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Hydrogen production from industrial wastes by photo catalysis

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Abstract

This review focuses on our research findings about efficiency of different nano materials synthesized by us for photocatalytic hydrogen production from industrial wastes. Lab-scale photocatalytic reactors were fabricated for hydrogen production from liquid phase alkaline waste streams and gaseous phase hydrogen sulfide. The effects of operating parameters namely pH, flow rate, light intensity, liquid depth, sulfide and sulphite concentration were investigated for 7 photocatalysts viz., CuGa₂-xFe_xO₄/RuO₂, Fe₂O₃-CdS/ZnS, Pd-Cr₂O₃/CdS, Ce-TiO₂, CdS-ZnS/TiO₂, CdS/ZnS, Ti-Cr-MCM-48. Among the photocatalysts used, CdS/ZnS nanosized photocatalysts have a much greater surface area and thus give a better hydrogen yield.

Keywords: Solar Photocatalysis; Liquid Phase; Gas Phase Photocatalysts; Hydrogen Production

1. Introduction

Hydrogen sulfide (H₂S) is a toxic gas harmful to human beings and the environment. It was generated due to various industrial activities and sewage treatment plants (STPs) (Supriya and Subrahmanyam 1997 and Linkous et al 2004). If the pH is less than 6, then H₂S is mainly in the gaseous form. When pH increases to 6 – 8, part of H₂S converts into hydrosulfide ion (HS⁻). At pH 6 – 8, there is a mixture of H₂S and HS⁻. For a pH of 8 – 12, the main ion is HS⁻ but there is still some H₂S. The sulfide ions are present in appreciable concentrations above pH 10.

H₂S is abundant in natural gas and petroleum. Natural sources include crude oil, natural gas, salt marshes, sulfur springs, and swamps. Sewers with low velocities encourage the growth of anaerobic bacteria in a slime layer coating the sewer. These bacteria reduce sulfur compounds such as sulfate, thereby producing sulfides. These compounds occur naturally in domestic wastewater but also can be concentrated in industrial waste streams (Priya, 2011 and Kalairasi, 2012). With the increasing consumption of crude oil, the amount of H₂S released from petroleum refining has gradually increased. H₂S is also contained in most natural gas wells. Caustic scrubbing is commonly applied for the removal of H₂S from biogas in STPs and acid gases in petroleum refineries. During this process, alkaline sulfide wastewater is generated. Sulfide wastewater is also generated from leather and pulp and paper industries. Of all the industries given, Refineries and Petrochemical industries were been regarded as a most important producer of sulfide waste stream in high concentration as well as in quantity (Priya and Kanmani, 2011 and Balamurugan and Kanmani, 2013).

The erratic nature and toxicity of sulfide depends upon the pH, refining processes, percentage of sulfur in crude oil. The impacts of the sulfide were been categorized as Aesthetic and Health, Mechanical and Environmental. Higher concentration effects range from choking to coma or death. High content of sulfur compounds in lubricating oils seems to lower resistance to oxidation and increases the deposition of solids as sludge in engines. Under alkaline conditions,

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sulfide remain largely as a solution but in lower pH, the higher rate of H₂S evolution will be there. Sulfide is less toxic than hydrogen sulfide and it have a high oxygen demand of 2mol O₂/L mol S²⁻ (Baratvaj and Kanmani, 2012) Hydrogen sulfide is a highly toxic compound to aquatic animal life in very low concentrations and has been the cause of mass fish mortality in aquaculture systems. The threshold limits value for fresh or salt water fish 0.5 ppm (Atlas and Byukgungor, 2008). In air emissions hydrogen sulfide should not exceed 10 mg/Nm³ and in the waste water discharge the sulfide limit is 1 mg/L (Kalaiyarasi and Kanmani, 2012).

Present existing pollution control methods are the Claus process and Wet absorption methods. These methods are used to treat H₂S in gaseous form. Chemical and biological removal methods are available for treating of sulfide wastewater. Other methods are thermochemical, electrochemical and photochemical methods. Current treatment technologies have some drawbacks. In absorption of H₂S into caustic, or oxidizing it in Cl₂, or potassium permanganate processes are costly as they require constant replacement of consumed catalyst and there is also the problem of disposal. In claus process, the H₂ component of H₂S is oxidized to H₂O and thus the H₂ is lost Additional tail gas treatment is necessary because the total conversion of the Claus process is not sufficiently high for hydrogen production (Priya and Kanmani, 2011).

