron mediators like methyl viologen and imposed potential (−0.55 V vs. SHE) in cathodic chamber of MEC, the study successfully recovered 83 mg/l of ethanol [73,75] from 50 mM acetic acid. Similarly, Steinbusch et al. [75] reported the recovery of carbon rich compounds like ethanol and butanol in the cathodic chamber. Also, the novel use of mediators to accelerate electron transport from cathode to bacteria, to influence their metabolism and hinder the parasitic reactions like methanogenesis, which can increase the undesirable butyrate concentration (Eq. (11)), were also discussed in the same study. The details of the half-cell reactions are summarized below:

Anodic reactions [77]:

$$\text{Fe(CN)}_6^{3-} + e^- \rightarrow \text{Fe(CN)}_6^{2-}$$  

Cathodic reactions:

Desirable reactions –

$$\text{CH}_3\text{COO}^- + 5\text{H}^+ + 4e^- \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O}$$  

Undesirable reaction –

$$2\text{CH}_3\text{COO}^- + 5\text{H}^+ + 4e^- \rightarrow \text{CH}_3\text{CH}_2\text{COO}^- + 2\text{H}_2\text{O}$$  

3.3. Medium chain triglycerides – the biological precursors of renewable fuels

Medium chain fatty acids which are naturally present in food, used in medicine and food products, can be recovered in BES to impart greater benefits [78]. Researchers have investigated the mechanism of producing medium chain fatty acids with a higher length than butyrate from acetate in BES with (or without) using external electron mediators and cathodic electron donors [74,79]. An-in-situ supply of electrons was mediated by the cathodic microorganisms that produced ethanol by utilizing hydrogen (H2 production pathway) or directly by

Fig. 3. Electro-catalytic reduction reactions for bio-fuel conversion in BES.

Fig. 4. Electrochemical conversion of acetate to ethanol in MEC.
cathode through bio-electrochemical hydrogen production.

A novel pathway of reduction of acetate by using $H_2$ as an electron donor to produce medium chain fatty acids, caproate (C–6) and caprylate (C–8), having a superior physical properties as a precursor to fuels and chemicals compared to ethanol and VFA, was discovered (Eqs. (12)–(15)). Few past studies exhibited the production of C$_2$–C$_4$ fatty acids and ethanol in MEC operated at an applied cathode potential of $-0.9$ V vs. SHE [74–77]. Configuration of MEC used was similar as depicted in Fig. 4 and 100 mM acetic acid was used as catholyte for production of medium chain fatty acids caproate and caprylate from acetate. Bio-electrochemical production of caproate (739 mg/L), caprylate (36 mg/L), butyrate (263 mg/L) and ethanol (27 mg/L), respectively, was reported by Eerten-Jansen et al. [74] during intermediate reduction of organics. Ethanol was produced by mixed culture of anaerobic bacterium, predominantly obtained as Clostridium kluyveri, Eubacterium pyruvativorans, Clostridium tyrobutyricum etc., in the cathodic chamber, thus avoiding its external addition in this study. The thermodynamic feasibility of step-wise reaction mechanisms are discussed below.

Ethanol production via $H_2$ pathway:

$$\text{CH}_3\text{COO}^- + 5 \text{H}^+ + 4e^- \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{H}_2\text{O} \quad \text{E} = -0.408 \text{ V vs. SHE} \quad \text{(12)}$$

Reduction of acetate to butyrate–intermediate and conversion to caproate and caprylate:

$$2 \text{CH}_3\text{COO}^- + 6 \text{H}^+ + 4e^- \rightarrow 2\text{CH}_3\text{CH}_2\text{COO}^- + \text{H}_2\text{O} \quad \text{(13)}$$

Caproate production:

$$\text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{CH}_2\text{COO}^- \rightarrow \text{CH}_3\text{CH}_2\text{CO}_2\text{H} + \text{H}_2\text{O} \quad \text{(14)}$$

Caprylate production:

$$2\text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{CH}_2\text{COO}^- \rightarrow 2\text{CH}_3\text{CH}_2\text{CO}_2\text{H} + 2\text{H}_2\text{O} \quad \text{(15)}$$

