



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 chemicals 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

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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 focussed 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) catalyse 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

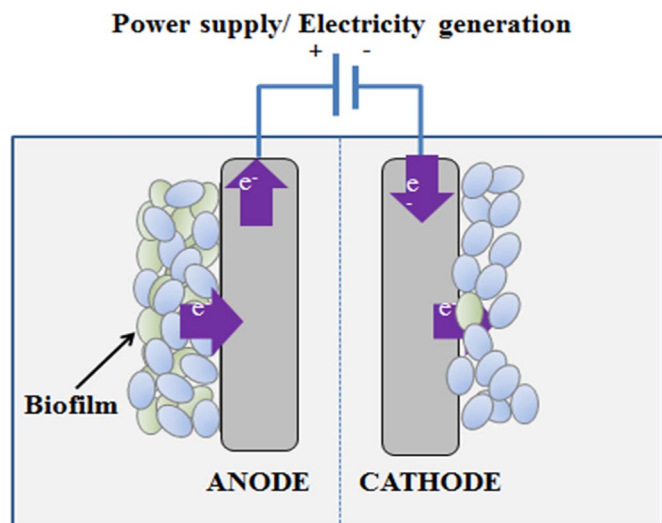


Fig. 1. Schematic diagram of bio-electrochemical system.

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

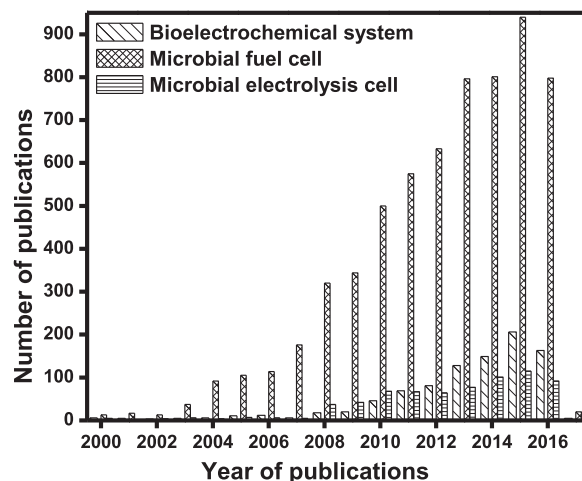


Fig. 2. Number of publications of the different modifications in bio-electrochemical system (Scopus data, accessed on January 15, 2017) [22].

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