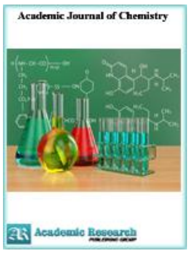

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Hydrogen Production Using Mediterranean Sea Water of Benghazi Shore and Synthetic Sea Water Electrolysis

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Abstract: Hydrogen production has attracted large attention due to depletion of fossil fuels and the threat of global warming, society. This research is concerned with overcoming the problem of efficient production of hydrogen at room temperature and uses it as energy storage and clean fossil fuel alternatives. The hydrogen production was measured from chemical solution such as sodium chloride and natural solution as sea water. Hoffmann voltmeter was used to estimate the production of hydrogen on sodium chloride and sea water at different applied potential 12, 9, 7.5, 6, 4.5, 3 and 1.5 volts and 1 Ampere for 2 hours. The following techniques pH meter and conductivity meter were used to investigate the effect of concentration of aqueous solution on volume of hydrogen gas produce of samples. In general, the production of hydrogen increased by increasing in voltage.

Keywords: Seawater; Water electrolysis; Hydrogen production; Conventional method; Renewable energy sources.

1. Introduction

During the twentieth century the world has been undergone a series of scientific and technological revolutions that led to increase in the role of energy resource as key factor in the economic and social development. The modern civilization has been based on the utilization of fossil fuel at present time fossil fuels coal petroleum and natural gas meet about 80 percent of the world energy demand [1]. However, the ever increasing consumption of fossil fuels reserves will eventually lead to its depletion and far before that to increase in energy prices more over. Rather than that fossil fuel have become a destructive force to the environment with its harmful ecological pollutants and health hazards [2]. However, to minimize greenhouse gas emissions, electricity generation using renewable energy technologies, such as wind, solar, geothermal, and hydroelectric power, nuclear energy, or coal and natural gas with carbon sequestration are preferred [3]. According to the literature, hydrogen has been used by for military, industrial and commercial purposes since late 19th century Producing hydrogen is receiving an increasing attention worldwide due to the huge energy potential. Hydrogen can be produced from water electrolysis using any power [4, 5]. All type of energy, renewable or non-renewable, can be traced back to either atmospheric activity in the past or to the present and future activities within the atmosphere. Hydrogen is the cleanest fuel, and has a heating value three times higher than petroleum. The hydrogen production can be produced from different sources such as oil, coal, biomass , natural gas, algae, alcohols, water electrolysis, wind-electrolysis, geothermal energy-electrolysis, photoelectrolysis. However, water electrolysis is more suitable for industry sectors that require very high purity hydrogen, like metallurgy, electronics and pharmaceuticals. Hydrogen can be produced from water electrolysis using any power [6].

Therefore, hydrogen bears a manufacture cost, which made it costing three times higher than the petroleum products. The theoretical principle of water electrolysis is the splitting of water into gaseous hydrogen and oxygen by the action of electricity can be expressed as,

$$H_2O_{(l)} + 2F \longrightarrow H_2\,(g) + 1/2\ O_2\,(g) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (1)$$

Where F is the Faraday constant representing the magnitude of electric charge per mole of electrons. (96487) As/mol, Eq. (1) shows that water electrolysis is an extremely clean process, since no polluting by-products are formed. However, it should not be forgotten that a technology cannot be cleaner than the energy source used to power it, [7, 8]. The electrochemical reaction of water electrolysis Eq. (2) is a well-established technique which consists of splitting water into its single components by using electrical energy. Therefore, if the energy source produces no carbon compounds for the required power generation, then the entire production process is carbon free.

$$H_2O \rightarrow {}^{1}\!/_{2}\,O_2 + H_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

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Alkaline electrolysis is well-developed technology which uses an aqueous solution (KOH or NaOH) as electrolyte. During the process of Hofmann voltmeter technique, water at the cathode consumes electrons to form hydrogen. Hydroxide ions are migrating through the solution towards the anode at which they release electrons and consequently, close the cycle. A diaphragm which separates both electrodes and their respective reaction enables to collect the generated gases afterwards. The half and overall reactions of the alkaline electrolysis can be written as:

