

ROLE OF MANGANESE ON HYDROGEN PRODUCTION FROM WASTE WATER

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Abstract - Hydrogen is the most abundant chemical element in the universe and has the highest energy content of any fuel source on the market today. Demand on hydrogen is not limited to utilization as a source of energy. Hydrogen gas is a widely used feedstock for the production of chemicals, hydrogenation of fats and oils in food industry, production of electronic devices, processing steel and also for desulfurization and reformulation of gasoline in refineries. Hydrogen production from the recycling of organic waste is considered as a greener technology compared to conventional hydrogen production methods. Present utilization of hydrogen is equivalent to 3% of energy consumption, and it is expected to grow significantly in the year to come. Bio-hydrogen production requires essential micronutrients for bacterial metabolism during fermentation. Sodium, magnesium, manganese, zinc and iron are all important trace metals affecting hydrogen production. Among them manganese is an important nutrient element.

Key Words: Manganese (MN), Waste Water (WW), Sludge (S),

1. INTRODUCTION

The worldwide energy need has been increasing exponentially, the reserves of fossil fuels have been decreasing, and the combustion of fossil fuels has serious negative effects on environment because of greenhouse gas emissions. Owing to widespread exploitation of fossil fuels severe environmental problems like global warming and ozone depletion have already been initiated, in turn adding to worldwide economic loss by environmental damage. At this juncture, the world is seeking cleaner energy resources to mitigate imminent fuel shortages to provide the energy necessary for future. Hydrogen is considered as the future energy carrier, due to its high energy content and non-polluting nature and also it can be considered as an environmental friendly alternative to fossil fuels and other fuels in automobiles so that impact on environment can be reduced.

Hydrogen is considered as a viable alternative fuel and “energy carrier” of future. Hydrogen gas is a clean fuel

with no CO₂ emissions and can easily be used in fuel cells for generation of electricity. Besides, hydrogen has a high energy yield of 122 kJ/g, which is 2.75 times greater than hydrocarbon fuels. The major problem in utilization of hydrogen gas as a fuel is its unavailability in nature and the need for inexpensive production methods.

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Bio-hydrogen production requires essential micronutrients for bacterial metabolism during fermentation. Sodium, magnesium, manganese, zinc and iron are all important trace metals affecting hydrogen production. Among them iron is an important nutrient element to form hydrogenase or other enzymes which almost all biohydrogen production needs fundamentally. Also compared to other metal ions, manganese has the benefits of high protection during handling as it scarcely reacts with water at low temperature, is easily recoverable, and is efficiently excavated. Thus, in the present study, batch experiments are designed to investigate the role of manganese concentration on hydrogen production from wastewater containing large amount of carbohydrate content.

1.1 Literature Survey

Dhanasekar et al, International Journal of Chemical Studies (2014) conducted a study based on the effect of aeration on microbial production of hydrogen from maize stalk hydrolysate. Enhanced production of hydrogen is obtained under micro aerobic condition when compared to strict anaerobic and partial aerobic condition and also the yield under micro-aeration conditions was found to be almost fivefold higher than the other two conditions. But in the project experiments

are carried out under strict anaerobic condition by sparging nitrogen in the reactor since the micro aeration condition is difficult to set up also the Hydrogen production under strict anaerobic condition was increased to 1.83 times using microbial electrolysis cell which is a technology related to microbial fuel cells.[2]

Zhang yu et al , International Journal Of Hydrogen Energy, (2008) conducted to find Hydrogen production characteristics of the organic fraction of municipal solid wastes by anaerobic mixed culture fermentation. It was investigated by using batch experiments at 37 degree celcius.7 varieties of typical components of OFMSW including rice, potato, lettuce, lean meat, oil, fat and banyan leaves were selected for hydrogen production.

SikShin et al International Journal of Hydrogen Energy, (2015) Conducted a study about the Feasibility of bio-hydrogen production by anaerobic co-digestion of food waste and sewage sludge. Food waste showed higher specific hydrogen production potential than sewage sludge. Carbohydrates are the preferred substrate for fermentative hydrogen producing bacteria. Volatile solids concentration and mixing ratios of waste water and sludge plays a crucial role in hydrogen production. The mixing ratios of food waste to sewage sludge were designed to be 100:0, 80:20, 60:40, 40:60, 20:80, and 0:100 on VS basis; however, the experiments at 20:80, and 0:100 for VS 3.0%, and 40:60, 20:80, and 0:100 for VS 5.0% could not be conducted due to low VS concentration of sewage sludge.

