UNIVERSITA' DEGLI STUDI DI PADOVA

Sede Amministrativa: Università degli Studi di Padova

Dipartimento di Ingegneria Idraulica, Marittima, Ambientale e Geotecnica

SCUOLA DI DOTTORATO DI RICERIA IN SCIENZE DELL'INGEGNERIA CIVILE ED AMBIENTALE

INDIRIZZO: INGEGNERIA PER L'AMBIENTE ED IL TERRITORIO

CICLO XX

INNOVATIVE TREATMENTS OF TANNERY SLUDGE

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DATA CONSEGNA TESI
31 gennaio 2008

Abstract

The Italian tan line of industrial activity is characterized by 2,400 companies and 30,300 workers. The companies are concentrated in four main industrial poles: S. Croce sull'Arno in Toscana, Arzignano and Valle del Chiampo in Veneto, Solofra in Campania and Turbigo Castano in Lombradia. The Italian tan activity is leader in the European Union and in the World too. The wastewater produced during the tan activity is collected to centralized industrial wastewater treatment plants. The most common depuration treatment of this wastewater is biological activated sludge. The excess sludge produced during the treatment process contents all the pollutants removed from water and it is still a waste to treat and dispose off. The tannery sludges are currently a big ecological and environmental problem in Europe and in Italy, too. The production in Italy is around 280.000 tons every year. No process carried out up to now, has been successful for a reuse of the sludge and the only possible destination remains the landfill.

The aim of the current research work is to analyze the capacity of some biological treatments to be applied in the management system of tannery sludge. The target is to reach the social and environmental sustainability of management system of tannery sludge.

The research work has regarded four topics: minimization of sludge and energy saving, aerobic stabilization of dry tannery sludge, biological hydrogen production from tannery sludge and environmental sustainability of tannery sludge landfill.

Energy saving can be achieved evaluating the optimal conditions for the thermal drying system of tannery sludge. The optimization of the thermal drying system aims to characterize the minimum value of total solids content of the sludge, that inhibits or that stops the biological activity of degradation of organic substances in the sludge. The minimum total solid content emerged in the research work seems to be 75%. Consequently an amount of moisture of 25% is not sufficient to support microbial activity, and the dry sludge does not show appreciable biological degradation processes, independently by he biodegradability of organic substances in the sludge.

Aerobic stabilization of mechanically dried tannery sludge before landfill, has the targets of stabilization of organic substances and reduction of water content. The advantages of a preliminary aerobic treatment are the reduction of environmental impacts of landfilling, better disposal conditions and low costs for treating plant investment and management. The results seem to be encouraging for the development of an aerobic treatment technology for the

stabilization of tannery sludge. The treatment seems to work though the negative characteristics of the tannery sludge. Volatile solid content has been reduced, moisture content has been reduced depending on aeration rate, leachability of metals has been reduce. Even the biological activity, measured by respiromentric test and fermentative test, has reached the values suggested in the international literature as stable waste conditions.

Biological hydrogen production is an interesting opportunity to produce hydrogen from renewable source, at low costs and sustainable environmental impacts. The biological processes are not only environmental friendly, but also they lead to open a new avenue for the utilization of renewable energy sources which are inexhaustible. For the investigation of the biological production of hydrogen by dark fermentation, laboratory tests have been conducted at a mesophilic process temperature of 35°C in batch operation. The results show a good production of hydrogen from glucose and also from Kitchen Waste. The hydrogen production from tannery sludge has been comparable with the results from kitchen waste but with slower production rate and long lag phase. The methane production has not been avoided. Probably the low biodegradability of tannery sludge and the fact that this substrate contents different types of biomass allows methanogenic bacterial to maintain or establish again their activity.

The last part of present research work has been set up to understand the behaviour of tannery sludge dispose of in sanitary landfill, especially when the barrier systems will fail and it has regarded the evaluation of the sustainability of landfill disposal of dry tannery sludge. The emission of biogas and quality of leachate indicate that the degradation of organic substances start quickly and the thermal drying treatment does not sterilize the sludge. The biogas emissions and the leachate quality do not indicate a sustainable condition. Comparing these conditions with lysimeters contatining aerobically stabilize tannery sludge, the good effects of pre-treatment can be observed. The biogas production has been very low. Comparing the concentration of metals of lysimeters containing pre-treated sludge and not pre-treated sludge, it is possible to understand the effects of biological stabilization of sludge and the advantages to reach the environmental sustainability of landfill.

