Anaerobic treatment of seafood processing waste waters in an industrial anaerobic pilot plant

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Abstract

Fish and shellfish canning industries produce waste waters whose characteristics depend upon the raw material processed which, in turn, varies throughout the year. Some production lines operate simultaneously, although it is possible to segregate or combine streams in order to optimise the treatment process. The main streams, produced in the cooking of mussel or tuna and in the manufacture of fish-meal, were treated individually or in combination at an industrial pilot plant, with an anaerobic central activity digester (CAD) of 15 m^3, for two years. The most noticeable characteristics of wastes are their high organic load (COD 20 to 90 g/ℓ) and the salinity (up to 14 g/ℓ of Cl^-). Another problem is the high ammonia content, up to 4.5 g/ℓ, produced after the degradation of proteins. A strategy for adapting sludges to the salinity and to the ammonia content was followed and specific methanogenic activities of 0.7 kg COD/kg VSS·d were achieved, with chloride, sodium and ammonia concentrations of up to 15.5, 9.7 and 3.5 g/ℓ, respectively. COD reductions, applied OLR and HRT ranged between 70 and 90%, 5 to 6 kg COD/m^3·d and 4.5 to 5 d, respectively. During the entire experimental period, nutrients addition was not necessary and pH remained neutral due to the high buffering capacity of the process (3 to 4 g $CaCO_3$/ℓ). Sudden changes in the influent composition did not affect the stability of the process, except when high suspended solids mixtures were treated. The biomass content in the digester varied around 11 g VSS/ℓ and the mean specific methane production was 301 ℓ/kg COD removed (15°C, 1 atm), with a biogas content of 60 to 65%. Hydrogen sulphide in biogas ranged from 1 to 4%. The mean anaerobic biodegradability was calculated for the main influents treated, being 84.9% for tuna-cooking effluents, 92.7% for mussel-cooking effluents, 79.4% for mixtures of tuna and mussel effluents and 71.4% for the tuna/mussel/fish-meal mixtures.

Notation

CAD	-	central activity digester
COD	-	chemical oxygen demand (mg/ℓ)
OLR	-	organic loading rate (g COD/ℓ·d)
TSS	-	total suspended solids (g)
VSS	-	volatile suspended solids (g)
IA	-	intermediate alkalinity
TA	-	total alkalinity
VFA	-	volatile fatty acids
HRT	-	hydraulic residence time

Introduction

Seafood processing is a very important industrial activity in those regions of long fishing tradition such as Galicia (NW Spain), where the largest number of these factories are found in Spain. They are mainly located on two broad estuaries where environmental problems have been detected because of the large volume of discharged waste waters. In previous work (Soto et al., 1990), waste waters produced in different factories were characterised. There are five major production lines that correspond to the main products processed in Galicia (Omil et al., 1994): tuna, mussel, sardine, octopus and fish-meal. In each of these lines different waste waters are produced. The characteristics of the final effluent largely depend upon the relative contribution of each of them, which is variable depending on the season.

High salinity (chloride, sodium, sulphate and other inorganic ions present in sea water), characteristic of these waste waters, may cause toxicity problems in biological treatment systems and the high protein content of these effluents can generate high levels of ammonia, which is a compound with significant toxic effects (Soto et al., 1991). Perhaps because of this, anaerobic treatment of these effluents has only been considered very recently (Carozzi, 1988; Méndez et al., 1992; Prasertsan et al., 1994, Veiga et al., 1994a; b). Anaerobic treatment of some particular streams, generated during different production lines, was considered in previous work carried out at laboratory-scale by Soto et al. (1995) and Guerrero et al. (1993), and at pilot-scale by Veiga et al. (1992).

Another peculiar characteristics of these factories is the frequent change of products to be processed (Soto et al., 1990) with concomitant changes in waste-water characteristics and stand-by periods, which bring about periodic restart phases of the waste-water treatment plant (Balslev-Olesen et al., 1990).

The objective of this paper was to study the anaerobic treatment of three main waste-water types: tuna-cooking effluent, mussel cooking effluent and fish-meal plant effluent, in an industrial pilot plant. Although these three effluents account only for 3% of the total flow, their organic load represents more than 40% of the discharged effluent. The study was carried out in the factory and the response of the process to common events, such as sudden change of raw material used, stand-by periods, etc., was also considered.

Experimental

Anaerobic pilot plant

The flow-sheet of the industrial pilot plant used in this work is illustrated in Fig. 1. It comprises a 7 m^3 predigester (where waste waters were collected and prepared), a 15 m^3 anaerobic digester; and a 3 m^3 clarifier.

The CAD (Fig. 1), is conceptually close to the anaerobic contact system, with its central cone working as an internal settler,

