Electrochemical Production of Hydrogen From Rice Mill Wastewater

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Abstract
Due to exhaustion of fossil fuels and water pollution caused by discharge of industrial wastewater, sustainable energy production and zero effluent discharge are now becoming the two main global environmental issues to be faced by the humanity. This study investigates the electrolysis of rice mill wastewater in the presence of sulfuric acid to produce hydrogen. High purity hydrogen gas (>99%) was produced by decomposition of organic compounds by the application of electricity. Effect of acid concentration was investigated and the results illustrate that the increase in acid concentration improves the rate of hydrogen production with reasonable COD reduction. Current efficiency of the electrolysis was found to be greater than 90%. Cumulative hydrogen production of 700ml per hour was obtained for 5V. Maximum energy efficiency (26%) of the process was achieved at acid concentration of 3wt% and applied voltage 4V. Platinum coated titanium electrodes used for electrolysis have not been etched during the operation. (Abstract)

Keywords—*Wastewater Treatment; Hydrogen Production; Electrolysis; (key words)*

I. INTRODUCTION

(Siz Hydrogen is the pollution free and best alternative to the fossil fuels. The production of hydrogen from waste is gaining importance at the current situation to meet increasing energy demand and to protect the environment economically. Commercially hydrogen is produced from fossil fuels through steam reforming, thermal cracking, partial oxidation and coal gasification [1]. Electrolysis contributes only five percent of commercial hydrogen produced worldwide. The majority of this hydrogen is produced in chloro-alkali industry as a side product along with chlorine. Successful electrolysis processes used for hydrogen gas production are alkaline electrolysis, proton exchange membrane (PEM) and solid oxide electrolysis cells (SOEC) [5]. Reported efficiencies of these electrolytic processes are in the range of 50–80%. Utilizing waste materials for the production of clean energy source make biological hydrogen production a novel and promising approach [2], [17]. Another important method to produce hydrogen is electrohydrogenesis, in which bacterial oxidation of organic materials assisted by external voltage [9-12]. However huge reaction time and sluggish rate of hydrogen production are the major problems associated with the scale up of electrohydrogenesis and microbial fermentation process [3]. On the other hand, direct electrolysis of organic waste for the production of hydrogen fined prominence due to its advantages such as increased production rate and less complexity [4]. The effluent of dark fermentation containing volatile fatty acids (VFAs) was used for hydrogen production by applying low voltage DC current using copper electrodes [6]. Hydrogen gas production by electrohydrolysis of vinegar fermentation wastewater was improved considerably by addition of scrap aluminum particles and salt to the solution [7].

Rice mill produces about 1.2 lit of parboiling wastewater during the processing of 1 kg of paddy [13-14]. Wastewater from rice mills contains large amount of carbohydrate waste that has to be treated to recover large amount of water. This research work is on electrolysis of rice mill wastewater using dimensionally stable electrode, platinum coated on titanium, in the presence of sulfuric acid. Proton exchange membrane was placed in the electrolytic cell to separate hydrogen from volatile organic compounds and carbon-dioxide. Therefore, further separation of hydrogen is not required. After completion of reaction residual sulfuric acid present in wastewater can be neutralized by adding sodium hydroxide, which resulted in further reduction of COD through coagulation.

II. MATERIALS AND METHODS

A. Feedstock

Rice mill wastewater was obtained from rice mill located at Kancheepuram, Tamil Nadu, India. It was stored at 4°C after sterilization in a well sealed container to avoid bacterial degradation. The characteristics of wastewater such as chemical oxygen demand (COD), biological oxygen demand (BOD), total dissolved solids (TDS), total suspended solids (TSS), total solids (TS), turbidity, pH, and electrical conductivity were determined by following APHA procedure. The characteristics of the wastewater studied are shown in Table.1. Wastewater was diluted slightly for the advantage of duplicating the experiments with constant initial COD.

