Mathematical Modelling of Photocatalytic Hydrogen Production from Glucose on Ru-Doped LaFeO$_3$

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Abstract

In the present work the authors proposed a simplified mathematical model for the renewable hydrogen production by the photocatalytic degradation of glucose over an optimized Ru-doped LaFeO$_3$ photocatalyst under UV irradiation emitted by light-emitting diodes (LEDs). To define the reaction system the analysis of liquid phase was coupled with the detection of reaction products in gaseous phase. The mathematical modeling of the system has been developed by using different kinetic approaches for glucose consumption. Model parameters estimation was realized by individuating the best agreement between the calculated values and experimental data as a function of irradiation time both for hydrogen production and glucose degradation degree evidencing that the best fitting has been obtained with zero order kinetic models. Finally, the accuracy of the model was tested in different experimental conditions, evidencing the ability of the mathematical model to be predictive.

Introduction

Hydrogen is considered as an ideal fuel for the future and it can be produced from clean and renewable energy sources and, thus, its life cycle is clean and renewable [1]. Solar and wind are the two major sources of renewable energy and they are also the promising sources for renewable hydrogen production [1]. Promising technology for production of green hydrogen from biomass by photocatalytic water splitting with TiO$_2$ has found increasing attention in recent years[2]. In many studies regarding the photocatalytic production of H$_2$, different substances (e.g., organic acids, alcohols, sulfide/sulfite) acting as electron donors, have been generally used [3,4].

In particular the photocatalytic hydrogen production from biomass glucose decomposition seems to become very powerful method for the practical and low cost technologies in the hydrogen–based energy system [5,7]. The most widely used semiconductor in photocatalysis is TiO$_2$ because of its physical and chemical properties, excellent stability, high availability and low cost [8]. With regard to the photocatalytic hydrogen production, the use of semiconductor (such as TiO$_2$ or ZnO) doped with metals (Au, Pt, Pd or Cu) has been extensively reported [9-12]. In particular, recent studies have shown a considerable efficiency of perovskites in the photocatalytic hydrogen production by aqueous solutions containing glucose or other sacrificial agents such as ethanol or methanol [13-15].

These semiconductors are particularly interesting because they has shown excellent photocatalytic activity due to its properties such as high stability, non-toxicity and small band gap energy[16,17]. Moreover, the effectiveness of perovskites in the photocatalytic H$_2$ production via water splitting in the presence of noble metals (Pt) as a co-catalyst has been investigated [18,19].

In particular, in our previous work we have reported the high efficiency of LaFeO$_3$ perovskite doped with ruthenium in the photocatalytic hydrogen production from glucose aqueous matrices under UV irradiation by light-emitting diodes (LEDs) [17,20]. In the present work, experimental investigations were extended in order to develop a simplified mathematical model able to simulate both hydrogen production and glucose degradation on the Ru-doped LaFeO$_3$, optimized in our previous paper [20].

Experimental Methods

Synthesis and photocatalyst characteristics

The Ru doped LaFeO$_3$ photocatalyts at 0.47 mol % of Ru were prepared by solution combustion synthesis, using citric acid as organic fuel and metal nitrate as metal precursor (oxidizer) [21,17]. In detail, 1.66 g of Fe(NO$_3$)$_3$·9H$_2$O (Riedel-deHaen, 97 wt%), 1.78g of La(NO$_3$)$_3$·6H$_2$O (Fluka, 99%), 0.86g of citric acid (Fluka, 99 wt%) and a specific amount of RuCl$_3$ (Sigma Aldrich, 99%) used as dopant, were completely dissolved in 100 ml of bidistilled water. The solution was kept stirred continuously at 60 °C for 5 minutes. Then, ammonium hydroxide (Carlo Erba, 37 wt %) was slowly added to regulate the pH of the solution up to 7.0. The solution was dried at 130° C and then calcined at 300° C for 3 hours to ignite the solution combustion reaction [17]. The Ru nominal loading is expressed as molar percentage and it was evaluated through

Equation 1:

$$\%molRu = \frac{nRu}{nLa=nFe} \cdot 100$$

Where nRu is the number of moles of RuCl$_3$ used in the synthesis;

nLa is the number of moles of La(NO$_3$)$_3$·6H$_2$O used in the synthesis;

and nFe is the number of moles of $Fe(NO_3)_3 \cdot 9H_2O$ used in the synthesis.

