Dairy Industrial Wastewater Treatment using AnMBR Technology

Universidad de Santiago de Compostela

Escuela Técnica Superior de Ingeniería

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Dairy Industrial Wastewater Treatment using AnMBR Technology

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INFORMAN:

Que la presente memoria, titulada "Dairy Industrial Wastewater Treatment using AnMBR Technology" constituye el Trabajo Fin de Máster realizado por Don Tomás Francisco Allegue Martínez bajo nuestra dirección con el objetivo de obtener el título de "Máster en Ingeniería Ambiental"

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Abbreviations

AnMBR: Anaerobic Membrane Bioreactor

CIP: Clean In Place

CSTR: Continuous Stirred Tank Reactor

EPS: Extracellular polymeric substances

FOG: Fat, Oil & Grease

GC: Gas Chromatography

HRT: Hydraulic Retention Time

NaOH: Sodium Hydroxide

OLR: Organic Loading Rate

PLC: Programmable Logic Controller

PVDF: Polyvinylidene Fluoride

SCOD: Soluble Chemical Oxygen Demand

SKN: Soluble Kjeldahl Nitrogen

SMA: Specific Methanogenic Activity

SMP: Soluble Microbial Products

SRT: Sludge Retention Time

SS: Suspended Solids

TCOD: Total Chemical Oxygen Demand

TKN: Total Kjeldahl Nitrogen

TMP: Transmembrane Pressure

TP: Total Phosphorous

TS: Total Solids

TSS: Total Suspended Solids

VFA: Volatile Fatty Acids

VLR: Volumetric Loading Rate

VS: Volatile Solids

VSS: Volatile Suspended Solids

1. Introduction

1.1 Background of the experimental work.

This research project was conducted at Biothane Systems International (subsidiary of Veolia Water Technologies), located in Delft (Netherlands), between November of 2013 and May of 2014.

Biothane has more than 35 years of extensive experience in the sector of biological wastewater treatment. During this time, their specialists have constructed 540 installations in more than 40 countries worldwide. Biothane represents a consolidated anaerobic wastewater treatment specialist company. Out of all the technologies provided by Biothane (anaerobic and aerobic), the anaerobic membrane bioreactor (Memthane®) is currently their largest focus and is under further development in their research laboratories.

Memthane® is an AnMBR which maximizes renewable energy production while producing a high effluent quality that can be reused or discharged directly to the sewer. The disposal costs are significantly reduced and simultaneously valuable gas is produced during the anaerobic treatment.

Memthane® accounts for the treatment of high-strength (high COD) and high-solids (high TSS) content streams, present in a wide range of industries including distilleries, dairies, bio-ethanol producers, instant coffee plants, etc. Attaining a low solids content effluent also facilitates the easy nutrients recovery in fertilizer production and water recycling to the plant.

Two different proven technologies are combined in this AnMBR treatment: Biothane´s anaerobic biological wastewater treatment process and Pentair´s® X-Flow ultrafiltration membrane separation process.

1.2 Scope of the thesis.

The main goal of this thesis was to investigate the anaerobic treatment feasibility of a high-strength dairy industrial wastewater, by using a Memthane® pilot plant (AnMBR technology).

The dairy wastewater is comprised of by three different kinds of feed: high-concentrated acid whey, DAF (from Dissolved Air Flotation treatment) and yoghurt (off-spec products). The ratio of these three components in establishing the resulting feed was altered throughout the experiment according to the client´s requirements.

During the majority of the trial, this resulting feed was characterized by a high COD (approximately 140 gCOD/l), a high SS value, as well as nutrient concentration (taking into consideration nitrogen, phosphorus and calcium content). During some stages of the experiment, a high FOG (Fat, Oil & Grease) content (21 g FOG/l), mainly induced, due to the DAF stream was measured.

It is important to note that due to the client´s required changes of the feed composition, the experiment will be extended for a longer period. This will be commented in more detail below in the section analysis and results. This testing will also present some interesting results and conclusions.

The monitoring of different biological parameters (such as COD removal efficiency, methanogenic bacteria activity, organic loading rate potential…) and membrane performance (permeability, TMP, flux) will be studied.

The ultimate aim is to use the test results to allow the design of a full-scale Memthane® plant for dairy wastewater treatment.

1.3 Use of anaerobic treatment for high-rate influents.

An increase in industrial efficiency of processes during the past years has led to more conscious and effective use of resources and raw materials.

This also applies to water use, which leads to more aggressive wastewaters production, trying to close industrial process water cycles. For this transcendent reason, anaerobic technology is continuously being developed.

Anaerobic treatment could be defined as a fermentation process, where the organic matter (COD) is degraded and biogas is produced. The biogas is mainly composed by CO_2 and CH_4, and, in less extent, by SH_2 and H_2. This process can take place in a low Redox potential (oxygen zero). Aeration supply is not a necessity for the system, representing one of the most significant costs in aerobic wastewater treatment

This kind of treatment has been used to treat industrial, agricultural and food processing wastewaters over the last decades. In 2003, nearly 1600 commercial anaerobic wastewater treatment systems were operating all over the world (Kleerebezem & Macarie, April, 2003).

1.3.1 Advantages of anaerobic treatment.

Anaerobic treatment has been quickly developed since the late 1960s. Nowadays, it represents one of the most cost-effective alternatives to remove an organic load from the given wastewaters. This success also noted by the biogas production also associated with the process, which can carry on to be utilised as an energy resource, owing to energy-neutral or even profitable treatment. This biogas produced may be combusted to produce heat and electricity.

The main advantages of the anaerobic technology include its characteristic organic matter removal efficiency, biogas production and the important decrease in sludge production it manages to achieve (Rajeshwari et al., 2000; van Lier et al., 2001; van Lier, 2008).

Low biomass yields and low growth rates represent one of the important advantages of anaerobic biotechnology, since they translate into the generation of low amounts of waste sludge, up to ten times less than during aerobic treatment. This is important since sludge management represents high costs for companies. However, during the first developments of anaerobic processes this feature represented a major drawback when trying to increase the biomass concentration in anaerobic reactors (Speece,1996). The treatment capacity is directly related to the amount of microorganisms that can be effectively retained in the treatment system.

It is possible to produce up to ten times less of sludge utilising anaerobic treatment. It also requires less space, due to compact design, since the decoupling between hydraulic retention time (HRT) and sludge retention time (SRT) is possible, due to granule formation and/or the presence of a membrane. Moreover, it can be associated with a lower energy consumption (no aeration) compared to aerobic treatment.

To attain successful high-rate wastewaters removal, an important consideration of vital importance is to keep the slow growing methanogenic bacteria inside the reactor. For that reason come the necessity of the decoupling between HRT and SRT is strictly necessary.

Other important advantages of the anaerobic technology included the storage ability if unfed for many months, the process has low nutrients and chemical requirements (anaerobic biomass presents lower growing rates than aerobic microorganisms. Therefore, much less nutrients concentration will be necessary). Another advantage includes pathogens-frees permeate

1.3.2 Disadvantages of anaerobic treatment.

On the other hand, this sort of treatment presents some drawbacks such as odour problems, the process is also very sensitive and vulnerable, a long period is required for the start-up. Another con is that generally some form of post-treatment is usually required after the process. Lettinga (1995) states that anaerobic treatment can be responsible for different mineral compounds such as ammonium, phosphate or sulphides, and therefore requires additional post-treatment to comply with a sustainable environmental protection practice.

1.4 Granular sludge bed reactors.

Granulation process represents a key factor in the operation of these high-rate anaerobic reactors. The granulation can be defined as the formation of well-setteable microbial aggregates with different functionalities (Hulshoff Pol et al., 2004), depending on several aspects, physico-chemical parameters, wastewater properties, and the hydraulic situation. It can be concluded that granule formation is a complex process involving physical-chemical as well as biological interactions

Three mechanisms are commonly used for biomass retention: settling, attachment and granulation. The latter is currently the most used of the three, as reflected by the significant amount of Upflow Anaerobic Sludge Bed (UASB), Expanded Granular Sludge (EGSB) and Internal Circulation (IC) that are used in industrial wastewater treatment (van Lier et al., 2001; van Lier, 2008). Close to 80% of anaerobic full-scale plants are sludge bed reactors, in which biomass retention is possible, due to granular sludge formation.

The UASB (Upflow Anaerobic Sludge Bed) and the EGSB (Expanded Anaerobic Sludge Bed) processes, require biomass with excellent settling properties. Different parameters have been studied to see which can effect most greatly the sludge granulation. Most of the configurations for these kind of systems, in the presence of a high SS/COD value, may have serious problems in seeing to the development of the granular sludge. For this reason, in such cases it would be necessary a wastewater pretreatment to remove the existent TSS.

The UASB reactor technology has been developed in the late 1970s, and became quickly widespread due to its high performances. This reactor is able to treat various high-strength industrial wastewaters, and most soluble (low presence of SS) wastewaters could be applied on it.

In the late 1980s a new anaerobic granular sludge reactor concept was developed, the EGSB reactor. UASB and EGSB share the same basic principle, i.e. a combination of a GLS (Gas-liquid-solid) separator and the use of granular sludge. Nevertheless much higher liquid up-flow velocities are applied. As a result the sludge bed is more expanded (better mixed) and it is possible to apply much higher volumetric loading rates. Maybe more importantly it is also possible to apply much higher upflow velocities in the settler. As a result surface area required for settling is much lower. Thus EGSB systems present smaller volumes and also smaller footprints than UASB reactors and are therefore cheaper to construct.

In spite of this EGSB lower costs, UASB reactors are still being used all over the world, since they can handle higher SS and FOG concentrations compared to EGSB.

The presence, in granular sludge bed reactors, of very high biomass concentrations inside the system enables high organic loading rates between 5-15 and 15-25 kg COD/m^3.day, with UASB and EGSB technology respectively. These values can vary depending on the kind of used wastewater. Both systems are characterized by the absence of some mechanical mixing, which is achieved rather via the gas and upwards flow movement.

Anaerobic granular sludge utilization, is currently the most successful factor of high rate anaerobic processes. But not all the industrial wastewaters can be treated with granular sludge. In presence of different extreme situations such as a high SS, FOG, temperature, toxicity, salinity, drastic OLR changes and HRT fluctuations, the sludge may suffer important negative impacts in the granulation or even de-granulation and biomass loss. With this kind of wastes, the biomass retention mechanisms will play an important role in anaerobic treatment.

1.5 Membrane Bioreactors for wastewater treatment. Description & configurations.

Since the use of anaerobic treatment is useful in the presence of high-rate streams, to maintain a satisfactory removal of organic matter, it is necessary a high sludge concentration. To achieve this, it is of vital importance that the biomass is retained in the system.

Membrane bioreactors represent an improvement on the conventional activated sludge treatment as they use membrane filtration as a means of biomass retention. In these reactors, the slow growing microorganisms and particulate organic matter, which in upflow reactors would be washed-out, is being physically retained inside the reactor, giving way to optimum organic matter and nutrients removal (Jeison, van Betuw, & van Lier, 2008) (Dereli, et al., 2012).

The membrane, also accounts for a faster start-up compared to other anaerobic reactor configurations (sludge bed reactors. The nature of the effluent is pathogen free, resulting in an important saving if reused or recycling is required, since sometimes, permeate post-treatment could not be necessary.

Anaerobic membrane bioreactor (AnMBR) is a relatively new reactor configuration that is becoming gradually more attractive for wastewaters treatment under extreme conditions that can impede granulation or reduce the activity of the sludge.

Depending on the membrane configuration, we may distinguish three different kinds of membrane bioreactors: side-stream, gas lift and submerged reactors. In gas-lift and side-stream reactors, membrane modules are located outside the reactor where the sludge is circulated over a recirculation system. On the other hand, in the submerged membrane reactors, the membrane is placed inside the Continuous Stirred Tank Reactor (CSTR).

The only different parameter between gas-lift and the side-stream configuration is how the membrane scouring is made. In the AnMBR is employed the own permeate, while in the gas-lift reactor, gas is used.

Side-stream membrane reactors, need a higher energy requirement due to the elevated volumetric flow necessary to reach the desired cross-flow velocity. For instance, in side-stream aerobic reactors the pumping energy consumption is around 60-80%, whereas the aeration energy consumption represents 20-40% of the total (Gander et al., 2000). However, with the AnMBR technology a significant biogas volume is being produced which compensates the energy consumption.

The main advantage of the side-stream reactors is that membrane cleaning may be performed in an easier way than submerged configurations, since membrane extraction must be done in the latter case.

Reactors with submerged membrane require less energy consumption (absence of a circulation loop), but lower permeate flux may be attained due to the lack of sufficient surface share, compared to side-stream reactors (Jeison D. , 2007).

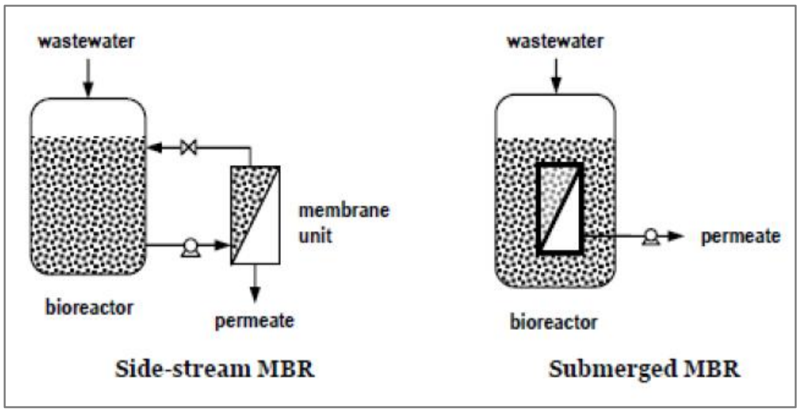

Figure 1. Membrane bioreactor configurations

There are two types of membrane filtration:

1. Dead-end membrane filtration: the feed flow, or sludge, goes against the membrane surface. In this case there is no any retentate, i.e all the feed flow is being converted into permeate.
2. Cross-flow membrane filtration: The feed flow, or sludge, goes in parallel direction to the membrane. There is retentate fraction since only a part of the sludge will be transferred to permeate.

For the dead-end filtration process, is quite easy to produce a thick cake layer on the membrane which requires high-frequency backwash application to have a stable membrane operation. On the other hand, the cross-flow filtration works much better if continuous operation is required (Judd., 2011).

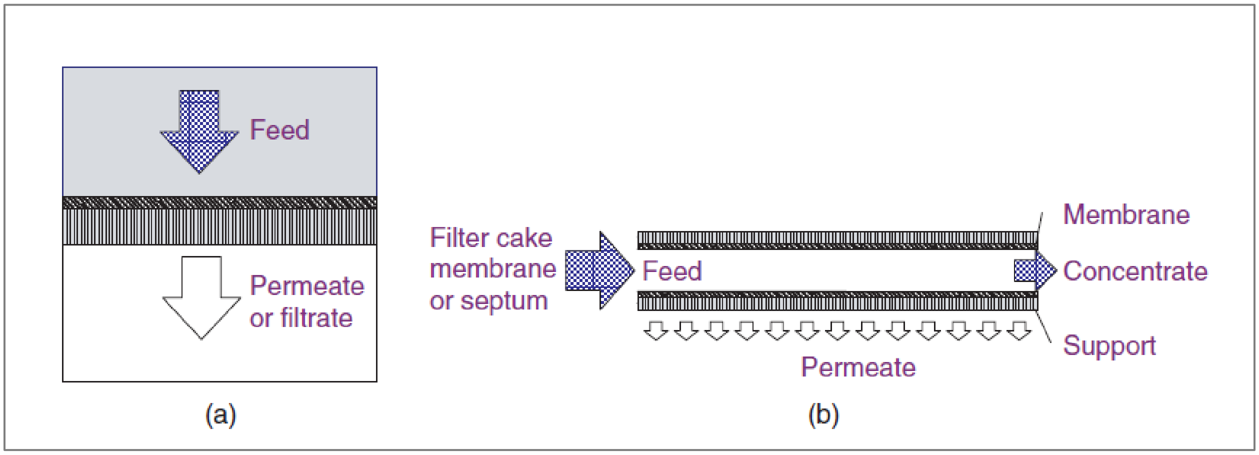

Figure 2. Dead-end (a) and cross-flow (b) filtration (Judd., 2011)

1.6 Anaerobic membrane bioreactors general description.

When sludge granulation is hampered or inhibited, the use of a membrane to benefit the biomass accumulation, it looks the most suitable mechanism to attain it, specifically by the using of the AnMBR technology.

Bed reactor systems as UASB, EGSB and IC represent a low-cost alternative to treat a wide set of wastewaters. On the other hand, MBR technology necessitates higher costs due to the membrane requirements, more complexity and more energy consumption (especially for the cross-flow velocity application). For this reason, the use of this modern system is mostly applied when is not possible to treat the influents with conventional granular sludge reactors. AnMBRs could fill in the gap between high-rate anaerobic treatment traditional systems and anaerobic digesters. These digesters are able to treat wastewaters with a huge amount of SS or a high FOG concentration, in presence of long hydraulic retention times, constituting an effective solids digestion technology.

Figure 3 (No numerical values are showed) shows a general approximation about which kinds of wastewaters may be treated using AnMBRs.

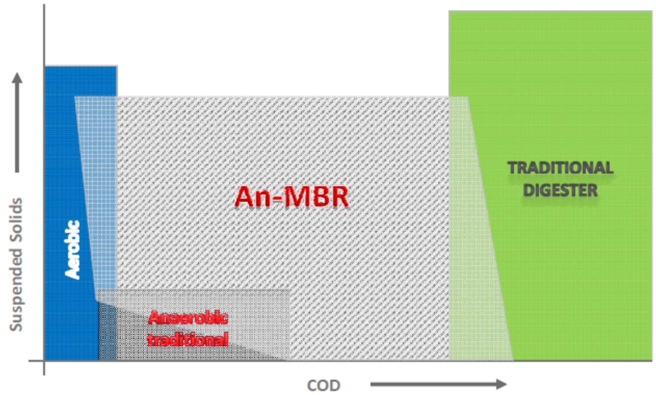

Figure 3. Memthane® application

Anaerobic membrane bioreactors (AnMBR) offer effluents with a high quality, free of solids and pathogen agents. Probably in a near future, this kind of wastewaters will be obtained as a result of cleaner industrial production processes, need of a water consumption decrease, water reuse and water recovery (van Lier et al., 2001; van Lier, 2008).

