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Effect of ammonia content in the biodegradability of the salmon industry wastes

R. Chamy, P. Poirrier, M.C. Schiappacasse, D. Alkalay, L. Guerrero

Abstract Lately, efforts put into solving the serious environmental problems caused by the accumulation of liquid, gaseous or solid industrial residues, have been greatly increased, being solid wastes the last ones to be considered. This work studies the anaerobic biodegradation of salmon waste produced by death in the farming process. The results obtained: 61.99% degradation (expressed in volatile solids abatement), with a methane productivity of 535.66 l $CH_4/kg_{d.k.}$ in studies done to samples with 1% w/v of dry residue, show that the anaerobic technology is adequate to treat these wastes. Runs performed with higher solid contents (7, 13 and 20% w/v) showed an ammonia accumulation, coming from protein degradation. They represent an upper limit of the system studied at a maximum value of ammonia nitrogen of 3.5 g/l attained, amount which hinders the further increase of solid matter in the tests. With the results obtained during this study, two inhibition models were analyzed (the Luong model and one proposed by the authors), which allow the prediction of the performance of the system studied.

List of symbols

NNE	non nitrogenous extract
COD	chemical oxygen demand
SVS	suspended volatile solids
VS	volatile solids
q_p	methane productivity
q_{po}	maximum methane productivity
I	salmon concentration
I_m	maximum salmon concentration
α	inhibition effect parameter
k_1	kinetic constant
k_2	parameter, indicates degree of affinity between the inhibitor and the microorganism(s) involved
h.b.	humid base
d.b.	dry base
d.r.	dry residue

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1
Introduction

Process industry in general produces large quantities of residues and subproducts which frequently generate serious environmental problems. Solid wastes, because of its easier confinement have had less attention and only lately there have been serious efforts to cope with them.

An important case are the fish rearing industries in which an important number of fish die in the fishfarms, which because of sanitary reasons can not be utilized in the fishmeal production. In the salmon farms the rate of death varies from 1% to 30%, depending on the technification of the installation, among other factors. On the other hand, heads, viscera and bones which come from the salmon processing can be used for fishmeal producing.

The dead fish residues have a high solid content (36%). Because of this, they have to be diluted before they may be processed in conventional biological reactors, with concentrations of solids between 5–10% (Wujcik & Jewell, 1980; Adams & Dougan, 1987; Colleran et al., 1983; Fouhy, 1993), since there does not exist a totally developed technology for their treatment. From an other point of view, the high humidity content of the crude waste and the normally great distance from agricultural farmlands, make less attractive alternative processes like composting or incineration.

A good solution is anaerobic digestion, which has some special advantages, through the production of usable subproducts, as: biogas and a sludge with soil remediation properties, which may improve the economic balance of the process (Vallés et al., 1980; Vochten et al., 1988; Mata-Alvarez & Cecchi, 1992; Rivard, 1993; Verstraete et al., 1996).

This work focuses on anaerobic biodegradability studies of the residue with concentrations from 1% to 20%, and the eventually inhibitory effect of ammonia accumulation. The latter is of great importance due to the high protein content of the waste and the ammonia evolution from the anaerobic digestion of aminoacids.

2
Materials and methods

Substrate: For the experimental work, whole salmons were provided by chilean fishfarms. The salmons were triturated to a homogeneous paste, so as to have a representative sample of the real waste.

Biodegradability tests: Biodegradability was determined at four total solids concentrations: 1, 7, 13 and 20% w/v, each of them duplicated and with one test of only sludge and one with pure waste.

The method used was adapted from the one developed for liquid residues by Field et al. (1988). The main modification is the addition of 1 g of bicarbonate per g of COD, to prevent the media acidification. The high organic load makes necessary to use a mixture of sodium and potassium bicarbonate to be sure to work below toxic levels of both cations (WPCF, 1987; Speece, 1993).

The experiments were performed in the system shown in Fig. 1.

The 300 ml batch reactor operated has a working volume of 150 ml. It is connected through a water trap to a gas meter which contains a sodium hydroxide solution of 50 g/l, which absorbs the CO_2, so as to measure only the methane produced.

As innoculants of the anaerobic degradation measurements, two different sludges were used, both coming from an anaerobic brewery waste treatment plant. The methanogenic activities of these sludges were 1.33 and 0.58 gCOD-CH_4/gVSS·d, measured at 37° using the method of Field et al. (1988).

A daily register of methane produced was conducted and the total solid contents, volatile solids and pH, were measured at the beginning and at the end of each run.

3 Results and discussion

3.1 Waste characterization

The characterization of the salmon wastes used is presented in Table 1.

