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Utilization of Wastewater with Optimized Voltage for Electrolytic Green Hydrogen Production: Experimental Study

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In this study, the electrolysis of industrial wastewater was carried out at different voltages for green hydrogen production rate (HPR). Voltages selected for the study are 1.3 V, 3 V, 6 V, 9 V, 12 V, and 15 V. It was found that at a high voltage range, the electrolytic hydrogen production rate was high, but the efficiency of the system did not follow a similar trend of increase with selected wastewater. It was found that with an increase in voltage (1.3 V to 15 V) the HPR increased up from 0.05 ml/hr to 8.45 ml/hr while the highest optimized efficiency of 20.68 % was achieved at 3 V with carbon electrodes.

Keywords: Green hydrogen; wastewater; electrolysis; water splitting; laundry wastewater

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Hydrogen (H_2) being a potential energy carrier is being seen as a hope to replace a major proportion of energy in the near future as a safe and reliable alternative fuel. Only a limited quantity of H_2 is present in its pure form. However, it can be separated from its pure forms such as fossil fuels and water (H_2O).

In the present scenario, H_2 is considered a desirable source of fuel because when it burns, it produces water as a byproduct. As a consequence, no greenhouse gas emissions, and no major air pollutants (CO, NO_x, SO_x, major particulate matters like aerosols etc.) are emitted into the atmosphere. Some other physio-chemical properties like high energy density, lighter weight, and quick dispersion rate during release, make it a part of attention in the research community. Although it is a colourless gas it is felicitated by colour codes as per their route of production, such as, black H_2 (from coal), grey H_2 (from natural gas), brown H_2 (from lignite), and green H_2 (from renewable energy sources and water electrolysis). The commercial H_2-producing technologies at present are steam methane reforming (SMR), coal and biomass gasification. Water splitting using electrolysis method can also be used for H_2 production. Recent research studies are also oriented towards H_2 production through electrolysis. The electrolysis incorporates three main technologies i.e. proton exchange membrane electrolysis (PEMEL), solid oxide electrolysis (SOEL), and alkaline water electrolysis (AEL) [1]. These methods provide unique advantages and are specifically designed for different H_2 production applications. Theoretically, a minimum voltage of 1.23 V (at 25°C/298K at 1 atm) is required to split H_2O into H_2 and Oxygen (O_2) [2]. Pure water due to the absence of any electrolytes does not conduct electricity but normal water such as tap water conducts electricity up to some extent due to the presence of ions such as Ca^{2+}, Mg^{2+}, Na^+, HCO_3^-, and SO_4^{2-}. In electrolysis, a Direct Current (DC) source is connected to water containing electrolytes in any form. In electrolysis, the electrolytic solution is connected to the anode and cathode using suitable electrodic materials (carbon/platinum/composite materials/coated materials). H_2 is produced at the cathode while O_2 is produced at the anode. During electrolysis, it is common to use a catalyst for water splitting. Water splitting is significantly enhanced by alkaline waste-water, because of its high pH levels. This creates ideal conditions for H_2 production. Dissolved particles in wastewater can act as catalysts, enhancing the rate of H_2 production. Similarly, the use of abundant electro-catalyst materials during the process of electrolysis is also an important parameter to increase the overall efficiency of the process at laboratory and commercial scales. Furthermore, electrocatalytic water splitting proceeds by green electricity i.e. high-grade electricity via renewable energy technologies (solar/wind/hydro/ geothermal etc.) is helpful in the production of H_2 with a minimum contribution to CO_2 footprints. In similar routes, wastewater may be a potential feedstock for green electrolytic H_2 production because dissolved particles in wastewater can act as catalysts, enhancing the rate of H_2 production due to the presence of ionic constituents.

These substances have high ionic conductivity and are resistant to chemical decomposition over high voltage conditions. Also, non-volatile nature of these materials acts as a buffer for stabilizing pH levels during H_2 production. Approximately 9-10 litres of water is needed for H_2 production through electrolysis. H_2 sector is projected to rise and will severely put pressure on freshwater resources in near future.

