Appendix

Table 1:- Amount of H_2S dissolved in different percentage of MEA (Figure 3-1).

Temp C°	10% MEA	20%MEA	30%MEA
0	0	0	0
30	2.5	1.75	1.5
40	2.5	2.25	1.75
50	2.75	2.25	1.75
60	3	2.5	2
70	3	2.75	2
80	3.25	2.75	2.25
90	3.5	3	2.25

Table 2:-Volume of hydrogen produced (mL) in different percentage of MEA (Figure 3-3a).

Time (min)	10%MEA	15%MEA	20%MEA	30%MEA	35%MEA
0	٠	0	٠	٠	٠
١٥	0.2	0.3	0.45	0.3	0.25
٣٠	0.45	0.45	0.8	0.5	0.45
٤٥	0.6	0.7	1.05	0.75	0.6
٦٠	0.96	0.95	1.15	1.05	0.85
٧٥	1.2	1.3	1.5	1.3	1.2
٩٠	1.65	1.7	1.9	1.5	1.45
١٠٥	1.7	1.8	2	1.55	1.45
١٢٠	1.7	1.85	٢	1.6	1.5

Table 3:- Volume of hydrogen produced (mL) using different catalyst (Figure 3-6).

Time (min)	2mg TiO_2	5mg ZnO	with out catalyst
0	0	0	0
١٥	0.45	0.05	0.05
٣٠	0.8	0.2	0.13
٤٥	1.05	0.35	0.23
٦٠	1.3	0.51	0.31
٧٥	1.54	0.72	0.43
٩٠	1.85	0.94	0.55
١٠٥	1.95	1.1	0.61
١٢٠	2	1.2	0.72

Table 4:- Volume of hydrogen produced (mL) using different load of titanium dioxide (Figure 3-7a).

Time (min)	0.5 mg TiO_2	1 mg TiO_2	1.5 mg TiO_2	2 mg TiO_2	2.5 mg TiO_2
0	0	0	0	0	0
١٥	0.33	0.13	0.25	0.3	0.15
٣٠	0.55	0.6	0.55	0.69	0.25
٤٥	0.7	0.85	0.7	0.91	0.44
٦٠	0.8	1.2	0.9	1.06	0.59
٧٥	1.09	1.49	1.21	1.405	0.82
٩٠	1.45	1.6	1.6	1.79	0.89
١٠٥	1.6	1.75	1.85	1.98	0.93
١٢٠	1.6	1.8	1.9	2	0.95

Table 5:- Volume of hydrogen produced (mL) using different percentage of hydrogen peroxide (Figure 3-9a).

Time (min)	With out H_2O_2	0.5% H_2O_2	1% H_2O_2	1.5% H_2O_2	2% H_2O_2
0	0	0	0	0	0
١٥	0.55	0.4	0.45	0.15	0.2
٣٠	0.96	0.75	0.6	0.35	0.45
٤٥	1.25	0.95	0.8	0.65	0.7
٦٠	1.61	1.2	1.3	0.95	0.95
٧٥	1.75	1.6	1.75	1.2	1.15
٩٠	1.9	1.85	2.1	1.5	1.25
١٠٥	1.95	2.05	2.2	1.75	1.5
١٢٠	2	2.1	2.25	1.8	1.6

Table 6:- Volume of hydrogen produced (mL) in different temperature with irradiation (Figure 3-10a).

Time (min)	278.15K	283.15K	293.15K	298.15K	303.15K	308.15K
0	0	0	0	0	0	0
١٥	0.6	0.4	0.4	0.55	0.3	0.25
٣٠	1.05	0.75	0.65	0.95	0.65	0.6
٤٥	1.35	0.9	0.95	1.25	0.8	0.75
٦٠	1.55	1.2	1.3	1.45	0.9	0.9
٧٥	1.8	1.6	1.55	1.75	1.05	1.1
٩٠	2.1	1.95	1.75	1.9	1.4	1.3
١٠٥	2.2	2.05	1.95	2	1.65	1.45
١٢٠	2.25	2.15	2.05	2.00	1.7	1.5

Table 7:- Volume of hydrogen produced (mL) in different temperature with out irradiation (Figure 3-10c).

Time (min)	278.15K	283.15K	293.15K	298.15K	303.15K	308.15K
0	0	0	0	0	0	0
١٥	0.02	0.05	0.05	0.05	0.047	0.12
٣٠	0.02	0.05	0.05	0.05	0.1	0.179
٤٥	0.02	0.05	0.05	0.1	0.131	0.226
٦٠	0.02	0.05	0.1	0.138	0.179	0.28
٧٥	0.02	0.05	0.1	0.2	0.248	0.318
٩٠	0.02	0.05	0.134	0.25	0.296	0.358
١٠٥	0.02	0.05	0.134	0.253	0.336	0.416
١٢٠	0.02	0.05	0.152	0.253	0.376	0.453

Table 8:- Volume of hydrogen produced (mL) in the case of addition different concentration of riboflavin (Figure 3-11a).

Time (min)	2mg TiO_2	2.5 mg (Rib)	2mgTiO_2 3mg Rib	2mgTiO_2 1mg Rib	2mgTiO_2 2mg Rib	2mgTiO_2 2.5mg Rib
0	0	0	0	0	0	0
١٥	0.55	0.141	0.25	0.45	0.45	0.6
٣٠	0.949	0.274	0.4	0.65	0.65	0.85
٤٥	1.235	0.486	0.6	0.9	0.9	1.1
٦٠	1.472	0.742	0.848	1.2	1.2	1.45
٧٥	1.75	1.042	1.157	1.65	1.65	1.85
٩٠	1.87	1.272	1.4	1.95	1.95	2.05
١٠٥	2	1.352	1.475	2.05	2.05	2.25
١٢٠	2	1.35	1.5	2.1	2.1	2.3

Table 9:- Scale of hydrogen meter as arbitrary unit *v*s. volume of hydrogen (Figure 3-12).

V_{H2}(mL)	Pure H_2	2mgTiO_2 2.5mg Rib	2mgTiO_2 1% H_2O_2	2mgTiO	With out catalyst
0	0	0	0.4	0	0
0.1	15	10	9	8	4
0.2	25	25	23	14	8
0.3	37	37	35	25	13
0.4	52	48	44	35.1	17
0.5	66	59	52	43	19
0.6	77.7	67	62	52	23
0.7	89	76	70	62	28
0.8	99.2	84	81	72	32
0.9	100	94	91	83	39
1	100	97	95	91	47

<u>Grammar Certification</u>

I certify that the thesis presented by Inam Hussein Ali titled: "**PHOTOPRODUCTION OF HYDROGEN FROM HYDROGEN SULFIDE IN AQUEOUS SOLUTIONS OF MONOETHANOLAMINE USING TITANIUM DIOXIDE AS PHOTOCATALYST**" was corrected from all grammar and expression mistakes present in it, and now it is suitable for discussion in the regard to expression and grammar side.

Signature
Dr. Salima Abdul –Zahra
Date: / /

INTRODUCTION

The main condition that all countries have agreed on about the future of earth is to keep it clean and free of pollution. For using energy and still keeping the earth clean, the final solution is to use alternative fuels. These fuels must satisfy at least three main requirements: (1)

- Being clean, meaning that no by-products harmful to the environment will be produced.
- Being abundant.
- Being economic.

Hydrogen, as an alternative clean fuel, would be a good choice because when it reacts with oxygen it gives only water. Using hydrogen as an alternative fuel rests upon the fact that it is both abundant and not harmful to the environment.

$$H_{2\,(g)} + 1/2\ O_{2\,(g)} \longrightarrow H_2O_{(g)}\ \Delta H = -242\ \text{kJ mol}^{-1} \text{...... (1-1)}$$

1.1 POLLUTING BY FOSSIL FUEL

The burning of fossil fuels is a source of environmental pollutants .Acid rain, which has been shown to be harmful to the environment, is believed to be partially a result of burning coal and petroleum .These fuels contain sulfur compounds that burn to give sulfur dioxide, which reacts in moist air to form sulfuric acid, a major component of acid rain (2). It appears that carbon dioxide, a main product in the burning of fossil fuel, may also be a major pollutant .The percentage of CO_2 in the atmosphere has risen steadily since the large-scale burning of fossil fuels began in the late nineteenth century. Carbon dioxide in the atmosphere acts like the glass on a green house, retaining the earth's heat energy (3). Climatologists believe that this green house effect is at last partly responsible for the recent increase in the average high temperature of the surface of earth and this global warming may increase because of the increasing concentration of carbon dioxide in the atmosphere from fossil fuel burning (4) .Controlling carbon dioxide emissions in the atmosphere is a difficult challenge, but the answer might lie in the conversion to hydrogen energy economy.

1.2 HYDROGEN FUEL

It is important to realize that hydrogen is not an energy source; mistake still made fairly often by other wise sophisticated .It is not primary energy like natural gas or crude oil existing freely in nature. It is an energy carrier a secondary form of energy that has to be manufactured like electricity (5).

1.2.1 Properties

When compared hydrogen to other common fuels on a per unit mass basis, hydrogen is found to have a considerably higher heating value than many of the hydrocarbons fuels in common usage .For example, hydrogen's heating value is 120kJ/g compared to 50kJ/g for natural gas and 45kJ/g for gasoline (6).Therefore, now the value of the fuels is measured as the ratio H/C increase. This makes hydrogen especially attractive for use where fuel weight is of considerable importance, such as in aviation or space applications .Although hydrogen offers a much higher heating value per unit weight, beside that hydrogen is not producing CO_2 gas. The energy required to ignite hydrogen is an order of magnitude less than that required to ignite hydrocarbons fuels ,but that energy must be supplied at a higher temperature than that required for hydrocarbon fuels(7).

1.2.2 Occurrence of Hydrogen

The spectroscope shows that hydrogen present in the sun and many stars. It makes up 0.9% of the mass and 15.1% of the atoms in earths crust. If we look beyond our home planet ,hydrogen atoms thought to make up 89% of the atoms on the sun ,and 85% to 95% of the atoms in the atmospheres of outer planets .In the universe as a whole ,about 90% of all atoms is H (the rest are mainly He). Only trace amount of free hydrogen(H_2) is found on earth; it must be obtained from its compounds(8) .Although hydrogen occurs in more compounds than does any other element, only a few compounds are economically viable source of the element .Water is the most abundant hydrogen-containing compound. Most of the earth's hydrogen is present as water, either in the ocean or trapped inside minerals and clays. Hydrogen is also found in the hydrocarbons that make up the fossil fuel: coal, petroleum, and natural gas (9).

1.2.3 Uses of Hydrogen

Nearly half of the hydrogen gas produced in the manufacture of ammonia (NH_3).Ammonia, in turn, is used in the manufacture of fertilizers, plastic, and explosive (10). The second most important use of hydrogen is the petrochemical industry .For example hydrogen is used to convert benzene to cyclohexane, acyclic hydrocarbon used as an intermediate in the production of nylon .Another chemical manufacturing process that uses hydrogen is the synthesis of methanol an industrial solvent and a raw material for making other organic compounds(11).

$$CO_{(g)} + 2H_2 \xrightarrow{\text{Catalyst}} CH_3OH_{(g)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(1-2)}$$

1.2.4 Production of Hydrogen Fuel

The principal commercial processes specific for the production of hydrogen are steam reforming, partial oxidation, coal gasification, and water electrolysis, however, these are not of equal economic importance.

Relatively small quantities of hydrogen are produced by these processes .World wide, hydrogen as a raw material for the chemical industry is derived as follows: 77% from natural gas /petroleum, 18% from coal, 4% from water electrolysis, and 1 % by other means (12).After the energy crisis and pollution of the earth by CO_2, researchers concentrate on the production of hydrogen from water because hydrogen can be produced with no negative environmental effects.

1.2.5 Water- Splitting Techniques

As the water is most abundant and cheap, breaking up the water molecules is a difficult process because of the strong chemical binding forces between hydrogen and oxygen. Water can be broken up in many ways, including directly, with extreme heat, with the help of chemicals in two or more steps; with a combination of heat and chemical; and by running an electrical current through water in electrolysis(5).

The water electrolysis is an old and proven process to convert water to hydrogen, and is used industrially on a limited scale .The main problem is that electricity used to drive the process is 3-5 times more expensive than fossil fuel-derived energy (13).However, it has been used to significant extent only in place where electricity is very cheap (such as Canada and Norway).The electrolysis of water is a very clean, reliable process, and hydrogen is very pure. Electrochemical water splitting occurs when two electrodes are placed in water and a direct current is passed between the electrodes (14).

Cathode $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$……………. (1-3)

Anode $2OH^- \longrightarrow \frac{1}{2}O_2 + H_2O + 2e^-$…………….(1-4)

Three types of electrochemical water - splitting processes have been employed:

1- An aqueous alkaline system.
2- A solid polymer electrolyte (SPE).
3- High temperature (700-1000°C) steam electrolysis.

The first two systems are used commercially; the last is under development (15) .Unfortunately, about half the energy associated with electricity is unavoidably converted to waste heat. An alternative is to use excess hydroelectric or nuclear power. Such power sources typically generate more power than can be immediately used, and this excess can not readily be stored as such for future use to produce hydrogen. The hope of the future is that either wind power or solar cell energy collected via photovoltaic collectors that convert light directly into electricity; this will be an economically viable means of providing electricity to generate hydrogen.

Even better would be the direct decomposition of water into hydrogen and oxygen by sunlight, though no practical, efficient methods have yet been devised to affect this transformation. One of the difficulties in using sunlight to decompose water is that H_2O does not absorb light in the (Visible) or (UV) regions; thus some substance must be found that can absorb sunlight, transfer the energy to the decomposition process, and finally be regenerated (16). The uses of semiconductors and sensitizers in process of photodecomposition of water using visible light were the major field of the researcher around the world since 1972 when Fujishima and Honda (17) discovered the photocatalytic splitting of water on TiO_2 electrodes using sunlight. Also Getoff (18) studied the production of hydrogen from water using solar energy and different types of semiconductor electrodes.

Anode $TiO_2 + 2h\nu \longrightarrow 2e^- + 2p^+ (TiO_2)$………….... (1-5)

$2p^+ (TiO_2) + 2H_2O \longrightarrow 2H^+ + O_2$ ……....... (1-6)

Cathode $2H^+ + 2e^- \longrightarrow H_2$ ………………………... (1-7)

In another work (19), using titanium dioxide supported by Pt and RuO_2 ($Pt/TiO_2/RuO_2$) was done to produce hydrogen and oxygen gases from water. The same results with higher efficiency were gotten after the addition of ruthenium trisbipyridine as the photosensitizer $[Ru (bipy)_3]^{+2}$ and methyl viologen (MV^{+2}) as the relay agent and EDTA and TEOA as the sacrificial electron donor agents (20).

Because of the low percentage of decomposition water and higher cost processes due to the strong bond of hydrogen and oxygen in water, another source of hydrogen must be found. The other suitable molecule which contains hydrogen is hydrogen sulfide, the hydrogen in H_2S is quite loosely bond compared to many other simple compounds that contain hydrogen such as water (H_2O) and methane (CH_4)(21).Because of the low energy of H-S bond, it is possible that lower cost processes could be devised by making hydrogen from hydrogen sulfide. The work in this thesis is the production of hydrogen from hydrogen sulfide.

1.3 HYDROGEN SULFIDE GAS

1.3.1 Physical and Chemical Properties of H_2S

Hydrogen sulfide is a colorless, flammable gas. At low concentration it has an odor similar to rotten eggs. Hydrogen sulfides relative molecular mass is 34.08 g/mole (22).

Hydrogen sulfide is soluble in water; the water solubility at 20°C is 1g in 242mL.The taste threshold for hydrogen sulfide in water between 0.05 and 0.1 mg/L (23). Hydrogen sulfide is also soluble in alkanol amines, alcohol, ether, glycerol, gasoline, kerosene, crude oil, and carbon dioxide (24).

The other physical properties of hydrogen sulfide as follow:-

Boiling point: -60.7 °C

Melting point: -85.5 °C

Density: 1.4 g/L at 25 °C

Dissociation Constant: PK_1=6.97, PK_2=12.9 at 25 °C (25-26).

1.3.2 Source of Hydrogen Sulfide

Hydrogen sulfide is produced naturally and as a result of human activity .Natural sources account for about 90% of the total hydrogen sulfide in the atmosphere (27). Hydrogen sulfide is produced through non-specific and anaerobic bacterial reduction of sulfates and sulfur-containing organic compounds (28). It is released primarily as a gas and found naturally in crude petroleum, natural gas, volcanic gas, and hot spring. Hydrogen sulfide is also found in ground water (29).

Significant quantities of acid gases are generated each year (more than 200,000 tons/day of hydrogen sulfide processing capacity is in place world wide (30). Estimates of the terrestrial emission rate of hydrogen sulfide range from 53 to 100 million tones of sulfur per year. Estimates of the emission rate from oceans range from 27 to 150 millions tones of sulfur per year (31). The principal source of hydrogen sulfide is recovery as a by-product in the purification of natural and refinery gases (32). It is a by -product of Kraft pulp and paper manufacturing of carbon disulfide production(33) .Ambient hydrogen sulfide concentration in the air near land fills indicate that landfills may be a source as well.

1.3.3Toxic Effects of Hydrogen Sulfide

Hydrogen sulfide is a very toxic gas at normal temperature .It posses a very serious inhalation hazard. Hydrogen sulfide is rapidly absorbed into the body, almost exclusively through inhalation (34). The acute toxicity of inhaled hydrogen sulfide is well documented and includes effects on the respiratory, cardiac and nervous systems (35). The chief toxic effects are associated with the deactivation of enzymes ,either through the cleavage of their disulfide bridges or by the binding of sulfide to metal co-factors such as Fe^{+2},Mg^{+2},Cu^{+2} (36,37).

A study of human health consequences associated with prolonged low-level exposure to hydrogen sulfide might be encountered under conditions of general urban air pollution, has not been carried out. No reports of toxic effects due to hydrogen sulfide present in drinking water have been found, it is worth noting that although sulfides can persist in water for long periods of time, they are not stable(38).

Physiological responses to acute exposure to hydrogen sulfide have been reported as follow (39)

10 ppm	Beginning of eye irritation
50-100 ppm	Slight conjunctivitis and respiratory tract irritation after one hour
>100 ppm	Coughing, eye irritation, loss of smell after 2-15 minutes. Altered respiration, pain in the eyes, and drowsiness after 15-30 minutes followed by throat irritation after one hour.

	Several hours' exposure results in gradual increase in severity of symptoms and death may occur within the next 48 hours.
200-300 ppm	Marked conjunctivitis and respiratory tract irritation after one hour exposure.
500-700 ppm	Loss of consciousness and possibly death in 30 minutes to one hour of exposure.
700-1000 ppm	Rapid unconsciousness, cessation of respiration, and death.
1000-2000 ppm	Unconsciousness at once, with early cessation of respiration and death in a few minutes. Death may occur if individual is removed to fresh air at once.

1.3.4 Hydrogen Sulfide Removal and Recovery

Hydrogen sulfide represents the largest source of recovered sulfur.Hydrogen sulfide is often present in natural gas or refinery streams, occurring naturally or as the by-product of processing operations such as hydro heating(40) .A number of processes have been developed to remove and recover hydrogen sulfide. These processes are generally categorized according to the primary mechanism, as adsorption, absorption, or conversion. It is also common for these processes to be classified on the basis of functionality, for example, as scavenger, redox, Claus, etc (41).

In Iraq, about 2200 tons a day of sulfur are extracted from H_2S through Claus process. The Claus process is the most widely used to convert hydrogen sulfide to sulfur at most locations that produce it. The process, developed by C.F.Claus in 1883, was significantly modified in the late 1930s by I.G.Fabenin industry AG, but did not become widely used until the 1950s (42). Figure (1-1) illustrates the basic process scheme of Claus unit. A Claus sulfur recovery unit consists of a combustion furnace, waste heat boiler, sulfur condenser, and a series of catalytic stage (43).

First H_2S is separated from the host gas stream using amine extraction. Then it is fed to the Claus unit, where it is converted in two steps:

1- Thermal step: The H_2S is partially oxidized with air .This is done in a reaction furnace at high temperature (1000-1400°C) .Sulfur is formed, but some H_2S remains unreacted, and some SO_2 is made.

2- Catalytic step: The remaining H_2S is reacted with the SO_2 at lower temperature (about 200-350°C) over a catalyst to make more sulfur.

A catalyst is needed in the second step to help the components react with reasonable speed (44).

The reaction is as follows:

$$2H_2S + SO_2 \longrightarrow 3S + 2H_2O \qquad (1\text{-}8)$$

Inevitably a small amount of H_2S remains in the tail gas. This residual quantity, together with other trace sulfur compounds, is usually dealt within a tail gas unit. The latter can give overall sulfur recoveries of about 99.8% which is very impressive indeed.

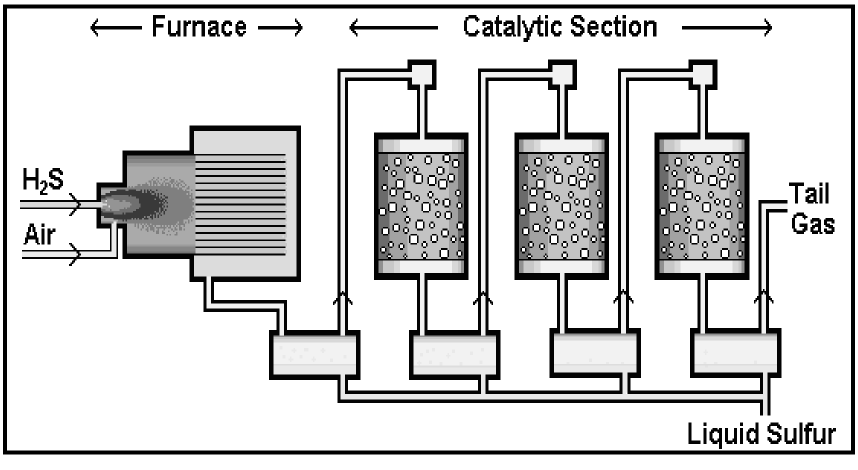

Figure [1-1] The basic process scheme of Claus unit.

But treating H_2S by Claus process leads to recovery only elemental sulfur and hydrogen in H_2S can not be recovered and it is finally wasted in the form of water (45).

Removal of hydrogen sulfide using alkanolamines, gas sweetening, was patented in 1930. Several amine solvents are available as of the mid 1990(46).The most widely used are mono ethanolamine, diethanoamine.The first alkanolamine to gain commercial acceptance was monoethanolamine (MEA) because it offers several advantages, primarily the lowest solvent cost and lowest hydrocarbon co-absorption (47). MEA typically requires higher solvent circulation rates and higher regeneration energy than competing amine process. In addition, the MEA process has shown a higher tendency toward corrosion and foam.

Photochemical cycles to produce hydrogen from hydrogen sulfide bring a revolution in the technology of energy. These cycles for production of hydrogen from splitting of hydrogen sulfide are energetically more favorable than those of water and should be considerably simpler to practice.