Cathode: $2H_2O + 2e^- \rightarrow 2OH^- + H_2$ ……………………………….. (3)

Anode: $2OH^- \rightarrow H_2O + {}^1/_2\,O_2 + 4e^-$ ......……………………… (4)

Sum: $H_2O \rightarrow H_2 + {}^1/_2\,O_2$ …………………….............. (5)

Alkaline electrolysis is a commercially mature technology and globally present on the hydrogen production market. The high gas production rate, the long stack lifetime and the relatively high efficiency made it an interesting candidate for large scale and stationary applications [9]. Water electrolysis is known as the H_2/O_2 cell, while for saturated brine electrolysis, it is described as the H_2/Cl_2 cell for caustic soda production. Hydrogen/oxygen is produced in the ratio of 2:1 in the former cell, while hydrogen/chlorine is produced in the molar ratio of 1 : 1. Nowadays, electrolytic hydrogen has a share 4% in the global production of the most abundant element of the universe. Electricity expense constitutes the largest fraction of hydrogen production costs [10]. Little consideration is given however, to the availability and the quality of the raw material used in the production of hydrogen; that is water. Under normal conditions of operation, the electrolysis cell behaves to produce H_2/Cl_2 rather than H_2/O_2. Experimental results are presented for the electrolysis of a wide range of saline water (0.5-7.0% TDS) and interpretations are given for two main cell-operating-characteristics. These are rate of hydrogen production and chlorine evaluation. This is attributed to high over potential of O_2 at practical current densities. The most promising way for the electrolysis of sea water in a H_2/O_2 cell is the use of oxygen-selective electrodes. Oxygen reaction depends rather upon the electrode material than the chlorine reaction does and at low overpotential with different electrode materials (a porous deposit coating containing about 100 mg/m^2 manganese or MnO_2 was reported by Bennett). Thus, in the interval of a pH between 0-3, Cl_2 evolution reaction potential is lower than O_2. Chlorine evolution at the anode replaces oxygen even for chloride concentrations lower than those of sea water. This shows how mass transfer and kinetics combine to make chlorine evolution the dominant anodic reaction product [11]. It is towards this objective that the current research is directed to consider saline water about range of 0.5-7% TDS (total dissolved solids) to be electrolyzed for hydrogen production. Abundant indigenous reserves are represented by underground water, sea water and rejects from water desalination MSF plants. [11]. However, there are some articles on production of hydrogen from electrolysis of sea water. Abdel-Aal et al. in 2010 studied the electrolysis of saline water for the production of hydrogen. In this paper, electrolysis is one of the acknowledged means of generating chemical products from their native state. This is true for hydrogen production from water. The use of sea water (sea water in particular) as a feedstock for producing hydrogen by electrolysis is examined in this work. Under normal condition of operation which are at room temperature in applying potential 1.5, 3, 4.5, 6, 7.5, 9, 12 V.

2. Materials and Methods

2.1. Materials

Sodium hydroxide was obtained from T-Baker and sodium chloride (NaCl) was Made in Mumbai, India. Electrolysis of synthetic sea water, alkaline prepared in the laboratory, and neutral sea water, from the Mediterranean sea of Benghazi in Libya. In analytical part, Hofmann voltmeter technique, pH meter, conductivity meter was utilized. In these experiments, electrolyzes of both synthetic sea water and alkaline water were carried out using a simple Hoffman electrolysis apparatus. Details of the experimental arrangement are given in reference [11].

2.2. Methods

An appropriate amount of potassium hydroxide (KOH) about 4.2 g was dissolved in double distilled water in volumetric flask 250. Sea water was simulated (synthetic sea water) using NaCl (3.5%) Sodium chloride (NaCl), we have used sodium chloride 3.5% M in volumetric flask 250 was diluted by using double distilled water. The experiment was carried out in a 250 ml electrolysis apparatus which uses the basic Hoffman arrangement.