B. Experimental Setup

Schematic diagram of the electrolytic cell is shown in Fig.1. It consists of core cathode chamber of volume 300ml and annular anode chamber of volume 200ml. Proton exchange membrane separates anode and cathode chamber by placing it on the curved surface of core chamber. In order to avoid leakage, PEM was sandwiched with rubber sheets and fastened on cathode chamber. Platinum coated on titanium electrodes of surface area 3 cm2 was used as both anode and cathode. Electrodes were kept at a distance of 1 cm apart.

C. Experimental Procedure

Experiments were conducted in the electrolytic cell with the working volume of 100 ml in the anode chamber. Anode chamber was filled with wastewater (COD: 5400mg L-1) containing varying concentration of sulfuric acid. Cathode chamber was filled with sulfuric acid slightly concentrated than that of anode chamber. Anode and cathode chamber lids were closed completely and sealed using Teflon tapes to avoid gas leak. When voltage is applied between electrodes in the presence of sulfuric acid, oxidation of organic compounds occurs in anodic chamber and produces decomposed organic compounds, electrons, and protons. Released electrons are assimilated by protons at cathode to produce hydrogen.

Organic compounds $\rightarrow$ *lower organic compounds + CO2 + H2* (1)

Cathodic reaction:

$$nH^+ + ne^- \rightarrow n/2\, H_2 \qquad (2)$$

Anodic reaction:

Organic compounds $\rightarrow$ ne- + nH^++ decomposed organics + CO_2 (3)

Since rice mill wastewater is a mixture of compounds, it is difficult to predict the exact mechanism of the electrolytic process. But the presence of carbon-dioxide in the anodic chamber indicates the contribution of organic compounds in electrolytic process. Carbon-dioxide produced is confirmed with the formation of white precipitate with Ca(OH)2. Electrolysis of water occurs simultaneously along with decomposition of organic compounds, which was confirmed using DO meter(Lutron DO-5509). The samples withdrawn at regular time intervals was subjected to COD analysis by open reflux method. The hydrogen gas produced was measured using an online monitor from H2 scan (HY-ALERTA, USA) [16].

Parameter	***Value***
Chemical Oxygen demand	5600 mg/L
Electrical Conductivity	2.31 m Mho/cm
Turbidity	153.8 NTU
pH	5.2
Biological Oxygen demand	3800 mg/lit
Odour	Foul
Total Dissolved solids	2300 mg/lit
Total suspended solids	780 mg/lit

Table.1 Characteristics of rice Mill Wastewater

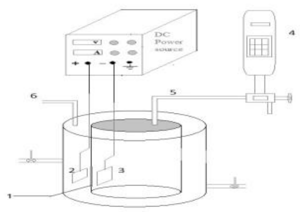

Fig. 1 Schematic Representation of Electrolysis of Rice Mill Wastewater (1) PEM (2) Anode (Platinum Coated Titanium) (3) Cathode (Platinum Coated Titanium) (4) H2 Scanner (5) CO2 and O2 (6) H2 gas.

The volume of hydrogen collected was determined by downward displacement of water.

D. Energy and Current Efficiency

The energy consumed for electrolysis was calculated using the mathematical expression given byFikret et al[8]:

$$E_e = VIt \qquad (4)$$

Where $E_e$is the electrical energy supplied to the system by the DC power supply; V is the applied DC voltage (V); I is the average current (A) measured by a multimeter for time period t(h). Electrical energy input was calculated by determined using Equation (4).

The mass of hydrogen gas collected was calculated by using the ideal gas law.

$$PV_{H_2}M = mRT \qquad (5)$$

Where P is the pressure (101325 Pa); V_{H_2} is the volume of the cumulative hydrogen gas; m is the mass of the cumulative hydrogen (g); M is the molar mass of hydrogen (2 g/mol); R is the

gas constant (8.314 J/mol K), and T is the absolute temperature (303 K).

