

Preliminary study of hydrogen production from local arid area algae in a bubble column

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Abstract: Fighting climate change and ensuring sustainable development is one of the greatest concerns nowadays. In this regard, energy production from biomass is already a reality and presents tremendous possibilities of use as an alternative source. Among the various technologies, hydrogen production from microalgae is a promising clean energy alternative. Indeed, some unicellular green algae have the ability to produce hydrogen simply in the presence of water and light. However, an important factor governing the efficiency of hydrogen production by microalgae depends on the method of production. Designing a suitable bioreactor is therefore very important in order to control the main production parameters. Hence, a suitable bubble agitation system, with proper bubble size, that keeps algal cells in suspension is proposed.

The present work foresees a tentative method of hydrogen production from *Chlamydomonas sp.*, a local alga from the arid area of Adrar (southern Algeria). This is performed in a photobioreactor of the type of a bubble column. It should be noted that a hydrodynamic study of the bubble column has been previously conducted. This has led to a proper choice of the diffuser and an approximate assessment of microalgae culture parameters. Moreover, various process parameters were monitored under a given light intensity, namely: pH, temperature, dissolved oxygen, etc. The observations show massive growth of the algae biomass which indicates a good adaptation of this type of photobioreactors for microalgae production, and subsequently hydrogen production as long as low rates are required.

Keywords: Renewable Energy, Hydrogen, Microalgae, Photobioreactor, Bubble column.

1. Introduction

World energy consumption can only grow given the accelerated growth of the population. It is largely dominated by fossil fuels (oil, natural gas and coal) as the sole energy source. Moreover, their massive use exposes the planet to two major problems: a devastating pollution caused by the emission of greenhouse gases and the depletion of fossil fuel reserves. The growing awareness about the risks of climate change and the conditions for sustainable development of the planet led to the search for alternative energy sources more environmentally friendly as substitute for fossil fuels. Ultimately, renewable energies are the best alternative. However, they have the disadvantage of not being competitive yet for many applications. More specifically, hydrogen appears to be the ideal alternative energy source and represents a serious hope to achieve an industrial era with considerably lower carbon dioxide emission. Indeed, it is considered as a viable alternative and as "the energy carrier of the future. Biologically produced hydrogen is a promising alternative to produce clean energy as it shares both advantages of being renewable and nonpolluting. In fact, from just water and solar energy, some unicellular green algae or cyanobacteria are known for their ability to provide hydrogen by photosynthesis [1]. However, for purely economic reasons, it is difficult to accept that biologically produced hydrogen may compete with other modes of production [2]. Bubble column reactors are mainly used in various industries such as: chemical, petrochemical, biological, bioenergetic...etc, due to their simple construction and their low operating costs. The gas holdup and the bubble size constitute important parameters for the study of the flow patterns in a bubble column. In addition, bubble size distribution, as well as

the gas holdup depends on some parameters such as: column geometry, operating conditions, physicochemical properties of the two phases put in contact and the type of gas sparger [3]. The liquid is assumed to be mixed by the motion of gas bubbles in it. However, the use of a gas sparger which generates small bubbles distributed with homogeneous way throughout the column ensures a better mixture [4].

The aim of the present work is to undertake preliminary test of photobiological production of hydrogen from microalgae strains isolated locally in Algeria. A Pyrex made bubble column type photobioreactor has been designed for this purpose with the possibility of controlling some of the culture parameters such as light intensity, thus allowing the optimization of certain operating conditions. To the dispersion of the gas phase, the total gas holdup, the bubble size distribution within the column are studied. So, the bubble diameter was measured by using a photographic method, with the help of a millimetre.

2. Methodology

2.1. Material and methods

2.1.1. Strain and culture medium used

Microalgae used in this study were isolated from freshwater samples collected from southern Algeria. The microalgal species used is a locally isolated *Chlamydomonas sp.* The culture medium used is tri-acetate phosphate (TAP) which is adjusted to pH 7.2. This medium is widely used for cultivation of microalgae for the purpose of hydrogen production.

2.1.2. Experimental set-up

The experimental set-up used in this study is a cylindrical Pyrex column of 0.04m internal diameter and 0.86m height, provided with several lateral pipes (Figure 1). Stirring provided by injecting air through a porous sintered glass diffuser of porosity 40 μ m, which is placed at the bottom of the column. The airflow is controlled by a flowmeter. It should be noted that a preculture is first prepared and inoculated in the column in 900 ml of culture medium. Bubbling with nitrogen is recommended to create anoxia (low dissolved oxygen) and counteract the inhibition of hydrogen production.