Hoffman's Apparatus is used for demonstrating the decomposition of water, determination of chemical composition by electrolysis and has applications in the evaluation of the electrochemical equivalent of hydrogen. The glass unit has two connected limbs, each of approximately 100 ml capacity (graduated 2 to 100 ml). Total volume is about 250 ml, integral reservoir tube and funnel-shaped bulb, with a stopcock at the top of each limb. The apparatus is filled with solution through the central funnel. The two stopcocks are opened briefly to remove the air from the graduated tubes. A DC current (H works well) and 1 ampere is passed through the electrodes when runs device. These bubbles free from the electrodes and rise up the side limbs to form a gas column under each tap. The cathode evolves oxygen and the anode hydrogen. Theoretically twice the volume of hydrogen is evolved than oxygen. However, oxygen is much more soluble in water than hydrogen, so the measured amount tends to be lower than expected.

The cell has two vertical graduated gas collecting tubes with stopcocks at the top, joined by a bridge-tube at the bottom which is connected to a reservoir as shown Figure 1a and b. The potassium hydroxide solution and synthetic sea water and natural sea water were used. The experiments were conducted in taking with 1.5, 3, 4.5, 6, 7.5, 9 and

12 volts and 1 Ampere for 2 hours. The volumes of hydrogen produced at the cathode and other gases at the anode were obtained and calculated.

Figure-1a. A sketch a Hofmann voltmeter

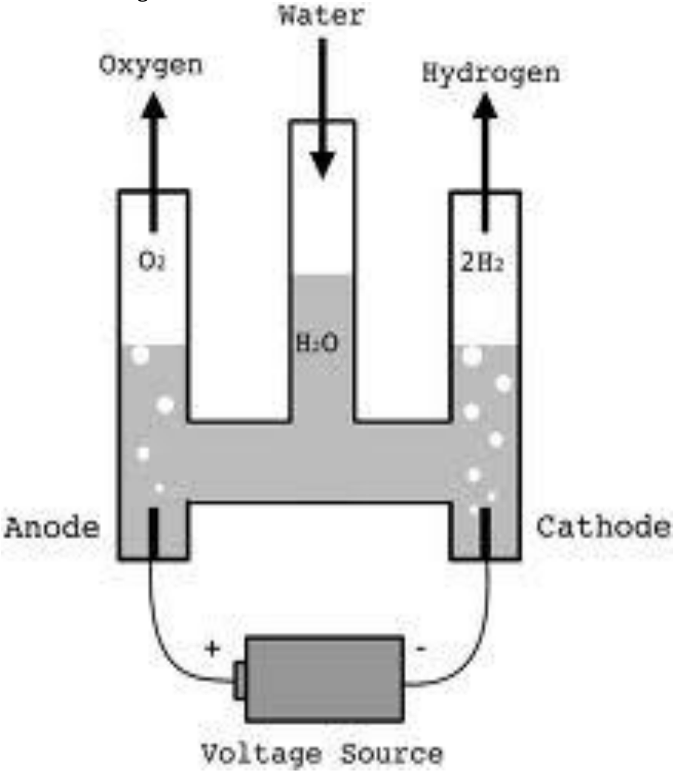
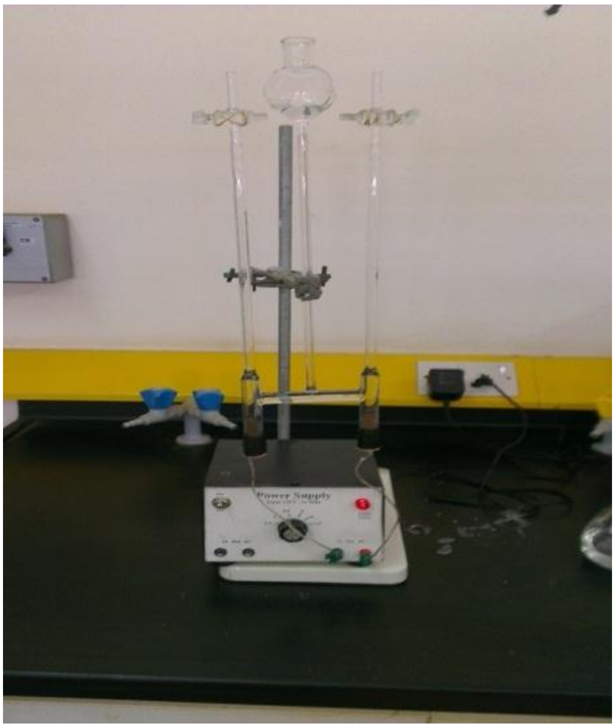


