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Articles

Biohydrogen from anaerobic treatment of brewery wastewaters: A preliminary study

Biohidrógeno a partir de la fermentación oscura de las aguas residuales de la industria cervecera: evaluación preliminar

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Abstract

Hydrogen gas is considered the energy of the future because it is renewable, clean, and does not generate greenhouse gas emissions. Among the existing processes for producing hydrogen, it is found biological production from residual wastewater with a high content of carbohydrates treated with an anaerobic process. The utilization of wastewater for hydrogen production is considered an economical alternative because the raw material is abundant and easy to access. In this sense, the present study assessed the hydrogen production from the wastewater of the beer industry treated by Up-flow Anaerobic Sludge Blanket Reactors (UASB). Then, it was applied a thermal shock (90 °C/15 min) to the inoculum, with a previous dark fermentation treatment. The results revealed that with an organic volumetric load of 9.1 gDQO/L.D., pH of 5.5, and a hydraulic retention time (HRT) of 2 h, the maximum percentage of hydrogen gas was 21 % which corresponds to a yield of hydrogen of 6.50 mMolH_2/l. According to the results was found that the initial compound of wastewater influenced the stability and continuity of hydrogen gas (H_2). Finally, this study identified the uncommon presence of methane gas (CH_4) with hydrogen gas, despite keeping pH values nearby to 5.5, and has applied a thermal shock to the inoculum.

Keywords: Clean energy, dark fermentation, hydrogen, industrial wastewater.

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Resumen

El gas hidrógeno se considera como la energía del futuro por ser renovable, limpia y no generar emisiones de gases de efecto invernadero como producto final de su combustión. Entre los procesos que existen para producir hidrógeno se encuentra la producción biológica a partir de aguas residuales con altos contenidos de carbohidratos mediante procesos anaerobios. La utilización del agua residual como fuente de biomasa para producir hidrógeno se considera una alternativa económica debido a que la materia prima es abundante y de fácil acceso. Con base en lo anterior, el presente estudio evaluó la producción de hidrógeno a partir de aguas residuales de la industria cervecera tratadas en un reactor anaerobio de manto de lodos y flujo ascendente (UASB) a escala de laboratorio. Para esto, se aplicó un choque térmico (90 °C/15 min) al inóculo, para inhibir a los microorganismos metanogénicos y promover la producción de H_2. Los resultados mostraron que con un valor de carga orgánica volumétrica de 9.1 gDQO/L.D., pH de 5.5 y un tiempo de detención hidráulica (TDH) de 2 h, el valor máximo de contenido porcentual de hidrógeno en el biogás fue de 21 %, lo que correspondió a un rendimiento de 6.50 mMolH_2/l. A partir de los resultados, se encontró que la variación en la composición inicial del agua residual influyó en la estabilidad y continuidad de la producción del gas hidrógeno (H_2). Por último, este estudio encontró la presencia de gas metano (CH_4) junto con el gas hidrógeno, a pesar de mantener los valores de pH próximos a 5.5, y haber aplicado el choque térmico al inóculo.

Palabras clave: agua residual industrial, energía limpia, fermentación oscura, hidrógeno.

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Introduction

Currently, 90 % of the world's energy is generated from fossil fuels, which are considered scarce and harmful to the environment and human beings. Among the alternative fuels potentially suitable for replacing fossil fuels is hydrogen. Hydrogen is a clean fuel that generates water as the only product during combustion and has 2.75 times more potential energy than hydrocarbons (Wei, Liu, & Zhang, 2010). Recently, the production of biohydrogen from different organic waste has become a low-cost and eco-friendly alternative. According to Zhong, Stevens, and Hansen (2015), at the First World Hydrogen Energy Conference held in 2006, hydrogen was identified as the first clean energy carrier of the future, not only because of its high energy density (143 MJ/kg) which is 2.6 times higher than methane and 3.3 times higher than gasoline, but also because its combustion only generates water as a by-product. Sivagurunathan, Sen, and Lin (2015) said that hydrogen production from dark fermentation has gained much attention at present mainly because there is a wide range of substrates that can be converted to hydrogen without additional energy expenditure. Among the substrates being studied most are industrial wastewaters with high carbohydrate content.