1.4 PHOTOCHEMICAL PROCESS

The primary photo chemical process comprises a series of events. These events begin with the absorption of a photon by a molecule, and end either with the disappearance of that molecule or with its conversion to a state such that its reactivity is statistically not greater than that of similar molecules in thermal equilibrium with their surroundings.

In the primary photochemical process there are usually a variety of paths for degradation of the electronic energy of excitation: (48)

- Photochemical paths

They include intermolecular rearrangement or the formation of free radicals and excited molecules which may react in secondary process to form new products of chemical interest.

$A^{*} \longrightarrow$ photo dissociation products…………………….. (1-9)

$A \xrightarrow{hv+O_2}$ photo oxidation products ………………………. (1-10)

$A \xrightarrow{hv+H_2}$ photo reduction products ……………………… (1-11)

- Photophysical paths

They do not lead to a net chemical change, yet are alternate paths for loss of the absorbed energy.

$A^{*} \longrightarrow A + h\nu$ (Radiative [Fluoresence, Phosphoresence])... (1-12)

$A^{*} \longrightarrow A$ + Heat (Non radative(IC, ISC)………………….. (1-13)

$A^{*} + B \longrightarrow B^{*} + A$ (Energy Transfer)…………………….. (1-14)

1.4.1 Photocatalysis

Catalysis refers to the process by which a substance (the catalyst) accelerates kinetically slow reaction and the catalyst is fully regenerated at the end of each catalyst cycle .When photons are also implicated in the process, photocatalysis is defined without the implication of some special or specific mechanism as the acceleration of the rate of a photo reaction by the presence of catalyst (49).

The catalyst may accelerate the photoreaction by interaction with a substrate either in its ground state or in its exited state and/or with the primary photoreaction. Therefore, the non descriptive term photo catalysis is a general label to indicate that light and some substance, the catalyst or the initiator, are necessary entities to influence a reaction. The process must be shown to be truly catalytic by some acceptable and attainable parameter (50).

Reaction [1-15] in which the titanium dioxide serves as a catalyst, may be taken as both a photocatalytic oxidation and a photocatalytic dehydrogenation.

$$CH_3\text{-}CH(OH)\text{-}CH_3 + \tfrac{1}{2}O_2 \xrightarrow{h\nu/\ TiO_2} CH_3\text{-}CO\text{-}CH_3 + H_2O \quad ....(1\text{-}15)$$

The photocatalyst employed, e.g., TiO_2 or ZnO, is inexpensive and can be supported on a suitable materials .This technology has industrial potential and research in photocatalysis has been driven by legislation in industrialized countries encouraging water decontamination destruction(51,52).

1.4.2 Heterogeneous Photocatalysis

Heterogeneous photocatalysis is a technology based on the irradiation of a semiconductor (Sc) photocatalyst, for example, titanium dioxide ($TiO_{2)}$, zinc oxide (ZnO), or cadmium sulfide (CdS) (53).

Semiconductor materials have electrical conductivity properties between those of metal and insulators, and have narrow energy gaps between the filled valance band and the conduction band (54, 55).

A number of electronic and photochemical processes occur following band gap excitation of a semiconductor. Figure [1-2] illustrates a sequence of photochemical and photophysical events and the possible redox reactions which might occur at the surface of the semiconductor particle in contact with solution. Absorption of light energy greater than or equal to the band gap (E_{bg}) of the semiconductor results in a shift of electron from the valance band (VB) to the conduction band (CB) and the creation of hole (h^+) in the valence band (56).

$$Sc + h\nu \xrightarrow{\qquad} h^{+}_{(VB)} + e^{-}_{(CB)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1\text{-}16)$$

These charges carry recombine ,radiatively and/or non radiatively ,in competition with rapid diffusion to the surface where the resulting non equilibrium distribution of electron and holes gives rise to reduction or oxidation processes of adsorbed species ;surface groups ,and the semiconductor components. When illuminated with light of sufficient energy, the semiconductor particle becomes part of a particulate system capable of mimicking a microphotoelectrochemical cell at which efficient reductive and oxidative processes may take place (57). The efficiency of these processes is largely determined by five factors:

1. Efficient absorption of solar light with minimal entropy production.
2. Fact charges separation after light absorption.
3. Separation of products in order to prevent reveres reaction.

4. Adjustment of the redox potentials of the excited state to the redox reactions which store the energy.
5. Long –term stability or continuous reproduction (58).

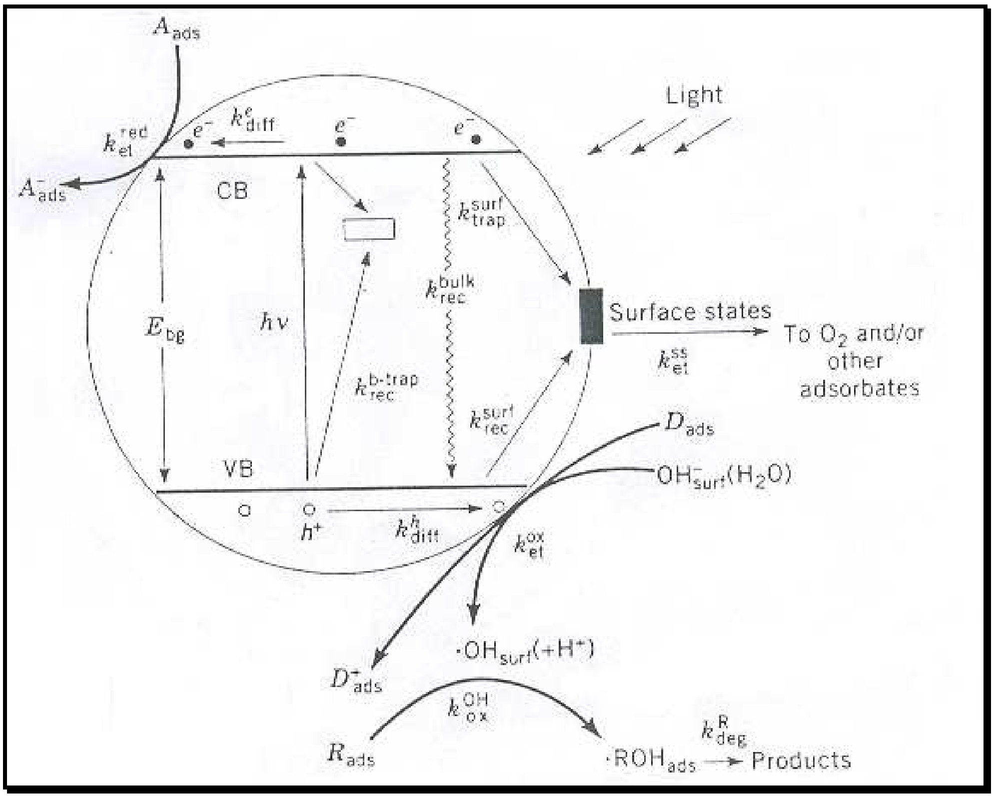

Figure (1-2) Photophysical and photochemical processes in a semiconductor cluster where A_{ads} and D_{ads} represent chemical species, adsorbed on the surface of the semiconductor particle, which are capable of undergoing reduction (A_{ads}) and oxidation (D_{ads}) at rates k^{red} and k^{ox}, respectively. The subscript et = electron transfer. Other reaction rates are designated according to the species undergoing the reaction, eg, k^{OH}. The subscripts diff, deg, ox, rec, surf, and trap refer to the processes of diffusion, degradation, oxidation, recombination, surface, and trapping, respectively. E_{bg}=band gap energy; CB and VB refer to the semiconductor conduction band and valance band, respectively.

The dominant competitive process to charge separation is e^-/h^+ recombination, which for semiconductor clusters primarily occurs via non radiative processes. Figure [1-3] illustrates band gaps and band edge positions in aqueous media for a number of semiconductor materials which have been explored in heterogeneous photocatalysis (59).

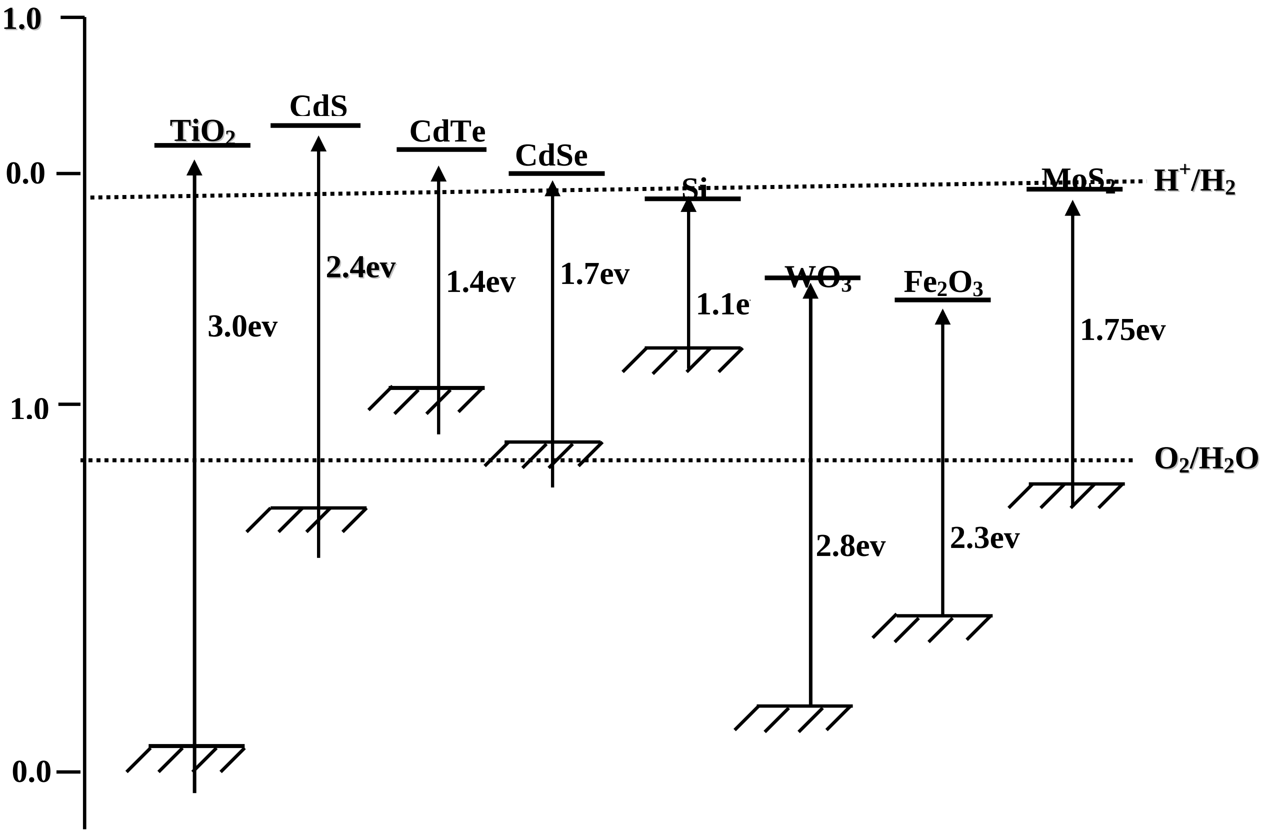

Figure (1-3) Band edge positions of several semiconductors.

1.4.3 Mechanism of Heterogeneous Photocatalysis on TiO_2

Titanium dioxide is a white pigment either in an anatase or rutile form. The history of this pigment is relatively recent compared to other white pigment (60) .Commercial production of this pigment was discovered in the early 1990s during the investigation of ways to convert ilmenite to iron or titanium-iron alloys (61).

Titanium dioxide can exist in one of the three crystal forms: rutile, anatase, and brookite. Both rutile and anatase crystallize in the tetragnol system, brookite in the rhombic system (62). Only anatase and rutile forms have good pigmentary properties, and rutile is more thermally stable .Anatase transforms rapidly to rutile at a temperature above 700°C (63).

Anatase is the most common and widely used polymorphs of TiO_2.Its crystal is formed by chains of distorted TiO_6 octahedra, and its tetragnol structure can be described in terms of three parameters: two cell edges a and c, and one internal parameter d (Fig1-4). In the most anatase phase the unit cell contains four TiO_2 units. Each Ti atom is coordinated to the six neighboring oxygens via two (long) apical and four (short) equatorial bonds, of lengths 1.979Å and 1.932Å ,respectively, at 15 K. Each O atom is coordinated to three Ti atoms via one long bond and two short bonds, lying in the same plane (64).

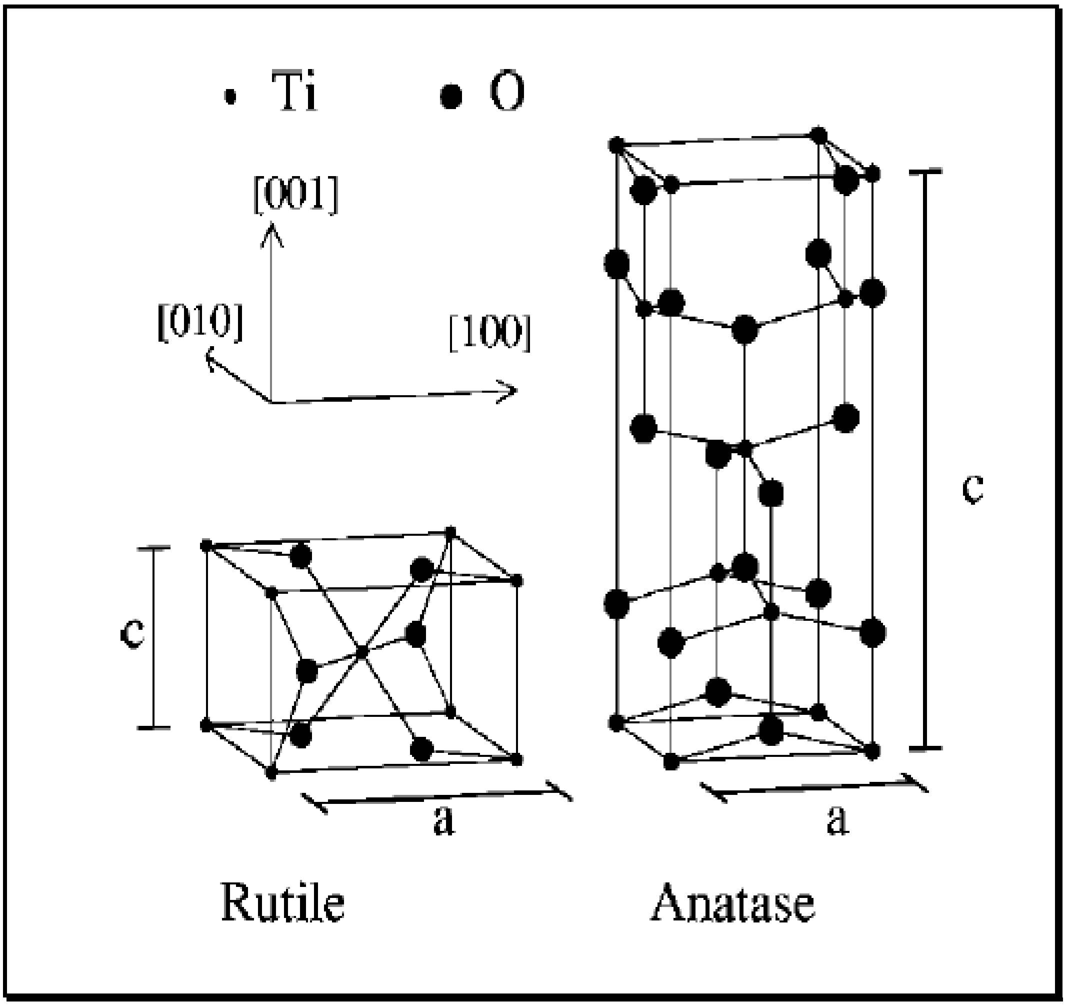

Figure (1-4) Bulk TiO_2 crystal structure in the rutile and anatase phases

Titanium dioxide as semiconductor can act as sensitizers for light-reduced- redox process due to its electronic structure, which is characterized by a filled valance band and an empty conduction band .When a photon with an energy of h*v* matches or exceeds the band gab energy (3.2ev), an electron e^- is promoted from the valance band VB into the conduction band CB, leaving a hole h^+ behind within a reaction time of only a few micro second. Figure (1- 5)(65).

The photocatalytic reaction occurred on the surface of the titanium dioxide comprise the following steps: (66)

1. Reactants are adhered to the surface of the titanium dioxide.
2. Illumination of TiO_2 leads to the formation of electrons and holes.
3. The electrons and holes are captured and provided on the surface of the titanium dioxide.
4. The electron and holes react with reactants to generate hydroxyl radicals.
5. An oxidation reaction between the hydroxyl free radicals and the reactants.
6. The product leaves the surface of the titanium dioxide.

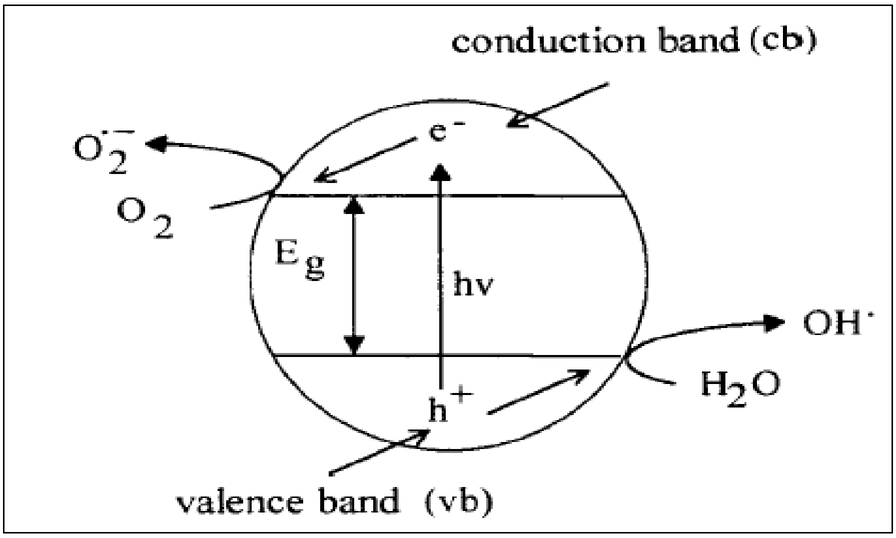

Figure [1-5] the TiO_2/solution interface under illumination

The overall processes occurring in and on a titanium dioxide particle after illumination can be summarized as follows: (67)

$TiO_2 \longrightarrow e^- + h^+$ …………………………. (1-17)

$(O_2)_{ads} + e^- \longrightarrow (O_2^{\cdot -})\ ads$……………….. (1-18)

$Ti\ (IV)\text{-}OH + h^+ \longrightarrow Ti\ (IV)\text{-}OH^{\cdot}$ ………….. (1-19)

$Ti\ (IV)\text{-}H_2O + h^+ \longrightarrow Ti\ (IV)\text{-}OH^{\cdot} + H^+$ …… (1-20)

$R + h^+ \longrightarrow R\ (oxidized)$ …………………. (1- 21)

1.4.4 Dye-Sensitized Photocatalyst

The disadvantage of using TiO_2 in photocatalyst is that only U.V light below 400nm can in principle be utilized to drive this process. Therefore, Kamat (68) first investigated the changes of photosensitization of TiO_2 by using appropriate dyes or other colored compound. These dyes which usually possess high extinction coefficient in the visible region could enhance the rate of photocatalytic reaction. For instance dyes such as anthracene, prophyrins, chlorophyllin, riboflavin (69).

Each dye material is adsorbed on the TiO_2 surface and thus extends the response of the visible region. The process of photosensitization involves initial excitation of the colored organic material, which is adsorbed on the semiconductor surface. Then electrons are injected from the excited state of the dye molecule into the conduction band of semiconductor particle (70, 71).Show (Fig 1-6)

$Sensitizer(S) + h\nu \longrightarrow S^*$ ……….......................... (1-22)

$S^* + A \longrightarrow A^* + S$ …………………................... (1-23)

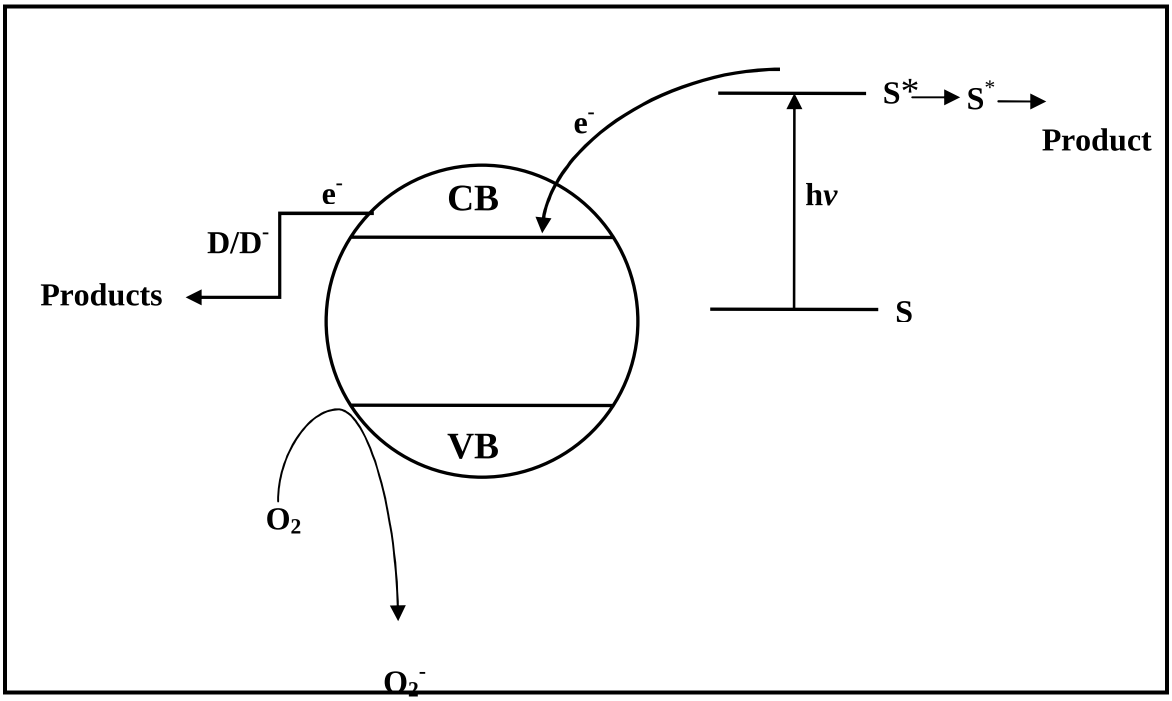

Figure (1-6) illustrates the charge injection from excited state of dye molecule into the conduction band of the semiconductor.

