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GENERATION OF ELECTRICITY AND HYDROGEN FROM WASTEWATER USING PHOTO FUEL CELL- A REVIEW

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Abstract: Due to increasing environmental problems, there has been urge to develop more products that would benefit our environment and can have minimum pollution. Researches has been carried on various methods of hydrogen generation as it is a green fuel. Hydrogen can be generated using Microbial fuel cell(MFC), Photofuel cell (PFC), etc. Disposal of wastewater has been an important area of research in these recent years. It is a tedious process as the organic pollutants are difficult to degrade by the conventional processes. To remove these organic pollutants they are subjected to the photocatalytic degradation process. Photofuel cell uses this method to produce hydrogen and electricity using various fuels such as alcohols, ammonia, wastewater, etc. Photo fuel is a Photoelectrochemical cell which converts chemical energy to electrical energy and thus produces electricity. It gives triple benefit such as generation of hydrogen and electricity along with the purification of waste water. Thus, this paper gives review about the techniques of generation of hydrogen and electricity, the materials used for it and their efficiency of the cell.

Keywords: Photochemical cell, Hydrogen production, Photocatalyst.

1. Introduction

There has been increase in environmental problems and so there is need for development of more and more eco-friendly products such as green fuel [60,25]. Renewable energy resources are encouraged due to environmental problems. The scientific research has proved that, there is an alternative way to produce electricity using photo-fuel cell from wastewater [121, 122]. In this case double benefits can be obtained such as electricity production and Hydrogen generation by using wastewater [60]. Photo fuel cells which are also called as Photocatalytic fuel cell (PFC) with attractive feature to produce electricity using inorganic and organic pollutants. The Photocatalytic degradation of organic pollutants results in production of electricity and also wastewater cleaning[118, 119]. The idea of Photofuel cell (PFC) was first introduced by Kaneko and co-workers [120]. Now this research is considered as an alternative way of energy resource. Photo fuel cell consist of two electrodes such as Photo-anode and cathode which are separated by an ion exchange membrane. The photo-anode consist of photo-catalyst, different materials can be used as photo-anode. Every material gives different results based on their properties. Various materials can be employed as cathode but typically platinum (Pt) is used as it is a noble metal. Basically, as the name suggest Photo-fuel cell absorbs sunlight (Visible light, ultraviolet rays) and the photo-anode consisting of photo-catalyst which excites the electrons from valence band to the conduction band thus the electron-hole pair are generated. Consumption of Holes are done by oxidising fuel and the electrons are carried by the external circuit to generate hydrogen and electricity.

A photo catalyst is material which absorbs light energy to get the higher energy levels and this bring out the excitation of electrons, thus chemical reaction takes place when this energy is provided to the reacting substance. One of the major candidates for photocatalysis is Titania (TiO2) because it is stable in nature and also it is readily available in the market at low cost [2]. Various fuels can be used in photo fuel cell such as textile wastewater, sewage water, food waste, industrial wastewater, etc.This wastewater can be purified by using various electrolytes such as NaOH, KOH, H2SO4 etc. Electrolyte is necessary to maintain the pH value as it helps in production of hydroxyl radicals (OH) and also plays a vital role in the destruction of organic pollutants. This review pays more attention in studies related to photo fuel cell and the effectiveness of hydrogen production from wastewater and discusses the different hydrogen and electricity generation devices such as Microbial fuel cell (MFC), Dual fuel cell, Bio-photo fuel cell, etc.

2. Hydrogen Production Techniques

2.1 Photocatalytic (PC) production of hydrogen

photocatalytic production of hydrogen can be done either by water splitting or by photoreforming of organic compounds. Photocatalytic water splitting requires a photocatalyst which is exited by photons, which in turn creates electron-hole pairs [95]. Electrons travel through external circuit to produce electricity. In this process the final product obtained is water because it is difficult to separate hydrogen and oxygen [1, 15, 52, 64]. In this method, electron and hole pairs are generated through redox reaction [101]. Hydrogen can only be produced in the absence of oxygen which can be achieved in PEC cell. Photocatalysis occurs due to the absorption of light where the excitation takes place due to which the electron and hole pair are generated i.e. the electron form valence band travel towards the conduction band this results in the separation of electron and hole [102]. But the major drawback in this process is the recombination of electron and hole pairs and hence, it effects the hydrogen production. Particularly the water splitting is studied when the sacrificial reagents or electrolytes. Hence depositing the TiO2 with nanoparticles, doping with metals or non-metals. The production of hydrogen can also be increased by the use of electron donor as a sacrificial agent which reacts with the photo generated holes or photo generated oxygen resulting suppressed recombination of electrons and holes [7].