Currently, most of the research has been developed in lab-scale, but it already may see an important number of full-scale plants running all over the world. There is still some lack of knowledge related to the design and operation of full-scale plants, since most of the research has been developed in lab-scale.

AnMBR constitutes a merging technology based on the biological treatment, in oxygen absence, allowing to treat industrial wastewaters at extreme conditions, such as high salinity and temperature, presence of toxicity and important concentrations of suspended solids that impede granulation and biomass retention, or reduce the biomass activity in sludge bed reactors (van Lier et al., 2001).

Basically, AnMBR technology is a combination between the CSTR and ultrafiltration membrane. The membrane enhances the complete solid-liquid separation. In AnMBRs the particulate organic matter and the biomass are physically retained in the reactor, leading to optimal conditions to organic matter degradation.

It would be possible, in theory, to have an infinite SRT with the AnMBR technology, but it is non-viable since a high sludge concentration affects negatively to membrane operation. From 20 to 25 g/l of VSS the membrane may work correctly.

Cake layer formation was identified as the most important fouling mechanism in AnMBR (Choo and Lee, 1998; Jeison and van Lier, 2007b; Xie et al., 2010). The fouling presence is inevitable, at least in long term, for this reason all the efforts currently are focused in how to reduce its build up. The sludge cross-flow velocity across the membrane surface serves as the main mechanism to reduce the cake-layer formation.

In the past, high costs of the membranes, unstable flux rates and membrane fouling, avoided the use of this modern technology to treat wastewaters. But, during the last years, membrane improvements and energy recovery as biogas, make this technology feasible. Other advantages are the later effluent utilization to save in fresh water consumption, and the use of the daily removed sludge on the fields to increase their productivity.

The laboratory-scale studies may provide reliable information about the wastewater treatability and membrane fouling, but different factors aspressure drops and hydraulic conditions in a small membrane module can be significantly different than in full-scale membrane modules. Besides, the shear effect of full-scale pumps on particle size distribution of the bioflocs and the sludge activity could be different than in laboratory-scale setups. The pilot-scale studies can provide more representative results in terms of attainable flux and membrane fouling.

1.7 Suitability of the AnMBR technology to treat this specific influent.

Anaerobic granular sludge is the most successful technology to treat high-rate wastewater treatment. But sometimes, due to some limiting characteristics of the feed is not possible its use. Some wastewaters could impact negatively to the granulation of the sludge or even provoke the de-granulation or its loss.

In this trial, it was decided to use the AnMBR technology instead of using granular sludge systems for the following reasons:

1. High suspended solids concentration.
2. The significant fats content in the feed.
3. High feed COD.

1) *High suspended solids concentrations*.

The accumulation of slowly degradable particulate matter and non-degradable solids in the sludge bed of UASB reactors, reduces the sludge methanogenic activity during long term operation, deteriorates effluent quality due to the presence of these compounds, leads to a worse sludge granulation and induce serious problems at influent distribution systems in sludge bed reactors. Industries as slaughterhouses, meat and potatoes processing generate an important amount of suspended solids, that´s the reason why a pretreatment step is required in UASB, EGSB and IC reactors, to decrease SS concentration in the feed.

With AnMBR reactors all biomass and suspended solids are completely retained in the system, impeding both, biomass loss (biomass retention is not dependent on granulation) and effluent quality deterioration.

In this kind of treatment, as all particulate matter is being kept into the reactor, by setting the appropriate SRT, a more complete digestion for non-easily biodegradable organic matter will be expected, improving digestion efficiency compared to a conventional slurry digester. Some inert particulate material can be accumulated in the reactor and this may necessitate some sludge discharge.

The presence of higher hydraulic retention times (HRT), compared to UASB and EGSB reactors, and membrane interventions assure a better capacity of removal, of these non-easily biodegradable particles, in AnMBR bioreactors.

SS concentration that AnMBR reactors can treat is not endless, so, if the concentration of these materials in feed is too high and sludge does not have time enough to consume them, a considerably build-up will take place, leading to a quick increase in membrane fouling.

2) *Significant fats content in the feed.*

The main problems associated with the treatment of high-lipids-content wastewaters are the toxicity of long chain fatty acids (LCFA) to methanogens and acetogens (Hwu, 1997), and the formation of a lipid layer around biomass which limits substrate and nutrients transportation (Pereira et al., 2005), resulting in biomass flotation (Rinzema et al., 1989). Even though It is evident that the granular sludge is more resistant to the LCFA presence than the flocculant sludge due to a lower specific surface area, many researchers have reported several operation problems during high lipid containing wastewaters treatment by using of high rate anaerobic reactor, such as granulation impairment, wash-out and flotation of biomass, foam accumulation at the top of the reactor, and suppression of the methanogenic activity.

A report from Hawkes et al. (1995) compared the different performance of UASB, EGSB, Anaerobic Filter and Anaerobic Contact Reactor for the treatment of ice cream wastewater with high-lipid content. The conclusion was that the anaerobic contact reactor presented a better COD removal compared to the others, due to the good mixing between the feed and the sludge. For this reason is usually requires a pretreatment step to treat these kind of wastewaters.

The presence of a good mixing in AnMBR reactors guarantees a good contact between substrate and microorganisms, improving this way the COD removal efficiency compared to the traditional systems that require a pretreatment step, to separate the fats before adding the feed to the system. Moreover no risk of biomass wash-out takes place with the membrane intervention.

3) *High feed COD*

The sludge granulation depends on several factors, such as hydraulic conditions, wastewater characteristics, physico-chemical parameters, etc. Successful sludge granulation can be attained by bacterial selection mechanisms. As a rule of thumb, a correct sludge granulation in high rate anaerobic reactors can be expected with low hydraulic retention times (HRT), i.e., <2 days.

Low HRT values are impossible to be reached with high influent COD value of this experiment (around 145 g COD/l). This high COD concentration requires much longer HRT to be properly treated. The limiting factor in this case would be the volumetric loading rate (VLR). No higher VLR values than 25 or 15 kg COD/m^3.day can be usually applied at EGSB and UASB reactors respectively.

1.8 Limitations of AnMBR technology

Although MBRs proportionate many advantages such as a low footprint and a smaller reactor volume, compared to conventional anaerobic biological treatment systems, it is also important takes into account their main weak point, what is represented by membrane fouling. This fouling will lead to a decrease in membrane lifetime, a flux reduction and an increase in membrane cleaning frequency. That's the main limiting factor to have a more widespread implementation of MBR technology (Rosenberger, et al., 2006). Figure 4 represents parameters affecting membrane fouling.

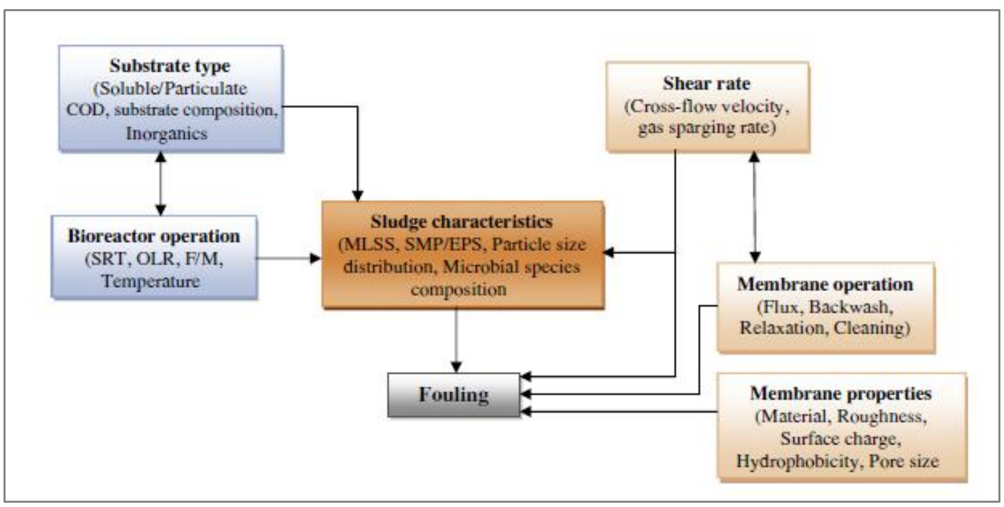

Figure 4. Factors affecting membrane fouling in AnMBR (Dereli, et al., 2012)

Membranes themselves represent a relevant capital cost, so everything that can reduce their lifetime or the applied flux will directly affect the economic feasibility of process. Moreover, membrane cleaning activities directly affect reactor operation due to the necessity for process interruptions

Table 1 shows different foulant definitions.

Table 1. Foulant definitions (Henze, 2008)

Practical	Mechanism	Foulant material type
Reversible/temporary • Removed by physical cleaning *Irreversible/permanent* • Removed by chemical cleaning *Irrecoverable/absolute* • Not removed by any cleaning regime	*Pore blocking/filtration models* • Complete blocking • Standard blocking • Intermediate blocking • Cake filtration	*Size* • Molecular, macro-molecular, colloidal or particulate *Surface charge/chemistry* • Positive or negative (cationic or anionic) *Chemical type* • Inorganic or organic • Carbohydrate or protein *Origin* • Microbial, terrestrial or man-made • EPS or SMP

Four types of membrane fouling can be identified:

1. Cake layer formation
2. Pore clogging
3. Inorganic Fouling
4. Adsorption

These four phenomena are responsible for membrane fouling, but cake layer formation has been identified as the main important factor governing the attainable flux.

Cake layer covers membrane surface protecting it from small sized particles deposition, preventing pore clogging, and retaining them inside the system. Jeison D., (2007) concluded that sludge concentration is the main operational parameter governing cake layer formation, as a sludge concentration increase would augment the convective flow of solids towards the membrane.

In side-stream MBRs a cross-flow velocity of 2-3 m/s it was applied to minimize cake layer formation. Nevertheless, these high flow velocities are able to disrupt the sludge flocs, resulting in accumulation of smaller particles on membrane surface (Lin, et al., 2009). Liao, Kraemer, & Bagley (2006) suggest that these high shear-rates could also affect to the activity of the sludge. For this reason, most of the investigations on MBRs have been conducted using lower cross-flow velocities (1 m/s normally used in full-scale plants) and patterns of relaxation or backwash.

Depending on operational conditions, each membrane will present a different critical flux value. Critical flux is defined as flux over which the relation between flux and TMP becomes non-linear (Wu et al., 1999). Therefore this value results very useful to characterize membrane fouling in membrane applications.

To have a good membrane performance is necessary to operate with a filtration flux value lower than the critical flux one. But still, AnMBR treatment without fouling cannot be expected, and throughout the time, a slow linear increase of TMP will be observed (Liao, Kraemer, & Bagley, 2006).

Operating in a short term at permeate filtration flux close to critical flux leads to a reversible cake layer formation that can be removed by mean of backwash utilization between filtration processes. In a long-term the consolidation of cake layer takes place, and even backwash use could be useless to remove it.

AnMBR use, to treat industrial wastewaters is more prone to inorganic fouling by precipitates of different elements (calcium, phosphorous, sulphur, etc.) than their aerobic counterparts. This is because of high presence of these elements in industrial wastewater of interest for AnMBR, the applied high volumetric loading rates and the chemistry of carbon dioxide equilibrium (Stuckey., 2010)

Struvite ($NH_4MgPO_4 \cdot 6H_2O$) is considered as one of the most significant precipitates affecting filtration performance of inorganic membranes (Choo and Lee, 1998; Choo et al., 2000; Kang et al., 2002)).

Inorganic fouling should not be underestimated when treating industrial wastewaters with ahigh nitrogen and phosphorous concentration. Inorganic species could interact with Soluble Microbial Products (SMP) enhancing the mechanical stability of the fouling layer.

This technology could be much cheaper if a good fouling control could be accomplished. Not only suspended solids (biomass) may affect to the membrane permeability. Also many others agents such as colloids (Choo, et al., 2000), soluble organic matter (Harada, Momonoi, Yamazaki, & Takizawa, 1994), inorganic particles (Choo & Lee, 1996b); (Yoon, Kang, & Lee, 1999) and EPS (Nagaoka, Ueda, & Miya, 1996); (Chang & Lee, 1998); (Cho & Fane, 2002) can play an important role on fouling apparition.

The main biological parameter responsible for the membrane fouling is the concentration of microorganism; this means the mixed liquor suspended solids concentration. The use of ultrafiltration membranes allows to keep all the microorganism into the system, since the biomass size is bigger than the ultrafiltration membrane pores. An increase in the MLSS concentration will provoke a permeate filtration flux value reduction, by the increased opportunity of cake layer formation.

The membrane material nature also presents a significant role in the membrane fouling. The utilization of an inorganic membrane with a smooth surface is less susceptible to clogging than an organic membrane with the presence of a rough and fibrous structure that provides a better adhesiveness for the biomass (In-Joong Kang et al., 2002).

2. Materials and methods

2.1 Materials

2.1.1 Influent characterization

The influent used to feed the AnMBR reactor, was a mixture of different wastewater streams from a dairy industry.

Throughout the trial is possible to distinguish 4 main stages, which correspond to 4 different kinds of feed used during 160 days. The first two feeds, ice cream, and afterwards, a mix between yoghurt and acid whey (ratio 2:5), were used for the acclimatization of bacteria, because DAF influent would not arrive to Biothane® until the 54th day. From that date, acid whey, yoghurt and DAF were introduced in the AnMBR (ratio 5:2:2). It was believed that this wastewater would be the definitive one, but on day 124, the dairy industry decided to vary the feed composition. The final stream was composed by 85% of acid whey, 7.5% water, 3.75% yoghurt and 3.75% DAF.

The first weeks, the dairy industry wastewater had not arrived yet, so, it was decided to use an influent with similar characteristics as agreed between the client and Biothane®. The chosen influent was ice cream because of high-fats and COD concentration. After using ice cream, biomass was fed with acid whey and yoghurt, but DAF was still no available to be treated.

The day 54, DAF influent came to Biothane, and a feed composed by acid whey, DAF and yoghurt (with the following proportions 5:2:2) was treated until the day 124.

Finally, the client decided to vary the wastewater composition, increasing considerably the acid whey proportion in the total feed (85% of Acid Whey, 7.5% water, 3.75% yoghurt and 3.75% DAF).

The new feed ratio resulted in lower fats content, since the acid whey is mainly formed by sugars (lactose) and, in less extent, by proteins. The presence of fats in this kind of wastewater is almost insignificant (0.2 g/l), compared to DAF and yoghurt influents which present a fat concentration of 70 and 30 g/l respectively.

Stage 1. *Ice cream*

During this acclimatization stage, diluted ice cream was used to simulate pretty similar characteristics as the feed in Stage 3 (big amount of fats and high TCOD). This stage last the first 21 days, where a quantity of 35.5 liters in total were consumed. Later, when analyzing the results, this phase will not be taken into account.

Stage 2. *Acid Whey and yoghurt (off-spec products)*

This phase will be briefly analyzed in the analysis and results part since only acid whey and yoghurt are being used.

DAF influent was not present yet, so this feed does not correspond to the final one.

The ratio employed was 5 (acid whey):2 (yoghurt). This stage took place from 22nd to 54th day, feeding the reactor with 85.8 liters. Table 5 shows the composition of the feed in Stage 2. Some influent characteristics to note are:

- The presence of a high TCOD value (151.7 g/l). This value was constantly high in all the experiment, not only in Stage 2.
- The quotient SCOD/TCOD is 0.84. This means that the 84% of the TCOD is soluble.
- The TSS and VSS values are pretty high (45 and 37 g/l respectively). This is one of the reasons why this technology was chosen to try to treat this dairy feed. This value is not too much reliable because only two TSS and VSS analysis were done.
- The quotient VSS/TSS is 0.83. It means that the 17% of the feed is formed by inorganic suspended solids and the 83% by organic ones.
- Nitrogen, calcium, phosphorous and magnesium concentrations were quite high, so none extra-nutrients addition was required in this period.
- DAF influent has not arrived yet, so, the fats concentration was not still the expected one.

Stage 3. *DAF (wastewater from Dissolved Air Flotation system), yoghurt (off-spec products) and Acid whey*

In principle, this would be the real feed that the dairy company really wanted to treat. The ratio employed was 2:2:5 respectively (day 54 to 124). Around 157.8 liters were consumed. The feed composition is depicted in Table 6. Some important characteristics of this feed are:

- The presence of a high TCOD value (158 g/l).

- The quotient SCOD/TCOD is 0.69. Therefore the 69% of the TCOD is soluble. This value would indicate a higher suspended solids concentration presence compared to the Stage 2 and 4.

- The TSS and VSS values are pretty high (42 and 39 g/l respectively). It is important to note that the standard deviation value at this phase was considerably far from 0. This occurred since the feed was not really homogeneous. These values should have been higher than at the stage 2, since DAF presents more SS than acid whey and yoghurt influents. With high suspended solids concentrations may be difficult to get good analysis.

- The quotient VSS/TSS is 0.92. It means that the 8% of the feed is formed by inorganic suspended solids and the 92% by organic solids.

- Nitrogen, calcium, phosphorous, magnesium concentrations were quite high, so none extra-nutrients addition was required in this stage.

- DAF already went incorporated to the system.

Stage 4. *DAF (wastewater from Dissolved Air Flotation system), yoghurt (off-spec products) and Acid whey*

The following proportion was added to the system: 85% of Acid Whey, 7.5% water, 3.75% yoghurt and 3.75% DAF. The water addition was carried out to reduce the COD of DAF, since in a future a different composition will be produced in the factory and that would be its real COD concentration value.

This last stage was performed from 124th to 160th day, feeding the anaerobic reactor with 170.65 liters. Table 7 shows the feed composition. Some of the interesting characteristics of the influent are:

- The presence of a high TCOD value (141 g/l). This value was constantly high in all the experiment, but compared to the other influents was the lowest. This could be mostly explained by the significant presence of acid whey in the feed (85%). DAF and yoghurt have higher COD concentrations.

- The quotient SCOD/TCOD is 0.89. This means that the 89% of the TCOD was soluble.

- The TSS and VSS values were not so high compared to the other stages (22 and 19 g/l respectively). This is because the acid whey presented the lowest suspended solids concentration of the three.

- The quotient VSS/TSS is 0.88. It means that the 12 % of the feed was formed by inorganic suspended solids and the 88% by organic solids.

