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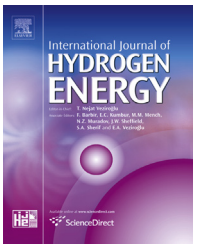

Methodology to determine the specific hydrogenic activity (SHA) of waste sludges

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ABSTRACT

Production of hydrogen is influenced by the pH, the concentration of organic matter, and the concentration of sludge. A short-term test is presented in which the specific hydrogenic activity of a waste sludge is calculated in order to quantify its hydrogen production capacity. To determine the ideal conditions for the measurement of SHA was used glucose in concentrations of 1000; 2000; 4000; 8000; 12,000; 16,000; and 20,000 mg O_2 L^{-1}; sludge in concentrations of 1250; 2500; 5000; and 7500 mg TVS L^{-1}; and pH adjustments of 5.0; 5.5; 6.0; and 6.5. Given the initial concentration of soluble COD of 12,000 mg O_2 L^{-1}, sludge concentration of 2500 mg TVS L^{-1}, and pH of 6.0, the highest SHA obtained was 483 mLH_2 g TVS^{-1} h^{-1}. As to volumetric measurements, given the initial concentration of organic matter of 8000 mg L^{-1}, biomass concentration of 5.000 mg TVS L^{-1}, and pH of 5.5, the volume of produced hydrogen per mass of soluble COD added reached a maximum of 38 mL $gCOD^{-1}$.

Introduction

Hydrogen is an energy vector to power fuel cell systems used in transportation or stationary applications. The benefit of using these systems is that only water is produced as the product which will help to reduce the emissions of greenhouse gases if they are used to replace engines or combustors which rely on carbon-containing fuels such as petrol and natural gas [1]. Hydrogen has emerged as one very promising alternative energy source because it is clean, efficient, and can be produced from a variety of means, including thermochemical processes or fermentation of plant biomass and organic residues [2].

The method of production of hydrogen by fermentative bacteria is technically simpler than the method that uses photosynthetic bacteria because in the fermentation process hydrogen is obtained from the decomposition of the carbohydrates that are present in the organic waste. The demerit of hydrogen production by photosynthetic bacteria is that these bacteria need light to convert organic matter in hydrogen [3].

Mixed cultures are complex microbial communities, as are the sources from which they are obtained. It is expected that those communities have a potential hydrolytic activity, and robustness to cope with environmental changes because various similar and complementary metabolic pathways

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occur simultaneously, even during the degradation of the same substrate [4].

There are several problems associated with the use of mixed cultures: as complex microbial communities, their composition varies with time, responding to changes in process parameters and from reactor to reactor [4].

The species *Enterobacter aerogenes, E. cloacae, Clostridium butyricum, C. pasteurianum, Desulfovibrio vulgaris and Escherichia coli*, found in mixed cultures in anaerobic sludges, are among the bacteria employed in the artificial generation of hydrogen [5].

The production of hydrogen by fermentation processes has several advantages such as [6]:

(a) high hydrogen production rates;
(b) potential 24-h continued production;
(c) high growth rates of the fermentative bacteria.

The sludge characteristics play an important role in the production of hydrogen. Microorganisms not sedimented, resulting from stratification in sludge sedimentation phase in a sequential batch reactor, were able to produce more hydrogen when compared to the sedimented ones. The high production was mainly attributed to the presence of the species *Clostridium butyricum* sp. and the absence of the species *Selenomonas* sp., which is associated with low hydrogen yield [7].

Sludge from wastewater treatment plants contain a mixed culture that requires a different nutritional medium used for the pure cultures. Further investigation is necessary to find nutritional formulations for this type of microflora in order to maximize their hydrogen-producing capacity [8].

In addition to the nutritional formulations, the pH is a determining factor in the hydrogen production due to the effects of the hydrogenases enzymes and on the metabolic pathways involved in the process [9] [10].

The optimum pH range for hydrogen production depends of the organic waste utilized. The optimum pH range is 4.0 to 4.5 for sucrose; 4.7 to 5.7 for starch; 5.5 for glucose; 6 to 7 for xylose [11]; and 6 for wastewaters from the food industry [12].