In conventional biological treatment processes, microorganisms are used to oxidize H₂S dissolved in liquid under aerobic conditions. Chemical removal methods are filtration of sulfide wastewater after liming and recycling and oxidation by oxidizers and air oxygen. In thermochemical methods, H₂ is produced directly. But it suffers from unfavorable thermodynamic equilibrium and a poor yield. The electrochemical and plasmochemical methods are not suitable for large-scale operation as it requires high input cost for electricity and electrodes. Of all these methods, solar photocatalysis has received attention in view of solar energy utilization for the promotion of useful chemical reactions (Balamurugan and Kanmani, 2013 and Kalairasi and Kanmani, 2012).

The past thirty decades witnessed an intense research on economically viable routes of solar energy conversion using semiconductor photocatalysts for hydrogen from various sources such as H₂O and H₂S (Gurunathan et al. 2008 and Preethi and Kanmani, 2013) Hydrogen sulfide under visible light to generate hydrogen is an attractive route of solar energy conversion, because hydrogen is 100% environment clean chemical fuel in its cycles of generation and utilization. On the other hand, there is scope for hydrogen sulfide as the raw source of hydrogen, because hydrogen sulfide splitting requires a very less energy ($\Delta G^\circ = 33.44$ KJ/mol) compared to that or water splitting ($\Delta G^\circ = 237.17$ KJ/mol). Also, hydrogen sulfide is available in millions tons of quantities in petroleum refineries (Baratvaj and Kanmani, 2012 and Preethi and Kanmani, 2013).

Among all of the visible light sensitive photocatalytic materials developed so far, CdS is one of the most active photocatalyst owing to its suitable band gap. However, CdS is prone to photocorrosion in photocatalytic reactions. Many attempt to improve CdS activity had been reported, such combining CdS with other semiconductors ,addition of cocatalysts using support materials as well as designing the nanostructures, such as CdS nanowires and nanorods. On the other hand, ZnS had been reported as a good photocatalyst for hydrogen production. However the band gap is too large for visible light response, therefore metal ions such as Ni²⁺, Cu²⁺, Ru²⁺, Pd²⁺ were doped into ZnS. Other approach for band gap engineering is combining ZnS with CdS to form solid solution. It was found that the band gap energy of the solid solutions by changing the composition.

2. Mechanism of Semiconduction Photocatalyst

A photocatalyst absorbs UV and/or visible (Vis) light irradiation from sunlight or an illuminated light source. The electrons in the valence band of the photocatalyst are excited to the conduction band, while the holes are left in the valence band. This, therefore, creates the negative-electron (e⁻) and positive-hole (h⁺) pairs. After photoexcitation, the excited electrons and holes separate and migrate to the surface of photocatalyst. The generated e⁻ reduces H⁺ ions into H₂. Therefore, the band gap energy (eV) of the photocatalyst should be >1.23 eV (< 1000 nm) to achieve water splitting. However, to use visible light, it should be < 3.0 eV (> 400 nm). The processes in the photocatalytic generation of H₂ includes light absorption of the semiconductor photocatalyst, generation of excited charges (electrons and holes), recombination of the excited charges, separation of excited charges, migration of the charges, trap of excited charges and transfer of excited charges to water or other molecules. All of these processes affect the final generation of H₂ from the semiconductor photocatalyst system (Gurunathan et al. 2008). The mechanism of the process is explained in Figure.1 and band gap energies value in Table 1. (Preethi and Kanmani, 2013).

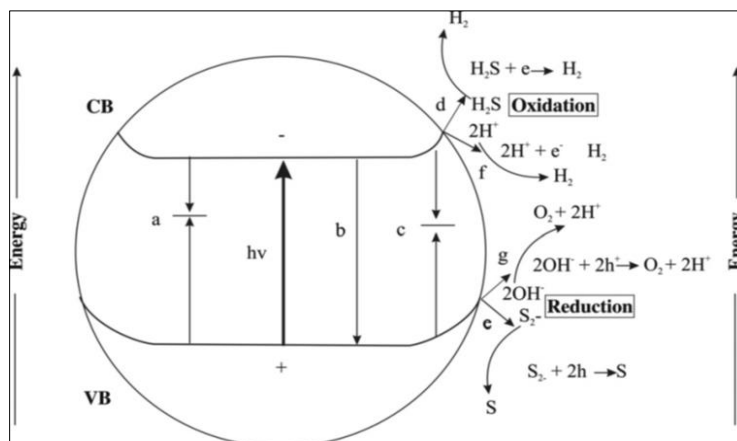


Figure 1 Processes in the photocatalytic generation of H_2 production

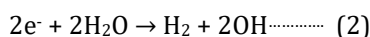
2.1. Mechanism of H_2S photolysis in liquid phase