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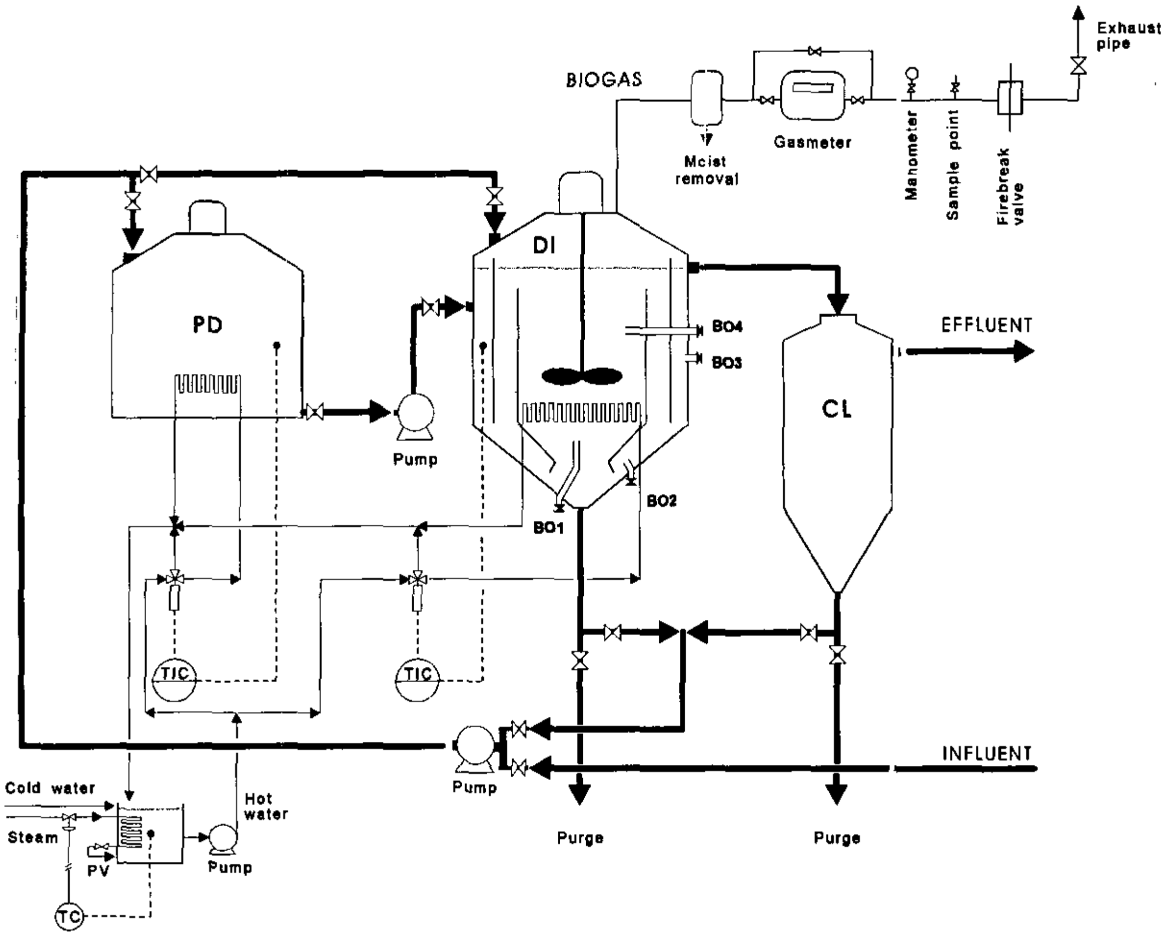


Figure 1
Scheme of the industrial pilot plant (PD: predigester, DI: digester and CL: clarifier)

TABLE 1
CONTROL OPERATION ROUTINE FOR THE PILOT PLANT

Influent		Digester		Effluent	
Flow	Daily	TSS and VSS	3 per week	TSS and VSS	3 per week
TSS and VSS	3 per week	COD	3 per week	COD	Daily
COD	Daily	pH	Daily	pH	Daily
pH	Daily	TA	3 per week		
Total carbohydrates	Monthly	IA	3 per week	**Biogas**	
Soluble protein	Monthly	Ratio IA/TA	3 per week		
Sulphate	Weekly	Ammonia	Weekly	Flow	Daily
Chloride	Weekly	Chloride	3 per week	Composition	3 per week

thus improving biomass retention. A stirring system allows internal recycling to be increased and therefore enhances sludge homogenisation. Because of its characteristics, waste waters with high suspended solids can be fed into this digester. However, cell retention is expected not to be as high as in other systems like the upflow anaerobic sludge bed (UASB) system (Lettinga and Hulshoff Pol, 1991) or the anaerobic filter (Young, 1991).

Temperature was maintained at mesophilic range (35 to 37°C) by a thermostat-controlled system. Four points (BO1 to BO4) were available for sampling sludge from the reactor.

Analytical methods

Most analyses (pH, TSS, VSS, NH_4^+, Cl^-, SO_4^{2-}, PO_4^{3-}, lipids) were performed according to *Standard Methods* (1985). Soluble protein was analysed by Lowry's method (1959) and soluble carbohydrates by means of the hydrazine sulphate/sulphuric method (Miller, 1959). COD was carried out using a semi-micro method adapted to high salinity waters (Soto et al., 1989). VFA was analysed by gas chromatography (Fernández et al., 1995). TA and IA due to VFA were determined by titration (Ripley et al., 1986). When the ratio

TABLE 2
AVERAGE CHARACTERISTICS OF THE MAIN WASTE WATERS TREATED IN THE PILOT PLANT: TUNA-COOKING EFFLUENT, MUSSEL-COOKING EFFLUENT AND FISH-MEAL PLANT EFFLUENT (COMPOSITION IN g/ℓ, EXCEPT pH)

	Effluent		
	Tuna	**Mussel**	**Fish-meal**
Composition (g/ℓ)			
COD	29.5	18.5	89.4
TSS	4.0	1.4	69.6
VSS	3.6	1.2	67.0
pH	6.2	7.0	6.4
Cl^-	14.0	13.0	3.5
$N\text{-}NH_4^+$	0.15	0.04	0.53
$P\text{-}PO_4^{3-}$	0.40	0.07	0.39
SO_4^{2-}	1.32	2.11	0.59
VFA	0	0	2.32
COD composition (%)			
Proteins	73.0	21.9	72.2
Lipids	23.5	3.6	21.4
Carbohydrates	8.5	74.5	6.4

TABLE 3
INITIAL CONCENTRATION OF SLUDGE IN THE REACTOR

	Sample point			
	BO1	**BO2**	**BO3**	**BO4**
TSS (g/ℓ)	39.92	41.52	39.24	38.52
VSS (g/ℓ)	16.00	16.84	16.44	16.24

IA/TA remains below 0.3 to 0.4 it indicates that no accumulation of VFA occurs. Total biogas flow rate was measured (at 15°C and 1 atm) and percentages of CO_2 and H_2S were determined with Orsat and Dräger tubes (Refs: CH-28101/29101) respectively, being the remaining volume assigned to methane. Digester samples were usually taken at point BO4.