- The nitrogen, calcium, phosphorous and magnesium concentrations were quite high, so none extra-nutrients addition was required in this stage. Compared to the other two feeds (Stage 2 and 3), this influent has a lower nitrogen concentration but a higher calcium content.

Table 2. Acid whey characterization

Parameter	Value	Units
pH	4.4	
TCOD	154,270 ± 7,552	mg/l
SCOD	151,566 ± 10,115	mg/l
TS	137,068 ± 668	mg/l
VS	119,156 ± 869	mg/l
TSS	2,601 ± 803	mg/l
VSS	2,468 ± 746	mg/l
TKN	1,512 ± 33	mg/l
NH4	722 ± 126	mg/l
Total-P	1,780 ± 62	mg/l
Ortho-P	1,487 ± 41	mg/l
$SO42^{-}$	305	mg/l
Cl^{-}	2,520 ± 221	mg/l
$Mg2^{+}$	289 ± 20	mg/l
$Ca2^{+}$	3,076 ± 107	mg/l
K^{+}	3,010 ± 438	mg/l
Fats	200	mg/l

Table 3. Yoghurt characterization

Parameter	Value	Units
pH	3.684 ± 0.16	
TCOD	162,833 ± 8,129	mg/l
SCOD	71,046 ± 2,720	mg/l
TS	112,176 ± 26,333	mg/l
VS	104, 753 ± 24,287	mg/l
TSS	78,457 ± 24,287	mg/l
VSS	76,821 ± 23,928	mg/l
TKN	6,216 ± 806	mg/l
NH4	1,296 ± 78	mg/l
Total-P	653 ± 59	mg/l
Ortho-P	515 ± 156	mg/l
$SO42^{-}$	660	mg/l
Cl^{-}	915	mg/l
$Mg2^{+}$	212 ± 78	mg/l
$Ca2^{+}$	1,016 ± 92	mg/l
K^{+}	803 ± 86	mg/l
Fats	30,000	mg/l

Table 4. DAF characterization

Parameter	Value	Units
pH	5.6	
TCOD	179,000 ± 23,081	mg/l
SCOD	13,901 ± 9,380	mg/l
TS	98,926 ± 22,868	mg/l
VS	81,292 ± 17,507	mg/l
TSS	94,576 ± 23,478	mg/l
VSS	81,200 ± 17,603	mg/l
TKN	3,863 ± 37	mg/l
NH4	1,269 ± 412	mg/l
Total-P	774 ± 167	mg/l
Ortho-P	388 ± 75	mg/l
Cl^{-}	1,008 ± 1,077	mg/l
$Mg2^{+}$	219 ± 181	mg/l
$Ca2^{+}$	918 ± 70	mg/l
Fats	70,000	mg/l

Table 5. Stage 2 (Feed characterization)

Parameter	Value	Units
pH	4.05 ± 0.1	
TCOD	151,790 ± 13,590	mg/l
SCOD	127,209 ± 7,430	mg/l
TS	120,796 ± 5,700	mg/l
VS	106,412 ± 5,365	mg/l
TSS	45,249 ± 9,859	mg/l
VSS	37,477	mg/l
TKN	2,867 ± 238	mg/l
$NH4^{+}$	359	mg/l
Total-P	1,500 ± 118	mg/l
Ortho-P	1,160 ± 42	mg/l
$SO42^{-}$	561 ± 103	mg/l
Na^{+}	3,243	mg/l
$Mg2^{+}$	381 ± 174	mg/l
$Ca2^{+}$	2,790 ± 60	mg/l

Table 6. Stage 3 (Feed characterization)

Parameter	Value	Units
pH	4.2 ± 0.27	
TCOD	159,219 ± 12,572	mg/l
SCOD	106,927 ± 14,538	mg/l
TS	116,445 ± 26,726	mg/l
VS	102,072 ± 26,672	mg/l
TSS	42,402 ± 16,574	mg/l
VSS	39,497 ± 15,362	mg/l
TKN	3,162 ± 238	mg/l
$NH4^{+}$	408 ± 206	mg/l
Total-P	1408 ± 121	mg/l
Ortho-P	1129 ± 60	mg/l
$SO42^{-}$	429 ± 99	mg/l
Na^{+}	675 ± 272	mg/l
$Mg2^{+}$	254 ± 111	mg/l
$Ca2^{+}$	2668 ± 536	mg/l

Table 7. Stage 4 (Feed characterization)

Parameter	Value	Units
pH	3,83 ± 0,25	
TCOD	141,329 ± 5.763	mg/l
SCOD	126,706 ± 7,382	mg/l
TS	110,759 ± 8,498	mg/l
VS	93,634 ± 8,242	mg/l
TSS	22,208 ± 6,178	mg/l
VSS	19,634 ± 5,472	mg/l
TKN	1,694 ± 53	mg/l
$NH4^{+}$	327 ± 9.62	mg/l
Total-P	1,632 ± 13	mg/l
Ortho-P	1,409 ± 33	mg/l
$SO42^{-}$	284 ± 17	mg/l
Cl^{-}	2.089 ± 258	mg/l
Mg^{2+}	329 ± 94	mg/l
$Ca2^{+}$	3,158 ± 359	mg/l

2.1.2 Pilot Plant Anaerobic Membrane Bioreactor (AnMBR)

This trial was carried out by using Biothane´s Memthane® technology. A modern pilot plant with a reactor capacity of 100 liters was employed to treat the dairy industry wastewater.

2.1.2.1 Pilot Plant components (configuration)

Figure 5. Memthane® layout

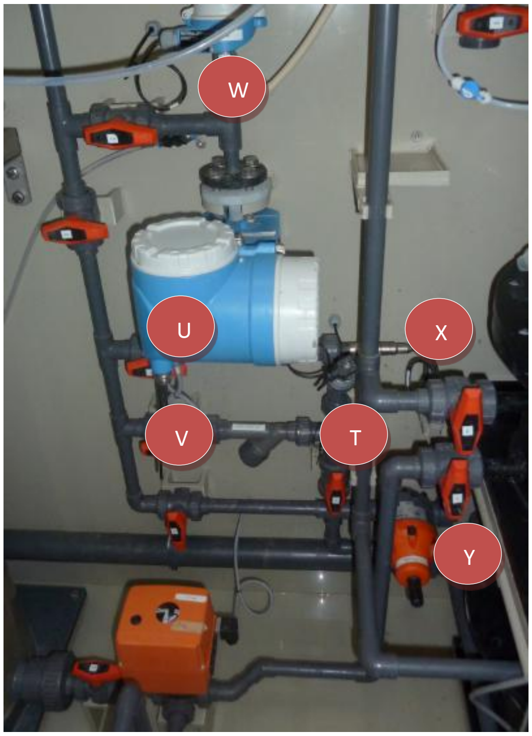

Figure 6. Memthane® layout

Figure 5 shows a picture taken before starting the experiment, but this not will be the definitive layout, since, in order to improve the system performance, some changes in the design that will be commented below were made. The Memthane® Pilot Plant P&ID is depicted in Figure 41 (last page of the thesis) where all the made changes are depicted.

Legend:

- A) Buffer Tank (T-400)
- B) Feed Pump (P-402)
- C) Heating Bath (X-3000)
- D) Antifoam Tank (T-5120)
- E) Caustic Tank (T-5000)
- F) AnMBR Stirrer (M-1101)
- G) AnMBR reactor (T-1100)
- H) Recirculation Pump (P-1102)
- I) Membrane skid (X6)
- J) Permeate tank (T-1700)

- K) Permeate pressure sensor (PT-1604)
- L) Pressure sensor (PT-1602)
- M) Pressure sensor (PT-1603)
- N) Gas meter
- O) Permeate filtration pump (P-1601)
- P) CIP tank (T-1800)
- Q) Draining tank (T-1900)
- R) Gas column (T-2000)
- S) Permeate recirculation pump (P-1701)
- T) Recirculation Pump pressure sensor (PT-1112)
- U) Sludge recirculation Flow meter (FIT-1107)
- V) Sludge recirculation strainer (S-1120)
- W) Temperature sensor (TT-1106)
- X) pH meter (AIT-1106)
- Y) Pressure valve (PV-201)

2.1.2.2 Pilot Plant components description

The anaerobic reactor was operated at mesophilic temperature, around 37°C, with a SRT, until the 136th day, of 50 days. Later on, due to the high inorganic (non-volatile suspended solids) and organic (volatile suspended solids) particles accumulation, it was decided to reduce the SRT up to 40 days. This SRT value of 40 days was employed until the end of the experiment.

The AnMBR could, in theory, operate with an infinite sludge retention time (SRT), but the non-removal of the sludge would provoke a sludge concentration increase in the system as a consequence of biomass growth and non-biodegradable particles build-up, and consequently, a grave membrane fouling would occur. In presence of this significant fouling, the flux filtration would suffer an important decline. A TSS concentration around 30 g/l may be considered worrying to have a proper membrane performance.

AnMBR reactor (T-1100)

The AnMBR reactor (T-1100) capacity is 100 liters. The sludge was continuously mixed with a mechanical stirrer (M-1101) at 132 rpm (Figure 7). These rpm represent the maximum capacity of this device, allowing this way a good mixing. At first, the velocity was around 50 rpm. But throughout the trial, it was observed an important accumulation of inorganic particles at the bottom of the reactor (no mixing enough). This could mean that some inorganic particles were falling down and were being accumulated there, instead of being removed from the sludge sample point (placed after the recirculation pump).

The digester (T-1100) has two level indicator transmitters (LIT-1102 A and LIT-1102 B; Figure 8, numbers 1 and 2 respectively), which give us a precise sludge volume value inside the reactor. They are located at the top and at the bottom of the AnMBR reactor respectively.

In order to get optimal digestion efficiencies for the microorganisms, an interval temperature value between 35-37°C is necessary (mesophilic conditions). To keep a desired sludge temperature value, the reactor is surrounded by a heating bath jacket, from where warm water coming from the heating bath is passing through.

Figure 7. Mechanical mixer (M-1101)

Figure 8. AnMBR reator (T-1100)

Recirculation pump (P-1102)

The Anaerobic membrane bioreactor was operated with a cross-flow velocity of 1 m/s. That´s the normal value used in a full-scale plant. This cross-flow velocity is necessary to move sludge all over the system, and represents one of the most important energetic costs of this technology.

In order to avoid possible damages to itself and to the system, the recirculation pump (P-1102), has a temperature (TT-1106) and a pressure sensor (PT-1112).

When pressure values, detected by the pressure transmitter (PT-1112) are higher than 2 bar, sludge would be released from the pressure valve (PV-201) as a mechanism of protection. To avoid this sludge loss, a high pressure alarm was installed in the system. The maximum allowed sludge recirculation pressure at the experiment was 1.5 bar. So, if the value detected by the pressure sensor (PT-1112) is higher, the Pilot Plant will go to out of service mode.

Figure 9. Recirculation pump (P-1102)

It is very important to note the immediate existence of a 1.4 mm pore size filter (S-1120) after the recirculation pump (P-1102), to try the collect as many particles as possible, to prevent possible membrane damages. In particular, this strainer was very helpful to collect every day a huge amount of $CaCO_3$ and $Ca_3(PO_4)_2$, located on the reactor walls. Logically, only the particles with bigger size than 1.4 mm could have been removed from the system. But this strainer did not solve the problem of the small inorganic particles accumulation in the system. The only way to remove them is by means of the sludge removal. Figure 10 shows how significant was the inorganics accumulation on the inside reactor surface.

Figure 10. Inorganic precipitates fixed to the reactor walls

Membrane skid

The Pilot Plant was equipped with an ultrafiltration membrane supplied by Pentair® and composed by PVDF (Polyvinylidene fluoride). The skid characteristics are:

- Number of membranes: 6
- Membrane length: 3 m
- Mean Pore size: 30 nm
- Membrane surface (1x): 0.049 m^2
- Total membrane surface (6x): 0.294 m^2
- Membrane tube opening (1x): 5.2 mm

During sludge recirculation two different modes can be used: normal and reversal cross-flow. They are called this way only to differentiate sludge direction movement. In normal cross-flow mode the movement is represented by the red lines (Figure 11).

In reversal cross-flow mode, sludge is moving along the membrane in the opposite direction (blue lines in Figure 11), from PT-1603 to PT-1602. This allows to membranes not being forced to do filtration always at the same point. In normal cross-flow most of the filtration is taking place close to PT-1602, and in reversal cross-flow happens close to PT-1603. This occurs since the main responsible for the permeate filtration is not the filtration pump (P-1601), but the recirculation pump (P-1102). This pump is providing pressure to extract permeate from membrane.

The orange valves (Figure 11) will automatically change their position every certain period of time (this time can be adjusted by the operator) to allow the change of mode, from normal to reversal cross-flow and the other way around.

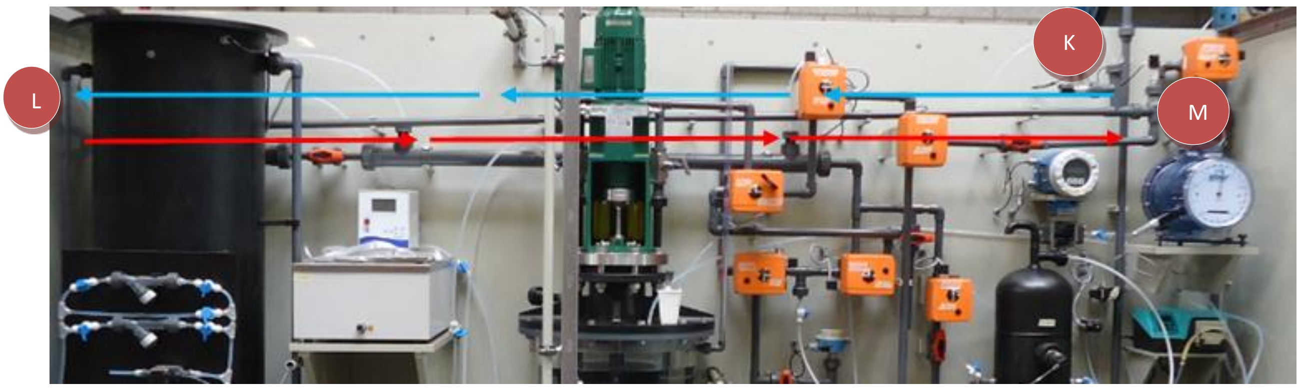

Figure 11. Sludge movement in normal and reversal cross-flow

The followed sequence in the experiment consisted of alternate 15 normal/reversal cross-flow cycles. In both modes, each cycle lasts 15 minutes. Between every cycle, a 10 seconds backwash took place with a flux value of 185 (maximum pump capacity).

On day 135, it was decided to increase this value up to 250 l/(m^2.h), to simulate the full-scale plant operation conditions. To accomplish this high value, an extra pump-head was installed in the permeate filtration pump (P-1601). This higher value it is supposed to reduce the existent membrane fouling.

The permeate filtration flux value was vaying throughout the experiment, in accordance to membrane fouling (measured by the TMP value). In the end, a stable 12 l/(m^2.h) value was considered suitable to do filtration.

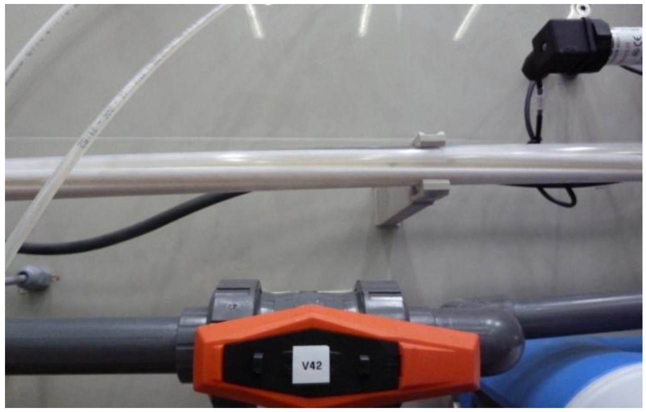

Figure 12. Membrane skid (longitudinal view)

Figure 13. Membrane skid 6x (sectional view)

Buffer tank T-400

The feed was kept inside a 250 liters buffer tank (T-400). This tank was provided with a submerged pump (P-401) to keep feed completely mixed.

In the experiment, due to high feed TCOD, the provided feed flow was quite low. This resulted in some acidification inside the buffer tank. The acidogenic bacteria consumed COD (TCOD and SCOD) to produce VFA. This means, to obtain a consistent COD mass balance, it was necessary to increase the feed TCOD and SCOD frequency analysis. The high feed VFA concentrations do not suppose a big concern. When feed pH value is lower than 4 the activity of acidogenic bacteria will be reduced and no more acidification will be carried out in the buffer tank.

Two strainers with a pore size of 2.2 mm (S-410 and S-420) are responsible for collecting different particles present in the feed line, as a mechanism to protect the membrane. Mainly these particles come from the yoghurt (some fruit pieces) and DAF. These strainers are located between the feed pump (P-402) and the anaerobic reactor (T-1100). The feed pump is exactly the same kind of pump as the filtration pump (P-1601) and the permeate recirculation pump (P-1701).

As can be observed in Figure 16, the pumps are protected with a plastic cover to avoid any possible damage at the back of the pump, where some water sensitive parts are located.

To control the feed volume, a level indicator transmitter (LIT-401) is employed. It is located at the bottom of the buffer tank. This level indicator shows how much feed there is in the tank. A low level alarm is presented to let us know if the feed volume is low.

Figure 15. Buffer Tank (T-400)

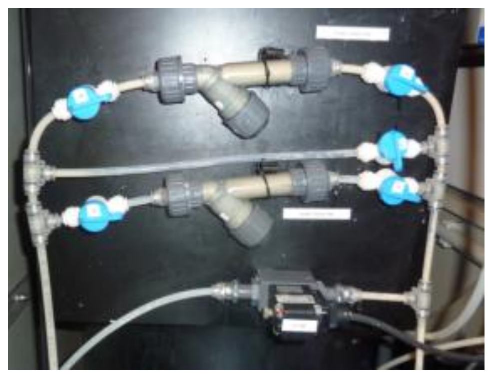

Figure 14. Strainers (S-410 and S-420)

Figure 16. Feed Pump (P-402)

Permeate tank (T-1700) and Permeate recirculation pump (P-1701)

When designing an AnMBR, the flux is one of the most critical parameter as it determines the amount of membranes required. This is very important as the membranes are a significant cost. Thus the higher the flux that can be applied the better in terms of the competitiveness of the solution. However it is also important to prevent fouling on membranes as this will rapidly decrease the flux that can be applied.