Hydrogen sulfide is an ideal source for hydrogen production. Hydrogen sulfide is a weak diprotic acid with pKa value of 7.0 and 11.96. At pH 13.5, the two acid dissociation reactions of hydrogen sulfide occur, yielding hydrosulfide HS^- and sulfide S^{2-} ions in equilibrium. On the bandgap excitation, the photocatalyst generates CB electrons (e^-_{cb}) and VB holes (h^+_{vb}). (Priya, 2011)

Light absorption, when a photon is absorbed by photocatalyst in the presence of S^{2-} and SO_3^{2-} , an e^-/h^+ pair is generated as explained in Equation (1).



The photogenerated electrons in the conduction band reduce the water to form H_2 , as explained in Equation (2)



The photogenerated holes in the valence band oxidize SO_3^{2-} and S^{2-} to form SO_4^{2-} and S_2^{2-} directly (Equations 3 and 4)

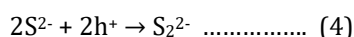
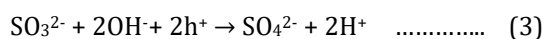


Table 1 Band gap energies for some semiconductor materials

Sl.No.	Photocatalyst	Band gap energy (eV)
1	Si	1.1
2	TiO ₂ (rutile)	3.0
3	WO ₃	2.7
4	ZnS	3.7
5	SnO ₂	3.5
6	CdS	2.4
7	SrTiO ₃	3.4
8	Fe ₂ O ₃	2.2
9	ZnO	3.3
10	TiO ₂ (anatase)	3.2
11	CdSe	1.7
12	Cu ₂ O	2.172
13	Ge	0.744
14	PbS	0.286

3. Review of photocatalytic activity of H₂ production from liquid waste stream

Priya and Kanmani (2011), synthesized a photocatalyst namely CdS-ZnS/TiO₂ by coprecipitation and hydrothermal methods in cylindrical and tubular reactor. The catalyst of 0.5g/l was mixed with 200ml of waste water with an aqueous solution of 0.35 M Na₂SO₃ and 0.25 M Na₂S. The physical characterization of the nanophotocatalysts had been carried out by XRD, TEM, FTIR, DRS UV-Vis, SEM, BET and XPS. It was observed that the synthesized nanoparticles sizes were less than 10 nm and active in UV-visible portion of sunlight. The H₂ generation rate over CdS NPs, ZnS NPs, TiO₂ NTs, CdS-ZnS NCs and CdS-ZnS/TiO₂ NCS was compared. The H₂ generation rate over CdS NPs, ZnS NPs, TiO₂ NTs, CdS-ZnS NCs and CdS-ZnS/TiO₂ NCs were observed to be 419, 157, 209, 838 and 4196 μmol/h, respectively. The highest volume of hydrogen produced after optimization is 4196 μmol/h at 3 sun lamps + 1 UV lamp light intensity, 0.1 M sulfide concentration, 0.2 M sulfite concentration, 11.3 pH, 300 mL photolyte volume, 0.5 g catalyst dosage and 18 mL/hr recycle flow rate. From the results, it was concluded that CdS-ZnS/TiO₂NCs was better than other nanophotocatalysts.