Organic sensitizer (Riboflavin) has been used in this work ,riboflavin vitamin B_2 or riboflavin, a yellow nitrogen containing alcohol that occurs abundantly in whey (watery part of milk) and in an essential nutrient for animals. It can be synthesized by green plants and by most bacteria and fungi $^{(72)}$.

Riboflavin consists of heterotricycle structure to which is attached to ribitol as shown in figure (1-7)

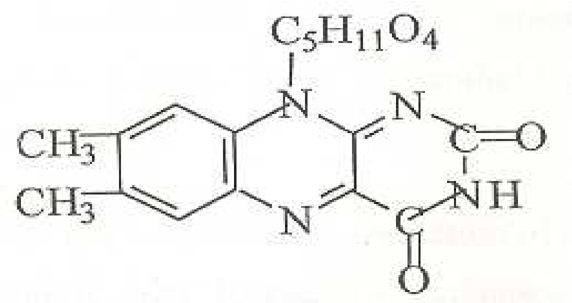

Figure (1-7): Structure of riboflavin.

In addition to its pale-yellow color, green fluorescence, and solubility properties, riboflavin is characterized by its stability towards mild oxidizing agent and reversible reduction to colorless, non fluorescing compounds by exposure to certain substance. Riboflavin is a component of an enzyme capable of combing with molecular oxygen (yellow product) release the oxygen in the cell with simultaneous loss in color (73, 74).

Riboflavin is stable against acids, air, and common oxidizing agents such as bromine and nitrous acid. Upon reduction by conventional agents such as sodium dithionite, $Na_2S_2O_4$, zinc in acidic solution, or catalytically activated hydrogen, riboflavin readily takes up two hydrogen atoms to form the almost colorless 1,5dihydroriboflavin, which is reoxidized by shaking with air. This oxidation-reduction system has considerable stability, and is probably responsible for the physiological functions of riboflavin (75).

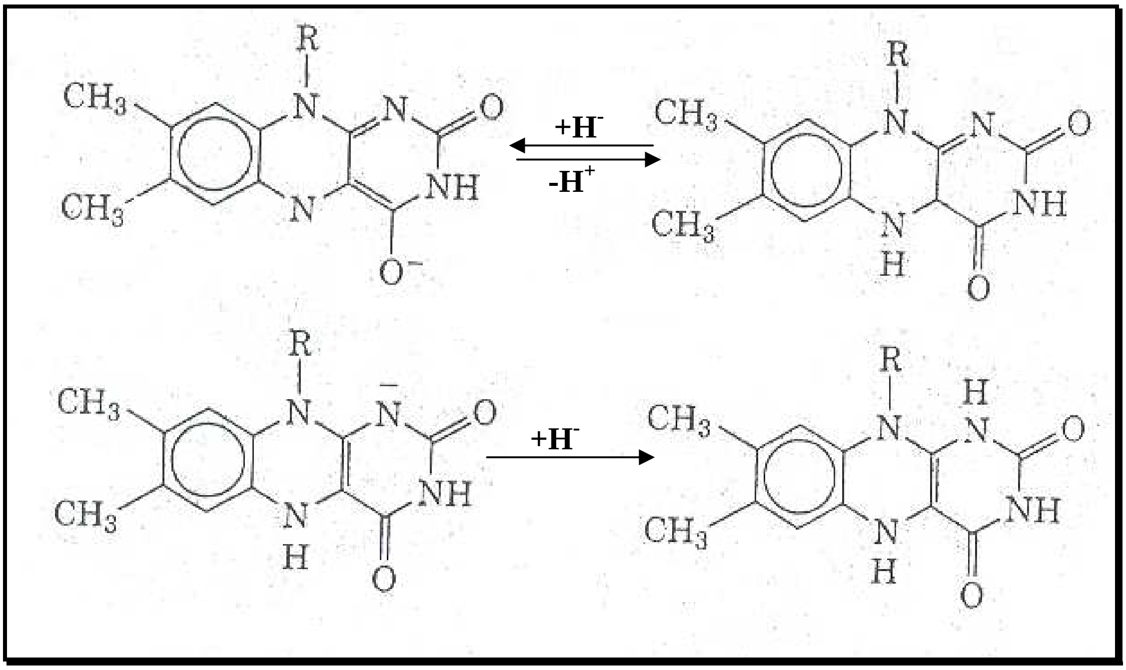

Figure (1-8) formation of dihydroriboflavin.

1.5 PRODUCTION OF HYDROGEN FROM HYDROGEN SULFIED

Attention has been given to the prospect of splitting H_2S as a source of hydrogen. The impetus is derived largely from the extensive source of hydrogen sulfide found in fossil fuels. Gas oil and residuum desulfurization in practical extensively in the petroleum industry (76).

A number of reaction processes have been proposed for splitting hydrogen sulfide, using energy derived from thermochemical, electrical, or microwave means, along with high temperature catalysis (77).

In Iraq, many experimental processes have been devised to produce hydrogen from hydrogen sulfide by many researchers, because of the percent of hydrogen sulfide in natural gas is between (10-15 %) was separated from the north-well natural gas in Kurkuk (78). A summary of these processes as follows:-

1.5.1 Photocatalytic Production

Photochemical processes using photocatalyst and colloidal semiconductor in liquid phase is one of the most interesting methods have been used for recovering hydrogen from hydrogen sulfide.

Gratzel (79) has illumination with visible light a CdS electrode immersed into aqueous sulfide solution containing H_2S and sulfide ions in the presence of RuO_2 and Pt catalyst, also Thewissen (80) has improved the photochemical splitting of H_2S by CdS suspensions using RuS_2 as a catalyst. Both Gratzel and Thewissen have found the production of hydrogen gas and sulfur deposited in solution, which may be rationalized in term of band gab excitation of CdS particles producing valance bands (h^+)of the semiconductor particles, the former reduce protons:-

$2e^-_{CB} + 2H^+ \longrightarrow H_2$ …………………. (1-24)

while the latter oxidize H_2S or HS^- to sulfur.

Naman and Al-Emara (81) studied the rates of hydrogen production from hydrogen sulfide with vanadium sulfides and oxides semiconductor mixture dispersions with different composition of doping materials (Pt and RuO_2) and electrolytes (Na_2S, Na_2SO_3, and H_2S) for long irradiation time by Xe-lamp 250W at 35°C. In another work, Naman and coworkers (82) studied the possibility of using aqueous vanadium sulfides dispersions loaded with RuO_2 under illumination by visible light for cleavage of hydrogen sulfide at room temperature and 35°C at different concentrations of Na_2S, Na_2SO_3 and $Na_2S_2O_3$ solutions. This process was very efficient when 0.1M Na_2S or Na_2SO_3 at pH=11 is used in aqueous media at 35°C,with 0.3g of vanadium sulfide and 0.9mg RuO_2 dissolved in 300ml water.

Cleavage of hydrogen sulfide into hydrogen and sulfur occurs in alkaline aqueous CdS dispersions under visible light illumination (400nm) was done by Borgarello and Serpone(83), in this work they loaded small quantities of a noble metal catalyst (RuO_2) onto CdS particles markedly improve the yield of hydrogen formation.

1.5.2 Thermochemical Decomposition

Although the direct thermal decomposition of hydrogen sulfide is possible, the equilibrium H_2 concentration is only about 13vol% at 1000°C (84).Therefore, studies were made on the simultaneous recovery of H_2 and S by using catalyst.

Kiuchi and coworkers (85) studied the thermochemical decomposition cycle of H_2S with nickel sulfide which mixed and dispersed in Al_2O_3 powder.

$$Ni_3S_2 + H_2S \longrightarrow 3NiS + H_2 \text{ ………….. } (1\text{-}25)$$

$$3NiS \longrightarrow Ni_3S_2 + S^\circ \text{ ……………… } (1\text{-}26)$$

$$\overline{\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad}$$

$$H_2S \longrightarrow H_2 + S^\circ$$

The results show that H_2 concentration of about 60vol% can be expected for the coexistence of Ni_3S_2 and NiS at 650°C.

In another work (86), Sugioka and Aomura studied the catalytic decomposition of hydrogen sulfide over molybdenum disulfide by the use of a closed circulation system at 500°C. The catalytic activity of MoS_2 was remarkably enhanced by reduction with hydrogen but was not considerably increased by increasing the evacuation temperature.

The thermaldecomposition of hydrogen sulfide to hydrogen and sulfur on alkali metal sulfides M_2S (M=Li, Na and K) and poly sulfides M_2S_x (x=2-4; M=Na and K) has been studied in a flow system at (400-800°C) (87).It was found that both Na_2S and K_2S are rapidly sulfided by H_2S to give the corresponding disulfides M_2S_2, where Li_2S acts as a catalyst for the thermal decomposition of H_2S.Chivers and Lau(88) studied the thermal decomposition of hydrogen sulfide to hydrogen and sulfur on V_2S_3 in a quartz reactor using either flow or circulating systems and in thermal diffusion reactors at 400-800°C. The use of thermal diffusion column reactors resulted in a much higher conversion of H_2S into H_2 than that was attainable in the circulating system using a quartz reactor. For that, they studied in another work (89) the thermal decomposition of hydrogen sulfide over transition metal sulfides.

Naman and Al-Shamaa (90) studied the thermal decomposition of hydrogen sulfide in a flow system using Pyrex tube reactor containing V_2O_5/Al_2O_3 catalyst. The conversion efficiency has been studied for different vanadium oxide /alumina percentage for a temperature range of 723 to 873K. The maximum conversion efficiency was 70% at 873K for 0.38min resident time for 5-10wt% V_2S_3/Al_2O_3 catalyst.

They also studied kinetically the thermal production of hydrogen from hydrogen sulfide by heterogeneous catalysis of vanadium sulfide in a flow system (91) .First and second order kinetic equations have been used for different concentration of catalytic for the temperature range at 723-873K.The Arrhenius activation energies were between 31-53 KJ mol^{-1} and the orders of the reactions were between zero and one, depending on catalyst and temperature.

David and coworkers (92) studied the thermolysis of hydrogen sulfide in a metal membrane reactor. The membrane contains a platinum coating layer on the feed side of membrane. This membrane has been used in a laboratory –scale membrane reactor to drive the decomposition of H_2S to greater than 99.4% of complete conversion. The by- products are hydrogen and sulfur; no sulfur oxides are formed.

The thermaldecomposition of hydrogen sulfide at low concentrations has been investigated(93) in the temperature range 1956K and 2600K, using the atomic resonance absorption spectroscopy (ARAS).The experiments have been performed in mixture of argon with small concentrations of H_2S (25 to 200 ppm) at total pressures of about 1.8-2.0bar.

The rate constants for reactions:-

$H_2S + M \longrightarrow HS^- + H^+ + M$………. (1-27)

$H_2S + H \longrightarrow HS^- + H_2$ ………….. (1-28)

were found to be given by

$K_1=7.7X10^{-10}$ exp (-41.500k/T) $molecule^{-1}$ cm^3 S^{-1}

$K_2=1.8X10^{-10}$ exp (-1500k/T) $molecule^{-1}$ cm^3 S^{-1}.

1.5.3 Photoelectrochemical Production

The Photoelectochemical conversion of hydrogen sulfide to hydrogen is an attractive process because it addresses three major problems. Firstly, it may provide insights chemical water splitting. Secondly, it may be a partial solution to the hydrogen fuel problem since it is a possible way of producing hydrogen on a large scale. Thirdly, it serves as a way to market wastes from the coal and petroleum industry since this process has the potential of converting H_2S wastes to useful produce (94).

Lowrence and coworkers (95) studied the photoelectochemical conversion of H_2S to H_2 using visible light as illumination source and cadmium sulfide as semiconductor. The redox reaction that results in photoelectrochemical conversion of H_2S to H_2 using visible light and as illumination source and cadmium sulfide as semiconductor are:-

$CdS + h\nu \longrightarrow h^+ + e^-$ …………… (1-29)

H_2S Dissociation: $H_2S + OH^- \longrightarrow HS^- + H_2O$ ………. (1-30)

Oxidation : $2HS^- + 2h^+ \longrightarrow S^{-2} + 2H^+$………. (1-31)

Reduction: $2H^+ + 2e^- \longrightarrow H_2$ ………………… (1-32)

Overall : $2H_2S \longrightarrow H_2 + H_2S_2$ ………….. (1-33)

The highest production rate was 113ml of H_2 in 4h using solar radiation and 2mg CdS.

Indirect electrochemical conversion of hydrogen sulfide using iodine oxidants and aqueous hydro iodide and strongly basic solutions was investigated by Kalina and Maas (96, 97).The electrochemical process utilized the basic indirect electrolysis of H_2S produces iodate oxidant (IO^{-3}) and hydrogen gas.

$I^- + 3H_2O \longrightarrow IO^{-3} + 3H_2$……………… (1-34)

$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$…………….. (1-35)

$$2I^- \longrightarrow I_2 + 2e^- \ldots\ldots\ldots\ldots\ldots\ldots\ldots..... \quad (1\text{-}36)$$

The reaction of hydrogen sulfide with iodate proceeds according to the reaction in equation (1-36)

$$3H_2S + IO^{-3} \longrightarrow 3S + 3H_2O + I^- \ldots\ldots\ldots\ldots\ldots\ldots..... (1\text{-}37)$$

1.5.4 Production of Hydrogen from Hydrogen Sulfide using Microporous Ceramic Membrance.

Hydrogen can be removed continuously from hydrogen sulfide via some form of semi-permeable membrane. Such a process cannot be established without finding a suitable selective diffusion membrane (98).

For the effective production of hydrogen from hydrogen sulfide, the gaseous diffusion membranes need theoretically to have a smaller mean pore diameter the mean free paths of the hydrogen gas molecules and hydrogen sulfide molecules, which are 1230 and 430 Å, respectively, at 25 °C under 1 atm. Since hydrogen sulfide starts to decompose measurably above 500°C, membranes should also not be degradable above 500°C. The membranes, however, could not be used above 500°C because they degrade in the presence of hydrogen sulfide at high temperature. Some porous ceramic membranes may be used above 500°C.Up to now, porous Vycor glass has been used as a separation membrane for many gas mixtures below 500°C in the absence of hydrogen sulfide; however, there are porous Vycor glass membrane and a new microporous alumina membrane for the effective production of hydrogen from hydrogen sulfide at temperatures up to 800°C (99).

The use of a Vycor-type glass membrane and a new microporous alumina membrane at the decomposition reaction conditions of hydrogen sulfide increase the yield of hydrogen rapidly by about twice the equilibrium one. Therefore, this microporous membrane can be used as separation membranes for the effective production of hydrogen from hydrogen sulfide at high temperature up to 1000°C without being degraded. An improved coating method on the coarse alumina membrane in order to get a mean pore diameter of 200-600 Å will increase the yield of hydrogen further and then this process will become attractive for the industrial production of hydrogen from hydrogen sulfide (100).

1.5.5 Production of Hydrogen from Hydrogen Sulfide in Aqueous Solutions of Ethanolamine.

Ethanolamines are the most frequently used solvents for the removal of hydrogen sulfide from natural gas, because of their reactivity and availability at low cost; ethanolamines have achieved a position of prominence in the gas sweetening industry, e.g. the Claus process in which hydrogen sulfide is converted to sulfur (101). The most widely used are monoethanolamine (MEA), diethanolamine (DEA), diglycolamine (DGA), and methyl diethanolamine (MDEA). Amine processes are generally applicable when hydrogen sulfide concentration in the feed gas is relatively low (eg 5-25 mol %) and high purity must be achieved in the treated gas (102).

The primary reactions of amine and hydrogen sulfide are those of a base with acid:-

$$2RNH_2 + H_2S \longrightarrow (RNH_3)_2S \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1\text{-}38)$$

$$(RNH_3)_2S + H_2S \longrightarrow 2RNH_3HS \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (1\text{-}39)$$

For that, many researchers focused much attention on the direct photocatalyst decomposition of hydrogen sulfide to produce hydrogen.

Naman and Gratzel (103) studied visible-light generation of hydrogen from hydrogen sulfide in aqueous solutions of ethanolamines containing vanadium sulfide dispersions using iodine lamp as a source irradiation and temperature range (30-80°C).They show that the maximum rate of hydrogen production from H_2S was observed at 20% MEA and at 15mg of vanadium sulfide in 35ml.When the semiconductor VS was doped with RuO_2, the rate decrease and the stability of the semiconductor was reduced. This may be due to the formation of complex between RuO_2 and the amines. In another work (104), Naman studied the photocatalytic production of H_2 from H_2S in ethanolamine aqueous solution containing CdSe and CdS semiconductor dispersion in the same range of temperature.

On the other hand, carbon dioxide also accompanies hydrogen sulfide in the same natural gas source, and hydrogenation of CO_2 to fuels could become a very important industrial process and is already of great academic interest (105). In a system containing a mixture of H_2S and CO_2, the hydrogen required for the hydrogenation of CO_2 may be obtained from H_2S either through thermal decomposition or photosplitting.

1.6 THE AIM OF THE PRESENT WORK

This work has aimed to produce hydrogen gas as clean and alternative fuel from hydrogen sulfide which found in high percent in natural gas in the north oil fields (Kurkuk) using photocatalyst process.

In addition, it has aimed to find the optimum conditions and parameters for the highest efficiency of photodecomposition of hydrogen sulfide such as using suitable photocatalyst, using visible radiation as a source of light, using ambient temperature, the addition of oxidant to the photocatalyst and the effect of addition of sensitizer to increase the activity of semiconductor catalytic under photo conditions.

Experimental Part

2.1 Chemicals

2.1.1 Semiconductors

● Titanium dioxide (TiO_2) type (Anatase) with purity of 99%, supplied by Fluka AG. The surface area of anatase is $18.2m^2g^{-1}$, while the band gap is 3.2ev and the density is 3.9 g mL^{-1}.

●Zinc oxide (ZnO): with purity of 99%, band gap 3.2ev, surface area $16.4m^2g^{-1}$ which was supplied by BDH.Ltd.A.R.Grade.

2.1.2 Other chemicals

●Riboflavin: ($C_{17}H_{20}N_4O_6$) with purity of 98%, supplied by Fluka, AG.Chemische Fsbrik CH- 9470Buchs.This sensitizer was prepared by dissolving in distilled water, then it was mixed with monoethanolamine.

● Ferrous sulfide (FeS): with purity of 97%, supplied by BDH. Ltd.A.R.Grade.

● Hydrochloric acid (HCl): with purity of 36% Analar, supplied by BDH. Ltd.A.R.Grade.

● Monoethanolamine (MEA): (C_2H_7NO) with purity of 99.9%, supplied by BDH. Ltd.A.R.Grade.

● Diethanolamine (DEA): ($C_4H_{11}NO_2$) with purity of 99%, supplied by BDH. Ltd.A.R.Grade.

● Hydrogen peroxide (H_2O_2): (18% aq solution) supplied from Aldrich (A.G.).

2.1.3 Gases

• Hydrogen Sulfide gas (H_2S)

Hydrogen sulfide gas was prepared from Kipp generator; it is a U-shaped tube with two bulbs. Into the constricted part of the left arm inserted gauze (a porcelain or copper plate with holes) on which pieces of ferrous sulfide (10g) are placed.

Through the left arm of the apparatus is introduced dilute (1:1) hydrochloric acid which reacts with FeS to form H_2S (106).

$$FeS + 2HCl \longrightarrow FeCl_2 + H_2S \uparrow \text{............} \quad (2\text{-}1)$$

If the stopcock of the gas-delivery tubing is shut, the evolving hydrogen sulfide will force the acid into the left arm of the tube and the reaction will be stopped. When the stopcock is opened, the reaction is resumed.

• Oxygen Gas

Oxygen gas of purity 99.99% was supplied by Al-Mansour Factory, Baghdad, Iraq. Oxygen gas was passed through aqueous solutions of ethanol amines.

•Hydrogen Gas

Hydrogen gas of purity 99.99% was supplied by Al-Mansour Factory, Baghdad, Iraq.

2.2 Photolytic System

The main parts of the photolytic system used in this work are shown in figure (2-1).

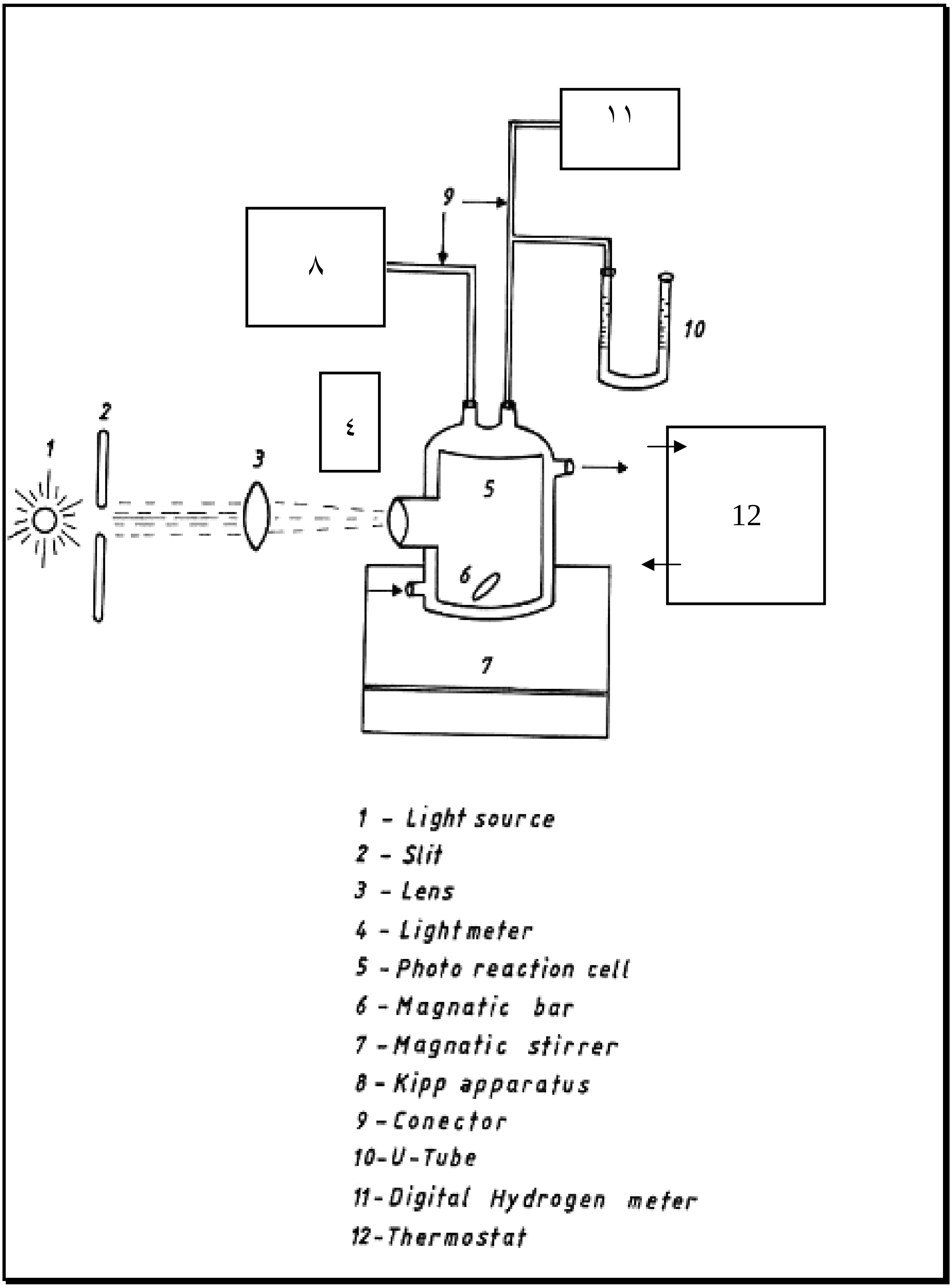

Figure (2-1) Schematic diagram of the experimental apparatus.