The flux can defined as the rate of flow of a fluid across a given area. It is the result of divide the permeate flow by the membrane surface. The flux value used in most of the trial was around 12 $l/(m^2.h)$.

The flux membrane surface used in the pilot plant was 0.295 m^2. This value is quite high compared to which was really required. But it is very useful to obtain more reliable experimental results. To keep a constant flux value, in presence of a big membrane surface, it is also necessary a high permeate flow. Therefore an extra permeate extraction will be carried out.

Using the flux formulae, the only way of obtaining a value of 12 $l/(m^2.h)$ is with a permeate flow of 3.5 l/h. This results in a daily permeate flow of 84 liters/day. But the feed flow in most of the trial was approximately 6 liters/day. For that reason, those extra 78 liters of permeate will come back to the reactor throughout the day by means of the permeate recirculation pump (P-1701).

The extracted overpermeate will be stored inside the 10 liters of capacity permeate tank (T-1700). Every time sludge volume is lower than a given value (specified by the operator), the permeate recirculation pump (P-1701) will be activated, introducing part of permeate located in the permeate tank back into the reactor. The permeate tank is provided with a level switch (LS-1701) to detect permeate low levels.

Figure 17. Permeate tank (T-1700)

NaOH (T-5000) Tank

The NaOH tank and the NaOH pump present a plastic protection cover to avoid any possible health risk.

The use of the NaOH pump (P-5001) was not required at any moment of the experiment, due to the sufficient quantity of nitrogen existing in the feed. The $NH4^+$ produced in anaerobic conditions, present an important buffer capacity.

If the case that nitrogen capacity was not enough and the pH value was lower than 6.8 (this value can be changed by the operator) the pump (P-5001) would be activated, pumping NaOH to the system until reaching the desired value for the operator. At that moment the pump would stop automatically.

The alkalinity formation, during the degradation of the proteins in the feed, kept the pH of the sludge constant. This alkalinity allows the neutralization of the VFA, preventing the reduction of the pH in the reactor. This could reduce the operational costs since no NaOH addition was required.

Antifoam (T-5120) tank

On the other hand, the use of antifoam was constantly required. Its use started after DAF feed addition to the system. This foam apparition presents an important problem, since may provoke interferences over the anaerobic reactor volume measurement. The level indicator transmitter (LIT-1102 A) could send a wrong signal to the PC, avoiding a proper operation.

Another possible foam accumulation problem could be the incorporation of some sludge inside the Permeate tank (T-1700), since the anaerobic tank (T-400) and the permeate tank (T-1700) are directly connected by a plastic tube. This connection was necessary to prevent wrong biogas production measurement (the permeate tank acts as a buffer). During the backwash period, part of the sludge could be incorporated at the outside part of the membrane.

But the main problem of this foam accumulation is the possible clogging of the gas line, which could lead to an increase in biogas pressure inside the anaerobic bioreactor. If the gas line is completely clogged there was no other way out for the biogas produced inside the digester.

Once the problem was detected, it was decided to install a 1 meter water-lock in the reactor, in order to prevent this pressure build-up. In this particular case, this water lock was filled up to 60 cm with water. So, by the time the pressure is higher than 60 mbar inside the reactor, the water-lock water will come out to the atmosphere (outside the anaerobic reactor), releasing the pressure excess. So, if the gas line is clogged, because of the foam presence, an extra way out is available to prevent any risk.

Figure 18. Water-lock

Throughout the experiment, the inorganic particles accumulation ($CaCO_3$, Ca_3PO4_2 and struvite) inside the spray nozzle (responsible for the good antifoam distribution in the anaerobic reactor), provoked an irreversible clogging, and as a consequence, the antifoam line was not used anymore. To solve this problem it was decided to add antifoam directly in feed.

Heating Bath (X-3000)

The heating bath keeps the sludge temperature constant inside the reactor, to have an optimum biomass performance. The highest anaerobic sludge activity will occur, in mesophilic conditions, with a temperature between 35-37°C. The existence of temperatures higher than 40°C would very likely result in biomass death. On the other hand, a temperature reduction will provoke a sludge activity decline.

To control the sludge temperature, a temperature sensor (TT-1106) is installed after the recirculation pump (P-1102). The temperature of this sensor does not correspond exactly with the real value inside the anaerobic reactor, since there is a cooling when the sludge abandon the anaerobic reactor and starts to run all over the pipeline. This means that temperature detected in the recirculation line by the sensor will be little lower than inside the reactor.

The heating bath (X-3000) has an internal pump which is able to pump warm water to the reactor jacket, (which completely surrounds the anaerobic reactor) allowing this way the sludge heating-up.

It is important to be aware that some water will occasionally evaporate. So, it will be necessary to fill the heating bath with water from time to time.

Figure 19. Heating Bath (X-3000)

Pressure sensors

Four pressure sensors were required in this experiment. Three of them were used to calculate the so important value of the Trans-Membrane Pressure (PT-1602; PT-1603 and PT-1604). The TMP value gives the fouling status of the membrane.

- The PT-1602 presents a pressure range between 0-2 bar (settings). No negative values measurement is needed.
- The PT-1603 presents a pressure range between 0-2 bar (settings). No negative values measurement is needed
- The PT-1604 pressure sensor will provide the pressure value during the filtration and backwash mode. It presents a pressure range between -1 to 1 bar (settings). In this part of the membrane it is possible to have negative pressure values.

Figure 20. Permeate pressure sensor (PT-1604)

The missing pressure sensor (PT-1112) or recirculation pump pressure sensor, presents a range between 0-2 bar (settings). No negative values measurement is needed.

Monitoring software

The different processes such as: reactor feeding, pH regulation, antifoam injection, reactor temperature, sludge recirculation, sludge extraction, membrane filtration, permeate recirculation, membrane cleaning etc… are implemented on a cRIO system (PLC), which will run independently of the PC. The PC is used for user interfacing and data collection. This installation may run continually, 24/7, being possible to control all the system from home thanks to Team Viewer program. For this reason the pilot plant could be monitored at any moment of the year.

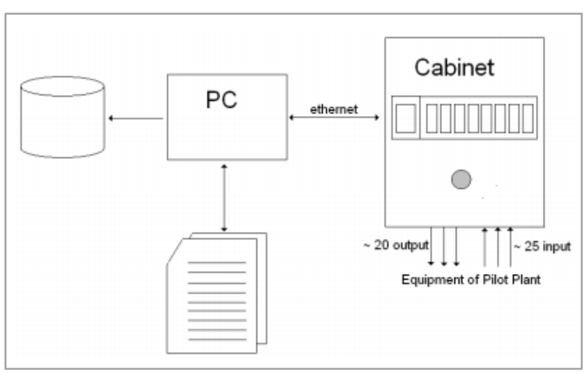

Figure 21. System Memthane Pilot Plant

The Graphical User Interface makes possible for the user to view a P&ID (Piping and Instrumentation Diagram) and provide navigation to settings, status information and trending.

In the P&ID (Figure 22) the process values and set points will be shown. Status of valves (orientation) will be indicated and can be operated from the P&ID.

All the following parameters were configured and monitored thanks to this interface:

- Sludge pH and temperature
- Buffer tank and AnMBR volume
- TMP (Transmembrane Pressure)
- Permeability
- Filtration flux
- Cross-flow, feed flow and permeate flow (filtration/backwash mode) velocities
- Biogas production
- Pressure difference (ΔP)
- Recirculation pump pressure and temperature
- Heating Bath temperature

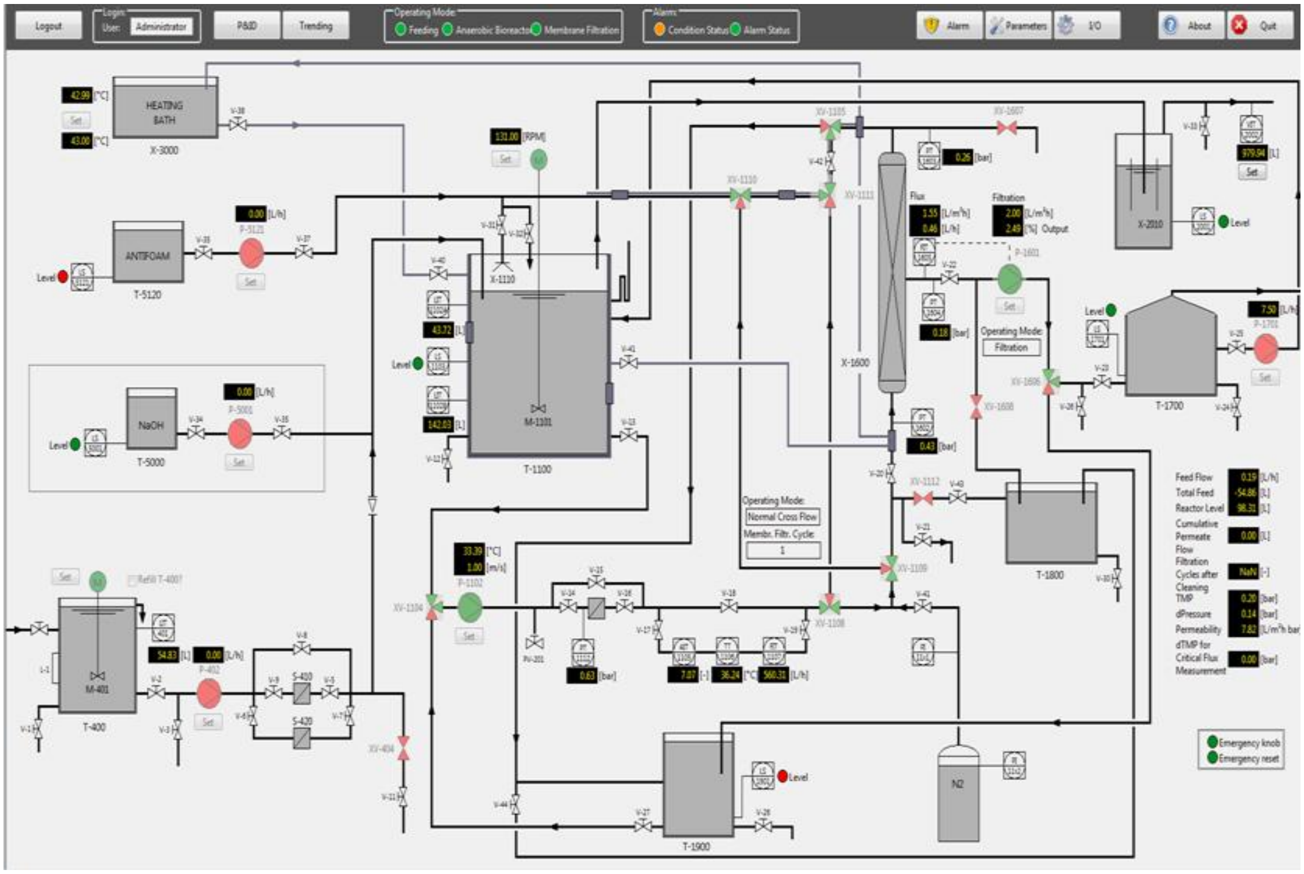

Figure 22. Piping and instrumentation diagram (screen)

The Trending screen (Figure 23), constitutes another important part of this interface, providing us graphical information about different parameters and their values.

- Feed pressure (In normal cross-flow measured by PT-1602; in reversal cross-flow by PT-1603)
- Retentate pressure (In normal cross-flow measured by PT-1603; in reversal cross-flow by PT-1604)
- Permeate pressure
- Filtration flux
- TMP
- Permeability
- Pressure difference (ΔP) (In normal cross-flow is the result of subtracting PT-1602 – PT-1603 value; in Reversal cross-flow PT-1603 – PT-1602 value)
- Biogas production

It may be seen in the trending, online information at the top part of the screen, and recorded information, during a desired period time, at the bottom part. At the top part the operator may check out whatever parameter value (showed above) during the last 24 hours and with online update. At the bottom part the operator could choose a starting and ending date (at any moment of the experiment), but without online visualization.

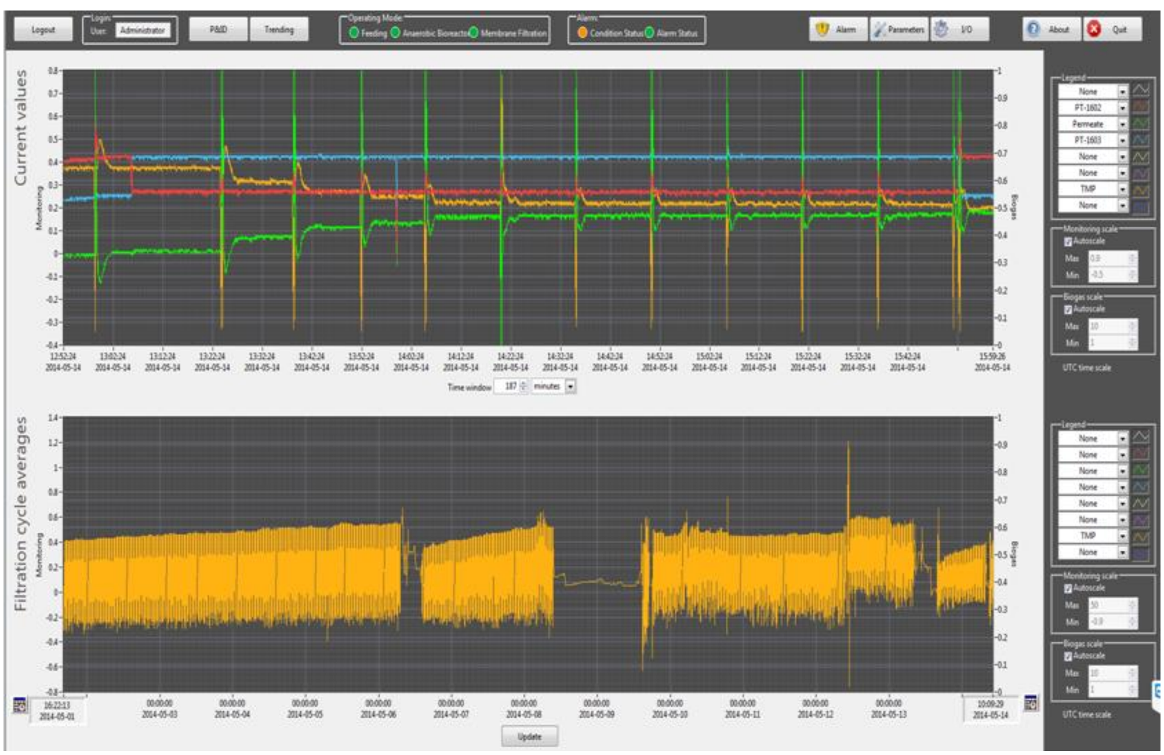

Figure 23. Trending screen; online data (top part) and recorded data (bottom part)

2.2 Methods

2.2.1 Analysis and sample treatment

Samples analyses were regularly carried on the feed, sludge, permeate and biogas as it is described in the analyses schedule for the Memthane® AnMBR trial (Table 8).

Table 8. Analysis schedule for the AnMBR

	Samples			
Analysis	**Feed**	**WAnS**	**Permeate**	**Biogas**
pH	1/w	c	1/w	
Temperature		c		
Biogas production				c
Biogas CH4-%				5/w
TCOD	2/w	1/w	5/w	
SCOD	2/w	1/w		
TS/VS	1/w	2/w	1/w	
TSS/VSS	1/w	2/w	1/w	
VFA	1/w		5/w	
TKN	1/w	1/w	1/w	
NH4-N	1/w		1/w	
Ptotal	1/w	1/w	1/w	
Anions (Cl-, SO42-, Ortho-P)	1/w	2/m	1/w	
Cations (Mg2+, K+, Ca2+)	1/w	1/w	1/w	
Capillary suction time		1/w		
Specific methanogenic activity		2-4/m		
SH_2				1/w

To analyze COD and SCOD of the feed, sludge and permeate Lange COD cuvette tests were used. To do the TCOD, no sample treatment was required. On the other hand, to analyze the SCOD the samples were centrifuged during 2 minutes at 14000 rpm, in a Hermle Z. 383 K centrifuge. After the centrifuge utilization, supernatants are filtered in a 0.45 µm filter, just in case some solids remain in the supernatant.

TSS, VSS, TS, VS, TKN, N-NH4, and alkalinity were measured according to Standard Methods (APHA, 1998). TSS and VSS were analyzed by gravimetric analysis with presence of a fiberglass filter. TS and VS were analyzed also by gravimetric analysis but without any fiberglass filter. The quantitative determination of the TKN was obtained by decomposition, distillation and titration. The NH_4-N value was obtained by distillation and titration.

The VFA measurement, feed and permeate, was done by using GC (Gas chromatography) model Agilent 7820 A, at 250 ºC, using N2 as gas carrier, previous centrifugation of the samples during 10 minutes at 14000 rpm.

TP and orthophosphate were measured using Lange cuvette tests (LCK 350, Hach Lange, Germany). The cuvettes were cooked in a Lange oven and subsequently read through a spectrophotometer, model Lange 3900 (HACH).

Mg and calcium were measured using Lange cuvette tests (LCK-327). Calcium and magnesium react with Metal phthalein giving a violet color.

The biogas composition was monitored daily, using a dedicated flask. The flask contains NaOH (1 M) solution and phenolphthalein as pH indicator. The sampled gas collected from the biogas line, was introduced with a syringe in the liquid filled column of the flask. CO2 is absorbed in the NaOH solution allowing only the not absorbed gas volume to be collected at the top of the column. Therefore, the gas volume accumulating in the flask represents the fraction of gas that is not CO2 (mainly methane) and the absorbed volume is the fraction of CO2. In the Figure 24 this simple but effective measurement method is depicted.