Sommario

Il settore conciario italiano è composto da circa 2400 aziende e 30300 addetti. The aziende sono concentrate in quattro principali poli industriali: S. Croce sull'Arno in Toscana, Arzignano and Valle del Chiampo in Veneto, Solofra in Campania and Turbigo Castano in Lombradia. L'industria conciaria italiana è leader sia a livello europeo sia a livello mondiale. Le acque reflue prodotte dall'attività conciaria sono collettate a grandi impianti di depurazione industriali centralizzati. Il processo depurativo più comune è quello a fanghi attivi. Il fango di supero, prodotto durante le fasi di depurazione è chiamato fango di concia e contiene tutti gli inquinanti rimossi dall'acqua reflua trattata. E' pertanto a sua volta un rifiuto da trattare e smaltire. I fanghi di conceria sono attualmente un grosso problema ambientale ed ecologico, sia in Europa che in Italia. La produzione di fanghi conciari in Italia è stimata pari a 280,000 tonnellate all'anno. Ad oggi, nessun processo ha avuto successo per il riutilizzo di questi fanghi e l'unica destinazione possibile rimane la discarica.

L'obiettivo del presente lavoro di ricerca è quello di analizzare le potenzialità di alcuni processi biologici per la loro applicazione nel processo gestionale dei fanghi di concia. Il fine è quello di raggiungere una situazione di sostenibilità sociale ed ambientale del processo gestionale e di trattamento dei fanghi conciari.

Il lavoro di ricerca si è articolato in quattro tematiche: la minimizzazione della produzione di fango e la minimizzazione della richiesta energetica per la gestione dei fanghi stessi, la stabilizzazione aerobica di fanghi disidratati meccanicamente, la produzione biologica di idrogeno da fanghi di conceria e la sostenibilità ambientale dello smaltimento in discarica dei fanghi.

Risparmi energetici nella gestione dei fanghi possono essere ottenuti individuando le condizioni ottimali nel processo di essiccamento termico. L'obiettivo è quello di individuare la minima concentrazione di solidi totali, oltre la quale i processi di degradazione biologici sono fortemente inibiti o fermati, per mancanza d'acqua. Il valore della concentrazione di solidi totali emerso dal presente lavoro sperimentale è pari al 75%. Conseguentemente un valore di umidità del 25% o inferiore, non è in grado di garantire lo svolgimento di processi degradativi batterici, indipendentemente dalla biodegradabilità del substrato organico nel fango.

La stabilizzazione aerobica di fanghi disidratati meccanicamente, prima della loro deposizione in discarica, ha l'obiettivo di stabilizzare la sostanza organica contenuta nei fanghi e ridurne il

contenuto d’acqua. I vantaggi di questo trattamento preliminare la discarica, sono da ritrovare nelle migliori condizioni di deposito, nella riduzione dello spazio necessario allo smaltimento in discarica, nella riduzione degli impatti di lungo termine delle discariche e nei bassi investimenti economici per la realizzazione e gestione di tali impianti. Il processo di stabilizzazione aerobica ha successo, nonostante le caratteristiche intrinseche dei fanghi conciari e i risultati ottenuti sono incoraggianti per la realizzazione in scala reale di tale trattamento. Si sono osservate riduzioni del contenuto di solidi volatili, riduzioni del contenuto d’acqua, dipendentemente dalle portate d’aria specifiche di insufflazione e diminuzione della lisciviabilità e della mobilità dei metalli pesanti contenuti. Anche i parametri di stabilità biologica, valutati sia con test resporometrici che fermentativi, hanno raggiunto i valori riportati nella letteratura scientifica internazionale indicativi di condizioni di stabilità per i rifiuti.

La produzione biologica di idrogeno rappresenta un interessante opportunità per produrre idrogeno da fonti rinnovabili, a bassi costi e con impatti ambientali sostenibili. I processi biologici di produzione di idrogeno, sono non solo ambientalmente accettabili, ma aprono una nuova prospettiva per l’utilizzazione di fonti energetiche rinnovabili, che sono inesauribili. Per lo studio della produzione biologica di idrogeno si sono svolte prove di fermentazione in batch, in condizioni mesofile. Si sono ottenuti buoni risultati di produzione di idrogeno utilizzando come substrato il glucosio e la frazione organica putrescibile dei rifiuti solidi urbani. La produzione di idrogeno dai fanghi conciari è paragonabile con quanto ottenuto dalla frazione organica putrescibile dei rifiuti urbani, ma con produzioni più lente e con fasi di adattamento più lunghe. Non si è riusciti ad evitare però la produzione di metano. Probabilmente la lenta biodegradabilità dei fanghi conciari e il fatto che i fanghi stessi contengano biomassa batterica, ha permesso ai batteri metanigeni di mantenere o ristabilire la loro attività degradativa.

L’ultima parte del presente lavoro di ricerca ha riguardato l’analisi del comportamento a lungo termine di fanghi conciari depositati in discarica. In particolare si sono analizzate le condizioni in cui i sistemi barriera delle discariche non garantiranno più la loro azione di contenimento. Le emissioni di biogas e di percolato hanno evidenziato che i processi di degradazione del fango depositato ripartono molto rapidamente e che il processo di essiccamento termico non realizza una sterilizzazione del fango. Le emissioni di biogas e la qualità del percolato prodotto nei test in lisimetro non indicano condizioni di sostenibilità ambientale di lungo periodo. Paragonando i risultati ottenuti con il comportamento in lisimetro di fanghi conciari trattati preliminarmente con un processo di stabilizzazione aerobico, si possono evidenziare i benefici di tale trattamento nel raggiungimento di condizioni di sostenibilità ambientale. Le produzioni di biogas sono state quasi impercettibili. Anche i parametri di qualità

del percolato hanno evidenziato ordini di grandezza inferiori rispetto al percolato prodotto da lisimetri contenenti fanghi conciari non trattati. Paragonando inoltre il contenuto di metalli nel percolato di fango trattano e non trattato, si possono evidenziare i positivi effetti di riduzione della mobilità dei metalli a seguito del trattamento aerobico.