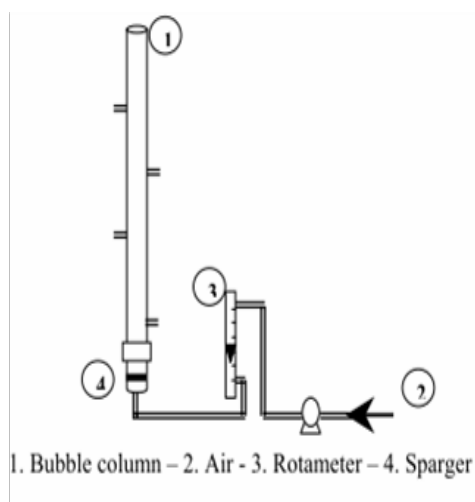


Fig. 1. Experimental set-up

2.1.3. Microalgae growth

The growth of microalgae is favorable in the presence of a culture medium rich in nutrients and exposed to sufficient luminous intensity. Different factors may influence the growth and the production of hydrogen from microalgae [5]. The experiments were performed in the bubble column inoculated with a preculture of *Chlamydomonas sp.*, which allowed us to follow the temporal evolution of biophysical parameters such as: dissolved oxygen, pH and Temperature, etc. Microalgal cell count was performed using a microscope. The count is carried out with a cell count, which allows us to check any contamination present in the medium. An average of three samples is performed for each test.

2.1.4. Gas retention

The gas retention is given according to superficial gas velocity and the type of the sparger. For bubble columns the gas holdup, ϵ_g , is given by the following relation:

$$\epsilon_g = \frac{\Delta H}{\Delta H + H_L} \quad (1)$$

Where:

H_L : Height of the liquid before injection of gas.

ΔH : Increase in the level of the liquid after gas expansion.

2.1.5. Bubble diameter

The average diameter of the bubbles is measured by a photographic method. The pictures of the bubbles were taken at a certain distance to the bottom of the column where the distribution of the bubbles is uniform with a using numerical photograph (SONY). Then, the photographs are treated and the diameter of the bubble is calculated using the software Matlab 6.5. The shape of the bubbles is generally ellipsoidal.

The local bubble diameter was calculated using the following relationship:

$$d_i = \sqrt[3]{a^2 b} \quad (2)$$

Where a and b are the diameter and the width of the ellipsoid respectively.

For each gas velocity, the average Sauter diameter is calculated from the following relation:

$$d_{32} = \frac{\sum_i n_i \cdot d_i^3}{\sum_i n_i \cdot d_i^2} \quad (3)$$

n_i : the number of the bubbles with an individual diameter d_i .

2.1.6. Axial dispersion

The model employed is the one used to characterize flows in tubular engines. It takes into account two effects: convection, which represents the flow in block, and dispersion, which results from the molecular and turbulent diffusion. There are two types of contributions to dispersion: radial and axial [6]. The radial effect is negligible compared to the axial effect

when the ratio L/D is greater than 4. With these considerations, the transient matter assessment in the tracer is written as:

$$\frac{\partial C}{\partial t} = D_z \frac{\partial^2 C}{\partial z^2} - u \frac{\partial C}{\partial z} \quad (4)$$

Where C is the concentration of the tracer, u the speed of the fluid, D_z the axial dispersion coefficient, z the axial co-ordinate and t, the time

The solution of equation (4) is then:

$$\frac{c(t, z)}{c_E} = 1 + \frac{2L}{\pi\beta} \sum_{n=1}^{\infty} \left\{ \frac{1}{n} \sin\left(\frac{n\pi}{L}\beta\right) \cos\left(\frac{n\pi}{L}z\right) \exp\left[-\left(\frac{n\pi}{L}\right)^2 D_z t\right] \right\} \quad (5)$$

3. Results and discussions

3.1. Gas retention

The mixing of the liquid phase is ensured by the injection of gas. The study of the dispersion of the gas phase can bring information on the flow within the column. The gas retention ε_g , which is one of the most important parameters characterising the hydrodynamics of the bubble column reactors, depends mainly on the superficial gas velocity and the type of gas sparger. According to M.S. Michaud, 2001 [4], there is no significant difference in the value of gas retention according to the type of sparger used.