1. Light source: A Tungsten-Halogen lamp, supplied by Ebec.
1000 Watt, the light intensity 2.132×10^{-7} Ein.$L^{-1}s^{-1}$.
and 500 Watt, the light intensity 7.43×10^{-8} Ein.L^{-1} s^{-1} were used.
2. Slit: by using box of wood to concentrate the light on the lens.
3. Lens: to give a good beam of light.
4. Light meter: to measure light intensity, supplied by KBM, Mod.776, 6108 Weiterstadt 2, Germany).
5. Photoreaction cell: A Pyrex photochemical reactor cylindrical shape; (volume 35 ml), equipped with a Pyrex window diameter (2cm),figure (2-3) shows absorbance spectra of this window, and surrounded by a thermostatically controlled water jacket. Dimensions of the photo cell are shown in Figure (2-2).

The cell is supplied with two openings of 0.5 cm diameter and these were used for hydrogen sulfide gas bubbling and hydrogen gas production.

6. Magnetic bar
7. Magnetic stirrer: to keep the aqueous solution in homogenous phase during photolysis experiments.
8. Kipp apparatus: to generate hydrogen sulfide gas.
9. Connector.
10. U-Tube: volume 10 ml, contain distilled water (3ml), to measure volume of hydrogen gas which produce from the photocatalytic cell.
11. Digital hydrogen meter: type GP, Japan. It was used to measure the percentage of hydrogen gas produced as arbitrary unit.
12. Thermostat: circulating thermostat type HAAKE FE2 controlled the reaction temperature.

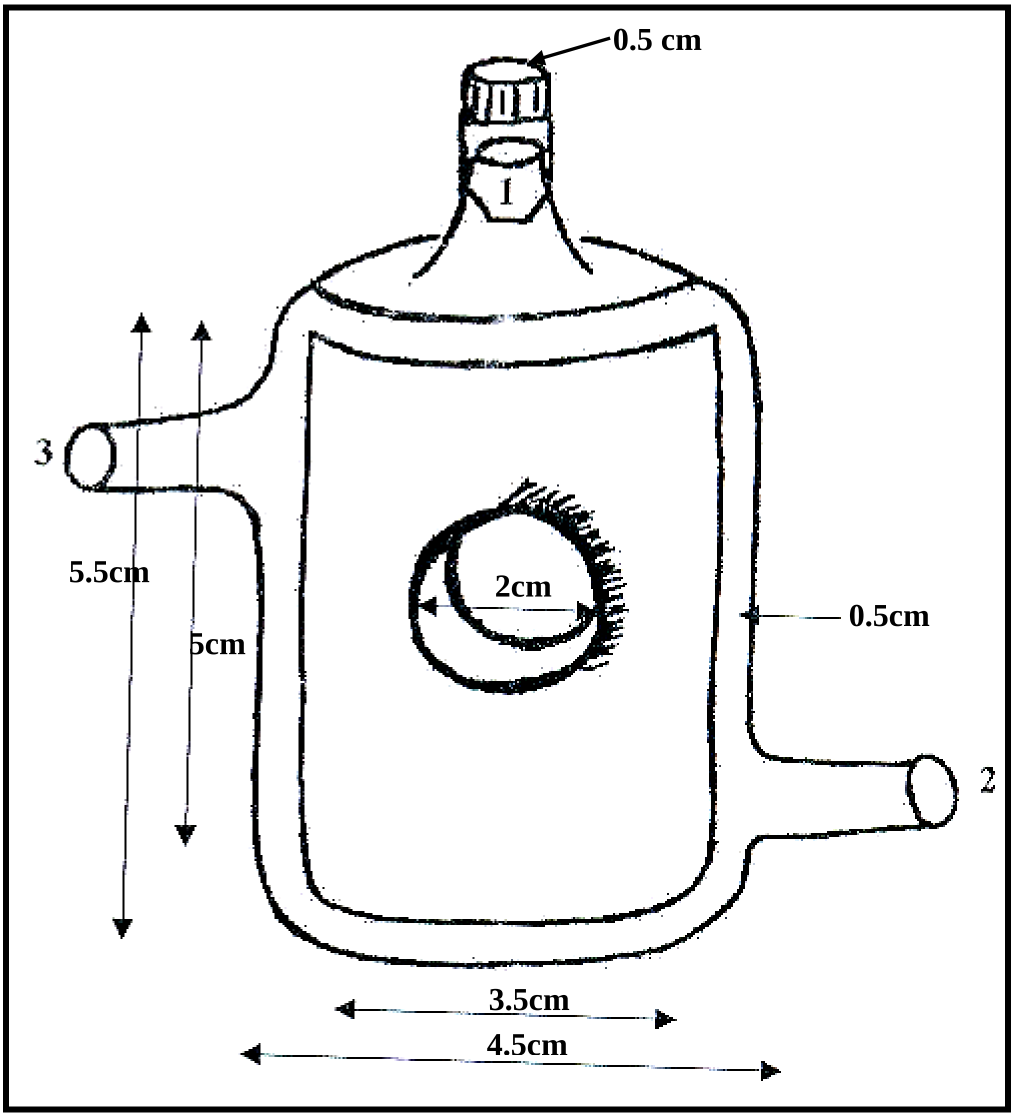

Figure (2-2): The schematic diagram of the photoreaction cell.

1. Gases inlet and outlet.
2. Water inlet.
3. Water outlet.

2.3 Procedure

1. Different percentage of monoethanolamine was prepared by mixing it with distilled water followed by the addition of titanium dioxide photocatalyst.
2. Hydrogen sulfide gas was passed from Kipp apparatus through these solutions for 10 minute, after finished bubbling H_2S was closed up.
3. Direct photolysis to these solutions was done.
4. The volume of hydrogen was produced from photolysis was measured every 15 minute using U- tube.
5. The amount of hydrogen sulfide which was absorbed in mono ethanolamine was calculated by reheating and evaporating H_2S, it was done at temperature between (30-90°C).

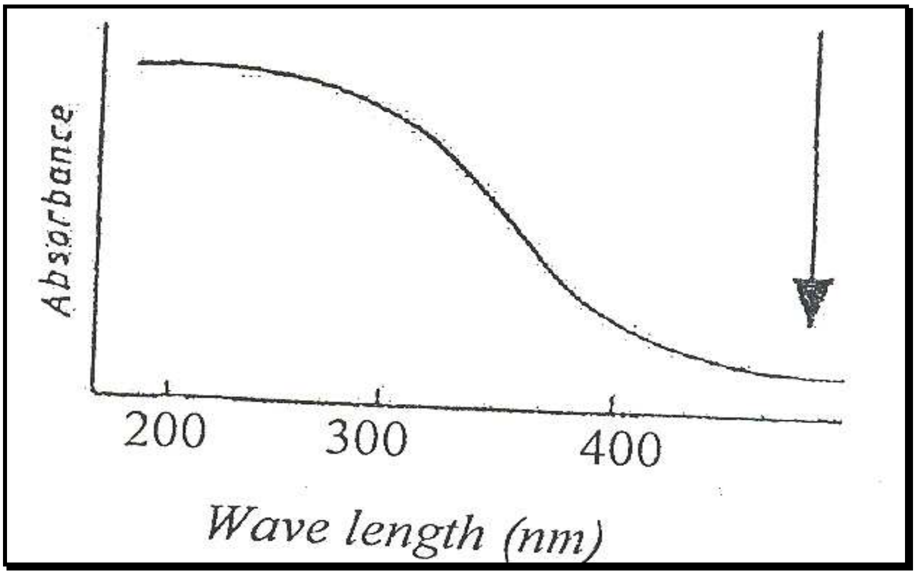

Figure (2-3) Absorption spectra of Pyrex window in the photo cell.

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Results and Discussion

In order to find the optimum conditions for the photocatalytic decomposition of hydrogen sulfide gas in aqueous solution of monoethanolamine to produce hydrogen gas, several experiments were conducted to study the effects of different conditions and parameters which are the most effective to increase the percentage decomposition of hydrogen sulfide. These conditions are for example:- type of solvent and percentage in water, effect of addition titanium dioxide photocatalyst and its load, air, addition of hydrogen peroxide, temperature, and the effect of sensitizer. The effect of these conditions was studied as in the following experiments:-

3.1. Solubility of H_2S in the different percentages of MEA

The amounts of hydrogen sulfide which can be absorbed by the different percentages of monoethanolamine in water have been measured by reheating and evaporating the mixture to 90°C. Figure (3-1) shows the volume of H_2S/35ml dissolved in solution at different temperature.

The primary reaction of monoethanolamine and hydrogen sulfide is an acid-base reaction. Hydrogen sulfide a Brønstead acid has a proton to donate and reacts extremely rapidly with the MEA (107).

$$2HOCH_2CH_2NH_2+H_2S \rightleftarrows (HOCH_2CH_2NH_3)_2S \quad (\mathbf{I}) \ldots\ldots.. (3\text{-}1)$$

$$(HOCH_2CH_2NH_3)_2S + H_2S \rightleftarrows 2\ HOCH_2CH_2NH_3HS\ (\mathbf{II}) \ldots (3\text{-}2)$$

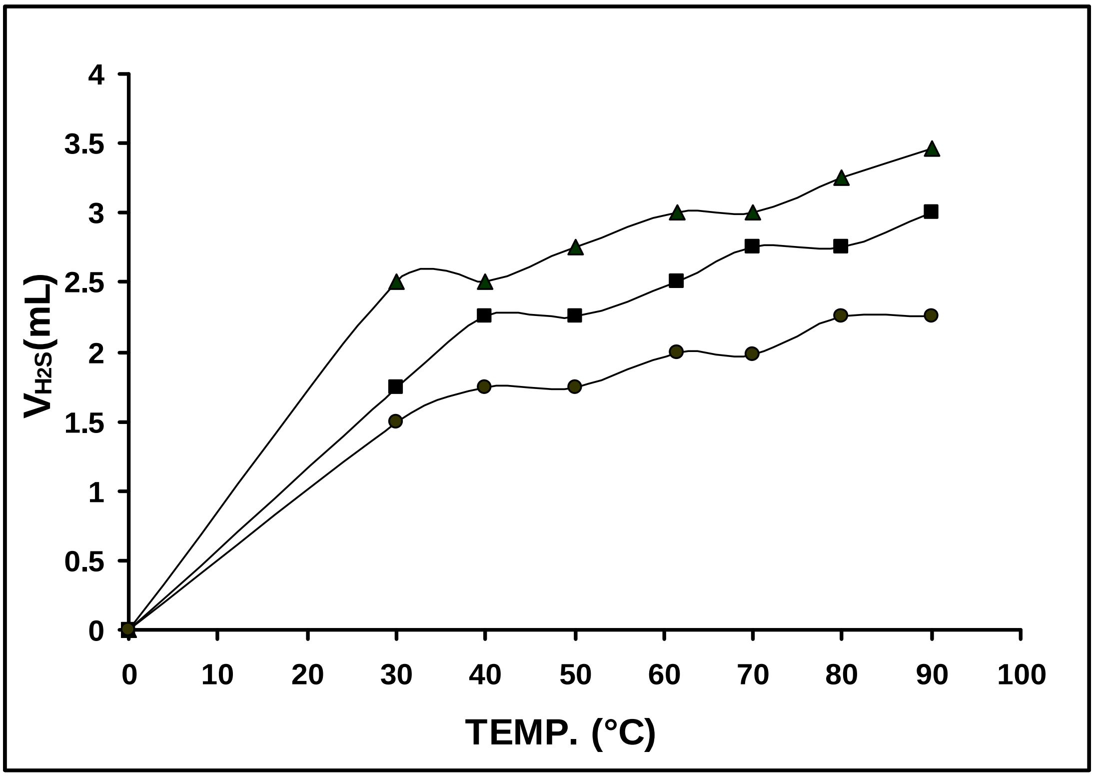


Figure (3-1) Amount of H_2S dissolved in different percentages of MEA aqueous solution.▲ 10% MEA ■ 20% MEA ● 30%MEA.

From these results, the maximum volume of H_2S which was absorbed in 10%MEA was 3.5 ml. It is clear that the solubility of H_2S increases in diluted solutions, this may be due to the formation of some bonding between these amine and hydrogen sulfide.

3.2 The effect of solvent on the photolysis of mixture.

In this study MEA is used and not DEA because the former has lower molecular weight of the common amines and a greater carrying capacity for acid gases (CO_2+H_2S) on a unit weight or volume (108).

In addition, MEA is photochemically stable, with a highest rate of hydrogen formation, which minimizes solution degradation and it can be separated easily from H_2S gas by steam stripping process (109).

Figure (3-2) shows the volume of hydrogen produced in the same percentage of ethanol amines (MEA, DEA) in the presence of titanium dioxide as semiconductor and using 1000W Tungsten-Halogen lamp as a source of light.

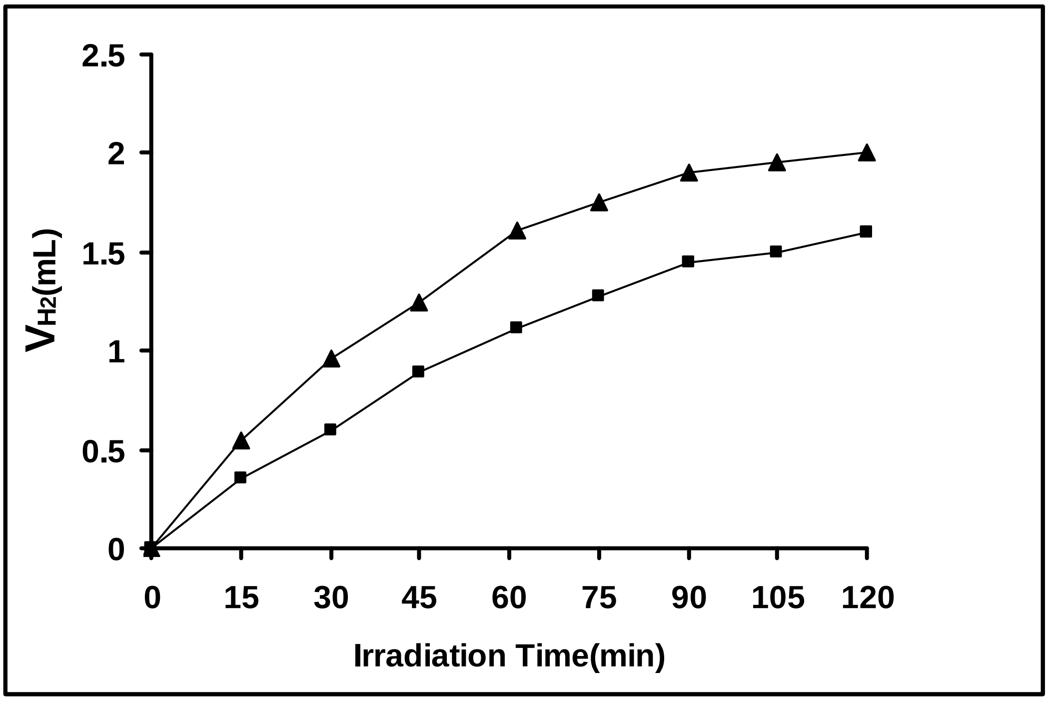


Figure (3-2) Volume of hydrogen produced as a function of irradiation time at room temperature using ▲20% MEA, ■20% DEA.

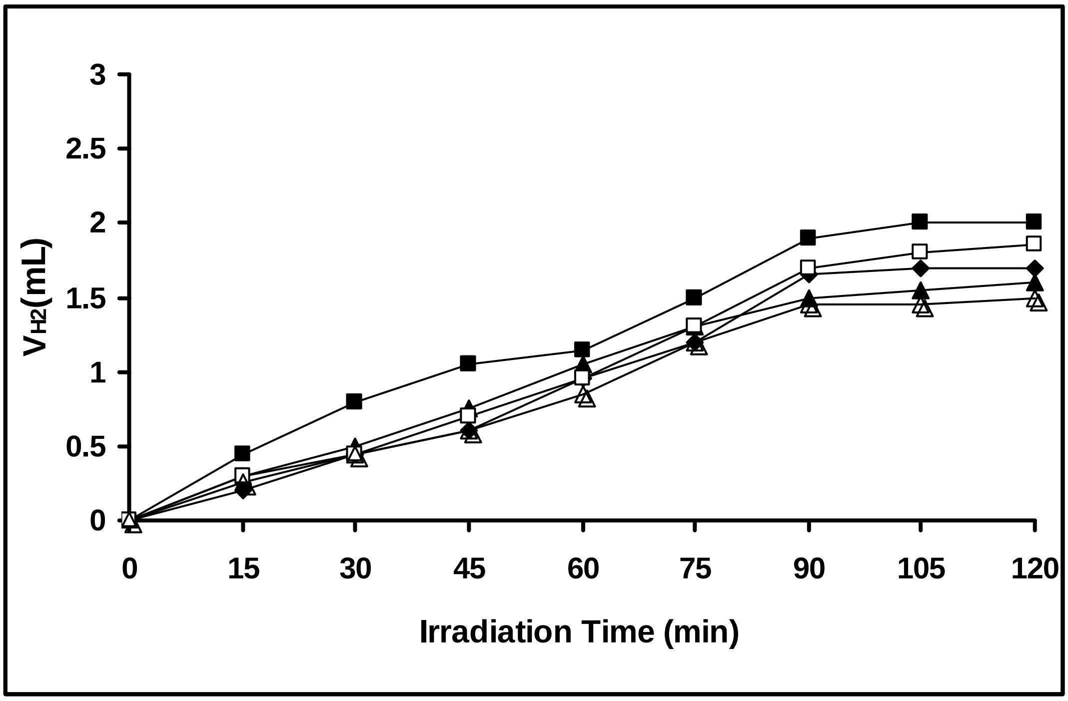
It was clear that the volume of hydrogen produced using MEA is more than in the case of using DEA, this is due to the formation of ammonia via decomposition of DEA in aqueous solution and this leads to decrease the photodecomposition of hydrogen sulfide in this amine.

The following reaction may explain the formation of ammonia in this system (110) in the case of DEA.

$(HOCH_2CH_2)NH + 2H_2O + h\nu \xrightarrow{Sc} 2HOCH_2CH_2OH + NH_3$.... (3-3)

3.3 Photocatalytic decomposition of hydrogen sulfide in different percentages of MEA.

Blank experiments were performed with different percentage of MEA for all experiments. Figure (3-3a) shows the volume of hydrogen produced in different percentage of MEA aqueous solution in the presence of titanium dioxide (load 2mg/35mL) as photocatalytic and 1000W Tungsten-Halogen lamp as a source of light.



Figure(3-3a)Volume of hydrogen produced as a function of irradiation time at room temperature(TiO_2 load 2mg/35ml) in different percentages of MEA : ■20%MEA □ 15%MEA ♦10%MEA ▲ 30%MEA∆35%MEA.

Figure (3-3b) shows that the best percent of MEA for maximum hydrogen produced from photolysis of H_2S is 20% MEA. (TiO_2 load 2mg/35ml of photo cell after 2 hours of irradiation.

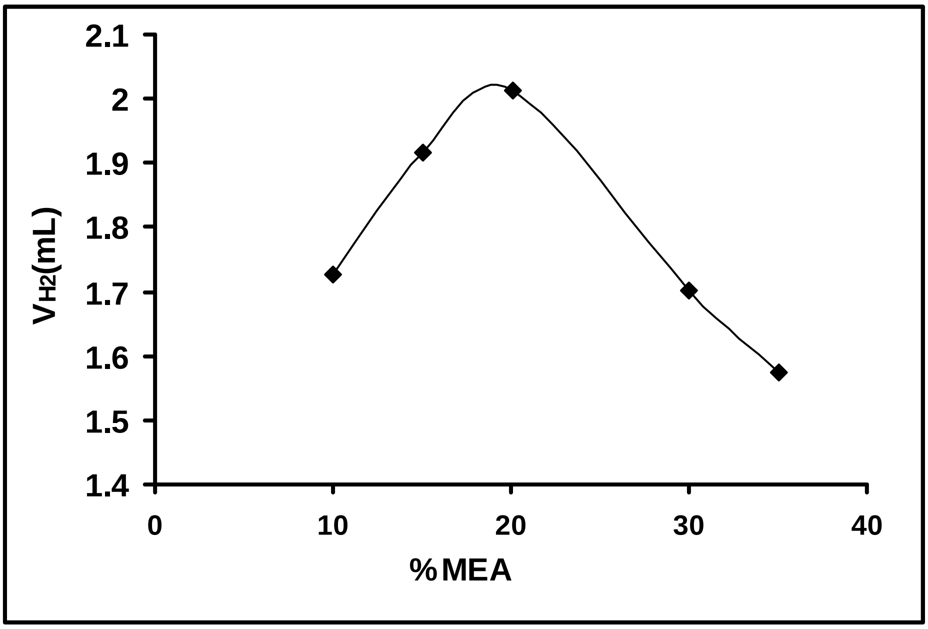


Figure (3-3b) Maximum volume of hydrogen produced with different percentage of MEA after 2hour of irradiation. (TiO_2 load 2mg/35ml photo cell.

3.4 The effect of light on the photocatalytic decomposition of hydrogen sulfide.

The effect of light was studied using visible light (1000W Tungsten-Halogen lamp) by measuring the volume of hydrogen gas produced from the photolysis of (20%MEA and hydrogen sulfide) mixture in the same conditions of temperature and amount of catalyst as shown in Figure (3-4).

