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Development and performance of bench-scale reactor for the photocatalytic generation of hydrogen

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ABSTRACT

In this study, a new novel bench-scale (5 L) tubular photocatalytic reactor was developed and its feasibility studies were conducted for optimizing the operating variables, namely concentration of sulfide ion, concentration of sulfite ion, pH, catalyst concentration, lamp power, volume of wastewater and recycle flow rates at batch recycle mode for the generation of hydrogen from aqueous sodium sulfide using CdS–ZnS/TiO_2 core–shell NPs (nanoparticles). The maximum H_2 generation was found at 0.05 M concentration of sulfide ion, 0.2 M concentration of sulfite ion, pH 11.3, 0.5 g/L catalyst concentration and recycle flow rate of 18 L/h. Reusability studies were conducted for analyzing stability of photocatalyst. The results showed that the generation of hydrogen depends on light intensity, photoreactor used, nature of photocatalysts and the operating conditions.

1. Introduction

Hydrogen sulfide (H_2S) is produced in large quantities as a byproduct in coal and petroleum industries, natural gas and oil wells, and geothermal plants. Sulfide wastewater is generated from STPs (sewage treatment plants), tanning of hides and pulp and paper industries. In most cases, this toxic H_2S gas and sulfide wastewater has to be converted into an environmentally less harmful form to comply with environmental regulations [1]. Various treatment processes are available for the removal of H_2S gas and sulfide wastewater. As these processes have some drawbacks, new emerging technologies viz., biological [2], thermochemical, electrochemical and photochemical are applied for the hydrogen (H_2) production through waste minimization. Among these approaches, photocatalysis has received attention as a possible method for photochemical conversion and storage of solar energy. Solar energy is the primary source for clean and renewable energy alternatives. Thus, simultaneous hydrogen (H_2) generation and H_2S decomposition in an alkaline solution is a highly desirable process that could satisfy both energy and environment requirements [3–5].

Hydrogen (H_2) is regarded as the fuel of the future and is one of the most suitable energy carriers in the context of sustainable development. Recently, biomass-based energy technologies employed for CO_2 capture and also for the production of H_2 [6]. H_2 is produced from fossil fuels as well as from biomass by established technologies [7] but the conventional sources should be replaced by alternative sources such as solar energy. H_2 generation from cheap raw materials like H_2S is a challenging method that could provide a solution for future energy needs. So far, many photocatalytic research studies have been focused on exploring new active photocatalysts on H_2 generation. The reported oxide photocatalysts, such as $NaTaO_3$ [8] and $Sr_2Nb_2O_7$ [9–10] exhibit high photocatalytic activities for H_2 generation from water, however, these oxide photocatalysts are only active under UV light which constitutes only 5% of the solar spectrum [11]. Therefore, it is indispensable to develop photocatalyst responding to visible portion of solar spectrum. Sulfide semiconductors, such as CdS and ZnS with narrow band gaps and valence bands at relatively negative potentials compared to oxide semiconductors can be good candidates for visible light driven photocatalysts. Titania (TiO_2) has attracted extensive attention for many applications such as photocatalysis, gas sensing, solar water splitting, dye-sensitized solar cells and solid state dye-sensitized solar cells. 1D (One dimensional) TiO_2 materials including nanotubes, and nanotube arrays are currently of great interest owing to the possibility for suppression of charge recombination [12–13]. The coupling of two or more semiconductors and nanomaterials can be effectively used for the generation of H_2 and also it eliminates the use of noble metals [14]. Employing artificial lamps for this

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technology is not advantageous. Harvesting of renewable and abundantly available renewable solar energy would be beneficial. Using of solar UV–visible light responsive photocatalysts would be a promising method to achieve the commercial application of this technology. For the transfer of this technology in society, the development of a suitable photocatalytic reactor is needed. Particularly in a subtropical country like India where sunlight is abundant almost throughout the year, research on solar photocatalytic generation of H_2 from H_2S in an alkaline solution will be quite promising.

Several parameters govern or influence the kinetics of the photocatalytic H_2 generation process. Kinetics of the process is needed for the scale-up of photocatalytic reactors. Very few studies were focused on the development of photoreactor for the generation of H_2 [15–20]. Linkous et al. [15–16] conducted pioneering work on development of photocatalytic reactors for the generation of H_2. Earlier batch recycle photocatalytic reactor with N_2 bubbling was developed in our laboratory for the decomposition of H_2S in alkaline solution for the generation of H_2 [17]. Jing et al. (2010) developed solar photocatalytic hydrogen reactor for the production of H_2. The maximum production rate amounted to 1.88 L/h [18]. Katherine Villa et al. (2013) CPC (Compound Parabolic Concentrator) solar reactor has been used to generate hydrogen from aqueous solutions of formic acid, glycerol, or a real wastewater, and using Pt/(TiO_2–N) and Pt/(CdS–ZnS) as photocatalysts. The approximate energy efficiencies calculated with the highest hydrogen production rates were 2.5% and 1.6% for Pt/(TiO_2–N) and Pt/(CdS–ZnS), respectively [19]. Recently, Jing et al. (2013) developed fluidized fluidized-bed photocatalytic reactor with H_2S bubbling. The reaction rate constant was 1.12 E^{-1} [20].