Our results, presented in figure 2, show clearly the influence of the type of sparger on the gas holdup. According to this figure, we observe that for superficial gas velocity lower than 0.03 m/s, the gas retention is similar for the two spargers. For high superficial gas velocity, however, the gas holdup obtained for sparger 1 is higher than that obtained in sparger 2. So the type of sparger does influence the gas holdup for high gas regimes. Indeed, sparger 1 (150 μ m) generates large bubbles and thus increases the gas retention in the whole column. Moreover, the gas retention increases with increasing gas velocity, which is in agreement with the observations of Thomas et al. (1989) [7].

The dependence of the gas holdup on the superficial gas velocity v_g , can be written as:

$$\varepsilon_g = C. (v_g)^\alpha$$

The experimental values of C and α obtained in this work are: C=12.091 and $\alpha=0.747$ for the sparger 1(150 μ m), which is in agreement with the work of Shah and al, 1982 [9]. According to this author, the exponent α varies usually from 0.7 to 1.2 for bubbly flow. As for sparger 2 (40 μ m), the constant C was 7.1511 and α was 0.6775 which corresponds to a heterogeneous flow where the exponent α ranged from 0.4 to 0.7 according to the same author. Figure 3 illustrates the experimental results compared to those found in the literature. For low superficial gas velocities our experimental results are in good agreement with those from the literature. However, for high gas velocities, the results diverge due mainly to the operating conditions and to the type of spargers used.

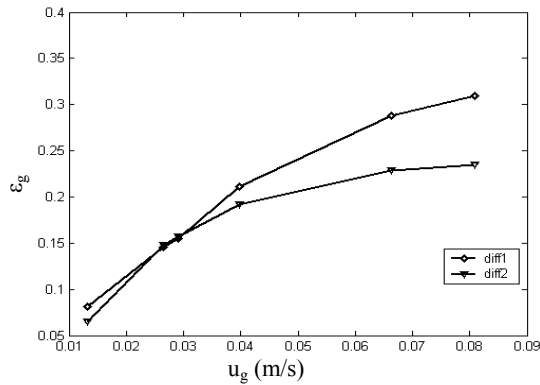


Fig. 2. Gas retention vs superficial gas velocity

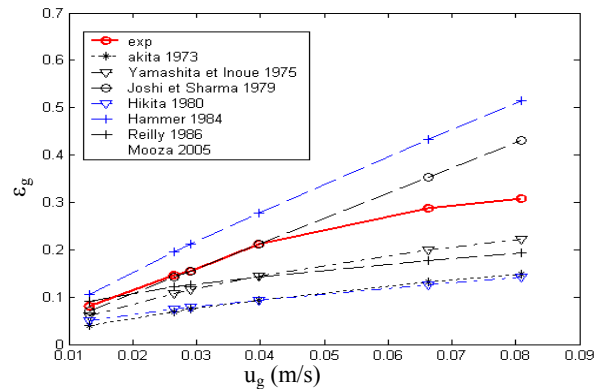


Fig. 3. Gas retention vs superficial velocity compared with the literature data

3.2. Bubble diameter

Bubble size is a very significant parameter for better understanding the gas dispersion within the column. In bubble column reactors, the variations of the average diameter of the bubbles depends on the type of gas sparger [8], and the Sauter diameter increases slightly with the increase of superficial gas velocity. For our study, the variation of the bubble size according to the superficial gas velocity is represented in figure 4, we notice that the average diameter of the bubbles increases with increasing gas velocity. We also observe a coalescence of the bubbles beyond a gas velocity of 0.033 m/s; at which point, the size of the bubbles becomes difficult to determine. The bubbles are generally ellipsoidal and for the porous spargers used, the bubble diameter ranges from 2,5 mm to 8,5 mm. For the two spargers, The Sauter diameter varies similarly according to the superficial gas velocity (Figure 5). However, for sparger 1, the Sauter diameter is about 5mm, while for sparger 2, the Sauter diameter is 7.5mm.

We also represent in the figure 4 and 5 the Sauter diameter and the average diameter for the two spargers. We note that the variation follows the same increasing pattern. However, sparger 1 presents larger bubbles than those generated by sparger 2.