Different techniques were used to characterize the photocatalyst from a chemical-physical point of view and the results were reported in our previous work [20]. In summary, the results showed the formation of orthorhombic perovskite type structure and that Ru^{3+} cation partially substitutes Fe^{3+} cation in the perovskite structure. Moreover the absorption edge of Ru-doped $LaFeO_3$ catalysts has a red shift and also a stronger absorption than the pure $LaFeO_3$ in the visible region due to the electronic transition from donor levels formed with Ru^{3+} to the conduction band of the host perovskite structure.
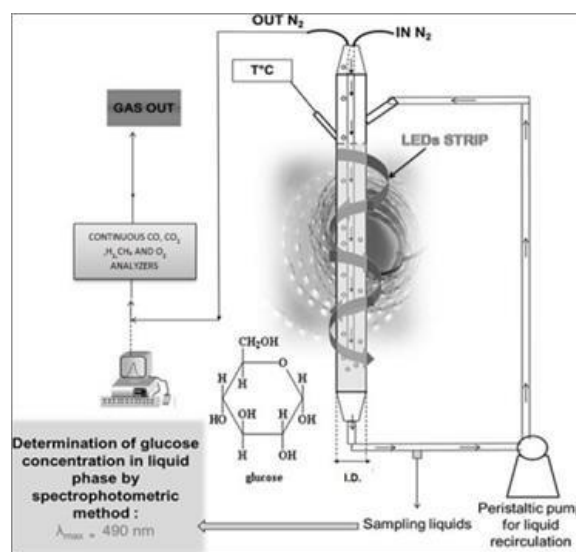
Photocatalytic Tests

With the aim to realizing a mathematical model for the evaluation of reaction kinetics, photocatalytic experiments considered for hydrogen production from glucose aqueous matrices were carried out in a photocatalytic pyrex cylindrical reactor [20,22-24] with internal diameter equal to 1.25 cm equipped with a N2 distributor device (Q=0.122 NL/min) [20]. The experimental set up is represented in (Figure 1).

In a typical photocatalytic test, 0.12 g of 0.47%Ru photocatalytst was suspended in 80 ml of an aqueous solution containing 1000 mg/L of glucose (D + Glucose VWR, Sigma-Aldrich). To ensure complete mixing of the solution in the reactor, a peristaltic pump was used. The photoreactor was irradiated with a strip of UV-LEDs positioned around the external surface of the reactor (nominal power: 10W) with wavelength emission in the range 375–380 nm. The suspension was left in dark conditions for 2 hours to reach the adsorption-desorption equilibrium of glucose on the photocatalyst surface, and then the

reaction was started under UV light up to 4 hours.

About 2 mL of samples were taken from the photoreactor at different times and filtered (filter pore size: 0.45 μm) in order to remove photocatalyst particles before the analyses.

Figure 1: Experimental set up for photocatalytic tests [20]

Chemical Analysis

The characterization of the gaseous phase coming from the photoreactor was performed by continuous CO, CO_2, O_2, H_2 and CH_4 analyzers (ABB Advance Optima). The concentration of glucose was measured by a spectrophotometric method [25] at 490 nm using UV-vis spectrophotometer (Lambda 35, Perkin Elmer). According to the method 2 mL of a carbohydrate solution was mixed with 1 mL of 5 wt% aqueous solution of phenol (Sigma-Aldrich) in a test tube. Subsequently, 5 mL of concentrated sulfuric acid (Sigma-Aldrich) was added rapidly to the mixture. The gluconic acid formed during the irradiation time was quantified by analyzing the UV absorption of liquid samples at 264 nm [26] using the same equipment.

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Mathematical Modelling

Water splitting reaction on 0.47%Ru photocatalyst

Before assessing the mathematical model of photocatalytic hydrogen formation from the degradation of glucose in aqueous solution, the ability of 0.47%Ru photocatalyst in the hydrogen production through water splitting reaction (without glucose) under UV irradiation was evaluated. The results are reported in Figure 1. The amount of hydrogen produced progressively increased as irradiation time increased, reaching a value of 64 μmol (after 4 hours of irradiation) corresponding to 2133 μmol/L, significantly lower than that obtained in presence of glucose that acts as sacrificial agent enhancing the hydrogen production [20]. The amount of hydrogen produced through water splitting reaction during the photocatalytic process followed a linear trend (Figure 2); accordingly, the zero-order kinetic model (Equation 2) perfectly represents experimental data:
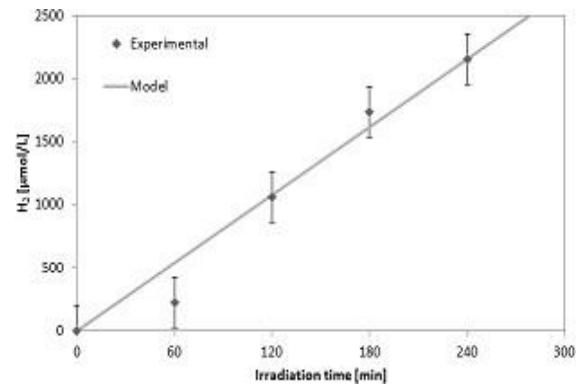
Equation 2:

$$\frac{dnH2}{dt} = K_{ws}.W$$

Where W is the amount of photocatalyst used in the test (0.12 g), nH$_2$ is the millimoles of hydrogen produced, t is the irradiation time (min) and k$_{ws}$ is the kinetic constant of water splitting reaction (mmol/(gcat*min).

The initial condition for Equation 2 was:

t = 0   nH$_2$=0

Equation 2 was solved with Euler iterative method together with the initial condition finding a kws value equal to 0.00513 mmol/ (g$_{cat}$*min).

Figure (2): Fitting of experimental data with zero-order kinetic model for water splitting reaction. Photocatalyst: 0.47%Ru; light source: UV-LEDs; catalyst dosage: 1.5 g/L

Adsorption of glucose on 0.47%Ru photocatalyst in dark conditions

Glucose adsorption on the active surface of the photocatalyst (0.47%Ru) (C*) was evaluated as a function of the equilibrium concentration (C$_{eq}$) under dark conditions (Figure 3).

Different assumptions were made to understand the best model able to fit the obtained experimental data. In particular a first fitting attempt was made with Langmuir isotherm

Equation 3:

$$C^* = \frac{C_m.b.C_{eq}}{1+b.C_{eq}}$$

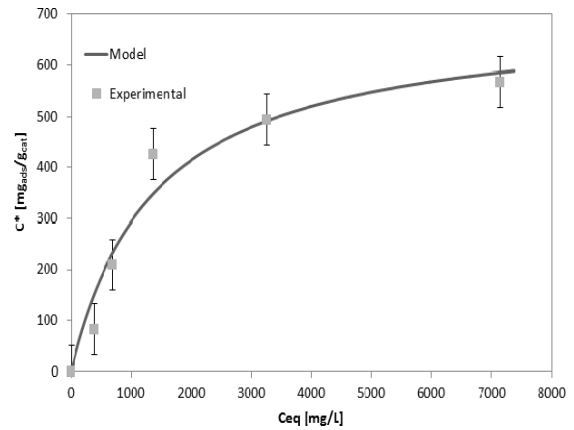Where C* is the amount of glucose adsorbed on catalyst surface [mg$_{glucose}$/g$_{cat}$];

C$_{eq}$ is the glucose equilibrium concentration after dark phase [mg/L];

C$_m$ is the maximum amount of glucose adsorbed on catalyst surface [mg$_{glucose}$/g$_{cat}$];

b is the adsorption equilibrium constant [L/mg].

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The values of b and C_m were achieved using nonlinear regression analysis of the experimental data to fit the Langmuir function for glucose adsorption as a function of C_{eq}. The nonlinear regression procedure was performed using the least-squares approach, based on the minimization of the sum of squared residuals, obtaining 0.00073 and 699 for b and C_m, respectively. Unfortunately, the calculated values did not fit well experimental data (Figure 3). This means that Langmuir isotherm is unable to well represent the behavior of glucose adsorption on the 0.47%Ru surface.

Figure (3): Evaluation of glucose adsorbed on 0.47%Ru sample. Catalyst dosage: 1.5 g/L

Figure (4): Fitting of adsorption experimental data with Langmuir–Hinshelwood (L–H) isotherm for the evaluation of adsorption constant b. Sample: 0.47%Ru; catalyst dosage: 1.5 g/L