2.2 Microbial fuel cell (MFC)

The MFC as the name suggests, in the MFC microbes are used as a fuel. MFC can be single or double compartment. As organic waste contains microbes which can potentially be used as fuel. Microbial fuel cell or bio-electrochemical cell produces electricity and hydrogen from microbes present in the water [4, 5, 10]. The recent study suggests that combining microbial fuel cell with photoelectrical cell improves the production of hydrogen [5]. Microbes enable faster excitation rate for electrons from valence band (VB) into semiconductors conduction band (CB). Like other fuel cell MFC also consist of anode and cathode it is two compartment cell separated by the membrane which can be salt bridge for the transfer of ions. MFC uses microbes which donate electrons which further travel to external circuit to cathode [23]. The main advantage of MFC is that the bacteria present in the organic wastes works as an electrolyte to enhance the reaction to generate electricity and hydrogen. The fig 2.1 describes the working of double chamber MFC, where organic substance is used, and the basic approach for this processes is that the microorganisms uses protons (H+) to sink with electron(e-) for hydrogen production. The basic reaction is as follows-

$$2H^+ + 2e^- \longrightarrow H_2$$

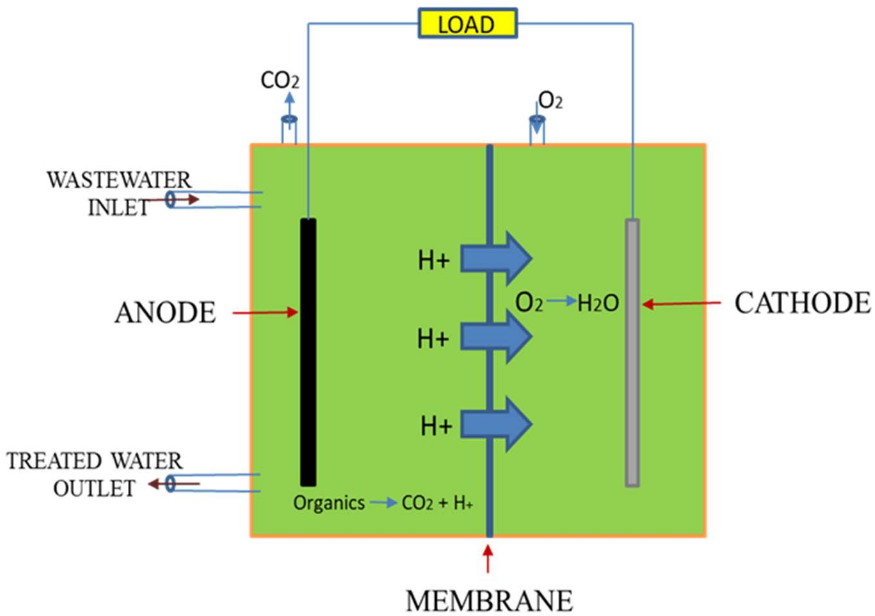

Fig 2.1

The primary application of MFC technology is to generate electricity. Generation of electricity depends upon various factors such as design of MFC, electrode material, membrane and operating conditions. Internal resistance of an MFC should be as low as possible to get optimum results. Microbial Fuel cell uses bacteria to oxidize the organic materials to produce hydrogen and electricity, but it has slow electron transfer and hence less power generation whereas, Photo fuel cell has more and better electron transfer and hence more power generation [82]. Carbon nanotubes can also be employed as anode material for MFC which can increase the current density of MFC [48]. Biofilm as an substrate can be used in MFC [50] in anodic chamber and also it is necessary to maintain the ph value for effective oxidation [49, 124].The intensity of the light affects in the power generation, when the light intensity ws in the range of 3500-7000 lux the power generation was increased upto544 mv, whereas power decreases when it was increased to 10,000 lux [19]. When microalgae was used as fuel and Pt as Photocatalyst it was found the maximum power density from Polarization and power density curve , was obtained 0.50 microalgal biomass and the illumination greatly affected the electric performance [16] .Another type of anode such as Bio-anode which can be also be used in MFC as described elsewhere [81], where they have used bio-anode and Pt cathode with different organic waste such as food waste and waste from dairy products, etc .In which the membrane used was cation/anion exchange membrane and bacteria as electrolyte and photocatalyst [81] and output obtained from food waste was highest compared to other fuels used [81]. Photocathode can also be used in MFC to increase the electricity. As TiO2 is an n-type semiconductor which behaves as conductor when a certain light intensity level is crossed [92]. It is also seen that the power increased to 12.03W/m3 when coated on graphite [93]. Various materials which can be used as photocathode such as copper indium sulphide (CuInS2), lithium-tantalat, cuprous oxide (Cu2O), etc [94]. When lihium-tantalat was irradiated with 500W UV/Vis lamp it produced (63 mW/m3) of output power [97]. Photocathode can also be employed for hydrogen production through microbial electrolysis cell (MEC) [92]. The hydrogen evolution reaction in photocathode requires a semiconductor with narrow band gap such TiO2 nanorods, they have been used as photocatalyst which is deposited on FTO coated glass. The hydrogen gas obtained was about 2.2 μL h−1 cm−2 under irradiation of 300W Xenon lamp [96]. A preferable replacement for TiO2 is Cuprous oxide (Cu2O) which has a narrower band gap than TiO2. It can be used in the form of nanowires which can be deposited on copper foils [98]. It has experimentally proved that Cu2O is more efficient than than TiO2 in the case of photocathode MECs [99]. But considering its toxicity for most of the microbes, which is higher than TiO2 it can be coupled with various other materials such as Cu2O/NiOx. A film of NiOx was coated on the surface and under irradiation produced 5.09 μLh−1 cm−2 of hydrogen which is comparatively higher than TiO2 [100]. Table 1 gives information about the performance of bio-electricity generation using various substrates.