1.2 Objectives

1. To find out the amount of hydrogen produced from waste water at different manganese concentrations.
2. To determine the manganese concentration at which maximum amount of hydrogen is produced.

1.3 Scope Of The Study

Use of fossil fuels has become a part of daily energy needs and their requirement is increasing with the passage of time. Consumption of fossil fuels gives rise to the greenhouse gas emissions in the environment and causes ambient air pollution, which have now become global concerns. This coupled with the limited reserves of fossil fuels have encouraged and promoted the development and use of new and renewable energy sources, including hydrogen energy as an energy carrier. The technologies for production of hydrogen from new and renewable sources of energy are in the process of development and demonstration. In order to meet the future energy demands in sustainable and environment friendly manner, technologies are required to be developed for the production, storage and applications of

hydrogen in transportation sector as well as for portable & stationary power generation. Green technologies for hydrogen production will be a blessing for the future generation as it produces less impact on the environment.

2. EXPERIMENTAL INVESTIGATION

2.1 Samples Collected

Dairy industry is one of the major food industries in India, and India ranks first among the maximum major milk producing nation. The dairy industry is one of a major source of waste water. The milk industry generates between 3.739 and 11.217 million m³ of waste per year (i.e. 1 to 3 times the volume of milk processed). Wastewater is generated in milk processing unit, mostly in pasteurization, homogenization of fluid milk and the production of dairy products such as butter, cheese, milk powder etc. Important contents of this waste water are proteins, carbohydrates, fats etc. Both waste water and sludge were collected. This sample was used since the major component in this waste is hydrogen and carbon which in turn helps in more hydrogen production. Sample for our project was collected from Hima milk project, Ereattupetta.

2.2 Tests Conducted

1. **pH:** Measurement of pH is one of the most important and frequently used tests in water analysis. pH is a measure of the degree of acidity or alkalinity of a substance or refers to the measure of hydrogen ion concentration in a solution and defined as the negative log of H⁺ ions concentration in water and wastewater. A pH meter is an electronic device used for measuring the pH (acidity or alkalinity) of a liquid. A typical pH meter consists of a special measuring probe (a glass electrode) connected to an electronic meter that measures and displays the pH reading.
2. **Total solids:** Total solids are the measure of suspended and dissolved particle in the wastewater. Suspended solids are those that can be retained on a water filter and are capable of settling out of the water column onto the stream bottom when stream velocities are low.
3. **Filterable Solids:** Total suspended solids (TSS) are the dry weight of particles trapped by a filter. It is a water quality parameter used to assess the quality of wastewater after treatment in a wastewater treatment plant. Non filterable residue is also called as Total suspended matter.
4. **Non Filterable Solids:** The filter paper used in the test of filterable solids was removed and dried in a hot air oven for 1 hour at 103-105°C, it is cooled, desiccated and weighed.



Fig-1: Experimental setup for filterable and non-filterable solid

2.3 Experimental setup

1. Batch Reactor

A batch reactor is a vessel used to mix chemicals under tightly controlled conditions. It is distinguished from a continuous reactor by its cyclic use, mixing one batch at a time, as opposed to the constant reaction carried out in a continuous reactor. In this project Batch hydrogen production experiments are carried out in a 250-ml Erlenmeyer flask which acted as batch reactor. The flask was tightly closed using a rubber cork with two outlets, one for sample collection and the other for hydrogen gas. The sample collection outlet was tightly closed using a clamp in order to prevent the entry of air from outside. The active working volume of the batch reactor was 100 ml.



Fig -2: Batch Reactor

Both waste water and sludge were added in different proportions. Sludge acts as the inoculum and waste water acts as the substrate. The substrate is a molecule upon which an enzyme acts. Enzymes catalyze chemical reactions involving the substrate. In the case of a single substrate, the substrate bonds with the enzyme active site, and an enzyme-substrate complex is formed. The substrate is transformed into one or more products, which are then released from the active site. The active

site is then free to accept another substrate molecule. In the case of more than one substrate, these may bind in a particular order to the active site, before reacting together to produce products whereas inoculum is a small amount of substance containing bacteria from a pure culture which is used to start a new culture.