The energy content of the produced hydrogen was calculated using the following equation

$$E_{H_2} = m * (122kJ/gm) \quad (6)$$

Where 'm' is the mass of the cumulative hydrogen produced. Energy efficiency was calculated using the following equation

Energy efficiency,

$$\eta_E = \frac{E_{H_2}}{E_e} \quad (7)$$

The current efficiency of hydrogen production expressed using expression given by [15].

$$\eta_C = \frac{V_{H2}}{V_{Th}} \quad (8)$$

V_{H2} $- Volume\ of\ hydrogen\ collected\ per\ hour\ \left(\frac{ml}{hr}\right)$

V_{Th} $- Volume\ of\ theoretical\ hydrogen\ production\ (ml/hr)$

Theoretical hydrogen production per hour is expressed as,

$$V_{Th} = \frac{(I*22.414*3600*1000)}{F*2} \text{ml/hr} \quad (9)$$

where I is the current applied(A), F is the faraday's constant - 96485 C/mol and 2 g/mol is the Molecular weight of hydrogen gas.

III. RESULTS AND DISCUSSION

A. Effect of Applied Voltage

The effect of applied voltage on rate of hydrogen production studied at different acid concentrations is shown in the Fig.2. The rate of hydrogen production increased linearly with increase in applied voltage. Significant increase in hydrogen production was observed with increasing acid concentration. The highest rate of hydrogen production was observed at 10V. Voltage applied is an important parameter for optimizing the process. Applied voltage determines the rate of decomposition by controlling the number of electrons involved in the process. The results show that at higher applied voltage hydrogen production increases (up to 10V) beyond 10 voltage economic efficiency of the process decreases.

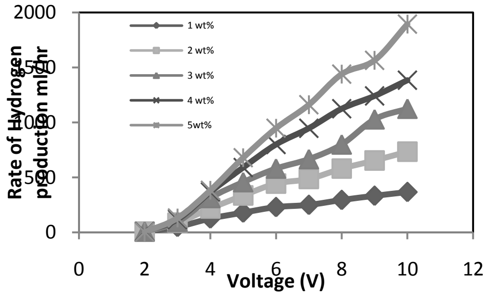

Fig. 2 Effect of Voltage on Rate of Hydrogen Production at Different Acid Concentrations (Temperature: 303 K)

B. Effect of Applied Voltage

Conductivity of the electrolyte is an important factor in determining the rate of electrolysis. Since rice mill wastewater shows high resistance to the current flow, adding sulfuric acid increases the conductivity of the cell. Sulfuric acid concentration at cathode has to be maintained same or slightly higher than anode cell, because the conductivity of the cell is fixed by the chamber containing lower acid concentration. PEM has very high conductance and does not affect the electrical conductivity. Experiments were conducted at different acid concentration from 1 to 5 wt% sulfuric acid, the highest rate of hydrogen production was observed at 5wt% acid. Increased acid concentration increases H3O+ ions they in turn increases the conductivity of the cell and this is the primary reason for the increase in rate of production of hydrogen. From the Fig.2 it is observed that increasing acid concentration increased the rate of hydrogen production. But acid concentration in the system should be limited due to its high corrosive behavior.

C. Effect of Applied Voltage

Effect of electrolysis time on cumulative hydrogen production at different acid concentration is shown in the Fig.3. The cumulative hydrogen production increases linearly with time irrespective of acid concentration. Increasing the time of electrolysis increased the amount of electrons admitted into the reactor which in turn increased the cumulative hydrogen production. Even though increase in time of electrolysis increased the cumulative hydrogen production, operating of electrochemical reactor for longer period may affect the economic viability of the process.

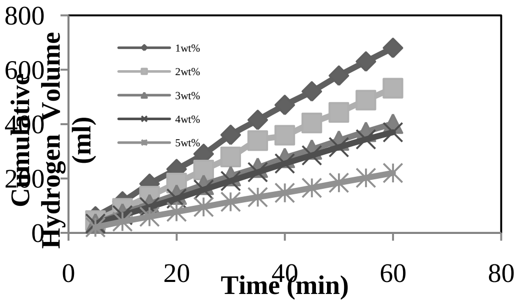

Fig.3Effect of Time on Cumulative Hydrogen Production at Different Acid Concentrations. (Voltage-5V)

Fig.4 shows the effect of electrolysis time on percentage of COD reduction. Percentage of COD reduction increases with increase in acid concentration and reaction time. The percentage of COD reduction was found to increase linearly with time (up to 75 min) after that there was no significant variation was observed. During electrolysis of rice mill wastewater with platinum coated titanium electrodes, there is possibility for the production of OH- radicals. These radicals are very strong oxidizing agents and might have oxidized the organic compounds present in the waste water. The increase in acid concentration also increases percentage reduction of COD this may be due to the fact that at higher acid concentration better conductivity can be achieved this enhances the production of oxidizing agents, which in turn increased the percentage of COD reduction.