Table 1

Types of MFC	Substrate	Power density	Ref.
Single Chamber	Glucose	68 mW/m^2	Logan(2004)
	Ethanol	820 mW/m^2	Logan and Regan(2006)
	Domestic Waste water	114 mW/m^2	Jiang et al (2014)
Dual Chamber	Glucose	855 mW/m^2	Chaudhuri and Lovely (2003)
	Waste water	2485 mW/m^2	Amend and Shock (2001)

2.3 Photoelectrochemical (PEC) production of hydrogen

The PEC cell comprises of single compartment or two compartment/dual chamber [33] consisting of a photoanode and a cathode [1, 61, 74]. Photoanode consist of photocatalyst typically a n-type semiconductor. Under irradiation photoanode absorbs photons and produces electron-hole pairs. For efficient working of the cell forward bias is necessary .Two different electrolytes were used to produce the bias [34, 51, 53]. Electrons are directed towards cathode through external circuit and holes oxidise the target substance liberating hydrogen ions [75]. Since oxidation site and reduction site are separated, H2 and O2 can also be easily separated [107]. Hydrogen is produced when oxygen is not present but when it exist the following reaction takes place, where output is water

$2H^+ + 1/2O_2 + 2e^- \longrightarrow H_2O.$

The basic configuration of Photoelectrochemical cell can be understood from the fig.2.2 where cathode and anode are connected by an external circuit.

