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THE TECHNOLOGY OF HYDROGEN GAS PRODUCTION FROM RESIDUAL WATERS IN TURKMENISTAN

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Introduction

At present, a considerable rise in world energy demand is under way due to population growth and the expansion of economies, mainly emerging ones. This implies a large growth in pollution, resulting in ever-larger green house gas emissions and global warming of the planet, with a consequent increase in the Earth's average temperature.

The need for a change in the world energy system and for an improvement in energy efficiency is obvious. Thus, the demands for efficient use of limited resources and the development of environmentally acceptable technologies are increasing, due to growing social awareness of reusing and recycling wastes.

Every day tons of wastewater are generated all over the world, for which no single treatment is able to reduce the water's contaminants to the permitted limits. Wastewater management is a challenge for many countries, as it is essential for human health, the environment, and sustainable economic development. The idea of using organic wastewater as a hydrogen source has arisen due to the difficulties in treatment of organic wastes. In addition, hydrogen generation is increasingly relevant due to its multiple applications and CO_2 zero emissions.

Hydrogen Economy

Hydrogen is the most abundant element in the universe, but is rarely found in a free form on Earth because of its chemical affinity. Usually, it appears combined with other elements, giving rise to compounds such as water, hydrides, or organic materials. It is an element having a higher energy yield, of 122 KJ/g. Hydrogen is not strictly an energy source, but a flexible energy carrier, which can be produced both from any primary energy source and locally available materials, such as biomass, wind, solar, geothermal, and organic waste.

For several years, the hydrogen vector concept has been developed as a complement to the electricity vector. Its main advantage over electricity is that it can be stored as a chemical energy support in gaseous, liquid, and solid (metal hydrides) phases. Stored hydrogen significantly benefits the reduction in gas emissions in the automotive sector, and aids in the decarbonization of industrial processes. In addition, it represents a high enthalpy storage mechanism for non-controllable renewable energy sources for real-time coupling of power flow generation and demand. Furthermore, fuel cells can transform hydrogen into electricity, as an energy source for applications that currently use fossil fuels. Hydrogen production processes have their origin in a wide variety of raw materials.

The main energy sources, renewable or otherwise, and some processes used for hydrogen production. Each of these technologies is at a different stage of development and offers different benefits, opportunities, and challenges. Most of these technologies are already commercially available for large-scale hydrogen industrial production. Other hydrogen production processes are still under development, such as the method here presented. Green means that it has no CO_2 emissions, grey means that it produces CO_2 emissions, and nuclear energy is represented by the colour violet. As there is not yet a wide market for hydrogen energy applications, more than 90% of the hydrogen generated is used on-site in the refinery industry, for desulphurization, in the chemical industry, as a chemical reagent for ammonia and fertilizer production, and in methanol production, with only 10% being used for other purposes.

The majority of hydrogen produced was obtained from fossil fuels, by-products in refineries or fossil with carbon capture and utilization; in contrast, the hydrogen production by fossil fuels with carbon capture and storage and electrolysis was much lower. The latter method, although less developed, holds great promise since, combined with renewable energy sources, it will considerably reduce the carbon footprint.

Electrolysis is being extensively studied and used for "green H₂" production, despite its negative energy balance, since the energy requirement for water electrolysis with an alkaline electrolyzer.

Wastewater: Impact and Types

Among the multiple organic residues, olive mill and biodiesel wastewaters are part of the residual waters group within residual organic liquids. Most urban, farming, and industrial activities require a large amount of water, which leads to the generation of a large quantity of wastewater. Most wastewaters are spilled onto the environment without any treatment due to weak regulations.

This has a detrimental impact on human health, economic productivity, freshwater resource quality, and the ecosystem. Sources of generated wastewater include domestic residences, commercial properties, industrial operations, cattle, and agriculture. Globally, about 80% of wastewater receives no treatment. Pollutants present in wastewater include pathogens (as bacteria, virus, and microscopic parasites), organic particles, soluble organic material, inorganic particles, toxins (e.g., herbicides, pesticides, dyes, or poisons), pharmaceuticals, household wastes, and even dissolved gases.

These wastewaters are a complex mixture of different organic and inorganic compounds, some of which are toxic and difficult to degrade, and are mainly treated by conventional technologies such as aerobic and anaerobic processes and chemical coagulation. As these techniques are not able to remove all of the harmful compounds, electrochemical treatments are being developed to complement them. Production processes give rise to large amounts of residual organic liquids such as beet root pulp, palm oil mill effluent, and wastewater from dairies, rice mills, chemicals, sago (large leaf palm), biomethanated distillate, paper and pulp, cheese whey, textile desizing, cassava, olive mills, protein, breweries, and biodiesel. Several research groups have used similar techniques to treat wastewater. NiFeMo hybrid film acts as cathode and anode materials in an electrolytic cell for hydrogen generation from urea electrolysis and the purification of urea-containing wastewater. They provide an easy method for synthesizing low-cost high-performance electrocatalysts.

