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Photocatalytic Hydrogen Production from Sulfide Wastewater

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Abstract

A novel Pd/CdS powder synthesized with by co-precipitation method was used for production of hydrogen from sulfide wastewater and water. SEM, XRD, UV-DRS, FT-IR were used for characterization of the product. SEM shows that spherical particles of irregular aggregates with pores. XRD pattern indicates particle size of 3.7 µm. The band gap energy of 2.33 eV and threshold wavelength of 530 nm were found using UV-DRS. The photocatalytic properties for the production of H_2 from simulated sulfide wastewater and water were studied using Pd/CdS a trapezoidal photocatalytic reactor. The results show that 0.2 g suspended in 100 ml of simulated wastewater irradiated at 300W visible lamp produced maximum $H_2$of 2500 µmol h-1.

Keywords: co-precipitation, Hydrogen, Pd/Cd, visible light.

I. INTRODUCTION

Oil refineries generate huge amounts of solid, liquid wastes and waste gas in the refining processes. Sulfide wastewater is also generated from leather and pulp and paper industriesThe presence of sulfide in the wastewater exerts a high biological oxygen demand of 2mol O_2/L mol S^{2-} which remains a threat to living organisms in water (Poulton *et al.*, 2002). Hence, if released to the water bodies without treatment can cause serious environmental effects causing adverse threat to the aquatic life and mass fish mortality (Altas and Buyukgungor, 2008). It causes serious health impacts on human beings and the environment. Considering the impacts, the treatment of sulfide from wastewater is often attempted through various treatment processes like adsorption, coagulation, chemical oxidation, wet air oxidation, membrane technologies, and biological processes to avoid the related environmental concerns but all of them are either expensive or not friendly to environment (El Naas *et al.*, 2009 and Demirci*et al.*, 1997). Furthermore, refineries are also in need of large quantities of hydrogen to purify sulfur rich crude oils (World diesel, 2003). To resolve both the problems by framing a suitable strategy, solar photocatalysis is the best and beneficial treatment process which has a high oxidation potential (estimated to be +2.8V) to mineralize all the organic pollutants and the catalyst itself is non-toxic, cost effective and readily available .

Hence the removal of sulfide ions from wastewater is necessary. However, the conventional process is costly in terms of energy. So it would be advisable to go for a more energy efficient process Hydrogen sulfide has to be converted to an environmentally less dangerous form. Claus process for the removal of H_2S is to burn it to water and sulfide. On the other hand, if H_2S is split into H_2 and S we also get a useful fuel.Hydrogen is a product that is fully capable of sustaining the world's energy needs now and in the future. If renewably produced, H_2 would be a fuel that does not contribute to environmental damage (pollution) and supports the well being of humans (Turner *et al.,* 2004).

Photocatalysts could convert solar energy into chemical energy by producing H_2 gas from H_2 containing compounds. Thus, H_2 generation by use of semiconductor photocatalysts has recently received much attention with this view. Since visible light accounts for the largest portion (ca. 42 %) of the solar spectrum, visible light driven photocatalysts that could produce H_2 from water splitting or aqueous electrolyte solutions under solar light have been actively sought (Kato et al 2003, Kudo 2007 and Jang et al 2007a). Particulate systems are attractive with respect to their economic advantages. They are very simple in construction and maintenance costs. The light absorption efficiency in suspensions can be very high and polycrystalline semiconductors can be used in particulate system as well. To date, a large number of photocatalysts such as $CuGaO_2$ and $CuGa_{1-x}ln_xO_2$ (Gurunathan et al 2008), $FeGaO_3$ (Subramanian et al 2008), nanospheres of Fe_2O_3 and Fe_2GaO_3 (Subramanian et al 2009), $CuCr_2O_4/TiO_2$ (Yan et al 2009), Pt-PdS/CdS (Yan et al 2009a), CdS nanoparticles on HY Zeolite pore (Bai et al 2011), CdS incorporated special glass (Liu et al 2010) and Ag_2S on CdS (Shen et al 2010) have been reported for splitting of water. However, most of the photocatalysts can produce H_2 only under UV light irradiation due to their wide band gaps. This property limits the practical use of the photocatalysts for H_2 generation from water under sunlight. For direct, efficient conversion of solar energy during water decomposition the optimum band gap of the semiconductor should be around 2.0 eV. In this aspect, CdS with the band gap of 2.4 eV, seems to be almost a perfect semiconductor photocatalyst for H_2 generation by sunlight.