3.4. Biopolymer synthesis

Polyhydroxyalkanoates (PHAs) having rheological properties similar to polypropylene, are a naturally degradable bio-plastics extracted from bacterial cells. However, high production cost of PHAs over the low cost petro-chemically derived plastics led to less importance in its production and research [80–82]. Recent researches on bio-electrochemical-synthesis of PHAs have created a renewed interest, demonstrating its production in cathodic chamber under ample availability of carbon and nutrient sources [25,83]. Also, PHA synthesis pathway by cathodic micro-aerophilic biofilm, utilizing CO$_2$ as the carbon source in BES, evidenced the yield of alcohols, carboxylic acids, diols and biopolymers such as poly-β-hydroxybutyrate, when an enforced cathodic reduction potential was implied by external power supply [84]. This concept was further developed by Srikanth et al. [85], demonstrating enhanced electrogenesis and accumulation of synthesized PHA in the cathodic chamber of MFC using aerobic consortia as biocatalyst.

3.5. Biorefinery intermediates

Hydrolysates produced by hydrothermal treatment of lignocellulosic feed-stocks, originating from agricultural and bio-refinery facilities, can be considered as a potential source of substrate in BES. It results in formation of high value reaction intermediates of poly-phenolic lignin, cellulose and hemicellulose residues upon further treatment [86–88]. Reduction of such reaction intermediates can be facilitated by hydrogen produced in cathodic chamber of MEC, finally yielding the poly-phenolic group of metabolites (equol and resveratrol), which is widely used as a natural antioxidant and composite material for bio-plastics [72,89–91].

4. Hybrid approach of wastewater treatment for efficient co-product recovery

With development in BES research, several studies came with an integration of one or more wastewater treatment processes with BES to increase the effluent quality and recover maximum available energy present in the wastewater. The products such as bio-hydrogen, biomethane, electricity, bio-fertilizer, caustic soda, hydrogen peroxide, etc. were formed during the integrated operation of hybrid BES. Hydrogen and methane production during such combined operation makes the hybrid system more attractive and efficient [92]. A methane producing MEC in combination with anaerobic digestion has been proposed as a polishing post-treatment for effluent received from anaerobic digesters [93]. The hybrid approach of MFC with anaerobic membrane bioreactor [94], integrated photo-bioreactor fuel cell [95], anaerobic digester (AD) [96], up-flow anaerobic sludge blanket reactor (UASB), MEC, rotating biological contactor [97], desalination cell [98], etc. were investigated to produce higher quality treated effluent and recover valuable by-products [9] (Fig. 5). With respect to energy production, assuming that the of energy recovery from the AD, MFC and algae treatment steps are 28%, 10% and 3%, respectively, in making total 41% of the chemical energy that can be recovered, which theoretically would turn the treatment process into a net energy producer by when the energy consumption of wastewater treatment was less than 10% of the energy content [99].

The hybrid system is capable to achieve higher levels of wastewater treatment and it can provide polishing treatment as well for removal of specific pollutants. The BES-centred hybrid treatment system is proposed as an example of integrating bio-electrochemical technology with relevant technologies for improving treatment sustainability. However, it demands high energy input and additional components to attach, which consequently increase the cost of fabrication. Also, difficulty with reactor scaling-up and primary barrier for hybrid systems (including MFC) due to the complexity of the combined treatment processes, strive its practical implementation. Therefore, a balanced evaluation and suitable modifications of all unfavourable factors are required to be duly addressed to guide the process design and operation of such hybrid processes.

5. Other chemical recovery options

Realizing the full poly-generation potentials, i.e. recovery of metals, production of bio-fuels and chemicals from reuse of CO$_2$ and clean water from waste streams can attain an economic and environmental upside of novel electrochemical synthesis processes. The wastewater
treatment producing reusable quality water and carbon capture along with recovery of sodium salt at cathode was achieved by employing the MFC technology [96]. About 9% (w/v) sodium salt was recovered in the form of sodium carbonate and sodium bicarbonate with use of Pt–free cathode in MFC, which might be attributed to the oxygen reduction reactions, water diffusion and electro-osmotic drag [100].