Figure-1b. A Hofmann voltmeter apparatus



3. Results and Discussions

3.1. The Effect of Different Applied Potential of Hydrogen Production Using Potassium Hydroxide

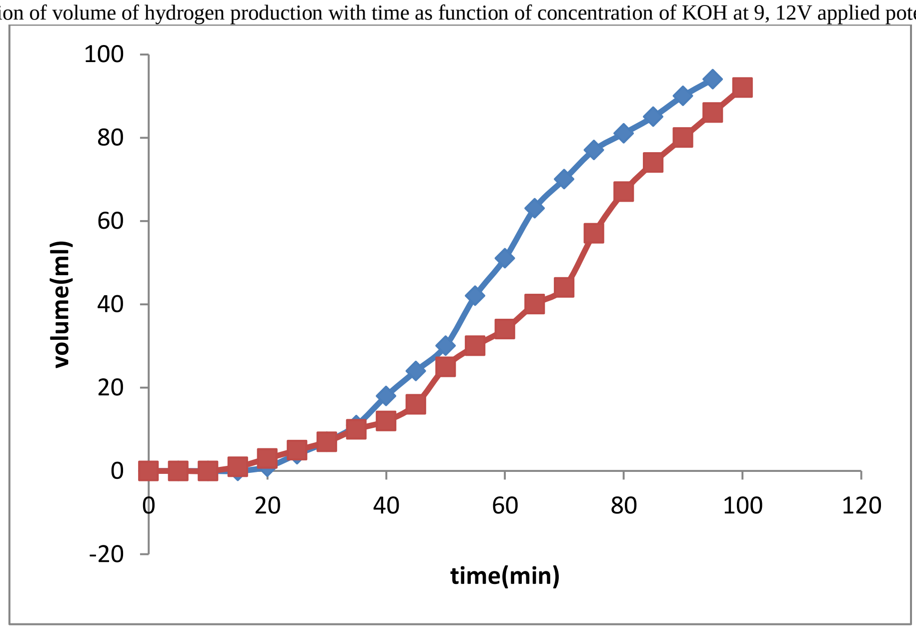
For the solutions investigated, it was found that the hydrogen production rate was dependent upon the applied voltage. Table 1 and Figure 2 display the effect of time on volume of hydrogen gas produced of KOH (0.2 M) for 120 min at 9, 12 V applied potential. There was no hydrogen volume observe at potential less than 9V.

From the Figure 2, we can verify that a greater hydrogen volume is produced in the same amount of time with a higher alkali concentration (and therefore, the reaction rate is higher). Yuvaraj and Santhanaraj [12] showed the influence of an applied voltage on the hydrogen evolution reaction can be studied over cylindrical graphite electrode at the temperature of 593 K with a 0.025 M concentration of KOH. pH and ionic conductivity of potassium hydroxide are 12.91 and 38.7 mS/cm. The applied voltage is varied from 9 to 12 V. It shows that, the rate of production of hydrogen gas gradually increases with increase in applied voltage. At 75 min the highest Hydrogen volume of potassium hydroxide was obtained at 12V. Potassium hydroxide is most commonly used in water electrolysis, avoiding the huge corrosion loss caused by acid electrolytes [1].

Table-1. The value of hydrogen gas produced volume of 0.2 M KOH at 9, 12V applied potential for 120 min.

Time (min)	Volume H_2 (ml) 9V	Volume H_2 (ml) 12V
0	0	0
5	N.d	1
10	1	1.5
15	9	8
20	12	19
25	16	30
30	18	41
35	30	50
40	35	55
45	42	65
50	48	72
55	55	80
60	58	87
65	65	90
70	68	92
75	70	94
80	73	-
85	78	-
90	80	-
95	85	-
100	87	-
105	90	-
110	92	-
115	94	-
120	-	-

Fig-2. The variation of volume of hydrogen production with time as function of concentration of KOH at 9, 12V applied potential for 120 min.