CONTENTS

Chapter 1

INTRODUCTION

The Italian tan line of industrial activity is characterized by 2,400 companies and 30,300 workers. The companies are concentrated in four main industrial poles: S. Croce sull'Arno in Toscana, Arzignano and Valle del Chiampo in Veneto, Solofra in Campania and Turbigo Castano in Lombradia.

The turnover of the Italian tan industries has been of 5.4 thousand millions in 2003. The Italian tan activity is leader in the European Union (65% of European turnover) and in the World too (20% of global turnover). The line of business is composed by small and medium concerns.
The wastewater produced during the tan activity is collected to centralized industrial wastewater treatment plants. The most common depuration treatment of this wastewater is biological activated sludge. The excess sludge produced during the treatment process contents all the pollutants removed from water. The disposal of excess sludge represent one of the main problem for managers of wastewater treatment plants, the cost for the disposal of dewatered sludge reaches an half of the whole plant management cost including energy, personnel and ordinary maintenance.

The possible solutions to solve the problems of sludge management can be different: composting, incineration, pyrolysis or gasification, solidification, use in brick or concrete industries, landfill disposal. Not all the above solution are practicable due to social and political reasons and or technical and economical reasons.

The aim of the current research work is to analyze the capacity of some biological treatments to be applied in the management system of tannery sludge. The target is to reach the social and environmental sustainability of management system of tannery sludge.

The sludge can be considered a solid waste and to find new solutions for the management of such waste, the waste management hierarchy has to be the pathway.

The first phase is minimization. Reduction of the amount of waste that a system has to manage is the first possibility to limit the impacts on the environment of current society. Minimization applied to wastewater treatment means to realize all the operation that reduce the

production of excess sludge that has to be disposed off. Minimization of excess sludge in biological wastewater treatments means to avoid the doubling of bacterial cells, to enhance the oxidation processes. The possibility to enhance the oxidation processes instead of cell replication, are both physics-chemical and biological. The phase of minimization includes also the reduction of the energy required for the management of sludge. One of the most intensive energy requirements takes place during dewatering of sludge.

The second step of waste management hierarchy is material recovery. The possibility to use the excess sludge as a resource and not as waste to dispose off, is the use as fertilizer in agricultural activity. The main advantage is the distribution of carbon and nutrients in the ground, to maintain a balanced amount of such elements that are taken up by intense cultivations. On the other hand the problems of the use of sludge in agriculture are the content of heavy metals, the overloading of nitrogen, the pathogens and the potential dangerous organic compounds.

The third step of waste management hierarchy is the energy recovery. The possibilities to use the sludge as energy source are different. The sludge can be use in thermal treatment as incineration, pyrolysis or gasification. Not all the cited treatments are actually developed at an industrial level, and often the realization of thermal treatment plants meets the opposition of communities living in the neighbourhood. The other possibilities are the biological treatments. Anaerobic digestion to produce methane is a mature, reliable technology that has been demonstrated in thousands of full-scale facilities worldwide. Biological hydrogen production is one of the most promising biological treatments to produce an energetic compound and it is also an interesting opportunity to produce hydrogen from renewable source, at low costs and sustainable environmental impacts.

The last step of waste management hierarchy is landfill disposal. Landfill disposal must be a sustainable system, as all the systems described before. The sustainability of landfill means a system “which meets the needs of the present without compromising the ability of future generations to meet their own needs”. A sustainable landfill has emissions that do not change in a considerable way quality of the surrounding air, ground and groundwater; therefore emissions that do not cause significant modifications to the surrounding environment can be considered as negligible. Mechanical and biological pre-treatments before landfilling are processes that contribute to the realization of a sustainable landfill. The objective of biological waste treatment is to minimize the reactivity of the waste and thus prevent subsequent unchecked emissions, and to match the chemical conversions to those in nature in terms of quantity and speed. By the biological waste pretreatment, processes taking place in the landfill over long periods of time will be shortened to a few years. The emission potential contained in the waste is reduced to a

large extent during pretreatment so that, compared to unpretreated wastes, only minor emissions occur, which can be controlled and treated with little expenditure.

The overall management system of tannery sludge should meet the above points. The intrinsic characteristics of this type of waste have to be evaluated to define the best available technologies to reach a condition not only economically sustainable but, first of all, environmentally sustainable.

