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Anaerobic digestion of tuna waste for the production of volatile fatty acids

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ABSTRACT

Fish canning industries generate a significant amount of solid waste that can be digested anaerobically into volatile fatty acids (VFA). The aim of this research was to study the effect of various pHs, ranging from 5.0 to 10.0, and percentage of total solids on the anaerobic digestion of tuna waste into VFA, both in batch assays and continuous reactor. The production of VFA was affected by pH and was significantly higher under alkaline conditions. At pH 8.0, the VFA production reached 30,611 mg COD/L. The VFA mainly consisted of acetic, propionic, *n*-butyric and *i*-valeric acids. Acetic acid was the main product at all the pHs tested. In terms of total solids (TS) the best results were obtained with 2.5% total solids, reaching 0.73 g COD_{VFA}/g COD_{waste}. At higher TS concentrations (5 and 8% TS) lower yields were reached probably due to inhibition at high VFA concentration.

1. Introduction

The fish canning industries are an important sector in Galicia, responsible for 86% of the total fish canning production in Spain. Tuna is currently the main product of the Spanish seafood processing industry. In fact, Spain is the second largest world producer and the largest producer in the EU of canned tuna, with 237,047 tons produced in 2009, behind Thailand. Galician cannery companies manufacture a high range of raw materials, and canned tuna represents 65.5% of the total production. The amount of solid waste generated in the fish canning industry is high. During the manufacturing process, the amount of raw materials leftover in the form of waste can amount to 50% by weight. That solid waste consists of offal, tails, heads and guts, and is a good candidate for anaerobic digestion because it contains high levels of potentially biodegradable materials.

The literature on anaerobic digestion of fish waste is scarce. Until now this type of waste had not been taken into account for the production of volatile fatty acids (VFA), although studies have been published on their use for the production of biogas (Eiroa et al., 2012). VFA are short-chain fatty acids (acetic, propionic, butyric acids), produced either synthetically from fossil resources or as metabolic intermediates of anaerobic digestion. The possibility to use VFA for various purposes as valuable chemical compounds has opened a new avenue for the treatment of waste by anaerobic fermentation. VFA may have many uses in the marketplace. They can be used for the production of biodiesel (Christophe et al., 2012; Fontanille et al., 2012). They are suitable as an energy source for the storage of lipids in microalgae (Prathima and Venkata, 2012). They are useful as potential substrates for the production of hydrogen via photo-fermentation (Nayale et al., 2013; Srikanth et al., 2009) or to produce polyhydroxyalkanoates (PHAs), in replacement of petroleum-based plastics (Ben et al., 2016; Mengmeng et al., 2009; Lee et al., 2014; Lagoa-Costa et al., 2017).

VFA production through acidogenic fermentation in bioreactors can be affected by several factors, such as the nature of the substrate and its concentration, hydraulic retention time (HRT), organic loading rate (OLR), temperature or pH.

It is believed that the hydrolysis of the organic material is the limiting factor in the anaerobic digestion of solid wastes (Eastman and Ferguson, 1981). If the organic matter of the waste is not adequately solubilized, only 30–50% of the total COD was found to be biodegraded in 30 days (Parkin and Owen, 1986).

Specific operating conditions for acetogenic-methanogenic stages have been previously studied, however relevant literature on the hydrolytic-acidogenic step is still scarce. In this context, the purpose of this study was to investigate the effects of pH and % Total Solids (TS) on hydrolysis, solubilization and VFA production from solid tuna waste, in order to provide optimal conditions for acidogenic fermentation.

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2. Material and methods

2.1. Substrates and inoculum

2.1.1. Inoculum

The inoculum used in the batch assays and for the acidogenic reactor was collected from an anaerobic digester fed with tuna waste and operated to produce biogas. This sludge was concentrated by sedimentation at 4 °C for 24 h and acclimatized to the new operating conditions. The percentage of volatile solids (VS) in the sludge used in all the experiments ranged between 70 and 91%. In the batch assays the initial inoculum concentration was 9% and the amount biomass remained practically constant throughout the assays.

2.1.2. Substrate

The residue used for the experiments came from a tuna cannery industry in Galicia (Spain). It consisted of heads, tails, bones and guts. The residue was dried in an oven at 100 °C until reaching a stable dry weight, after 24–48 h. Then, the tuna waste was triturated to a size smaller than 2 mm using a kitchen mixer. The composition is shown in Table 1. The organic fraction of the dry waste was high, reaching 84%; therefore, the fish waste is a good candidate for anaerobic digestion because it contains high levels of potentially biodegradable materials. Moreover, high amounts of nitrogen and fat present in the waste can result after its anaerobic conversion to ammonium and VFA, which could inhibit the process depending on the final amount.

