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Possibilities of Pharmaceutical Wastewater Generating Hydrogen Gas Potential Hydrogen Production from Pharmaceutical Wastewater

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ABSTRACT

Over the past fifty years, there has been a sharp surge in the search for clean, high-energy fuels. Fossil fuels, which are a primary source of energy, release harmful air pollutants into the environment which are posing a substantial air pollution issue. Compared to fossil fuels, hydrogen gas is a clean and having a high heating value. Hydrogen is thought to be the main energy carrier of the future and can be utilised in fuel cells to produce electricity. The present paper gives an insight for hydrogen gas (H_2) production from the pharmaceutical wastewater. Out of the many technologies available for hydrogen production form the water, sludges & sewage &/or wastewater, electro-hydrolysis is one of the most researched technologies from production of hydrogen from waste & wastewaters. The lab scale electro-hydrolysis treatment was given having iron electrodes to real treated pharmaceutical wastewater. The wastewater samples were collected from each stage of the treatment plant in order to evaluate the treatment efficiency. The hydrogen gas production after electrolysis treatment was confirmed with the flame testing method.

KEYWORDS

Hydrogen gas, Electrolysis, Pharmaceutical wastewater, Electrodes, flame testing method

1. Introduction

There is growing worldwide agreement that coordinated action is required to bring global warming to levels less than 2 ℃ and if possible, to a maximum of 1.5 ℃ above pre-industrial levels. Various counties across the globe have pledge about emission reduction through transitions from fossil fuel to clean hydrogen. India has also committed to net zero targets. In order to achieve these targets, set under the Green Hydrogen Policy in India by Ministry of power in year 2022, the hydrogen generation from water via electrolysis using renewable energy resource & from biomass. **[1]** . To combat this, a substitute usage of green energy from H2 gas is more advantageous. Today, consumptions of non-renewable energy such as crude oil and other are on the approach of exhaustion. Countries like India concentrate on reducing carbon emissions and expanding the use of renewable energy sources. One of the programmes that focuses on producing hydrogen gas from renewable sources, including solar energy, is the green hydrogen policy. India wants to produce as much H_2 as possible because it has many benefits and is seen as having a bright future. **[2]** Large potential for companies to supply some of the generated gas are created by the rising demand for H_2 gas. The need of that industry will largely determine how that gas is used.

Electrolysis one of the most proven technologies for the generation of the H_2 gas from the water. Electrodes are used during the chemical-free electro-hydrolysis process. During the procedure, electrodes and effluent are both contained in a closed vessel.**[3]** In terms of both pollution remediation and hydrogen production, electro-hydrolysis of wastewater can be thought of as an alternative to the current treatment procedures.

The electro-hydrolysis technique has gained popularity in recent years because it can simultaneously remove pollutants in wastewater and provide higher yields of hydrogen energy. Pharmaceutical wastewater has a complicated composition that is typically high in organic matter, microbially toxic, high in salt, and difficult to biodegrade **[4,5]**. Treated pharmaceutical wastewater can act as a good source of raw material for H_2 production. There are numerous locations where energy can be produced treatment plant of pharmaceutical industry. Starting with untreated wastewater, it has enough hydrocarbons and other compounds to be transferred to better energy sources. Sludge, which has the potential to contain energy and can be converted into methane and hydrogen, is another current form of energy extraction. Last but not least, because other sources are less effective than this one, we hoped to obtain hydrogen from treated wastewater.**[2]** The current study was conducted in an important endeavour to apply technique that maximises the use of treated wastewater and is also economical and environmentally benign for possibility of hydrogen gas production.