1.1 RESEARCH TOPICS

The research work has regarded the following four topics:

- Evaluation of the optimal conditions for the thermal drying system of tannery sludge. The thermal drying system of excess sludge shows possibility of optimization to guarantee the minimization of energy requirement. The thermal drying system has the aim to reduce the volume of sludge to dispose off, due to evaporation of water content of sludge, and the reduction of biological activity connected with the degradation or fermentation of biodegradable organic substances because of the high reduction of moisture content. The optimization of the thermal drying system aims to characterize the minimum value of total solids content of the sludge, that inhibits or that stops the biological activity of degradation of organic substances in the sludge.
- Aerobic stabilization of mechanically dried tannery sludge. The targets of the treatment are the stabilization of organic substances and the reduction of water content, differently by a composting process the target of which is the production of an agricultural fertilizer. The advantages of a preliminary aerobic treatment are the reduction of environmental impacts of landfilling, better disposal conditions and lower costs for treating plant investment and management when compared, for example, to a thermal treatment plant.
- Biological hydrogen production from tannery sludge. Hydrogen is receiving higher interest to avoid fossil fuels consumption and climate changing. It cannot be considered as a primary energy source but it could be transported, stored and used like other primary energy sources. Hydrogen is strategically important as it has low emission, is environmental-benign, cleaner and more sustainable energy system. Biological Hydrogen Production is an interesting opportunity to produce hydrogen from renewable source, at low costs and sustainable environmental impacts. The biological processes are not only environmental friendly, but also they lead to open a new avenue for the utilization of

renewable energy sources which are inexhaustible. In addition, they can also use various waste materials, which facilities waste recycling.

- Evaluation of the sustainability of landfill disposal of dry tannery sludge. The research work has been set up to understand the behaviour of landfill, especially when the barrier systems will fail. The actual landfill regulation imposes clay liners on the bottom and on the top of landfill, to avoid infiltration of water and uncontrolled leachate emissions. It is well known that these systems have a life time of some decades and they do not guarantee the perfect isolation of landfill from the environment to the eternity. The research work has been set up to understand the behaviour of landfill, especially when the barrier systems will fail. The actual landfill regulation imposes clay liners on the bottom and on the top of landfill, to avoid infiltration of water and uncontrolled leachate emissions. It well known that these systems have a life time of some decades (Cossu et al., 2005) and they do not guarantee the perfect isolation of landfill from the environment to the eternity.

The four topics cover three of the four steps of waste management hierarchy: minimization, energy recovery, sustainable landfill. No topics have been proposed for the second step of waste management hierarchy, due to intrinsic characteristics of tannery sludge. The high concentration of heavy metals in tannery sludge makes the utilization of such material not allowed for agricultural scopes. Even if the legislative limits can be respect by mixing tannery sludge and other waste materials to decrease the overall concentration of metals under the limit values, this practice do not seem ethic and sustainable. The solution of tannery sludge disposal problems can not be find spreading this material at small doses in large part of agricultural land.

1.2 TANNING PROCESS AND IMPACTS

The tanning process is composed by a sequence of mechanical and chemical processes. The sequence and the type of such processes depends to the desired characteristics of finished product. Traditionally the tanning process can be divided in three phases:

- Preliminary processing
- Tanning process and dyeing process
- Post tanning process and finishing

There are two types of tanning, vegetable tanning and chromium tanning. This process consists of the following steps:

- Soaking: The preserved raw hides regain their normal water contents. Dirt, manure, blood, preservatives (sodium chloride, bactericides) etc. are removed.
- Pickling: Pickling increases the acidity of the hide to a pH of 3, enabling chromium tannins to enter the hide. Salts are added to prevent the hide from swelling. For preservation purposes, 0.03 - 2 weight percent of fungicides and bactericides are applied.
- Tanning: After pickling, when the pH is low, chromium salts (Cr^{3+}) are added. To fixate the chromium, the pH is slowly increased through addition of a base. The process of chromium tanning is based on the cross-linkage of chromium ions with free carboxyl groups in the collagen. It makes the hide resistant to bacteria and high temperature. The chromium-tanned hide contains about 2-3 dry weight percent of Cr^{3+}.
- Basification: Fixing of the chrome with oxide of magnesium and fungicide's addition (antifungal).

The next step it to realize the mechanical operations necessary to give hides the needed thickness (Squeezed, divided and reduced). Finally, the leather neutralizes each other with formiato-bicarbonate of sodium to be able to lubricate (synthetic oils) to give them the softness and the needed touch.

The overall process requires high quantity of water and it uses large amount of chemical compounds. For this reasons the tan industries is commonly knows to have high environmental impacts and it traditionally associated with bad smells and pollution. Tannery waste includes proteins, hair, lime, salt, acids, tannins, dyes and oils and most of such compounds are present in the wastewater stream.

The main environmental impacts are following reported.