CdS has a sufficiently negative flat-band potential and good absorption property in the visible zone of the solar spectrum. Furthermore, it has been reported that the activity of CdS can be improved by combining other semiconductors having different energy levels. For examples, Fe_2O_3 /CdS (Preethi and Kanmani, 2014). On the other hand, ZnS is another metal sulfide that has been extensively studied for water splitting. The band gap of ZnS is 3.66 eV, that is activated on UV irradiation (Kudo 2007). Therefore, metal ions (i.e., Ni^{2+}, Pb^{2+} and Cu^{2+}) were doped into ZnS in order to shift the absorption edge of ZnS into visible light region (Tsuji et al 2004 and Kudo 2007).Coupling of two or more semiconductors can be used effectively for the photocatalytic decomposition of H_2S in an alkaline solution, which decreases the extent of e^-/h^+ recombination and also enhances the interparticle electron transfer. Several literatures suggest that ZnS is not active under visible light for photocatalytic H_2 evolution. On the other hand, the activity of CdS was achieved lower rate of hydrogen production (Lu Wang *et al.,* 2010 and Yabo Wang *et al.,* 2012). The combination $Cd_{1-X}Z_XS$ got higher rate of H_2 production than CdS and ZnS (Yabo Wang *et al.,* 2012 and Melody Kimi *et al.,* 2012). Therefore in this study $Cd_{1-X}Z_XS$ (x=0.4) photocatalyst was selected. Compared to the non-doped sample, Ni doping can give rise to 86% increase in the Hydrogen production. Gurunathan*et al.,* (2008) found that the hydrogen production was higher with Ruthenium doped spinel photocatalyst than NiO.In this study, Pd doped CdSwas prepared by the simple co-precipiation method under ambient condition using Na_2S and Na_2SO_3 as the source.

II. CATALYST PREPARATION AND EXPERIMENTAL PROCEDURE

A. Preparation of photocatalysis

All of the chemical reagents were analytical grade and used without further purification.

B. Synthesis of Pd doped CdSnanocomposite

The CdSwere prepared using co-precipitation method by adding ($Cd(CH_3COO)_2$) into a 500 mL of distilled H_2O. The solution was well mixed using magnetic stirring. Na_2S solution was added drop by drop during stirring condition.After one hour, the solution was removed from magnetic stirrer and washed with isopropyl alcohol and distilled H_2O to split particles from each other. The precipitate was allowed to settle and dried in oven for 150 ºC. After that $PdCl_2$powder was added to the above prepared nanophotocatalyst sample and add hydrochloric acid 5 to 6drop in it. Then the prepared nanophotocatalyst was kept in ultra sonication for 3 minutes, the sample was dried at 110 ºC for 2 hours and Sintered at 350 ºC for 1.5 hours to form final nanaphotocatalyst.

C. Characterization of photocatalyst

The photocatalyst was conducted at room temperature using X-Ray Diffraction measurement (XRD, CuKα1, λ= 1.54 nm, PANalytical, Netherlands). The particle size was determined using Scherrer equation. Scanning Electron Microscopy (Hitachi S-3400N, Tokyo, Japan) was used to analyze the particles morphology and the agglomeration. UltraViolet – Visible Spectroscopy (UV-DRS,) was used to find out the threshold wavelength and bandgap energy.Elemental analysis was characterized by energy dispersive X-ray spectroscopy (EDS).