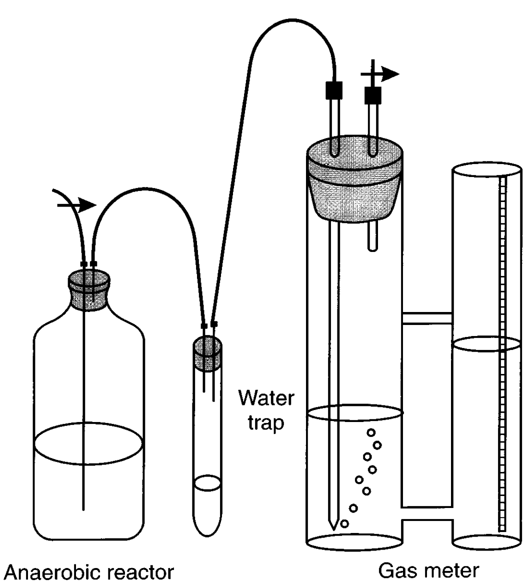

Fig. 1. System for measuring biodegradation

Table 1. Characterization of salmon

Characterized parameter	Units	
Humidity	% h.b.	64.63
Total solids	% h.b.	35.37
Volatile solids	% d.b.	94.50
Ashes	% d.b.	5.50
Proteins	% d.b.	41.52
Lipids	% d.b.	39.17
Total soluble sugars	% d.b.	0.31
NNE	% d.b.	13.51
Carbon (C)	% d.b.	51.22
Nitrogen (N)	% d.b.	6.66
C/N Ratio	–	7.70
Ammonia Nitrogen	% s.b.	0.00134
Total COD	mgO_2/g d.r.	1365.97
Soluble COD	mgO_2/g d.r.	542.90
pH	–	6.00

3.2 Biodegradability kinetics

In Fig. 2, the rates of methane generation is shown at the four solid levels studied.

In the graph an inverse proportionality between solid content and total gas production can be appreciated. Methane productivity is shown in Table 2.

From the other part, for each solids level tested, the biodegradability kinetics show a high initial rate of degradation, which is representative of the consumption of easily degradable nutrients. In general, this first step of microbial activity is followed by a substrate solubilization stage, which is easily observed in the 1% run. In the other runs, the methanogenic activity ceases completely after this first stage. This could mean some kind of inhibition of the system which hinders the degradation of more complex molecules (second phase of the tests).

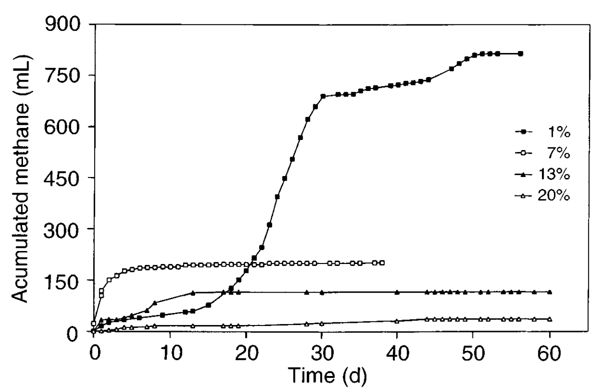

Fig. 2. Kinetics of salmon degradation. 1, 7, 13 y 20% w/v TS measurements

Table 2. Methane productivity at the four salmon content levels

Solids level (% w/v)	Productivity L CH_4/$kg_{dry\ residue}$
1	535.66
7	19.98
13	6.92
20	1.4