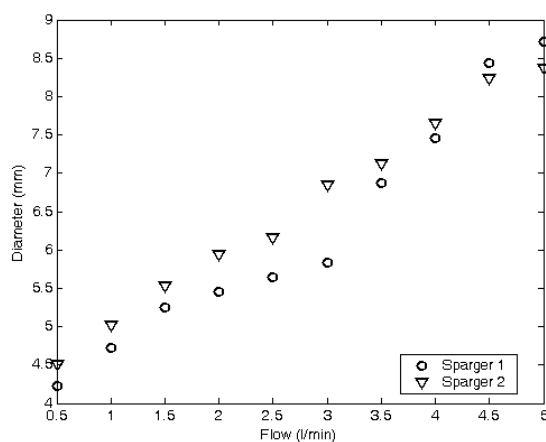


Fig. 4. Mean bubble diameter versus the injection gas velocity.

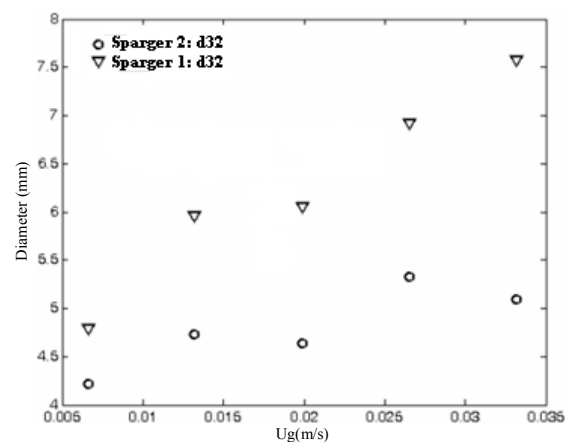


Fig. 5. Sauter diameter vs superficial gas velocity

3.3. Modelling of the column

The computed curves are generated using a model with axial dispersion. The results obtained are represented in figure 6 and 7 for each flow and each type of diffuser. The experimental data points are represented and compared with the model of axial dispersion. The parameters of the model are adjusted in order to obtain a good adjustment of the model to the experimental data using MATLAB 6.5. We note that for a bubble column in batch mode, the SDR fits the model of axial dispersion almost perfectly. The expression used is that of Eq. 5 and the results of this model seem to be in agreement with the experimental data. Figure 7 represent the exit of the tracer for diffuser 1 (150 μ m) for flow gas of $Q_G = 3$ l/min.

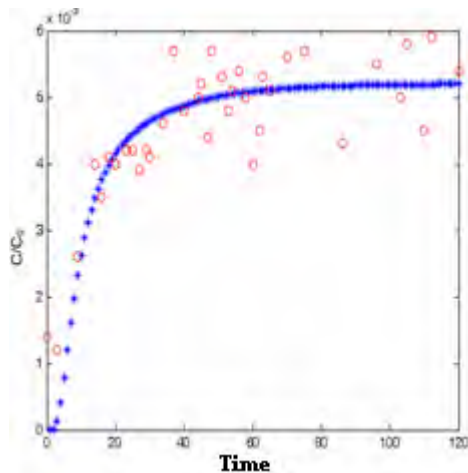


Fig. 6. Exit-tracer concentration in batch mode
($D=150\mu\text{m}$, $Q_G=1$ l/min)

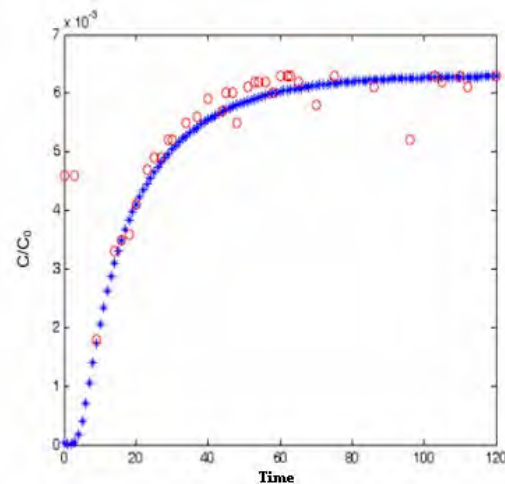


Fig. 7. Exit-tracer concentration in batch mode
($D=150\mu\text{m}$, $Q_G=3$ l/min)

3.4. Microalgae growth

For a light intensity of 7800 lux, a considerable evolution of microalgal biomass is observed over time. Figure 8 shows the change in optical density vs. time and informs us about the temporal evolution of the growth of microalgae. It is noted that this curve actually reflects the growth kinetics of the *Chlamydomonas sp.* Strain, reaching a maximum after 98 hours of cultivation, then a stationary phase where the concentration of biomass is stable