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Addressing these challenges requires exploration of alternatives to freshwater. One potential alternative could be utilizing wastewater for electrolysis. For making H_2 as the future fuel collaborative efforts on global scale are required for drafting and implementing national-level policies supporting utilization of waste-water for H_2 production. The wastewater should have strong ionic conductivity and require resistance to chemical breakdown on exposure to high voltage ranges. It should be non-volatile and act as a buffer for stabilizing pH levels during electrolysis.

In this research study, one of the causes of pollution in urban wastewater, collected from a waste stream near the laundry industry, is being explored for its potential to be utilized for green H_2 production (a clean alternative fuel) via the electrolysis process. Laundry wastewater is a part of discharge from both point and non-point sources. According to the literature, there are two major types of laundries: commercial and industrial. Commercial laundries are large, while industrial laundries include hotels, hospitals, local dry cleaners, etc. The primary sources of laundry wastewater are small-scale industries. These industries consist mainly of small-scale cloth-washing facilities found in all cities and towns. This sector is experiencing rapid growth due to high demand. Laundry wastewater harms human health, deteriorates the quality of freshwater resources, and also leads to a higher rate of eutrophication [3]. The treatment of laundry waste-water is complex and time-consuming due to the presence of a wide range of organic substances such as soap, detergents, chlorinated solvents, aromatic compounds, fats [4], and grease, as well as inorganic contaminants such as heavy metals, dirt, clay, silt, and various metallic ions.

The characteristics of laundry wastewater depend greatly on the type of detergent, the quality and the quantity of water used for processing. This experimental study is a novel investigation into the utilization of wastewater (a source of contamination and freely available resource) for the production of green H_2. The wastewater selected for the study having high TDS content enhances its electrical conductivity, offering favorable conditions for wastewater electrolysis and reduces the need of electrolytes required for water splitting. This conductivity boosts ion mobility for wastewater splitting. Furthermore, the application of laundry wastewater in the production of green H_2 not only serves to reduce environmental pollution but also favours maximum utilization of resource from readily available wastewater stream and preventing the discharge of wastewater into freshwater or under-ground waterbodies.

EXPERIMENTAL

Methodology

The wastewater was collected in an amber-coloured bottle from runoff in a sewage canal near a laundry. The wastewater was immediately transported to the laboratory for storage and different physiochemical analyses. Upon arrival, the sample was visually examined for colour and any apparent particles. Tests were performed to analyse the colour, pH level, temperature, total solids (TS), total dissolved solids (TDS), total suspended solids (TSS), and conductivity. Table 1 shows the parametric values of the wastewater selected for the study.

Table 1. Physio-chemical analysis of selected wastewater.

S.No.	Parameters	Value/Range
1.	Colour	Grey
2.	Temperature	22.5°C
3.	pH	7.96
4.	TS	2932
5.	TDS	2087
6.	TSS	845
7.	Conductivity	4174 μS/cm

*Except colour, temperature, pH, and conductivity, all values are in parts per million (ppm).