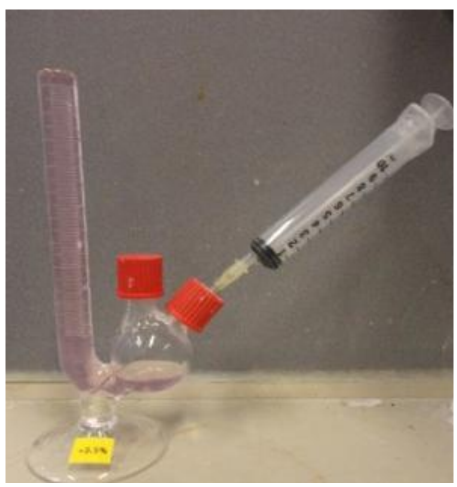

Figure 24. Biogas composition measurement

2.2.2 Supporting batch tests – Sludge methanogenic activity

Anaerobic biomass activity tests were carried out using Oxitop® equipment as shown in Figure 25 AnMBR sludge samples (duplicates) were mixed together with a known quantity of acetate (from a pH-neutralised stock solution).

The headspace of the bottles was made oxygen-free by flushing with a N_2:CO_2 mixture as the HCO_3^-/CO_2-buffer provides a near-neutral pH. The bottles were placed on a rotary shaker in a temperature-controlled cabinet at 36 ± 1 °C. Gentle stirring assured good contact between the liquid phase and the anaerobic biomass. Biogas production was measured from the build-up of pressure, which is registered every 20 minutes by the manometric Oxitop® heads. Biomass activity was measured as the maximum slope of the pressure vs. time curve and expressed in g CH_4-COD g^{-1} VSS d^{-1}.

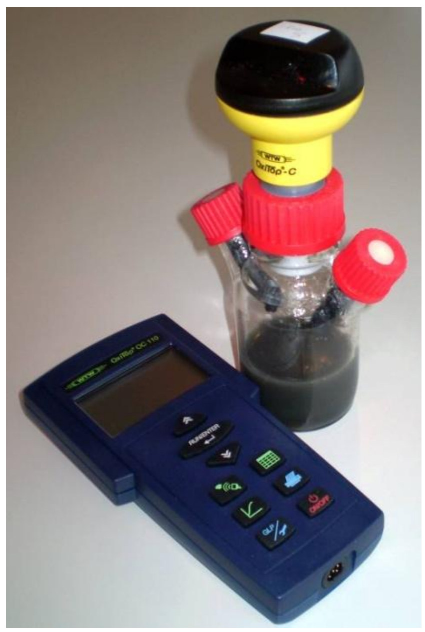

Figure 25. Oxitop ® equipment used for biomass methanogenic activity

2.2.3 Capillarity suction time (CSTR)

The CST equipment is a practical method for the determination of sludge dewaterability, providing a rapid comparison of the effects of different agents and dosages in waste water.

The rate at which the filtrate passes through the paper filter is influenced by the characteristics of the sludge. The Capillary Suction Time (CST) is calculated by the time that the water from the sample takes to travel from one electrode to another.

The equipment is formed by, the reader apparatus, two different cells, the filter support and the upper plate (Figure 26)

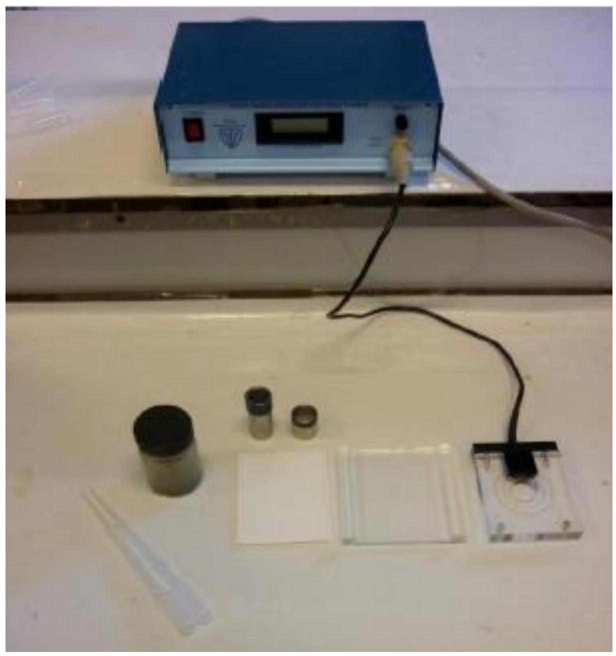

Figure 26. CST analysis equipment

Procedure to assemble and operate the CST equipment

1. The equipment should be disconnected (Off signal)
2. Connect the signal reader to the upper plate (with the electrodes)
3. Put the filter in the paper filter support. Take care to put the filter on the right side (weaving part on the filter support)

4. Assemble the upper plate on top of the filter, with the electrodes down touching the paper filter

5. Put the chosen cell in the upper plate, making sure that is touching the paper filter completely

6. Pour the sample into the cell (should be totally full and present a meniscus, see picture 9)

7. Turn the switch ON

8. Depending on the type of sample the measurement will take more or less time, a beep signals when the filtrate reaches the first electrode and also when the second set of electrodes is reached.

2.2.4 Membrane cleaning (CIP)

Every certain period of time, due to the fouling of the membrane responsible for the increasing in the TMP value, a clean in place (CIP) process is required. The point is to remove from the membrane, first, inorganic particles with citric acid ($C_6H_8O_7$) at 1%, and then, the organic matter with hypochlorite (NaOCl) at 500 ppm. During the CIP the AnMBR reactor will be completely isolated, protecting the sludge from the chemicals. The CIP process lasts around 6 hours. During the CIP no feed was added, that explains why the VLR some days was lower than the agreed. No backwash was used during the cleaning.

This CIP presents the following sequence:

1. Draining
2. Rinsing
3. Acid CIP with citric acid (1%)
4. Rinsing
5. Hypo CIP
6. Rinsing

The CIP phases will be further described below:

1. **Draining**: First of all, is very important to remove with water as much sludge as possible from the membrane to have better chemicals performances. This phase is called draining. It is necessary to fill the CIP tank (T-1900) with clean water. Then, the recirculation pump will send water all over the system to try the remove sludge from membrane and pipeline. Finally, the dirty water will be collected in the draining tank (T-1800). This phase will be ended when the CIP tank is empty.

2. **Rinsing**: After draining, is required a water recirculation over the system to try to remove from the membrane more sludge. It wants to get ready the membrane for the use of chemicals. This rinsing phase lasts 10 minutes with a filtration flux of 20 LMH and a cross-flow velocity of 1 m/s. This time is enough to replace the existent water outside the membrane. To know which values are suitable is important to calculate the HRT outside the membrane. 10 minutes lasts this phase.

3. **Acid CIP**: Citric acid at 1% is used to remove the presence of inorganic particles responsible for the membrane fouling. 25 liters of citric acid will be poured in the CIP tank with a temperature around 35°C (If the temperature is higher the chemicals activity will be higher, but it is not possible to use really high temperatures since the membrane could suffer important damages) and a pH around 2.5. In the fourth cycle, the old citric acid solution was replaced (10 liters) by a new one, in order to get a better fouling removal. It is not possible to keep the temperature constant, so this one will decrease throughout the CIP.

   If better results are desired, some extra stronger acid addition, as HCL, could be added in order to get lower pH_s. At this phase, 8 filtration/soak cycles will be necessary. The filtration and soak times are 6 and 9 minutes respectively. The filtration flux is 20 LMH and the cross-flow velocity is 1 m/s.

   To avoid damages in the sludge recirculation flow meter (FIT-1107) and the permeate flow meter (FIT-1605), by means of chemicals addition (citric acid and hypo), the use of different by-pass are strictly necessary.

4. **Rinsing**: It is important this phase to replace the citric acid present inside the system (pipes and inside/ outside the membrane) by water. The mix between hypochlorite and citric acid would provoke Chlorine gas formation which is really dangerous for the people´s health. The HRT value outside the membrane must be exceeded to assure the complete citric acid removal. The rinsing time is 10 minutes.

5. **Hypochlorite CIP:** this compound is useful to remove the organic matter fouling at the membrane. 12 filtration/soak cycles are required to clean properly the membrane. The filtration and the soak times were 6 and 9 minutes respectively. The filtration flux is 20 LMH and the cross-flow velocity 1 m/s. Initially, 25 liters) of this compound (35°C and pH 4) were poured inside the CIP tank, and after 6 cycles, 10 liters of the initial solution were replaced by new solution.

6. **Rinsing:** The point of this rinsing, is to remove the Hypo present in the system. After this last rinsing, the sludge recirculation can be restarted.

3. Results and discussion

3.1 Start-up procedure

To carry out this trial was used pure granular sludge from an EGSB reactor, stored at room temperature in the lab. The granular sludge was crushed and sieved before being introduced in the system.

Prior to introduce the required sludge quantity inside the reactor, a TS analysis has been done. After crushing the pure granular sludge the TS concentration was 106 g/l. Since normal start-up TS concentration used is 10 g/l and the capacity of the anaerobic reactor is 100 l, it has been necessary 9.46 l of crushed sludge.

Apart from the sludge, 500 g of bicarbonate were added, what it means 5 g/l of ($HCO3^-$), to keep a constant pH value inside the reactor. With the bicarbonate adding, it wants to avoid the acidification of the system which may lead to the sludge activity decay. This is because sludge is not still adapted to the system, so it needs an acclimation period of time.

Before the feed addition, the reactor was flushed with N_2 in order to displace all the present O_2 which considerably inhibits the sludge activity.

Finally, a low quantity of feed was introduced (0.7 l), corresponding to a VLR of 0.86 g COD/l/day, to get the microorganism acclimation to the given feed. It is important to note that ice cream, with a TCOD mean value of 123 g/l, was used during 21 days to simulate the real feed characteristics, since the original dairy industry wastewater had not arrived yet. This ice cream presented a COD value and a fat content quite similar to the original feed.

As a rule of thumb, during this period of adaptation, is not recommended to increase VLR value more than 20% of itself, which could lead to serious problems of acidification, since microorganism populations are not still acclimatized to the present feed. Selection natural mechanisms are still interfering.

Table 9 summarizes the time-scale and the main parameters applied during most of the experiment.

Table 9. Timeline of the experiment and main parameters

Parameter	
Starting date	16/01/2014
Ending date	21/05/2014
Total time	17 weeks
Biological parameters	
Temperature	37 ºC
Volumetric Loading rate (target)	Initially 8 g COD/L/d ; Finally 6 g COD/L/d
Sludge Retention Time	Initially 50 days ; Finally 40 days

Membrane parameter

Cross-flow velocity	1 m/s
Filtration time	15min
Backwash time	10 sec
Bacwash flux	Initially 170 L/m^2/h ; Finally 250 L/m^2/h
Recirculation flow	570 L/h
Permeate flux (target)	12 L/m^2/h

3.2 Biological processes performance

3.2.1) Volumetric loading rate (VLR) and removal efficiency

Before starting to analyze results it must be known that the main parameter to detect any loss of performance in anaerobic treatment is the permeate VFA concentration. This parameter was measured daily. Generally, a limit of 5 meq/l VFA was applied. If the value is higher, methanogenic sludge activity will be considerably inhibited and an organic load reduction must be applied to reduce its concentration. A VFA concentration increase would indicate that the system was operating at or above its maximum capacity.

On the other hand, the F:M (Feed:Microorganim) value expressed in gCOD/(gVSS·d) refers to the balance between feed supply and biomass concentration in the system in terms of VSS/l. This ratio F:M affects to the organic removal efficiency, sludge properties and microbial composition (Liu., 2012).

Three lines (green, blue and yellow) separate the four different stages at the below figures:

- Stage 1: From the first day to the green one
- Stage 2: From the green line to the blue one
- Stage 3: From the blue line to the yellow one
- Stage 4: From the yellow one to the last day

Stage 2

Figure 30 shows the VLR applied during the testing. At the stage 2 (Between the lines green and blue) could be appreciated the gradual increase in the VLR without any worrying VFA presence in the AnMBR. Only on day 25 the VFA concentration exceeded the 5 meq/l. But later on, that value significantly decreased.

The average VLR at the stage 2 was 5.23 g COD/l/d and the average permeate VFA concentration was 1.4 meq/l. The VLR target value (8 g COD/l/d) in this short period had not been reached yet. But it was not because of a high VFA concentration problem, but for some problems, like for example a leaking in the filtration pump that stopped the reactor during 3 days. In Table 10, total and soluble COD removals are depicted:

Table 10. COD removal in the stage 2

Parameter	Influent g/l	Permeate g/l	Removal %
TCOD	151.5	0.249	99.84
SCOD	129.5	0.249	99.81

Extremely high removal efficiencies have been obtained during the testing in the stage 2. More than 99% of the COD contained in the feed has been removed.

Stage 3

This stage was characterized by some interesting problems apparition, such as the presence of a leaking at the heating bath and the big amount of inorganic particles build-up inside the reactor. These problems obliged to stop the reactor during some days. That explains the zero VLR values applied in several days of this long stage 3:

- Leaking at the heating bath: The first problem was the detection in the 66th day of a leaking at the bottom of the heating bath jacket (possibly the initial glue addition was not made correctly). To fix the problem was required a powerful glue that cannot work properly in wet conditions, so, four days without any operation the reactor was completely stopped. In Figure 27 the leaking can be detected, at the bottom of the anaerobic reactor (T-1100), by the presence of a water drop (a red arrow is indicating the problem).

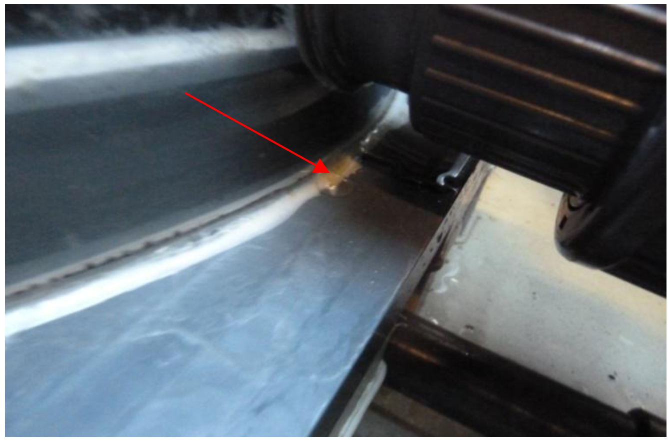

Figure 27. Water leaking detected at the bottom part of the jacket reactor

- The second and most important problem was the loss of a big amount of sludge in the system (around 60 liters) across the pressure valve (PV-201). This means the pressure in the recirculation pump was higher than two bars (that is the minimum value responsible for the activation of this safety valve which is taking sludge out the system to avoid damages in the system in presence of high-pressure values).

  It is true that there is an alarm to stop reactor when the pressure reaches a given by the operator value, but this alarm system was not correctly installed and the alarm did not go off. After this problem, it was decided to install a low reactor volume alarm, so, when the sludge volume in the reactor is lower than a desired by the operator value, all the system goes to out of service operation, impeding the sludge release through the pressure valve.

  If pressure values detected by the recirculation pump pressure sensor (PT-1112) is high, it means that the pump has some problems to suck the sludge from inside the reactor because something is impeding the proper sludge recirculation.

  The main hypothesis was that inorganic compounds as $CaCO_3$ and $Ca_3(PO_4)_4$ impeded a correct sludge circulation through the needle valves. These needle valves (placed straight at the top of the reactor) represent a critical point in the system since their diameter opening size is only of 5 mm. But these valves are placed there because with normal ball valves it would be impossible to regulate the flow. Moreover, the spray nozzle was also completely clogged with inorganics and it was not possible to use it again anymore. This spray nozzle facilitates a good distribution of the antifoam over the reactor to get a good foam removal.

Inorganic particles accumulation could be accentuated because the stirrer was only working at the beginning of the testing at 50 rpm, so possibly an important quantity of particles could be at the bottom of the reactor instead of being removed from the sludge removal point. Days later the incident, the stirrer velocity was increased up to the maximum capacity, 131rpm.

Besides, a 1.4 mm pore size strainer (S-1120) was installed after the recirculation pump to try the collect the biggest particles inside the system. These particles normally were formed attached to the anaerobic reactor (T-1100) walls and inside the pipeline (fixed to the surface) placed just before the needle valves. Eventually, they were released to the sludge and were moving around the system, resulting in some clogging.

A continuous strainer use was not possible. Usually, every 6 hours the filter was almost completely clogged and had to be cleaned afterwards, leading to an increase in the sludge recirculation pressure (PT-1112), with the subsequent activation of the high pressure alarm. So, it was decided, during the night, keep the strainer closed and use a by-pass. But this by-pass could provoke that some particles, in that period of time, run all over the system leaving the reactor without any kind of protection, and mostly the most sensitive parts. Fundamentally, this problem could importantly affect to the most sensitive parts of the Pilot plant, such as membrane and needle valves.

In Figure 28 these inorganic particles are showed. In particular, these precipitates were collected mechanically (brushing) from the pipes, placed just before the needle valves (V-31 and V-32). The particles collected from the strainer (S-1120) presented the same composition but less thick.

