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Bio-hydrogen production during acidogenic fermentation in a multistage stirred tank reactor

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ABSTRACT

The objective of this study was to evaluate the production of hydrogen in a two-stage CSTR system – both reactors having the same volume – and compare its performance with a conventional one-stage process. The lab-scale two-stage and one-stage systems were operated at five pHs and five hydraulic retention time (HRTs). The maximum volumetric hydrogen productivity and yield obtained with the two-stage system were 5.8 mmol L^{-1} h^{-1} and 2.7 mol H_2 mol glucose^{-1}, respectively, at an HRT of 12 h and pH 5.5. Overall, the two-stage system showed, at steady state, a better performance that the one-stage system for all the evaluated pHs. However, a comparison between the one-stage system, operating at 6 h of HRT, and the first reactor of the two-stage system at the same HRT did not show any significant difference, highlighting the positive impact of having a two-stage process. The determination of the ratio between the experimental measured H_2 in the gas phase and the theoretical H_2 generated in the liquid phase (discrepancy factor) indicated that an important part of the hydrogen produced in the first reactor was transferred into the second reactor instead of being desorbed in the headspace. Therefore, the improving of hydrogen production in the two-stage system is rather attributed to the increased transfer of hydrogen from liquid to gas than an actual total hydrogen production increase.

1. Introduction

There are several operational variables that influence the hydrogen production by anaerobic digestion among the most important ones: pH, hydraulic retention time (HRT), partial pressure of hydrogen and liquid/gas equilibrium of the system [1–4]. In regards to the HRT (which is the inverse of the dilution rate), it is advisable to use a dilution rate less than 0.17 h^{-1} or greater than 6 h HRT, when using continuous reactors with suspended biomass, since the maximum specific growth rate (μ_{max}) of hydrogen producers in an anaerobic mixed inoculums is less than that value. Despite this hydraulic constraint, different operational HRT ranges have been used depending on the type of substrates, reactor and inoculum as well as the pretreatment applied to eliminate the methanogens. In any case, it is clear that as HRT increases, the hydrogen production decreases, being the maximum reported value for HRT to produce hydrogen in a continuous operation between 14 and

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17 h [5]. On the other hand, it is usually accepted, although this is still unclear, that hydrogen accumulation, which is related to the partial pressure of hydrogen in the reactor headspace, might inhibit hydrogen producers [6]. In this context, different strategies have been used to minimize this effect, for example, the dilution of the biogas by sparging an inert gas and vacuum application [7–9]. However, these strategies may increase the cost of the process and it is necessary to investigate new and more economically feasible alternatives to reduce the effect of hydrogen partial pressure. One possible option is the use of multistage stirred tank reactors in series which are characterised by having several states across the reactors. This configuration is well suited for processes in which a certain degree of product inhibition may occur [10,11]. Therefore, using two continuous stirred tank reactors (CSTR) in series could, first of all, enhance the selection of hydrogen producers by washing out the methanogens, while at the same time, reducing the hydrogen partial pressure that a one-stirred tank reactor with the same total volume would have.

On the other hand, the reactors geometry may also influence the bio-hydrogen reactor performance since the transfer of hydrogen from the liquid to the gas phase depends on the interfacial specific area from the liquid to the gas. The aim of this study was to assess the bio-hydrogen production in a two-stage series system in terms of hydrogen yield and volumetric productivity compared to a classical one-stage continuous system.

2. Materials and method

2.1. Experimental set-up

Three glass-made reactors were designed and implemented at lab-scale. A conventional one-stage CSTR system with a volume of 4 L and a two-stage system, composed by two CSTR reactors in series of 2 L each, were used. Each reactor was connected to auxiliary equipment: temperature and pH sensors for monitoring, peristaltic pumps for influent feeding and effluent draw off, pH control pump by adding a bicarbonate solution, a mechanical stirrer and a heating jacked-type system. Both systems were maintained at 37 °C and operated in parallel.

2.2. Wastewater and inocula

For the experiments, synthetic glucose-based wastewater and suspended biomass were used (Table 1). For the reactors seeding, granular anaerobic inoculum was taken from a full-scale anaerobic plant treating tobacco wastewater with a concentration of 13 g VSS L^{-1} and an acidogenic and methanogenic activity of 0.17 g COD CH_4 $gVSS^{-1}$ d^{-1} and 7.74 g COD $C_6H_{12}O_6$ g VSS^{-1} d^{-1}. A volume of this inoculum equal to the 25% of the reactor volume was added for each experiment, resulting in an initial concentration of 4 g VSS L^{-1}. In order to wash out the methanogenic biomass from the inoculum, a biokinetic strategy based on the use of low HRT (in case of CSTR, HRT is equal to the solid retention time, SRT) was applied (6–14 h).

Table 1 – Synthetic wastewater composition (adapted from Bruce et al. [27]).

Nutrient	Chemical formula	Concentration (g/L)
Glucose	$C_6H_{12}O_6$	5
Ammonium bicarbonate	NH_4HCO_3	2
Potassium dihydrogen phosphate	KH_2PO_4	1
Magnesium sulphate heptahydrate	$MgSO_4 \cdot 7H_2O$	0.1
Ferrous chloride	$FeCl_2$	0.00278
Sodium chloride	NaCl	0.01
Sodium molybdenum oxide dihydrate	$NaMoO_4 \cdot 2H_2O$	0.01
Calcium chloride dihydrate	$CaCl_2 \cdot 2H_2O$	0.01
Manganese sulphate monohydrate	$MnSO_4 \cdot H_2O$	0.0094

2.3. Systems evaluation and comparison

2.3.1. Determination of the optimal conditions for the systems

Both systems were operated at five HRTs: 6, 8, 10, 12, 14 h aiming to find the best hydraulic conditions in terms of hydrogen yield and productivity. Each reactor of the two-stage system were operated at the same HRT i.e. half of the total one. Each HRT condition was evaluated at five pHs 4.0, 4.5, 5.0, 5.5 and 7.0. The influence of these variables was assessed by using the response surface methodology (RSM) in order to assess the effect of each variable as well as their combined influence. The analysis was carried out using the software Statgraphics Plus®.

2.3.2. Experimental running

The experiment sequence was randomised (i.e. randomly selected HRT and pH) in order to minimized the experimental bias. Furthermore, for each condition, the reactors were reseeded with the same original inoculum (non-adapted anaerobic biomass) and were kept until steady state conditions were reached, usually after 3 HRTs of operation, although, the reactors were maintained at each condition for around 40 HRTs.

2.4. Analytical methods

For each experiment, measurements of the influent and effluent of each reactor were carried out in order to characterize the system performance. Chemical oxygen demand (COD) was determined using Method 5220C, standard methods [12], and glucose concentration was measured using 3,5-Dinitrosalicylic acid, DNS [13]. Prior to COD and glucose determination, samples were centrifuged at 15,000 rpm for 10 min in order to remove suspended solids. The production of volatile fatty acids (VFA) and ethanol was determined by gas chromatography (Shimadzu GC8 and PerkinElmer 500, respectively). The biomass concentration was measured by determining the volatile suspended solids (VSS) in the reactor