Table 1 shows the control routine followed in the experiments carried out in the plant.

Waste-water characteristics

The influent fed into the pilot digester was collected from the tuna- and mussel-cooking operations and from the fish-meal plant effluent. Table 2 shows the main characteristics of these effluents.

It is interesting to point out the qualitative and quantitative differences between these effluents, which will be responsible for the variations on the behaviour of the system, when relative proportions in the influent change. The fish-meal factory produces a waste water with extremely high TSS content, mainly made up of proteins and lipids, while the mussel-cooking plant generates a stream with a major proportion of sugars (glycogen). Proteins and lipids are predominant in tuna-cooking effluents. Therefore, an increase in ammonia concentration is foreseeable when tuna-cooking and, especially fish-meal effluents are treated because of the high protein content.

Fresh- and sea water, as well as the general effluent of the factory, were used to adjust influent COD and salinity content to the required level during each stage. Main characteristics of the general effluent are: relatively low COD (1 to 4.5 g/ℓ) and high chloride concentration (from 13 to 19 g/ℓ). The chloride content of sea water is approximately 19.5 g/ℓ.

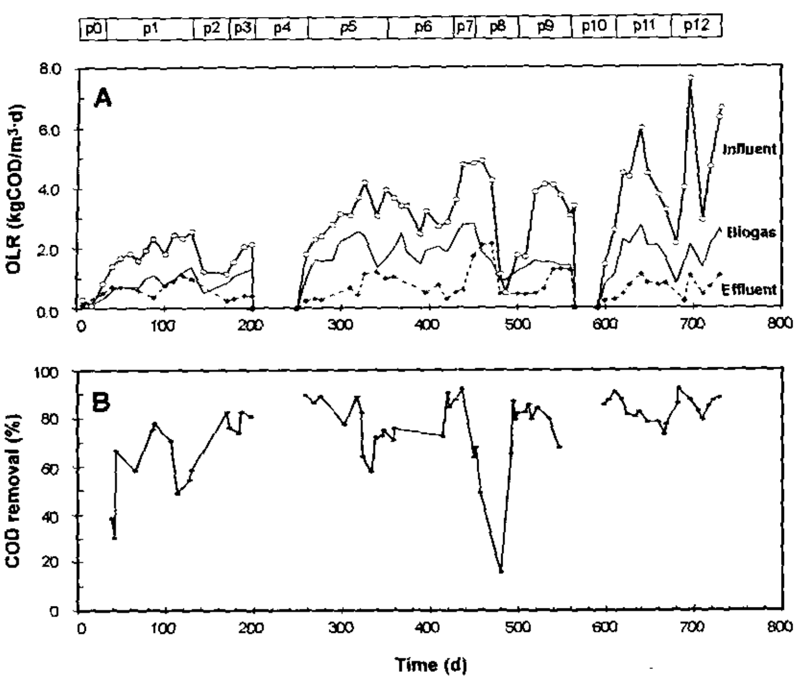
Results and discussion

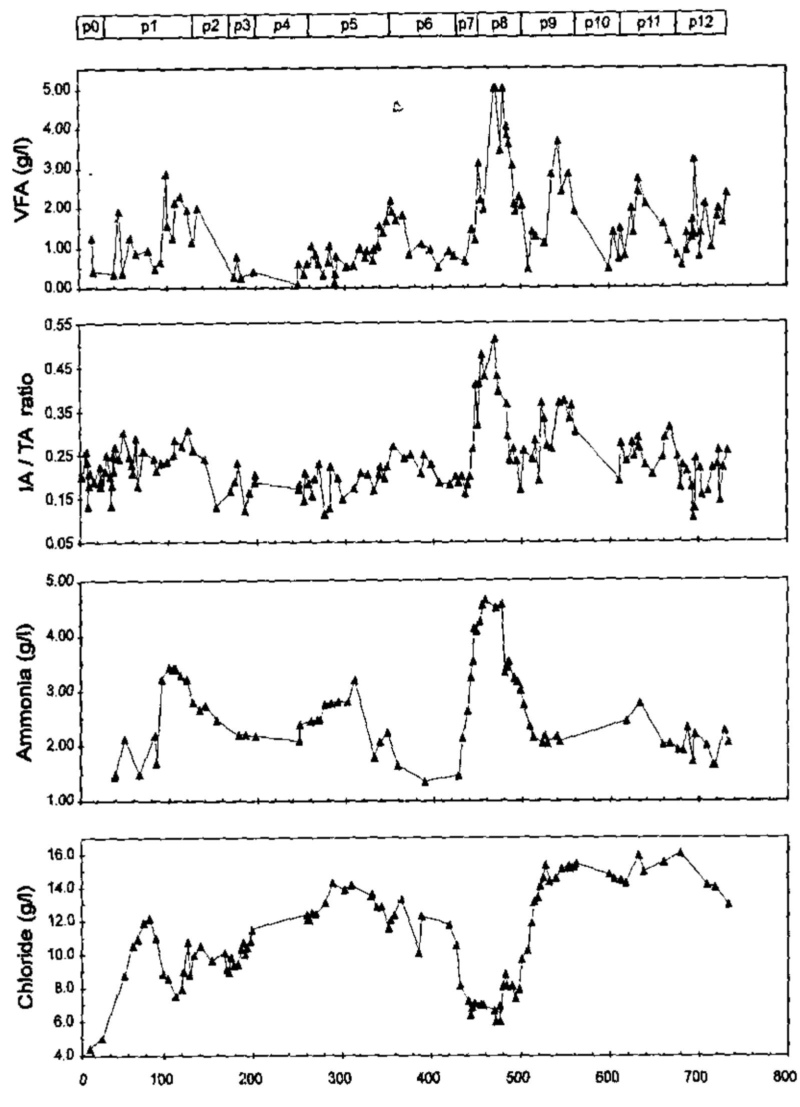
Analysis of operational periods

The digester was seeded with a 15 m^3 mixture of sludges from two industrial anaerobic digesters: an urban waste-water plant and a paper factory waste-water plant. A stirring velocity of 65 r/min was selected, thus allowing homogenisation and preventing disaggregation of sludge floccules. Settling curves of sludges, taken from the four sampling points (Fig. 1), were determined. The initial sludge concentration in the digester is shown in Table 3, and the methanogenic activity of this mixture was 0.047 g COD/gVSS·d (Omil et al., 1995).

TABLE 4
OPERATIONAL PERIODS IN THE INDUSTRIAL PILOT PLANT

Period	Days	Effluent treated	Objective
0	0-29	Tuna	Start-up
1	30-130	Tuna	Increasing of OLR and salinity adaptation
2	131-170	Tuna	Stabilisation
3	171-200	Tuna	High dilution treatment
4	201-260	Tuna	Stand-by and restart
5	261-350	Tuna, mussel	Adaptation to new influent
6	351-430	Mussel	Adaptation to new influent
7	431-447	Tuna, fish-meal	Tuna waste-water treatment
8	448-497	Tuna, fish-meal	Organic overloading and recovery
9	498-564	Tuna, general effluent	Tuna waste-water treatment
10	565-609	Tuna, general	Stand-by and restart
11	610-674	Tuna, mussel	Maximum OLR determination
12	675-732	Tuna, mussel, fish-meal	Adaptation to complex mixtures





After the start-up period (days 0 to 29), several studies were carried out during more than two years, with the main objectives shown in Table 4.