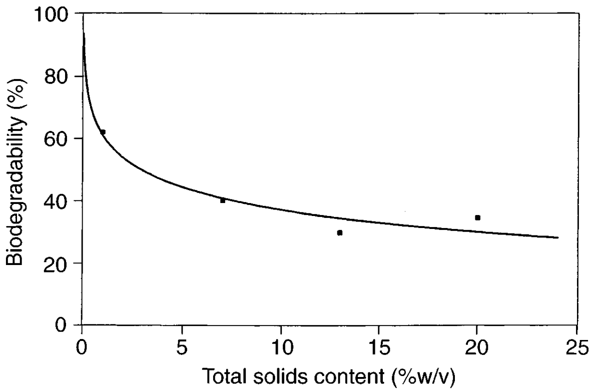

Fig. 3. Salmon biodegradability correlation with total solids content

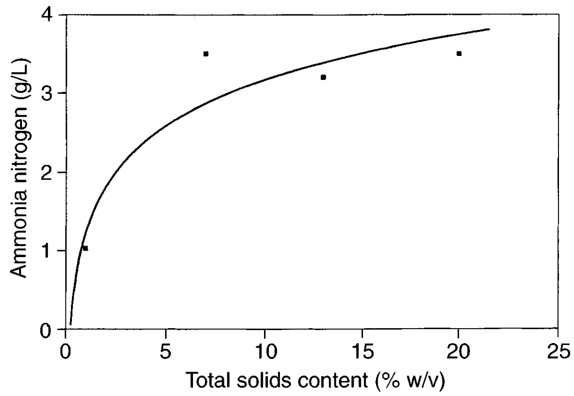

Fig. 4. Correlation between ammonia nitrogen produced and total solids content

The biodegradability of the waste at the four concentrations studied was determined through the consumption of the organic matter present, represented by the difference in volatile solids between the initial and final conditions. This is shown in Fig. 3, where a clear correlation is observed between solids content and the biodegradability measured. The tendency of the curve is asymptotic.

For the more diluted run the results obtained correspond to the "true" anaerobic biodegradability of the waste, because in this condition there are no inhibition nor toxicity problems, or mass transfer restrictions, as in higher solid concentration runs (13% and 20%).

The former was proved with tests performed with solid contents below 1%, where similar biodegradabilities were obtained.

Analyzing the results obtained in the tests performed and presented before, and taking into account the proteic nature of the waste studied, the possible accumulation of ammonia nitrogen was considered and its eventually harmful consequences to the anaerobic population. The effect of different ranges of ammonia contents on anaerobiosis is shown in Table 3.

This hypothesis proved true after determining the final concentrations of ammonia at the end of the biodegradability runs. The final values found, were inhibitory and even toxic for the three higher concentration runs of 7%, 13% and 20%, reaching a value of 3.5 g/l in the first of them. This is shown in Fig. 4. The 1% run showed an ammonia nitrogen content of 1.08 g/l.

All the runs above 1% were sustained for some time after the methane production ceased, with the purpose of trying to find an eventual adapting of the microorganisms to high ammonia contents, but to no avail, as shown in Fig. 4.

Table 3. Ammonia nitrogen effect on anaerobic media (WPCF, 1987)

Concentration (mg/l)	Effect Observed
300–500	beneficial
500–1000	not adverse
1500–3000	inhibitory
>3000	toxic

In this figure a tendency to saturation of the systems is appreciated, due to the reaching of a limiting ammonia value in the media. This saturation could further be explained at the 13% and 20% concentrations to restrictions in mass transfer due to the high solids content which could have produced a lesser nutrient degradation.

The values of ammonia shown in Fig. 4 for runs under 1%, correspond to tests which were performed trying to corroborate the data obtained at higher solids contents.

3.3 Model for ammonia inhibition

Ammonia inhibition was analyzed and a model of product inhibition was used, under the supposition that the salmon content in the tests is proportional and directly related to the inhibitor concentration.

Four alternative models were considered: Aiba & Shoda (1968), Ghose & Tyaghi (1982), Luong (1985) and one proposed by the authors. The latter two showed the best correlations.

Luong's model shows a good correlation for ethanol inhibited processes, and is represented as follows (Chamy et al., 1995):

$$q_p = q_{\mathrm{po}} \cdot \left(1 - \left(\frac{I}{I_m}\right)^{\alpha}\right) ,$$

where,
q_p: methane productivity (l CH_4/gVS $\cdot$ d)
q_{po}: methane productivity when the salmon content tends to zero (l CH_4/gVS $\cdot$ d)
I: salmon concentration (g/l)
I_m: salmon concentration for which methane productivity tends to zero (g/l)
α: inhibition effect parameter

The result obtained by the model is presented in Fig. 5, where the points represent the experimental values and the line the model. In this model the initial solid content was considered as parameter (which is proportional to the ammonia generated by the protein degradation), because it is easy to measure and to be used in the design of industrial scale reactors. In any case, the correlations obtained are very similar to the ones obtained when ammonia itself is used as parameter.

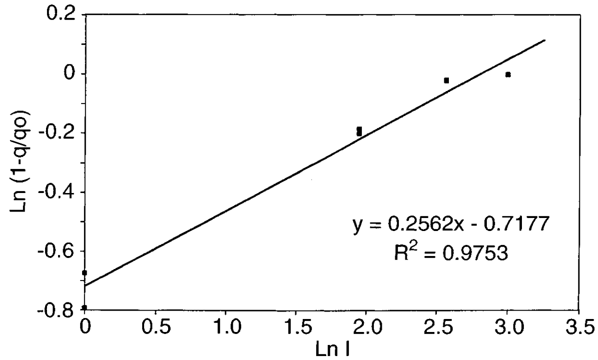

Fig. 5. Fitting of experimental values to Luong's model

From the adjusted correlation, the following values for the model parameters were obtained: α: 0.2562, I_m: 16.46 g/l for a value of q_{po} of 0.0185 (l CH_4/gVS · d), obtained from extrapolation in Fig. 6, for the case in which the solid residue tends to zero, point in which the inhibitor content is null.