Recently developed technique of microbial desalination cell (MDC) has been implemented to recover chemicals like HCl and NaOH, when a bipolar membrane (BPM) is placed next to the anodic chamber into the MDC, forming a microbial electrolysis desalination and chemical—production cell. With application of electric field in MDC, the water dissociation reaction resulted into generation of protons and \( \text{OH}^- \) ions. Furthermore, the \( \text{H}^+ \) ions migrated into the acid production chamber through cation exchange membrane (CEM), resulting in generation of HCl (2.1 mM). Similarly, the generated \( \text{OH}^- \) ions migrated to the anodic chamber via anion exchange membrane (AEM) to produce NaOH (2.1 mM), along with removal of NaCl and biological processes. In BES, the stillage streams from bio-refineries can be effectively used as a substrate to recover value added products; hence, coupling of MES with waste refineries can be useful to increase the efficiency of recovery of resources [102]. In MES, the mixed microbial community growing on the cathode can convert glycerol reductively to 1,3-propanediol [103]. They presented a combined approach for 1,3-propanediol production and propionate extraction in three chamber reactor system, which leads to recovery of additional 3–carbon compounds in BES.

### 6. Perspectives

In about one decade of research and development in the field of environmental electrochemistry, the functionality of microbial electrochemical technologies has expanded dramatically with modified and improved performance. Along with the main products (hydrogen, electricity, etc.), BES shows capabilities of recovering other valuable products such as heavy metals, nutrients, industrial chemicals and gaseous fuels. As discussed in this review article, BES carries great prospects for resource recovery; however, some biotechnological barriers and economic challenges are yet to be solved before it can be implemented at large scale and to be considered as an attractive alternative to the existing wastewater treatment methods. The negative energy balance of present wastewater treatment systems can be reversed if BES technology is utilized to recover the energy from organic carbon and phototrophic technologies are implemented for nutrients and other by-products recovery [104]. Based on the life cycle assessment (LCA) studied by Foley et al. [28], performance of MFC needs to be improved to produce more power, so as to establish it as a commercially viable and competitive solution comparable with existing anaerobic treatment technologies. This particularly demands attention in developing the low cost catalysts and efficient electrode materials to accelerate the oxygen reduction reaction on cathode for reducing the cathodic overpotential and to support higher current densities.

The production efficiency (or yield efficiency) of inorganic nutrients, heavy metals and organic chemicals by the aforementioned mechanisms in BES are listed in Table 2. Major BES studies have been conducted in laboratory scale and the technology is still having profound limitations for real world applications for wastewater reclamation and recovery of resources. However, further research efforts are required to upgrade the performance of BES by modifying the electrodes and separator assembly with low-cost, fouling resistant, conductive and bio-compatible materials to reduce the kinetic losses and develop a deeper understanding of bio-electrochemical processes to enable process optimization. Detailed economic and possible life cycle analyses are essential to understand the costs and benefits of specific resource recovery processes by BES, before scaling up for real-world applications. Future studies should emphasize more on resource