Figure 2 shows the variation in the OLR and the percentage of COD removal over an 800 d period. The OLR refers to the inlet, biogas and effluent, and each point represents an average of 10 d of operation.

Figure 3 shows the values of the main parameters used to monitor the behaviour of the process during the different experimental periods: VFA concentration; alkalinity ratio (IA/TA); ammonia and chloride concentration.

Start-up

The reactor was started by feeding tuna-cooking waste waters previously diluted to give COD values of less than 20 g/*ℓ*. The average inlet OLR was 0.3 kg COD/m³·d, which accounts for approximately 25% of the maximum methanogenic capacity of these sludges (Omil et al., 1995). This was considered adequate to achieve an adaptation of sludges to the salinity level present in the fish effluents.

At the end of this period (day 29), total alkalinity increased from 4.0 to 4.6 g $CaCO_3$/*ℓ*, the IA/TA ratio varied from 0.2 to 0.3 (Fig. 3), and pH varied from 7.6 to 7.8. These values were considered as indicative of a stable performance of the anaerobic process and therefore, the OLR was increased in the next period. Table 5 shows a summary of the results obtained during this period.

Period 1: Increasing OLR and salinity

After day 30 the applied OLR was gradually increased from 1.5 to 3 kg COD/m³·d by increasing the influent flow from 1 to 2.1 m³/d. This increase was controlled to ensure that COD removal percentage did not decline substantially when the OLR was increased. The influent consisted of tuna-cooking waters previously diluted to an adjusted COD value of approximately 20 g/*ℓ*. For these dilutions, fresh- and sea water were used alternatively to modify step-by-step (according to a predefined strategy) the content of chloride in the digester, up to concentrations of around 10 to 12 g/*ℓ*.

Daily production of biogas ranged from 10 to 12 m³/d, with a 70% methane content, 30% CO_2 and

Figure 2 (top)
The performance of the pilot plant: a) evolution influent OLR, biogas and the effluent; and b) COD removal obtained

Figure 3 (bottom)
The variation of VFA, alkalinity ratio, ammonia and chloride in the digester, as found during the experimental studies

TABLE 5
SUMMARY OF THE MAXIMUM OPERATIONAL CONDITIONS REACHED (T: TUNA, M: MUSSEL, FM: FISH-MEAL)

	Start-up	Acclimatisation	Individual treatment		Mixtures treatment		
	Period 0	Period 1	T	M	T + FM	T + M	T+M+FM
OLR (kg COD/m³·d)	0.4	3.0	4.5	4.0	5.3	6.0	6.0
Influent flow (m³/d)	0.4	2.1	3.3	3.0	2.0	3.4	3.1
COD removal (%)	-	61.0	71.7	81.9	69.0	81.8	87.4
Influent COD (g/ℓ)	12.0	19.0	17.3	15.5	35.0	22.8	33.7
Effluent COD (g/ℓ)	-	7.4	4.9	2.8	11.0	4.1	4.2
Biogas flow (m³/d)	1.7	12.2	13.2	20.3	25.0	28.0	22.4
V_{CH4} (ℓ/kg CODremoved)	-	409	319	305	271	245	222
CH_4 (%)	81.2	77.0	65.0	53.8	61.2	61.6	61.4
CO_2 (%)	16.4	21.9	32.5	42.5	37.6	35.8	35.6
H_2S (%)	2.4	1.1	2.5	3.7	1.2	2.6	2.9

0.8% H_2S. These values are similar to those obtained in laboratory-scale studies (Soto et al., 1995). Table 5 summarises the operational values reached during this stage.