3.2. The Effect of Different Applied Potential of Hydrogen Production Using Sodium Chloride

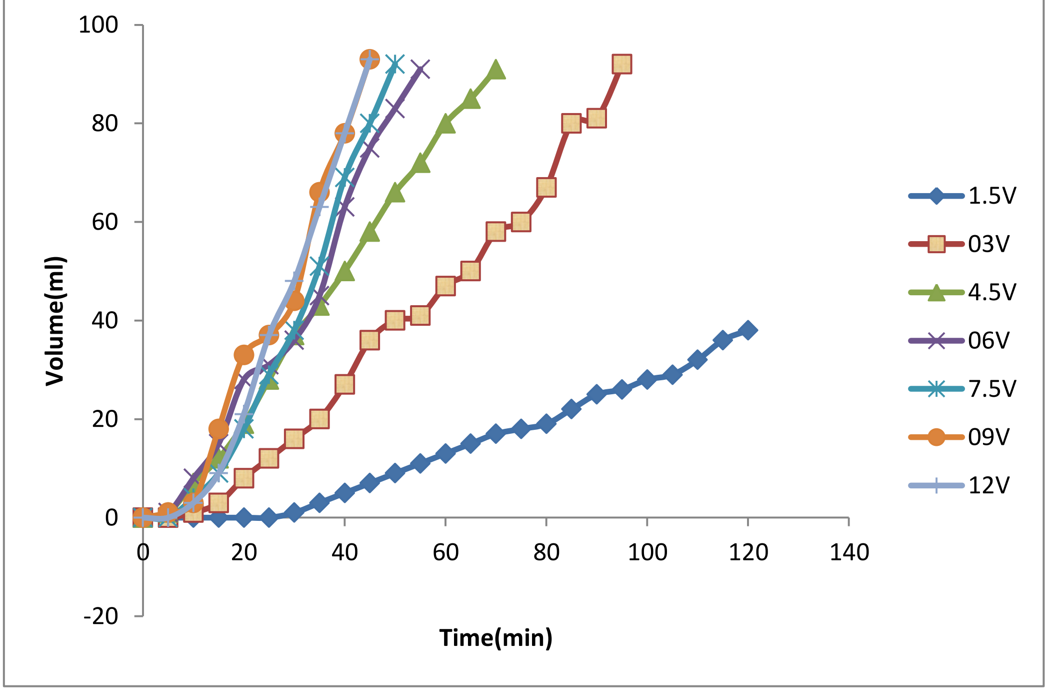
The effect of different applied potential on the production of hydrogen using sodium chloride 3.5% (w/v), Table 2 and Figure 3 show the effect of different the applied potential 1.5, 3, 4.5, 6, 7.5, 9 and 12 volts on the rate hydrogen produce for 120 min. The study revealed that the hydrogen production gradually increases with increasing in applied potential as listed in Table 2 and Figure 3. where pH and ionic conductivity of sodium chloride were 7.54 and 53.7 mS/cm. At 45 min the highest hydrogen volume of potassium hydroxide was obtained at 12v. The highest hydrogen volume of seawater was 93 ml at 9v for 45 min. Brine is a solution of sodium chloride (NaCl) and water (H_2O). The process of electrolysis involves using an electric current to bring about a chemical change and make new chemicals. The electrolysis of brine is a large-scale process used to manufacture chlorine from salt. Two other useful chemicals are obtained during the process, sodium hydroxide (NaOH) and hydrogen (H_2) [13]. The reason why the water took so long to decompose could possibly be due to the fact that the bonds between the hydrogen and oxygen are very strong and so much energy is needed to separate them (hence the long time). Because water is a polar covalent molecule, the hydrogen atoms have partially positive charges and the oxygen a slight negative one.

Table-2. The value of hydrogen gas produced volume of synthetic sea water using 1.5 to 12 V for 120 min.