Bhatavaj and Kanmani (2012), synthesized a photocatalyst namely Ce-TiO₂ powder by sol-gel method. This catalyst was used for production of hydrogen from sulfide wastewater. SEM, XRD, UV-DRS, FT-IR were used for characterization of the product. SEM shows that agglomeration of particles was due to cerium. XRD pattern indicates that crystal is tetragonal, body centred cubic lattice in anatase phase with particle size of 34.06 nm. The band gap energy of 1.7 eV and threshold wavelength of 700 nm were found using UV-DRS. Also, the surface adsorption was determined using FTIR. The photocatalytic properties for the production of H₂ from simulated sulfide water were studied using Ce-TiO₂ a tubular photocatalytic reactor. The results show that 0.1 g suspended in 500 ml of simulated wastewater (10000 mg/L) irradiated at 150W visible lamp produced maximum H₂ of 5189 μmol h⁻¹ by converting sulfide (200 mg/L). The highest volume of hydrogen produced after optimization is 5189 μmol/h at 150 W/m² light intensity, 0.25 M sulfide concentration, 0.2 M sulfite concentration, 12 pH, 500 mL photolyte volume, 0.1 g catalyst dosage and 30mL/hr recycle flow rate. The comparison of performance also reveals that Ce-TiO₂ was better than Nano TiO₂ and TiO₂.

Balamurugan and Kanmani (2013), synthesized a photocatalyst namely CdS by coprecipitation method in cylindrical reactor. The catalyst has been characterized using X-ray diffraction and Scanning electron microscope to reveal a colloidal solution of CdS aggregates with particle size 3.7 μm. The feasibility studies were carried out by varying the treatability parameters and it was found that maximum hydrogen production occurs at their respective optimum values. The highest volume of hydrogen produced after optimization is 1910 μmol/h at 220 W/m² light intensity, 0.2 M sulfide concentration, 0.2 M sulfite concentration, 10 pH, 300 mL photolyte volume, 0.5 g catalyst dosage and 30mL/hr recycle flow rate.

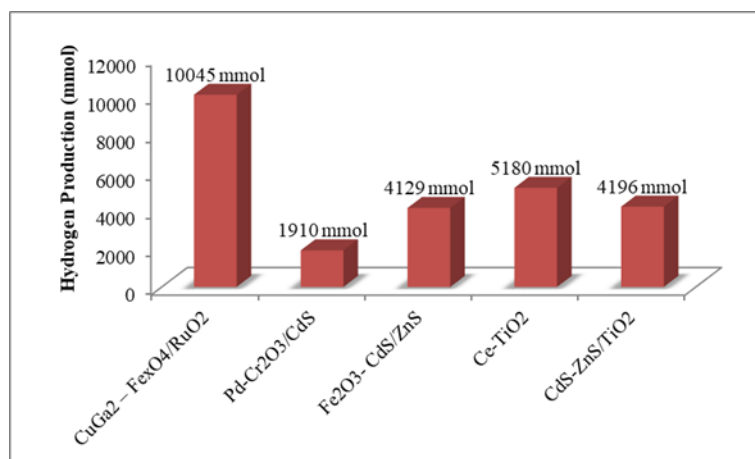


Figure 2 Typical results for nanocomposite material for H₂ production

Preethi and Kanmani (2013), synthesized a photocatalyst namely Fe₂O₃- CdS/ZnS by coprecipitation by using cylindrical reactor. The catalyst of 0.5g/l was mixed with 400ml of distilled water with an aqueous solution of 0.35 M Na₂SO₃ and 0.25 M Na₂S. The light source was 150- W tungsten halogen lamp. The highest volume of hydrogen produced after optimization is 4129 μmol/h at 219 W/m² light intensity, 0.2 M sulfide concentration, 0.2 M sulfite concentration, 11 pH, 0.5 g catalyst dosage and catalyst reuse for one time.

Preethi and Kanmani (2012), synthesized a photocatalyst namely $\text{CuGa}_2 - \text{Fe}_x\text{O}_4/\text{RuO}_2$ by coprecipitation by using cylindrical reactor. The catalyst of 0.2 g was mixed with 400 mL of 0.5M aqueous solution. The light source was 150- W tungsten halogen lamp. The highest volume of hydrogen produced after optimization were 10,045 $\mu\text{mol/h}$ at 219 W/m^2 light intensity, 0.25 M sulfide concentration, 13pH, 0.3 g catalyst dosage and catalyst reuse for one time.

From the results, we observed that maximum hydrogen production in liquid phase achieved in cylindrical photoreactor and the catalyst usage was $\text{CuGa}_2 - \text{Fe}_x\text{O}_4/\text{RuO}_2$ with different operating parameters Viz., 219 W/m^2 light intensity, 0.25 M sulfide concentration, 13pH, 0.3 g catalyst dosage and catalyst reuse for one time. Typical result of photocatalytic hydrogen production listed in the Figure 2 for several photocatalysts reactor.