Individual treatment of main effluents

Tuna and mussel production lines are the main ones in these factories and can be functioning simultaneously or during different periods of time. Therefore, the individual treatment of tuna-cooking and mussel-cooking effluents is of interest, whereas the individual treatment of the fish-meal plant effluent was not considered, since this plant is always associated with the tuna section.

Tuna-cooking effluent

The tuna-cooking effluent was treated during several periods (1, 2, 3 and 9). During the first periods (1 to 3), the dilution with alternative use of fresh- and sea water allowed control of the chloride content in the digester, in which an adequate biomass adaptation was considered important.

Once the chloride content in the digester reached the maximum level present in these waters (up to 14.5 g/ℓ), during the 9th period (days 498 to 564), the general effluent of the factory was used for dilution. Influent COD ranged from 12 to 23 g/ℓ and due to the high salinity of the general effluent, the chloride concentration reached 15.5 g/ℓ. The inlet flow was increased from 1 to 3.3 m³/d, giving maximum OLR values of 4.5 to 5 kg COD/m³·d (Fig. 2). An inlet flow of between 3 and 3.3 m³/d was determined to be the maximum operative level possible in order to avoid biomass washout, since the effluent solids content increased drastically above these values.

Table 5 shows the values of the main operational parameters throughout the 9th period. This period is considered to be the most representative phase in the treatment of tuna-cooking effluents, since the highest values of applied OLR and flow were reached.

Mussel-cooking effluent

These effluents were treated individually during the 6th period only (from day 351 to 430). As the chloride content in the digester had reached maximum values in previous periods and the organic content of these waters was not very high (always below 20 g/ℓ), no dilution was used.

The inlet flow was maintained at a constant level of 3.0 m³/d, and therefore the applied OLR ranged from 2.7 to 3.7 kg COD/m³·d. No disturbances occurred during this period: the VFA concentration always remained under 1.0 g/ℓ and the alkalinity ratio (IA/TA) below 0.25 (Fig. 3). The COD removal efficiency was consistently higher than 70%, with an average value of 81%.

Due to the low protein content of mussel-cooking waste waters, ammonia content decreased to below 1.5 g/ℓ, in the same way as total alkalinity, that oscillated around 3.0 g/ℓ. The chloride concentration also decreased to 11 g/ℓ.

Biogas production increased to 21 m³/d and higher. An increasing H_2S percentage was observed, reaching 4% and remaining stationary throughout this period. This fact is due to the high sulphate concentration in these waters (approximately 2.15 g/ℓ, compared to 1.1 in tuna-cooking effluents). The characteristic operational values are shown in Table 5.

Treatment of waste-water mixtures

Fish and shellfish canning industries depend on the availability of raw materials, which varies according to the season. Therefore, several production lines can coexist for a period of time and afterwards some line can be stopped or be substituted by another. For this reason, it was of interest to study the behavior of the treatment system, taking into consideration abrupt changes in the characteristics of the waste waters.

For several periods, mixtures of these effluents were treated: mussel- and tuna-cooking effluents during periods 5 and 11, tuna-cooking and fish-meal plant effluents during Period 7, and tuna, mussel and fish-meal effluents during Period 12.

Tuna/mussel mixtures

A mixture of similar volumes of both waste waters were treated from days 261 to 350 (Period 5). The COD of these mixtures ranged from 20 to 22 g/ℓ and they were fed without prior dilution. The inlet flow was set at 1.3 m³/d and was increased progressively to reach 2.6 m³/d, which was assumed to be a maximum applied OLR of 3.8 kg COD/m³·d with a COD removal efficiency of 87.4%.

Between days 610 and 674 (Period 11), these mixtures were fed again to determine if the system had the potential capacity to treat higher OLR, after the adaptation of biomass occurred in former periods. This hypothesis seemed possible because the feed flow ranged from 2.5 to 3.4 m^3/d, reaching an applied OLR of 6 kg COD/m^3·d with a COD removal efficiency of 81.8%.

During these periods the anaerobic process remained at its optimum operating range (low VFA content and IA/TA ratio) with a COD removal efficiency higher than 81% (Table 5). Salinity was about 15 g Cl^-/*ℓ*, showing that the maximum level could be attained by these effluents.

Tuna/fish-meal mixtures

Mixtures of tuna-cooking and fish-meal effluents were treated between days 431 and 447 (7th period), in a proportion higher than that existing in the factory (6:1 compared to 17:1). Fish-meal plant effluent has a low flow but a very high organic content (occasionally reaching 90 g COD/*ℓ*), which relates to its high content of suspended solids.

As these loads represented the most difficult situation that can be expected, it seemed worthwhile to study the treatment of these mixtures. The average COD of these mixtures was about 35 g/*ℓ*, with 45% being from suspended solids. The feed flow was maintained at 2.0 m^3/d, which assumes an OLR of approximately 5 kg COD/m^3·d.

