Nāsadīyam
A Multi-Disciplinary National Research Journal (Annual)
Peer Reviewed/Refereed
Available online at: https://nasadiyam.dmmkkr.ac.in/
Volume 2, Issue 1 (Jan – Dec), 2023, Pp 71-84

Harnessing the Energy Potential of Wastewater: A Pathway towards Sustainable Hydrogen Production

Mr. Gurvinder
Research Scholar (Department of Physics)
Kurukshetra University
Kurukshetra, Haryana, India
Email Id : gurvindersingh765@gmail.com
Mobile No.: 8950215939

Mrs. Prabhjot Kaur
Assistant Professor (Department of Mathematics)
Dayanand Mahila Mahavidyalaya
Kurukshetra, Haryana, India
Email Id :prabhjotkaur0117@gmail.com
Mobile No. : 8950115939

ABSTRACT

With the growing demand for clean and sustainable energy sources, the exploration of alternative options has become imperative due to environmental concerns associated with fossil fuel usage. Hydrogen has emerged as a promising candidate owing to its high energy content and environment friendly combustion, which results in only water vapor as a by-product.Wastewater, generated from domestic, industrial, and agricultural activities, presents an attractive opportunity for hydrogen production. Traditional wastewater treatment methods typically focus solely on pollutant removal and often overlook the energy potential inherent in wastewater. This review discusses different approaches, such as electrochemical, photocatalytic, and microbial electrolysis processes, which harness the energy present in wastewater for hydrogen generation. Advantages and limitations of each method have been discussed in the light of materials used for hydrogen production.

Keywords: Hydrogen Production, Electrolysis, Green House Gas Emission

INTRODUCTION

Energy plays a crucial role in driving social, economic, and political development towards safer and cleaner living standards [1]. However, the exploitation of fossil fuels to meet the global energy demands has led to numerous challenges. The excessive use of fossil fuels has not only resulted in oil crises and subsequent price hikes but has also contributed to the higher concentration of greenhouse gas emissions. These emissions have led to adverse effects such as the increase in average global temperature, climate change, ozone depletion, and negative impacts on both human and animal life [2]. Therefore, there is an urgent need for sustainable, efficient, and clean energy sources to meet the growing energy demands.

Among the available options, hydrogen is emerging as a major clean fuel. It boasts a high energy content of 122 kj/g and does not produce any secondary emissions since water is its only by-product. Hydrogen is also the most abundant element in nature according to the periodic table. It can be utilized across various energy sectors including transportation, industry, power generation, and the production of chemicals like methanol, ammonia, and agricultural fertilizers [1]. Additionally, hydrogen fuel cells show promise in reducing CO_2 emissions, thus contributing to environmental preservation.

Hydrogen, however, exists in a combined form, primarily as water, due to its highly reactive nature, and lacks fuel value in its molecular form [3]. Currently, most hydrogen production processes rely on conventional fuels, which hinder the realization of clean and sustainable technology. As industrialization continues to expand, the demand for water and energy intensifies, resulting in significant pollution, health hazards, and threats to ecosystems due to the improper disposal of wastewater. Shockingly, globally, approximately 80% of wastewater remains untreated. Traditional wastewater treatment methods focus on pollutant degradation but require a substantial amount of chemical energy.

In recent years, the simultaneous treatment of wastewater and the generation of eco-friendly fuel, such as hydrogen, has gained attention. Various methods for producing hydrogen from wastewater have been explored, including electrochemical, photocatalytic, and microbial electrolysis processes. Thus, present literature predominantly focuses on process aspects, and role of different materials involved in wastewater treatment and hydrogen production.