2. MATERIALS AND METHODS

2.1 Wastewater composition

One of the pharmaceutical wastewaters treating common effluent treatment plant (CETP) situated in Gujarat is selected for carrying out the experimental work. The 8 hours composite wastewater samples were collected from each stage of the treatment plant as shown in the treatment flow diagram in **Figure No:1**. The characterization of wastewater sample is as mentioned in **Table No:1**

2.2 Experimental Setup

The experimental set up consists of 1 L glass reactor bottles containing 700 mL treated wastewater sample), 2 iron or steel electrodes for each bottle, and 2 silicon stoppers for sealing the reactor entrance and fixing the electrodes. Both iron or steel electrodes are 25 cm long and 0.6 cm wide. The electrodes attached through electric wires in reactor. All the containers are insulated with silicone to prevent leakage of gas. Once the reactors are ready to be processed, the electrodes are connected to direct current (DC) power source. The generated hydrogen gas was collected in 1000 ml batch with the gas collecting pipes which is made from plastic, the gas compositions were determined using a flame test using IV set on the candle. Apart from this, oxygen was also transferred like hydrogen in separate container for collection purpose. Rest of the wastewater was allowed to settle down after that supernatant of it got collected. Executed experimental setup depict in **Figure No:2.**

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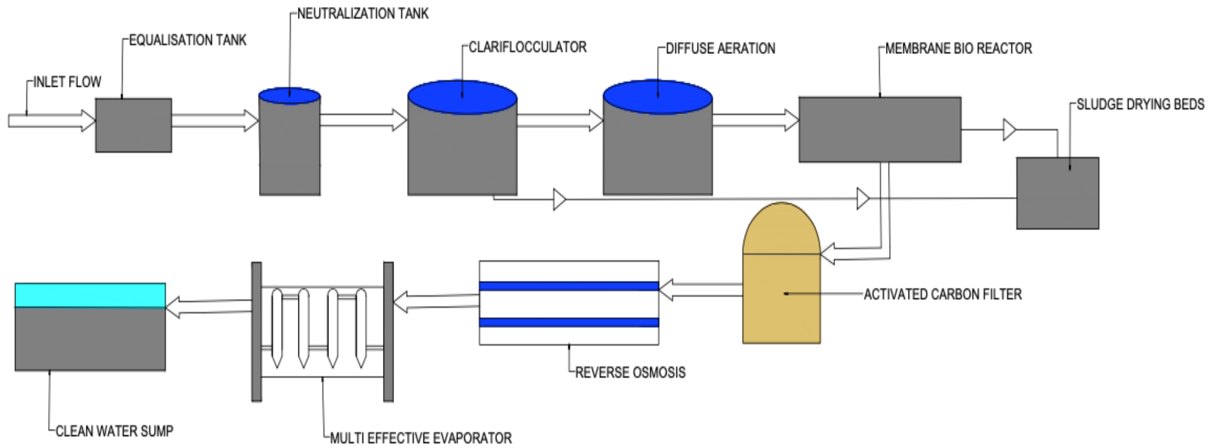