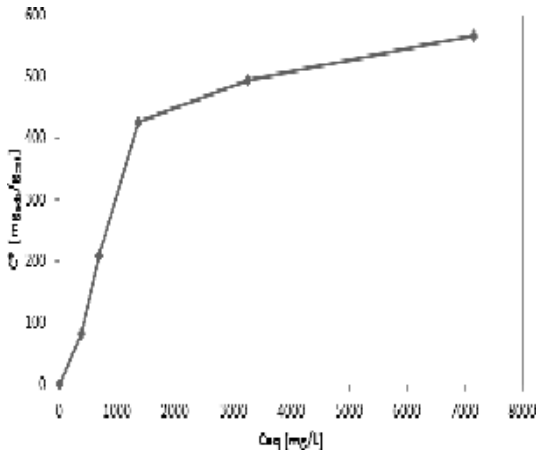The second attempt to find an adsorption law able to fit experimental data was made with Freundlich isotherm

Equation 4:

$$C^* = K. \, C_{eq}^{1/n}$$

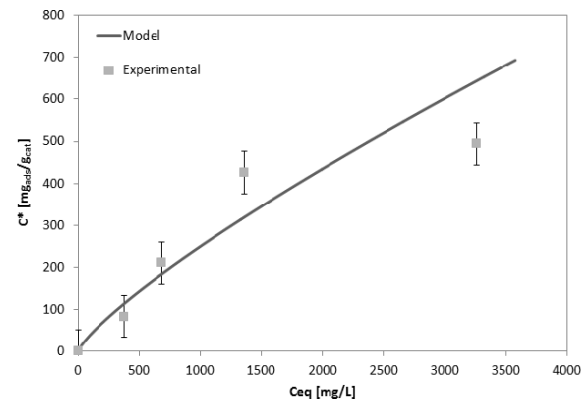Where k is the Freundlich constant that corresponds to adsorption capacity [27];

n is the adsorption intensity [27]

Constants k and 1/n were evaluated as 0.97 and 0.80, respectively by fitting the experimental data as a function of C_{eq} (Figure 5).

Figure (5): Fitting of adsorption experimental data with Freundlich isotherm. Sample: 0.47%Ru; catalyst dosage: 1.5 g/L
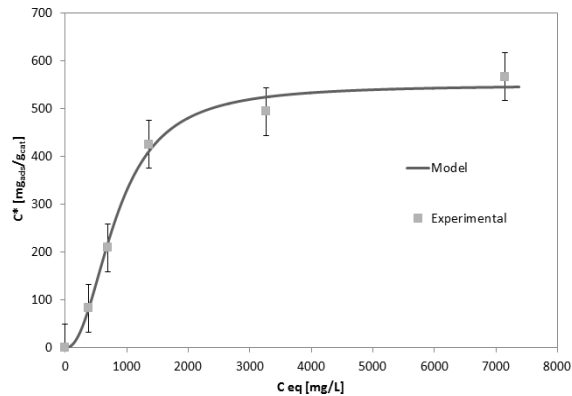
Unfortunately, also Freundlich isotherm model was not able to well represent the behavior of the experimental data. However, possible alternative approach for the definition of an adsorption model in catalytic reactions is represented by the Langmuir-Freundlich isotherm [28]. The Langmuir-Freundlich isotherm is a versatile isotherm expression that can simulate both Langmuir and Freundlich behaviors [29]. A general form of Langmuir-Freundlich isotherm can be written as follow (Equation 5):

$$C^* = \frac{C_{m.}(b.C_{eq})^n}{1+(b.C_{eq})^n}$$

Also in this case the fitting procedure was finalized by using the least squares approach, whose results are reported in Figure 6. The fitted values of b and n are 0.0012 and 2.21, respectively.

Figure (6): Fitting of adsorption experimental data with Langmuir-Freundlich (L-F) isotherm. Sample: 0.47%Ru; catalyst dosage: 1.5 g/L

The comparison between the experimental data and those ones calculated by isotherm equation (Equation 5) clearly indicates that the Langmuir-Freundlich can be used to describe the behavior of the amount of adsorbed glucose as a function of its equilibrium concentration. The non-linear behavior occurring for glucose concentrations lower than 1000 mg/L may happen because adsorbate-adsorbate interactions are stronger than adsorbate-adsorbent interactions [28].

Kinetic modelling of the photocatalytic glucose degradation and hydrogen production on 0.47%Ru photocatalyst

Before to develop the kinetic modeling of the photocatalytic glucose degradation and hydrogen production on 0.47%Ru photocatalyst, the fluid dynamics of the system was preliminarily evaluated by the determination of the Reynolds number Equation 6:

$$Re = \frac{D.V.P}{\mu} = 15963$$

Where D is the reactor diameter = 1.25 cm;

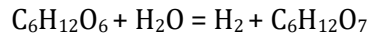v is the velocity of the liquid inside the reactor = 118 cm/min;

ρ is the density of the liquid solution (approximately equal to that water)= 1 g/cm3;

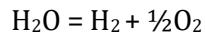μ is the water dynamic viscosity= 0.01 g/cm s.