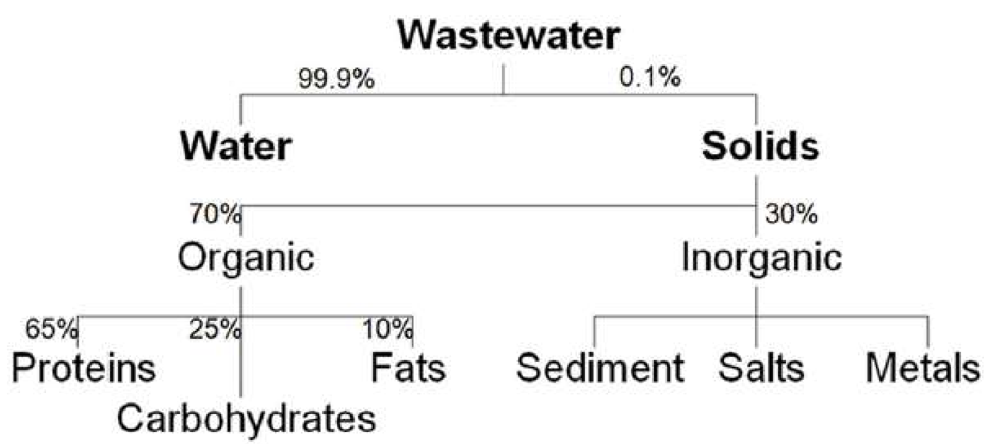
WASTEWATER AND ITS TYPES

Water is an essential resource for the survival of biodiversity, but human and industrial activities consume vast amounts of water, leading to the generation of enormous wastewater. While some level of water pollution occurs naturally, most of it is a result of human activities. Wastewater, also known as sludge, is a combination of liquid or water-carried waste from residences, industries, and institutions, which includes groundwater, surface water, and stormwater. It contains suspended solids that consist of human waste, food waste, metals, organic and inorganic solids, as well as disease-causing pathogens as depicted in figure 1 [4].

In developing countries, the pollution of rivers and streams with industrial chemicals and agricultural toxins like pesticides and fertilizers poses a significant environmental problem, contributing to diseases such as cancer, cholera, and diarrhoea [2].

Wastewater can be classified into four categories based on the source of contamination:
(A) Domestic wastewater, further classified as grey and black wastewater, refers to water discharged from residences and commercial institutions. Greywater or sullage originates from laundries, washrooms, and kitchens, excluding feces, while blackwater consists of urine and feces.
(B) Industrial wastewater comprises discharges from industries and agriculture, including pharmaceuticals, textiles, and paper mills.
(C) Infiltration refers to contamination with sewage water through leaking joints, cracks, and porous walls.
(D) Stormwater runoff is the mixing of sewage water with floodwater due to rain [5]. It occurs when water enters drains or sewers from streets, backyards, terraces, etc.

Figure 1: The typical approximate composition of wastewater.



Other terminologies used for wastewater are as follows: sewage refers to blackwater once it enters the sewerage system, septage is the term for blackwater when it joins the septic tank, influent is wastewater before it enters the treatment plant, and effluent is the term used for discharged wastewater from the treatment plant. The semi-solid waste left behind in operational units is known as sludge. On-site systems involve wastewater disposal without transportation, such as dry methods within houses, while off-site systems dispose of wastewater away from the production site, including vaults containing pour-flush toilets and traditional sewerage systems [6].Most types of wastewater contain a large amount of organic pollutants that significantly harm the environment. Some of these pollutants are highly toxic, even in low concentrations, posing serious health hazards. Therefore, the development of well-established techniques to remove these pollutants has become a focal point for researchers [7-10]. Some studies have shown that the organic pollutants present in wastewater can serve as good electron donors, making them important as a potential source of energy [11]. Conventional wastewater treatment methods, such as membrane separation, activated carbon adsorption, and ozone oxidation technology, have achieved remarkable treatment results [12]. However, these methods primarily focus on the separation, destruction, and degradation of toxic compounds, leaving a substantial amount of chemical energy unused. Therefore, the effective processing of wastewater and the utilization of the electrons produced in this process have become areas of great concern [13].

In this regard, Microbial Fuel Cells (MFCs) offer a solution by using microorganisms to convert the chemical energy present in wastewater into electrical energy during the treatment process [14, 15]. However, due to their relatively low conversion efficiency, MFCs are often hybridized with photo electrocatalysis for more effective hydrogen production. By harnessing wastewater, solar light, and photoactive materials, the combination of Photoelectrochemical Cells (PECs) and MFCs can be employed for electricity or hydrogen production [16,17]. This work will delve into the details of the materials used in wastewater treatment as a source for hydrogen production, along with various treatment methods.