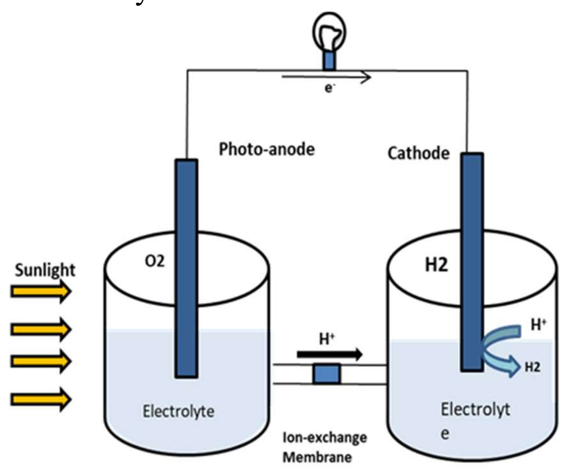

Fig. 2.2

Photo Fuel Cell (PFC) which is nothing but Photoelectrochemical (PEC) cell uses light energy to produce electricity [63, 74]. Photoanode can be made of different electrodes doped with various materials such as FluorineTin Oxide (FTO) or Indium Tin Oxide (ITO) which is reported by many researchers [9, 34,53]. Photoanode carries phototcatalyst which absorbs photons and generate electron-hole pairs. This holes oxidized the organic substances, thus purification of waste water occurs, and the positive ion from anode chamber travels through the membrane in the cathode chamber , containing electrolyte . Thus, the positive ion and the electron combine to form hydrogen i.e. hydrogen is generated [34, 106]. Typically TiO2 is used as photocatalyst, in 1972 when Fujishima and his co-author first used Ultra Violet (UV) light to photocatalytically split water by employing a TiO2 photoelectrode in [18].Under irradiation the photogenerated electrons travels from anode to cathode through external circuit and holes diffuse through electrolyte and passes through ion exchange membrane to cathode. Various membranes can be used such as Proton Exchange Membrane (PEM), solid oxide membrane, etc. Nafion is widely used as a proton exchange membrane because of its excellent thermal and mechanical property. In order to enhance the electromotive force drives electrons from anode to cathode, a bias is needed. Bias can be applied externally through DC or internally by using two different electrolytes [34, 53]. Electrons arriving from anode reduce into hydrogen ions to produce molecular hydrogen in cathode. Hydrogen gas is monitored by Gas Chromatography (GC) and can be further used for numerous applications. The efficient interaction between catalyst, light and reactants are essential for efficient hydrogen production [103, 104]. Thus, using solar energy, not only the wastewater can be purified but also the electricity can be generated simultaneously, with hydrogen generation [27, 108, 109]. Another material such as iron (Fe) can doped on titania for improved performance. Under light irradiation holes and electrons are generated on Fe dope titania. Fe2+ and Fe4+ is formed when Fe3+ traps the electron and holes respectively. These holes and electrons can return to form stable Fe^{3+}ions. Hydrogen is formed when electrons reacts with water or H^+ and the holes react with organic pollutants like CH_3OH to form CO_2 and water. Thus, the hydrogen production and degradation of organic compounds is enhanced [11]. The PFC mainly UV rays are absorbed from sun rays, but for visible light to absorb doping is done [21, 29, 52, 77]. Photo fuel cell has a vast range of benefits compared to Microbial fuel cell like:

1. PFC directly uses light as an energy source which enables fast and direct production of photo generated electrons which can be transferred directly to the cathode.
2. PFC can degrade the organic pollutants more effectively than microbial fuel cell.
3. Photo fuel cell can use toxic organic compounds as a substrate which cannot be digested by the bacteria [6].

3. Materials used for making PFC

3.1 Photoanode

Photo anode is a anode, as name suggests "photo" it means that it uses sun rays to operate the cell. It can be made up of various photocatalyst such as Platinum(Pt), Titanium(TiO_2), Cadmiumsulphide (CdS), Graphite (Gr), Carbon Cloth etc. deposited on the electrodes. In most of the cases Titanium(TiO_2) is used because it is stable in nature, non-toxic and easy availability in the market. Titania in the form of films are deposited on the transparent electrode. The only disadvantage of TiO_2 is it only absorbs UV radiation and only 3-5 % (below 400nm) which falls on the surface of Earth. Visible light absorption can be possible by combing with Cds or by doping of metal or non-metals. The deposition of films can be done with a simple chemical process such as sol-gel process. Another photocatalyst g-C_3N_4 can be used which can be coupled with TiO_2 to improve the performance. The photoelectrons transfer to the conduction band of TiO_2 and the photo generated holes transfer to the valence band of g-C_3N_4 thus accomplishing the separation of charge carriers. The composite photoanode of g-C_3N_4/TiO_2 showed a very good performance which is 1.4 times greater than the bare TiO_2[13]. The choice of photoanode depends on various factors such as atmospheric conditions, type of fuel, etc.

3.2 Electrodes for photoanode

It can be a transparent electrode made up of Fluorine-doped tin oxide (FTO) or Indium Tin Oxide (ITO). These two are the favourable choices for the choice of electrode because it is commercially available and have been used by many researchers in their studies [15, 24, 28] and got optimum results with it [35]. These are used as substrate for the photoanode and mainly used in touch-screen displays, thin film photovoltaic, etc. but it can be also used in PEC application. Many researchers have coated TiO_2 on a transparent conductive electrode (TCO) which is employed as photoanode in the cell.

Some cases photocatalyst such as carbon cloth is deposited on conductive electrode which is inspired from the fuel cells. Table 2 gives information about the electrode and the radiation absorption.

Table 2

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Transparent conductive Electrode (TCO)	Photocatalyst	Radiation	Reference
Indium Tin Oxide (ITO)	Platinum	UV rays	[117]
	Titanium dioxide	Only UV rays	[34]
	Cadmium sulphide	Visible light	[34]
Fluorine-doped tin oxide (FTO)	Titanium dioxide	UV rays only	[34]
	Platinum	UV rays	[117]
	Cadmium sulphide	Visible light	[34]

3.3 Photocatalyst

The term Photocatalysis can be defined as the activation of energy level due radiation , leading to excitation of electrons in an energy band [53, 72]. During initial condition the valance band (VB) is completely filled with the electrons and the conduction band (CB) with relatively high energy is empty. During the process of photocatalyst the energy is absorbed from semiconductor, the energy absorbed is higher or equal to band energy gap then the photo-generated electrons will travel from valence band to conduction band leaving holes in valance band [54, 114]. Fig 3.3 shows the basic principle of photocatalyst.