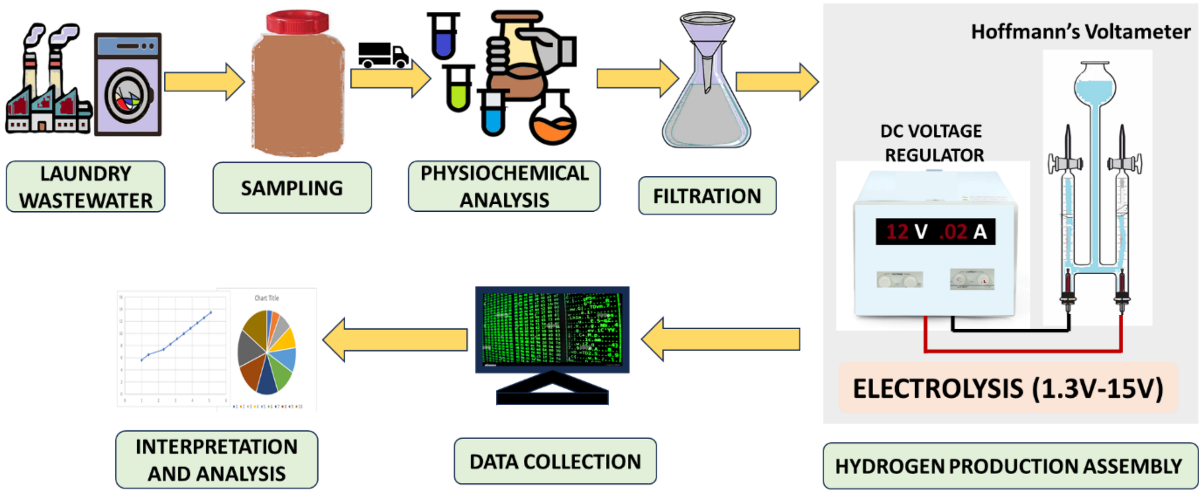

Figure 1. Schematic sketch of wastewater electrolysis.

Experimental Setup

The electrolysis process was conducted using a Hoffmann apparatus where gases generated at the cathode and anode were collected by the displacement of wastewater. Carbon electrodes (having a diameter of 0.8 cm, length of 4.2 cm and surface area of 11.59 cm^2) with rubber cork at the end were fixed at the lower tube ends of Hoffmann's apparatus. The apparatus was connected to a DC source having a varying voltage and current range (0-30 V/ 0-1 A, CES). The experiment was performed at varying voltages from 1.3 V, 3 V, 6 V, 9 V, 12 V, and 15 V. The volume of wastewater for the experiment was kept at 150 ml. To increase the pH of the wastewater, alkaline solution was added in a small amount. The experimental setup is represented in Figure 1 via a schematic sketch. A basic electrolysis unit consists of a source of Direct Current (DC), electrolytic solution, electrodes, glass container (for experimental demonstration we have used Hoffmann's voltameter).

System Efficiency (η):

In the context of green electrolytic H_2 production, system efficiency refers to the ratio between the chemical energy of produced H_2 and the electrical energy input provided during electrolysis. The electrolysis efficiency (η) of the conducted experiments was derived using the following equation [5]:

$$\eta = \frac{mh_{RP}}{VI}$$

Where η refers to the efficiency of the system (in %), m refers to the mass flow rate of H_2 ($kg.s^{-1}$), h_{RP} is the enthalpy of combustion ($J.kg^{-1}$), V is the voltage of the DC source (Volts), and I refers to the current (Amperes).

RESULTS AND DISCUSSION

The H_2 production was observed in wastewater samples in the specific voltage range. The wastewater was subjected to breakdown via electrolysis from 1.3 V to 15 V. The highest HPR of 8.45 ml/hr was observed at 15 V. The efficiency of the H_2 production increased up to 20.68 % at 3 V and further, it started to decrease again. Initially, the current of the wastewater sample reached 0.046 A at 12 V which began to reduce and became stable at 0.023 A after 1 hour of the electrolysis process. It could be mainly due to the flocculation of ionic concentration present in waste-water. The flocculation process was also visualized during the experiment. After the flocculation reached equilibrium, the conductivity of the water became stabilized and continuous H_2 production was observed.

Table 2 represents HPR (ml/hr) and the efficiency (%) of electrolysis at different voltages. Figure 2 depicts the H_2 production during different time intervals during experimental investigation. It has been observed that H_2 production increases with the increase in voltage and current (Figure 3). Whereas, the efficiency rate for the process does not show significant improvement with the increase in voltage and has decreased with an increase in input voltage (from 6 V to 15 V). Figures 3 and 4 show the graphical representation of the respective HPR, current flow and efficiency of the process respectively. When discussing electrolysis in wastewater, higher voltages might lead to greater overpotential because of interactions with the electrolyte found in the wastewater. The elevated overpotential observed at higher voltages could have potentially led to reduced efficiency in the electrolysis process.

Table 2. Hydrogen Production Rate (HPR) at different voltages with efficiency (%).