However, biogas is not the only product of anaerobic digestion that has energy value, the biological conversion of carbohydrate-rich substrates generates intermediates such as volatile fatty acids (VFAs) which in turn are constituents of other high value-added products such as polyhydroxyalkanoates (PHA), bio alcohols such as ethanol, butanol and hydrogen gas (*i.e.,* by-products of dark fermentation). The production of hydrogen and other intermediates occurs through the dark fermentation process. Strategies to ensure effective production of hydrogen and organic acids include ensuring that the system has essentially hydrogen-producing organisms and optimizing operational conditions to ensure that this production is continuous and stable (Barca, Soric, Ranava, Giudici-Orticoni, & Ferrasse, 2015). The physiological differences between acidogenic bacteria and methanogenic archaea represent the fundamental basis for developing mechanisms to accumulate hydrogen and organic acids. A review of the literature shows that one of the most common strategies is the elimination of methanogenic organisms (Castelló *et al*., 2020).

The brewing process involves a large number of batch processes in the processing of raw materials into the final product. Large quantities of water are used for beer production, as well as for general washing of floors, cellars, packaging, and on-site cleaning. These waters discharge a significant volume of wastewater, with high concentrations of organic pollutants characterized by high biochemical oxygen demand (BOD), chemical oxygen demand (COD), and total suspended solids (TSS)

(Arantes *et al*., 2019). The most commonly used treatments are generally those that use anaerobic processes due to the high organic load and high biodegradability of the water (Arreola-Vargas, Flores-Larios, González-Álvarez, Corona-González, & Méndez-Acosta, 2016; Montiel-Corona & Razo-Flores, 2018). This technology in combination with aerobic processes such as activated sludge will not only allow the system to comply with discharge regulations but also generates the option of taking advantage of energy production in the form of biogas rich in methane (CH_4) or hydrogen (H_2). The production of CH_4 by anaerobic digestion (AD) in this type of water is an established and widely known technology, while the biological production of H_2 has not yet been widely studied (Arantes *et al*., 2019).

There are several studies on hydrogen and methane production from both single and two-stage anaerobic processes using wastewater from the alcoholic beverage industry. Arreola-Vargas *et al*. (2016) evaluated energy recovery using the two-phase and one-phase anaerobic digestion process from the treatment of water from the tequila industry. Their results showed that using the two-phase methane production was 3.3 times higher than when operating in a single phase. Sinbuathong, Somjit, and Leungprasert (2015) treated real water from the brewery industry in 0.12 l anaerobic batch reactors to produce hydrogen. They varied the pH between 4 and 7 and applied three different types of pretreatments to the inoculum, i.e., heat shock acidification, and chloroform addition. It was mainly found that the methane-producing archaea in the sludge from UASB of the brewery tolerated the temperature change, in addition to the pretreatments by chemical additives, which led to the fact that there is no total inhibition of these microorganisms, therefore, these authors indicated that the brewery wastewater and sludge were suitable for producing methane instead of hydrogen.

It is important to mention that one of the biggest disadvantages of biohydrogen production by dark fermentation is the presence of different organisms, consumers, and/or inhibitors of hydrogen gas.(Sikora, Błaszczyk, Jurkowski, & Zielenkiewicz, 2013). Bundhoo y Mohee (2016) indicate that there are various groups of inhibitors, among which are: H_2 –consuming bacteria (homoacetogenic bacteria, propionic acid fermenting organisms, methanogenic archaea), organisms that compete for the same substrate (e.g., lactic acid bacteria), and can also occur due to the presence of by-products of the same fermentation (*e.g.,* acid accumulation).In this sense, to avoid the presence of these bacteria and increase the production of H_2, it is important to develop methods to inhibit the activity of these microorganisms. Following Castelló *et al*. (2020), the procedure that has shown the best results is the application of pretreatments to the inoculum. In this sense, the objective of this study was to evaluate the production of biohydrogen through dark fermentation by applying a heat shock pretreatment (90°C/15min) to the inoculum in an up-flow anaerobic sludge blanket reactor (UASB) at a laboratory scale treating wastewater from a brewery industry.

Materials y methods

Wastewater

The wastewater comes from a brewery located in the city of Bogota. The samples of wastewater were collected once a week for a year from the Parshall flume located at the entrance of the Wastewater Treatment Plant (WWTP). Once the samples were collected, they were preserved and stored for later analysis. For water characterization, analyses such as total suspended solids (TSS), total dissolved solids (TDS), total solids (TS), total alkalinity, total volatile acids (TVA), sulfates (SO4-2), chemical oxygen demand (COD), pH, total nitrogen, and phosphates (PO4-2) were performed using the HACH model DR5000 spectrophotometer and following the recommendations of APHA (2012).