Fig:1 The Pharmaceutical wastewater treating CETP flow diagram

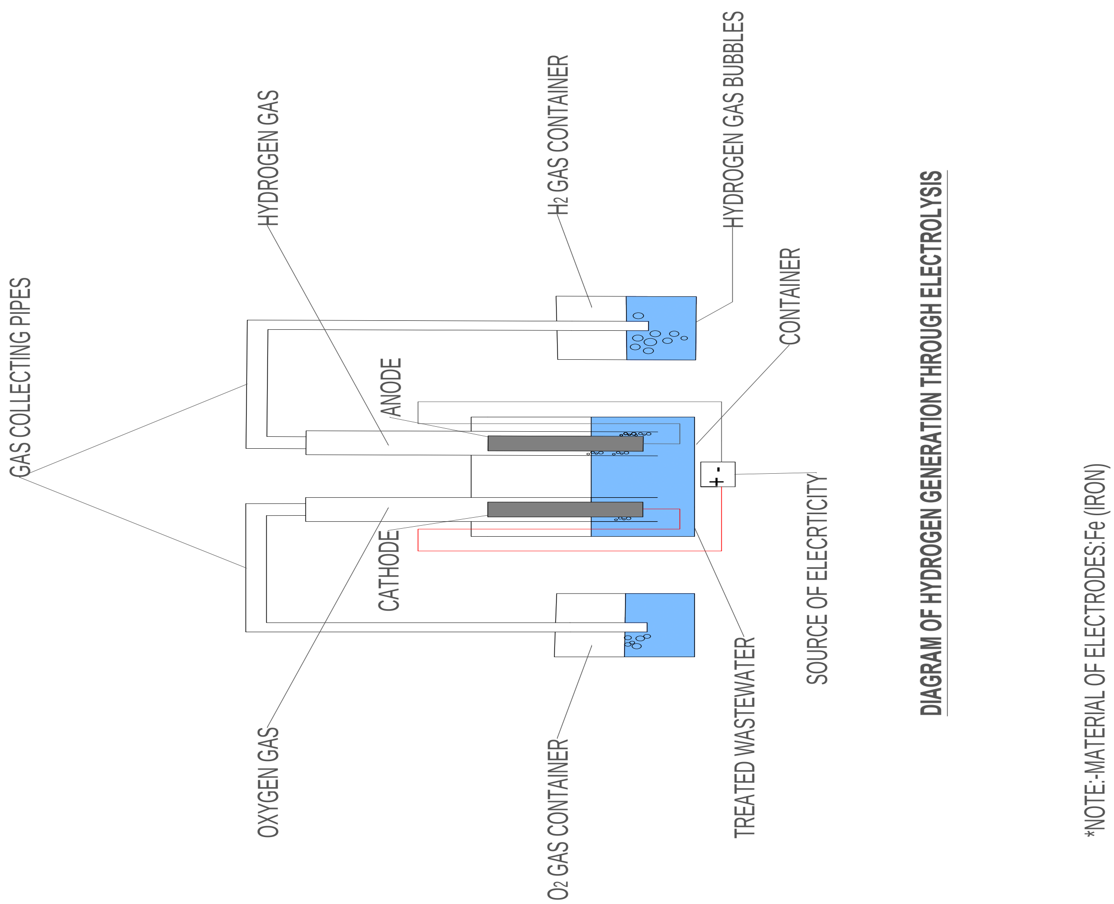

Fig:2 Line diagram of Laboratory Experimental Setup

Table No: 1
Intel & Outlet Wastewater Characteristics

Pollutant Parameters	Inlet (in mg/L)	Outlet (in mg/L)
pH	6.97	7-8
TSS	100	20
TDS	2940	600
COD	1800	40

3. Results and discussion

Pharmaceutical wastewater particularly due to certain reasons; among all one of the crucial one is currently; India is one of the leading countries around the globe. It is the world's 3rd largest by volume and 14th largest in terms of value. India contributes the network of 3,000 drug companies and around 10,500 manufacturing units. So, the opportunity is enormous to having treated wastewater which opens broad way to produce a gas which has a ability to replace conventional fossil fuels.

In general, the composition of pharmaceutical wastewater is complex, which has high concentration of organic matter, microbial toxicity, high salt, and it’s difficult to biodegrade. In addition, most of pharmaceutical industries are in batch process, and there are different raw materials and production process, which causes huge varieties in different wastewater. Electrolysis uses direct current (DC) electricity to split water into its basic elements, hydrogen and oxygen.

3.1 CHEMISTRY OF ELECTROLYSIS

Wastewater electrolysis is a chemical reaction that separates hydrogen and oxygen gases by passing an electric current through them. The electrolysis of wastewater is mainly carried out to yield pure hydrogen and oxygen gases. It involves passing an electric current through the wastewater which results in the decomposition of wastewater into hydrogen and oxygen.