Figure 28. Inorganic particles collected from the pipeline

Inorganic accumulation over that particular part of the pipeline (indicated by the blue line in the Figure 29) is because the citric acid, during the CIP, never reaches that place to avoid the chemicals incorporation into the anaerobic reactor (T-1100), so it could be considered a dead point. Therefore, in order to avoid some clogging in the needle valves, this part of the system must be cleaned apart. In Figure 29 the needle valves and the pipes affected by the scaling are indicated:

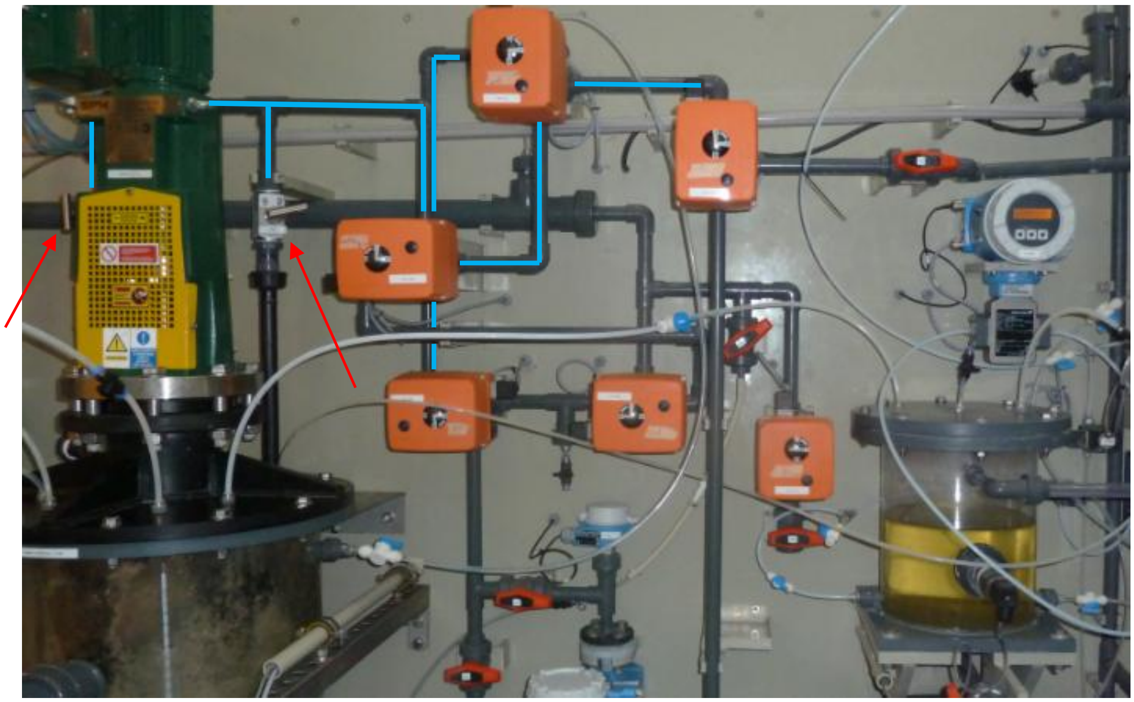

Figure 29. Needle valves position (red arrows) and pipeline portion affected by scaling (blue lines)

Before the sludge loss a VSS (biomass concentration) value around 19 g/l was present in the system. After the incident only around 5 g/l remained, so, some new sieved anaerobic sludge (6 liters with a VS concentration of 89 g/l) was introduced in the anaerobic reactor to reach a 10 g VSS/l approximately.

The effectiveness of the AnMBR to consume COD in this influent is extremely high. So, It can be noted that the Pilot plant can work properly with a mean VLR value of 6.87 gCOD/l/day, without any high VFA value. Only the day 74th a high peak was observed after the new sludge addition (7.6 meq/l), that is why the new sludge is not properly adapted to the feed characteristics.

Table 11. TCOD and SCOD removal percentage in the Stage 3

Parameter	Influent g/l	Permeate g/l	Removal %
TCOD	159.2	0.273	99.82
SCOD	106.9	0.273	99.1

Stage 4

At this stage, it can be observed how the obtained VLR was quite stable during all that period of time since the reactor was working in quite stable conditions. Few incidents took place compared to the before stage.

The 147th day, it was decided to reduce the VLR target to 6 gCOD/l/d. This decision was made to reduce sludge growth and the inorganic particles formation since the VSS and TSS values were increasing extremely (Figure 36). High concentrations can provoke a serious fouling on the membranes. Besides, the SRT was also varied from 50 to 40 days to try to collect more inorganic particles with sludge removal.

On day 149, after making those two decisions, TSS and VSS values were already too high. To solve the problem, 28 liters of sludge were removed from the reactor to reduce TSS and VSS values up to 28 and 21 g/l respectively. From now on, the new SRT and VLR values will try to avoid high suspended solids concentrations presence.

Regarding TCOD and SCOD percentage removal as in the rest of the stages was really high (Table 12). So, it can be concluded that with a VLR mean value of 7.51 gCOD/l/d, the TCOD and the SCOD removal efficiency were 99.76 and 99.73% respectively without any important VFA increase (never was higher than 5 meq/l). This testing proved that is possible to operate with that VLR without any apparent sign of toxicity.

Before varying the SRT from 50 to 40, a light VFA increase can be observed (Figure 31), this could mean that biomass is working close to maximum capacity (is still not worrying), but after reducing the value to 6 g COD/l/d the values came back to be very low

Table 12. TCOD and SCOD removal percentage in the stage 4

Parameter	Influent g/l	Permeate g/l	Removal %
TCOD	141.6	0.343	99.76
SCOD	127.5	0.343	99.73

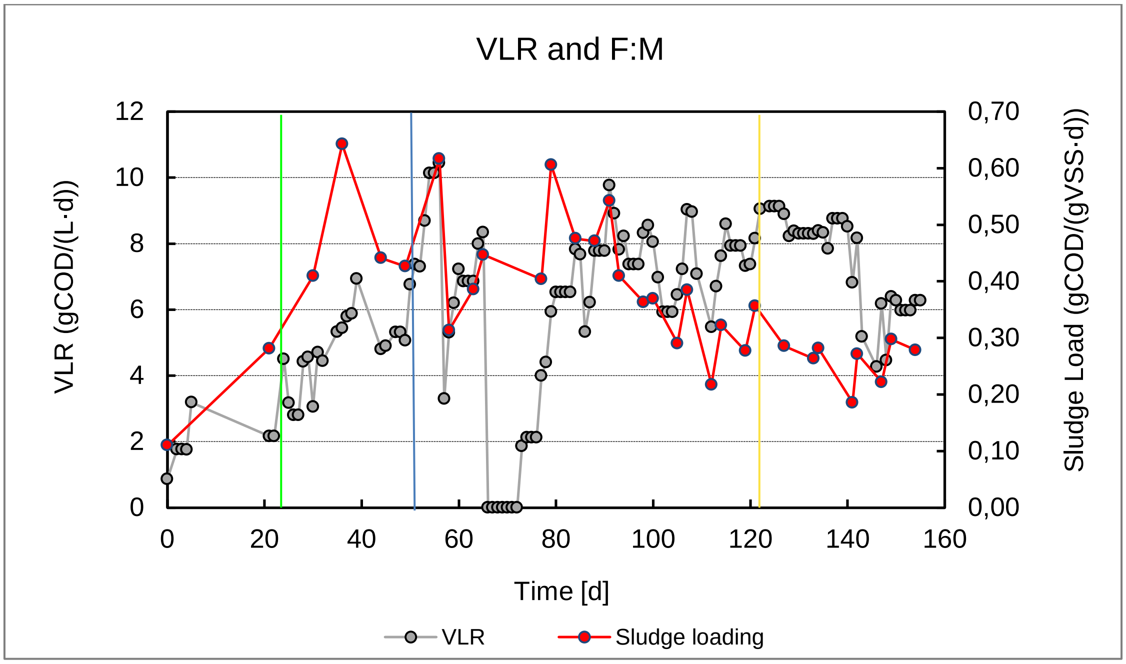

Figure 30. VLR and F:M

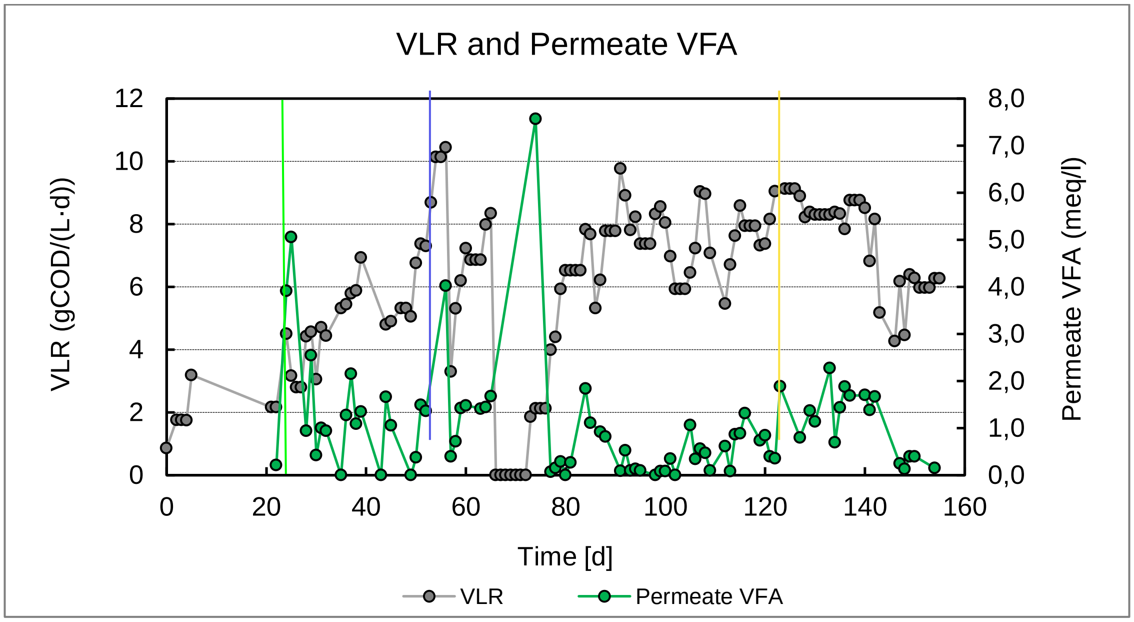

Figure 31. VLR and permeate VFA concentration

3.2.2 COD mass balance

Whereas reactor showed remarkable performances in terms of COD removal (see previous section), it should be noted that not all COD in influent was converted into biogas, or discharged in permeate. In most cases, a certain COD fraction is undigested and remains in sludge. For this reason, another approach to assess reactor performance is to make a COD mass balance.

In an AnMBR COD can leave the system by three ways, in biogas, in permeate and in excess sludge. The fraction of COD that is converted in the biogas is typically referred to as the digested fraction.

Tables 13 and 14, show the COD balance of the system during the stages 3 and 4. The stage 2 and the beginning of the third one are not described, because biogas results are not reliable. The biogas flow measurement was not accurate, and some changes in the permeate tank design were made to avoid wrong values. During backwash, with the old design, some air sucking was happening, and therefore, the measured values were lower than they really were. The 78th day the new design was installed, and the permeate tank (T-1700), from now on, will act as a buffer, giving this way accurate results.

The old permeate tank (Figure 33) was completely black and nothing could be seen inside it. While the new tank (Figure 32) is transparent, so it can see all what is going on inside. The main problem of this change is that, from that moment, the anaerobic reactor is in direct contact with the permeate tank (by mean of a tube) and, if some foam in the anaerobic tank is formed, it could reach, first, the permeate tank (Figure 32) and, after backwash, the outside part of membrane, resulting in a serious fouling problem. In Figure 32 is possible to appreciate as some foam came into the system. To solve the problem a precise antifoam dose should be applied.

With the old design, the anaerobic reactor was in direct contact with the gas column (T-2000). Now between them, the permeate tank is present.

Figure 33. Old permeate tank (T-1700)

Figure 32. Transparent permeate tank (T-1700)

Stage 3

The stage 3 with a VLR of 6.87 g COD/(l·d), 74.77% of COD is converted into biogas, 8.47% remains in sludge and 0.08% in permeate. Nevertheless, the total COD recovered is only 83.2%. Some possible explanations of the 16.8% gap in COD balance can be:

- The main possible reason to get this COD recovery could be explained by Biological conversion existing in the Buffer tank (T-400) (e.g. fermentation of carbohydrates concerns conversion of sugars into organic acids, acohol and hydrogen). Organic acids and alcohols are volatile and hydrogen is a gas, all of which can escape from liquid phase. In fact, measurements showed that COD concentration is decreasing every day. A solution made, at the stage 4, after these inaccurate values, was to increase the frequency of the COD analysis from 2 to 3 days per week.

- Another reason could be the existence of a non-homogeneous feed. Some particles present in feed (fats for example) could vary COD analysis results.

Table 13. COD mass balance in Stage 3

	Stage 3 From 78th day to 124th VLR 6.87 g COD/(L·d)	
	COD (gCOD/d)	%Feed
Influent	716.8	100
Permeate	0.6	0.08
Sludge	60.73	8.47
Biogas	535.01	74.77
Total recovered	596.34	**83.2**

Stage 4

The stage 4 with a VLR of 7.51 g COD/(l·d), 93.17% of the COD is converted into biogas, 11.79% remains in the sludge and 0.14% in the permeate. The total COD recovered is around 93.17%. After increasing the COD analysis frequency and due to the presence of a more homogeneous feed (less fats and less particles), a much better COD mass balance was obtained at this stage.

Table 14. COD mass balance in Stage 4

	Stage 4 From 124th day to 160th VLR 7.5 g COD/(L·d)	
	COD (gCOD/d)	%Feed
Influent	751.22	100
Permeate	1.07	0.14
Sludge	88.6	11.79
Biogas	610.27	81.25
Total recovered	699.94	**93.17**

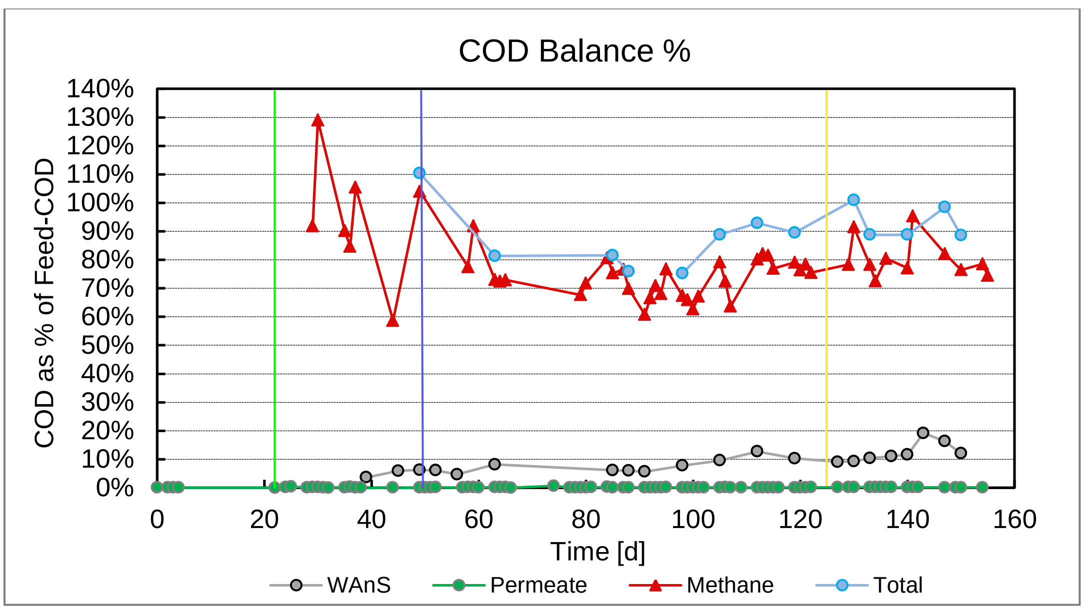

Figure 34. COD mass balance

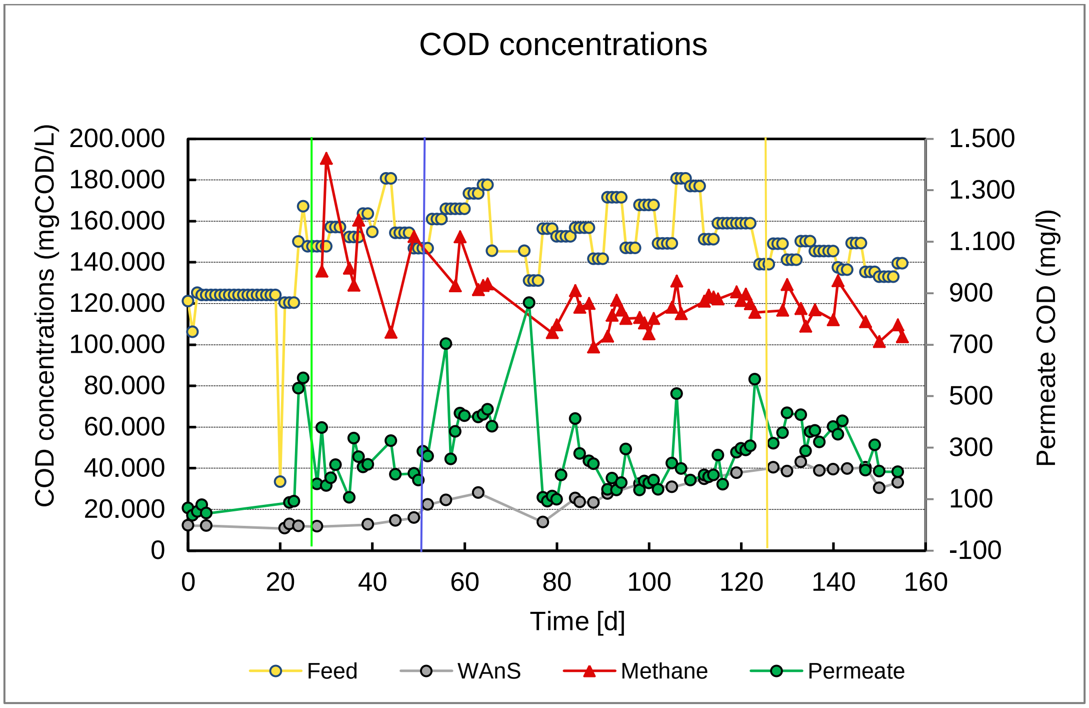

Figure 35. TCOD concentrations

3.2.3 Sludge production

Stage 3

Biomass concentrations were monitored regularly (twice per week) throughout the trial.

On day 77 TSS and VSS concentrations suffered an important decrease due to the loss of 60 liters of sludge in the system. Some new sludge was introduced to have a VSS value of 10 g/l. From that moment a gradually increase in TSS and VSS concentration can be seen. At this stage, both, TSS and VSS presented a quite similar behaviour. At the end of the stage 3 TSS and VSS concentrations look quite constant, around 30 gTSS/l and 25 gVSS/l respectively. At this ending moment, possibly, the steady state was reached but due to the requirements of the client the new feed (85% of acid whey) was introduced in Buffer tank.

VSS/TSS mean value over the stage 3, with a SRT of 50 days, is 83%. So, the 17% of TSS are formed by inorganic compounds and the remaining 83% are organic.

VSS/TSS ratio remained stable at ca. 0.84, indicating an equilibrium between inorganic precipitation and organic sludge growth.

Stage 4

With the utilization of new feed, an important increase in TSS and VSS concentrations was observed. VSS value could be explained because when varying feed (mostly sugars are presented in acid whey), bacteria population could have also varied. It seems that this new set of microorganism, present higher growing rates than in previous stages, hence a significant augmentation of VSS concentration can be noted.