Experimental set-up

A laboratory-scale UASB reactor was used, built-in acrylic, with a diameter (D) of 50 mm and a height (A) of 590 mm, and a useful volume of 940

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ml, which resulted in a length to diameter (L/D) ratio of 12 (Figure 1) by the recommendations of Chaparro et al. (2010). The conventional UASB reactor was operated continuously for 62 days with a hydraulic retention time (HRT) of 2 h. This HRT value was chosen based on what was suggested by authors such as Preethi et al., (2019) and an average volumetric organic load of 9.41 gDQO/L.D. The inoculum was obtained from the UASB reactor that treats wastewater from the brewery industry. A heat shock treatment was applied to this inoculum at 90ºC for 15 min, following the recommendations of Lay *et al*. (2019), and Wang, Fang, Fang, and Bu (2010). The pH value was adjusted to 5.5 with 1N sodium hydroxide or hydrochloric acid (10 mol/l), as appropriate.

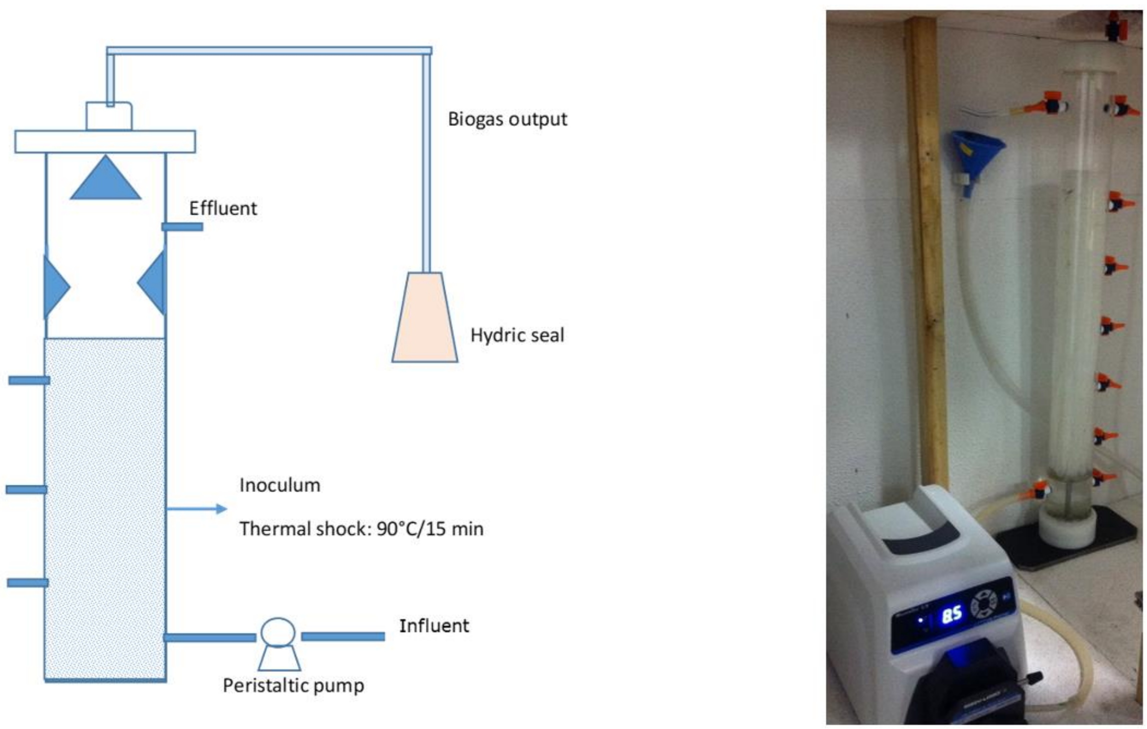

Figure 1. Experimental set-up and photograph, reactor UASB. Own elaboration.

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Analytical determinations

To evaluate the performance of the UASB reactor, the following analyses were performed: chemical oxygen demand, total volatile acids, total alkalinity, partial alkalinity, intermediate alkalinity, total solids, suspended solids, total volatile solids, suspended volatile solids, and pH; under the methodology described in APHA (2012), and Ripley and Boyle (1986). All determinations were carried out three times a week in duplicate. The composition of the biogas, including hydrogen gas and methane gas, was analyzed in the Chromatograph brand Agilent model 7890A, equipped with a thermal conductivity detector with helium as carrier gas and a Carboxen 1010 Plot column. The temperature of the injector and the detector were maintained at 200 and 230 °C, respectively. The flow of the carrier gas was 1.5 ml/min. The volume of the sample injected was 0.7 ml.