The obtained value for Reynolds number (15963) indicates a very turbulent regime inside the reactor, being Re > 2100. This result allows to assume the absence of external mass-transfer limitations since the simultaneous presence of the flow turbulence and a good stirring is usually enough for the effect of external transfer to vanish [30]. Moreover it was possible to neglect the liquid-gas transport phenomena in the kinetic model. Considering these simplifications with together the experimental results obtained in our previous work [20] and those ones presented in (Figure 1), the mathematical modeling on 0.47%Ru was developed

Vaiano V, Lervolino G, Sannino D, et al. (2007) Mathematical Modelling of Photocatalytic Hydrogen Production from Glucose on Ru-doped LaFeO$_3$. J Adv Eng; 1(1): 1-106.

considering that, in the batch photoreactor, occur mainly the following reactions:

Equation 7:

$C_6H_{12}O_6 + H_2O = H_2 + C_6H_{12}O_7$

Equation 8:

$H_2O = H_2 + \frac{1}{2}O_2$

In order to determine the best kinetic model for the degradation of glucose using the experimental data with an initial concentration of glucose equal to 2000 mg/L, three different models were evaluated: Langmuir-Freundlich-Hinshelwood (L-F-H) kinetic type model, first order kinetics; and zero-order kinetics.

The L-F-H kinetic model can be written as follows:

Equation 9:

$$V\frac{dC}{dt} = -k.\frac{C_m.(b.C_{eq})^n}{1+(b.C_{eq})^n}.W$$
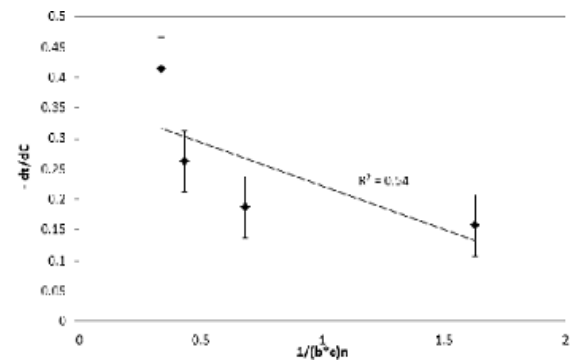
This equation can be arranged as:

Equation 10:

$$\frac{dt}{dC} = \alpha.\left(\frac{1}{(b.C)^n}\right)$$

Equation 11

$$\alpha = \frac{V}{K.W.C_m}$$

Where b and n are the constant previously evaluated, C is the glucose concentration during the irradiation time, k is the apparent kinetic constant, V is the solution volume and t is the irradiation time. The experimental data as well as the correlation coefficient (R^2) are shown in (Figure 7).

Figure (7): Langmuir-Freundlich-Hinshelwood (L-F-H) kinetic model for the evaluation of k. Initial glucose concentration: 2000 g/L; photocatalyst: 0.47%Ru; light source: UV-LEDs; catalyst dosage: 1.5 g/L

Unfortunately, the correlation coefficient R^2 in this case was equal to 0.54, indicating that the L-F-H kinetic model is not able to describe the degradation of glucose during the irradiation time.

The second assumption was the first order kinetic. The first-order model describes the systems where degradation rate depends on the amount of glucose molecules in the solution
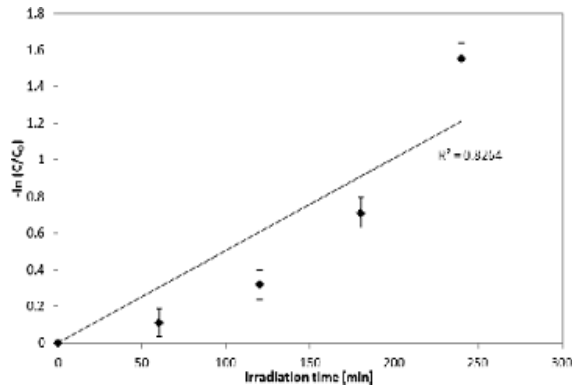
Equation 12:

$$-\ln\frac{C}{C_0} = K.\frac{W}{V}.t$$

Where C_0 is the concentration of glucose in aqueous solution after the dark phase.

