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Influence of the Carbon/Nitrogen Ratio on the Hydrogen Production in a Fixed-bed Anaerobic Reactor

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This study evaluated the effect of the carbon/nitrogen (C/N) ratio on the hydrogen production from a sucrose-based synthetic wastewater. Up-flow fixed-bed anaerobic reactors with recycled low-density polyethylene for biomass attachment were operated at 25°C and with a 2-h hydraulic detention time. Several C/N relationships were studied (40, 90, 140 and 190), using sucrose and urea as carbon and nitrogen sources, respectively. Average values of hydrogen yield of 0.6 mol-H₂.mol-sucrose⁻¹, 1.3 mol-H₂.mol-sucrose⁻¹, 2.7 mol-H₂.mol-sucrose⁻¹ and 1.7 mol-H₂.mol-sucrose⁻¹ were reached when the reactors were operated with C/N of 40, 90, 140 and 190, respectively. It was estimated an optimal value for C/N of 137, which would result in maximum hydrogen yield of 3.5 mol-H₂.mol-sucrose⁻¹. Biogas produced was composed of H₂ and CO₂, with average H₂ content of 53%, 49%, 61% and 52% for C/N of 40, 90, 140 and 190, respectively. The main intermediary fermentation products were similar for all the C/N ratios, being specially detected acetic acid, butyric acid and ethanol. Under excess of nitrogen, the biomass growth was higher with negative effects on hydrogen production while deficiency of nitrogen permitted the control of biomass growth and resulted in higher hydrogen yields.

1 Introduction

In the last decades high population growth has increased the demand of energy, leading to excessive use of fossil fuels. Due to this crescent demand and need of clean fuels, many studies focused on the hydrogen production as alternative energy source. Biological hydrogen production is interesting due to two main reasons: the use of a renewable energetic source and the easy operation of the productive plants at ambient temperature and pressure [1]. The use of cheaper sources, as wastewater with considerable amount of organic fraction, makes the hydrogen production a sustainable process, since the treatment of the wastewater is mandatory for pollution control and hydrogen is a by-product of this process [2]. Several factors affect the hydrogen production in anaerobic reactors as temperature, pH, type and operational condition of reactor, procedure of inoculation, source and processing of the inoculum, wastewater type, among others. The characteristic of the wastewater is extremely important since hydrogen production will depend on the organic contents, being the carbohydrates the main compounds of interest in the process. Moreover, the composition of macro (N, P, S) and micronutrients (K, Mg, Ca, Fe, Mn, Co, Cu, Mo, Zn) is essential for the metabolism and can affect hydrogen production. Among the macronutrients, nitrogen is the most requested for the microorganism and metabolism can be altered due to deficiency or excess this nutrient in the medium. Concerning hydrogen production, the

nitrogen availability can be a factor of great importance to increase hydrogen yield, as shown by Lin & Lay (2004) and Peixoto (2008) [3, 4].

This paper reports on the influence of the carbon/nitrogen (C/N) ratio on the hydrogen production in an up-flow fixed-bed anaerobic reactor.

2 Experimental Setup

The up-flow fixed-bed anaerobic reactor was comprised of acrylic tubes with 80 mm internal diameter, 88 mm external diameter and 750 mm long, with total volume of 3,77 L. Recycled low-density polyethylene was used as inert support for biomass attachment and the synthetic wastewater was composed by sucrose as carbon source, urea as nitrogen source and with micronutrient composition according to Leite *et al.* (2008) [5]. pH was maintained close to 6,5 with addition of NaHCO_3 (500 mg.L^{-1}) and HCl ($0,45 \text{ mL.L}^{-1} - 10 \text{ mol.L}^{-1}$). The reactor was inoculated according to the procedures described by Leite *et al.* (2008) [5].

Four experiments were carried-out, each one with a different C/N ratio (40, 90, 140 and 190). In each stage, the reactor was operated for 60 days at 25°C and with hydraulic detention time of 2 h.

In each experimental stage influent and effluent samples were collected for pH, temperature, chemical oxygen demand (COD) and volatile suspended solids (VSS) analyses according to Standard Methods [6]. Biogas composition, volatile acids, alcohols and acetone analyses were performed by gas chromatography (GC-2021 and GC-2010, Shimadzu, Tokyo, Japan). Sucrose was determined as proposed by Dubois *et al.* (1956) [7] and the volume of produced biogas was measured with a gas meter (Type TG1, Ritter Inc., Germany).