Results and discussion

Wastewater from the brewery industry is generated from several activities during production, such as cleaning of equipment and facilities, refrigeration and boiler circuits, packaging, sanitation, and factory consumption in general. As shown in Table 1, these wastewaters are characterized by high variability in most of the parameters measured. One explanation for this result may be that the sample was taken in the Parshall Flume at the entrance of the WWTP, just before the homogenizer.

Table 1. Characteristics of wastewater from the brewing industry.

Parameter	**Unit**	**Median**	**±**	**D.S.***
COD	mg/l	868	±	174
pH	--	7	±	1.1
Total Alkalinity	mg $CaCO_3$/l	1 628	±	492
TVA	mg HAc/l	1 720		317
TS	mg/l	4 915	±	1 279
TSS	mg/l	356	±	40
SO_4^{-2}	mg SO_4^{-2}/l	97	±	61
PO_4^{-2}	mg PO_4-^{2}/l	76	±	43
Cl	mg Cl^{-1}/l	144	±	37
TN	mg TN/l	32	±	10

*S.D.: Standard Deviation. Own elaboration.

From the results in Table 1, it can be said that the composition of the water could favor the production of hydrogen by anaerobic means. Additionally, the sulfate toxicity was evaluated with the COD/SO_4^{-2} ratio, which resulted in an average value of 12.2. By (Chernicharo (2007) a COD/SO_4^{-2} ratio greater than 10 does not cause toxicity problems due to the presence of sulfates in the anaerobic process. Finally, it was observed that the nitrogen and phosphorus content was high, mainly because of the yeast contributions to the wastewater (Gugulethu-Erogan, 2014).

Hydrogen production

Figure 2 shows that the percentage production of hydrogen was not constant and did not reach a steady state. The steady-state is considered to be reached when the H_2 production does not present a variation of about 10 % as suggested by Tapia-Venegas *et al*. (2015). The maximum yield achieved was 6.50 mMolH_2/l, which corresponded to 21 % of the biogas composition for operating day 12. Hydrogen production using real industrial wastewater as feedstock has shown favorable results in different studies, but under very different operating conditions, which does not allow establishing a pattern or defining values for design and operating parameters on a real scale. For example, Amorim, Alves, Martins and Amorim (2014), using an anaerobic fluidized bed reactor treating wastewater from cassava extraction with an HRT value of 2 h produced 1.2 molH2/mol glucose. Pachiega *et al*. (2019) also studied hydrogen production from brewery wastewater, adjusting the pH value to 5.5, in anaerobic Batch reactors but with an HRT of 180 h; the maximum production was 15 molH_2/mol fructose. Yu, Zhu, Hu and Zhang (2002) treated wastewater from rice production under thermophilic conditions at pH 5.5 and HRT of 2 h and their maximum yield was 2.14 molH_2/mol hexose.