Time (min)	Volume H_2 (ml) NaCl (1.5V)	Volume H_2 (ml) NaCl (3V)	Volume H_2 (ml) NaCl (4.5V)	Volume H_2 (ml) NaCl (6V)	Volume H_2 (ml) NaCl (7.5V)	Volume H_2 (ml) NaCl (9V)	Volume H_2 (ml) NaCl (12V)
0	0	0	0	0	0	0	0
5	N.d	N.d	1	1	N.d	1	N.d
10	N.d	1	7	8	4	3	3
15	N.d	3	12	15	9	18	9
20	N.d	8	19	28	18	33	21
25	N.d	12	28	31	29	73	37
30	1	16	37	36	38	44	48
35	3	20	43	45	51	66	63
40	5	27	50	63	69	78	78
45	7	36	58	75	80	93	93
50	9	40	66	83	92	-	-
55	11	41	72	91	-	-	-
60	13	47	80	-	-	-	-
65	15	50	85	-	-	-	-
70	17	58	91	-	-	-	-
75	18	60	-	-	-	-	-
80	19	67	-	-	-	-	-
85	22	80	-	-	-	-	-
90	25	81	-	-	-	-	-
95	26	92	-	-	-	-	-
100	28	-	-	-	-	-	-
105	29	-	-	-	-	-	-
110	32	-	-	-	-	-	-
115	36	-	-	-	-	-	-
120	38	-	-	-	-	-	-

ND: not detectable at level of 1 ml.

Fig-3. The influence of various times on volume hydrogen gas produced using 3.5 % NaCl (synthetic sea water) and 1.5, 3, 4.5, 6,7.5,9 and 12V applied potential for 120 min.



3.3. The Effect of Different Applied Potential of Hydrogen Production Using Seawater

The effect of different applied potential on the production of hydrogen using seawater have been studied, Table 3 and Figure 4 show the effect of different the applied potential 1.5, 3, 4.5, 6,7.5, 9 and 12 V on the rate of hydrogen produce for 120 min. Figure 4. illustrates the relationship between the applied potential and time of hydrogen volume production. As can be observed the hydrogen volume increased as amount of voltage. The highest hydrogen volume of seawater was 93 ml at 9v for 45 min. From data, shown down, we have found that the rate of hydrogen production increases ohmically (follows Ohm's law) with the increase in voltage for natural and synthetic seawater. However, the rate of increase at low values of voltage, say 1.5-12V, is rather slow, since the production rate is dependent on the current density. At higher voltages (10 V and above), the initial conductivity is no longer affecting the current density and the solution behaves like a resistance, with lower resistance at high TDS hence, the increase in salinity level gives a proportional increase in the hydrogen productivity.