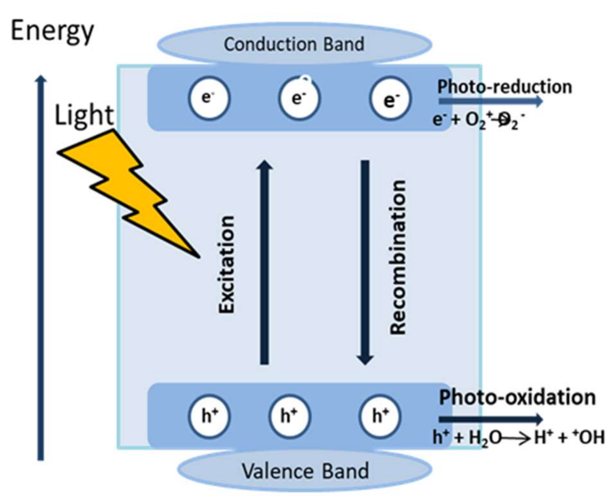

Fig. 3.3

In last few years it was found that the metal oxide such as TiO2 , WO3,ZnO, Fe2O3 has been widely used due to their advantages such as reserve , eco-friendliness, and stable nature[53,114]. High band gap limits the optimum absorption of TiO2 in UV domian. Gadolinium (Gd) doping is an effectual way as it has half-filled electronic configuration and high absorption sufficiency. Also, Gd2O3is decorated on the TiO2 surface to enhance the charge separation. Thus Gd+3 doped TiO2

NRA decorated with Gd2O3 microsphere is made by hydrothermal treatment [12].Another metal oxide ZnSO3 is working excellent due to its properties such as stable ,wide band gap, high electron mobility (>80%)[53]. Photocurrent density of about 1.1 mA/cm2 which is five times greater than that of pure Cds nanorod array photoanode when compared with 3D Cds NRA [44,55]. The Table3 given below shows the properties of photoanode.

Table-3

Photoanode	Properties
$ZnSO_3$	High electron mobility, wide ban gap
Indium Tin Oxide / Fluorine doped oxide	Stable , Commercially available
TiO_2 , Wo_3 ,ZnO , Fe_2O_3	Stable , Eco-friendly
3D CdS@Ni(OH)2 nanorod array	In comparison to the Cds NRa its has better performance in terms of water splitting and photo current.

TiO2 has gained much attention since Fujishima and Honda first employed semiconductor for photocatalytic activity[18]. It is also vastly used for its advantages such as stability and non-toxicity. Titanium can be classified into three main forms: a) Anatase, b) Rutile and c) Brookite [53]. Among these three forms rutile having band gap of 3.03eV is most stable but anatase TiO2 is preferred over them because of its better photocatalytic activity hence increasing hydrogen production. Anatase TiO2 has a band gap of 3.2eV [22] which is less as compared to ZnO(3.35eV) and SnO2(3.6eV) [53] and since TiO2 absorbs only UV light which is only about 3-5% of solar spectrum it is doped with materials to absorb visible light [53]. Hence to absorb visible light photocatalyst must have narrow band gap. Several methods to increase the performance of photocatalytic activity such as metal doping, non-metal doping, etc. Another photocatalyst ZnO can be employed as photoanode in the absence of TiO2 which has similar bandgap along with the similar configuration for Valence Band and Covalent Band levels to that of TiO2 [52]. Also it has been proved that charge carrier separation efficiency was when TiO2 coupled with ZnO [32]. Basically the performance of photocatalyst depends upon the factors such as method of composing, nanoparticle size, crystallinity, etc [52]. ZnO is more active photocatalyst as it gives the current doubling effect. It is observed that the nanostructure of ZnO is easy to construct and conserve than those of TiO2. ZnO can be synthesized in various forms such as nanoneedles, nanorods , nanofibers, nanowires etc [30]. Current doubling is the property of ZnO which doubles the current in presence of HCOONa, chemical reaction takes place in which they react with HCOO- ions and produce radicals species.

HCOO- + h+ HCOO

The radical is unstable and so it is decomposed by liberating electron and hydrogen ion.

HCOO. CO2 + H+ + e-

But due to the current doubling effect the semiconductor undergoes the photo corrosion so it is disadvantage of using ZnO [30]. The current doubling effect under ethanol is better adsorbed on n-TiO2 than compared with glycerol and xylithol have been proved by the Evangelos Kalamaras and Panagiotis Lianos in their research paper [56]. Comparison of various other catalyst combined with TiO2 is shown in Table-4.