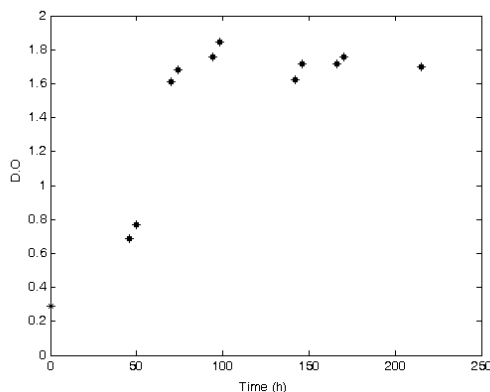


Fig. 8. Evolution of optical density vs Time

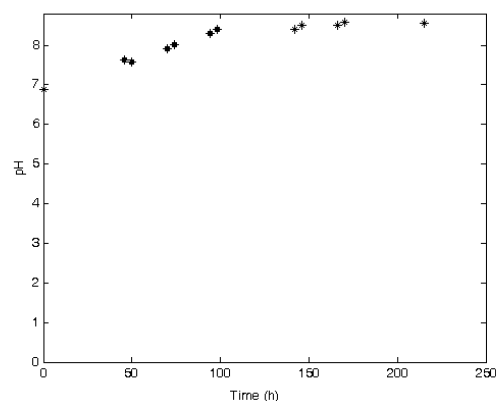


Fig. 9. pH vs time in growth algae

An increase of pH, while remaining within the range of 6.9 and 8.5, is also observed during growth (Figure 9). This increase reflects the growth of microorganisms. The pH increase is due to the microalgae photosynthetic activity. Given the fact that microalgae absorb CO_2 very

rapidly, the pH of the medium moves to values above 7.5 in the case where CO₂ demand of microalgae is higher than its supply to the middle. The variation of dry matter is shown in Figure 10 an increase in dry matter over time is observed, reflecting the concentration in the cell culture medium. However, a decrease of dry matter towards the end of growth is noted. The evolution of dissolved oxygen during growth is also monitored. Overall, dissolved oxygen increases over time during the period of illumination.

This also reflects the photosynthetic activity and hence the growth of microalgae (Fig. 11). The measured dissolved oxygen concentrations are in the range of 2.9 to 11.7mg/L.

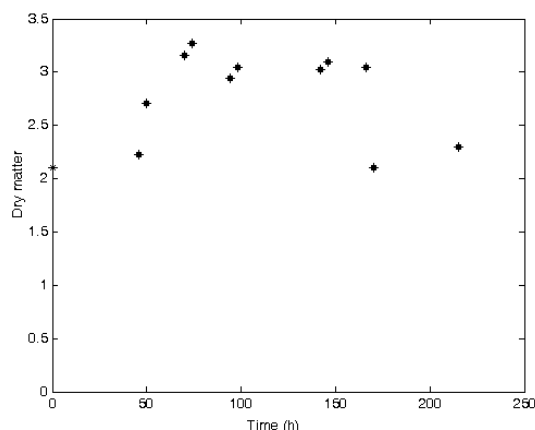


Fig. 10. Dry matter vs time

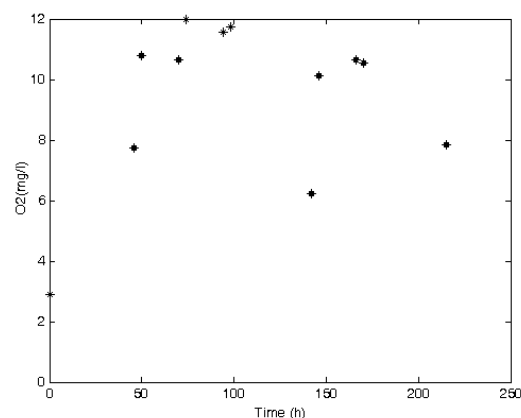


Fig. 11. Dissolved oxygen vs time

Preliminary tests of hydrogen production by the *Chlamydomonas sp.* strain are undertaken in the bubble column serving as a photobioreactor. The column is equipped with a mechanical agitation system to keep algal cells in suspension and prevent them from settling. It is noteworthy that during the hydrogen production testing, nitrogen bubbling is performed to achieve anoxia and induce the production of hydrogen [9, 10]. At the beginning of culture, the dissolved oxygen content is relatively constant. Beyond 20 minutes, it increases due to photosynthesis (O₂ release). However, a short period after the cultivation initiation, we note the formation of small bubbles through the capillary tube leaving the bubble column type photobioreactor (gas trapping system). This can be explained by the fact that culture was in anoxia which favored the production of hydrogen (transcription of the Fe-hydrogenase). This is followed by an increase of oxygen dissolved in the medium which inhibits the production since bubbles are no longer observed. These observations are consistent with those reported by [11].