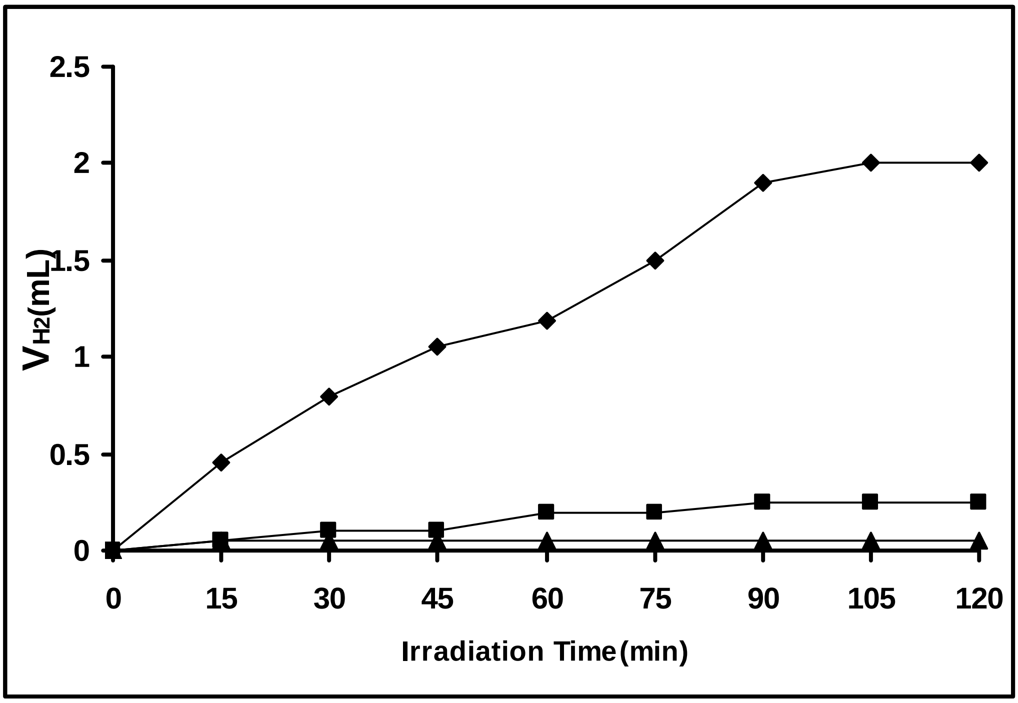


Figure (3-4) Volume of hydrogen produced as a function of irradiation time at room temperature using:-

♦visible light with TiO_2 photocatalyst.

■with TiO_2 photocatalyst, in the dark.

▲ with out TiO_2 photocatalyst, in the dark.

As it is seen from the results, the effect of light on the photolysis was very important because the role of the light is irradiating of the semiconductor particles. This is achieved through the absorption of a photon of ultra band gap energy of semiconductor which results in the promotion of an electron e^- from the valance band to the conduction band, creation a positive hole (h^+) in the valance band.

$$TiO_2 + h\nu \longrightarrow e^-_{(CB)} + h^+_{(VB)} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3\text{-}4)$$

$$(HOCH_2CH_2NH_3)_2S + e^- \longrightarrow 2HOCH_2CH_2NH_2 + H_2 + S_2 \ldots\ldots\ldots (3\text{-}5)$$

$$(HOCH_2CH_2NH_3)_2(SH)_2 + e^- \longrightarrow 2HOCH_2CH_2NH_2 + 2H_2 + S_2 \ldots (3\text{-}6)$$

3.5 The effect of incident light intensity

To study the effect of incident light intensity on the photocatalytic decomposition of hydrogen sulfide, two types of lamp were used (1000W, 500W Tungsten-Halogen lamp) at the same conditions of temperature and amount of catalyst. The results shown in figure (3-5).

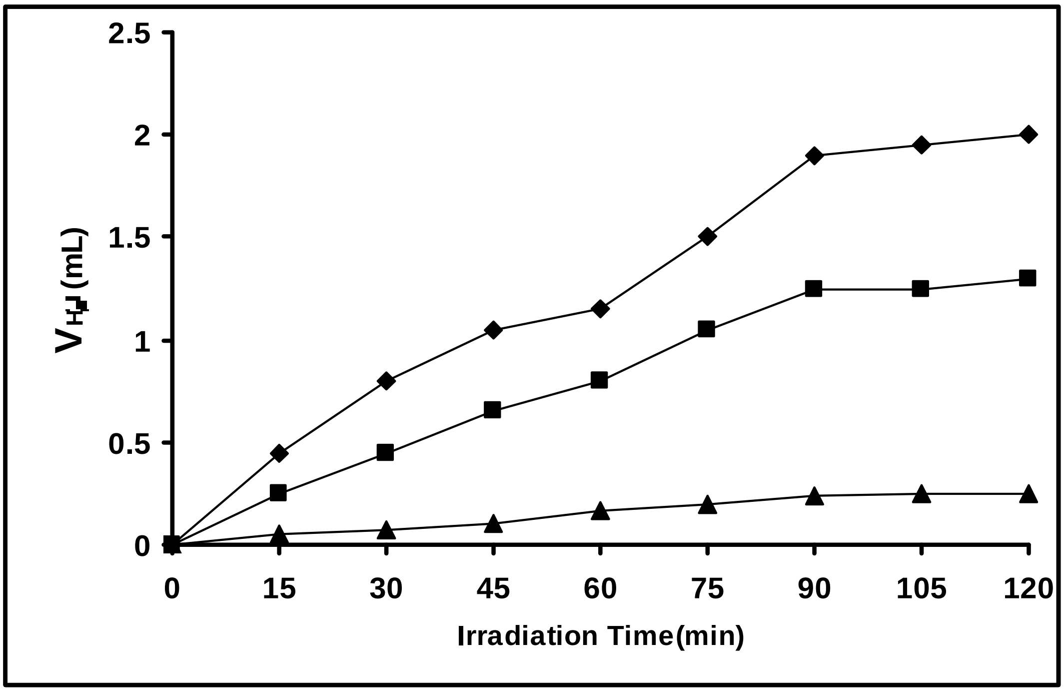


Figure (3-5) Volume of hydrogen produced as a function of irradiation time using:-

♦ 1000 W Tungsten-Halogen lamp.

■ 500 W Tungsten-Halogen lamp.

▲ In the dark.

The Figure (3-5) shows that higher light intensity will give higher volume of hydrogen produced. For that the volume of hydrogen produced decreases when using 500W Tungsten-Halogen lamp because the absorption of titanium dioxide to the energy using 1000W Tungsten-Halogen lamp is better than 500W Tungsten-Halogen lamp. This is obvious, due to the fact that increasing light intensity will increase the number of photons being absorbed by the semiconductor. Furthermore, the addition of catalyst without light had a negligible effect on the photodecomposition of hydrogen sulfide.

3.6 Effect the types of photocatalyst on the photodecomposition of hydrogen sulfide.

The ability of the semiconductors to act as sensitizers and consequently to enhance the photodecomposition of hydrogen sulfide is attributed to their electronic structure which is characterized by filled valance band and an empty conduction band. When the semiconductor is illuminated with energy greater than their band gap energy E_{bg}, excited high- energy states of electron and hole pairs(e^-/h^+) are produced.

$$TiO_2 + h\nu \longrightarrow h^+ + e^- \text{........................ (3-7)}$$

$$ZnO + h\nu \longrightarrow h^+ + e^- \text{........................ (3-8)}$$

These species can either recombine or react with electron donors or electron acceptors adsorbed on the semiconductors surface or within the surrounding electrical double layer of the charged particles (111).

Two types of semiconductors (ZnO, TiO_2) were studied to get the higher efficiency of photodecomposition of hydrogen sulfide at the same conditions of temperature and percentage of MEA. The photodecomposition of hydrogen sulfide in the presence of the two semiconductors catalyst is presented in Figure (3-6). Illumination of solution in the absence of a catalyst showed that the process occurs at a slower rate.

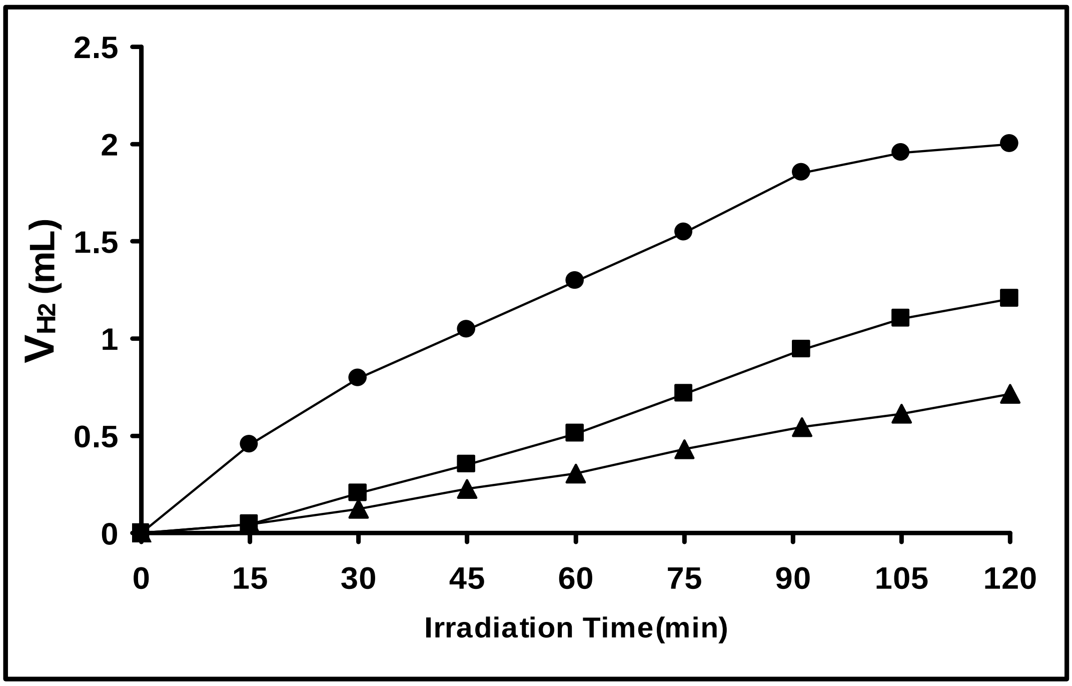


Figure (3-6) Volume of hydrogen produced as a function of irradiation time at room temperature using:-

● Titanium dioxide 2mg/35ml.

■ Zinc oxide 5mg/35ml.

▲ with out catalyst.

The absorption of light by the molecules **I** and **II** in equations (3-1),(3-2) respectively, may split H_2S to give hydrogen and elemental sulfur due to energy or electron transfer reactions in mixtures containing MEA and H_2S.

$\mathbf{I} + h\nu \longrightarrow \mathbf{I^*} \longrightarrow 2MEA + H_2 + S$ ……… (3-9)

$\mathbf{II} + h\nu \longrightarrow \mathbf{II^*} \longrightarrow 2MEA + 2H_2 + S_2$…..... (3-10)

The volume of hydrogen produced from such mixtures is 0.7ml/35ml of photo cell after two hours of irradiation. When semiconductor particles are present in the photochemical mixture, the volume is about 2ml/35ml of photo cell after two hours of irradiation using 2mg from titanium dioxide and 1.1 ml using 5mg from zinc oxide at the same conditions.

Initially, e^- and h^+ are produced by the titanium dioxide semiconductor as in equation (3-7).The electron and holes then react with molecules **I** or **II** to split hydrogen sulfide to give hydrogen and sulfur(probably molecule **II** more than molecule **I**).

I or II + $e^- \longrightarrow H_2$ or $2H_2$ …………… (3-11)

I or II + $h^+ \longrightarrow S$ or S_2 ……………. (3-12)

In aqueous solutions of MEA, there is an equilibrium reaction between H_2S and its ions:-

$H_2S \longrightarrow HS^- + H^+$……………………. (3-13)

$HS^- \longrightarrow H^+ + S^{2-}$ …………………….. (3-14)

The electrons and holes generated by the semiconductor can react with these ions and produce hydrogen and sulfur reactions.

$2H^+ + 2e^- \longrightarrow H_2$ …………………… (3-15)

$H_2S + 2h^+ \longrightarrow 2H^+ + S$ …………….. (3-16)

The volume of hydrogen produced in the case of using titanium dioxide is higher than in the case of using zinc oxide, this may be due to the small surface area of zinc oxide which decreases the absorption of light on its surface. This agrees with other studies (112,113). For this reason a larger load of ZnO was selected to work with throughout the work (5mg/35mL).

3.7 Effect of titanium dioxide load on the photocatalytic decomposition of hydrogen sulfide

The influence of the photocatalyst load on the photodecomposition of hydrogen sulfide has been investigated employing different load of TiO_2 varying from 0.5 to 2.5 mg/35mL of photocell. Figure (3-7a) shows the volume of hydrogen produced from mixtures containing 20% MEA, H_2S and different load of TiO_2 using 1000W Tungsten-Halogen lamp as a source of light.

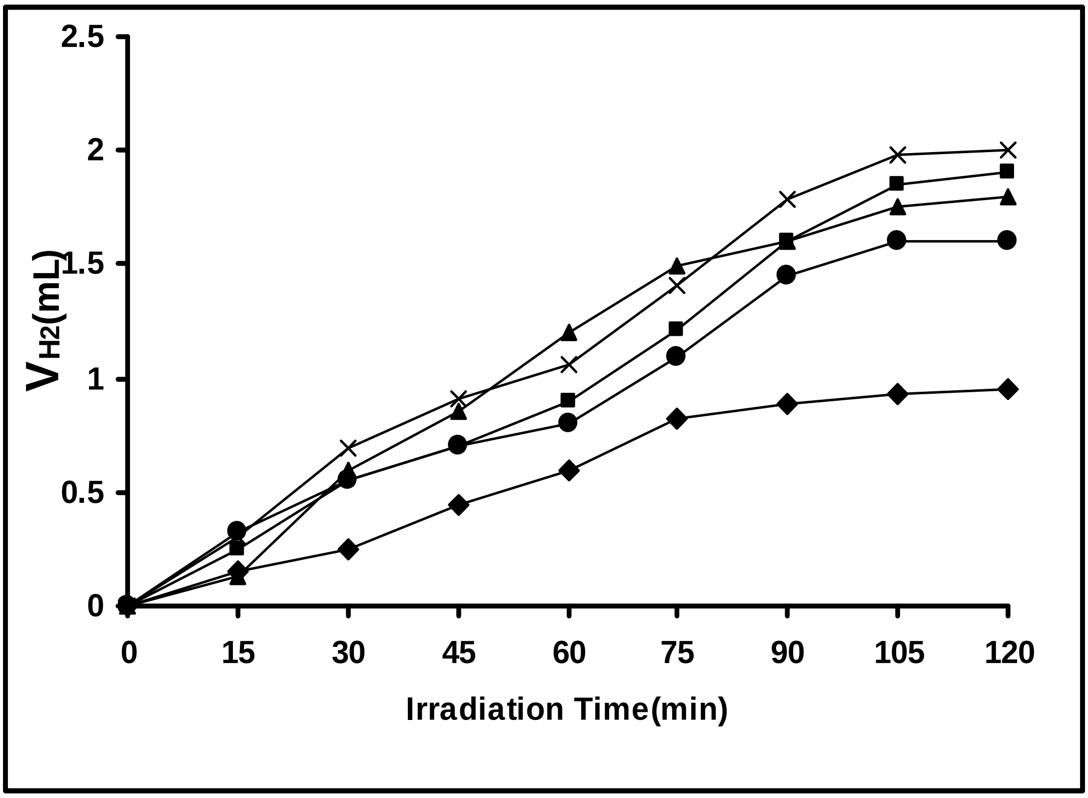


Figure (3-7a) Volume of hydrogen produced as a function of irradiation time at room temperature using different load of titanium dioxide.

x **2mg TiO_2.**

■1.5 mg TiO_2.

▲ 1mg TiO_2.

●0.5 mg TiO_2.

♦2.5 mg TiO_2.

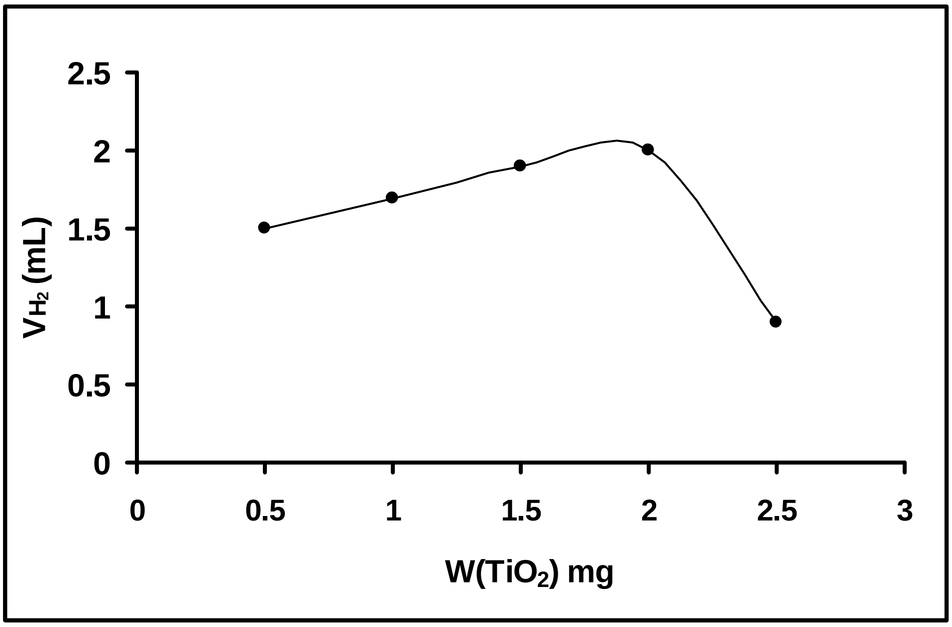


Figure (3-7b) Maximum volume of hydrogen produced with different load of titanium dioxide at constant temperature after two hour of irradiation.

The production of hydrogen gas increased until 2mg/35mL then it decreased due to the fact that the light is not absorbed, because most of it will scatter, and Beer-Lambert Law can be applied. These results are similar to other workers when they used the system of semiconductor for photocatalysis photodegradation of polluted molecules (114,115).

3.8 The effect of air on the photocatalytic decomposition of hydrogen sulfide

Oxygen gas was passed through solutions of MEA after and before hydrogen sulfide bubbling at the same conditions (20%MEA, 2mg TiO_2, 1000W, and at room temperature) in order to study the effect of the presence of O_2 in the photocatalytic decomposition process. Figure (3-8) shows the variation of the volume of hydrogen gas produced with irradiation time in presence and absence of oxygen.

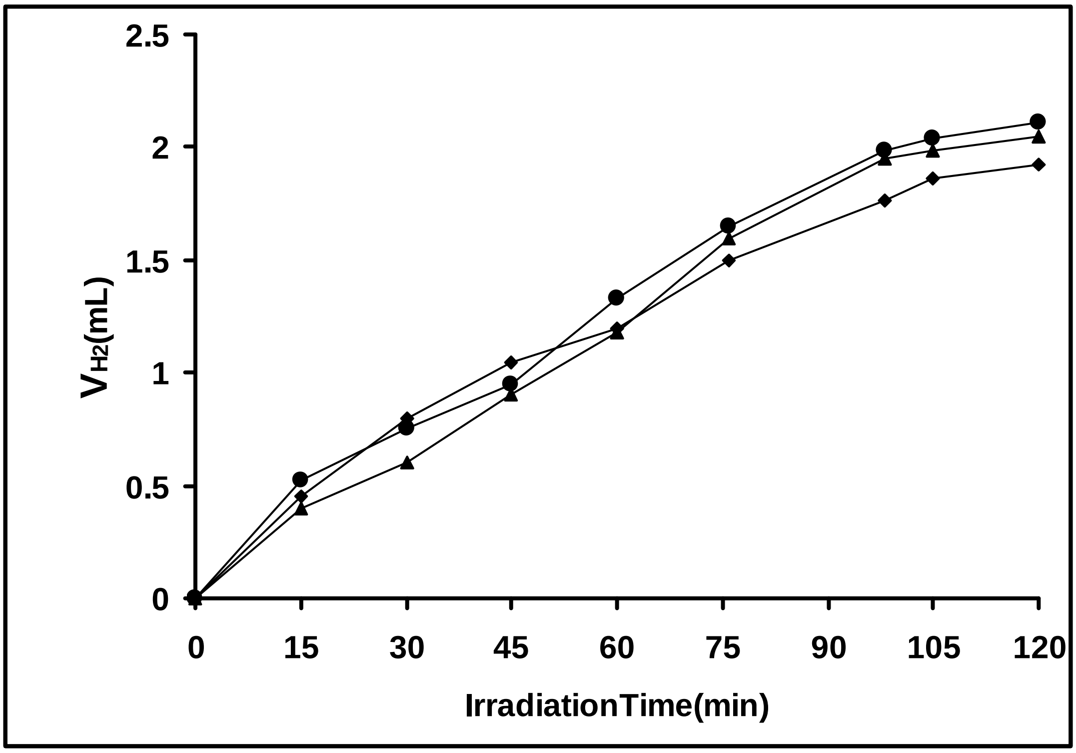


Figure (3-8) volume of hydrogen produced as a function of irradiation time by:

● passing oxygen gas after hydrogen sulfide bubbling.

▲ with out passing oxygen gas.

♦ passing oxygen gas before hydrogen sulfide bubbling.

From the results above it seems that the effect of oxygen on the photodecomposition of hydrogen sulfide is not significant, but oxygen adsorbed on surface of catalyst will increase the activity of catalyst, but in general oxygen gas in solution deactivate the exited state of molecules due to the unpaired electron of oxygen.

$H^{\bullet} + O_2 \longrightarrow HOO^{\bullet} \xrightarrow{\mathbf{H_20}} H_2O_2 + {}^{\bullet}OH$............ (3-17)

$H^{\bullet} + {}^{\bullet}OH \longrightarrow H_2O$.. (3-18)

Beside that the rate of hydrogen production decreases when oxygen gas is passing before hydrogen sulfide bubbling because hydrogen sulfide and oxygen react over the catalyst via the following reaction:-

$2H_2S + O_2 \longrightarrow S_2 + 2H_2O$ …………………...... (3-19)

3.9 The effect of hydrogen peroxide on the photocatalytic decomposition of hydrogen sulfide.

The addition of powerful oxidizing species (such as H_2O_2) to TiO_2 suspensions is well known procedure and in many cases leads to an increase of the rate of photooxidation (116,117). H_2O_2 is considered to have two functions in the process of photocatalyst. It accepts a photogenerated electron from the conduction band and thus promotes the charge separation (eq. 3-20).It also forms OH radicals according to eq (3-21).

$$H_2O_2 + e^- \longrightarrow {}^-OH + {}^\bullet OH \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (3\text{-}20)$$

$$H_2O_2 + O_2^{\bullet -} \longrightarrow {}^\bullet OH + {}^-OH + O_2 \ldots\ldots\ldots\ldots\ (3\text{-}21)$$

Different experiments have been performed on the photolysis of H_2S in MEA in the presence of TiO_2 and H_2O_2, and the volume of hydrogen produced has been measured at the same conditions (20%MEA, 2mg TiO_2, 1000W lamp, and at room temperature). The result in Figure (3-9a) shows the addition of hydrogen peroxide into a semiconductor suspension has been proven to enhance the volume of hydrogen produced.

Figure (3-9b) shows that the volume of hydrogen produced depends on the amount of H_2O_2 and has a maximum at 1% H_2O_2. It is obvious that small amount of hydrogen peroxide enhance the process. The reaction goes slower when the concentration of hydrogen peroxide is more than 1%; it seems to suppress further decomposition of hydrogen sulfide because it can act as a hole or ${}^\bullet OH$ scavenger (113).