- Water consumption: the processing of leather requires large amount of water in the preliminary phases and during the tanning process. The soaks are often changed in the same process phase and also between two different processing. The ratio between the amount of water per unit of weight of leather can reach 400%.
- Wastewater: the wastewater from tan activity is characterized by high concentration of organic compounds, bad smell and turbidity. The pollutants are both organic compound and inorganic compounds due to substances removed from the hair and chemicals added during the processes. Ammonia, sulphate and chlorides are the main inorganic compounds in the wastewater. The chlorides come from the high salinity of hide, sulphates derives from the large use of sulphuric acid.

- Atmospheric emissions: odours are the typical impacts of tan industry. The main smelling compounds emitted are hydrogen sulphide, ammonia, volatile organic compounds, vapours of formaldehyde and dusts.
- Soil: soils can be contaminated by chrome. The chrome is used as tanning agent in wet blue tanning processes. The chrome discharged in wastewater, is concentrated in primary and secondary sludge produced in the wastewater treatment plants.

1.3 TANNERY SLUDGE MANAGEMENT

Tannery sludge is produced during the biological treatment of wastewater from tan activity. The wastewater coming from tanneries are characterized by high concentration of organic compounds, high concentration of nitrogen compounds and high concentration of dissolved and suspended solids. Moreover these characteristic chlorides and sulphates, biological refractory compounds and sulphides are largely present in the wastewater. The sludge is generated during the depurative process, one part from the primary settler and one part from excess sludge from the secondary settlers.

The sludge are later thickened and treated. The possibilities of further treatment are anaerobic digestion or dewatering. Dewatering is generally preferred instead off anaerobic digestion, in small wastewater treatment plants or when the lack of space for digesters do not allows the realization of this process. The dewatering system can be composed by a mechanical and a thermal system. The mechanical drying system can reduce the moisture content to about 70%, while the thermal drying system can theoretically reach the complete dewatering of sludge. The normal target of thermal drying system is moisture content lower then 10%. At this point the dried tannery sludge can be dispose off in sanitary landfills.

The tannery sludge are characterized by a high content of organic matter, like the sludge from an urban wastewater treatment plant, a high content of chlorides, sulfates and heavy metals. Table 1.1 and Table 1.2 report the characterization of tannery sludge used in this research work. The characteristics of sludge are not constant but they vary depending on the type of processing carried out in tanning activity.

Table 1.1 Characterization of tannery sludge.

TOC	TKN	NH_3	NO_3^-	S^{2-}	$SO4^{2-}$	Cl^-	IR7	B21
[%TS]	[mgN/KgTS]	[mgN/KgTS]	[mgN/KgTS]	[mgS/KgTS]	[mgS/KgTS]	[mgCl/KgTS]	[mgO2/gTS]	[ml/gTS]
50-55	45000-50000	17000-19500	5-15	400-500	1800-2300	6500-7500	160-190	60

Table 1.2 Metal content of tannery sludge.

Cr	Cu	Fe	Ni	Pb	Zn
[mg/KgTS]	[mg/KgTS]	[mg/KgTS]	[mg/KgTS]	[mg/KgTS]	[mg/KgTS]
65000-85000	75-105	21000-26000	35-50	15-35	1300-5500

The fingerprint of this sludge is the high concentration of chrome and zinc, which are largely used in tanning process, high concentration of iron which is added in the wastewater treatment plant as floating agent, and high concentration of ammonia, chlorides and sulphur compounds which are sub-products of tanning processes.

The tannery sludges are currently a big ecological and environmental problem in Europe and in Italy, too. The production in Italy is around 280.000 tons every year. No process carried out up to now, has been successful for a reuse of the sludge and the only possible destination remains the landfill.

Chapter 2

MINIMIZATION

Biological wastewater treatment involves the transformation of dissolved and suspended organic contaminants to biomass and evolved gases (CO_2, CH_4, N_2 and SO_2). The activated sludge process is the most widely used biological wastewater treatment for both domestic and industrial plants in the world. One of the drawbacks of conventional activated sludge processes is high sludge production. Currently, production of excess sludge is one of the most serious challenges in biological wastewater treatment. In many wastewater treatment plants at international level, the cost for the disposal of dewatered sludge reaches an half of the whole plant management cost including energy, personnel and ordinary maintenance (Andreottola, 2006). Main alternative methods for sludge disposal in EU are landfill, land application and incineration, accounting for nearly 90% of total sludge production in EU (Davis, 1997). Land application of sewage sludge is restricted to prevent health risks to man and livestock due to potentially toxic elements in the sewage sludge, for example heavy metals, pathogens, and persist organic pollutants. Declines in available land space, coupled with increasing stringent regulations governing the design and operation of new landfills, have caused the cost of siting, building, and operating new landfills to rise sharply. Generally, incineration is the final option for sewage sludge disposal. The process generates ash, which tends to go to landfill as it cannot be disposed elsewhere due to the high heavy metals content and general toxicity.

2.1 SLUDGE MINIMIZATION

An ideal way to solve sludge-associated problems is to reduce sludge production in the wastewater treatment rather than the post-treatment of the sludge produced. Microbial metabolism liberates a portion of the carbon from organic substrates in respiration and assimilates a portion into biomass. To reduce the production of biomass, wastewater processes must be engineered such that substrate is diverted from assimilation for biosynthesis to fuel exothermic, non-growth activities.