The value for I_m agrees with the data obtained and described before. In these, it was found that for the run with 20%, the methane productivity decayed notoriously reaching a value of 1.03 l CH_4/$kg_{d.r.}$. Referring to the α parameter; looking at the equation it may be concluded that the value found indicates that the inhibitor acts slowly on the system.

So, the Luong model, somehow gives a physical interpretation to the inhibition phenomenon.

From the other side, the model proposed by the authors assumes the existence of an affinity factor between the inhibitor and the microorganism(s) (of the competitive inhibition type):

$$1 - \frac{q_p}{q_{po}} = \frac{k_1 \cdot I}{k_2 + I} ,$$

where k_1 and k_2 are constants of the model, of which the latter describes the affinity mentioned before. The rest of the parameters in this equation are the ones defined for the Luong model.

The adjustment of the experimental values are presented in Fig. 7.

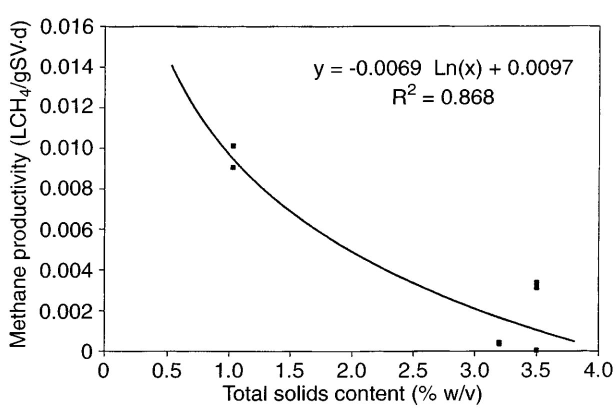

Fig. 6. Correlation between solids content and the productivities attained

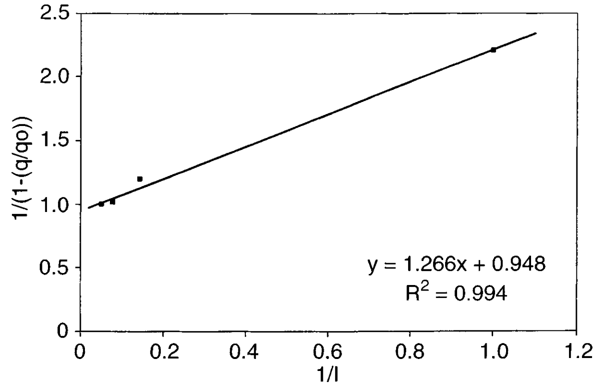

Fig. 7. Adjustment of the experimental values to the proposed model

The parameters found for this model have the following values: k_1: 1.05, k_2: 1.33 for the same q_{po}. The correlation coefficient obtained was 0.994, which means a good adjustment of the model to the system studied. The value of k_2, indicates that when $k_2 = I$ the inhibition of the system is 50%. This way, for the lower level of solids studied, $I = 1\%$, the system will be 45% inhibited.

4
Conclusions

According to the results obtained it is clear that the salmon industry residues are possible to be treated by anaerobic processes. However there exists a serious limitation of the process proposed due to the accumulation of ammonia in the media, caused by the high protein content of the residue studied, tending to a saturation point, from which there is not possible to increase the solid content to obtain further degradation. This limiting value corresponds to an ammonia nitrogen content around 3.5 g/l.

Alternative solutions to this problem are: the pH control of the media so as to diminish the amount of nitrogen in its inhibitory form (ammonia), favoring the ionized state (ammonium); to implement a nitrification-denitrification process or strip out the ammonia. All these possibilities have to be analyzed thoroughly and the corresponding experiments performed, for which the model developed in this work allows to predict the behavior of the system.

The anaerobic biodegradability of the salmon residues under conditions free of inhibition or mass transfer restrictions, which is the 1% test, is a 61.99% after 56 days, with a methane productivity of 535.66 l CH_4/$kg_{d.k.}$. These values are similar to those obtained with concentrations of total solids below 1%.

Finally, from the results obtained, two models were analyzed (Luong and one from the authors), both of which showed a good agreement with the experimental data, allowing the prediction of the behavior of the system studied.

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