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Photocatalytic valorization of glycerol to hydrogen: Optimization of operating parameters by artificial neural network

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ABSTRACT

Glycerol is a considerable by-product of biodiesel production from biomass. Photocatalytic glycerol valorization to hydrogen is an attractive approach from the sustainable development point of view. This study investigates the individual and interaction effects of main operating parameters of the photocatalytic hydrogen production process from glycerol using Pt/TiO_2 photocatalyst. Four key operating parameters (i.e. glycerol%, catalyst loading, Pt% and pH) were selected as independent variables, and the amount of produced hydrogen was considered as the dependent variable (response). Experiments were conducted based on the Box-Behnken design. Response surface methodology (RSM) and Artificial Neural Network (ANN) models were developed based on the experimental design approach to predict hydrogen production. The predictive capacity of the two models was compared based on R^2, R^2_{adj}, *RMS*, *MAE* and *AAD*. The ANN model was found more accurate and reliable, and it was therefore employed for the optimization of H_2 production and parametric investigation. Analysis of the results showed that the operating parameters can also influence each other's optimum value. Increasing glycerol% shifts the optimum values of catalyst loading, Pt%, and pH to higher values; however, Pt% has a negligible effect on the optimum values of the other parameters. Moreover, the catalyst loading and pH have no effect on the optimum value of glycerol%, but the increase of each of these two parameters reduces the optimum value of glycerol% and Pt%. The Genetic Algorithm along with the ANN model was also utilized for the optimization and it was found that the overall optimum of the system was 50% glycerol (v/v), 3.9 g/L catalyst loading, 3.1% Pt, and pH 4.5. Finally, Garson's method was employed to obtain the relative importance of each variable in the system. This analysis revealed that the variation of glycerol% and catalyst loading had, respectively, the least and the most effect on the amount of produced hydrogen.

1. Introduction

In recent years, global energy crises have led to the development of renewable energies like biodiesel and hydrogen [1]. Due to abundance of water on earth, water splitting using solar light driven photocatalysts is a promising alternative for future energy production. Despite vast research in this area, still more studies are required to increase the efficiency of the photocatalysis process. One the other hand, the price of glycerol, one of the biodiesel byproducts, has decreased significantly due to overproduction [2]. Valorization of sustainable glycerol to green fuels is therefore another promising alternative for future energy production. In addition, investigation of glycerol photo-reforming can assist with clarifying the mechanisms of photocatalysis. This knowledge is also beneficial to increase insight into water photo-splitting as well as glycerol photo-conversion to valuable liquid products.

TiO_2 is the most common photocatalyst which benefits from advantages like very high photocatalyst activity, low cost, suitable chemical and thermal stability, and low toxicity [3,4]. These advantages make TiO_2 a promising photocatalyst; however, more research is required to achieve an economically viable hydrogen production process on an industrial scale. One of the most efficient techniques to increase the photocatalytic activity of TiO_2 is incorporating metals or metal oxides as co-catalysts [5]. The presence of co-catalysts could provide hydrogen reaction sites, favor the charge separation reaction, trap photo-generated electrons and extend light absorption toward the visible range [6].

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Table 1
Experimental ranges and levels of variables for hydrogen production experiments.

Variables	−1	0	+1
Glycerol% (A, v/v)	0.5	25.25	50
Catalyst loading (B, g/L)	0.05	2.525	5
Pt% (C, wt%)	0.02	2.51	5
Initial pH of solution (D)	2	7	12

Among the metals used as co-catalysts in the photocatalytic glycerol conversion to hydrogen, like Pt [7–21], Cu [16,20,22–31], Au [12,13,21,32–34], Pd [12,13,21,35], Ni [21,30,36,37], Co [21,38], Ag [21,39], Mn [21], Cr [21], and W [21], Pt is the one most commonly used. Fu et al. [40] found that Pt decorated photocatalysts exhibited the highest hydrogen production rate and the photocatalytic activity decreased in the order of Pt > Au > Pd > Rh > Ag > Ru. In another work, Pt was found to be the most active co-catalyst for hydrogen production by investigating the vast range of Pt, Pd, Ir, Au, Ru, Rh, and Ni [41]. Recently, López-Tenllado et al. [13] reported the order of Pt > Pd > Au for propan-2-ol and Pt ≈ Au > Pd for glycerol photocatalytic valorization to hydrogen.

Although there is much research on the synthesis of photocatalyst and feasibility of hydrogen production from glycerol, this field suffers from the lack of optimization of operating parameters. On the other hand, it is very challenging to develop a consensus on the optimum value of operating parameters due to significant differences and contradictions in previous work [42]. These conflicts may be attributed to the application of a 'one-variable-at-a-time' approach and to a disregard for the interaction effect of the parameters [43].

