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A short-term test for the evaluation of hydrogen and volatile fatty acids production from industrial effluents

The use of a short-term test to evaluate organic matter concentration from industrial effluents for the production of hydrogen and volatile fatty acids

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ABSTRACT

A short-term test (time interval < 24 h) is proposed to evaluate the concentration of organic matter from industrial effluents for the production of hydrogen. Organic substrates selected were: protein effluent from a soybean processing plant; glycerol, from the production of biodiesel; Tebuconazole, a fungicide; and glucose, used as a reference substrate. Volatile fatty acids (VFA) and the degree of acidification of each substrate are also determined. After glucose (average hydrogen release of 24.8 mL g COD^{-1}), protein effluent provided the highest hydrogen yield (1.74 mL g COD^{-1}). Acetic and butyric acids presented the highest VFA concentrations. Fermentation of Tebuconazole presented the highest degree of acidification. Some considerations are made about the biological processes involved in hydrogen production.

Introduction

The need for a shift from fossil-based energy generation systems to more clean hydrogen-based systems is not only related to the risks associated with climatic changes, but also the depletion of fuel resources [1].

The use of hydrogen as an energy carrier offers advantages when compared to fossil fuels because its combustion produces only water (no carbon dioxide) and its heat capacity is almost three times higher than that of gasoline [2].

Biological hydrogen production comes from anaerobic degradation of complex organic substrates where polysaccharides, proteins and lipids are hydrolysed by enzymes

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into sugars, amino acids and fatty acids. These are further converted by acidogenic microorganisms into volatile fatty acids (VFA), carbon dioxide and hydrogen [3].

The criteria used to select organic substrates as suitable sources of hydrogen include their availability, cost and biodegradability. Simple sugars like glucose, sucrose and lactose are the most studied substrates for hydrogen production since they are easily biodegradable but their costs restrict the biogeneration of hydrogen in large-scale applications [4].

Biological hydrogen may also be produced from the fermentation of domestic, agricultural, livestock, and industrial organic waste. Effluents from food, biofuel and fungicide industries are potential sources of hydrogen and VFA due to their high concentration of carbohydrates and proteins. Nevertheless, the complex nature of these substrates affects their biodegradability because each component requires different environmental conditions to produce hydrogen [4]. In addition, it is important to determine the rate of influent organic matter to maintain the balance between acid-producer and acid-consumer microorganisms, taking into account the fluctuations in load and composition of the industrial effluents.

VFA produced during the fermentation of complex organic substrates may be used in processes of biological nutrient removal since these compounds are sources of biodegradable carbon [5]. A study demonstrated that it is possible to totally remove nitrate by the addition of VFA formed during the fermentation of effluents from the processing of potato [6]. The study found that the denitrifying microorganisms use carbon derived from acetic, butyric, and propionic acids.

VFA produced in anaerobic fermentation may also be used in the industrial synthesis of biodegradable polymers to replace petroleum (this adds more value to the fermentation process [7–9]), or as additives in the production of heat-resistant fibbers [10].

This work presents a fast and reliable tool (a short-term test) for evaluating the organic matter concentration of some selected effluents and its relation to the production of biohydrogen and volatile fatty acids (acetic, propionic and butyric). The substrates were submitted to standardized batch fermentation conditions and their degree of acidification was measured after a bioreactor operation time less than 24 h (some authors reported the need for a larger hydraulic retention time, more than 1 d, to determine VFA production [11–15]).

Material and methods

Effluents

The organic substrates employed were: glycerol (of low commercial value) from the production of biodiesel; protein effluent from the processing of soybean; effluent from the production of the fungicide Tebuconazole; and glucose, used as a reference substrate, in concentrations of 1000, 2000, 4000, 8000, 12,000, 16,000, and 20,000 $mgO_2\ L^{-1}$, expressed as COD.

Biomass

A granular sludge was collected in an UASB reactor from the participant soybean processing plant and used as biomass. The sludge was autoclaved at 120 °C during 30 min to eliminate methanogenic microorganisms [16]. Concentration of total volatile solids (TVS) was 2500 mg L^{-1}. Initial pH of 6.0, adjusted by adding HCl or NaOH 1 mol L^{-1} to the substrates.

Nutritional solution

Each bioreactor was supplied with a nutritional solution required by the acidogenic microorganisms composed by micro and macronutrients containing 40 mg L^{-1} of $MgCl_2 \cdot 6H_2O$; 1000 mg L^{-1} of $CaCl_2 \cdot 2H_2O$; 50 mg L^{-1} of NH_4Cl; 2.5 mg L^{-1} of $ZnCl_2$; 3.8 mg L^{-1} of $MnSO_4 \cdot 4H_2O$; 10 mg L^{-1} of $Na_2MoO_4 \cdot 2H_2O$; 5 mg L^{-1} of $CuSO_4 \cdot 5H_2O$; 130 mg L^{-1} of KCl; 1000 mg L^{-1} of $Na_2HPO_4 \cdot 12H_2O$; 2550 mg L^{-1} of $NaH_2PO_4 \cdot 2H_2O$; 2.5 mg L^{-1} of $NiCl_2 \cdot 6H_2O$; 12.5 mg L^{-1} of KI; 1000 mg L^{-1} of NaCl; 1 mg L^{-1} of $FeSO_4 \cdot 7H_2O$; and 2.5 mg L^{-1} of $CoCl_2 \cdot 6H_2O$ [17,18].

Operating procedures

The experiment was carried out in a system developed for inspecting the specific methanogenic activity (SMA) in anaerobic reactors [19], composed by eight 450 mL magnetically stirred glass bioreactors. Temperature and pressure were kept constant at 35 °C and 1 atm). Biogas releasing from each reactor was controlled by a device consisted of three-way solenoid valves actuated by low pressure manometers. Gas volume was measured semicontinuously and the lowering of its hydrogen content determined the end of each testing procedure.

Analytical procedures

The produced biogas was analysed by a gas chromatograph Dani GC 1000, with thermal conductivity detector (TCD) and Molecular Sieve column 80/100 [20], using helium as the carrier gas (25 mL min^{-1} flow). Sample volume of 1 mL.

Volatile fatty acid concentrations (acetic, propionic and butyric acids) were determined by a gas chromatograph Dani GC 1000, with flame ionization detector (FID) and capillary column AT 1000 (30 m × 0.32 mm × 0.25 μm), using helium as the carrier gas (1 mL min^{-1} flow). Sample volume of 1 μL [21].

Samples were centrifuged for 30 min and filtered in a glass fiber filter with pore size of 0.6 μm, to remove suspended solids.

The degree of acidification was determined by the ratio between the equivalent COD of the products (acetic, propionic and butyric acids) and the amount of biogas produced (hydrogen) related to the initial COD [8].

Results and discussion

Characterization the organic substrates

Table 1 shows the characteristics of the effluents analysed. Notice the high content of organic matter and the suitability of anaerobic processes to obtain organic compounds at low costs with the added benefit of bioenergy production.