The influence of several experimental variables such as effect of concentration of sulfide ion [21–27], concentration of sulfite ion [24,25,28–30], pH [27,31], catalyst concentration [32–35], lamp power [32,34–35], volume of wastewater [36–37] and recycle flow rates [17,38] on the rate of photocatalytic H_2 generation from aqueous sodium sulfide was reported for various catalytic systems. Developing photoreactors and conducting kinetic studies for optimization of operating variables are an important issues for scale up. Compared to other configurations, a cylindrical shape is better suited for transmitting the light radiation. The need of the hour is to generate H_2 by the utilization of solar energy using efficient nanophotocatalysts and appropriate photoreactors.

In this present study, CdS–ZnS/TiO_2 core–shell NPs (nanoparticles) was synthesized for the photocatalytic H_2 generation from aqueous sodium sulfide solution and the performance of photocatalytic reactor with respect to various process parameters such as concentration of sulfide ion, concentration of sulfite ion, pH, catalyst concentration, lamp power, volume of wastewater and recycle flow rates were studied.

2. Material and methods

All chemicals used were reagent grade or high quality used as supplied. The solutions of sodium sulfide and sodium sulfite were purged with high purity N_2 gas for 30 min prior to illumination. All the studies were conducted with distilled and de-ionized water.

2.1. Materials

Cadmium acetate ($Cd(CH_3COO)_2$), zinc acetate ($Zn(CH_3COO)_2$), sodium sulfide ($Na_2S.9H_2O$), sodium sulfite (Na_2SO_3), titanium dioxide (Degussa P25), thiourea, sodium hydroxide and hydrochloric acid from MERCK were procured. Other chemicals were used of analytical reagent grade.

2.2. Development of BTR (bench-scale tubular photocatalytic reactor)

The schematic diagram of the experimental setup for bench scale tubular photocatalytic reactor operated in batch recycle mode is shown in Fig. 1. The reactor shape was chosen to optimize the exposure of the catalyst to the light. By building the reactor in a cylindrical shape and surrounding it with the lamps, most of the light energy could be used. The plexiglass made tubular reactor was developed with a capacity of 5 L (diameter: 10 cm and height: 63.7 cm). The reactor consists of two inlets, i.e., one for purging of N_2 gas and another for solution feeding and two outlets, i.e., for collection of H_2 gas and solution. In the batch recycle mode of operation, an additional port was used for recirculating the Na_2S/Na_2SO_3 solution. The irradiation was carried out by using three sun lamps (Philips) of power 100 W each (wavelength ranges from 400 to 700 nm and light intensity ranges from 510 to 646 W/m^2) and one UV lamp of power 8 W (365 nm). The emission intensity of UV lamp was 183 μW/m^2.

2.3. Synthesis of CdS–ZnS/TiO_2 core–shell NPs

The CdS–ZnS/TiO_2 core–shell NPs was synthesized by two steps. It included hydrothermal synthesis of TiO_2 NTs [39] and co-precipitation of CdS–ZnS nanoparticles on TiO_2 NTs. In a 2 L beaker, each 500 mL of 0.1 M cadmium acetate and zinc acetate were stirred. 7.6 g thiourea, 3.5 g of TiO_2 NTs and 0.2 M Na_2S were added to it. The crystallized products were separated by ultracentrifugation, washed thoroughly with de-ionized water, isopropanol and dried at 110 °C in an oven. The weight ratio of the synthesized catalyst was 1:1:1 (CdS:ZnS:TiO_2 NTs). Typical particle sizes and band gap energy of the synthesized core–shell NPs as estimated from XRD studies and diffuse reflectance UV–visible absorption spectroscopy, respectively were about 3.2 nm and 2.88 eV.

2.4. Conducting feasibility studies for the optimization of operating variables

The nanophotocatalysts were suspended in the solution containing sodium sulfide and sodium sulfite (Na_2S and Na_2SO_3). The suspensions were deairated with N_2 gas for 30 min to prevent uptake of photogenerated electrons by dissolved oxygen. The air space above the solution in the reactor was flushed with N_2 for 1 h in each experiment. The flow rate of the N_2 gas was controlled by the rotameters. The part of the liquid was recycled by the peristaltic pump. The temperature of the photoreactor (25 °C) was maintained by using exhaust fans. The effluent gas was collected in the collection tank by downward displacement of water. The gas samples were analyzed for hydrogen with a Gas chromatograph (Chromatograph and Instruments Company) having a Porapak Q column and thermal conductivity detector. N2 was used as a carrier gas. The influence of operating variables viz., concentration of sulfide ion, concentration of sulfite ion, pH, catalyst concentration, lamp power, volume of wastewater and recycle flow rate were studied. At optimized conditions, solar studies were conducted for the generation of H_2. In outdoor solar studies, temperature of the photoreactor was maintained by external water circulation. The percentage conversion (X_A) was calculated by using the following equation (1) [40],

$$X_A = \frac{\text{Moles of } H_2 \text{ generated}}{\text{Moles of } Na_2S \text{ fed}} \times 100 \quad (1)$$

The apparent energy conversion efficiency of the system (η_c) can be calculated by following equation (2) [12],

$$\eta_c = \frac{G_{H_2}\ R_{H_2}}{W_S\ A} \times 100 \quad (2)$$