METHODS FOR WASTEWATER TREATMENTS

Wastewater treatment and its safe disposal is a great challenge and researchers, environmentalists are looking for sustainable and suitable technologies for its treatment and reusability. Wastewater treatment processes designs to remove suspended solids and biochemical oxygen demands. The extent of wastewater treatment depends upon the quality of receiving water and the purpose of reusability of treated water and these are monitored by various government agencies which sets the degree and quality requirements of the purification process. In view of nature of contaminants, wastewater treatment can be classified into physical, chemical, and biological processes. Physical unit operations involve the application of physical force for removing the contaminants and various physical methods are screening, communication, flow equalization, sedimentation etc. Whereas, in chemical treatment methods various elimination and conversion of contaminants carried out by addition of chemicals or by chemical reaction, these involves chemical precipitation, disinfection, dichlorination.Biological unit operations utilize various biological activities to remove toxic chemicals like nitrogen, phosphorous, sulphates and biodegradable organic substances into gases that escapes to atmosphere. These unit processes combined with operations in a treatment plant depending on the degree of treatment can be categorized into three levels called primary, secondary, and tertiary treatment.

(A) Primary Treatment units

Primary treatment unit involves preliminary treatment of wastewater including only physical operations to remove coarse solids and other large materials found in water. The objective of this treatment is to either eliminate or reduce the size of large suspended or floating solids comprise of large woods, plastics, clothes, debris, metal pieces etc. which commonly called as grit. After these preliminary treatments the primary treatment involves screening, sedimentation, filtration. To remove large solids of floating and suspended matter, water is passed through sets of inclined parallel bars of height of 18 to 75 mm and width of 25- 75 mm called screen bars and passed to grit chamber where sand. Gravel or other solids with specific gravity about 2.65 are removed by allowing free settling of solids. For the optimum efficiency the width of the grit chamber should be in between 1 m to 1.5 m. However, oil, grease, soap, vegetables, fruit skins remain in the water. To remove this kind of stuff, skimming tanks are used which consist of a designed chamber with provision of compress air supply. This led to floatation of matter, oil and prevent settling of heavy solids until these are removed and process is called floatation. Finally, the effluent from skimming tank is passed to primary sedimentation tank with sloppy walls where the water is detained for 90 – 150 minutes resulting in removal of readily settable solids. Primary treatment led to removal of 25- 50% Biochemical oxygen demand (BOD), 50-70% suspended solids and up to 65% of the oil and grease from water [18,19].

(B) Secondary Treatment

Secondary treatment of water can be done either by chemical unit processes such as chemical oxidation, chemical precipitation etc. or by employing biological route in which bacteria in presence of or absence of oxygen are used as catalyst for removal of pollutants. Currently, biological treatment processes are most used for converting colloidal and dissolved carbonaceous organic matter into various gases like CO_2, NH_3, and cell tissue. For efficient biological treatment wastewater must be free from toxic organic and inorganics as it includes aerobic and anaerobic digestion of water.

- **Aerobic Process**

In the presence of dissolved oxygen in wastewater, biodegradable organic matter undergoes aerobic decomposition caused by aerobic and facultative bacteria, resulting in CO_2, water, bacteria, and by-products like methane etc.

$$\text{Organic matter} + O_2 + \text{Bacteria} \rightarrow CO_2 + H_2O + \text{Bacteria} + \text{By-products} \quad (1)$$

Biological reactor for aerobic decomposition of organic matter consists of filters (tricking filters), activated sludge process (ASP), and oxidation ponds etc. The bacterial cells are disposed off after separating from secondary settling tanks. Trickling filters are made up of round shaped tank filled with volcanic rock, gravel, or synthetic material. As the wastewater tickles through the filter media, a biological slime consisting of aerobic bacteria builds up around the media surface. This film after growing to certain thickness falls off the filter. This process is called sloughing. Detached layer is removed by under drainage system and transferred to clarifier for its removal. This process continues and is efficient enough to remove upto 90% of the biodegradable organics. Activated sludge process consist of aeration in an aeration tank for flow of air that led to formation of flocs of bacteria (activated sludge) which stabilizes the organic matter. In this process, some part of the organic matter is converted into new cells and other part is oxidized to drive energy. This removes BOD and suspended solids. Biomass generated in aeration tank is separated in secondary settling tank. In order to maintain the concentration of active bacteria in the tank, some portion of the activated sludge is recycled into the aeration tank. This treated wastewater is transferred to secondary settling tank (SST) where the thickening of sludge takes place followed by compression. Finally, sludge drying beds are used to dewater the sludge prior to final disposal. This includes either filtration of water through sand or evaporation. This filtered water is sent for further purification treatment.