To assess the interaction effect of various operating parameters, a comprehensive model is required. Response Surface Methodology (RSM) and Artificial Neural Networks (ANN) are two useful modeling methods that can be applied for complex processes like photocatalytic hydrogen production because they do not require knowledge about the fundamentals of the photocatalytic process [44]. RSM is a statistical method to design experiments, develop a model, investigate effects of parameters, assess the interaction effect of the parameters, and optimize the desired responses [45,46]. ANN was inspired by biological neural networks taking advantage of some simple and non-linear models [47]. The Genetic Algorithm (GA) can be further employed to optimize the output of ANN models. GA utilizes a robust optimization procedure that mimics the process of natural selection, and its global optimizing capability is more powerful in comparison with other heuristic optimization methods [48].

To the best of our knowledge, a single statistical analysis on glycerol conversion to hydrogen has been reported to date. Bastos et al. [49] examined the glycerol valorization to hydrogen using a simple factorial design statistical model. The critical point which was obtained corresponded to a minimum, i.e., no optimization could be performed using this model. On the other hand, there is no publication in this field using other powerful methods such as RSM or ANN. Moreover, no statistical analysis study was found on the optimization of glycerol valorization to hydrogen using a TiO_2 based photocatalyst (as the most common photocatalyst).

Herein, we investigated individual and interaction effects of four key operating parameters (including catalyst loading, Pt%, glycerol%, and pH) on the photocatalytic glycerol valorization to hydrogen rate using Pt/TiO_2. Two approaches of RSM and ANN were employed to model the process, and their predictive ability for photocatalytic hydrogen production reactions was compared. Moreover, GA was applied to optimize the response of the ANN model. Finally, the level of influence of each operating parameter on the amount of produced hydrogen was calculated.

2. Materials and methods

2.1. Materials

The commercial TiO_2 Aeroxide P25 (≥99.5%) photocatalyst was provided by Evonik Industries. Hexachloroplatinic acid (IV) ($H_2PtCl_6{\cdot}6H_2O$, ≥37.50% Pt) was obtained from Sigma–Aldrich to be used as the platinum precursor. Glycerol (≥99.5%) and ethyl alcohol (99.99%) were supplied by Caledon and Commercial Alcohols, respectively. pH adjustment was made using NaOH (≥97%) and HCl (36.5–38.0%) which were purchased from VWR. Milli-Q water was utilized in the synthesis of photocatalysts.

2.2. Preparation of Pt/TiO_2 photocatalyst

Platinum deposition on TiO_2 was performed based on the photodeposition method [18]. Briefly, a suspension of 1 g TiO_2 and 120 ml ethyl alcohol solution (10%) was sonicated for 30 min using a Hielscher UP400S Ultrasonic Processor. Hexachloroplatinic acid solution in water was then added to the suspension in order to obtain Pt loadings of 0.02, 2.51, and 5 wt%. The mixture was purged with nitrogen for 15 min to remove the oxygen present in the mixture. A photoreactor equipped with four 20 W Black-Ray® mercury tubes (365 nm) was used to perform the photocatalytic experiments. The irradiation was maintained for 3 h under continued nitrogen flow and constant 500 rpm magnetic stirring in all experiments. Finally, the Pt/TiO_2 material was filtered, washed and dried overnight at 110 °C.

2.3. Photocatalyst characterization

Powder X-ray diffraction (XRD) patterns of the prepared samples were obtained using a Bruker SMART APEXII X-ray diffractometer equipped with Cu Kα radiation source (λ = 1.5418 Å). The patterns were measured from 2θ = 10–80° at a step of 0.02° and a scan rate of 1.2 min^{-1}. The Anatase:Rutile ratio of the samples was calculated using Eq. (1) [50]:

$$\%Rutile = \frac{1}{\left[1 + 0.8(I_A/I_B)\right]} \times 100 \quad (1)$$

where I_A and I_B are, respectively, the intensities of anatase (101) and rutile (110) reflections. TEM images were collected using a JOEL JEM 1230 operated an accelerating voltage of 120 kV. To prepare the samples for the analysis, they were dispersed in water and sonicated using a Hielscher UP400S Ultrasonic Processor and then placed on carbon coated copper TEM grids.

2.4. Hydrogen production experiments

The photocatalytic hydrogen production experiments were carried out in gas-tight Pyrex reaction cells using the prepared photocatalysts. In each experiment, predetermined amounts of glycerol, water, and photocatalyst (Table 2) were introduced into the cells. After sonication of the suspensions for 5 min to ensure proper dispersion of photocatalysts, the pH was adjusted using NaOH and HCl solutions. The volume of suspensions was ensured to be kept at 5 ml. Before irradiation, the reaction cells were purged with nitrogen (20 ml/min) for 15 min to remove oxygen and stirred in the dark for 20 min to allow the adsorption of glycerol on the catalyst surface. The cells were then irradiated with a light intensity of 1600 μW/cm^2 in a photoreactor equipped with four 20 W Black-Ray® mercury tubes. The spectral chart of the mercury tubes is illustrated in Fig. S1. During the experiments, the mixtures were maintained at constant 500 rpm magnetic stirring using Thermo-Scientific™ Cimarec™ 15-Position magnetic stirrer. The