Also in this case, the kinetic model doesn't fit the experimental data. In fact, the R^2 value was equal to 0.82 (Figure 8).

Figure (8): First-order kinetic model. Initial glucose concentration: 2000 g/L; photocatalyst: 0.47%Ru; light source: UV-LEDs; catalyst dosage: 1.5 g/L

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The last hypothesis investigated was the zero order kinetic models

Equation 13:

$$C - C_0 = -K.\frac{W}{V}.t$$

In this case (Figure 9) the experimental data are well described by the zero order kinetic model, being the R^2 value equal to 0.95. This model was used for the estimation of the apparent kinetic constant of glucose degradation.

Figure (9): Zero-order kinetic model. Initial glucose concentration: 2000 g/L; photocatalyst: 0.47%Ru; light source: UV-LEDs; catalyst dosage: 1.5 g/L
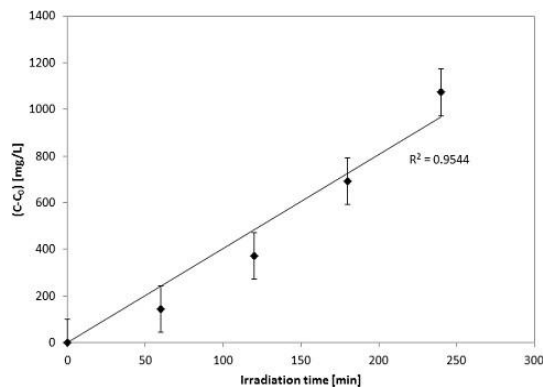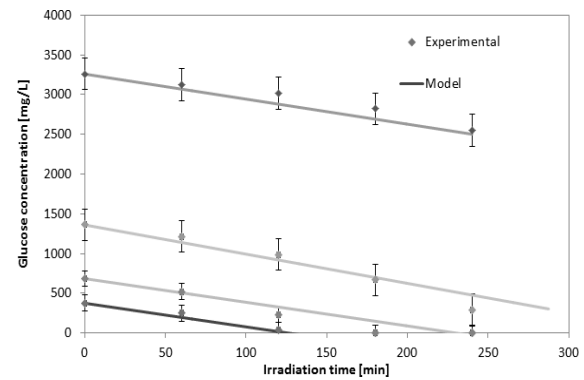

Considering the amount of photocatalyst (W=0.12 g) and the solution volume (V= 80 mL) used in the experimental test, the slope of the straight line reported in (Figure 9) allows to obtain the value of k, which resulted equal to 2.1 ± 0.3 [mg/ (g min)]. Finally, the experimental data obtained with different initial glucose concentrations were compared with the calculated values to analyze the ability of the model to predict the experimental data at 500, 1000, 2000 and 4000 mg/L initial glucose concentration.

Figure (10): Comparison between model calculation and experimental data for different glucose concentrations. Photocatalyst: 0.47%Ru; light source: UV-LEDs; catalyst dosage: 1.5 g/L

The calculated values are in good agreement with all the experimental data (Figure 10). It is important to note that also for the higher initial sugar concentration (4000 mg/L), this system is able to predict the glucose degradation trend with a single value of kinetic constant.

Using the k value of the glucose degradation, it was calculating the value of water splitting kinetic constant (kws) in presence of the target sugar in the aqueous medium using the experimental data with an initial glucose concentration of 2000 mg/L and optimizing the model for the hydrogen production that can be expressed as:

Equation 14:

$$\frac{dnH_2}{dt} = k \cdot \frac{W}{Mw} + k_{ws} \cdot W$$

Where M$_w$ is the molecular weight of glucose and nH$_2$ is the millimoles of hydrogen produced during the irradiation time.
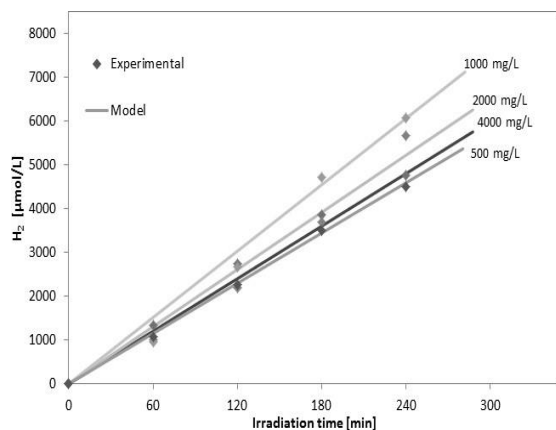
The initial condition for Equation 14 was:

t = 0   nH$_2$=0

The calculated data and the experimental ones in terms of H$_2$ production for the different initial concentration of glucose are included in supplementary material (Figure 11).