- **Anaerobic Treatment**

In last few decades anaerobic treatment is more preferred then aerobic treatment to treat complex organic solid wastes. Due to limited past knowledge anaerobic reactors were more expensive and less stable but these limitations have been overcome by the new technologies, providing a pathway for economical viable alternative to aerobic treatment. Anaerobic and facultative bacteria digestion convert organic matter into nitrogen, ammonia hydrogen, methane etc. which are valuable industrial chemicals. Also, no oxygen and low nutrient requirement makes this process attractive over aerobic treatment.

$$\text{Organic matter} + \text{bacteria} \rightarrow CO_2 + CH_4 + \text{Bacteria} + \text{byproduct}$$

Anaerobic biological conversion involves three processes. First process is called hydrolysis in which high molecular mass is converted into simpler compound which are source of energy like hydrogen, CO_2, fatty acids, alcohol etc. In second step, known as acidogenesis, conversion of of compounds obtained from first step to lower molecular mass compounds like acetic acid, hydrogen etc. takes place. In the final step which is a slow reaction process due to slow doubling rate called methanogenesis converts the intermediate compounds like methane and CO_2. Only in third step BOD is reduced while it remains unchanged in first two steps.Production of these energy source chemicals is a great advantage of anaerobic process over the aerobic process. However, anaerobic process efficiencies are strongly dependent on temperature, pH and concentration of toxic substances. With new technologies these limitations will be overcome making this process most preferred for wastewater treatment[18,20,21].

(C) Tertiary Treatment

Tertiary treatments are also known as advanced treatments and are combinations of two or all three processes units i.e., physical, chemical, and biological unit processes used after the secondary treatment. Tertiary treatment involves removal of organic matter, sewage nutrients and killing of pathogens. Tertiary treatment is final treatment before discharging water to sea, river, lake, ground etc. Tertiary treatment includes distillation, Crystallization, evaporation, ion exchange, reverse osmosis etc. Depending upon the source of wastewater and degree of purification, combination of above-mentioned processes are used. Distillation is very common process in which water is heated up to 100° C resulting in vaporization which on cooling converted into liquid water. This method is useful when impurities are either non-volatile or have boiling temperature greater than that of water. However, it is a costly process. Wastewater from fired boilers, paper and dying industries is usually treated by crystallization in which pollutant concentration is increased till crystallization occurs by evaporating water with the help of other solvents that lead to lowering of temperature of water. This results in good quality water but this method is not cost effective. Evaporation is another commonly used method for wastewater excreted from fertilizers, petroleum, and pharmaceutical companies. In this process water molecule evaporates under natural condition resulting in pure water in collection tanks. Ion exchange is another innovative method for removing toxic ions present in the wastewater. Ion exchangers are in the form of resins and are capable of exchanging cations and anions depending upon the nature of the resin. Most used resins are zeolites, polystyrene, sulphonic acid etc. Although it is very effective method but rising cost of resins are replacing this technology with superior membrane reverse osmosis in which pressure greater than the osmotic pressure is applied to remove the pollutants up to nano range. This method can remove up to 99% of the solids, organic dissolved matter, and bacteria. To increase the efficiency of this process micro and ultra-filtration cartridges are used before this process, to remove particles of 0.04 µm to 1 µm in size. Despite of these processes there are other processes like oxidation, electrodialysis which can accompany above mentioned tertiary methods to increase the purity of treated water[18,21].