Table-4

Photocatalyst		Reactor/Parameter	Hydrogen Production	Reference
Metal modified	Au/TiO_2	300W Xeon light source	3550 μmol $g^{-1}h^{-1}$	[35]
	Fe/TiO_2	Pyrex glass 300W Xeon acr light source	174.3 μmol $g^{-1}h^{-1}$	[36]
	Ni	Pyrex reactor	26,000 μmol $g^{-1}h^{-1}$	[37]
	Pd/TiO_2	Pyrex glass 400W Xeon lamp –UV light	38 mL $g^{-1}h^{-1}$	[38]
	Pt/TiO_2	Pyrex reactor 400W mercury lamp(λ=325nm)	1023.71 μmol $g^{-1}h^{-1}$	[39]
Semiconductor coupled with TiO2	TiO2/g-C_3N_4	Pyrex reactor 300W Xeon acr light source	2160 μmol h^{-1} g^{-1}	[40]
	Cu2O	Quartz reactor 300W Xeon light source , λ > 400nm	2142 μmol m^2 h^{-1}	[41]
	g-C_3N_4/TiO_2	300 W Xeon light source, λ > 420nm	513 μmol $g^{-1}h^{-1}$	[42]
	TiO2/CuO	Pyrex reactor 500W Xeon light source	8230 μmol h^{-1} g^{-1}	[43]
	CdS/TiO_2	Pyrex reactor 300W Xeon light source , λ > 400nm	128300 μmol $g^{-1}h^{-1}$	[44]

3.4 Membrane

Membrane is the selective barrier, which allows some things to pass through, but stops another [59, 76, 112, 125]. There is an great importance of membrane in photofuel cell, membrane are selected based on its properties such as particle retentivity, capillary flow rate, extent, surface properties, porosity [58]. Membrane is added in the photofuel cell it becomes two compartments otherwise it cell acts as one compartment. There are different types of membrane such as proton exchange, Glassfiber, Polyester, Nitrocellulose, PVDF cellulose, etc [58, 76].In all the above membrane the most widely used membrane is Nafionmembrane due excellent thermal and mechanical stability [57]. The Nafion membrane polymer can be used in different shapes such as tubing , film, etc. [76] The performance of Nafion can be increased by undergoing different process electro spinning, blending, etc [58]. Above can improve mechanical properties, reduction of methanol cross-over in direct methanol fuel, improving Nafion performance with synergetic effect [57, 58] . It is found that at high temperature the membrane undergoes corrosion along with losses it durability [57] so the HT-polymer electrolyte membrane is used which is chemically stable, durable, high temperature [76]. Table 4 given below shows properties and advantages of membrane.The membrane can be UV responsive Photocatalytic membrane: The use of UV responsive PFs membrane is very effective in removal of organic pollutants and is excellent germicide [90, 91]. The table-5 given shows the membrane and its fabrication method. Table-6 shows membrane and its advantages.

Table-5

Coating	Membrane type	Fabrication method	Reference
TiO2 coated membrane	PVDF	Dip Coating	[79]
	Al2O3	Atmospheric plasama spray	[84]
TiO2 blended membrane	PDVF	Phase separation	[80]
	PES	Phase inversion	[85]
ZnO coated membrane	AL2O3	Dip coating	[86]
	Stainless steel mesh	Spray coating	[87]
ZnO blended membrane	PES	Phase inversion	[88]
	PSF	Wet-phase inversion	[89]

Table-6

Membrane	Function	Use	Advantages	Reference

Nafion	Ion exchange	Transfers ion and molecules	Chemically stable, high conductivity, durable.	[18, 53, 57, 58]
Glassfiber	Sample	Hydrophilic membrane, Low pressure drop.	Implemented in sugar, salt, etc ,.	[65]
Polyster	Conjugation	Prevents corrosion	High mechanical strength along with absorption capacity.	[66]
Nitrocellulose	Blocking	Mainly used to move proteins and nucleic molecules.	Works with the water based solutions.	[67]
PVDF	Blocking	Strong hold on to move proteins.	Increases the detection sensitivity.	[68]