from industrial contamination wastewater has Nitrate become a common environmental problem. The electrochemical reduction in NO_3^- from wastewater, aiming to enhance the efficiency of NO_3^- elimination and the selectivity of NO_3^- to N_2 . Results indicated that acidic conditions were suitable for direct and indirect nitrate reduction, while NO₃⁻ was mainly reduced via direct reduction under alkaline conditions. A laboratory-scale reactor to study the feasibility of the energetic valorization of winery effluents into hydrogen by means of dark fermentation and its subsequent conversion into electrical energy using fuel cells. The acidogenic fermentation generated a gas effluent composed of CO_2 and H_2 (55%), resulting in a hydrogen yield about 1.5 L per liter of fermented wastewater at standard conditions. An integrated bio-refinery concept combining two biological platforms for the valorization of palm oil mill effluents and for simultaneous production of high market value products, such as microbial oils and bio-energy. Palm oil mill effluents were aerobically fermented to produce lipids, and subsequently the effluent from the fermentation was used as influent feedstock in an anaerobic digester for biogas production. A maximum of 74% of the theoretical methane yield was achieved during continuous reactor operation. Other applications use microbial electrochemical cells (MECs) to produce renewable hydrogen and, simultaneously, wastewater treatment. Krishnan et al. indicated that MEC have the potential to convert organic wastewater into hydrogen and valueadded chemicals such as methane, ethanol, and hydrogen peroxide.

Compared to other conventional methods, MECs offer a high H₂ yield with a small energy input of 0.4–0.5 V. The principal components of the MEC are similar to those of the electrolysis process, i.e., the anode and cathode electrodes, semi-permeable membrane, electrochemically active microbes, and the power supply unit. Several types of wastewater, such as agricultural, domestic, and industrial wastewater, were analyzed. Microbial electrolysis cells of palm oil mill effluents for biological H₂ production can be successfully derived using modeling processes. These findings indicate that the maximum H₂ production rate can be affected by the incubation temperature, the initial pH, or the influent dilution rate. Experimental analysis revealed that under the optimum conditions of T = 30.23 °C, pH = 6.63, and a 50.71% dilution rate of the influent.

Electrolytic Process

In electrolytic processes, a compound is split into elements in the presence of an electric field. Among these processes are:

Electrolysis

Electrolysis consists of the dissociation or breakdown of the water molecule by the action of an electric field. Liquid water is split into its elemental components, molecular hydrogen and oxygen, according to:

$$H_2O \rightarrow H_2(g) + 1/2O_2(g)$$

This is a non-spontaneous reaction that requires an external energy input. The cell voltage required for water dissociation is 1.23 V under standard conditions. However, the main drawback, which limits the efficiency of the process, is the sluggish kinetics of the water–oxygen couple (both the oxidation of water into oxygen and the reduction of oxygen into water) under near-room temperature conditions.

When the electrolysis cell is operated with current densities of at least 1 A/cm², to obtain a high hydrogen production rate at the cathode, a high overvoltage occurs. As a result, cell voltages of 1.8-2.0 V are generally required to reach significant hydrogen production rates, leading to energy conversion efficiencies of less than unity. This overvoltage is responsible for the energy cost of hydrogen production by water electrolysis. Cell voltages in the range of 2.5-4.5 V were applied in the tests carried out for this research.

The process takes place in an electrolyzer, which consists of two electrodes, i.e., an anode and a cathode, facing each other and separated by a thin layer of ionic conductor, called the electrolyte. Electrodes plugged in to an external power supply provide the energy required to generate free hydrogen at the cathode.

To maintain the charge balance, when a voltage is applied to the electrodes, electrons flow from the negative terminal (anode) to the cathode, where they are consumed (reduced) by protons to form hydrogen. At the same time, ions travel through the electrolyte to the corresponding electrode, where a reaction occurs, giving up electrons that return to the power supply terminal. The charges carried by the ionic compounds, such as OH^- , H^+ , or O^{2-} , move through the electrolyte to maintain the system electrical neutrality. According to the ionic conducting electrolyte, there are three types of electrolyzers: alkaline, proton exchange membranes (PEMs), and high



temperature solid oxides (SOEs).

Figure 2. Classification of water electrolyzer. Electro-Oxidation

The biological processes of wastewater primary treatment are not capable of degrading colored compounds, and are only suitable for wastewater having a low content of biodegradable materials. Wastewater treatment by electrochemical processes gives rise to chemical reactions aimed at the elimination of these contaminants. Electrochemical wastewater treatment is carried out using different techniques: electrocoagulation, electrofloculation, electrodeposition, and electro-oxidation, among others. In the electro-oxidation process, oxidants are produced during in situ treatment, either directly on the surface of the electro-oxidation process is either the total oxidation (or mineralization) or partial oxidation (conversion of organic matter to simpler, more easily degradable and less polluting compounds) of organic matter.

An electro-oxidation process can also be defined as an electrolysis process with the presence of an organic compound as an energy source. The electrolysis process has a variable cost depending on the energy consumption per kilogram of hydrogen produced. Therefore, it is essential to reduce the quantity of energy used to be competitive with conventional industrial hydrogen production processes. The presence of organic matter having a low oxidation potential implies a reduction in the cost of the hydrogen production.

Conclusions

The current work presents an electrolysis system based on an own-design reactor, and the process to obtain hydrogen by alkaline electrolysis assisted by two types of wastewater, i.e., olive mill and biodiesel wastewaters, and two organic compounds, i.e., glycerol and methanol for comparative purposes. Hydrogen was generated with different purity levels, a low production of undesired gases, such as O_2 , CO, CO₂, N_2 , and CH₄, and simultaneous reduction in the organic contaminants.

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