D. Production of H_2 from sulfide wastewater

The experiment was carried out in trapezoidal reactor of 500 mL capacity was irradiated using visible lamp. The reactor has two openings. One for purging with (N_2) gas for 1 hour to remove oxygen from solutionand the other to collect H_2 gas by inverted water displacement apparatus where there is a septum through which the gas can be sampled and determined by GC (Shimadzu 14B, Molecular sieve -5 A column, TCD detector and N_2 carrier gas).

III. RESULTS AND DIXSCUSSION

A.Characterization

Particle size

The XRD measurements were performed using a powder diffractometeroperating in the reflection mode. The X-ray diffraction pattern of Pd/CdS NCs was illustrated in Figure 3.1. The average crystal sizes of (calculated for intense reflection) Pd/CdS NCs was found to be 3.27 nm,derived from Debey–Scherrer Equation.

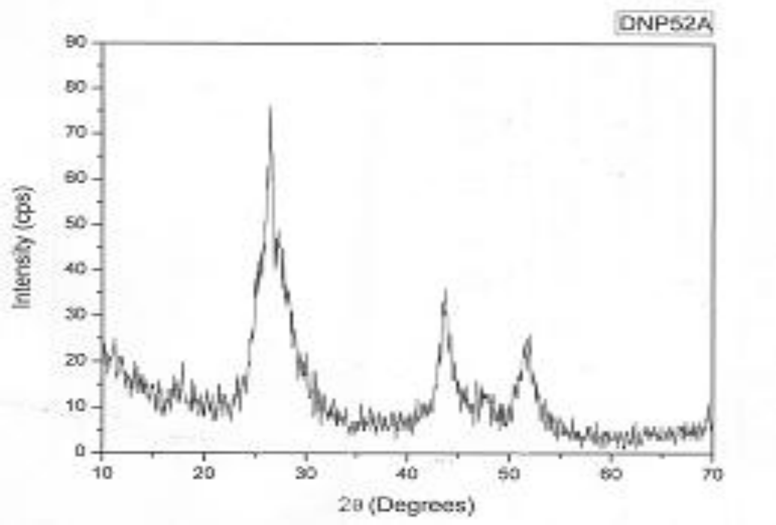

Fig. 3.1 XRD pattern ofPd/Cd**S**

Morphology

The SEM image of Pd/CdS was shown in Figure 3.2. The crystals were platy type with different sizes. Each plate should be composed of nanoparticles. Therefore, spherical particles were of irregular aggregates with pores.

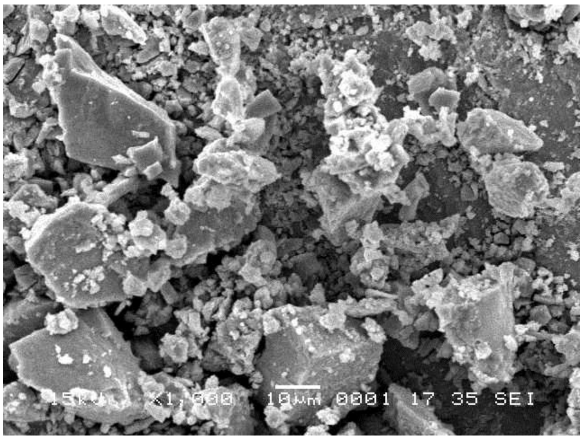

Fig. 3.2 SEM image of Pd/CdS

Band gap

DRS UV-Vis spectra of Pd/CdSphotocatalyst is shown in Fig. 3.3. The band gap excitation of CdS NPs occurred at longer wavelength whereas $PdCl_2$ NPs occurred at shorter wavelength. The band gap excitation due to Pd/CdS NCs did not show two steps corresponding to CdS NPs and PdCl2 NPs. Hence Pd/CdS NCs was a single compound and the excitation of Pd/CdS NCs appeared similar to CdS NPs. Hence there might be the isomorphic substitution of Cd by Pd in CdS lattice.In the case of Pd doped CdS, the spectrum can be distinguished to two bands at 530 nm, while the CdS spectrum can be distinguished to two bands at 610 nm. The bandgaps of CdS NPs and Pd doped CdS were 2.03 and 2.33 eV, respectively. The Pd/CdS NCs exhibited higher photocatalytic activity than the CdS. It was due to the excitation of nanocomposites by the visible light.