4. Review of photocatalytic activities of hydrogen production from gas-phase

Sujitha and Kanmani (2013), worked with the highly photoactive Ti-containing Cr-modified MCM-48 photocatalyst was prepared by a facile one-step method at room temperature. A combination of various physicochemical techniques such as X-ray diffraction (XRD), diffuse reflectance UV-vis spectra (DRS) and scanning electron microscopy (SEM) were used to characterize the properties of the synthetic catalysts. The characterization and experimental results indicated that tetrahedral Ti oxide moieties as dominant Ti oxide were loaded into the mesoporous structure and there was a synergistic interaction between the Ti species anchored on the walls and the Cr ions presented in the MCM-48 framework, which was considered to be directly correlated to the photoactivity. The maximum hydrogen production (333.41mL) from hydrogen sulfide was achieved at the catalytic dosage of 2 g under visible light, being the Cr^{6+} species primarily responsible for this photoactivity. Under optimized conditions, it was found that 30 minutes of irradiation gave maximum hydrogen sulphide degradation 83% The maximum hydrogen production was found with 2 g, 722 W/m^2 and 60 min of catalyst dosage, light intensity and irradiation period respectively.

Kalaiyarasi and Kanmani (2012), studied the decomposition of hydrogen sulphide in gas phase using a photocatalytic reactor of 500 ml capacity containing CdS/ZnS coated on vermiculite material. The BET result showed that surface area was 10.5 m^2/g and the diffraction study (X-ray Diffractometer) showed that particle size and structure of the photocatalyst was 26.59 nm and finally morphology result showed that the average diameter of the particles was equal to 37.8 nm. The photocatalytic reactions were carried out by varying the reaction conditions viz., irradiation time, catalyst dosage and light intensity. Under optimized conditions, it was found that 30 minutes of irradiation gave maximum hydrogen sulphide degradation 92 % in gas phase. CdS/ZnS samples prepared by co-precipitation method exhibited highest surface area, lowest crystallite sizes and showed highest activity towards photocatalytic decomposition of hydrogen sulphide.

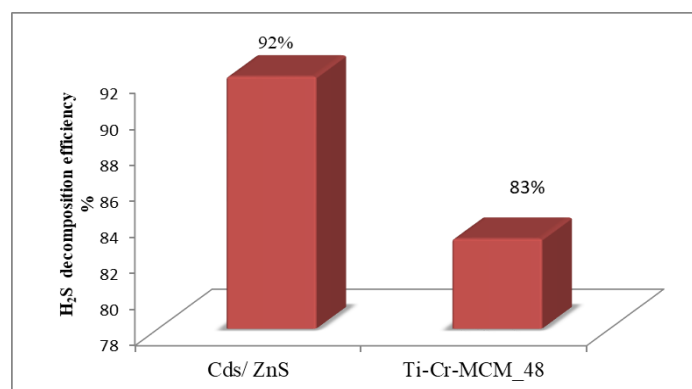


Figure 3 Typical results for nanocomposite material for H_2 production

From the results, we observed that maximum H_2S decomposition in gas- phase was achieved in packed bed tubular reactor and the catalyst usage was CdS/ZnS with different operating parameters viz., 722 W/m^2 light intensity, 2 g catalyst dosage and flow rate 50 ml/min.

5. Conclusion

In our research the various photocatalysts studied, among organic and inorganic sacrificial agents, sulfide ions are found to be the best sacrificial agents as they can act as hole scavengers. Sulfite ion instead of sulfide ion gives very little yield of H_2 , but a mixture of sulfide and sulfite is ideal. Both gas and liquid phase reactor, CdS is highly efficient in H_2

generation in an aqueous medium under visible light. The photoactivity of CdS can be improved by the addition of wide band gap semiconductors such as ZnS. Compared to non doped sample, doped sample is highly active and stable compound hydrogen production under visible light irradiation prepared by coprecipitation method. Among the three gas phase photocatalytic reactors packed bed photocatalytic reactor achieved the maximum hydrogen recovery. Based on the detailed literature review, the rare earth material more active in solar light and enhance hydrogen production.