Different strategies are currently developed for sludge reduction in an engineering way based on these mechanisms: lysis-cryptic growth, maintenance metabolism, uncoupling metabolism and predation on bacteria.

2.1.1 Lysis-cryptic growth

Cell lysis will release cell contents into the medium, thus providing an autochthonous substrate that contributes to the organic loading. This organic autochthonous substrate is reused in microbial metabolism and a portion of the carbon is liberated as products of respiration, and then results in a reduced overall biomass production. The biomass growth that subsequently occurs on this autochthonous substrate cannot be distinguished from growth on the original organic substrate, and is therefore termed as cryptic growth (Wei et al, 2003). There are two stages in lysis-cryptic growth: lysis and biodegradation. The rate-limiting step of lysis-cryptic growth is the lysis stage, and an increase of the lysis efficiency can therefore lead to an overall reduction of sludge production.

Sludge lysis and subsequently cryptic growth could be promoted by physical, chemical and combined ways in order to reduce sludge production, such as:

- Thermal treatment;
- Chemical treatment using acids or alkali;
- Mechanical disintegration using ultrasounds, mills, and homogenizers;
- Freezing and thawing;
- Biological hydrolysis with enzyme addition;
- Ozonation;
- Chlorination;
- Integration of thermal/ ultrasonic treatment and membrane;
- Integration of alkaline and heat treatment;
- Increase of oxygen concentration.

The treatment of sludge for inducing its reduction can be achieved by introducing an additional stage that can be integrated within the recirculation flow, before oxidation tank or before the anaerobic digestion, after thickening and before dewatering. In both cases the additional treatment realizes two simultaneous effects, the dispersion of biological aggregates and activated sludge flocs, with release of biodegradable soluble and colloidal substrates, and the breakage and death of microorganisms due to the disruption of cellular membrane with the release of

intercellular compounds. The result is the enhancement of sludge biodegradability due to the microbial cell lysis and the solubilisation of particulate COD (Andreottola, 2006).

In the current activated sludge theory, sludge retention time (θ_c) is defined as the average time a unit of biomass remains in the treatment system. Much research has shown that qc is the most operational parameter in activated sludge process. For steady state system, the qc is inversely related to the specific growth rate. It has been demonstrated that the relationship between sludge yield (Y_{obs}) and sludge retention time can be described by the following expression:

$$\frac{1}{Y_{obs}} = \frac{1}{Y_{\max}} + \frac{\theta_c K_d}{Y_{\max}} \tag{1}$$

where Y_{max} is the true growth yield; and K_d is specific endogenous rate. Equation (1) shows that the observed growth yield is inversely dependent on the sludge retention time and endogenous rate in steady state activated sludge process. This equation also provides a theoretical basis for in-plant engineers to control the total sludge production by adjusting the θ_c during the wastewater biological treatment.

Sludge reduction can be achieved by cryptic growth of microorganisms as microbial growth on its lysates. For this purpose, some cell breakage techniques have been developed, such as sludge treatment by thermal, alkaline, acid and their combination (Rocher et al., 1999, 2001). It was found that in thermal–chemical hydrolysis, sodium hydroxide was the most efficient for inducing cell lysis (Rocher et al., 1999). Cryptic growth can also be amplified at an increased sludge age through microbial endogenous respiration, a longer sludge age would result in a lower sludge production. Sodium hydroxide and energy input are required to maintain and adjust system pH and temperature. Sludge hydrolysis by chemical means produces high BOD/N waste, and one can easily calculate the amount of chemical oxygen demand (COD) and ammonia produced from each gram of dry biomass with an empirical formula of $C_5H_7NO_2$. It should be pointed out that complicated process operation/control and reactor corrosion limit the application of this chemical-assisted sludge reduction technique in full-scale wastewater treatment plants.

Most biological wastewater treatment processes are temperature sensitive, and thus increasing process temperature is effective for reducing sludge production. Low temperature operation can lead to the increase of sludge production. The possible explanation of higher sludge production at low temperature is a net accumulation of cell protoplasm within flocs in the form of COD because the hydrolysis of the organisms is the reaction rate-controlling step of the endogenous respiration (Lishman et al., 2000) temperatures can also be combined with acid or alkaline treatment to reduce or condition excess sludge. Different cell lysis techniques (thermal,

combination of thermal and alkaline or acid) were then compared with break Alcaligenes eutrophus and wasted activated sludge (Rocher et al., 2001). Their results showed that alkaline treatment by NaOH addition combined with thermal treatment (pH 10, 60_C for 20 min) was the most efficient process to induce cell lysis and produce biodegradable lysates. The coupling of this lysis system to a biological wastewater treatment bioreactor allowed a 37% reduction in the excess sludge production compared with the classic aerobic system process. Using thermal or thermo-chemical treatment corrosion is the major problem, thus high-grade materials are required. The costs for spare parts and maintenance constitute a large part of the total running costs of the treatment. Odor problem is another major drawback for the thermal treatment (Muller, 2001).