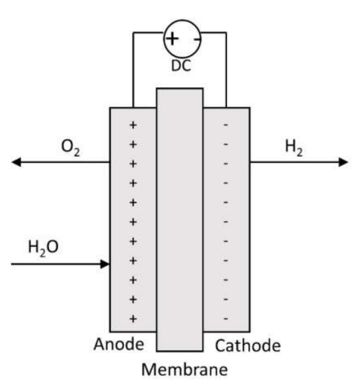
HYDROGEN GENERATION FROM WASTE WATER

Several methods commonly used for hydrogen production from wastewater are as follows:

(A) Electrochemical Methods:

- **Electrolysis:** Electrolysis is a well-known method for hydrogen production. In this process, an electric current is passed through system consisting of electrodes and water, leading to the electrolysis of water molecules into hydrogen gas (H_2) and oxygen gas (O_2). Electrolysis can be performed using different electrolytes, such as alkaline, acidic, or solid oxide electrolytes. The schematic diagram of electrolysis has been shown in figure 2. It offers high purity hydrogen production but requires energy input for the electrolysis process. Wang etal. [22] has studied the $NiCo_2O_4$ nanosheets to produce hydrogen from urea. Hu et al. [23] studied the electrolysis process with ammonia, urea, and hydrazine. Huang Lijun et al. [24] reported the production of hydrogen using wastewater.

Figure 2 : Schematic view of electrolysisreaction



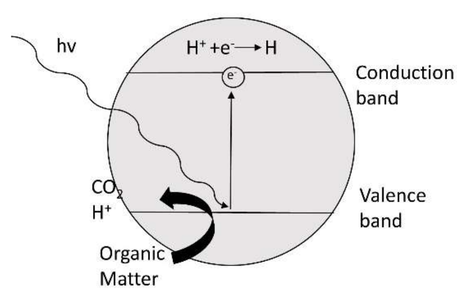
- Microbial Electrolysis Cells (MECs): MECs are a variant of electrolysis that employs microorganisms to enhance hydrogen production. In MECs, bacteria or archaea are used as catalysts to facilitate the electrochemical reactions at the anode. The microorganisms oxidize organic matter in the wastewater and transfer electrons to the anode, resulting in the generation of hydrogen gas at the cathode. MECs offer the advantage of utilizing organic matter in wastewater as a renewable energy source for hydrogen production.Jayabalanet al.[25] has studied the production of dihydrogen from wastewater of sugarcane industry using metal oxide/graphene-based catalyst and reported the hydrogen recovery of around 20%.

Electrolysis method offers the advantage of high purity hydrogen, separation of nitrogen from waste water but this technology is still in R& D phase and requires costly electrolytes.

(B) Photocatalytic Methods:

Photocatalysis is a promising approach for hydrogen production that utilizes light energy and a photocatalyst to drive the reaction. Semiconductor materials, such as titanium dioxide (TiO2), zinc oxide (ZnO), or modified metal oxides, are commonly used as photocatalysts. When these materials are exposed to light, they absorb photons and generate electron-hole pairs, which can facilitate the decomposition of organic pollutants in wastewater as depicted in figure 3. As a result, hydrogen gas is released as a by-product of the photocatalytic reaction. Photocatalytic systems offer the advantage of simultaneously treating wastewater and producing hydrogen, making them environmentally friendly. Vaiano et al.[26] has reported Ru-modified ZnO for dyewater treatment. Carbon nitridebased composites have extensively used in photocatalytic methods for simultaneous wastewater treatment and hydrogen production[27].

Figure 3 : Schematic view of Photocatalytic reaction



The main advantage of this method is that sunlight can be used as light source however, the solar light to hydrogen conversion efficiency is limited. In addition, the use of toxic materials as photocatalyst makes this method less attractive.

(C) Microbial Methods:

Microbial processes involve the use of specific microorganisms to produce hydrogen through metabolic pathways. Two common microbial methods for hydrogen production are:

- Dark Fermentation: Dark fermentation utilizes anaerobic bacteria to ferment organic matter in wastewater in the absence of light. The bacteria break down complex organic compounds into simpler compounds, producing hydrogen as a metabolic byproduct. Dark fermentation can be an effective method for hydrogen production, particularly from complex organic substrates. However, the hydrogen production is limited to anaerobic digestion process.
- Photo fermentation: Photofermentation employs photosynthetic bacteria that can utilize light energy to convert organic matter into hydrogen gas. These bacteria, such as purple non-sulphur bacteria, use light as an energy source for their metabolic activities, resulting in the production of hydrogen gas. Photofermentation is a promising method due to its ability to directly harness solar energy for hydrogen production. Most commonly microalgae Chlamydomonas reinhardtian species for photofermentation. Tao et al. [28] reported rhodobactersphaeroides for the hydrogen production from wastewater containing Carbon. Rhodobacterspheroids also used for treatment of wastewater from diaries and sugar industries.