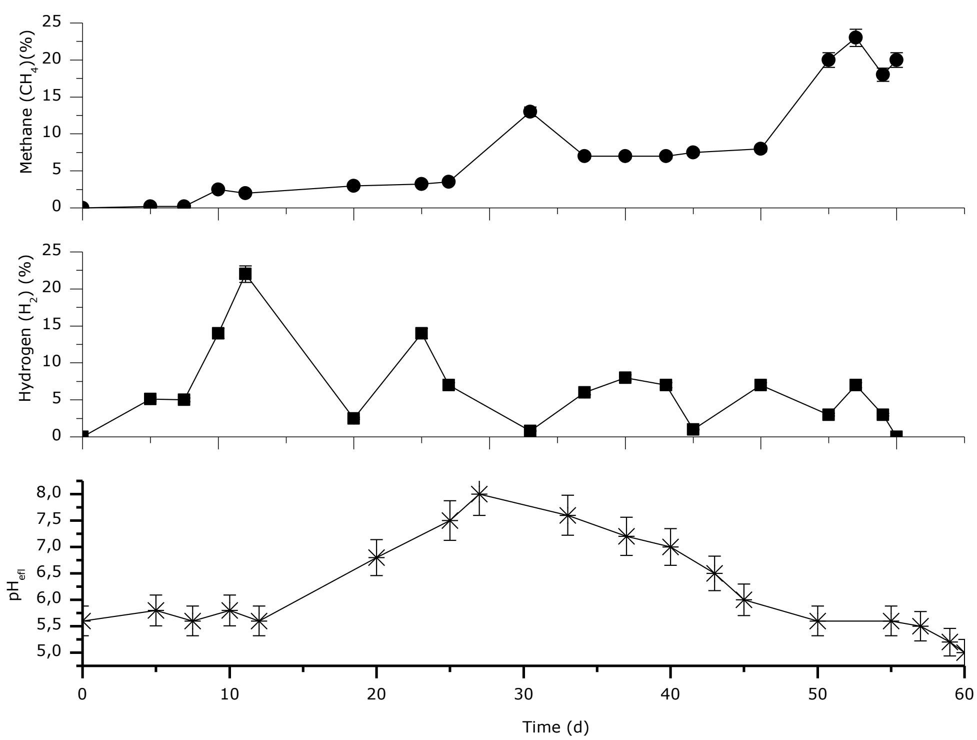

Figure 2. Temporal variation of hydrogen production, methane production, and pH in the effluent in the UASB reactor. Own elaboration.

Note: The values of the percentage production of hydrogen and methane are the result of three measurements made internally by the gas chromatograph.

Hydrogen production was unstable over time but continuous; this result can be attributed to different factors, including changes in the bacterial communities, the present consumers and/or inhibitors of H_2, the reactor configuration, or the chosen hydraulic detention time. Castelló *et al*. (2020), in a wide critical review of factors influencing the stability of hydrogen production, stated that there is as yet no consensus on operational parameter values and reactor configurations for producing hydrogen from real industrial wastewater. Several studies on hydrogen production from anaerobic digestion, particularly operating in the dark fermentation phase in waters of industrial origin, noted that from approximately the 25th day of operation, there is a tendency for hydrogen production to decrease and not return to initial values (Anzola-Rojas & Zaiat, 2014; Moureira, Lima, Kmiecik, & Zaiat, 2013; Penteado, Lazaro, Sakamoto, & Zaiat, 2013).

Notwithstanding the above, some findings can be established in this study, first, H_2 production was not only not stable, but also did not recover over time. Approximately from day 20 of operation, it decreased until it stopped completely around day 60. This observation was similar to other authors such as Bundhoo and Mohee (2016); Sivagurunathan, Anburajan, Kumar, and Kim(2016), and Si *et al*. (2015). Particularly, Si *et al*. (2015) state that one of the causes leading to the decrease in hydrogen production is the presence of homoacetanogenic microorganisms.

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Inoculum preparation plays a key role in the continuous and stable production of hydrogen, authors like Bundhoo y Mohee (2015) did an extensive review on the effect of various pretreatments on hydrogen production from dark fermentation. Among their main findings these authors indicated that, among the technologies reviewed for inoculum pretreatment, heat and acid pretreatments are the most studied and most effective. In addition, they noted that further research is needed to determine optimal pretreatment conditions before definitive conclusions can be drawn.

It is important to mention that in this study in every sample of biogas and biohydrogen was a presence of Methane gas (CH_4) in small proportions (Figure 2). A possible explanation for this phenomenon is that, despite the thermal pretreatment of the inoculum, it was not sufficient to inhibit or eliminate the methanogenic archaea. Despite the adjustment of the pH value to 5.5 in the reactor effluent, the effluent showed average values of 6.21, except for the first 8 days of operation, when values close to 8.0 were reached, similar results were obtained by Hawkes, Hussy, Kyazze, Dinsdale y Hawkes (2007), y Palomo-Briones *et al*. (2019).

Variation of total volatile acids

Anaerobic fermentation is always accompanied by the production of volatile acids. One aspect to take into account in this study is that on several occasions the wastewater already had high concentrations of total volatile acids, indicating that the water was already partially fermented. Therefore, the values were initially higher than > 1 500 mgHAc/l, and on average during the observation time the increase was not higher than 20 %, as a result, an average value of 1 800 mgHAc/l was reached, which indicated that there was no internal production of VTA as stated by Chernicharo (2007).

Hydrogen production can be inhibited by H_2 itself and by volatile fatty acids produced during the fermentation process. Fermentation with acetic and butyric acid produces 4 moles of H_2 per mole of glucose and 2 moles of H2 per mole of glucose, respectively. These are the main metabolic pathways by which H_2 is produced in dark fermentation Sikora *et al*. (2013). This indicates that to obtain a high H_2 production, this should correlate with high acid production, a situation that does not always occur, mainly due to the way the acid is in the medium. Both acetic acid and butyric acid are weak acids that will depend on the pH value, in this sense, if the acid does not dissociate it is more likely to enter the cytoplasm of the microorganisms, causing an imbalance in the pH value, acidifying the medium and increasing the energy requirements. As a result, an imbalance in the process will be generated, and for this reason, authors like Lee, Chua, Yeoh y Ngoh (2014), Mamimin *et al*. (2015), y Ghimire *et al*. (2015) proposed that one of the best strategies to produce hydrogen from wastewater with significant variations in organic load, pH values in the acid range mainly originated in the industry, should implement the anaerobic process in two stages. In this way, the operating parameters such as HRT, and pH, among others, are optimized in each of them, mainly favoring the microorganisms involved in each of these stages.