Ozone is a strong chemical oxidant and has been commonly used in water disinfection process. Ozonation-assisted sludge reduction process is based on the idea that part of activated sludge is mineralized to carbon dioxide and water, while part of sludge is solubilised to biodegradable organics that can be biologically treated. The ozonation of sludge results in both solubilization (due to disintegration of suspended solids) and mineralization (due to oxidation of soluble organic matter), and the recycling of solubilized sludge into the aeration tank will induce cryptic growth. Ozone is a strong cell lysis agent. When sludge is kept contact with ozone in the ozonation unit, most activated sludge microorganisms would be killed and oxidized to organic substances (Liu, 2003). There is evidence that more than 50% of the carbon obtained after ozonation is readily biodegradable (Deleris et al., 2000). This is reason why those organic substances produced from the sludge ozonation can then be degraded in the subsequent biological treatment. It had been reported that the sludge settleability in term of sludge volumetric index was highly improved as compared to control test without ozonation (Kamiya, 1998). Apparently, both operation and capital costs of the ozonation-activated sludge process should be high due to energy required for ozone production. However, economical estimate suggests that the operation costs of the whole process was lower than that of conventional activated sludge process if the costs of sludge dewatering and disposal were taken into account (Yasui et al., 1996).

As an alternative solution to ozonation, recently a chlorination-combined activated sludge process had been developed for minimizing excess sludge production (Saby et al., 2002). This chlorination-combined activated sludge process is similar to the ozonation-activated sludge process, i.e. excess sludge was subject to a chlorine dose, and the chlorinated liquor was then returned to the aeration tank. From the point of view of operation cost, the chlorination- activated sludge process would have advantages over the ozonation-activated sludge system as described

earlier. Since chlorine is a weak oxidant as compared to ozone, the dosage of chlorine used in the chlorination-activated sludge process is about 7–13 times higher than that of ozone applied in the ozonation-activated sludge process. It is well known that ozone has much higher oxidation power than chlorine, releases limited by-products, and is non-reactive with ammonia (Wojtenko, 2001). However, in the chlorination-activated sludge process, the formation of undesirable chlorinated by-products would occur.

Low sludge yield has been commonly observed in pure oxygen aeration activated sludge process. This implies that high dissolved oxygen concentration could promote sludge reduction. Compared to conventional air aeration activated sludge process, the growth yield can be lowered by up to 50% in purified oxygenation activated sludge system (Liu, 2003). These support a basic idea that high dissolved oxygen could promote sludge reduction. Additional benefits of high dissolved oxygen biological process include repression of filamentous growth, ability to maintain a higher biomass concentration in the aeration tank; better sludge settling and thickening; higher oxygen transfer efficiency and more stable operation. Two hypotheses had been proposed to interpret high dissolved oxygen-induced sludge reduction. The high dissolved oxygen concentration would produce a higher level of active biomass, and hence, a lower true sludge loading rate that would be measured relative to a low dissolved oxygen system. The lower true sludge loading rate would result in a relatively lower sludge production rate at the same apparent measured value of the sludge loading rate. However, Abbassi et al. (2000) considered that the increase of the oxygen concentration in the bulk liquid promoted a deep diffusion of oxygen that subsequently led to an enlargement of the aerobic volume inside the flocs. As a result, the hydrolysed biomass in the floc matrix could be aerobically degraded and sludge quantity is thus reduced.

Ultrasounds application presents a good technical state of the art and a good operational stability. Cavitation is the phenomenon of the formation, growth and subsequent collapse of microbubbles occurring in short times and producing high levels of pressure and temperatures. The main mechanisms of floc breaking induced by ultrasonic irradiation are the following: extreme temperature and pressure gradients within the bubbles during cavitational collapse, combustion or pyrolysis pathways occurring during bubble implosion and production of high reactive free-radicals (Andreottola 2006).

2.1.2 Maintenance and endogenous metabolism

Part of energy source for bacteria is used for maintaining living functions, which is so-called maintenance metabolism. Microorganisms satisfy their maintenance energy requirements in preference to producing additional biomass, and this recognition has revealed possible methods for sludge reduction during biological wastewater treatment. The importance of maintenance metabolism is that the maintenance-associated substrate consumption is not synthesized to new cellular mass. Thus, the sludge production should be inversely related to the activity of maintenance metabolism. The energy available to microorganisms is determined by the supply of substrate. By increasing biomass concentration it would theoretically be possible to reach a situation in which the amount of energy provided equals the maintenance demand. In the environmental engineering literature, endogenous respiration is usually the so-called autodigestion of biomass. In a continuous culture growth, endogenous metabolisms could occur concurrently. The major advantage of the endogenous metabolism is that the incoming substrate could be finally respired to carbon dioxide and water, while results in a lower biomass production. It should be realized that the control of endogenous respiration would have much practical significance as does the control of microbial growth and substrate removal in wastewater treatment processes.