(D) Thermochemical Methods:

Thermochemical processes involve the use of high temperatures to drive chemical reactions for hydrogen production. Two common thermochemical methods are:

- Gasification: Gasification is a process where organic components in wastewater are heated in the presence of a controlled amount of oxygen or steam. The high temperature breaks down complex organic compounds into simpler gases, including hydrogen, carbon monoxide, and carbon dioxide. The produced syngas can be further processed to separate and purify the hydrogen gas.

- In pyrolysis process degradation of chemical molecules takes place in inert atmosphere in temperature range of 300 °C to 900 °C leading to formation of liquid fuels, hydrogen, char, methane, and water vapours. Methane and water vapours are further processed to produce more hydrogen.

Thermochemical methods offer advantage of high hydrogen production potential, compatibility with different types of organic matter, and the ability to utilize waste heat from other processes. However, it has limitations of high energy input requirement, complex reactor design, potential for carbon formation and catalyst deactivation, and the need for gas clean up to obtain pure hydrogen.

CONCLUSION

The utilization of wastewater as a source for hydrogen production offers a promising avenue for addressing energy demands while simultaneously tackling environmental concerns. This review has shed light on the potential of wastewater as a valuable resource for clean energy generation. By incorporating energy recovery mechanisms into wastewater treatment processes, we can harness the untapped energy potential and convert it into hydrogen gas.

Various methods, such as electrochemical, photocatalytic, and microbial electrolysis processes, have been explored to extract energy from wastewater and generate hydrogen. These approaches demonstrate promising results in terms of hydrogen production efficiency. Additionally, the integration of advanced materials, such as $NiCo_2O_4$ nanosheets, holds great potential for improving the performance of wastewater treatment and hydrogen production systems.

In conclusion, the integration of wastewater treatment and hydrogen production offers a dual benefit of addressing energy needs while mitigating environmental concerns. Further research and development in this field are crucial to optimize energy recovery efficiency, explore new materials, and enhance the scalability and cost-effectiveness of wastewater-based hydrogen production systems. By harnessing the power of wastewater, we can contribute to a sustainable and clean energy future.

REFERENCES

1. Lee, R. (2011). The outlook for population growth. *Science*, *333*(6042), 569-573.
2. Hoffmann, P. (2019). *The forever fuel: the story of hydrogen*. Routledge.
3. Sharma, S., & Ghoshal, S. K. (2015). Hydrogen the future transportation fuel: From production to applications. *Renewable and sustainable energy reviews*, *43*, 1151-1158.

4. Templeton, M. R., & Butler, D. (2011). *Introduction to wastewater treatment*. Bookboon.
5. Sonune, A., & Ghate, R. (2004). Developments in wastewater treatment methods. *Desalination*, *167*, 55-63.
6. Bani, R. (2011). Wastewater management. In *Waste water-Evaluation and management*. IntechOpen.
7. Ali, I. (2012). New generation adsorbents for water treatment. *Chemical reviews*, *112*(10), 5073-5091.
8. C. C. Wang, J. R. Li, X. L. Lv, Y. Q. Zhang and G. Guo, Energy Environmental Science, 2014, 7, 2831-2867.
9. Shi, H., & Zhao, G. (2014). Water oxidation on spinel NiCo2O4 nanoneedles anode: microstructures, specific surface character, and the enhanced electrocatalytic performance. *The Journal of Physical Chemistry C*, *118*(45), 25939-25946.
10. Yang, G., Zhang, G., & Wang, H. (2015). Current state of sludge production, management, treatment and disposal in China. *Water research*, *78*, 60-73.
11. Strataki, N., Antoniadou, M., Dracopoulos, V., & Lianos, P. (2010). Visible-light photocatalytic hydrogen production from ethanol–water mixtures using a Pt–CdS–TiO2 photocatalyst. *Catalysis Today*, *151*(1-2), 53-57.53-57.
12. Martínez-Huitle, C. A., Rodrigo, M. A., Sirés, I., & Scialdone, O. (2015). Single and coupled electrochemical processes and reactors for the abatement of organic water pollutants: a critical review. *Chemical reviews*, *115*(24), 13362-13407.
13. Cambie, D., Bottecchia, C., Straathof, N. J., Hessel, V., & Noel, T. (2016). Applications of continuous-flow photochemistry in organic synthesis, material science, and water treatment. *Chemical reviews*, *116*(17), 10276-10341.
14. Yuan, H., & He, Z. (2015). Graphene-modified electrodes for enhancing the performance of microbial fuel cells. *Nanoscale*, *7*(16), 7022-7029.
15. Yang, W., Kim, K. Y., Saikaly, P. E., & Logan, B. E. (2017). The impact of new cathode materials relative to baseline performance of microbial fuel cells all with the same architecture and solution chemistry. *Energy & Environmental Science*, *10*(5), 1025-1033.
16. Wang, H., Qian, F., Wang, G., Jiao, Y., He, Z., & Li, Y. (2013). Self-biased solar-microbial device for sustainable hydrogen generation. *ACS nano*, *7*(10), 8728-8735.