Finally, it is relevant to note that the production of hydrogen from real wastewater from the brewery industry is an attractive option for industries to comply with the discharge limits established in the environmental regulations and also to recover energy through the by-products generated during the treatment of their effluents. For this, the anaerobic treatment must be carried out in two stages, the first a dark fermentation phase to optimize the production of hydrogen (H_2), and the second a phase to produce methane gas (CH_4). In particular, it is recommended to increase the pretreatment time with heat shock for inhibition of methanogenic archaea, 15 minutes is not enough as observed in this study, despite the low hydraulic detention time used and also the pH value of 5.5. Given the heterogeneity of the raw water, trials should be conducted under factorial experiments to find the optimal range of operational parameters.

Conclusions

In this study, a preliminary evaluation of the feasibility of producing hydrogen from dark fermentation by treating real wastewater from a brewery industry was carried out. It was found that it is feasible to produce hydrogen with this type of effluent using a conventional anaerobic UASB reactor from dark fermentation. The maximum yield achieved was 6.50 $mMolH_2/l$, which corresponded to 21 % of the biogas composition with a volumetric organic load value of 9.1 gCOD/L.D. However, it was not possible to maintain the stability and continuity of the process despite the application of thermal shock to the inoculum and pH control. It is important to mention that future studies must evaluate how factors such as variability in the composition of the wastewater, the configuration of the reactor, how the inoculum pretreatment is carried out, and its origin influence to improve of the stability of the biological process and consequently the continuity in the generation of hydrogen gas.

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References

Amorim, N. C. S., Alves, I., Martins, J. S., & Amorim, E. L. (2014). Biohydrogen production from cassava wastewater in an anaerobic fluidized bed reactor. *Brazilian Journal of Chemical Engineering*, 31(3), 603-612. Recovered from https://doi.org/10.2166/wpt.2019.041

Anzola-Rojas, M., & Zaiat, M. (2014). *Estratégias para a produção contínua de hidrogênio em reator anaeróbio de leito fixo* (tese de Doutorado em Ciência). Escola de Engenharia de São Carlos Departamento de Hidráulica e Saneamento, Brazil.

APHA, American Public Health Association. (2012). *Standard methods for examination of water and wastewater* (22nd ed.). Washington, USA: American Public Health Association.

Arantes, M. K., Sequinel, R., Alves, H. J., Machado, B., Fiorini, A., & Da Silva, E. A. (2019). Improvement of biohydrogen production from brewery wastewater: Evaluation of inocula, support and reactor. *International Journal of Hydrogen Energy*. Recovered from https://doi.org/10.1016/j.ijhydene.2019.07.208

Arreola-Vargas, J., Flores-Larios, A., González-Álvarez, V., Corona-González, R. I., & Méndez-Acosta, H. O. (2016). Single and two-stage anaerobic digestion for hydrogen and methane production from acid and enzymatic hydrolysates of *Agave tequilana* bagasse. *International Journal of Hydrogen Energy*, 41(2), 897-904. Recovered from https://doi.org/10.1016/j.ijhydene.2015.11.016

Barca, C., Soric, A., Ranava, D., Giudici-Orticoni, M. T., & Ferrasse, J. H. (2015). Anaerobic biofilm reactors for dark fermentative hydrogen production from wastewater: A review. *Bioresource Technology*, 185, 386-398. Recovered from https://doi.org/10.1016/j.biortech.2015.02.063

Bundhoo, M. A. Z., & Mohee, R. (2016). Science direct inhibition of dark fermentative bio-hydrogen production : A review. *International Journal of Hydrogen Energy*, 41(16), 6713-6733. Recovered from https://doi.org/10.1016/j.ijhydene.2016.03.057

Bundhoo, M. A. Z., Mohee, R., & Hassan, M. A. (2015). Effects of pre-treatment technologies on dark fermentative biohydrogen production: A review. *Journal of Environmental Management*, 157, 20-48. Recovered from https://doi.org/10.1016/j.jenvman.2015.04.006