D. Efficiency of the Process

Current efficiency is a direct measure of charge actually utilized for the electrolysis. Effect of applied voltage on current efficiency is shown in Fig.5. In the applied voltage range from 5 to 10 V 90% current efficiency was observed. Current efficiency was found to be low for lower voltages (1-4V). This may be due to low rate of hydrogen production not able to create enough pressure gradients to flow. The current efficiency depends on amount of hydrogen collected, so the collection of hydrogen without leak is important to determine the current efficiency without discrepancies. Energy conversion efficiency is the measure of energy recovered as hydrogen energy from the system. Effect of voltage on Energy conversion efficiency is shown in the Fig.6. Energy efficiency was found to be high in the voltage range of 3-4V and attains maximum of 26% at 4 V with 3wt% sulfuric acid. Energy efficiency decreases gradually for applied voltage greater than 4V.

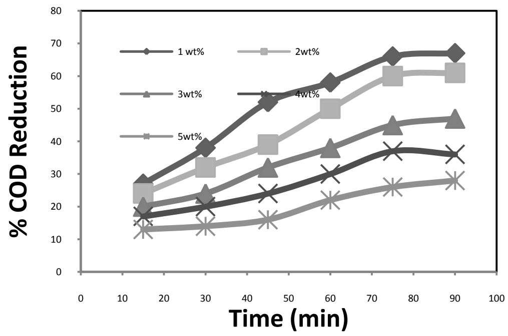

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Fig.4 Effect of Time on COD at Different Acid Concentrations.(Voltage-5V)

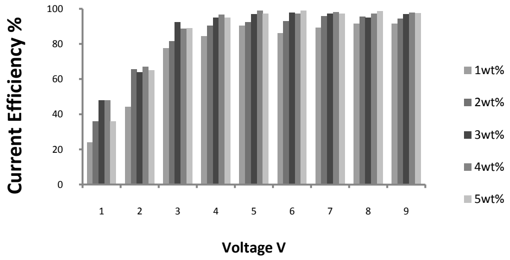

Fig. 5 Effect of Voltage on Current Efficiency of Electrolysis at Different Acid Concentrations

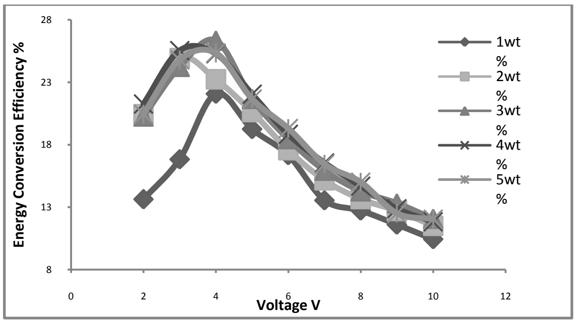

Fig. 6 Effect of Voltage on Energy Conversion Efficiency at Different Acid Concentration

IV. CONCLUSION

Electrolysis using dimensionally stable electrodes was found to be effective for the treatment of rice mill wastewater with significant COD reduction (67%) and high rate of hydrogen production. Unlike other biohydrogen production processes, this method is substrate independent. Platinum coated titanium electrodes used for the treatment were not etched during the operation even at high concentrations of sulphuric acid. Current efficiency of the electrolysis was found to be greater than 90% and cumulative hydrogen production of about 680 ml/h was obtained at an operating voltage of 5V and 5 wt% sulphuric acid. Maximum energy efficiency of the process was found to be around 26%.

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