17. Arun, J., SundarRajan, P., Pavithra, K. G., Priyadharsini, P., Shyam, S., Goutham, R., ... & Pugazhendhi, A. (2024). New insights into microbial electrolysis cells (MEC) and microbial fuel cells (MFC) for simultaneous wastewater treatment and green fuel (hydrogen) generation. *Fuel*, *355*, 129530.
18. Sonune, A., & Ghate, R. (2004). Developments in wastewater treatment methods. *Desalination*, *167*, 55-63.
19. Quach-Cu, J., Herrera-Lynch, B., Marciniak, C., Adams, S., Simmerman, A., & Reinke, R. A. (2018). The effect of primary, secondary, and tertiary wastewater treatment processes on antibiotic resistance gene (ARG) concentrations in solid and dissolved wastewater fractions. *Water*, *10*(1), 37.
20. Campos, C. J., Avant, J., Lowther, J., Till, D., & Lees, D. N. (2016). Human norovirus in untreated sewage and effluents from primary, secondary and tertiary treatment processes. *Water Research*, *103*, 224-232.
21. Koivunen, J., & Heinonen-Tanski, H. (2005). Peracetic acid (PAA) disinfection of primary, secondary and tertiary treated municipal wastewaters. *Water research*, *39*(18), 4445-4453.
22. Wang, D., Vijapur, S. H., Wang, Y., & Botte, G. G. (2017). NiCo2O4 nanosheets grown on current collectors as binder-free electrodes for hydrogen production via urea electrolysis. *International Journal of Hydrogen Energy*, *42*(7), 3987-3993.
23. Hu, S., Tan, Y., Feng, C., Wu, H., Zhang, J., & Mei, H. (2020). Synthesis of N doped NiZnCu-layered double hydroxides with reduced graphene oxide on nickel foam as versatile electrocatalysts for hydrogen production in hybrid-water electrolysis. *Journal of Power Sources*, *453*, 227872.
24. Huang, L., Fang, C., Pan, T., Zhu, Q., Geng, T., Li, G., ... & Yu, J. (2024). Hydrogen Production via Electrolysis of Wastewater. *Nanomaterials*, *14*(7), 567.
25. Jayabalan, T., Matheswaran, M., Preethi, V., & Mohamed, S. N. (2020). Enhancing biohydrogen production from sugar industry wastewater using metal oxide/graphene nanocomposite catalysts in microbial electrolysis cell. *International Journal of Hydrogen Energy*, *45*(13), 7647-7655.
26. Vaiano, V., & Iervolino, G. (2019). Photocatalytic removal of methyl orange azo dye with simultaneous hydrogen production using Ru-modified ZnO photocatalyst. *Catalysts*, *9*(11), 964.

27. Zhang, L., Zhang, J., Xia, Y., Xun, M., Chen, H., Liu, X., & Yin, X. (2020). Metal-free carbon quantum dots implant graphitic carbon nitride: Enhanced photocatalytic dye wastewater purification with simultaneous hydrogen production. *International Journal of Molecular Sciences*, *21*(3), 1052.
28. Tao, Y., He, Y., Wu, Y., Liu, F., Li, X., Zong, W., & Zhou, Z. (2008). Characteristics of a new photosynthetic bacterial strain for hydrogen production and its application in wastewater treatment. *International Journal of Hydrogen Energy*, *33*(3), 963-973.