The processes that occur at the electrode’s surface are described by following;

$$\text{Cathode: } 2\,H^+_{(aq)} + 2\,e^- \rightarrow H_{2(g)} \qquad (E^0 = 0.00\text{ V } vs.\text{ SHE})$$

$$\text{Anode: } H_2O_{(l)} \rightarrow 1/2\,O_{2(g)} + 2H^+_{(aq)} + 2e^- \ (E^0 = 1.23\text{V} vs.\text{SHE})$$

$$\text{Overall: } H_2O \rightarrow H_2 + 1/2\,O_2. \qquad (E_0 = -1.23\text{ V } vs.\text{ SHE})$$

The electrochemical reactions occurring at the cathode and anode are given by following ;

Cathode: $2\,H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^-$ ($E^0 = -0.83$ V *vs.* SHE)

Anode: $2\,OH^- \rightarrow 1/2\,O_2 + H_2O + 2\,e^-$ ($E^0 = 0.40$ V *vs.* SHE)

Generation of hydrogen molecules is doubled than the number of oxygen molecules. After electrolysis of wastewater, hydrogen is collected at anode and oxygen is collected at cathode. Volume of Hydrogen observed two time greater than oxygen. The minimum necessary cell voltage to start water electrolysis is the potential 1.229 V. This results in at least a 21% unavoidable loss of efficiency. **[6,7]**

3.2 Comparison of various types of electrodes

Steel and iron are the most commonly used for electrodes for electrolysis of water These electrodes are used as anodes and are sacrificed in electrolysis because the anode rusts (oxidizes) and the cathode rusts (reduces).

Organic material:

Carbon is a non-metallic element which is used due to high biodegradability and low reactivity. The conductivity of carbon (1.25 x 103 S/m) is very low compared to steel and platinum, but the cost of the material is very low. The carbon is used as an electrode material with a specific area of 23 ± 1.5 cm2 with 99.05 % purity The material is organic in nature and economical to use from a sustainable perspective

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Inorganic material:

Steel and platinum were used as inorganic electrode materials during the research. The steel is an electrode material with moderate conductivity (1.45 106 S/m) and cost. The surface area of steel electrode is 1.07 ± 0.23 cm2 with 99.57% purity index. Platinum electrode is used to examine the rate of hydrogen production rate due to its high conductivity (9.43 106 S/m) and purity 99.02% with surface area of 0.1 ± 0.02 cm2. Platinum is one the noble metals found on earth with very less reactivity and high conductivity. **[7]**

3.3 Performance of electrolysis process for different wastewater

Type of Wastewater	Operating Condition	% COD Reduction	Hydrogen Production . mL	References
Domestic	120-L microbial electrolysis cell to produce virtually pure hydrogen gas	33.7	9 mL/day	Purwono,&Oktiawan,W.&Hardiyanti,Nila. (2017).
Leachate	Effect of applied electrohydrolysis time on hydrogen production and	77	5,754 ml H_2/L at fermentation	Fikret Kargi et al. (2011)

	pollution removal		temperature of 37 ± 1°C	
Olive Oil	Aluminum electrode, 3 V	44	30 NmL·min−1 of pure H2	Canan Can Yarımtepe et al. (2019)
Textile wastewater	The Sono-Hydro-Gen process	87.2	45-65 ml/min	Atin K. Pathak, Richa Kothari, V.V. Tyagi, Sanjeev Anand(2020).
Vinegar wastewater	Aluminum electrode, 4 V	12	3197 mL	Kargi, et al. (2013)
Wasted sludge	Aluminum electrode, 2 V	84	2775 mL	(1) Kargi, F., et al. 2011.

3.4 Hydrogen generation Potential:

As technology advances, there are many ways to measure hydrogen. One of the methods is described in this paper with an example. Then find the actual pressure of hydrogen; Calculate the actual contribution of hydrogen to room pressure by multiplying the pressure of hydrogen by the sum of the volume and water. Use the ratio of moles of reactants to determine and calculate the expected amount of hydrogen gas. Give the amount of hydrogen gas released during the experiment as a percentage by multiplying the exact amount of hydrogen gas by 100 percent divided by the expected result. PV = nRT represent ideal gas law equation; the following denotes "P" is pressure, "V" is volume, "n" is the number of moles of gas and "T" is temperature. "R" stands for gas constant, which is 8.314472. The gas constant allows you to work with the Kelvin standard units for temperature, gas volume, pressure in pascals, and volume in cubic meters.