2. Water displacement method

The water displacement method is the process of measuring the volume of an irregularly shaped object by immersing it in water. This method served as the basis for the principle developed by the Greek philosopher Archimedes. The principle states that a body immersed in a fluid is buoyed up by a force equal to the weight of the displaced fluid. The principle applies to both floating and submerged bodies and to all fluids, i.e., liquids and gases. The obtained gas is collected in an inverted jar either graduated or not. If it is graduated the amount of gas can be easily calculated and if it is not suitable methods are adopted to calculate the amount of obtained gas.

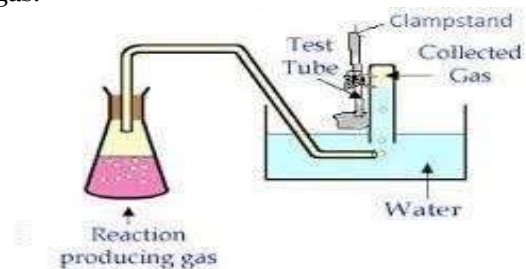


Fig-3: Experimental setup of water displacement method (Source: abridgingscience.blogspot.com)



Fig-4: Adopted Experimental Setup

3. RESULTS AND DISCUSSIONS

3.2 Hydrogen Production Without Mn

3.1 Before Production Of Hydrogen

Table-1: pH

Percentage of waste water and sludge	pH value
50% waste water 50% sludge	5.2
40% waste water 60% sludge	5.4
30% waste water 70% sludge	6.39
20% waste water 80% sludge	7.3
10% waste water 90% sludge	7.67

Table-3: H Production

Hydrogen production	Time in hours	
	12	24
50% waste water 50% sludge	7.3	8.5
40% waste water 60% sludge	7.9	8.8
30% waste water 70% sludge	8.4	9.7
20% waste water 80% sludge	9.9	10.6
10% waste water 90% sludge	10.3	11.6

Table-2: Solids

Parameter (mg/l)	Before hydrogen production				
	50% ww 50% S	40% ww 60% S	30% ww 70% S	20% ww 80% S	10% ww 90% S
Total solids	173.3	143	129	114	95
Filterable solids	72	47	41.5	44.6	54.4
Non filterable solids	101.2	96	87.5	69.4	40.6
Total fixed solids	79.6	67.3	48.9	30.7	25.7

3.3 Hydrogen production with Mn-24 hours

Table-4: Hydrogen Production

Hydrogen production in ml	Gram of Mn added		
	0.1	0.15	0.2
50% waste water 50% sludge	9.8	13.7	15.2
40% waste water 60% sludge	10.2	14.6	15.6
30% waste water 70% sludge	11.2	13.3	16.4
20% waste water 80% sludge	13.4	14.5	19.6
10% waste water 90% sludge	14.5	17.4	22

3.4 After Production of hydrogen

Table-6: pH

Percentage of waste water and sludge	pH value
50% waste water 50% sludge	5.1
40% waste water 60% sludge	5.5
30% waste water 70% sludge	6.58
20% waste water 80% sludge	7.6
10% waste water 90% sludge	7.67

Table-7: Solids

Parameter (mg/l)	Before hydrogen production				
	50% ww 50% S	40% ww 60% S	30% ww 70% S	20% ww 80% S	10% ww 90% S
Total solids	86.65	120	120	108	85
Filterable solids	68	47	47	33.5	53.5
Non filterable solids	59.6	85	85	58.6	35.5
Total fixed solids	70.6	67.3	67.3	20.6	24.3

4. CONCLUSIONS

Concerns about climate change and diminishing nature of petroleum reserves leads to the search for alternative, renewable fuels. Among the possible alternatives one of the important fuel is hydrogen, and there is on-going research for its production, storage and utilization. One requirement for a sustainable hydrogen economy is a renewable source of hydrogen fuel. Conventional commercial hydrogen synthesis processes typically involve the use of fossil fuels, water, or biomass as resources. About 98% of the annual globally produced hydrogen gas is obtained via the reforming of hydrocarbons, which are derived from fossil fuel reserves, resulting in the production of carbon dioxide which is a key player in global warming. A variety of processes are potentially available, among them microbiological hydrogen production.

In this project we have conducted experiments to produce hydrogen with the use of manganese and it is evident that manganese helps in increasing the rate of hydrogen production. The important conclusions obtained from the project are;

- In this dairy wastewater sample maximum production of hydrogen occurs at 0.2g of manganese concentration.
- Maximum hydrogen production occurs in 90% waste water and 10% sludge.
- Amount of solids get reduced after this experiment.

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