<table>
<thead>
<tr>
<th>Elements</th>
<th>Reactor/method used</th>
<th>Removal efficiency</th>
<th>Energy/current capture efficiency</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic carbon</td>
<td>ASBR (Anaerobic sequencing batch reactor)</td>
<td>58%</td>
<td>17.7 ± 10.1%</td>
<td>[104]</td>
</tr>
<tr>
<td></td>
<td>UASB (Upflow anaerobic sludge blanket)</td>
<td>69%</td>
<td>12.2 kJ/g COD</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ABR (Anaerobic baffled reactor)</td>
<td>90.3%</td>
<td>[24.0 ± 11.4%]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>AFB (Anaerobic fluidized bed)</td>
<td>82%</td>
<td>7.3 kJ/g COD</td>
<td></td>
</tr>
<tr>
<td></td>
<td>AnMBR (Anaerobic membrane bioreactor)</td>
<td>86.7%</td>
<td>[47.5 ± 4.5%]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MEC</td>
<td>78%</td>
<td>33.8 ± 12.9%</td>
<td></td>
</tr>
<tr>
<td></td>
<td>MFC</td>
<td>83%</td>
<td>9.7 kJ/g COD</td>
<td></td>
</tr>
<tr>
<td>Nitrogen</td>
<td>HRAp (High rate algal pond)</td>
<td>67.1%</td>
<td>[35.4 ± 26.8%]</td>
<td></td>
</tr>
<tr>
<td>PBR (Photobioreactor)</td>
<td>78.5%</td>
<td>14.3 ± 14.4%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stirred tank</td>
<td>62.3%</td>
<td></td>
<td>0.48 kJ/g COD</td>
<td></td>
</tr>
<tr>
<td>ATE (Algal turf scrubber)</td>
<td>70.5%</td>
<td>[1.6 ± 1.4%]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MFC</td>
<td>47–83%</td>
<td>[55,115,117]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Integrated photo–bio-electrochemical (IPB) system</td>
<td>63%</td>
<td>[116]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phosphorus</td>
<td>HRAP</td>
<td>52.1%</td>
<td>[104]</td>
<td></td>
</tr>
<tr>
<td>MFC</td>
<td>27.82%</td>
<td>[50,55]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PBR</td>
<td>93.2%</td>
<td>[104]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stirred tank</td>
<td>78.2%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MEC</td>
<td>78.6%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MEC</td>
<td>20–40%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH4: CO2 to CH4 in BES (at –0.65 V Ec vs. SHE)</td>
<td>0.055 ± 0.002 m mol/(day, mg VSS)</td>
<td>80%</td>
<td>90%</td>
<td>[59]</td>
</tr>
<tr>
<td>MEC by electromethanogenesis (at &lt; -0.7 V Ec vs. Ag/AgCl)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MEC (at –0.55 V Ec vs. SHE)</td>
<td>0.006 m3/m3 day</td>
<td>51.3%</td>
<td>[65]</td>
<td></td>
</tr>
<tr>
<td>H2 Bio-catalyzed electrolysis (applied voltage: 0.5 V)</td>
<td>0.02 m3/m3 day</td>
<td>53 ± 3.5%</td>
<td>[67]</td>
<td></td>
</tr>
<tr>
<td>Biocatalyzed electrolysis (at –0.7 V EC vs. SHE)</td>
<td>0.63 m3/m3 day</td>
<td>49%</td>
<td>[68]</td>
<td></td>
</tr>
<tr>
<td>H2O2</td>
<td>BES (applied voltage: 0.5 V)</td>
<td>1.9 ± 0.2 kg/m3/day</td>
<td>83.1 ± 4.8%</td>
<td>[64]</td>
</tr>
<tr>
<td>Ethanol</td>
<td>BES (at –0.7 V EC vs. SHE)</td>
<td>13.5 ± 0.7 mM</td>
<td>74.6 ± 6%</td>
<td>[72]</td>
</tr>
<tr>
<td>Triglycerides</td>
<td>Flat plate electrochemical cell (at –0.9 V EC vs. SHE)</td>
<td>Caprate: 739 mg/L</td>
<td>26%</td>
<td>[74]</td>
</tr>
<tr>
<td></td>
<td>Caprylate: 36 mg/L</td>
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<td></td>
</tr>
</tbody>
</table>
recovery to make the energy balance positive and develop better understanding of related mechanisms.

7. Conclusion

Bio-electrochemical system (BES) has been widely investigated for electrical energy recovery, bio-mediation, intermediate chemical production and recently, for useful resource recovery. This review mainly emphasized on third generation BES research for its potential to recover the other by-products i.e., heavy metals, nutrients, industrial chemicals, etc. from the wastewater. The recent development of bio-electrochemical technology offers a flexible platform for both oxidation and reduction oriented reactions leading to recovery of value added products while treating wastewaters. Further efforts are necessary to develop better understanding of the different mechanisms of resources recovery and the economic feasibility of engineering applications of field-scale BES technology.

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References