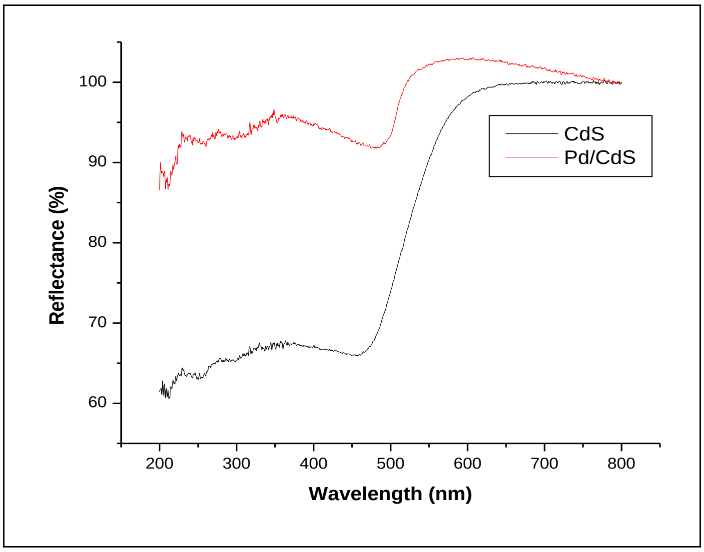

Fig.3.3. UV-DRS for Pd/CdS

Composition by EDX

Energy Dispersive X-ray analysis (EDAX) examination revealed to analyze the chemical components in the visible photocatalyst Pd doped CdS under SEM.X-ray data is processed to obtain the percentage of each measured element present in the individual particles. From Figure 3.4, it was evident that the Pd doped CdS mixture was composed of cadmium, palladium and sulfide elements. The maximum rate depends upon the percentage composition of catalytic material in the particulate mixture.