4. Conclusion

Bubble columns equipped with porous spargers offer a greater gas-liquid contact area as bubbles created by this type of spargers are numerous and far smaller. The use of porous spargers seems to be advantageous compared to the other types because of the multiple points of injection. According to the experimental results obtained, the type of sparger influences the gas retention for high superficial gas velocities. Moreover, the diameter of the bubbles increases with increasing gas velocity. We also note that the gas holdup and the Sauter diameter agree well with results reported in the literature. In the present study, the culture of locally isolated microalgae in a bubble column type photobioreactor is tested; followed by a preliminary investigation of hydrogen production.

The growth and massive evolution of algal biomass in this reactor type demonstrate the suitability of this type of reactor for the cultivation of microalgae. Subsequently, preliminary tests of the biological production of hydrogen by microalgae show that anoxia is achieved by nitrogen bubbling in the culture medium; which allowed observation a hydrogen production but for a short period of time only.

Thus, the preliminary tests of photobiological production of hydrogen by an algal strain and in a bubble column remain conclusive despite its transient character under the present conditions. The question that arises is how to maintain the conditions of the onset of hydrogen production for longer periods of time so to make it economically viable.

In order to elucidate a number of phenomena hitherto unexplained, this work is to be pursued and deepened to address these questions and more particularly in regard to the implementation of more adapted micro algal strains for hydrogen production in photobioreactors

References

- [1] H. Gaffron, J. Rubin, Fermentative and photochemical production of hydrogen in algae, *J Gen Physiol*, 1942, 26: 219–240
- [2] I. Akkerman, M. Janssen, J. Rocha, R. H. Wijffels, Photobiological hydrogen production : photochemical efficiency and bioreactor design”, *International Journal of Hydrogen Energy*, 2002, 27 :1195–1208
- [3] E. Camarasa, C.Vial, S. Poncin, G. Wild, N. Midoux, J. Bouillard, Influence of coalescence behaviour of the liquid year D of gas sparging one hydrodynamics and bubble characteristics in A bubble column. *Chemical Engineering and Processing*, 1999, 38, 329-344
- [4] M.S. Michaud, Hydrodynamic and biological study of one proceeds of methanisation has biofilm: the engine has turbulé bed opposite. Thesis of doctorate, I.N.S.A. France, 2001
- [5] M. J. G. V. Barbosa, Microalgal photobioreactors: scale up and optimization, Thesis, Wageningen University, Wageningen, The Netherlands, 2003
- [6] A. Behkish, Hydrodynamic and mass transfer parameters in large-scale slurry bubble column reactors, Ph.D. University of Pittsburgh, School of engineering, 2004
- [7] D. Thomas, A. Bernis, Incidence of the aptitude for the coalescence of the fluid on the hydrodynamics of the bed fluidized triphasic reverse functioning with counter-current; *Recent Progress in Genius of the Processes*, 1989 3(89), 161-166
- [8] Y.T. Shah, B.G. Kelkar, S.P. Godbole, W-D. Deckwer, Design parameters estimates for bubble column reactors. *A.I.Ch.E. Newspaper*, 1982, 28, 353 –379
- [9] S. Fouchard, A. Hemschemeier, A. Caruana, J. Pruvost, J. Legrand, T. Happe, G. Peltier, L. Cournac, Autotrophic and Mixotrophic Hydrogen Photoproduction in Sulfur-Deprived *Chlamydomonas* Cells, *Applied and Environmental Microbiology*, 2005, p. 6199–6205
- [10] S.A. Markov, E.R. Eivazova, J. Greenwood, Photostimulation of H₂ production in the green alga *Chlamydomonas reinhardtii* upon photoinhibition of its O₂-evolving system, *International Journal of Hydrogen Energy*, 2006, V. 31, 1314 – 1317
- [11] A. Melis, L. Zhang, M. Forestier, M.L. Ghirardi, M. Seibert, Sustained photobiological hydrogen gas production upon reversible inactivation of oxygen evolution in the green alga *Chlamydomonas reinhardtii*, *Plant Physiol*; 2000, V. 117, n°1, 29 – 39