The current lack of industrial applications of this technology can mainly be attributed to two reasons: the low photocatalytic efficiency due to large size photocatalysts and the resulting lack of agreement on how to quantify this efficiency, in particular for nanosized photocatalysts and reactor configurations. Therefore, for nanosized catalysts, reactor design and cost reductions for large-scale applications have to be given special priority. The other challenge is successful scale-up of laboratory scale photocatalysis to an industrially relevant scale. These two issues have been the object of our research and will also be the focus of our study in the future.

Compliance with ethical standards

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Disclosure of conflict of interest

The author has no conflicts of interest in connection with the research topic, results and research tools with other authors.

References

- [1] Altas, L. and Buyukgungor, H.(2008), ‘Sulfide removal in petroleum refinery wastewater by chemical precipitation’, *Journal Hazardous Material*, Vol. 153, pp. 462-469, 2008.
- [2] Balamurugan, K.R. and Kanmani, S. (2013), ‘The photocatalytic activity of Pd-Cr₂O₃/CdS along with batch process with passive mixing’ M.E thesis, Anna university, CES centre, Chennai.
- [3] Bharatvaj, J. and Kanmani, S. (2012), ‘Hydrogen production from sulphide waste stream waste water using Ce doped TiO₂’, M.E thesis, Anna university, CES centre, Chennai.
- [4] Gurunathan K., Baeg J., Lee S., Subramanian E., Moon S. and Kong K. (2008), ‘Visible light assisted highly efficient hydrogen production from H₂S decomposition by CuGaO₂ and CuGa_{1-x}X_xO₂ delafossite oxides bearing nanostructured co-catalysts’, *Catalyst Community*, Vol. 9, pp. 395-402.
- [5] Linkous, C.A., Huang, C. and Fowler, R. (2004) ‘UV photochemical oxidation of aqueous sodium sulfide to produce hydrogen and sulfur’, *Journal Photochemical Photobiology*, Vol. 168, pp. 153-160.
- [6] Preethi V. and kanmani S. (2013). ‘Photocatalytic hydrogen production’, *materials science semiconductor processing*, Vol. 36, pp.561-575.
- [7] Preethi V. and kanmani S. (2012) ‘Photocatalytic hydrogen production over CuGa₂ - Fe_xO₄/RuO₂ spinel’, *International journal of hydrogen energy*, Vol. 37, pp. 18740-18746.
- [8] Preethi V. and kanmani S. (2013) ‘Photocatalytic hydrogen production using Fe₂O₃ based nanoparticle with Z_nS and CdS’, *International journal of hydrogen energy*, Vol. 39, pp. 1612-1622.
- [9] Priya R. and Kanmani S. (2008), ‘Solar photocatalytic generation of hydrogen from hydrogen sulphide using CdS-based photocatalysts’, *Current Science*, Vol. 94, pp. 102-104.
- [10] Priya R. and Kanmani S. (2009), ‘Batch slurry photocatalytic reactors for the generation of hydrogen from sulfide and sulfite streams under solar irradiation’, *Solar Energy*, Vol. 83, pp. 1802-1805.
- [11] Priya R. and Kanmani S. (2010), ‘Solar photocatalytic generation of hydrogen under ultraviolet-visible light irradiation on (CdS/ZnS)/Ag₂S + (RuO₂/TiO₂) photocatalysts’, *Building Material Science*, Vol. 33, pp. 85-88.
- [12] Sakthivel, S., Neppolian, B., BanumathiArabindo., Palanichamy, N. and Murugesan, V. (2000), ‘TiO₂ catalysed photodegradation of leather dye: Acid green 16’, *Journal Science Industrial Resources*, Vol. 59, pp. 556-562.

- [13] Sherif S.A., Barbir F. and Veziroglu T.N. (2003), 'Principles of hydrogen energy and production, storage and utilization', Journal Science Resource., Vol. 62, pp. 46-63.
- [14] Supriya, V., Tambwekar, D. and Subrahmanyam, M. (1997), 'Photocatalytic generation of hydrogen from hydrogen sulfide an energy bargain', International. Journal of hydrogen energy, Vol. 22, pp. 959-965.
- [15] Kalaiyarasi, D, Kanmani, S,(2012), 'Development of gas phase photocatalytic reactor for decomposition of hydrogen sulphide', M.E thesis, Anna university,CEScentre, Chennai.
- [16] Sujitha M, Kanmani S, (2013), 'Recovery of hydrogen from hydrogen sulfide using gas phase photocatalytic reactor', M.E thesis, Anna university,CEScentre, Chennai.