3.4 Electrolyte

Electrolyte is a substance that, when added in water produces electrically conducting solution i.e.it gives mobility of ions. There are various electrolyte used such as NaOH, KOH, NA2SO4, H2SO4, etc. Electrolyte is added in water to make solution conducting which enhances electricity production. It gives hydroxyl ion , which are good hole scavenger which stops the recombination of holes and electrons. Electrolyte can be acidic or basic which can already present in the wastewater or can be added externally to improve the performance. Generally in a two compartment cell, a basic electrolyte in anode chamber and an acidic (H2SO4) electrolyte in cathode compartment is added in order to get the chemical bias. Adding an acidic electrolyte in the cathode chamber also increases the hydrogen ion mobility. Same electrolytes can also be used in both the compartments as used by Josef Krysa and SistoMalato [51]. They used the same basic (1.0 Molar NaOH) in both of the compartments along with it, it was tested under UVA radiation which can photocatalytic degrade organic substance to produce electricity without any external bias [51]. Some authors used Na2SO4 as an electrolyte in Bio- photofuel cells in which the organic pollutants were used as photodegradable substance. Frequent adding of electrolyte also helps in maintaining the pH which enhances the performance of the cell. Maintaining the pH contributes to the generation of electricity. As the value of pH decreases there is an increase in generation of electricity and proper degradation of organic compounds can be obtained [21].

3.5 Cathode

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Cathodes are made up of different materials such as Platinum (Pt), Palladium (Pd), Graphite (Gr), Carbon cloth, etc. It is essential to choose the cathode material wisely because on cathode side reduction process takes place. Electrons coming from anode reduce at cathode which completes the circuit to produce molecular hydrogen. Many researchers are using Platinum wire or Platinum foil as a cathode electrode [31, 52]. The reason of using Pt is that it is noble metal and has high conductivity. Although graphite is cheaper than platinum but still platinum is used because of its noncorrosive nature. Deposition of catalyst on the electrode is done, preferable platinised platinum is used for the choice of cathode. The distance between electrodes effects the generation of electricity, if the distance between electrodes is less than the internal resistance decreases, so generation of electricity is more [14]. It also affects the fill factor. If the distance between electrode increases then ff deceases and vice vesra [14]. Thus, the distance between electrode should be minimum [72]. The dual photoelectrode PFC has been developed to consume organic substrate, to develop electricity .i.e. the photoanode made up of Ti and photocathode made of Cu is used, the electrons from photoanode and the holes from photocathode combines to produce hydrogen and the electrons driven out form anode chamber to produce electricity [111]. Purging of various gases such as N2, O2,Ar, etc. is done in cathode chamber to effectively remove oxygen present in it. Purging of O2 results in improved rate of electron consumption as described elsewhere [52] whereas when N2 was purged in the same experiment the electron consumption rate was restricted due to low light quantum yield [52]. The charge transfer resistance depends on how efficiently the cathode works. This in turn reflects the fill factor(ff). Fill factor is directly related to performance of cell, can be calculated by the formula given below ff = Pmax / JSCVoc [53]. It is the ratio of max power density obtained by PFC to the product of short circuit current(ISC) and open circuit voltage (VOC). The valve of ff should be as high as possible for better performance [53]. Table-7gives different materials of cathode and its advantages.

Table-7

Cathode	Advantage/ Disadvantage	Use
Platinum	Stable Non-corrosive	Most widely used
Graphite	Excellent electrical conductivity Less stable compared to platinum	Less used compared to Platinum
Palladium	Expensive	Not used more
Carbon cloth	Stable High thermal and electrical conductivity	Used widely

4. Fuels

Various types organic fuels can be used in photo fuel cell [52]. The organic fuel such as sewage water, textile water, industrial water, food waste water, etc, [1, 18, 70] can be used in the photo fuel cell [110]. Sometimes there is no need to add extra electrolyte because in wastewater as electrolyte may already present in it for Ex. in textile water [52]. The main reason for using these fuels is there is large problem of disposal of waste water. Using waste water as a fuel has an advantage i.e. it is reused, water is purified, hydrogen and electricity generation. As environmental problems are growing day by day, use of waste water is encouraged.Hydrogen can be produced with the various feed stock [62, 69, 105]. The waste dye from industries such as Rodamine (RB), methylene blue(MB), and basic orange (BO) can also be used as fuel , and it as found that the Rodamine gives the highest yield of electricity compared to the other two [21]. The organic fuel such as alcohols, methanol, ethanol, glycerol, ammonia, etc , are also used because they increase the rate of reaction . The authors Maria Antoniadou and Panagiotis Lianos produced electricity as cathode was run under aerobic conditions and found that, addition of organic reagents in anode compartment increased the overall efficiency of the cell. The overall efficiency of 10.5% was observed when glycerol (20% v) was used which was comparatively high compared to other fuels used [34]. Also the hydrogen production using organic reactants is decreasing in the order of glycerol>ethylene>glycol>methanol>ethanol [54]. The interaction of different fuels such as Methanol, Ethanol, Glycerol with anode and cathode electrode is different depending upon neutral and acidic medium in it [115, 116]. Formic acids showed the highest hydrogen generation as the formic acid has high redox potential than methanol and glycerol hence it oxidize the CO_2 very easily and hence providing electrons for the photocatalytic process [8]. Biomass has been a sustainable way of hydrogen production in recent years. Bio hydrogen can be produced using fermentative conversion of biomass which has been an important method in past 10 years. It is an efficient transportation fuel and a low source of carbon for production of hydrogen and electricity. Bio conversion is done by the help of Microbes which takes place either in absence or presence of sunlight which is known as dark fermentation or photo fermentation respectively. The integrating approach of dark and photo fermentation hydrogen production has maximum production of hydrogen. Also the addition of nanoparticles to fermentative medium has increased the hydrogen production upto 6 times compared to non additive fermentation system [3].