Voltage	HPR (ml/hr)	Efficiency (%)
1.3V	0.05	11.23
3V	0.85	20.68
6V	2.65	11.724
9V	4.1	7.824
12V	6.15	6.235
15V	8.45	5.483

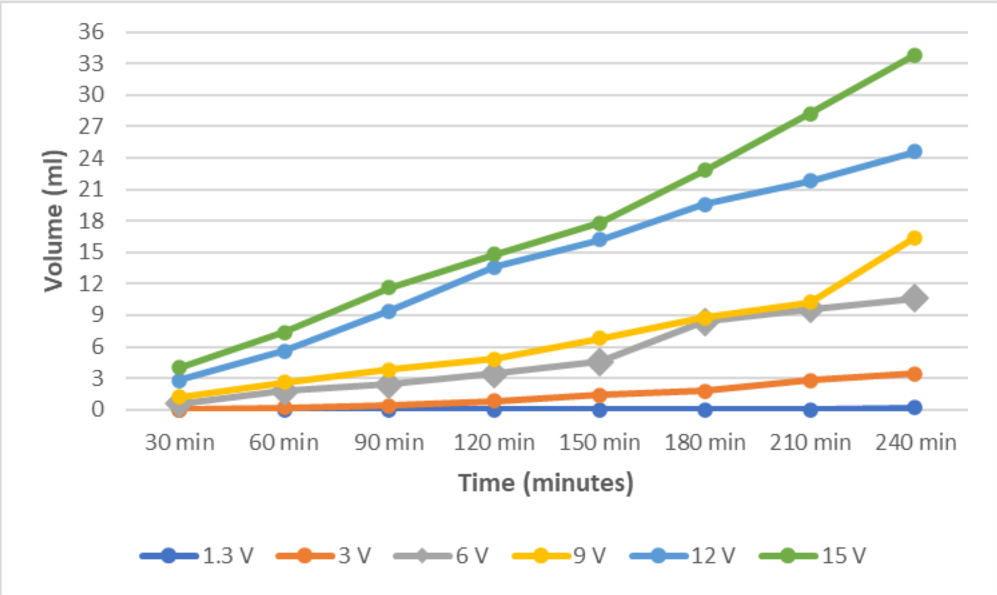

Figure 2. Hydrogen produced at different voltages with selected time intervals.

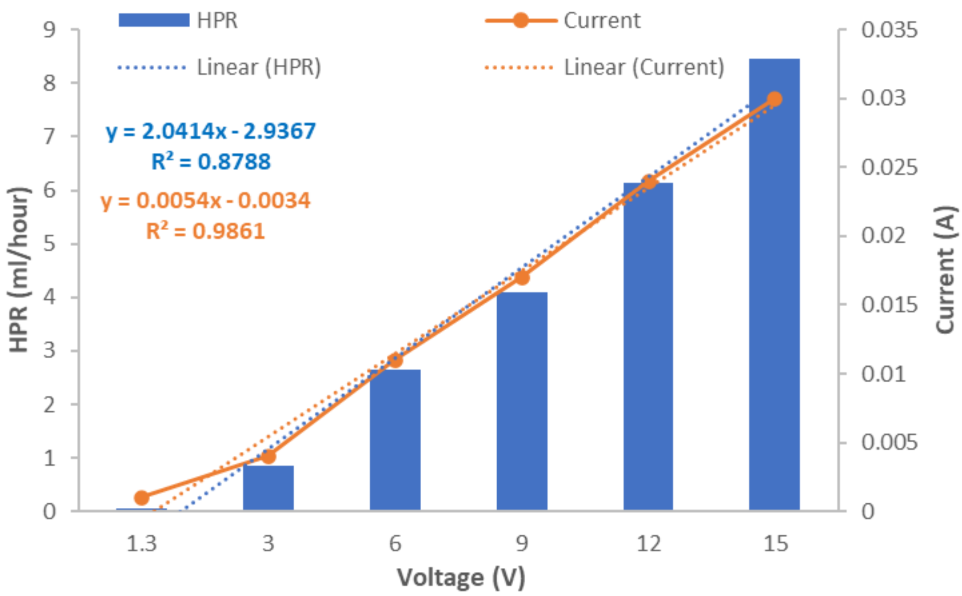

Figure 3. Effect of voltages on the rate of hydrogen production (ml/hr) with current (A).