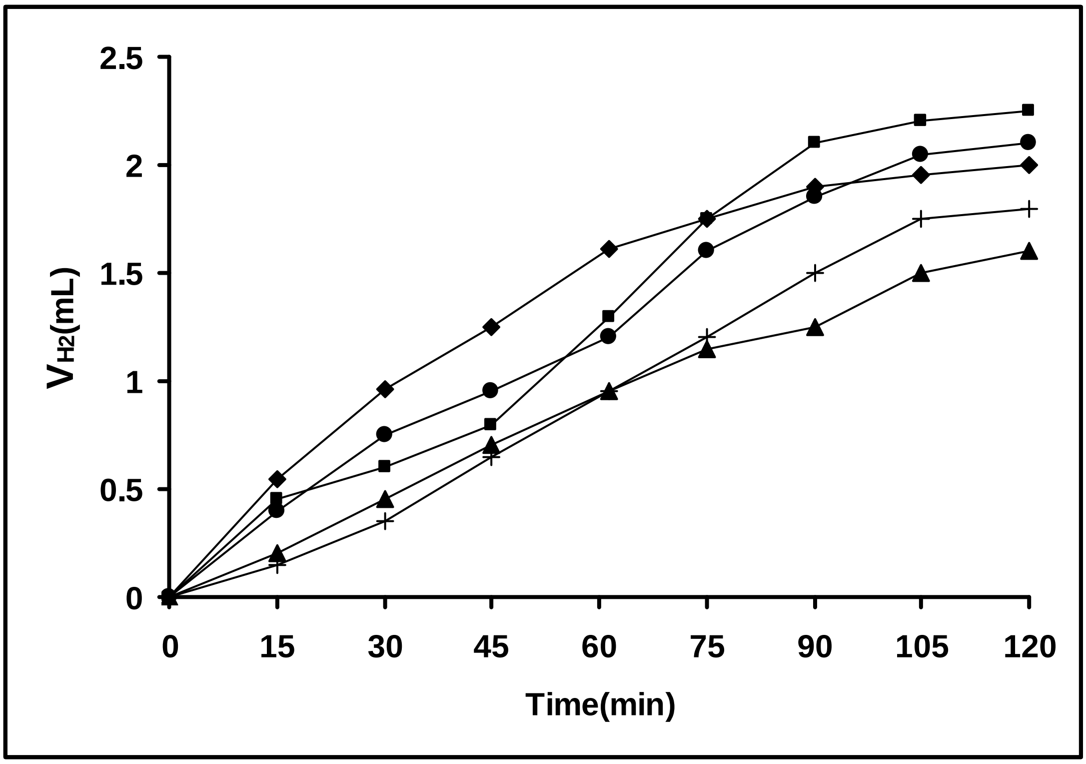


Figure (3-9a) Volume of hydrogen produced as a function of irradiation time by using different percentage of hydrogen peroxide:
■ 1% H_2O_2, ● 0.5% H_2O_2, ♦ with out the addition H_2O_2
+ 1.5% H_2O_2, ▲2% H_2O_2.

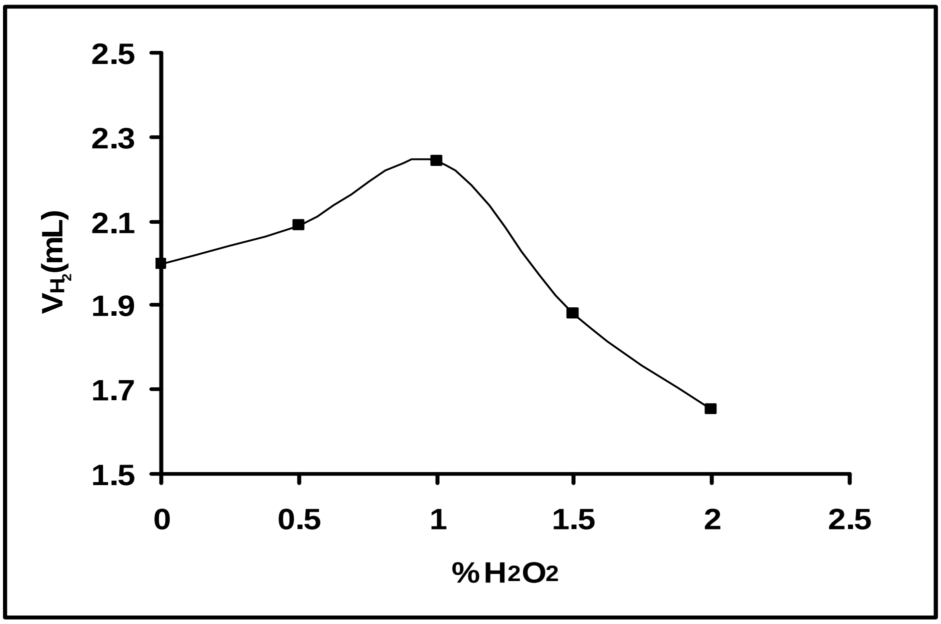


Figure (3-9b) Maximum volume of hydrogen produced in different percentage of H_2O_2 after two hours of irradiation.

3.10 The effect of temperature on the photocatalytic decomposition of hydrogen sulfide.

A series of experiments was carried out to study the effect of temperature on the photocatalytic decomposition of hydrogen sulfide; the range of temperature between (5-35°C) was studied at the same conditions (20%MEA, 2mg TiO_2, and 1000W lamp). Figure (3-10a) shows the volume of hydrogen produced using different temperature.

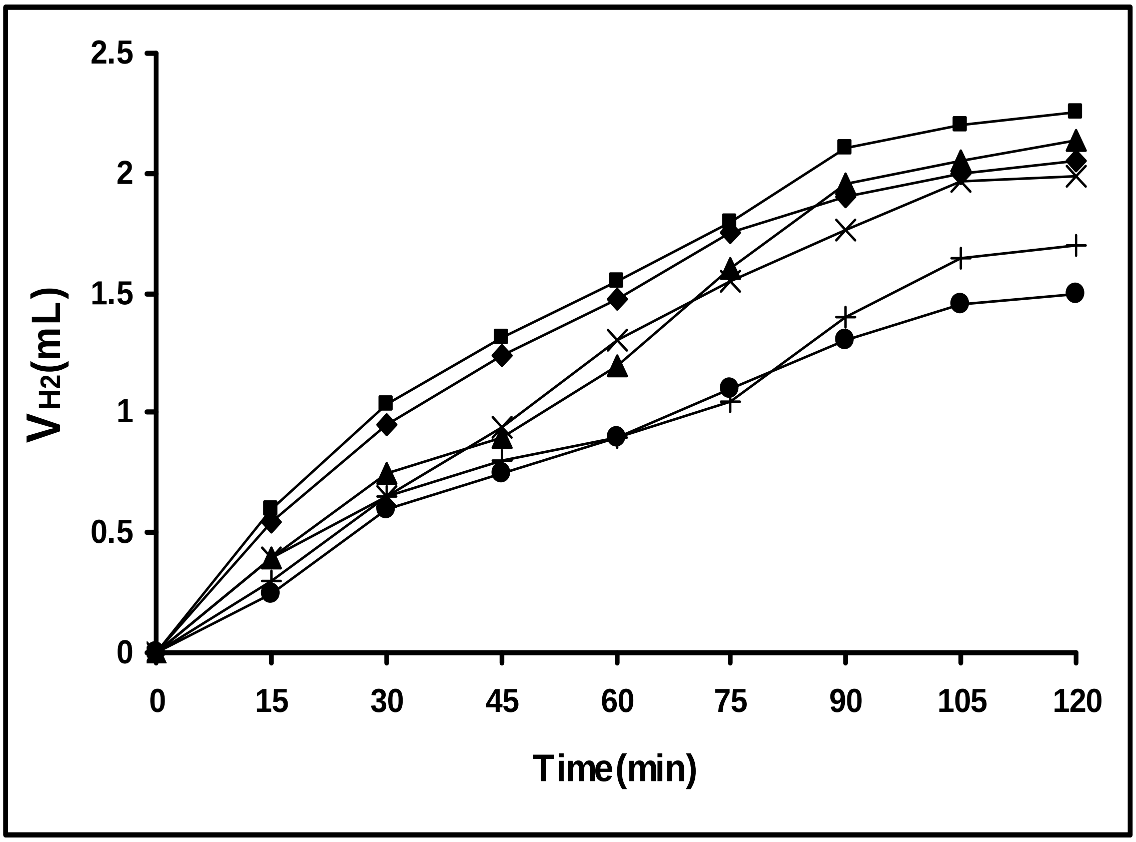


Figure (3-10a) Volume of hydrogen produced as a function of irradiation time in different temperature:

■ 278.15 K ▲283.15K ♦293.15K x **298.15K +303.15K ●308.15K**

The results show that hydrogen production is high at low temperature, but it decreases with an increase in temperature. This may be due to the decreasing of hydrogen sulfide solubility in solution of monoethanolamine.

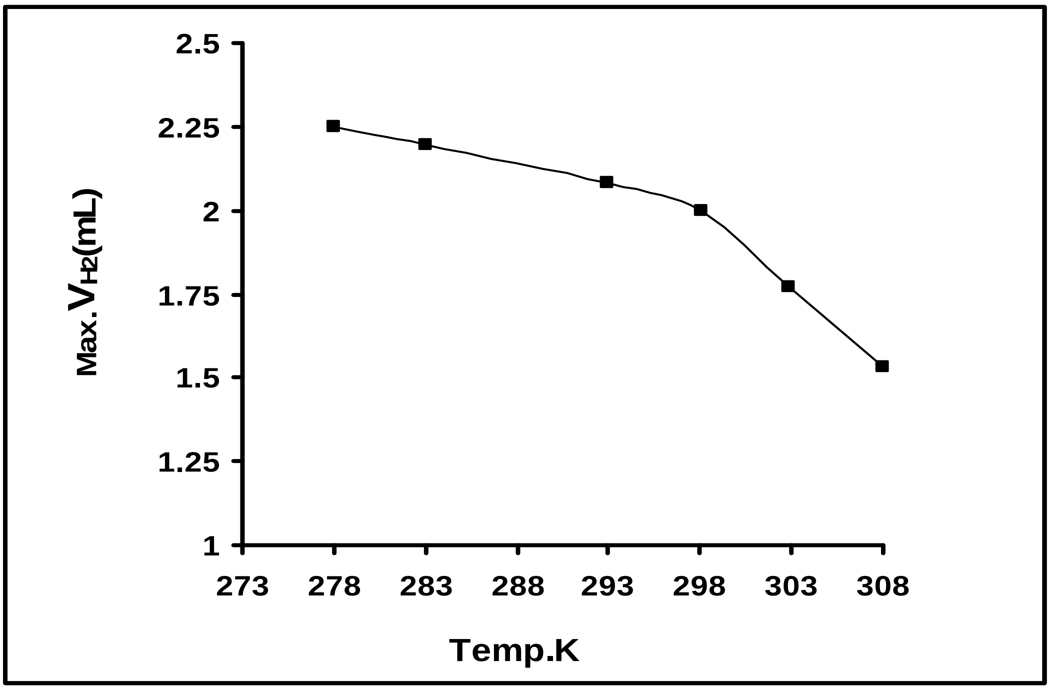


Figure (3-10b) Maximum volume of hydrogen produced in different temperatures after two hours of irradiation.

The results in Figure (3-10b) show that the maximum volume of hydrogen production is 2.25ml/35ml of photocell at low temperature in 278.15K. On another hand when the results compared with thermaldecomposition of hydrogen sulfide without irradiation, it shows that the volume of hydrogen production increases with an increase of temperature but in very low efficiency. The enhancement of the thermaldecomposition with the increase of temperature is probably due the increasing collision frequency of molecules (118). Figure (3-10c) shows the volume of hydrogen production to mixture ($MEA+H_2S+TiO_2$) as a function of heating time.

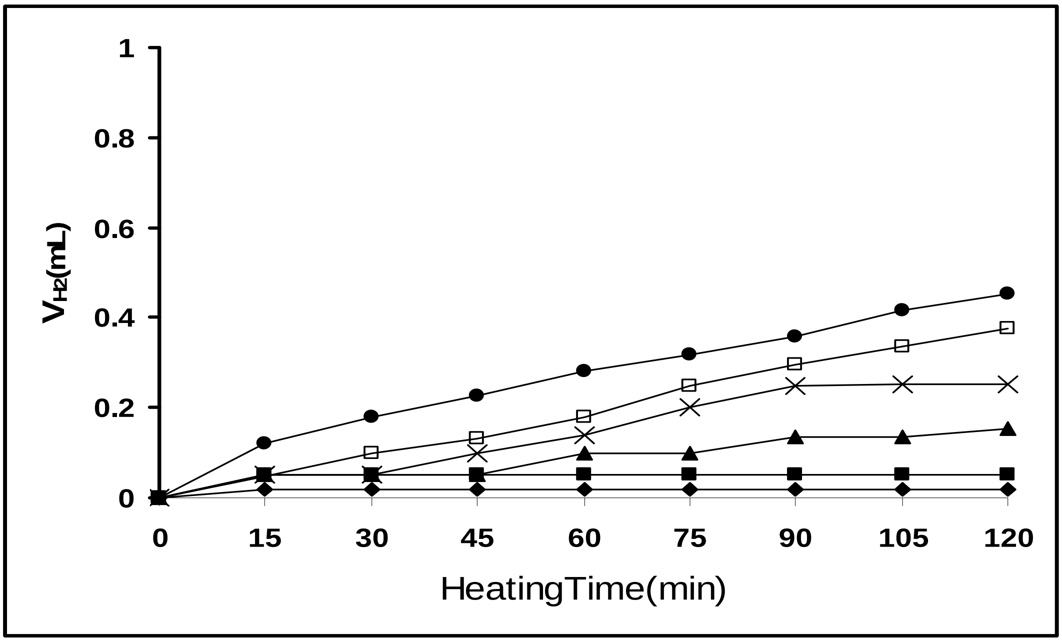


Figure (3-10c) Volume of hydrogen produced as a function of heating time from mixture contained (20%MEA+H_2S+2mg TiO_2)/35ml photocell.●308K , □303K , x298K , ▲ 293K, ■283K, ♦278K.

Figure (3-10d) shows that the maximum volume of hydrogen production is 0.45ml/35ml at 308 K of photocell. Irradiation is believed to be the primary source of e-/h+ pairs at ambient temperature because the band gap is too high to overcome by thermal excitation (119).

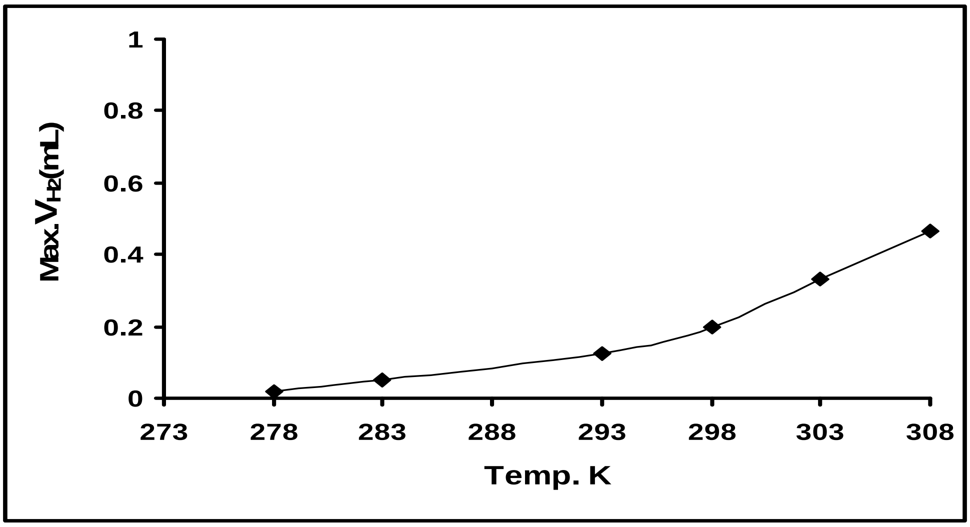


Figure (3-10d) Maximum volume of hydrogen production as a function of temperature after two hours of heating to mixture contained (MEA + H_2S + TiO_2) without irradiation.

3-11 Effect of addition of sensitizer to the titanium dioxide semiconductor

Many workers suggest the addition of sensitizer to the colloidal TiO_2 suspended aqueous solution in order to increase the absorption of new wavelength by the photoreaction mixture.

Figure (3-11a) shows the addition of different concentration of riboflavin to the mixture which contains (20%MEA, 2mg TiO_2) using 1000W Tungsten-Halogen lamp and at room temperature.

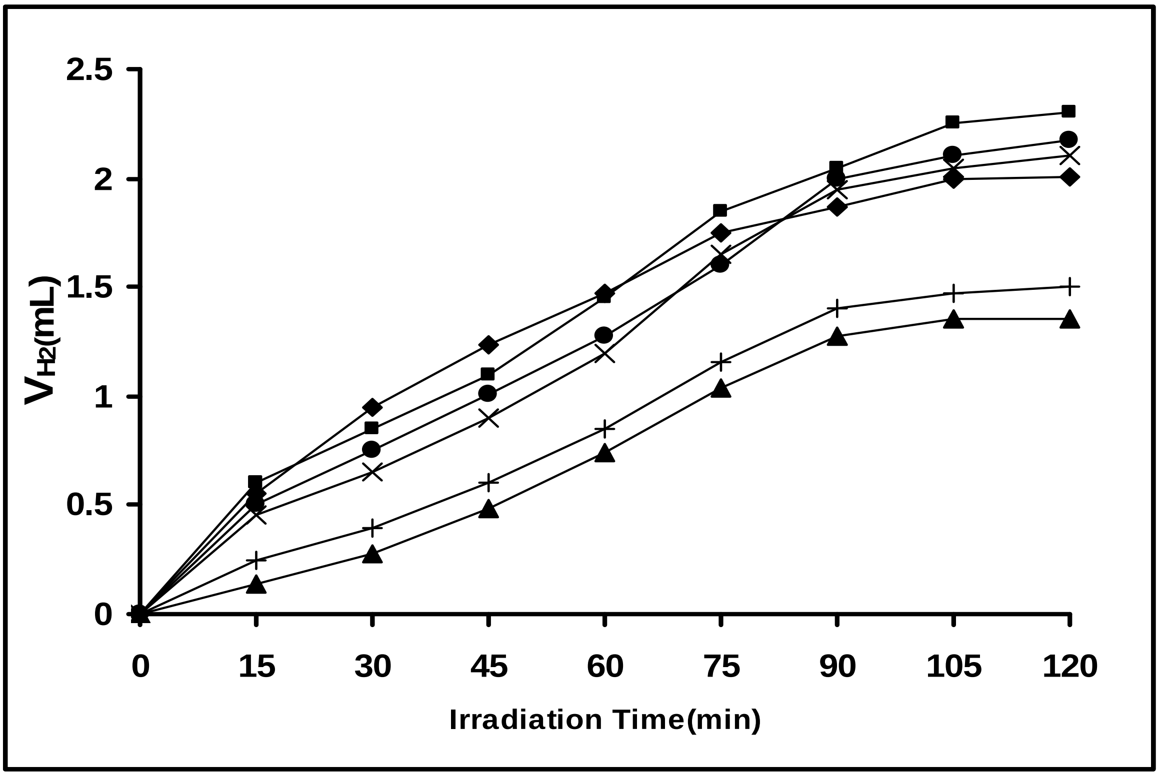


Figure (3-11a) Volume of hydrogen produced as a function of irradiation time using:-

■ **(2mg TiO_2 + 2.5 mg Riboflavin)/35ml.**

● **(2mg TiO_2 + 2 mg Riboflavin)/35ml.**

x **(2mg TiO_2** + 1 **mg Riboflavin)/35ml.**

♦ **(2mg TiO_2)/35ml**.

+ (2mg TiO_2+ 3 mg Riboflavin)/35ml.

▲ **(2.5 mg Riboflavin)/35ml (without TiO_2).**

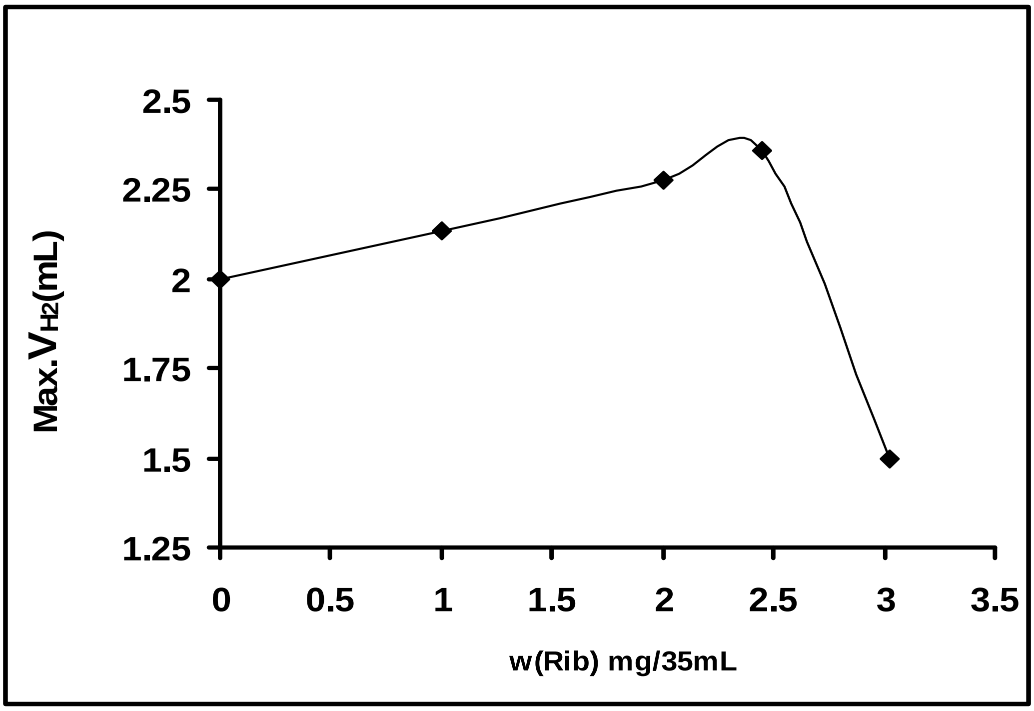


Figure (3-11b) Maximum volume of hydrogen production with different concentration of riboflavin.

The results show that 2.5mg/35ml Riboflavin is the best to produce hydrogen from the photocatalytic decomposition of hydrogen sulfide; that may be due to the absorption of new wavelength by riboflavin and titanium dioxide. The rate of hydrogen production increases when sensitizer was added because the electron transfers from sensitizer after irradiating it to the conduction band of semiconductor and that leads to increase the rate of decomposition of hydrogen sulfide and then the volume of hydrogen produced was increased.