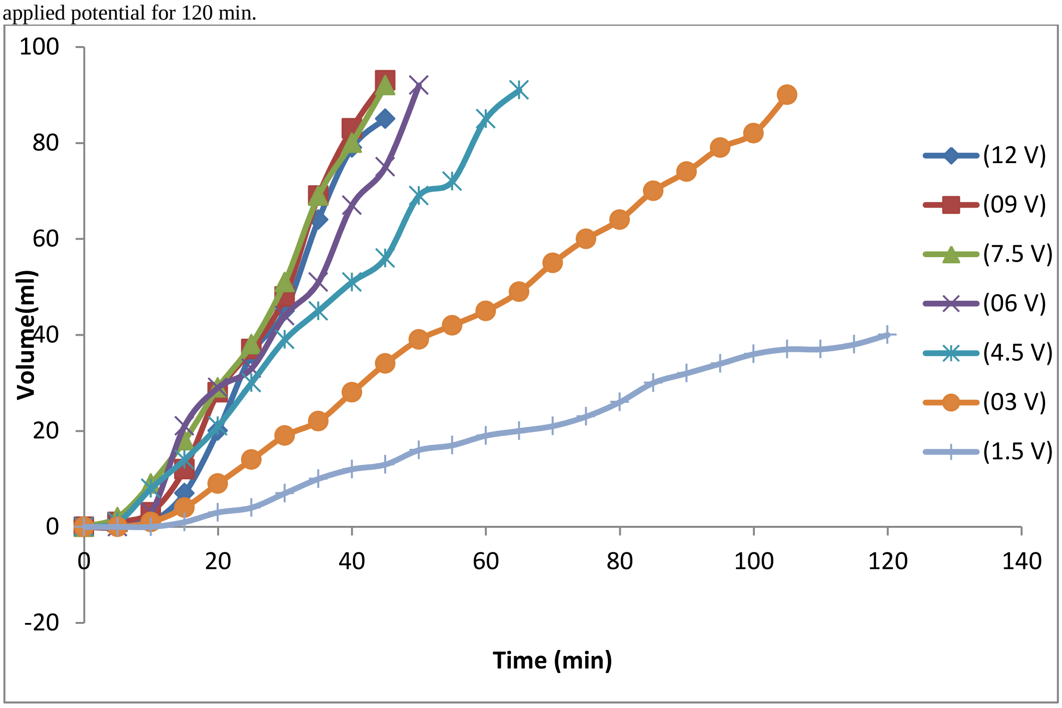
pH and ionic conductivity of sodium chloride are 7.93 and 56.7 mS/cm. Electrolysis is one of the acknowledged means of generating chemical products from their native state. This is true for hydrogen production from water. The use of saline water (sea water in particular) as a feedstock for producing hydrogen by electrolysis. Little consideration is given. However, to the availability and the quality of the raw material used in the production of hydrogen; that is water. Under normal conditions of operation, the electrolysis cell behaves to produce H_2/Cl_2 rather than H_2/O_2. [4, 11]. Direct electrolysis of seawater would have two distinguished outcomes, depending on the voltage supplied to the cell. One of the earliest studies on the direct electrolysis of seawater has shown that hydrogen is evolved at high current efficiency at the cathode of the electrolysis cell, while chlorine is produced in the form of sodium hypochlorite (NaOCl) in large quantities at the anode [13].

Table-3. The value of hydrogen gas produced volume of sea water using 1.5 to 12 V for 120 min.

Time (min)	**Volume H_2 (ml) seawater (1.5V)**	**Volume H_2 (ml) seawater (3V)**	**Volume H_2 (ml) seawater (4.5V)**	**Volume H_2 (ml) seawater (6V)**	**Volume H_2 (ml) seawater (7.5V)**	**Volume H_2 (ml) seawater (9V)**	**Volume H_2 (ml) seawater (12V)**
0	0	0	0	0	0	0	0
5	N.d	N.d	1	N.d	N.d	1	N.d
10	N.d	1	8	3	4	3	1
15	1	4	14	21	11	12	7
20	3	9	21	71	29	28	20
25	4	14	30	33	36	73	36
30	7	19	39	44	43	48	45
35	10	22	45	51	54	69	64
40	12	28	51	67	68	83	79
45	13	34	56	75	79	93	85
50	16	39	69	92	85	-	-
55	17	42	72	-	-	-	-
60	19	45	85	-	-	-	-
65	20	49	91	-	-	-	-
70	21	55	-	-	-	-	-
75	23	60	-	-	-	-	-
80	26	64	-	-	-	-	-
85	30	70	-	-	-	-	-
90	32	74	-	-	-	-	-
95	34	79	-	-	-	-	-
100	36	82	-	-	-	-	-
105	37	90	-	-	-	-	-
110	37	-	-	-	-	-	-
115	38	-	-	-	-	-	-
120	40	-	-	-	-	-	-

ND: not detectable at level of 1 ml.

Fig-4. The influence of various times on volume hydrogen gas produced using seawater and 1.5, 3, 4.5, 6, 7.5, 9and 12V applied potential for 120 min.



4. Conclusion

Interestingly, From above result, we noted that the rate of hydrogen production increases ohmically (follows Ohm's law) with the increase in voltage for alkaline natural and synthetic seawater. The highest hydrogen volume achieved in this work was 93 ml at 45 min. This may be due to the highest of ionic conductivity. It was found that seawater show the production in volume in less time where seawater shows the highest than sodium chloride and potassium hydroxide. It was conducted that seawater show high value of production of hydrogen. The highest hydrogen volume was obtained at approximately 45 min for seawater. Overall, seawater shows the highest hydrogen volume than potassium hydroxide and sodium chloride. The reason behind that is that seawater has high ionic conductivity.

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