3 Results and Discussion

3.1 Hydrogen production

This research demonstrated clearly the influence of C/N ratio in the biogas production, indicating that the biogas production increased as the C/N ratio was increased from 40 to 140, thus decreasing for higher values of C/N ratio (Figure 1a). It is important to note that, although the C/N ratio has influenced biogas production in the reactors, the behaviour along the experimental time was the same for all C/N ratios. Biogas production increased up to 25th day of operation, with subsequent drop toward null values of biogas flow-rate around the 60th day of operation. Therefore, stabilization of the biogas production was not observed in any experiment. However, the analysis of the liquid phase indicated stabilization of the fermentative process after approximately 25 days of operation, as observed for sucrose conversion (Figure 1b).

Sucrose conversion efficiencies were similar in all C/N ratios, with values above 88%, similar to those observed by Fernandes (2008) [8]. The content of hydrogen in the biogas ranged from 49% for C/N ratio of 90 and 61% for C/N of 140. This hydrogen content was similar to that observed by O-Thong *et al.* (2008) in up-flow anaerobic sludge blanket (UASB) reactor fed with sucrose [9]. Carbon dioxide ranged from 28% for C/N ratio of 40 and 35% for C/N of 140. Methane was not detected in the biogas during the experiments, indicating absence of methanogenic activity in the reactors under all C/N ratios. Maximum values of hydrogen molar flow-rate ($16.2 \text{ mmol-H}_2\text{.h}^{-1}$) and hydrogen yield ($3.5 \text{ mol-H}_2\text{.mol-sac}^{-1}$) were obtained

when reactor operated with C/N ratio of 140. This yield value is 43.5% of the theoretical maximum value, established by the reaction stoichiometry and considering that sucrose would be converted only in acetic acid. Maximum value of hydrogen volumetric production was $162.5 \text{ mL-H}_2\cdot\text{h}^{-1}\cdot\text{L}^{-1}$, also achieved with C/N ratio of 140.

The same behaviour of biogas production, hydrogen molar flow-rate and hydrogen yield was observed for all C/N ratio assayed (Figure 1c). The decrease of the nitrogen concentration in the medium resulted in favourable conditions for hydrogen production with hydrogen yield 3.5 times higher when C/N ratio was increased from 40 to 140. It is worth mentioning that, in this range of C/N ratio, the increase in hydrogen yield was proportional to the decrease in the nitrogen concentration. This behaviour can be related to the metabolic pathway. Under excess of nitrogen (low C/N ratios), energy was mainly used to cell assimilation and growth, thus resulting in lower hydrogen production. However, as the C/N ratio was increased, nutritional deficiency probably prevents the use of energy for growth, with positive effect in hydrogen production. The drop in hydrogen production under the highest C/N ratio can indicate severe nutritional deficiency, thus suggesting an optimal C/N ratio for the process. These results are according with those described by Lin & Lay (2004), who suggested that less nitrogen contents can be insufficient for cell growth [3]. The hypothesis of cell growth favoured by low C/N ratio could be checked through biomass concentration (as total solid - TS) in the reactor. Biomass concentration decreased as C/N ratio increased, with stabilization for C/N ratio 140 and 190. The decrease in the biomass concentration indicates that specific organic load increased as the C/N ratio was increased, causing a positive effect in hydrogen production due to unbalance of the anaerobic process, essential for hydrogen production.