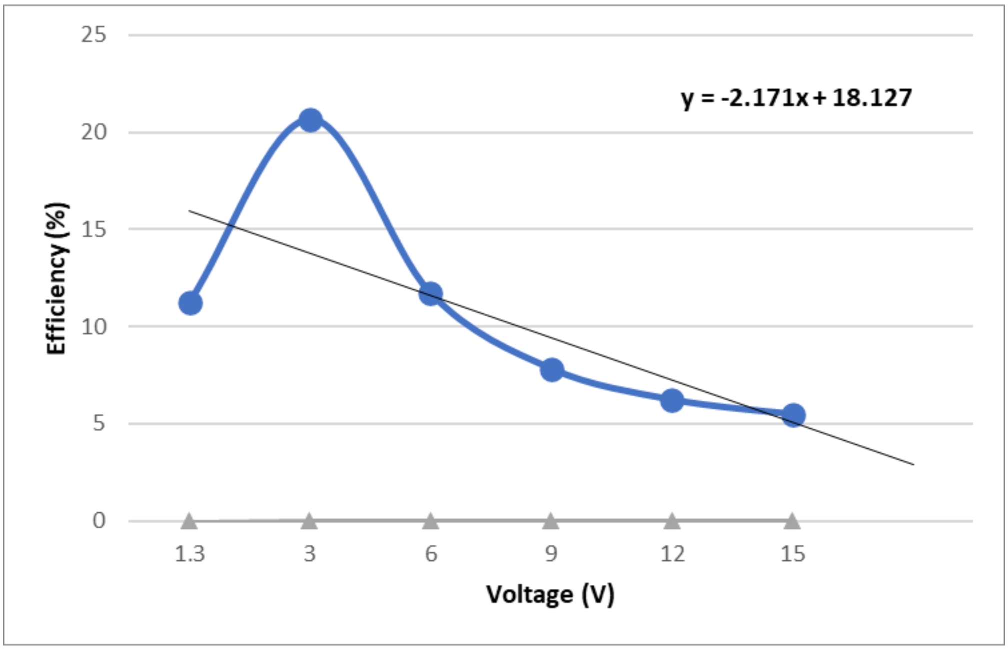

Figure 4. Effect of voltage on efficiency.

In Figure 4, the efficiency is seen to increase up to 3 V and then decreases with an increase in voltages from 6 V onwards up to 15 V. High levels of suspended solids/dissolved solids present in wastewater may be a reason for support of the rise in HPR with an increase in voltages for the present study. Buddhi et al. [6] observed that the concentration of ions in an electrolyte significantly influences the electrolysis process. Industrial wastewater contains a range of cations and anions, including sodium, potassium, magnesium, calcium, sulphate, phosphate, chloride, nitrate, etc.

Therefore, it may be concluded that higher conductivities due to ionic constituents are one of the reasons for efficiency decrease with an increase in input voltage present in the selected wastewater. Also, after 40 hours of continuous electrolysis at 12 V, slight corroding of carbon electrodes was observed. As the colour of wastewater started turning light brown to black over continuous electrolysis. From this observation, it was concluded that, possibly at a higher pH range, the carbon electrodes tend to corrode. A similar trend was also observed at different voltages. This novel approach of green H_2 production from wastewater as a resource provides new insight into energy recovery.

CONCLUSION

The experimental study depicts that the yield of electrolytic H_2 gas increases with the increase in voltage with real wastewater while the optimized system efficiency was obtained at 3V with carbon electrodes. Hence, the rate of H_2 production was found to be directly proportional to the increase in voltage but the efficiency did not change much with the increase in voltage. This study aligns with the approach of wastewater reuse for green H_2 production via water splitting. This method is in line with initiatives to enhance resource efficiency and promote environmental sustainability in water management procedures for green H_2 production.

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