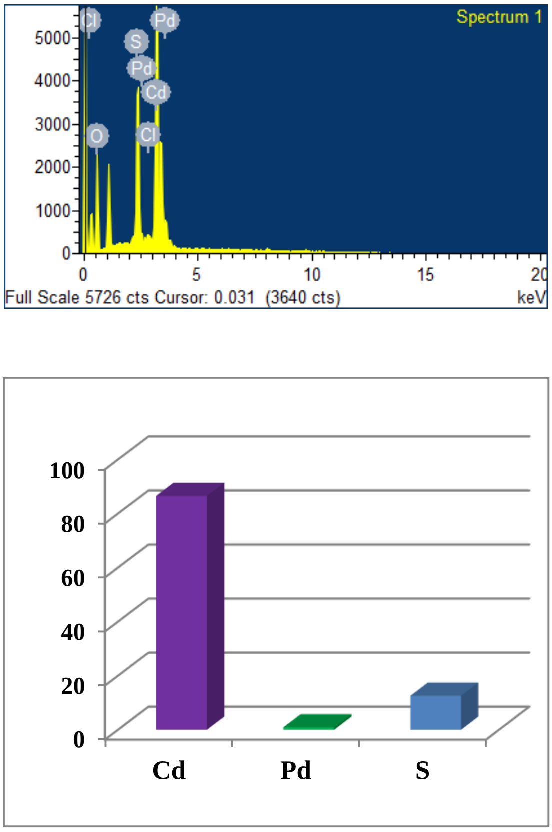

Fig.4. EDX spectrum image for Pd/CdS

B. Photocatalytic evolution of hydrogen

The photocatalytic hydrogen production from Pd doped CdSnanophotocatalyst was conducted in aqueous solutions under visible light irradiation. The effect of concentration of sulfide ion on the generation of H_2 was studied by varying the concentration of sulfide ion in the range of 0.1 to 0.3 M. Concentration of sulfite ion, catalyst dosage, pH, volume and light intensity were kept constant as 0.2 M, 0.2 g, 12, 200 mL and 100 W respectively. The hydrogen production was recorded for 1 hour. It was observed that increase in the concentration of sulfide ion, the hydrogen production increased and reached a maximum at 0.25 M is shown in Fig 4.1. Further increase in concentration of sulfide ion led to a decreased in hydrogen production, because It was due to the formation of yellow polysulfides which absorbed part of the visible-wavelength photons by which it could contribute to CdS Photocatalysis (Furlong et al 1986 and Bao et al 2008). The formations of polysulfide cause catalyst deactivation as well as consumption of donor. The poisoning of active catalyst surfaces was due to the adsorption of sulfur containing compounds. It was due to the blockage of the adsorption of hydronium cations at the surface active sites. Sulfide and sulfite ions behaved as a quenching agent of ions and radicals (Cui et al 2004), and more ions and radicals were quenched with the increase in concentration of sulfide ion.

The effect of concentration of sulfite ion on the generation of H_2 from simulated sulfide wastewater was studied at different sulfite ion concentration in the range of 0.1 to 0.3 M was shown in Fig 4.2. Concentration of sulfide ion, catalyst dose, pH, volume and lamp source were kept constant as 0.25 M,0.2 g, 12, 200 mL and 100 W respectively.The maximum hydrogen production rate was found of 1830 µmol/h at 0.2 M of sulfite ion concentration for 1 hour simulated sulfide wastewater and all other parameters were kept constant. The volume of H_2 production decreased with increase in sulfite ion concentration. It was due to the competitive absorption of sulfide and thiosulfate on the active site of photocatalyst (Grzyll*et al*. 1989 and Preethi and Kanmani, 2014).

In the presence of sulfite (SO_3^{2-}) ions, hydrogen production occurs continuously with the oxidation of (SO_3^{2-}) ions to sulfate and dithionate (Raj Kumar Arya, 2012). In the solution containing SO_3^{2-} ions formation of thiosulfate ions occurs concomitantly with hydrogen production. After the formation of thiosulfate ions, hydrogen production continues with a smaller rate due to further oxidation of thiosulfate ions to tetrathionate. The disproportionate of tetrathionate leads to formation of SO^{2-} ions that can further oxidized to sulphate. The increasing concentration of thiosulfate ions decreases the rate of hydrogen formation attributed to their reduction by conduction band electrons (Raj Kumar Arya., 2012).