2.2. Reactor

A double-walled glass reactor was used and allowed to maintain the temperature at 37 °C using a thermostatic bath. It had a working volume of 2L and was maintained with continuous stirring by means of an electric shaker at 120 rpm to keep the mixture well-stirred. The reactor was inoculated with anaerobic sludge, reaching a concentration of 30.81 g TS/L and 26.41 g VS/L. It was fed 2 days a week with pre-ground dried tuna waste.

The reactor was started up with an OLR of 2 g COD L^{-1} d^{-1}, which was maintained during 40 days (baseline data not shown), to be subsequently increased to 4 g COD L^{-1} d^{-1}.

Initially a hydraulic retention time (HRT) of 10 days was applied, which was later increased to 20 days. The reactor was operated under conditions of thorough mixing; therefore the hydraulic retention time was equal to the solids retention time (SRT).

The pH was automatically controlled through the addition of a 2 N NaOH solution and the reactor was operated at different pHs, starting at pH 5 to be progressively increased to pH 6, 7, 8, 9 and 10. At each pH the reactor was operated until reaching steady state conditions (when the concentration of the soluble chemical oxygen demand (SCOD) and the VFA content in the effluent were stable) and it was then maintained under such conditions for a period of 4 times the HRT.

The biogas produced was measured with a liquid metering device biogas displacement (Veiga et al., 1990).

Table 1
Composition of the dried and grounded tuna residue.

	Tuna waste
g COD/g waste	1.29
g TS/g waste	0.96
g VS/g waste	0.84
g N/g waste	0.10
g C/g waste	0.51
g fat/g waste	0.29
g protein/g waste	0.63
C/N	5.10

2.3. Batch fermentation experiments (batch tests)

The biodegradability assays were performed in 21 glass flasks of 120 ml with a working volume of 50 ml, closed with butyl rubber stoppers, and sealed with aluminum caps (Angelidaki et al., 2009). All assays were undertaken in triplicate, the initial pH values were adjusted to 5, 6, 7, 8, 9, and 10 by adding 2 N NaOH or 2 N HCl. Bicarbonate (5 g/L) was added to maintain suitable alkalinity. After adding the medium, the grounded waste and the inoculum, the headspace was flushed with N_2/CO_2 (80/20, v/v) and Na_2S was added as reducing agent (1 mM).

A control, called "Blank", was prepared in triplicate similarly as the rest of the flasks and subjected to the same operational parameters, but without adding the waste, both in the test on the effect of pH as well as in the assay on the effect of the concentration of TS.

The vials were then incubated at 37 °C and the pressure increase was monitored using a handheld pressure transducer.

2.4. Analytical methods

Total and volatile solids, ammonia and total Kjeldahl nitrogen (TKN) were measured according to Standard Methods (APHA et al., 1998). The total and soluble chemical oxygen demands (COD and SCOD, respectively) were assessed by digestion of the sample with dichromate at 150 °C.

The acids: formic (HFor), acetic (HAc), lactic (HLac), propionic (HPr), butyric (HBu), *n*-valeric (HVa), *i*-valeric (*i*-HVa) acids were determined by high performance liquid chromatography (HPLC) using a Hewlett Packard chromatograph equipped with supelcogel C-610 a column and two detectors connected in line, one ultraviolet detector (UV) and a refractive index detector (RI). The VFA concentration was the sum of the various acids and was expressed as the chemical oxygen demand (COD) by using a conversion factor (Henze et al., 1995). A solution of 0.1% phosphoric acid was used as mobile phase with a flow rate of 0.5 ml/min. The column was maintained at 30 °C. The detection wavelength was set at 210 nm. VFA concentrations were calculated using a calibration curve ranging from 25 to 3000 mg/L. All samples were analyzed after centrifugation at 10,000 rpm for 10 min and filtration through a 0.2 μm membrane.

On the other hand, when acids are produced they can either be dissociated (A^-) or undissociated (HA) depending on the pH of the medium and the pKa of the acids. The p*K*a values of the obtained acids are: 3.74 (HFor); 4.75 (HAc); 4.87 (HPr); 3.86 (HLac); 4.83 (HBu) and 3.86 (HVa). The undissociated acid concentration of an acid (HA) "i" was calculated with Eq. (1) (Infantes et al., 2012):

$$C_{HAi} = \frac{C_{Total}}{1 + 10^{(pH - pKa)}} \quad (1)$$

The dissociated acid concentration of an acid (A^-) "i" was calculated with Eq. (2):

$$C_{Total=} C_{HAi} + C_{Ai^-} \quad (2)$$

The production of methane is defined as the highest plateau attained in the methane production curves after correction for the residual methane present in the inoculum divided by the amount of waste initially added as substrate.

The methane content of the biogas was analyzed on a gas chromatograph equipped with a thermal conductivity detector (TCD) and a Poropack-Q column. Helium was used as the carrier gas at

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