Castelló, E., Nunes-Ferraz-Junior, A. D., Andreani, C., Anzola-Rojas, M. del P., Borzacconi, L., Buitrón, G., Carrillo-Reyes, J., Gomes, S. D., Maintinguer, S. I., Moreno-Andrade, I., Palomo-Briones, R., Razo-Flores, E., Schiappacasse-Dasati, M., Tapia-Venegas, E., Valdez-Vázquez, I., Vesga-Baron, A., Zaiat, M., & Etchebehere, C. (2020). Stability problems in the hydrogen production by dark fermentation: Possible causes and solutions. *Renewable and Sustainable Energy Reviews*, 119(May). Recovered from https://doi.org/10.1016/j.rser.2019.109602

Chaparro, T. R. (2010). Tratamento anaeróbio seguido de processo oxidativo avançado. In: *Tratamento de efluentes de branqueamento de polpa celulósica em reator anaeróbio seguido de processo oxidativo avançado*. Sao Paulo, Brasil: Universidad de Sao Paulo.

Chernicharo, C. (2007). *Anaerobic reactors*. New Delhi, India: IWA Publishing.

Ghimire, A., Frunzo, L., Pirozzi, F., Trably, E., Escudie, R., Lens, P. N. L., & Esposito, G. (2015). A review on dark fermentative biohydrogen production from organic biomass: Process parameters and use of by-products. *Applied Energy*, 144, 73-95. Recovered from https://doi.org/10.1016/j.apenergy.2015.01.045

Gugulethu-Erogan, I. (2014). *Treatment of soft drink industry wastewater using an integrated anaerobic / aerobic membrane bioreactor*. Cape Peninsula University of Technology, October, 154. Recovered from http://digitalknowledge.cput.ac.za/jspui/bitstream/11189/2441/1/200679315_erdogan_ig_mtech_chem_eng_2014.pdf

Hawkes, F. R., Hussy, I., Kyazze, G., Dinsdale, R., & Hawkes, D. L. (2007). Continuous dark fermentative hydrogen production by mesophilic microflora: Principles and progress. *International Journal of Hydrogen Energy*, 32(2), 172-184. Recovered from https://doi.org/10.1016/j.ijhydene.2006.08.014

Lay, C. H., Vo, T. P., Lin, P. Y., Abdul, P. M., Liu, C. M., & Lin, C. Y. (2019). Anaerobic hydrogen and methane production from low-strength beverage wastewater. *International Journal of Hydrogen Energy*, 44(28), 14351–14361. Recovered from https://doi.org/10.1016/j.ijhydene.2019.03.165

Lee, W. S., Chua, A. S. M., Yeoh, H. K., & Ngoh, G. C. (2014). A review of the production and applications of waste-derived volatile fatty acids. *Chemical Engineering Journal*, 235, 83-99. Recovered from https://doi.org/10.1016/j.cej.2013.09.002

Mamimin, C., Singkhala, A., Kongjan, P., Suraraksa, B., Prasertsan, P., Imai, T., & O-Thong, S. (2015). Two-stage thermophilic fermentation and mesophilic methanogen process for biohythane production from palm oil mill effluent. *International Journal of Hydrogen Energy*, 40(19), 6319-6328. Recovered from https://doi.org/10.1016/j.ijhydene.2015.03.068

Montiel-Corona, V., & Razo-Flores, E. (2018). Continuous hydrogen and methane production from *Agave tequilana* bagasse hydrolysate by sequential process to maximize energy recovery efficiency. *Bioresource Technology*, 249(August 2017), 334-341. Recovered from https://doi.org/10.1016/j.biortech.2017.10.032

Moureira, D., Lima, F., Kmiecik, W., & Zaiat, M. (2013). Comparison of the use of sucrose and glucose as a substrate for hydrogen production in an up flow anaerobic fixed-bed reactor. *International Journal of Hydrogen Energy*, 38(35), 15074-15083. Recovered from https://doi.org/10.1016/j.ijhydene.2013.09.003

Pachiega, R., Rodrigues, M. F., Rodrigues, C. V., Sakamoto, I. K., Varesche, M. B. A., De-Oliveira, J. E., & Maintinguer, S. I. (2019). Hydrogen bioproduction with anaerobic bacteria consortium from brewery wastewater. *International Journal of Hydrogen Energy*, 155-163. Recovered from https://doi.org/10.1016/j.ijhydene.2018.02.107

Palomo-Briones, R., Celis, L. B., Méndez-Acosta, H. O., Bernet, N., Trably, E., & Razo-Flores, E. (2019). Enhancement of mass transfer conditions to increase the productivity and efficiency of dark fermentation in continuous reactors. *Fuel*, 254(June), 115648. Recovered from https://doi.org/10.1016/j.fuel.2019.115648