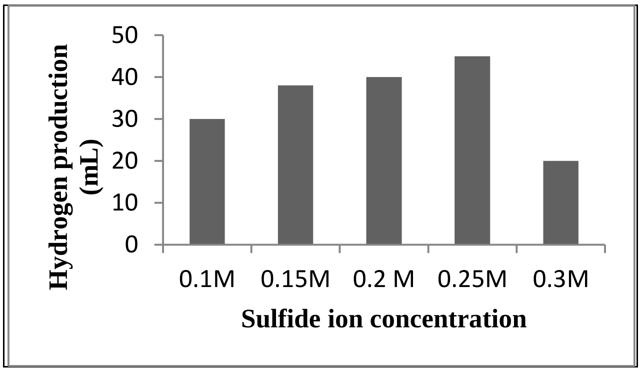

Fig.4.1. Effect of sulfide ion concentration

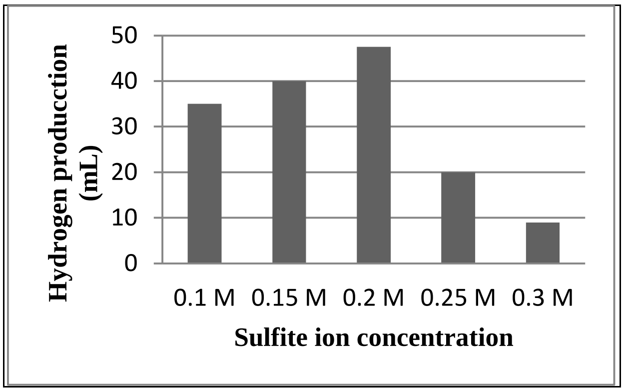

Fig.4.2. Effect of sulfite ion concentration

The effect of catalyst dosage on the generation of H_2 from simulated sulfide wastewater was studied by varying the catalyst dose in the range of 0.1 to 0.5 g. Concentration of sulfite ion, concentration of sulfide ion, volume, light intensity and pH were kept constant as 0.2 M, 0.25 M, 200 mL, 100 W and 12 respectively. The increase in the catalyst dosage from 0.1 to 0.3 g resulted in increase in hydrogen production. It was due to the presence of more active sites in the added photocatalyst. Further increase in the amount of photocatalyst from (0.3 – 0.5) g led to decreased in hydrogen production. It reduced the light absorption of inner particles of the solution (Preethi and Kanmani, 2014) and also increased concentration of suspended particles with negative effects in terms of shadowing and screening phenomena (Raj Kumar Arya, 2012) shown in fig 4.3.

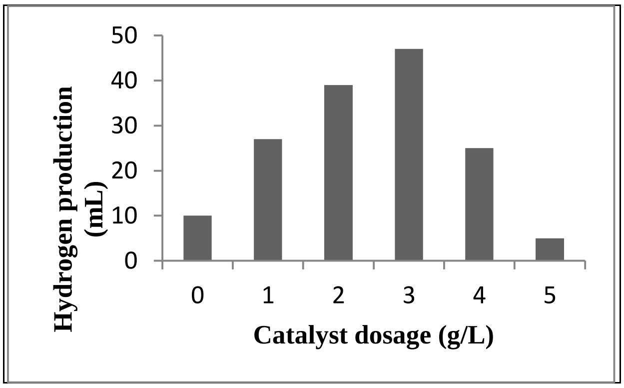

Fig.4.3. Effect of catalyst dosage

Following the sulfite, sulfide and catalyst dosage optimization, pH optimization should be carried out because of its prominent role in existing nature of the sulfur compounds. If pH value increase from 9 to 12, hydrogen production also get increased. Further increase pH from 12 to 13, hydrogen gets decreased were shown in fig 4.4. It was due to the increase OH^- ion concentration. When the hydroxide ions concentration becomes too high, many photogenerated hydrogen ions interacted with hydroxide ions producing water (Strataki*et al.* 2010 and Bao *et al.* 2008). The photocatalyst decomposition at high alkaline condition was also an additional factor for reduced hydrogen production (Preethi and Kanmani, 2012).