Because of the high protein content in both waste waters, ammonia concentration increased quickly from 1.5 g/*ℓ* to values greater than 4 g/*ℓ*. Accordingly, total alkalinity ranged between 2.8 and 5.5 g/*ℓ*.

The COD removal efficiencies were around 67 to 70% at the end of the period. The VFA remained constantly below 1.5 g/*ℓ*, and the alkalinity ratio IA/TA below 0.3. The chloride concentration decreased to the range 6 to 7 g/*ℓ*.

Tuna/mussel/fish-meal mixtures

During the final study period, from day 675 (12th period), mixtures of tuna-cooking, mussel-cooking and fish-meal plant effluents were treated. This situation corresponds to the existing conditions in the factory, when these three production lines are running simultaneously. The flow ratio of these three effluents in the factory is 17:32:1 respectively.

The mixture was composed of 3 m^3 tuna effluent, 3 m^3 mussel effluent and 0.5 m^3 from the fish-meal plant effluent, which is relatively more difficult to treat than the actual effluent from the factory. This is a result of the higher proportion of fish-meal and the lower proportion of mussel effluents (effluent most difficult and easiest to degrade, respectively). The COD of this mixture ranged between 30 and 35 g/*ℓ* and suspended solids were about 5.8 g TSS/*ℓ* and 4.8 g VSS/*ℓ*.

The feed flow rate was maintained constant at 3.1 m^3/d, with the inlet OLR ranging from 6 to 7 kg COD/m^3·d. The control variables did not reflect any significant overloading (VFA and IA/TA ratio below 2 g/*ℓ* and 0.3, respectively) and the COD removal efficiencies remained in the range 77 to 88%. Table 5 shows the characteristic values of the optimal operating conditions obtained during the treatment of these mixtures.

Stand-by periods

Anaerobic treatment is particularly suited to for industries operating seasonally, because of the low maintenance requirements of the anaerobic community (Balslev-Olesen et al., 1990). Seafood processing industries usually have two or more periods in a year when the production is temporarily discontinued. Throughout this study, the factory stopped its production twice, once for a period of 45 days and another for 30 days (4th and 10th periods respectively).

In the 4th period the restart of the operation was prolonged for 13 d. The feed flow rate was increased from 1 to 1.6 m^3/d using tuna-cooking waste water previously diluted. OLR values of up to 2.3 kg COD/m^3·d were quickly reached (Fig. 2), with a COD removal efficiency of up to 90%.

The second stand-by period corresponded with the 10th period and restart was carried out from day 592 to 609. It was fed the same mixture as considered in the 9th period, starting with 1 m^3/d and reaching 2.5 m^3/d after 5 d. Thus, the inlet OLR increased from 1.6 to 3.1 kg COD/m^3·d (Fig. 2) with a COD removal efficiency of approximately 77%.

Mixtures with high protein content: Overloading and recuperation

The behaviour of the process in an overload situation was studied during the 8th period. A mixture of tuna-cooking and fish-meal waste waters, with a lower proportion of tuna than the mixture employed in the 7th period, was fed to the digester with a flow rate of 2 m^3/d. The COD ranged between 35 to 45 g/*ℓ*, which resulted in an applied OLR of more than 6 kg COD/m^3·d.

The ammonia content increased quickly to the range 4 to 4.5 g/*ℓ*. The alkalinity ratio (IA/TA) (Fig. 3) was higher than 0.5 and the VFA content exceeded 5 g/*ℓ* on day 470, accounting for acetic (4.5 to 5 g/*ℓ*) and propionic acid (1 to 1.8 g/*ℓ*) and other acids with longer chains (n-butyric, isovaleric and n-valeric) which indicates an overloading situation (Myburg and Britz, 1993).

This evolved as a result of several factors: high applied OLR, high proportion in suspended organic matter (which makes the process slower due to the need of a pre-hydrolysis step) and the high ammonia content that produced a significant toxic effect as reported in previous work (Soto et al., 1991).

As a consequence, the COD removal efficiency decreased from 49% on day 457 to 30% on day 470. During this period feeding was discontinued for 6 d to enhance degradation of accumulated acids. Afterwards, 2 m^3/d of mixtures of tuna/general effluent were fed for 3 d (COD of 13 g/*ℓ*), and a further decrease in the COD removal efficiency was observed (16% on day 480), with VFA concentrations higher than 5 g/*ℓ*.

A progressive biomass reduction was observed since the beginning of this period: on day 480 the lowest level was reached (6.5 g TSS/*ℓ* and 5.6 g VSS/*ℓ*), whereas normal values were around 22 and 11 g/*ℓ* respectively. This low biomass content could explain the difficulties observed during process recovery using mixtures of tuna/general effluent (low COD content).

Therefore, a similar strategy to that used during start-up was adopted in order to recover the normal conditions in the digester and enhance biomass growth. The strategy consisted of:

- feeding an organic load that represented 10 to 25% of the theoretical methanogenic capacity of the biomass; and
- use of tuna-cooking waste waters, diluted previously with freshwater, to reduce the organic content to 10 g COD/*ℓ* and also to reduce the salinity.

In accordance with the methanogenic activity of the biomass and its concentration in the digester (Omil et al., 1995), the applied OLR to be used would be between 0.4 and 0.9 kg COD/m^3·d.