3.12 Analysis of the products using digital hydrogen meter

Hydrogen gas produced from photodecomposition of hydrogen sulfide was analyzed using digital hydrogen meter by injection 1mL of hydrogen from samples and compared it with pure hydrogen. Figure (3-12) shows scale of hydrogen meter as arbitrary unit with volume of hydrogen.

The percent of hydrogen in gas produced from photolysis of different mixtures decreases in comparison with pure hydrogen due to the sensitivity of digital hydrogen meter.

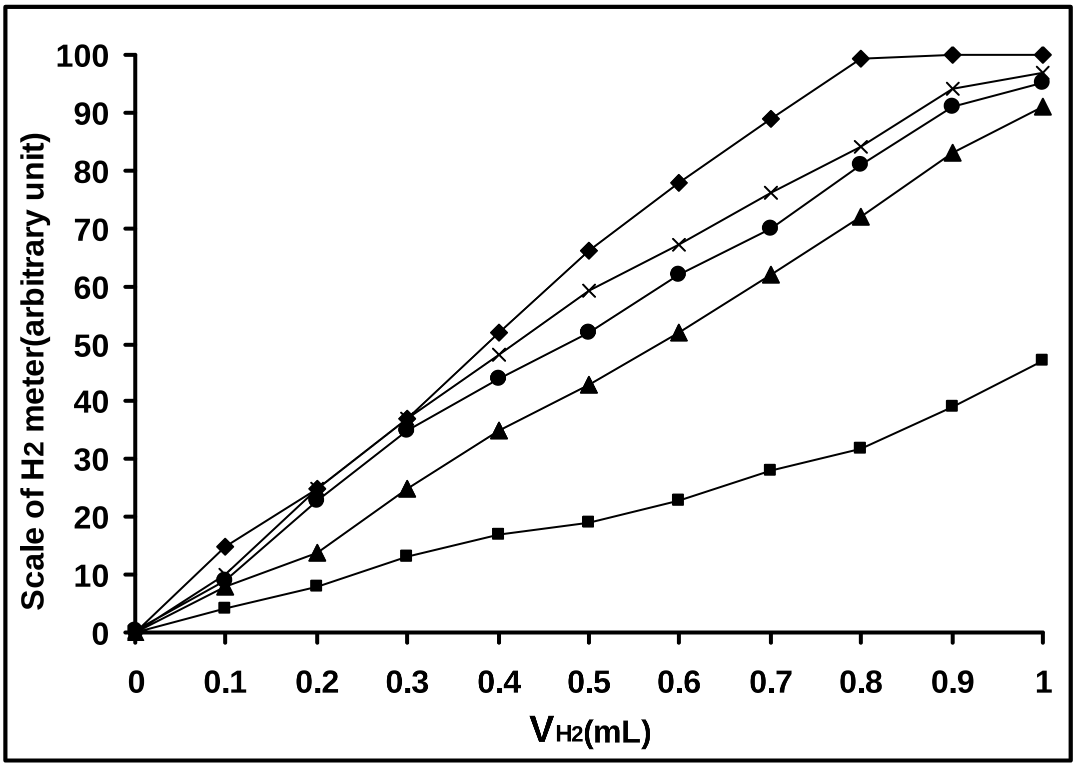


Figure (3-12) Scale of hydrogen meter as arbitrary unit *v*s. volume of hydrogen:

♦ pure hydrogen.

x Hydrogen produced from photolysis mixture (35ml) contained (MEA+H_2S+2mgTiO_2+2.5mg Riboflavin) at room temperature using 1000W Tungsten-Halogen lamp.

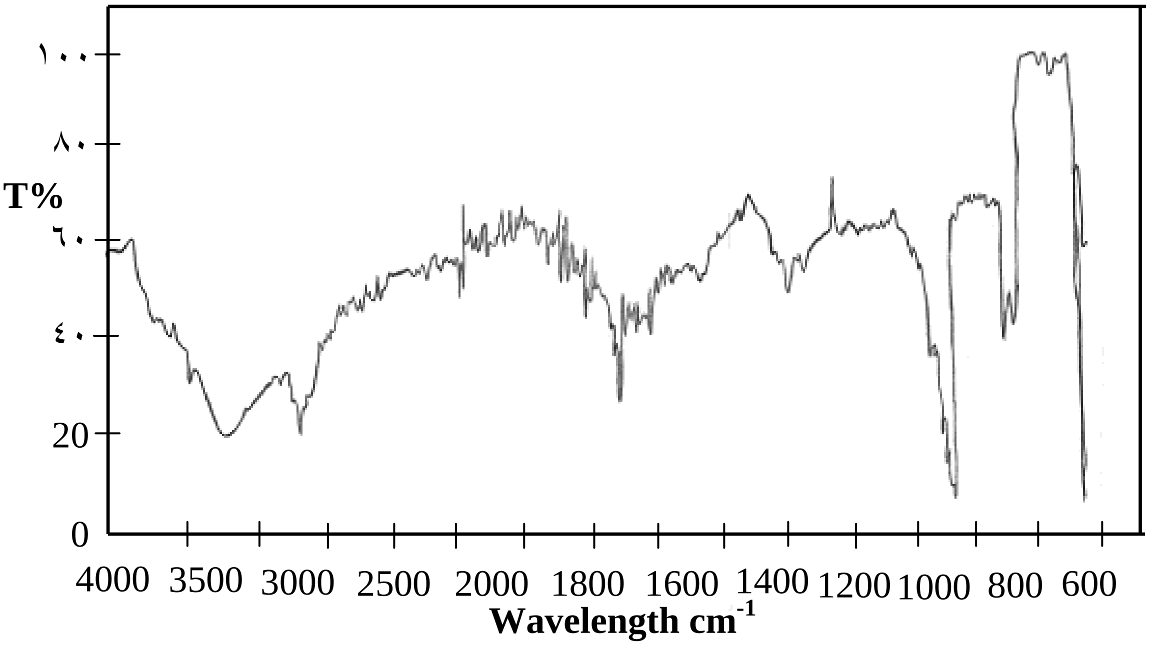
● Hydrogen produced from photolysis mixture (35ml) contained (MEA+H_2S+2mgTiO_2+1% H_20_2) at room temperature using 1000W Tungsten-Halogen lamp.

▲ Hydrogen produced from photolysis mixture (35ml) contained (MEA+H_2S+2mgTiO_2) at room temperature using 1000W Tungsten-Halogen lamp.

■ Hydrogen produced from photolysis mixture (35ml) contained (MEA+H_2S+) at room temperature using 1000W Tungsten-Halogen lamp.

3.13 Infra Red Spectra analysis studies

The analysis of the products using IR spectra was investigated (Figure3-13) to mixture (20% MEA, H_2S, 2mg TiO_2 filtered using filter paper) before and after irradiation at room temperature and it shows that the solvent molecule of monoethanolamine is not affected by photodecomposition of hydrogen sulfide.



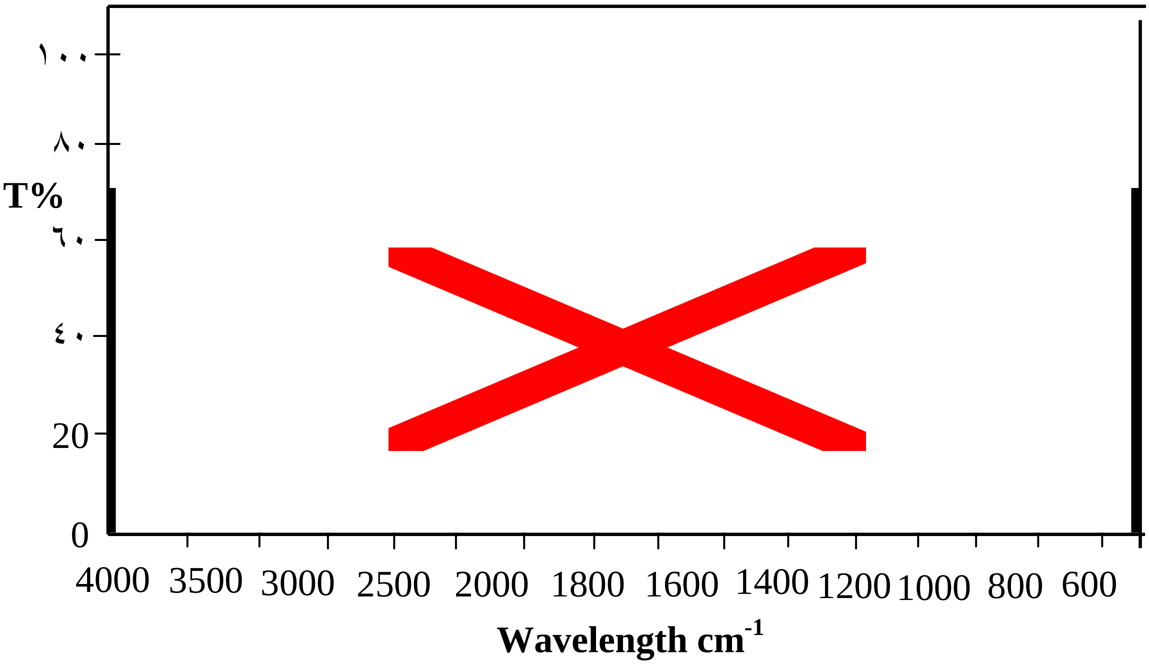


Figure (3-13) IR spectra analysis.

3.14 U.V visible spectra studies

U.V visible spectra was also studied to the same mixture (20% MEA, H_2S, 2mg TiO_2 filtered using filter paper) before and after irradiation and it shows that even UV visible spectra has not affected solvent molecules of monoethanolamine because the four peaks of this spectrum have not been changed.

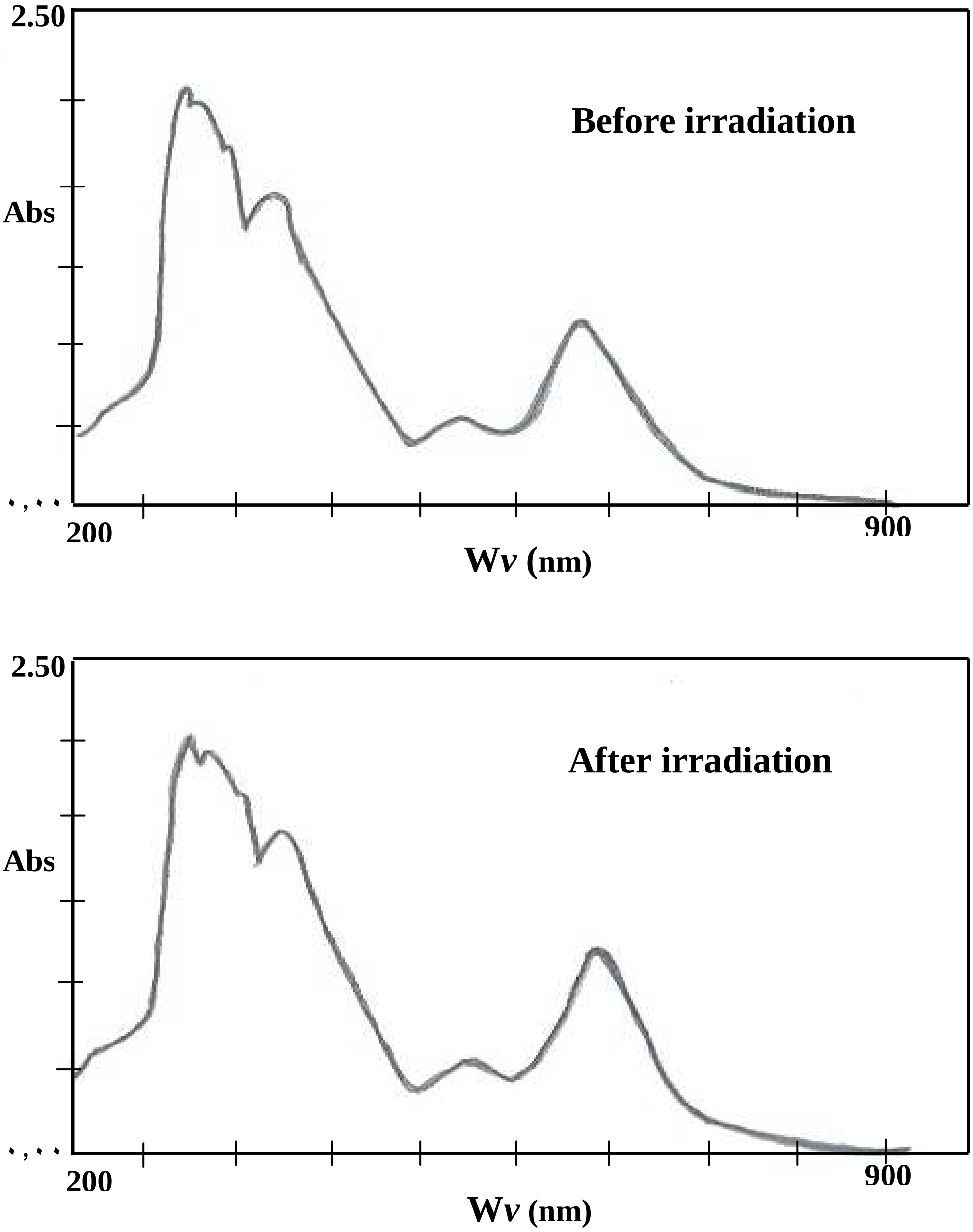


Figure (3-14) U.V visible spectra of mixture (20% MEA, H_2S, 2mg TiO_2) before and after irradiation.

3.15 Determination of Reaction Order

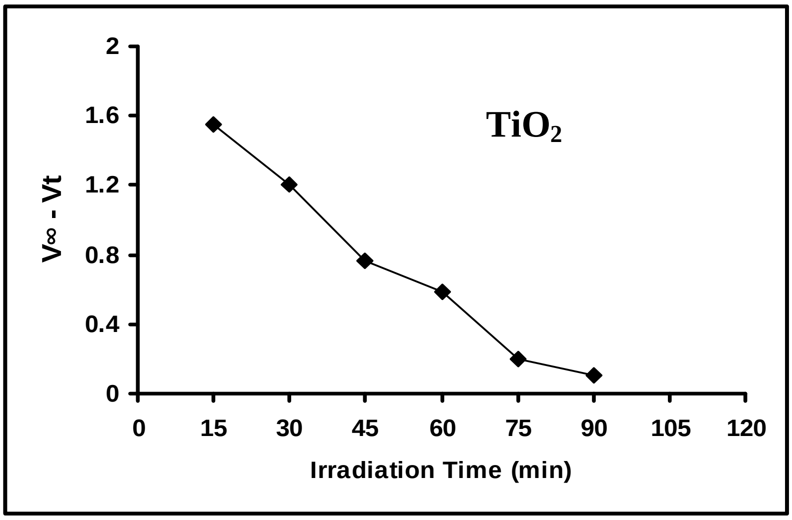
In order to obtain a best fit to a set of experimental rate data, it is necessary to obtain an integrated rate equation. Rate equations are differential equations and in many commonly occurring reactions analytical integration is straightforward (120,121). However, the rate of the decomposition of hydrogen sulfide was measured by equation:-

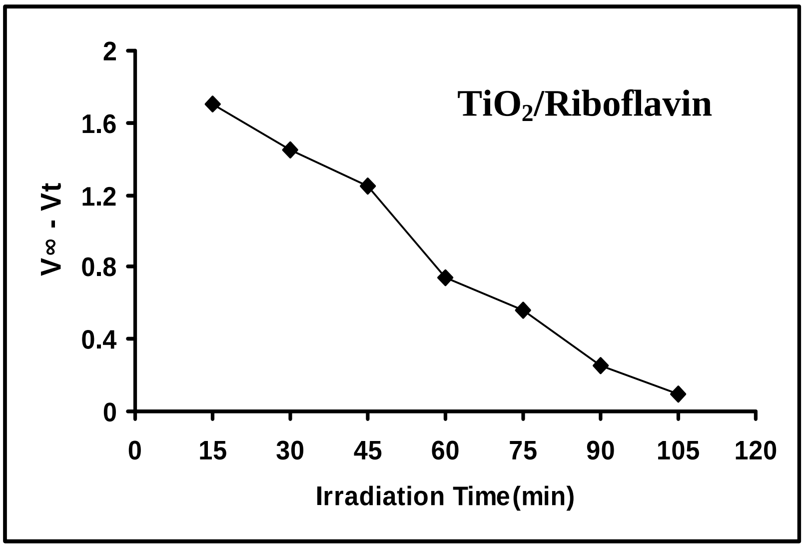
$$-d\,[H_2S]/dt = d\,[H_2]/dt = K\,[H_2]^{\mathbf{n}} \quad \text{............................} \quad (3\text{-}22)$$

Where K is the rate constant for the production of hydrogen, n is the order of reaction and $[H_2]$ is the concentration of hydrogen gas from hydrogen sulfide (91).

Kinetics analysis has been done to find the behavior of hydrogen production from hydrogen sulfide at room temperature for three experiments (1-using 2mg TiO_2, 2- using 2mg TiO_2+2.5 mg Riboflavin, 3- using 2mg TiO_2+1% H_2O_2) by plotting (V∞ –Vt) against time (Figure 3-15a) as a zero order test, plotting log [V∞/ (V∞ –Vt)] against time (Figure3-15b) as a first order test and [Vt/ V∞(V∞ – Vt)] against time (Figure3-15c) as a second order test. Where V∞ is the volume of hydrogen at infinite time and Vt at time t.

The results in these plots show the decomposition behavior is first order reaction because it shows a good straight line and the rate constant calculated has been the same in every step.





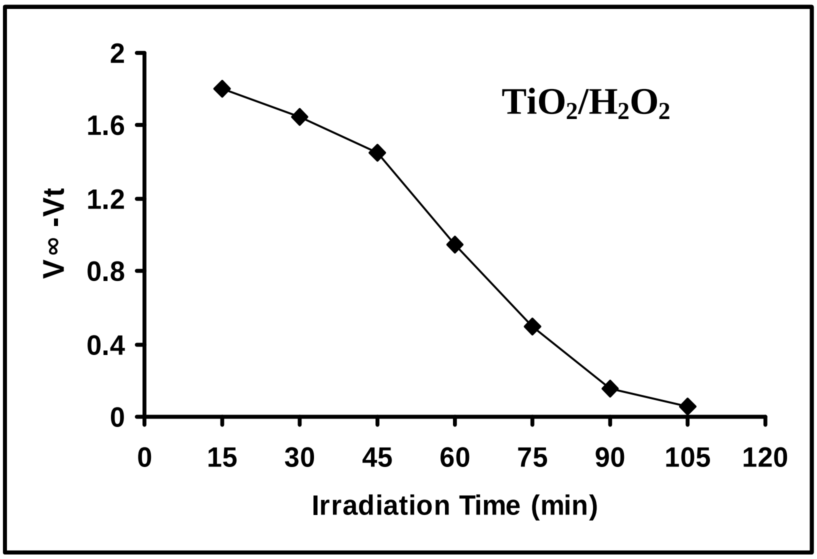
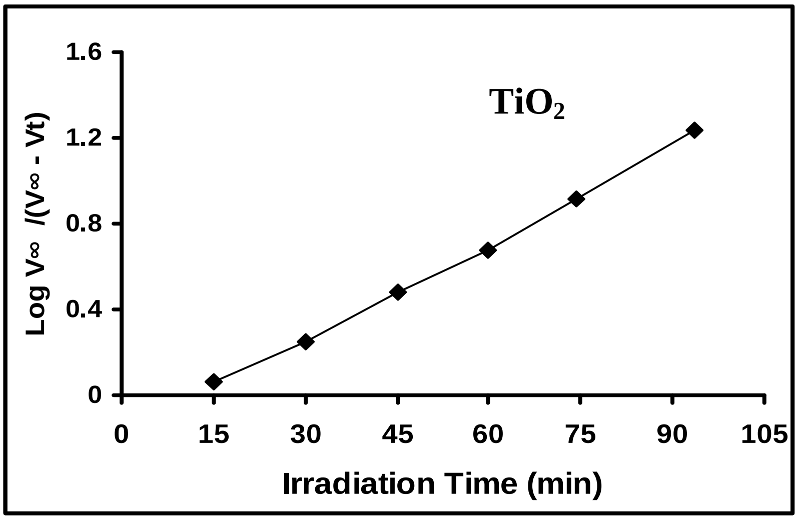
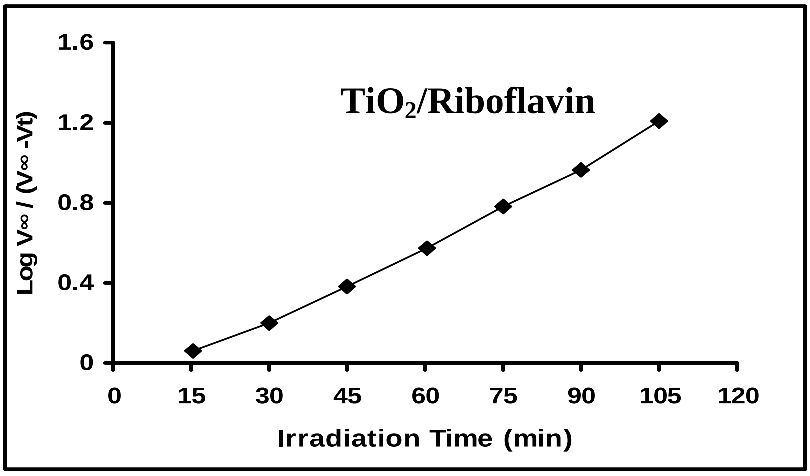


Figure (3-15a) Zero order plot for hydrogen production from H_2S (V∞ - Vt) against Irradiation time (min) at 298.15K.