- Add 273.15 to Celsius (C) temperature to convert to Kelvin (K). For example, if hydrogen is collected at 20 C, this temperature corresponds to 293.15 (273.15 + 20) K. It is usually expressed as 101,325 atmospheric pressure (atm) to convert to the international system of pascals (Pa). For example, if the gas is collected at a pressure of 2 atm, 101,325 x 2 atm = 202,650 Pa will be changed.
- Convert the volume of gas collected to cubic meters. For example, if it is given in liters (L), divide by 1000. Therefore, 25 liters corresponds to 0.025 (25/1000) cubic meters.
- To calculate moles of hydrogen gas, multiply the volume and pressure and divide the product by the temperature and molar gas. For example, the amount of hydrogen is 202.650 x 0.025 / 293.15 x 8.314472 = 2.078 moles.
- Use the mass of hydrogen gas to directly calculate moles of gas; divide the weight of hydrogen by the mass of 2 g/mol. For example, 250 grams (g) of hydrogen gas is equal to 250 g/2 g/mol = 125 mol. **[9]** The total amount of hydrogen produced will be one of the important information in this experiment. This article talks about the data on the amount of H2 measured. mainly depends on the current parameters of the treated wastewater. However, 0,700 kg was captured for the 50–55 kW (180–200 MJ) of pharmaceutical wastewater tested. The generation of hydrogen can be confirmed by a flame test. Hydrogen shows a tendency to contact fire, with a blue flame indicating the

presence of hydrogen. This diagram shows the H2 gas supply pipe that delivers the hydrogen gas to the container water. The H2 gas then rises in a bubble that passes through the needle and the tip of the needle is ignited by a gas lamp collected from the container and reaches the needle, where the blue flame of hydrogen is clearly visible when contact is made between the flame of the gas lamp. the end point of the needle. The experimental tests performed are shown in Figure 3.

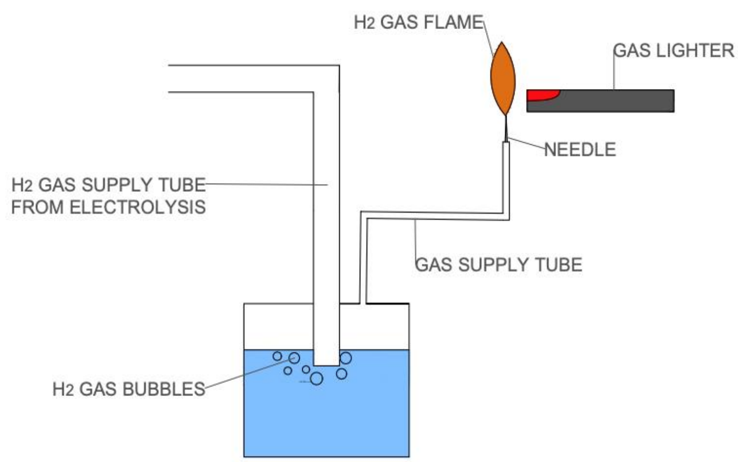

Figure No: 3 Flame test for presence of Hydrogen gas

4. CONCLUSIONS :-

This paper described the potential of pharmaceutical wastewater as a source of green hydrogen generation, energy recovery using electrolysis. It is more efficient and environment advantageous than the production of hydrogen from fresh water splitting. Hydrogen generation cost can be measured under every different operating conditions and the systematic procedure for evaluation of various compounds for electrodes and hydrogen rate. This method may found costly for an instance but that limitation can be overcome by use of solar panel. Requirement of electricity and its cost is negligible if source of it is solar panels which makes this whole process more feasible. Use of solar panels helps to boost up the state's solar energy capacity in order to contribute to India's overall renewable energy targets keeping in mind India's commitments under International climate agreements.**[10]**Moreover, The hydrogen generation from wastewater leads to degradation of pollution present in it which enhance the quality of treated wastewater.

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