The fitting procedure was finalized using the same procedure used for the estimation of the kinetic constant of glucose degradation, obtaining the k$_{ws}$ value equal to 0.003 ± 0.2 [mmol/ (g min)], different from the kws evaluated in the water splitting experiment (section 3.1).

Figure (11): Comparison between model calculation and experimental data for hydrogen production at different glucose initial concentrations. Photocatalyst: 0.47%Ru; light source: UV-LEDs; catalyst dosage: 1.5 g/L

In particular, in the presence of glucose, the kws value was lower than that one obtained in the water splitting reaction (without glucose in aqueous solution), indicating that the hydrogen production preferentially comes from the glucose degradation reaction that inhibits the water splitting reaction. The calculated values are in good agreement with all the experimental data also for the photocatalytic hydrogen production obtained at different glucose initial concentrations.

Conclusion

The photocatalytic hydrogen production from glucose aqueous solutions using Ru-doped LaFeO$_3$ photocatalyst under UV light emitted by LEDs was investigated in a batch photoreactor, performing mass balance on glucose in liquid medium and hydrogen in gaseous phase at different operating conditions. The obtained results allowed to develop a simplified mathematical model based on zero order kinetic both for glucose degradation and hydrogen production. Model parameters estimation was realized by individuating the best agreement between the calculated values and experimental data as a function of irradiation time. On the basis of these results, the accuracy of the model was tested for different initial glucose concentration evidencing a very good fitting between experimental and model data.

References

1. Ni M, Leung MKH, Leung DYC, et al. (2006) A review and recent developments in photocatalytic water-splitting using TiO2 for hydrogen production. Renewable Sustainable Energy Rev; 11(3): 401-425.

2. Ruppert AM, Weinberg K, Palkovits R (2012) Hydrogenolysis goes bio: from

Vaiano V, Lervolino G, Sannino D, et al. (2007) Mathematical Modelling of Photocatalytic Hydrogen Production from Glucose on Ru-doped $LaFeO_3$. J Adv Eng; 1(1): 1-106.

3. carbohydrates and sugar alcohols to platform chemicals. Angew Chem Int Ed Engl; 51(11): 2564-2601.

4. Zieliñska B, Borowiak-Palen E, Kalenczuk RJ (2008) Photocatalytic hydrogen generation over alkaline-earth titanates in the presence of electron donors. International Journal of Hydrogen Energy; 33(7):1797-1802.

5. Antoniadou M, Vaiano V, Sannino D, et al. (2013) The Chemical Engineering Journal and the Biochemical Engineering. Journal; Chemical Engineering Journal; 224: 144- 148.

6. Gomathisankar P, Yamamoto D, Katsumata H, et al. (2013) Photocatalytic hydrogen production with aid of simultaneous metal deposition using titanium dioxide from aqueous glucose solution. Int J Hydrogen Energy; 38(14): 5517-5524.

7. Kawai T, Sakata T (1980) Conversion of carbohydrate into hydrogen fuel by a photocatalytic process. Nature (London); 286: 474-476.

8. Wu G, Chen V, Zhou G, et al. (2008) H2 production with low CO selectivity from photocatalytic reforming of glucose on metal/TiO2catalysts. Sci China Ser B Chem; 51(2): 97-100.

9. Schneider J, Matsuoka M, Takeuchi M, et al. (2014) Understanding TiO2 Photocatalysis: Mechanisms and Materials. Chem. Rev. (Washington, DC, U. S.); 114(19): 9919-9986.

10. Vaiano V, Iervolino G, Sarno G, et al. (2015) Simultaneous Production of CH4 and H2 from Photocatalytic Reforming of Glucose Aqueous Solution on Sulfated Pd-TiO2 Catalysts. Oil and Gas Science and Technology; 70(5): 891-902.

11.

Wu MC, Chang IC, Huang WK (2014) Correlation between palladium chemical state and photocatalytic performance of TiO2–Pd based nanoparticles. Thin Solid Films; 570: 371-375.

12. Clarizia L, Somma ID, Onotri L, et al. (2017) Kinetic modeling of hydrogen generation over nano-Cu(s)/TiO2 catalyst through photoreforming of alcohols. Catal. Today; 281(1): 117-123.