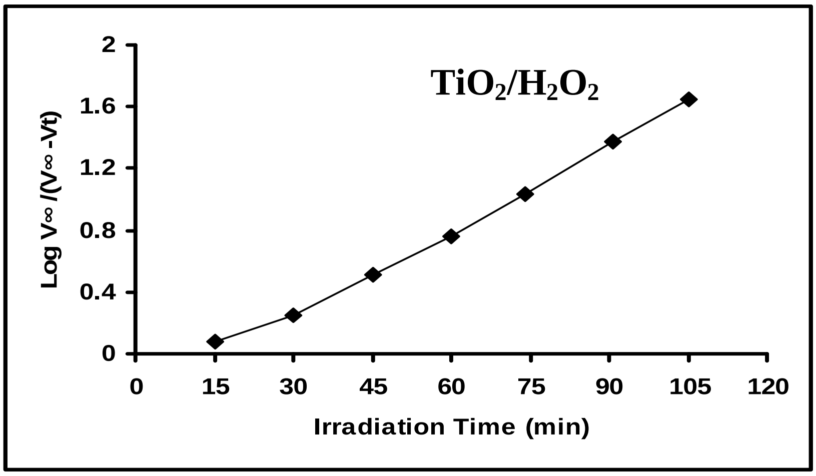
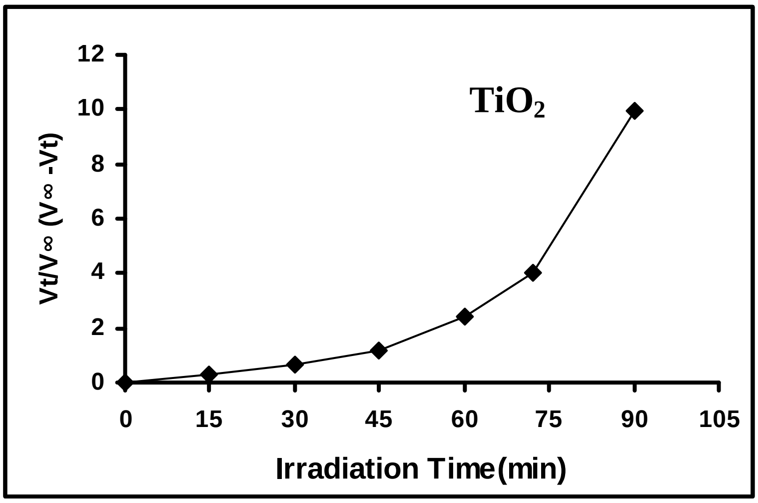
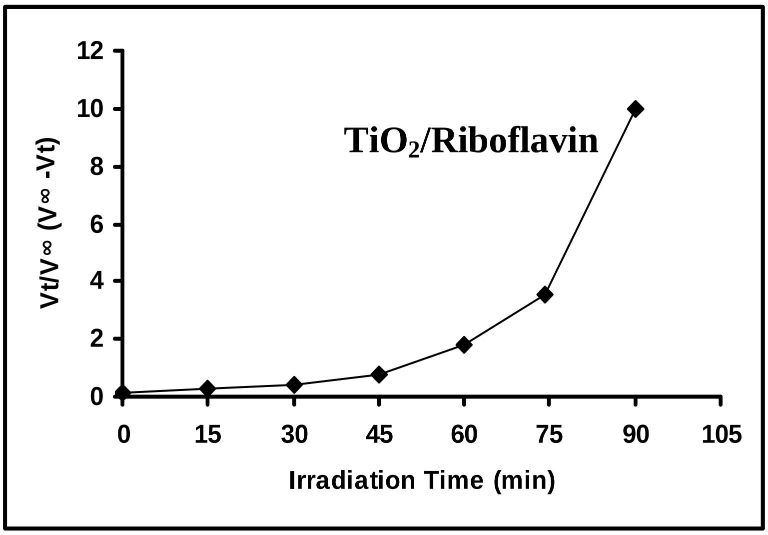


Figure (3-15b) First order plot for hydrogen production from H_2S log V∞ / (V∞ - Vt) against Irradiation time (min) at 298.15K.





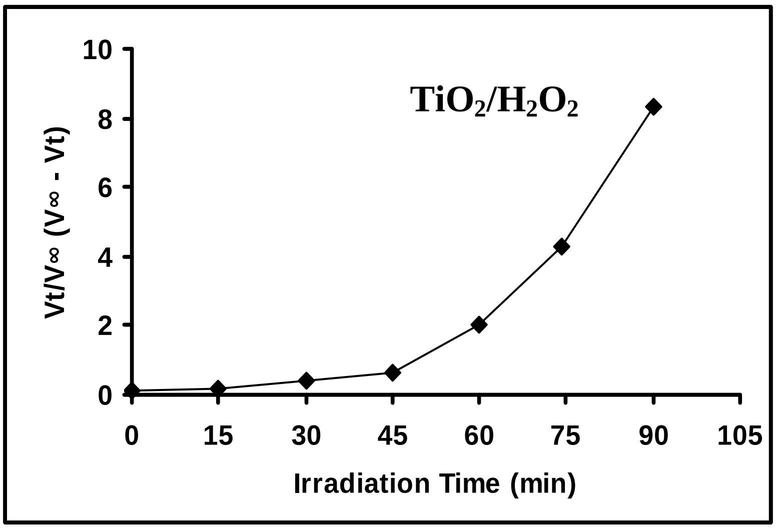


Figure (3-15c) Second order plot for hydrogen production from H_2S [Vt/ V∞ (V∞ - Vt)] against Irradiation time (min) at 298.15K.

3.16 Determination of Activation energy

The activation energy for the production of hydrogen from mixture contained (20% MEA, hydrogen sulfide, 2mg TiO_2) was calculated for temperature range (278 to 308 K) using 1000W Tungsten-Halogen lamp. Arrhenius plot for first order has been plotted in figure (3-16).

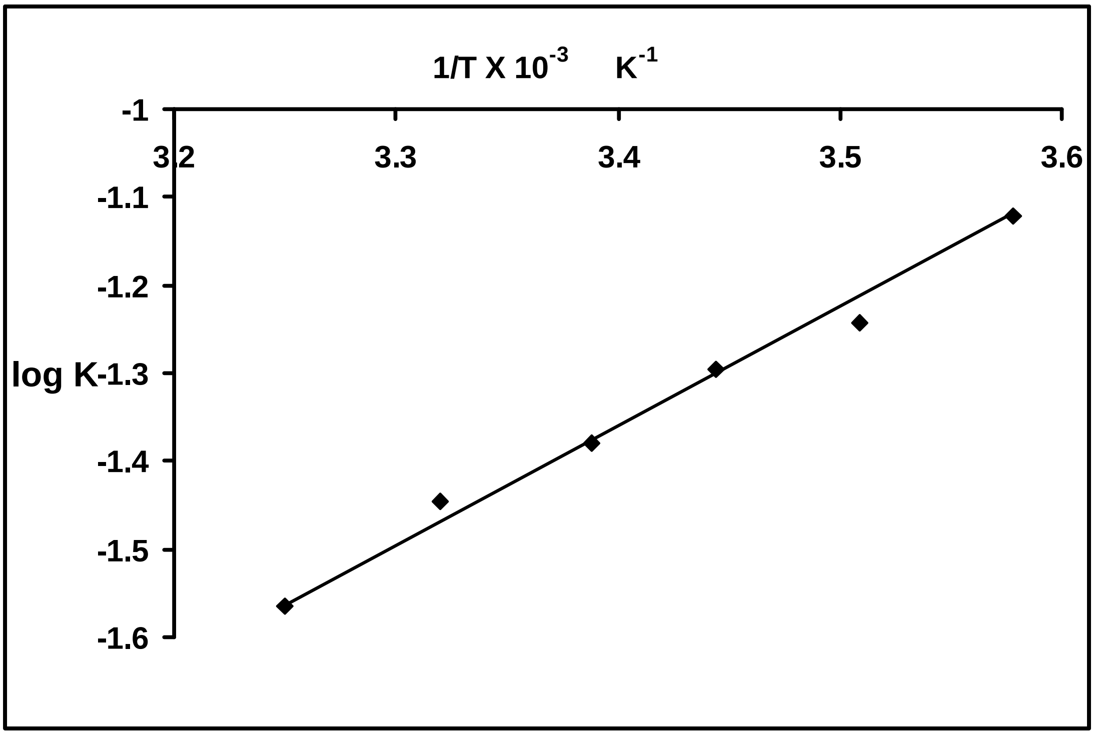


Figure (3-16) Arrhenius activation energy plot for the first order assumption for hydrogen production. Plot of logK against the reciprocal of the absolute temperature.

From the slope of straight line activation energy was found equal to 25.32 kJ /mole.

3.17 Mechanism of Photochemical Reaction

From kinetic data the following mechanism may be proposed for the reaction of hydrogen sulfide and MEA in aqueous colloidal suspended of semiconductor of titanium dioxide.

Monoethanolamine reacts and dissolves H_2S molecules according to this equation:-

$2HOCH_2CH_2NH_2 + H_2S \longrightarrow (HOCH_2CH_2NH_3)_2S$............ (3-26)

The product reacts with another molecule of hydrogen sulfide according to this equation:-

$(HOCH_2CH_2NH_3)_2S + H_2S \rightleftarrows (HOCH_2CH_2NH_3)_2(SH)_2$..... (3-27)

The new molecule in equation (3-27) is in equilibrium with reactants (MEA and H_2S) and the bonding between sulfur and nitrogen is very weak. For that when these molecules absorbed light, it was exited and decomposed according to these equations:-

$(HOCH_2CH_2NH_3)_2S + h\nu \longrightarrow [(HOCH_2CH_2NH_3)_2S]^* \longrightarrow MEA + H_2 + S$....... (3-28)

$(HOCH_2CH_2NH_3)_2(SH)_2 \longrightarrow [(HOCH_2CH_2NH_3)_2(SH)_2]^* \longrightarrow MEA + H_2 + S_2$..(3-29)

The elemental sulfur have detected as a pure yellow crystal precipitated on the wall of photocell during the photolytic experiments.

When semiconductor particles are present in the photochemical mixture the following mechanism was suggested:-

$TiO_2 + h\nu \longrightarrow e^- + h^+$

$(HOCH_2CH_2NH_3)_2S + e^- \longrightarrow 2MEA + H_2 + S$................ (3-30)

$(HOCH_2CH_2NH_3)_2(SH)_2 + h^+ \longrightarrow 2MEA + 2H_2 + S_2$...... (3-31)

3.18 Conclusions

1. Hydrogen gas as a clean fuel can be produced from photodecomposition of hydrogen sulfide in aqueous solutions of monoethanolamine in the presence of photocatalyst.
2. Titanium dioxide proved to be more efficient photocatalyst than zinc oxide since the decomposition of hydrogen sulfide proceeded at higher production of hydrogen.
3. 2mgTiO_2/35ml was the optimum load of titanium dioxide used in the experiments.
4. No significant effect was shown when oxygen gas was passing through these solutions and sulfur atom may increase the recombination of electron and hole on the surface of titanium dioxide.
5. In the case of addition of hydrogen peroxide into illuminated TiO_2 suspensions synergistic effect was observed leading to an enhancement of the process.
6. The effect of organic sensitizer (Riboflavin) on the photodecomposition of hydrogen sulfide will lead to the increase the efficiency of the process according to its ability of scavenging light and thus increasing the decomposition of hydrogen sulfide.
7. The photodecomposition of hydrogen sulfide followed first order kinetics and parameters such as temperature, light intensity and the percentage of monoethanolamine play an important role affecting the reaction rate.
8. The results give that 2/3 percent of dissolved gas has been converted to hydrogen and sulfur.

3.19 Recommendations

1. Study the production of hydrogen gas from hydrogen sulfide in aqueous solution of ethanolamines using another type of semiconductors such as CdSe, CdTe, CdS, and WO_3.
2. According to the higher solubility of mixture (CO_2+H_2S) in aqueous solution of ethanolamines, another study can be investigated by photoreduction carbon dioxide to formic acid and formaldehyde by hydrogen produced from decomposition of hydrogen sulfide.
3. Study the efficiency of process using another type of titanium dioxide polymorphs such as rutile and brookite.
4. Study the thermal production of hydrogen from hydrogen sulfide in aqueous solution of ethanolamines using temperature between (40-90) °C.
5. Using another type of sensitizers such as Hydroquinone, Resorcinol, P-Nitrophenol in the photodecomposition of hydrogen sulfide in the presence of titanium dioxide.

Republic of Iraq
Ministry of Higher Education
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College of Science for Women
Chemistry Department

PHOTO PRODUCTION OF HYDROGEN FROM HYDROGEN SULFIDE IN AQUEOUS SOLUTIONS OF MONOETHANOLAMINE USING TITANIUM DIOXIDE AS PHOTOCATALYST

A THESIS
SUBMITTED TO THE COLLEGE OF SCIENCE FOR WOMEN
BAGHDAD UNIVERSITY
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF MASTER OF SCIENCE IN CHEMISTRY

BY

INAM HUSSEIN ALI MOHMMED AL-MOSAWI

B.Sc.BAGHDAD 2000

2005 *1426*

بسم الله الرحمن الرحيم

ويسئلونك عن الروح قل الروح من أمر ربي
وما أوتيتم من العلم الا قليلا

صدق الله العظيم

(سورة الاسراء/٨٥)

الى أرواح شهداء فاجعة الكاظمية

«تغمدهم الله بفسيح جناته»

انعام

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I wish to express my deep gratitude to all my friends for their encouragement and assistance that cannot be forgotten.

ABSTRACT

In the present work, the production of hydrogen fuel from photodecomposition of hydrogen sulfide in aqueous solution of monoethanolamine, using titanium dioxide as photocatalyst has been investigated. The influence of various parameters such as the percentage of monoethanolamine, the load of the catalyst, the effect of addition of sensitizer, the effect of addition of an oxidant and the increase of temperature is also studied.

All photochemical experiments have been carried out in a Pyrex cylinder cell of capacity 35mL. The volume of hydrogen produced is measured using U- tube.

The blank experiments for either illuminated aqueous solutions of monoethanolamine and hydrogen sulfide or the suspension containing titanium dioxide have showed that both illumination and the catalyst are necessary for the decomposition of hydrogen sulfide.

The photochemical processes are monitored at different percentages of monoethanolamine (10%, 15%, 20%, 25%, 30%, 35%), different sources of light (1000W, 500W) Tungsten-Halogen lamp, different temperatures (278.15, 283.15, 293.15, 298.15, 303.15)K and different load of titanium dioxide photocatalyst (0.5mg, 1mg, 1.5mg, 2mg, 2.5mg)/35ml of photocell. The results have shown that higher hydrogen production was achieved using 20% MEA at 278 K using 1000W Tungsten-Halogen lamp with 2mg load of TiO_2.

The effect of passing oxygen gas was investigated and no significant effect was shown. The addition of an oxidant using hydrogen peroxide was studied and the volume of hydrogen produced is increased.

The organic sensitizer (Riboflavin) can be sensitized the photocatalytic decomposition of hydrogen sulfide. It is generally found

that the volume of hydrogen produced is increased and at maximum using 2.5 mg of sensitizer in 35 mL of photocell.

U.V visible and IR spectra analysis was investigated and no significant effect was shown.

According to the kinetic results, the reaction is first-order, with activation energy of 25.32 kJ /mole.

Reaction mechanism has been suggested for this reaction in absence and presence of titanium dioxide photocatalyst.

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Chapter Two: - Experimental Part

Chapter Three: - Results and Discussion

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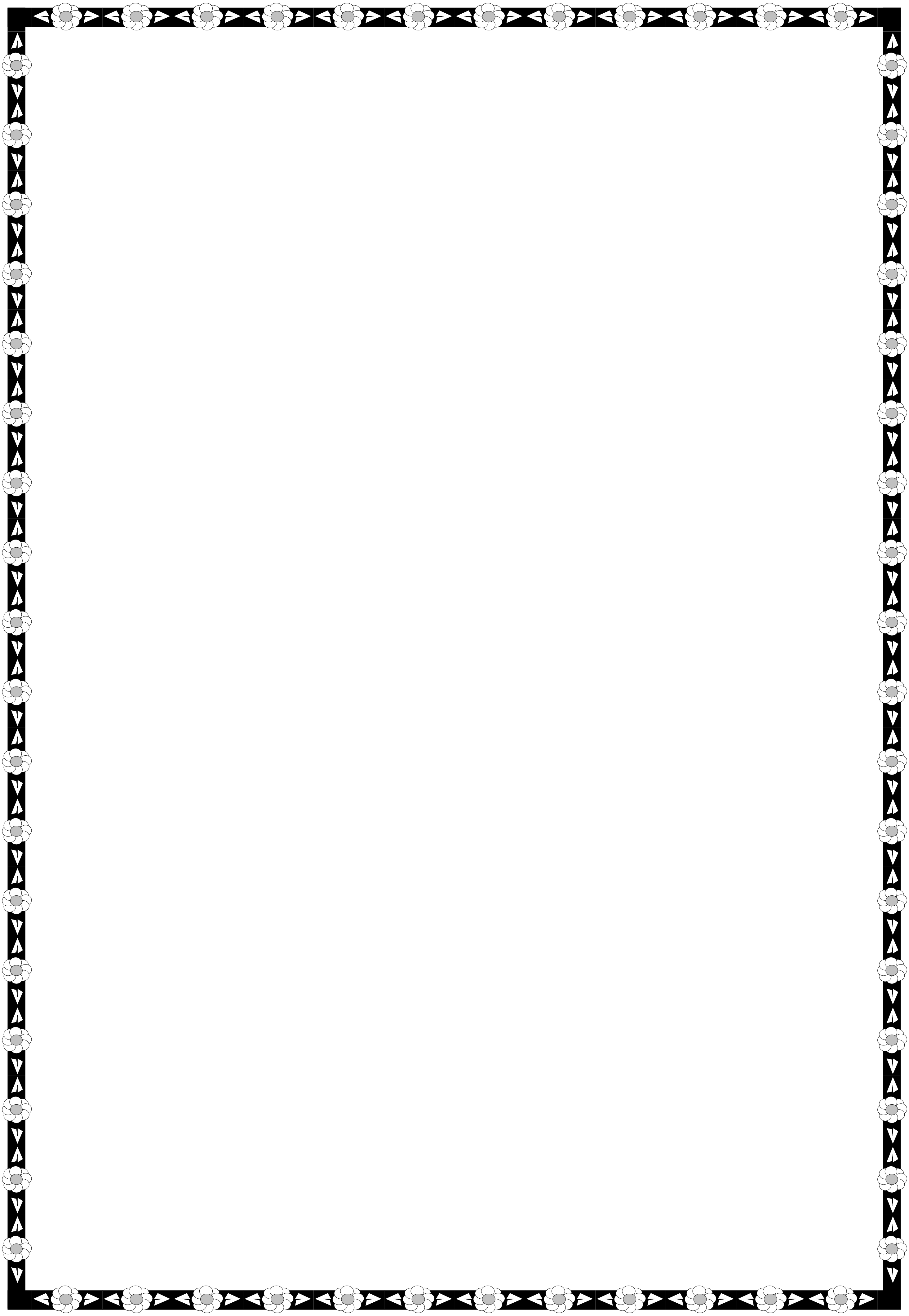
Chapter One: - Introduction

Chapter Two:-Experimental Part

Chapter Three:-Results and Discussion

LIST OF ABBREVIATIONS

Abbreviations	Meaning
CB	Conduction Band
VB	Valance Band
E_{bg}	Energy band gap
UV	Ultra Violet
MEA	Monoethanolamine
DEA	Diethanolamine
DGA	Diglycolamine
MDEA	Methyldiethanolamine
SPE	Solid Polymer Electrolyte
MV	Methyl Viologen
EDTA	Ethylene Diamine Tetra Acetic Acid
TEOA	Triethanol amine
IC	Internal Conversion
ISC	Inter System Crossing
Sc	Semiconductor
h^+	hole
e^-	electron
S	Sensitizer
ARAS	Atomic Resonance Absorption Spectroscopy



جمهورية العراق
وزارة التعليم العالي و البحث العلمي
جامعة بغداد/كلية العلوم للبنات
قسم الكيمياء

انتاج الهيدروجين ضوئيا من كبريتيد الهيدروجين في المحاليل المائية لاحادي ايثانول امين باستعمال ثاني اوكسيد التيتانيوم كمحفز ضوئي

رسالة مقدمة الى
كلية العلوم للبنات- جامعة بغداد
كجزء من متطلبات نيل درجة ماجستير علوم في الكيمياء

من قبل

أنعام حسين علي محمد الموسوي

بكالوريوس كيمياء ٢٠٠٠

جامعة بغداد

١٤٢٦ ٢٠٠٥

الخلاصة

تم خلال البحث الحالي دراسة انتاج الهيدروجين كوقود من التفكك الضوئي لغاز كبريتيد الهيدروجين الذائب في المحاليل المائية لاحادي ايثانول امين بأستعمال ثاني اوكسيد التيتانيوم كمحفز ضوئي.

كذلك تم دراسة تأثير تغير بعض العوامل مثل تركيزالمذيب وكمية المحفز المضافة وتاثير اضافة متحسس ضوئي وكذلك اضافة عامل مؤكسد مثل بيروكسيد الهيدروجين بالاضافة الى تاثير زيادة درجة الحرارة على التفاعل.

تم اجراء تفاعل التفكك الضوئي في خلية ضوئية اسطوانية الشكل سعة ٣٥مل مزودة بنافذة من البايركس. و لمتابعة سير التفاعل تم قياس حجم الهيدروجين الناتج بمرور الزمن باستعمال أنبوب زجاجي على شكل حرف U .

لقد اثبتت التجارب الاولية التي اجريت على مزيج التفاعل في الضوء و الظلام و بوجود او غياب ثاني اوكسيد التيتانيوم ان كل من الضوء والمحفز ضروريان لاتمام عملية التفكك الضوئي لكبريتيد الهيدروجين.

لقد تم اجراء التجارب المختبرية لتفاعل التفكك الضوئي بتراكيز مختلفة من احادي ايثانول امين(١٠%، ١٥%، ٢٠%، ٣٠%، ٣٥%) وبأستخدام مصباح التنكستن–هالوجين بشدة(500W,1000W) كمصدر للضوء وفي درجات حرارية مختلفة(٢٧٨، ٢٨٣، ٢٩٣، ٢٩٨، ٣٠٣)كلفن ، وبأضافة كميات مختلفة من المحفز الضوئي(2.5mg, 2mg,1.5mg, 1mg, 0.5mg). فكان اعلى معدل لانتاج الهبدروجين عند استعمال ٢٠% من احادي ايثانول امين بدرجة حرارة ٢٧٨,١٥ كلفن باستخدام مصباح

التنكستن-هالوجين بشدة(1000W) مع افضل كمية محفز مضافة وهي 2mg لكل٣٥ مل لحجم الخلية.

كذلك تم دراسة تاثير امرار غاز الاوكسجين على مزيج التفاعل فكانت النتيجة غير مؤثرة، اما عند اضافة عامل مؤكسد مثل بيروكسيد الهيدروجين الى التفاعل فان كمية الهيدروجين المتحرر قد ازدادت بنسبة مؤثرة.

وقد تم في هذا البحث محاولة زيادة كفاءة نظام التفكك الضوئي وذلك باضافة المتحسس العضوي الرايبوفلافين الممدص على سطح ثاني اوكسيد التيتانيوم حيث اوضحت القياسات ان معدل انتاج الهيدروجين قد ازداد عند اضافة2.5mg من المتحسس لكل ٣٥ مل لحجم الخلية الضوئي.

لقد تم تحليل نواتج التفاعل بأستخدام مطيافية الاشعة فوق البنفسجية والمرئية ومطيافية الاشعة تحت الحمراء فلم تكن مؤثرة في تشخيص نواتج التفاعل.

ان الدراسات الحركية اوضحت ان سرعة التفاعل هي من المرتبة الاولى، اما طاقة التنشيط فكانت تساوي ٢٥,٣٢ كيلو جول /مول.

وعلى ضوء تاثير هذه العوامل المختلفة تم اقتراح ميكانيكية لتفاعل التفكك الضوئي بوجود و بغياب المحفز الضوئي.