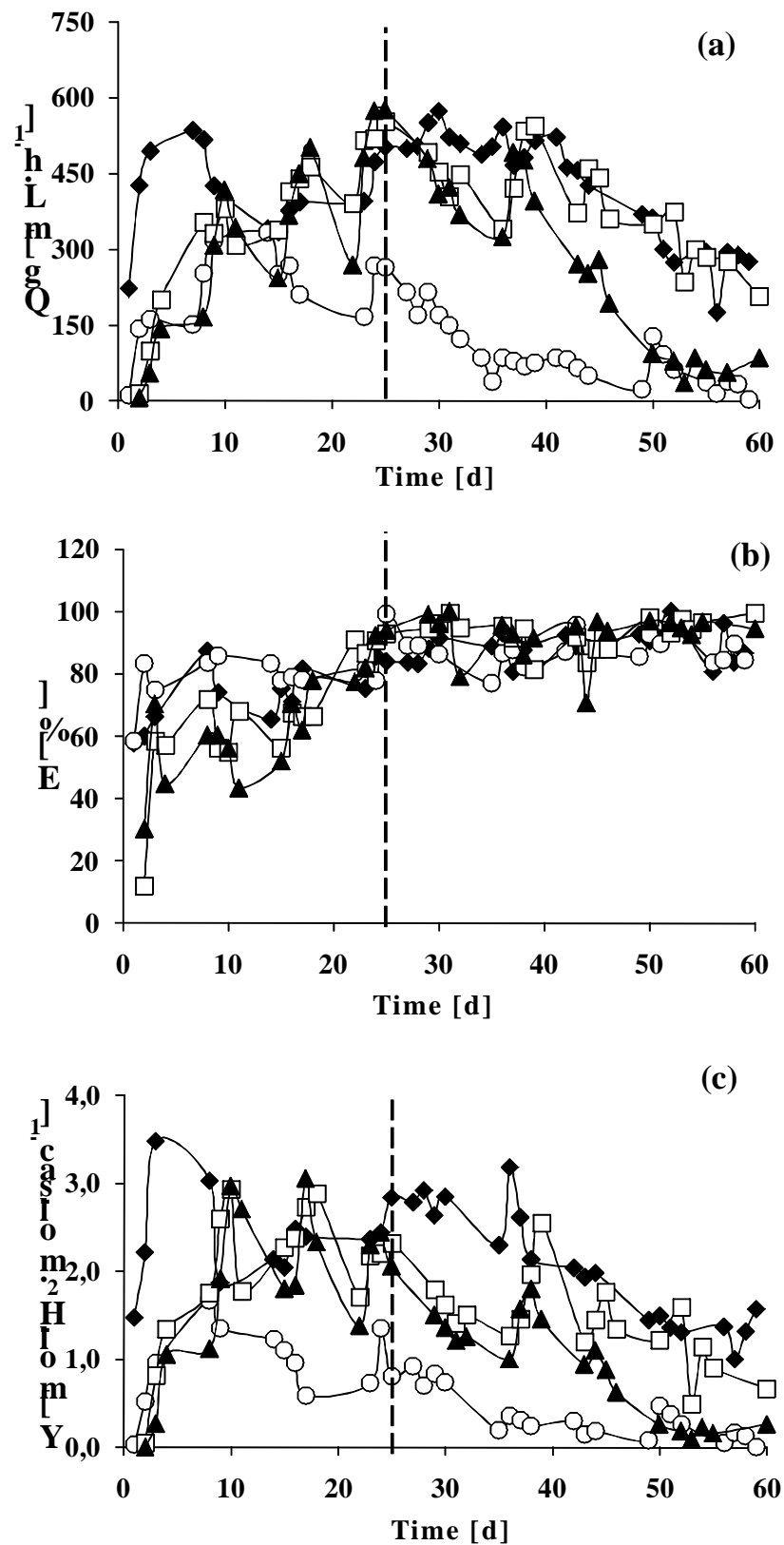


Figure 1: Biological hydrogen production with C/N ratio of 40 (○), 90 (▲), 140 (◆) and 190 (□). (a) Biogas production (Qg). (b) Sucrose degradation (E). (c) Hydrogen yield (Y).

3.2 Fermentation products in liquid medium

The composition of soluble products was similar in all experiments independent of the C/N ratio, being predominant acetic and butyric acids, related to maximum hydrogen production [10], besides the ethanol, undesirable when hydrogen is the desirable product. Other detected products were propionic acid, n-butanol, acetone, isobutyric acid, methanol, caproic, valeric and isovaleric acids.

4 Conclusions

The C/N ratio affected biological hydrogen production in anaerobic fixed-bed reactor. Maximum molar flow-rate, yield and volumetric production amount were $16.2 \text{ mmol-H}_2\cdot\text{h}^{-1}$, $3.5 \text{ mol-H}_2\cdot\text{mol-suc}^{-1}$ e $162.5 \text{ mL-H}_2\cdot\text{h}^{-1}\cdot\text{L}^{-1}$, respectively, obtained under C/N ratio of 140. The biogas was composed mainly by H_2 and CO_2 , with hydrogen average percentages of 53%, 49%, 61% and 52% with C/N ratio of 40, 90, 140 and 190 respectively. The main organic acids produced in the process were acetic and butyric, and the main solvent produced was the ethanol.

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