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Integrated Bioelectrodialysis for Hydrogen Production from Biological Waste

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The ever-increasing need for energy and, at the same time, the depletion of fossil fuel resources have forced governments to find alternative energies. Renewable energies such as bio-energy can be worthy of attention from different aspects, including energy sources, energy efficiency and sustainable production, and preserving the environment and replacing fossil fuels. There are different types of bio-energy, including bio-ethanol, biogas, bio-diesel, and bio-hydrogen [1, 2]. Biological hydrogen is the hydrogen that is produced in biological processes, and is one of the cleanest sources of energy in the world [3]. Bio-hydrogen has a high energy density and produces only water vapor in the process of combustion. Therefore, unlike other conventional fuels, it does not have adverse environmental effects [4, 5]. Many waste materials (solid and industrial waste, wastewater sludge, waste from livestock and poultry industries, etc.) can be converted into biological hydrogen, which can also help in eliminating many environmental pollutants [6]. That is why there is an increasing interest in the field of hydrogen production.

Processes and microorganisms involved in the production of biological hydrogen

Hydrogen can be produced using non-biological methods such as electrolysis of water or the use of fossil fuels with partial oxidation of hydrocarbons or gasification process [7]. However, these methods, in addition to creating greenhouse gases and environmental pollutants, are not economically viable. Hydrogen production by biological processes is done using several techniques [8]:

1- Biophotolysis (direct and indirect)
2- Microbial water-gas conversion
3- Light fermentation
4- Dark fermentation
5- Microbial electrolysis

Among these, biophotolysis and photofermentation processes are dependent on light [9]. Direct and indirect photolysis produce purer hydrogen than the processes of dark fermentation and fermentation in the light. The biological hydrogen produced in the latter two processes, in addition to hydrogen and carbon dioxide, is accompanied by other gases such

as methane, carbon monoxide, hydrogen sulfide, and smaller amounts of ammonia, which require extensive purification processes [10]. Light-requiring processes are carried out in photobioreactors and dark fermentation processes are conducted in fermenters [2]. Different bacteria can participate in the production of biological hydrogen, including *Escherichia coli*, *Citrobacter*, *Enterobacter spp*, *Thermoanaerobacterium*, *Thermotogales*, *purple bacteria*, *Aeromonos spp*., etc. [11].

One of the recent technologies to produce clean hydrogen, which has recived much attention, is microbial electrolysis cell (MEC). MEC technology is very similar to microbial fuel cells and has great potential for wastewater and wastewater treatment. This system consists of an anode and a cathode separated by an ion exchange membrane (Figure 1) [1].

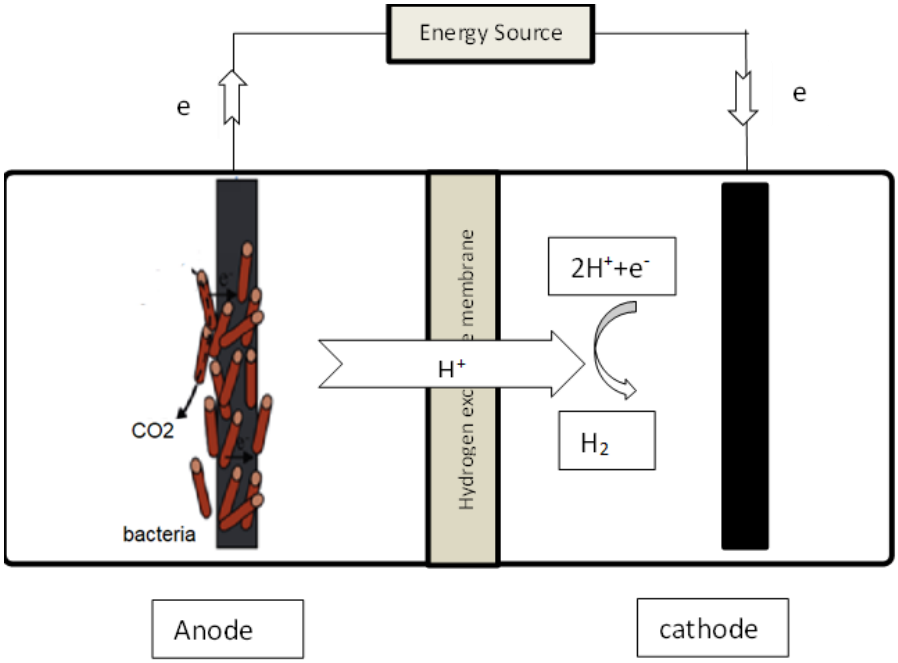

Figure 1: Schematic of a MEC

In MECs, microorganisms oxidize organic substrates in the anode, and the produced electrons reach the cathode through an external circuit, while the produced protons pass through an ion exchange membrane [12]. In this system, there is also an external electrical energy source to provide the necessary energy for the regeneration of protons and the production of molecular hydrogen in the cathode. It is due to the fact that the reaction does not take place spontaneously in terms of thermodynamics [13]. According to the type of substrate, the efficiency of hydrogen production will be different. Various microorganisms such as archaea, cyanobacteria and some bacteria such as Desulfitobacterium species and Dehalococcoides species and methanogenic and hemostogenic microorganisms can be used in this process [14].

Substrates for biohydrogen production

A wide range of substrates and residues are used to produce this biofuel according to the reaction method. Today, the increase in population has caused the accumulation of waste and residues to be one of the major problems of urban societies. However, using these wastes to produce hydrogen is a way to reduce these accumulated waste materials, which can simultaneously produce a product with high added value [15]. Also, many of these sources can be among the best substrates in biological hydrogen production due to having abundant nutrients such as lipids, minerals, and vitamins [3, 14]. One of the most available substrates for hydrogen production is lignocellulosic biomass, which has been receiving much attention for various reasons, including its abundance,

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renewability, and availability for hydrogen production. Waste from forests, agriculture, and animal manure are rich in these lignocellulosic sources [5]. These lignocellulosic masses are composed of three main parts, including cellulose (40%), hemicellulose (25%), and lignin (20%) (the remaining 15% are also very small components of inorganic compounds). Flax and hemp plant products, which are part of the strong structures for plant cells, can be rich sources of cellulose [16]. In order to use each of these components, it is necessary to carry out decomposition reactions to create monomeric units, which can be carried out by physical (hydrothermolysis - steam pressure), chemical (acid and base) and biological methods [12].

Limitations of bio-hydrogen production

Despite the major advantages of hydrogen production as biofuel, there may be problems with the production process. For example, when polymers such as cellulose are used as a substrate, some methods such as enzymatic hydrolysis are needed to break it down into monomeric units, which can be one of the most troublesome and costly steps [11]. In terms of engineering and designing suitable reactors for photo-fermentation, there are problems to provide suitable light for the process. Also, the exploitation and use of pure hydrogen and its storage is problematic, and there are limitations for supplying hydrogen as fuel in transportation [4]. In the production of hydrogen using the electrolysis method, the cost of production has become an important obstacle for the commercialization of the technology. Another issues is the availability of suitable electrodes in this field, which has recently been solved by using composites based on biopolymers such as bacterial nanocellulose [15]. Bacterial nanocellulose, despite its unique properties in this regard, it can be prepared on a large scale by microbial fermentation from inexpensive sources [12].

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