On day 480, 1 m^3/d of this mixture was fed to the digester at an OLR of 0.6 kg COD/m^3·d and after 10 d the values of the control

TABLE 6
OLR BALANCE (kg COD/m³·PERIOD) IN TERMS OF PERCENTAGE FOR EACH PERIOD OF OPERATION AND FOR THE OVERALL PERIOD. THE OLR FED TO THE DIGESTER WAS DISTRIBUTED BETWEEN THE BIOGAS (METHANE PRODUCTION), BIOMASS (SLUDGE ACCUMULATION) AND EFFLUENT (VFA, VSS AND SOLUBLE RESIDUAL ORGANIC MATTER)

Periods	Organic loading rate					
	Influent	Biogas	Accumulated sludges	Effluent VFA	Effluent washout	Effluent residual (soluble)
P1, P2	100	59.1	-5.4	6.8	19.9	19.6
P3, P4	100	75.5	9.0	2.4	5.7	7.3
P5	100	69.2	-7.1	4.1	13.2	20.6
P6	100	70.8	5.3	8.6	8.0	7.3
P7	100	81.2	11.9	2.1	3.7	1.2
P8	100	60.1	-17.6	9.2	12.9	35.4
P9, P10	100	58.2	3.7	12.3	10.6	15.1
P11	100	56.5	2.5	9.0	9.3	22.7
P12	100	49.8	-2.3	5.4	18.6	28.6
Total	100	61.8	-0.8	7.4	12.3	19.3

parameters recovered to their normal ranges: VFA below 2 g/ℓ and alkalinity ratio under 0.25 (Fig. 3). The reduction in organic content of the feed also resulted in a dramatic reduction in ammonia concentration. From there on, the applied OLR was progressively increased and, on day 501, the biomass concentration reached normal values: 29.2 g TSS/ℓ and 12.8 g VSS/ℓ.

Reactor yield evaluation

Methanisation and anaerobic biodegradability

A balance, in terms of percentage of OLR, was calculated for each operational period and the results are shown in Table 6. Columns 1 to 3 refer to the influent (applied OLR), that is the calculation basis; biogas (methanised OLR); accumulation of sludges, calculated from the variation of the concentration of biomass during each period (Omil et al., 1995); and the columns 4 to 6 correspond to the different fractions of organic content in the effluent. These include: VFA; VSS, mainly related to the biomass washout, although non-hydrolysed solids can also be included; and soluble organic matter.

Methanisation varied between 49.8 and 81.2%, with an average value of 61.8%. The lowest levels were obtained when the mixtures containing high solids were treated and the applied OLR was high (Period 12). During Period 7, even though the influent had high solids content, the methanisation was high due to the longer HRT employed which favoured their complete hydrolysis.

During Period 1, Period 5 and Period 8, significant losses of biomass were experienced due to the lower operational HRT. During the other periods, washout was mainly related to the biomass and ranged between 3.7 and 10.6%. The values in Table 6 (accumulated sludges), show that there was no significant change in the biomass concentration in the digester during the entire experimental period, with an overall decrease of 0.8%.

The residual effluent (last column of Table 6) represents the soluble organic matter not converted into short-chain fatty acids, which probably relates to the products formed during the first stages of solids hydrolysis, although this hypothesis requires further research. The treatment of mixtures with high solids content and the unstable conditions in the digester produced a high value during Period 8 (35.4% of the influent OLR), whereas during Period 12 the value obtained (28.6%) was mainly due to the contribution of the initial days of adaptation to the high applied OLR levels. This also occurred during other periods (1, 2, 5, 11) where the routine occurrence of increased OLR caused a temporary efficiency decrease. When the applied OLR was maintained, these values were lower (7.3% and 1.2% for Periods 6 and 7, respectively).

The anaerobic biodegradability (obtained by adding the data corresponding to biogas, effluent VFA and effluent VSS) was 80.7% for the overall period of operation and the results for main periods of operation were: 84.9% during the treatment of tuna-cooking waste waters, 92.7% for mussel-cooking waste waters, 79.4% for mixtures of tuna and mussel-cooking effluents, and 71.4% for the mixtures fed during Period 12.

Methane production to COD removal ratio

The ratio between the volume of methane produced and the organic matter removed was calculated for each period of operation (Table 5). The overall value calculated, using a weighted average and referred to throughout the entire experimental period, was 301 ℓ CH_4/ kg COD removed (moist methane at 15°C and 1 atm).

Figure 4 shows the specific methane production and the removed OLR related with the applied OLR. It can be seen that the obtained values for methane production varied between 200 and 400 ℓ CH_4/ kg COD removed, fluctuating more at low applied OLR values, when the digester was in start-up periods or the applied conditions were changed. This distribution can also be observed for the OLR removal (the diagonal line represents 100% applied OLR removal).

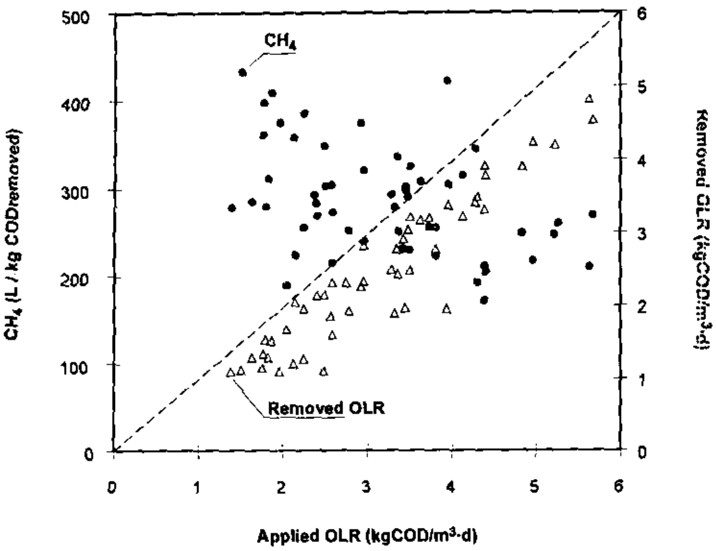


Figure 4
Specific methane production (measured at 15°C and 1 atm) and removed OLR vs. applied OLR (the diagonal line represents 100% OLR removal)