Regarding the high values of non-volatile suspended solids concentration, the main explanation could be a higher calcium content in new feed (3,158 mg/l), higher feed flows (since the new feed COD is lower at this stage) and the presence of higher VLR (average value of 7.51 gCOD/l/d), compared to the stage 3. As can be seen in Figure 36, the distance between TSS and VSS value are much higher than in previous stages. The formation of $CaCO_3$ and $Ca_3(PO4)_2$, at anaerobic conditions, can be significantly favoured.

A maximum value of 47 gTSS/l and 34 gVSS/l in sludge were reached in the stage 4. These values could present important problems to have a proper permeate filtration leading to severe fouling formation. It is recommended a maximum TSS concentration around 30 g/l and a VSS concentration around 25 g/l to have good membrane performances.

For this reason it was decided to short the SRT from 50 to 40 and reduce the VLR from 8 to 6 gCOD/l/d in order to reduce the concentration of these two parameters. If VLR is reduced, the amount of ions and total COD incorporated to the system will be lower, then, less inorganic precipitates formation and biomass growing will occur. Reducing SRT more sludge will be extracted and then more biomass and more inorganic particles will be removed from the system. With this step it wants to have a stable VSS and TSS concentration.

VSS/TSS average value was 74%. In this case the proportion of inorganic particles (26%) in the system is quite worrying.

In spite of reducing VLR and SRT value, an important quantity of inorganic particles may be formed in the reactor. To remove more inorganics SRT should be lower, but if SRT is reduced, more sludge would be also removed (less VSS concentration), reducing this way the capacity of the biomass of consuming organic matter.

An interesting solution to try to prevent these inorganic particles accumulation, could be the installation of a settler to try to collect as many particles as possible. This is considering that sludge settling velocity is inexistent in presence of flocculant sludge. So, mostly inorganic particles, no sludge, would be removed from the settler. But, no results are presented in this thesis due to the lack of time.

In term of TSS, the anaerobic reactor (in all the trial) showed a TSS removal efficiency of 100%. This is unsurprising as UF membrane effectively retains all solids

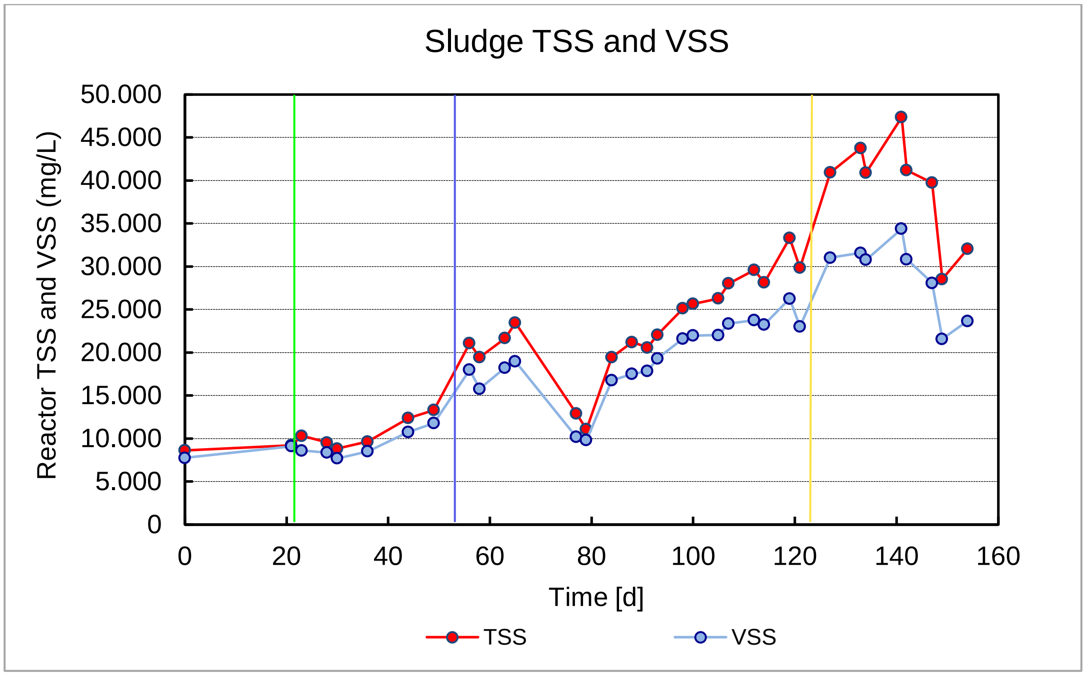

Figure 36. Evolution of Sludge TSS and VSS during the experiment

3.2.4 Nutrients Balance

Nutrients are the basic cellular building blocks for growth and ensure that cells are able to produce enzymes and cofactors that drive the metabolic and biochemical reactions.

According to the relative quantities required by biomass is possible to distinguish two different kinds of nutrients:

- *Macronutrients*: are essential to microbial growth. Nitrogen and phosphorous are the most requires ones. Other important macronutrients are sulphur, calcium and magnesium. Normally these nutrients are present in wastewaters.

  Macronutrients utilization (N and P) in anaerobic digestion is, in general, less than those in aerobic system, but thanks to inorganic precipitates formation and the subsequent removal along with sludge, this technology will allow important removal percentages.

- *Micronutrients*: this group is composed of different trace metals that form part of enzymes cofactors. They are essential to growth and activity of the biomass. Iron, Zinc, Cobalt, Nickel, Molibdenum, Manganese, Selenium and Copper. These micronutrients are not usually presented in the wastewaters in concentrations enough, so, some extra addition could be added. Biothane®, in particular, uses Vithane® solution. At this experiment, in order to have a good sludge performance some Vithane® was introduced in the feed. Another compound used in this project was FeCl, to guarantee the iron availability in the system.

3.2.4.1 Nitrogen

Figure 37 shows the TKN concentration in feed, permeate and sludge. TKN could be defined as the total concentration of organic nitrogen, ammonium and ammonia in a sample. (TKN = Non-ammoniacal-N + NH_4-N + NH_3-N)

There are two mechanisms of nitrogen removal in the system, the nitrogen consumed by the microorganism to grow up (only a small fraction will be used by the biomass due to the slow-growth rates existing in anaerobic sludge) and the most important one, the non-biodegradable inorganic compounds formation as struvite ($NH_4MgPO_4 \cdot 6H_2O$) or ammonium salts. These inorganic particles cannot go through the membrane and the only way to remove them is thanks to the sludge extraction.

The nitrogen represents between 8-10% of the sludge VSS concentration.

The NH4-N (Ammonium) represents an extremely important nutrient for the biomass. The concentration of this compound in permeate should be higher than 10 mg/l. If it is not, some nitrogen addition may be needed.

In Table 15 the average nitrogen removal percentages are represented. The stage 4 is characterized by the lowest TKN concentration of the feeds. This is an advantage compared to the others feeds, due to less inorganic particles with presence of this element will be produced with this sort of feed. The removal percentages are quite similar in all of the stages.

Regarding the sludge TKN a gradually increase can be viewed until the 60^{th} day, this could be explained by the increase of the biomass concentration and the containing nitrogen inorganic precipitates (struvite and ammonium salts). Then an important reduction TKN value was obtained since 60 liters of sludge were lost. After that incident, the TKN sludge concentration, is gradually increasing more than likely due to biomass is incorporating this macronutrient to its structure.

The reduction in the TKN sludge concentration, at the stage 4, was due to the removal of 28 liters from the reactor to reduce the TSS content, and because the reactor was cleaned twice with citric acid to remove the scaling presented in the system. In this cleaning process some sludge was lost since it was not possible to recover all the sludge from the system (especially at the bottom of the reactor and in the pipes.

The nitrogen percentage removal cannot be higher than the values presented in the Table 15, since there is an equilibrium between the nitrogen in phase solid and liquid. In presence of these anaerobic conditions, no more quantities can go from the liquid to solid phase (producing inorganic precipitates).

Table 15. TKN removal percentages

Stage	Feed TKN mg/l	Permeate TKN mg/l	Removal %
2	2,867	418	85.42
3	3,197	423	86.77
4	1,694	387	77.1

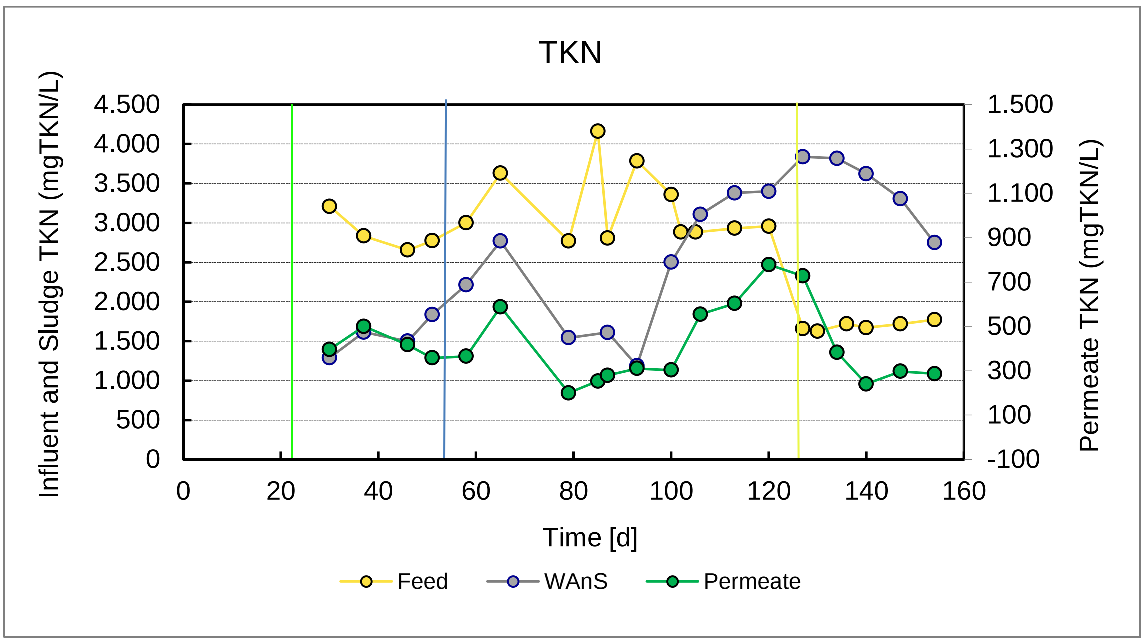

Figure 37. TKN concentration

3.2.4.2 Total phosphate

The phosphorous is another important macronutrient for biomass, which represents between the 2-2.5 % of the sludge VSS concentration. Orthophosphate is the form assimilated by biomass. If the concentration of this compound in permeate is lower than 5 mg/l, an extra dosing could be required.

The total phosphate permeate concentration in this trial was always higher than 5 mg/l, so, no any extra orthophosphate addition was required. TP and orthophosphate permeate values should be equal. The big-size compounds with presence of phosphorous in their structures, cannot go through the membrane, and are retained inside the anaerobic system. Only soluble particles should be in permeate. The same happens with the TKN and $NH4^+$ in permeate (should be equal).

The assimilation of nitrogen and phosphorous by the microorganisms depends on anaerobic biomass production. Usually a 5 % of the feed TCOD goes to the biomass growth, but this percentage is related to several factors.

The Total phosphate value was practically the same at the 3 different stages. Only in the stage 3 mention a light increase of the feed value up to 1.6 g/l instead of the 1.4 g/l presented in the stages 2 and 3.

TP sludge concentration, is gradually increasing more than likely due to biomass is incorporating this macronutrient to its structure. In the stage 4 the biomass growth is the highest, so, more phosphorous incorporation is being carried out. The removal percentages in all the stages are satisfactorily good.

Table 16. TP removal percentages

Stage	Feed TP mg/l	Permeate TP mg/l	Removal %
2	1,500	57.	96.2
3	1,408	37.95	97.3
4	1,632	25	98.5

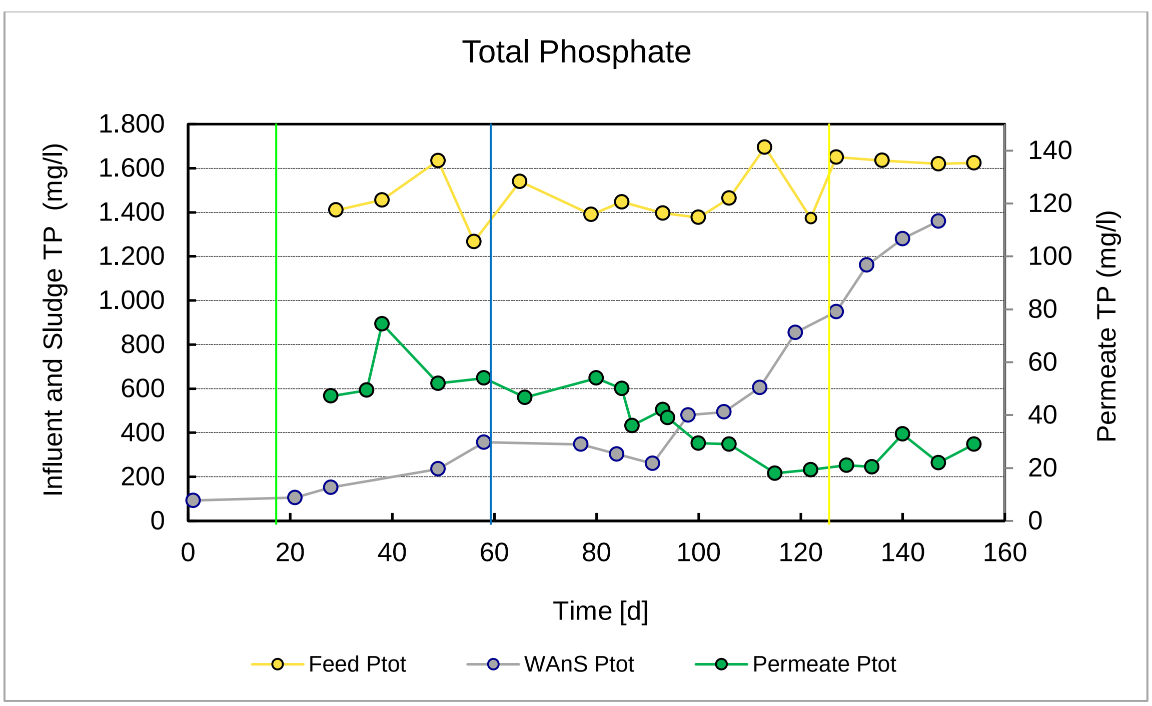

Figure 38. TP concentrations

3.2.4.3 Calcium

Regarding the calcium, it can be noted the high concentration present in all the feeds (all about at the stage 4) and the significant removal percentages. Its presence was responsible for the huge amount of inorganic precipitates in the sludge.

Table 17. Calcium removal percentages

Stage	Feed Ca^{2+} mg/l	Permeate Ca^{2+} mg/l	Removal %
2	2,790	115	95.8
3	2,688	225	91.6
4	3,158	247	92.2

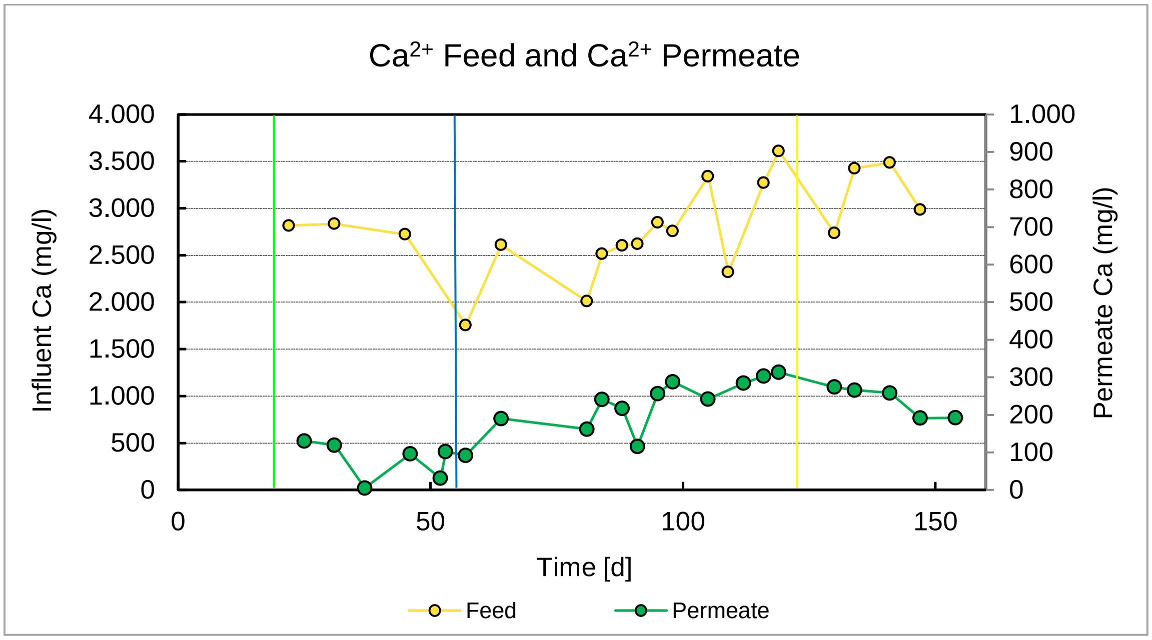

Figure 39. Calcium concentrations

This element represents one of the most important problems in this trial because of the calcium precipitates accumulation on the reactor surface. From time to time, these particles were released and moved around the system. The strainer (S-1120) was installed to try to collect as many particles as possible.

During daytime the filter was used, and important amounts of inorganic could be collected and removed. The problems came during the night, when the strainer was not used, since the particles build-up inside the strainer provoked an important increase of the sludge recirculation pressure (>1.5 bar) and the Pilot plant, in hours, would go to out of service mode. So, if it wanted to operate continuously, it was not possible to leave the strainer open during the nighttime. Therefore, when the reactor worked without the strainer, all these particles could move all along the pipes, leading to some possible clogging concerns.

The picture (Figure 10) was taken on day 124 when it was decided, first, to take all the sludge out the system, and then, recirculate citric acid 1% all over the system, to try to dissolve all these calcium precipitates. The same process was made again on day 163. These particles could provoke important pipes clogging.

The decision of emptying the reactor and cleaning all the system (with citric acid) was made, since the pressures detected along the system were pretty high (all pressures increased at the same time). After cleaning the reactor, normal pressure results were attained, showing that this cleaning process was effective to dissolve these inorganic compounds.