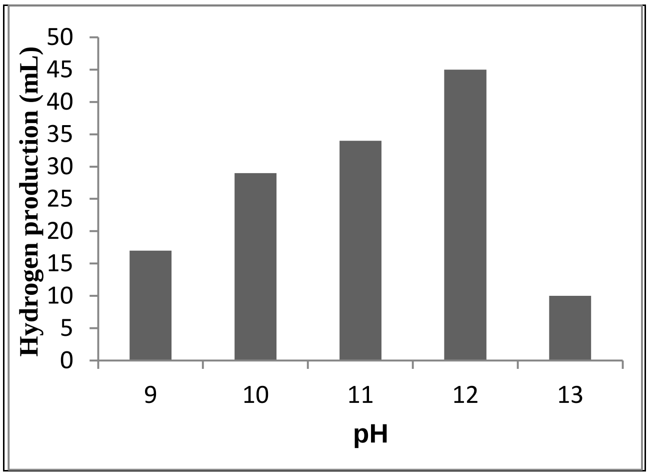

Fig.4.4. Effect of pH

In order to study the lamp source (100 W to 300 W), it was observed that the hydrogen production increased with increases in light intensity was shown in fig 4.5. It was due to the fact that with increase in intensity of light, large number of electron/hole pairs might be generated that lead to be higher hydrogen production (Rita *et al.* 2010, Linkous *et al.* 2004 and Preethi amdKanmani, 2014). Thus more electrons might be available for reducing the H^+ ions for hydrogen production in the equation 1 to 3.

H_2S dissociation:

$H_2S+OH^- \Rightarrow HS^-$ (bisuflide ion) + H_2O 1

Oxidation:

$2HS^- + 2h^+ \Rightarrow S_2^-$ (Polysulfide) + $2H^+$ 2

Reduction:

$2H^+ + 2e^- \Rightarrow H_2$ (hydrogen) 3

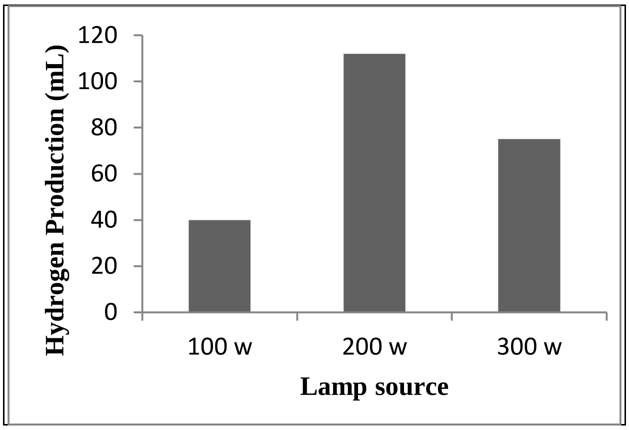

Fig.4.5. Effect of Lamp source

From the fig 4.6,the increases the volume of sample decreases the hydrogen production due to low penetrate into the reactor and screening effect was occurred. The dark color was found into the reactor and hydrogen production decreased.

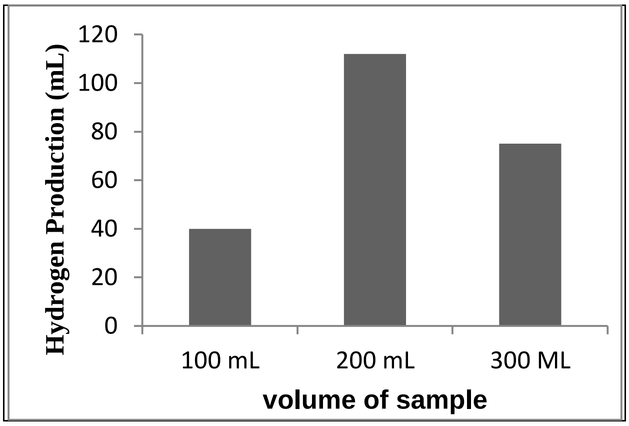

Fig.4.6. Effect of pH

The feasibility studies had been carried out in order to optimize the operating variables such as concentration of sulfide ion 0.2 M, concentration of sulfite ion 0.25 M, pH 12, catalyst amount 0.3g, lamp power 300 W and volume of wastewater 100 mL, the maximum hydrogen production rate was 112 mL (5000 µmol h^{-1}).

IV. CONCLUSION

In this study, nanophotocatalystPd/Cd_0S had been synthesized by co-precipitation method. The light intensity increases the hydrogen production also increased was noticed. There is a decrease in hydrogen production, when the volume of sample increased. The maximum hydrogen production was observed with Pd/CdS shell nano particles of 5000 µmol/h.

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