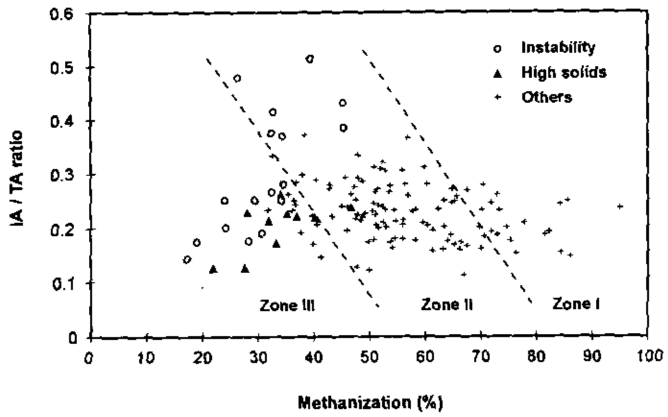


Figure 5
Distribution of alkalinity ratio values vs. percentage of methanisation. Three zones can be approximately distinguished according with the different conditions imposed to the process and the performance COD removal efficiencies obtained during the different stages of operation

Methanisation and alkalinity

Figure 5 represents the obtained values of the alkalinity ratio vs. percentage of methanisation. In general, data points are distributed in a triangular area, showing that the highest percentages were obtained when the alkalinity ratio was low. According to the influent composition (solids content), the conditions of operation (start-up, acclimation, recovery and stable periods) and the COD removal efficiencies, the experimental data obtained can be approximately distributed in three zones:

- Zone I includes the data points obtained that correspond to the optimal operation of the digester due to maximum efficiency of micro-organisms.
- Zone II includes the data points obtained that correspond to an intermediate activity. For a given IA/TA ratio, methanisation is lower, due to an inhibited microbial activity, which results in lower efficiency.
- Zone III represents the zone with the lowest activity, with very low methanisation percentages which correspond to adaptation periods (restarts) or temporal unstability caused by increases of flow and/or unsuitable applied OLR.

Conclusions

Start-up, process stability and efficiencies

Effective anaerobic treatment of these waste waters could be reached after a short start-up period (29 d), using a mixture of sludge from two different waste-water treatment plants as inoculum.

A sudden change in the characteristics of the influent had no important effect on the process, except when mixtures with high solids content were treated. In this case, a longer HRT has to be used (7.5 d instead of the 5 d HRT normally used), in order to achieve similar efficiencies.

The digester remained for two stand-by periods (45 and 30 d) without feeding, stirring and heating. In the subsequent restarts, normal operational values were reached in 5 to 10 d.

The COD removal efficiency was in the order of 70 to 90% and the addition of nutrients was not necessary. The methane percentages obtained in the biogas ranged between 60 and 65% and hydrogen sulphide ranged between 1 and 4%, depending on the sulphate content of the influent. The average methane production, measured at 15°C and 1 atm, was 301 ℓ/kg COD removed.

The average anaerobic biodegradability values obtained during the operation were: 8[illegible].9% for tuna-cooking waste waters, 92.7% for mussel waste waters, 79.4% for mixtures of tuna and mussel waste waters and 71.[illegible]% for the mixtures used in Period 12.

Operational characteristics of the equipment

In order to calculate the expected capacity of an anaerobic digester, three factors have to be considered: biomass retention; maximum methanogenic activity of biomass; and possible inhibitory effects due the presence of sodium and other sea salts. In our particular case, these three factors can be evaluated as follows:

- Biomass retention in a CAD reactor depends mainly on the inlet flow applied, although a value of 11 g VSS/ℓ can be considered as characteristic (Omil et al., 1995).
- Specific methanogenic activity was carried out according to Soto et al. (1993). Maximum values obtained ranged between 0.5 and 0.75 g COD/g VSS·d (Omil et al., 1995).
- Previous results (Omil et al., 1995) show that 20 to 50% of toxicity may be expected under the maximum sodium content of these waste waters (around 9 to 10 g/ℓ). This toxic effect could possibly be lower if the antagonistic effect caused by other sea salts over sodium toxicity is considered, as was reported in previous work (Feijoo et al., 1995).

From the data, the maximum operating capacity of this reactor can be estimated to be in the range 2.8 to 6.6 kg COD/m^3·d. Maximum values applied in the pilot plant that were compatible with a stable regime, were 5 to 6 kg COD/m^3·d. These values agree with the predetermined estimates, which took into account the biomass concentration and the specific methanogenic activity of the sludges.

Tolerance to high salinity and ammonia

Chloride and sodium concentrations in steady-state operation reached values of up to 15.5 g/ℓ and 9.7 g/ℓ, respectively. A stepwise procedure was followed to achieve successful adaptation of the biomass. This process was favoured by antagonistic phenomena, due to the presence of cations and anions in these effluents, which significantly alter the inhibitory effect caused by sodium (Feijoo et al., 1995).

High protein content (especially from the tuna-cooking and fish-meal plant) produced a high ammonia concentration, ranging between 1.5 and 3.5 g/ℓ. In spite of that and in agreement with previous studies, in which it was concluded that after an adequate adaptation period it is possible to operate successfully at relatively high ammonia concentrations (Soto et al., 1991), an efficient and stable operation could be achieved.

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