3.2.4.4 Magnesium

Compared to the other macronutrients the magnesium composition was not so high. Important removal percentages took place during all the stages. The magnesium is one of the components which form part of struvite ($NH_4MgPO_4{\cdot}6H_2O$). Accumulation of this compound inside the system may provoke important damages to membrane and pipelines. Moreover, high TSS values can be an obstacle to get good membranes performances. In Table 18 are depicted the obtained removal percentages in anaerobic bioreactor.

Table 18. Magnesium removal percentages

Stage	Feed Mg^{2+} mg/l	Permeate Mg^{2+} mg/l	Removal %
2	381	25.6	93.3
3	254	56.7	77.7
4	329	80.5	75.5

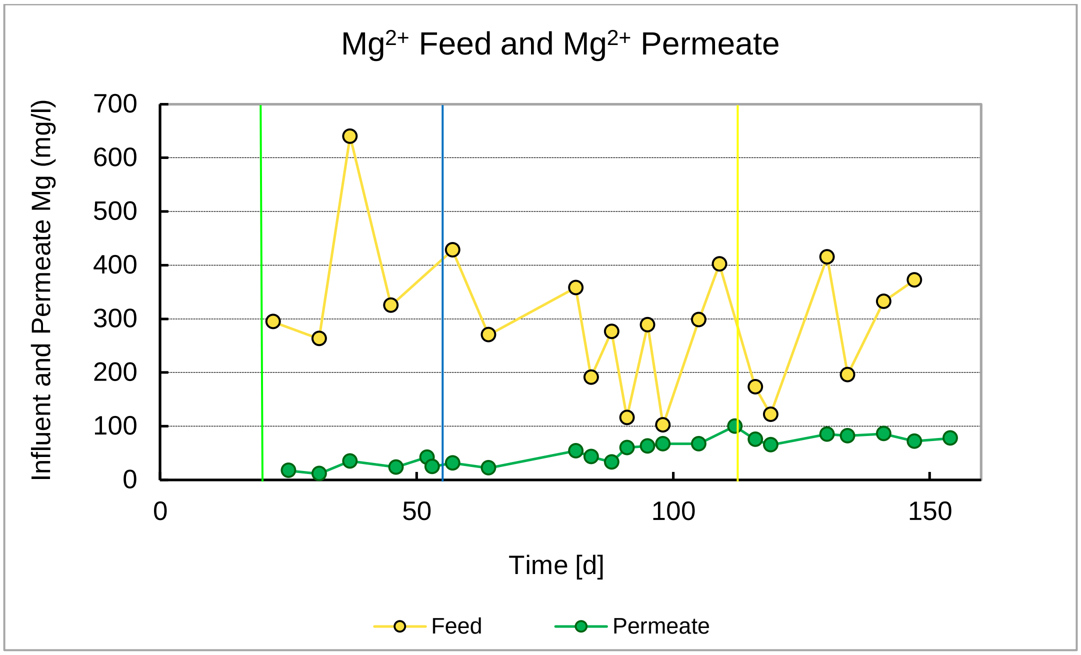

Figure 40. Magnesium concentrations

3.2.5 Membrane performance

Compared to the lab-scale experiments, the use of a Pilot Plant, as in this testing, allows us to have more similar results with full-scale systems. This is mainly because the length of the membrane, the cross-flow velocity applied and the backwash value are exactly the same as full-scale systems.

Transmembrane pressure (TMP) and the permeate flux have been measured daily and the results are represented in the Figure 41.

TMP represents a good fouling level indicator. So, the higher is the TMP value, the more important will be the existent fouling. It is recommended not to exceed a TMP value of 800 mbar to avoid possible membrane damages. In this experiment if the TMP was higher than 600 mbar, CIP would take place.

The system has been operated at a flux of approximately 12 LMH. At the beginning, the obtainable flux was much higher due to the membrane was completely new and the suspended solids concentration in the sludge was quite low. Over time, the flux value was decreased up to 12 LMH. The higher the flux applied, the higher the obtained TMP value.

When designing an AnMBR, the flux is one of the most important parameters, as it determines the number of membranes required in the system. This is of vital importance, since the membranes represent a high cost for the clients, so the higher the flux than can be applied, the lower required membrane surface will be.

Only the results at the stages 3 and 4 will be analyzed.

In order to reduce the TMP at the stage 2, the flux was reduced from 25 to 15 LMH, since the sludge concentration started to increase, as well as the fouling velocity. At the beginning of the experiment, the sludge was introduced in the system mixed with water, therefore, in that period of time was much easier for the membrane to filtrate the sludge. That water, with the passage of time, will be replaced by water, increasing the viscosity of the sludge. So, initially the related to membrane operation results were not reliable.

The day 67^{th}, the sludge loss took place. That is the reason why the TMP value decreased considerably, up to really low values, less than 100 mbar.

Around the day 100^{th} a non-explained event occurred. After cleaning the membrane the TMP value increased significantly from 100 to 400 mbar. This was unexpected and has not been explained at the moment.

In the day 110^{th} the Flux was reduced until 12 LMH. This would be the employed value for the rest of the experiment. The obtained flux values were quite stable (12 LMH) during that final period of time.

The sludge filterability can also be evaluated through the capillary suction time (CST). The CST is a static filtration test that measures the filtration rate (time for free water to pass between two electrodes) using filter paper as the medium. The lower the CST the easier to filter the sludge is, typical the CST for aerobic sludge is less than 100 s. However for an AnMBR a CST < 1,500 seconds is excellent but it can go up to 2,000-3,000 seconds.

It is difficult to make any conclusion about obtained CST values throughout the experiment. After losing 60 liters of sludge the CST (Figure 42) remained always quite low and stable. However, it is quite curious, in spite of these low values, the fouling velocity was pretty high during this period of time. This could be explained for the high concentration of inorganic particles present in the sludge, making difficult to compare CST with TMP. The CST, in this case, is not giving us reliable information about how easy filtrate the sludge is.

From the day 100^{th}, due to the characteristics of the feed almost every week the CIP was performed.

Regarding the permeability, it makes sense that it was was gradually decreasing until reaching the 108^{th} day stable values. The CST is also stable when that permeability value was obtained.

After losing 60 liters of sludge the permeability value increased because of the reduction in the suspended solids concentration. In addition, to fill the reactor again up to 100 liters, 30 liters of water were necessary since no more than 30 liters of permeate have been stored so far. This also resulted in a permeability increase.

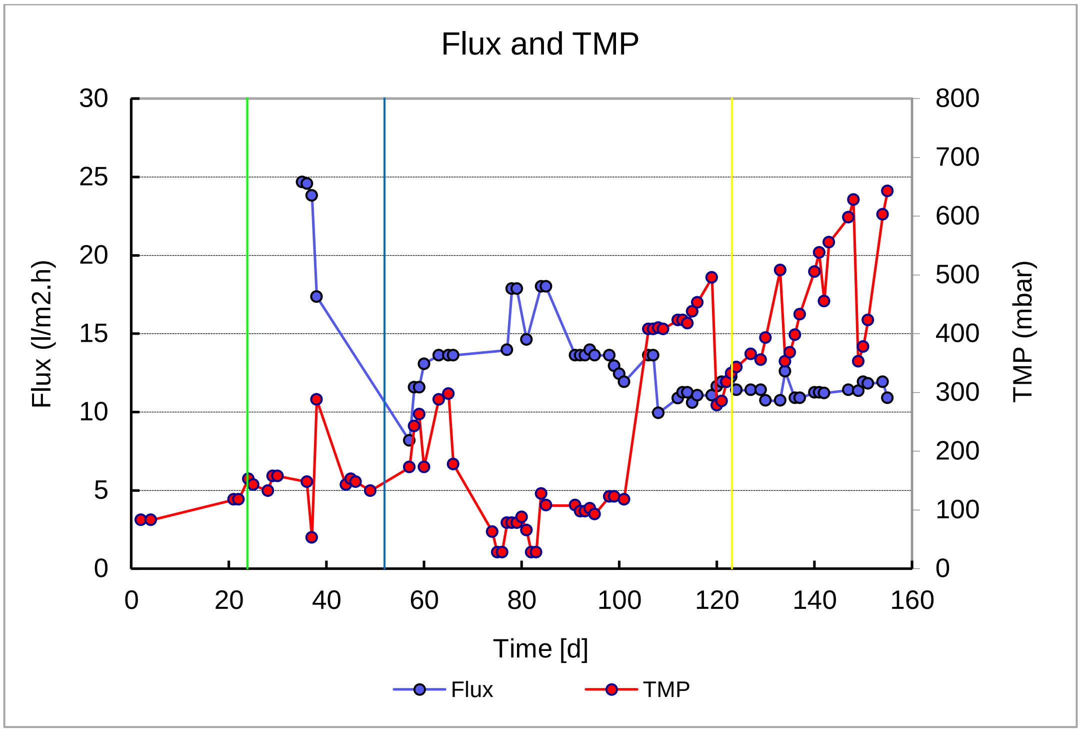

Figure 41. Evolution of TMP and Flux during operation

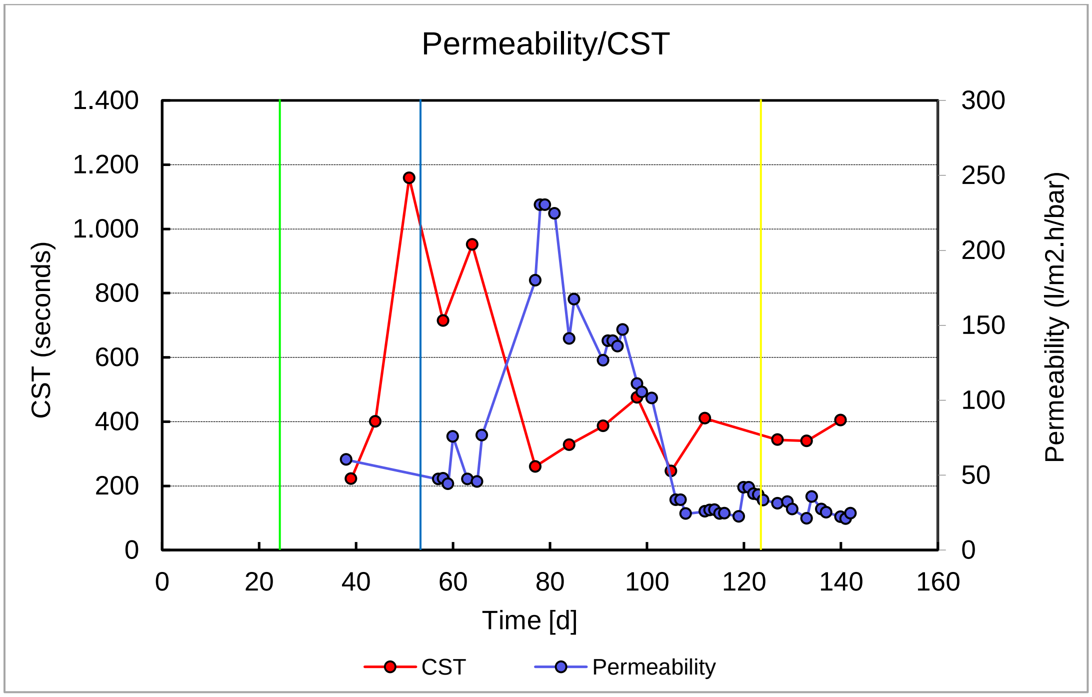

Figure 42. Evolution of permeability and CST during operation

3.2.6 Activity test results

The sludge methanogenic activity has been measured regularly during the trial and the results can be seen in Figure 43. The results show that the sludge activity is gradually decreasing until the 59th day.

After that day, the loss of 60 liters of sludge happened and new biomass was added to the system. For this reason the following activity value was around 1 gCOD/(gVSS.d).

Afterwards, sludge methanogenic activity dropped, mainly due to the adaptation of bacteria communities in the reactor, since a part of the sludge added to the AnMBR reactor was not adapted.

Over the time, the activity looks to be stable around 0.27 gCOD/(gVSS.d). Sludge methanogenic activity, is an additional test that gives us a good indication of the volumetric loading rate that bacteria can handle. Assuming for example a sludge concentration (157th day) of 23.5 g VSS/L, and a activity value of 0.27 gCOD/(gVSS.d), the result of multiply both values gives a maximum loading rate of 6.34 g COD/(l·d). This means, at this particular moment when it is being applied a VLR of 6 g COD/(l.d), we are close to the maximum VLR that methanogenic biomass is able to treat.

Essentially, during the course of the experiment, the permeate VFA concentration was never higher than 5 meq/l. This could be a result of the applied VLR was not higher than the maximum allowed value for the system. Only, at the beginning of the stage 4, is possible to see a light increase of the permeate VFA concentration, this could indicate we were close to the maximum capacity.

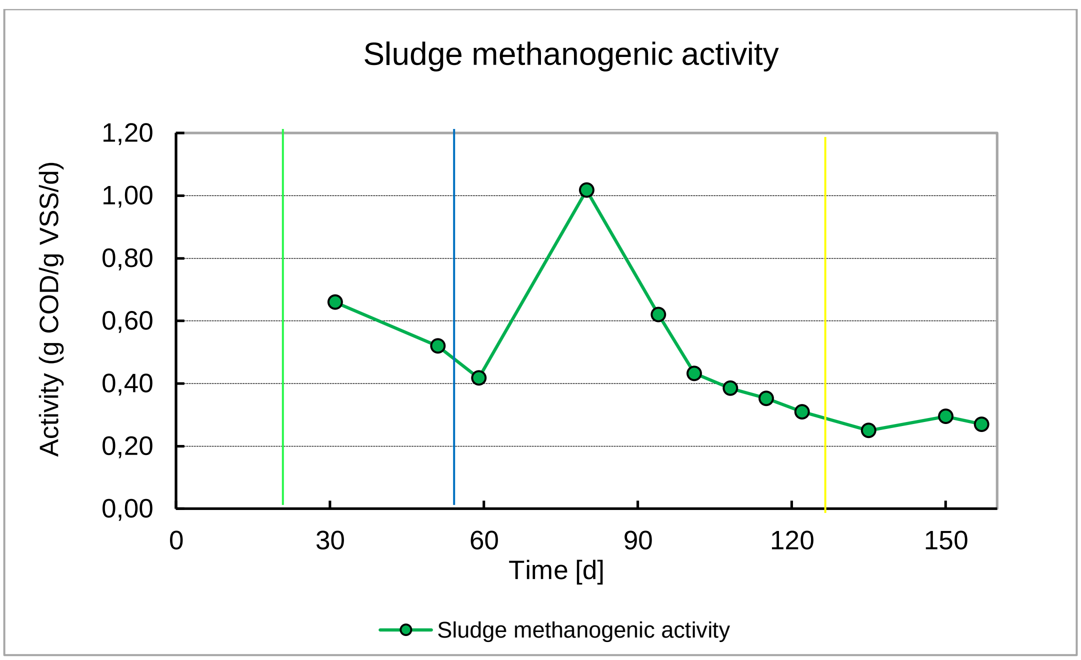

Figure 43. Sludge methanogenic activity

4. Conclusions

The objective of the Memthane® pilot plant test was to investigate the feasibility of the anaerobic membrane bioreactor to treat wastewaters from a dairy industry. All the collected data and results will be used to issue the final design of the full-scale Memthane® AnMBR.

AnMBR proved to be an efficient system to treat wastewaters in extreme conditions. In this particular case, a high COD and suspended solids concentration and an important FOG content favored the use of this technology, instead of using granular sludge bed reactors as EGSB or UASB.

The first two stages at this testing represent an acclimation period and are not further commented in the thesis project.

Two important different feeds were treated during these 160 days of experiment. The feed used in the stage 3 was finally changed at the 124th day due to dairy industry requirements. The client preferred to vary the feed ratio increasing the percentage of acid whey in wastewater.

It is very important to note that all the required nutrients for biomass were presented in the feed. In addition, just to assure good nutrients availability, Vithane® and FeCl were added.

UF membrane retained the biomass and the inorganic particles inside the reactor, which led to an effluent clear of SS (100% free of solids permeate) and an excellent COD percentage removal, of 99.8 and 99.76% in the stages 3 and 4 respectively.

Even though this study was not a completed one ending with the optimum biological and filtration performance, it was worthwhile to explore the alternatives to treat cheese whey in a more efficient and economical way.

The target volumetric loading rate, at the beginning of the experiment, was 8 gCOD/l/day. But due to the high biomass growth and the huge amount of inorganic particles formation in the system forced us to decrease the value up to 6 gCOD/l/day. At any time the VFA concentration supposed a concern in this trial. This means the biomass was working with a suitable organic load for them.

The digestion efficiency in the stage 3 was of 73.5%. This result is quite low because of the problem in the biogas flow measurement. In the stage 4, with that problem completely solved, the digestion efficiency was 80%.

The initial SRT was 50 days. But, this value was also changed up to 40 days to try to remove more inorganic particles and reduce the VSS concentration in the sludge. This decision was made in order to prevent severe fouling problems.

Regarding nutrients removal, in the stage 3 was obtained a removal of TKN, TP, calcium and magnesium of 87%, 97%, 92% and 78% respectively. Most of these nutrients were removed with sludge extraction and only a small percentage was consumed by the microorganisms.

In the stage 4 was obtained a removal of TKN, TP, calcium and magnesium of 77%, 98%, 92% and 75% respectively.

About other nutrients as sodium and potassium were not followed with the same interest, since they are no reactive and they will no produce some inorganic particles. Anyway the minimum required concentrations were presented in the wastewater.

No caustic adding was applied in at any time of the experiment.

Once the reactor looked be stable was decided to clean the membrane every week in order to remove the present fouling. A stable flux of 12 LMH was used most of the experiment.

The CST value did not proportionate any conclusive information about the filterability of the sludge since the CST value was very low but the TMP value was considerably high. This could be explained by high inorganic particles presence.

To have more reliable results in the stage 4, more time would be necessary, but so far, it can be concluded that if it is possible to reduce the presence of inorganic calcium precipitates, because of the high calcium concentration in the feed, it would be plausible to use the AnMBR technology to treat this dairy wastewater. An interesting experiment to try to solve this problem may be the installation of a settler to try the collect by gravity this kind of substances than can provoke serious fouling in the membrane.

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