5. Types of reactors

The reactor mainly depends upon its design. The material of the reactor also contributes to performance of the cell. Depending upon the light source the glass material of the reactor is employed. Different type's glass material such as Pyrex, Quartz, and Borosilicate are used and among these, Pyrex glass is preferable used as it more efficient to transfer the light, means its transparency is more as compared to others.

5.1 Optical fiber reactor

In optical fiber reactor, difference in refractive index the light splits into two beams. Light reflects and transmits, while the rest which penetrates excites the photoanode and generates electron and hole pairs. The benefit of using optical fiber is that, it has high uniform distribution and so it leads to high excitation rate and is economic [53]. But the drawback of using it is it has less surface area for the reaction [54]. More development are going on for improvement of design of optical fiber [54].

5.2 Monolith reactor

In monolith reactor there are small chambers , the advantages of using this type of reactor is that it has low pressure drop , better porosity, good mechanical strength. In recent research it has been proved that Monolith reactor are better than the commercial reactors and it can absorb both UV and visible light Inside the reactor there can be coating of various photo catalyst such as TiO2 , Au, etc [54]. In another paper Ming Xia and authors have used the same monolithic design but was used under membrane less conditions by process of sol-gel. Photo-catalytic fuel cell (PFC), which is an integration of the photo-catalysis and fuel cell technologies, a membrane-less monolithic micro PFC with an airbreathing cathode was developed in the study. The photo-anode and cathode were arranged with a shoulder-to-shoulder design in this study, forming two planer electrodes. To demonstrate micro PFCs, methanol was used as a model fuel, it is mainly consist of a cover, a photoanode, a cathode and a baseplate. The cover and baseplate was made of polydimethylsiloxane (PDMS). In this cover, there are two microchambers for photoanode and cathode, each microchamber had one inlet and one outlet. The photoanode was fabricated by coating TiO2 on FTO glass and cathode was made up of pt coated carbon paper. In the middle, the conducting layer was removed by the etching method to separate the photoanode and cathode and avoid the short circuit. A rectangular shape hole was drilled on the cathode side of the microchamber for breathing oxygen from air [28, 30].

5.3 Slurry reactor

The slurry reactor can absorb both UV and visible light[54].This is special reactor where it can have catalyst in form of powder .Annular reactor is slurry reactor mostly used. Design of slurry reactor is very simple but separation of catalyst is difficult[53]. Table 8 gives information about reactors and its advantages.

Table-8

Reactor	Advantage	Limitations
Optical Fiber	Large surface area High uniform distribution	Surface area for reaction is less
Monolith	Low pressure drop Good mechanical strength.	Efficiency of light is less
Slurry	Continuous flow pattern can be obtained	Due to continuous stirring it becomes costly

.

6. Conclusion

This review gives brief idea about the various hydrogen generation techniques from waste water, such as MFC, PFC, etc. The basic working principle of the process has not changed much in the recent years. From various researches done on this topic it can be said that, PFC consumes organic and inorganic substances and produces electricity and hydrogen. It is found that various photo-

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anodes can be used but TiO2exhibits best photocatalytic activity and hence it is widely used. Visible light absorption can be done by deposition of materials on photoanode. Depending upon the type of photo-anode and the photocatalyst the performance of PFC is affected. Same can be said for the choice of cathode, mainly it is found that Pt is used more because it is non-corrosive in nature and produces best results .The various design of reactors can be used depending upon conditions and fuel, still the research on the design of reactors may be a subject of interest in the future. Different types of wastewater can be used for the production of Electricity and Hydrogen by degrading organic substances with wastewater cleaning as by-product. Same can be said in the case of MFC, the choice of photocatalyst, photoanode affects the performance of cell. Thus, the review presented in this manuscript, focuses on Photo Fuel Cell which can be effectively used to get triple benefits such as generation of hydrogen and electricity along with purification of wastewater.

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