Temperature is another factor that influences the physiological activity of microorganisms and the rate of formation of fermentation products. If the temperature of the medium is changed, the process becomes unstable, since the microorganisms are sensitive to thermal variations. They take a while to return to a steady production at a given temperature. This occurs because temperature affects their physiological activity and the rate of formation of fermentation products [13].

The present work proposes a short-term test (24 h) to evaluate the specific hydrogenic activity of a waste sludge and calculate its maximum productivity. Moreover, the volume of hydrogen produced per mass of soluble COD added is determined as a function of pH and TVS. Control parameters are suggested to improve hydrogen release in acidogenic reactors.

Material and methods

Organic substrate

Glucose in concentrations of 1000; 2000; 4000; 8000; 12,000; 16,000 and 20,000 mg O_2 L^{-1}, expressed as COD.

Inoculum source

Granular sludge collected in an UASB reactor from a soybean processing plant, autoclaved at 120 °C for 30 min to eliminate methanogenic microorganisms [14]. Adopted concentrations of total volatile solids (TVS): 1250; 2500; 5000 and 7500 mg L^{-1}. Initial pH of 5.0; 5.5; 6.0; and 6.5 for TVS concentrations of 2500; 5000 and 7500 mg L^{-1}. Initial pH of 5.5 and 6.0 for TVS concentration of 1.250 mg L^{-1}. Either HCl or NaOH used for making pH adjustments (1 mol.L^{-1}).

Nutritional solution

Each bioreactor was supplied with a nutritional solution of micro- and macronutrients composed by: $MgCl_2 \cdot 6H_2O$ (40 mg L^{-1}); $CaCl_2 \cdot 2H_2O$ (1,000 mg L^{-1}); NH_4Cl (50 mg L^{-1}); $ZnCl_2$ (2·5 mg L^{-1}); $MnSO_4 \cdot 4H_2O$ (3.8 mg L^{-1}); $Na_2MoO_4 \cdot 2H_2O$ (10 mg L^{-1}); $CuSO_4 \cdot 5H_2O$ (5 mg L^{-1}); KCl (130 mg L^{-1}); $Na_2HPO_4 \cdot 12H_2O$ (1,000 mg L^{-1}); $NaH_2PO_4 \cdot 2H_2O$ (2,550 mg L^{-1}); $NiCl_2 \cdot 6H_2O$ (2.5 mg L^{-1}); KI (12.5 mg L^{-1}); NaCl (1,000 mg L^{-1}); $FeSO_4 \cdot 7H_2O$ (1 mg L^{-1}); and $CoCl_2 \cdot 6H_2O$ (2.5 mg L^{-1}) [8] [15].

Method for SHA measurement

The experiment was carried out in an equipment developed for inspecting the specific methanogenic activity (SMA) in anaerobic reactors [16], composed by eight 450 mL magnetically stirred glass reactors. Temperature and pressure were kept at 35 °C (±2 °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. The manometric fluid used was water and the gas volume in the reactors was measured semi continuously by displacement of 10 mL water. With this displacement the water reached an electrical contact to open the solenoid valve and releasing the gas contained in manometer. Each valve actuation an electrical signal was recorded by the data acquisition software. The gas volume in each reactor was obtained by the total number of signals recorded multiplied by the gas volume displaced in manometer calibration.

The following operational steps were taken to determine the SHA of the sludge:

- Sludge autoclaving;
- Addition of sludge and nutrient solution in equal volume [8];
- pH adjustment;
- Bubbling of nitrogen (1 min) into the digester to remove atmospheric air;
- Adjustment of the temperature at 35 °C;
- Acclimation of the sludge (12–14 h);
- Addition of glucose (organic substrate) in predetermined concentration;
- pH adjustment;
- Bubbling of nitrogen to remove residual atmospheric air;
- Collection of biogas samples every 2 h for measurement of the hydrogen percentage.

Small amounts of hydrogen (below 1%) in the collected biogas, or a reduction in the biogas volume, marked the end of the experiment.

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