13. Iervolino G, Vaiano V, Murcia JJ, et al. (2016) Photocatalytic hydrogen production from degradation of glucose over fluorinated and platinized TiO2catalysts. Journal of Catalysis; 339: 47-56.

14. Gallego J, Mondragon F, Batiot-Dupeyrat C, et al. (2013) Simultaneous production of hydrogen and carbon nanostructured materials from ethanol over LaNiO3 and $LaFeO_3$ perovskites as catalyst precursors. Appl Catal A; 450: 73-79.

15. Sun X, Xie Y, Wu F, et al. (2015) Photocatalytic Hydrogen Production over Chromium Doped Layered Perovskite Sr2TiO4. Inorg Chem; 54(15): 7445-7453.

16. Lu L, Ni S, Liu G, et al. (2017) Int. J. Hydrogen Energy.

17. Li S, Jing L, Fu W, et al. (2007) Photoinduced charge property of nanosized perovskite-type $LaFeO_3$ and its relationships with photocatalytic activity under visible irradiation. Materials Research Bulletin; 42: 203-212.

18. Iervolino G, Vaiano V, Sannino D, et al. (2016) Production of hydrogen from glucose by $LaFeO_3$ based photocatalytic

Vaiano V, Lervolino G, Sannino D, et al. (2007) Mathematical Modelling of Photocatalytic Hydrogen Production from Glucose on Ru-doped LaFeO$_3$. J Adv Eng; 1(1): 1-106.

process during water treatment. International Journal of Hydrogen

19. Tijare SN, Joshi MM, Rayalu SS, et al. (2012) Photocatalytic hydrogen generation through water splitting on nano-crystalline LaFeO$_3$ perovskite, ACS National Meeting Book of Abstracts; 37(13):10451-10456.

20. Parida KM, Reddy KH, Martha S, et al. (2010) Fabrication of nanocrystalline LaFeO$_3$: An efficient sol–gel auto-combustion assisted visible light responsive photocatalyst for water decomposition. International Journal of Hydrogen Energy; 35: 12161-12168.

21. Iervolino G, Vaiano V, Sannino D, et al. (2017) Enhanced photocatalytic hydrogen production from glucose aqueous matrices on Ru-doped LaFeO$_3$. Appl Catal B; 207: 182-194.

22. Hwang Y, Kang DS, Park MH (2010) Solution combustion synthesis and surface properties of LaFeO$_3$ powders. Journal of Ceramic Processing Research; 11(3): 397-400.

23. Vaiano V, Sacco O, Stoller M, et al. (2014) Effect of solar simulated N-doped TiO2 photocatalysis on the inactivation and antibiotic resistance of an E. coli strain in biologically treated urban wastewater. International Journal of Chemical Reactor Engineering; 144:369-378.

24. Vaiano V, Sacco O, Sannino D (2015) Nanostructured N-doped TiO2 coated on glass spheres for the photocatalytic removal of organic dyes under UV or visible light irradiation. Ciambelli, Applied Catalysis B: Environmental; 170-171, 153-161.

25. Vaiano V, Sacco O, Sannino D

Energy; 41(2): 959-966.

(2015) Photocatalytic removal of spiramycin from wastewater under visible lightwith N-doped TiO2 photocatalysts. Chemical Engineering Journal; 261: 3-8.

26. Dubois M, Gilles KA, Hamilton JK, et al. (1956) Colorimetric Method for Determination of Sugars and Related Substances. Analytical Chemistry; 28(3): 350-356.

27. Li Y, Wang J, Peng S, et al. (2010) Photocatalytic hydrogen generation in the presence of glucose over ZnS-coated ZnIn2S4 under visible light irradiation. International Journal of Hydrogen Energy; 35: 7116-7126.

28. Desta MB (2013) Batch Sorption Experiments: Langmuir and Freundlich Isotherm Studies for the Adsorption of Textile Metal Ions onto Teff Straw (Eragrostis tef) Agricultural Waste. Journal of Thermodynamics 1.

29. Jeppu GP, Clement TP (2012) A modified Langmuir-Freundlich isotherm model for simulating pH-dependent adsorption effects. Journal of Contaminant Hydrology; 129-130, 46-53.

30. Nahm MH, Herzenberg LA, Little K, (1977) A new method of applying the Sips equation. Journal of Immunology; 119(1): 301-305.

31. Bouchy M, Zahraa O (2003) Photocatalytic reactors. International Journal of Photoenergy; 5(3): 191-197.