Penteado, E. D., Lazaro, C. Z., Sakamoto, I. K., & Zaiat, M. (2013). Influence of seed sludge and pretreatment method on hydrogen production in packed-bed anaerobic reactors. *International Journal of Hydrogen Energy*, 38(14), 6137-6145. Recovered from https://doi.org/10.1016/j.ijhydene.2013.01.067

Preethi, T. M., Banu, J. R., Gunasekaran, M., & Kumar, G. (2019). Biohydrogen production from industrial wastewater: Advancement towards commercialisation. *Bioresource Technology Reports*, 7, 1002, https://doi.org/10.1016/j.biteb.2019.100287.

Ripley, L. E., & Boyle, W. C. (1986). Improved alkalimetric monitoring for anaerobic digestion of high-strength wastes. *Journal of Water Pollution Control Federation*, 58(5), 406-411.

Si, B., Li, J., Li, B., Zhu, Z., Shen, R., Zhang, Y., & Liu, Z. (2015). The role of hydraulic retention time on controlling methanogenesis and homacetogenesis in biohydrogen production using up flow anaerobic sludge blanket (UASB) reactor and packed bed reactor (PBR). *International Journal of Hydrogen Energy*, 40(35), 11414-11421. Recovered from https://doi.org/10.1016/j.ijhydene.2015.04.035

Sikora, A., Błaszczyk, M., Jurkowski, M., & Zielenkiewicz, U. (2013). Chapter 21. In: *Lactic Acid Bacteria in Hydrogen-Producing Consortia: On Purpose or by Coincidence?* Recovered from https://doi.org/10.5772/50364

Sinbuathong, N., Somjit, C., & Leungprasert, S. (2015). Feasibility study for biohydrogen production from raw brewery wastewater.

International Journal of Energy Research, 39(13), 1769-1777. Recovered from https://doi.org/10.1002/er.3321

Sivagurunathan, P., Anburajan, P., Kumar, G., & Kim, S. H. (2016). Effect of hydraulic retention time (HRT) on biohydrogen production from galactose in an up-flow anaerobic sludge blanket reactor. *International Journal of Hydrogen Energy*, 41(46), 21670-21677. Recovered from https://doi.org/10.1016/j.ijhydene.2016.06.047

Sivagurunathan, P., Sen, B., & Lin, C. Y. (2015). High-rate fermentative hydrogen production from beverage wastewater. *Applied Energy*, 147, 1-9. Recovered from https://doi.org/10.1016/j.apenergy.2015.01.136

Tapia-Venegas, E., Ramirez-Morales, J. E., Silva-Illanes, F., Toledo-Alarcón, J., Paillet, F., Escudie, R., Lay, C. H., Chu, C. Y., Leu, H. J., Marone, A., Lin, C. Y., Kim, D. H., Trably, E., & Ruiz-Filippi, G. (2015). Biohydrogen production by dark fermentation: Scaling-up and technologies integration for a sustainable system. *Reviews in Environmental Science and Biotechnology*, 14(4), 761-785. Recovered from https://doi.org/10.1007/s11157-015-9383-5

Yu, H., Zhu, Z., Hu, W., & Zhang, H. (2002). Hydrogen production from rice winery wastewater in an upflow anaerobic reactor by using mixed anaerobic cultures. *International Journal of Hydrogen Energy*, 27(11-12), 1359-1365. Recovered from https://doi.org/10.1016/S0360-3199(02)00073-3

Wang, H., Fang, M., Fang, Z., & Bu, H. (2010). Bioresource technology effects of sludge pretreatments and organic acids on hydrogen production by anaerobic fermentation. *Bioresource Technology*, 101(22), 8731-8735. Recovered from https://doi.org/10.1016/j.biortech.2010.06.131

Wei, J., Liu, Z. T., & Zhang, X. (2010). Biohydrogen production from starch wastewater and application in fuel cell. *International Journal of Hydrogen Energy*, 35(7), 2949-2952. Recovered from https://doi.org/10.1016/j.ijhydene.2009.05.035

Zhong, J., Stevens, D. K., & Hansen, C. L. (2015). Optimization of anaerobic hydrogen and methane production from dairy processing waste using a two-stage digestion in induced bed reactors (IBR). *International Journal of Hydrogen Energy*, 40(45), 15470-15476. Recovered from https://doi.org/10.1016/j.ijhydene.2015.09.085