2.1.3 Energy spilling and uncoupling conditions

Bacteria have complex metabolic pathways to control growth, replication and other processes. Catabolism is the reaction series that reduces the complexity of organic compounds produces the free energy. Anabolic paths involve the use of free energy to build the molecules required by cell. Energy transfer between these paths is in the form of adenosine triphosphate (ATP). Metabolism is the sum of biochemical transformations that includes interrelated catabolic and anabolic reactions, and the behaviors of a microbial culture are determined by the catabolism and anabolism. There is evidence that under some conditions, such as existence of organic protonophores, heavy metals, abnormal temperature and alternative aerobic-anaerobic cycle, the variation in respiration would be far greater than the amount that could be ascribed to ATP production, i.e. catabolism no longer couples to anabolism (Tsai, 1990; Cabrero et al., 1998; Mayhew, 1998; Liu, 2000). There is evidence to show that under energy uncoupling conditions, the microorganisms are able to overconsume substrate and a higher substrate consumption rate is observed (Cook, 1994; Liu, 1999; Low et al., 2000). This indicates that cells could dispose of their intracellular energy by dissipation of membrane potential, ATP hydrolysis and futile cycles,

and a major part of the substrate would be oxidized to carbon dioxide under energy uncoupling conditions. In this case, the energy generated was used to drive futile cycles of the energy, but no significant effect was imposed on the substrate removal rate (Liu, 2001). It must be realized that the specific feature of energy uncoupling is the breakdown and reformation of substrate by microorganisms, but without a corresponding change in cell mass. In an environmental engineering sense, the concept of energy uncoupling can be extended to the phenomenon in which the rate of substrate consumption is higher than that required for growth and maintenance. As a result, under energy uncoupling conditions the observed growth yield of activated sludge would be reduced markedly. In theory, reduction in the growth yield means that sludge production can be cut down by an equivalent percentage. This exhibits a promising way to reduce excessive sludge production by controlling metabolic state of microorganisms in order to maximize dissociation of catabolism from anabolism.

For most aerobic bacteria, ATP is generated by oxidative phosphorylation, in which process electrons are transported through the electron transport system (ETS) from a source of electrons at elevated energy levels (substrate) to a final electron acceptor (oxygen). The molecules directly using the proton gradient built up by electron transport is considered proton-ATPase pumps that can be forced to reversibly operate. If operating in forward direction, the pumps would use energy released by ATP hydrolysis to drive proton across a membrane, but in cellular systems producing ATP, the pumps are driven in reverse by the magnitude of the proton gradient produced by electron transport. It has been known that such chemiosmotic mechanisms of oxidative phosphorylation can be effectively uncoupled by organic protonophores, such as 2,4-dinitrophenol (dNP), para-nitrophenol (pNP), pentachlorophenol and 3,30,40,5-tetrachlorosalicylanilide (TCS). In the presence of organic protonophores, the majority of organic substrate would be oxidized to carbon dioxide rather than used for biosynthesis. As a result, the growth efficiency is much lowered in uncoupler-containing activated sludge process. Based on the above principle, much research has been focused on development of uncoupler-induced energy spilling process for minimization of excess sludge production.

However, it should be pointed out that most of the organic protonophores are xenobiotic and potentially harmful to the environment, thus their application in wastewater treatment practice would not be very prudent.

Oxic-settling-anaerobic (OSA) process is a modification of conventional activated sludge technology by inserting an anaerobic reactor in the recycling bypass of sludge. The OSA system consists of an oxic completely mixed tank, followed by a settling tank and an anaerobic tank, situated in the returned sludge circuit of the OSA system. This process has been successfully

employed to repress the growth of filamentous organisms. For aerobic microorganisms, ATP is generated from the oxidation of exogenous organic substrate. When the microorganisms are subject to anaerobic condition without food supply, they are no longer able to produce the energy and have to use their ATP reserves as energy source. During the anaerobic starvation period, the ATP would be exhausted. After microorganisms return to food-enriched aerobic reactor, they have to rebuild necessary energy reserves prior to biosynthesis because cellular synthesis could not proceed without a certain intracellular stock of ATP. In this case, the substrate consumption should thus go to catabolic metabolism to satisfy the energy requirement of microorganisms (Liu, 2001). Maximized energy uncoupling would result in a minimized sludge yield. The energy uncoupling induced by alternative aerobic and anaerobic treatment constructs theoretical basis of oxic-settling anaerobic technique designed for excess sludge minimization. In view of industrial scale application, the oxicsettling-anaerobic process provides a promising technique for efficiently reducing sludge production, while improving the stability of process operation

2.1.4 Predation on bacteria

A biological wastewater treatment process can be considered as an artificial ecosystem, and activated sludge is an ideal habitat for several organisms other than bacteria. One way to reduce sludge production is to exploit higher organisms such as protozoa and metazoan in the activated sludge processes that predate on the bacteria whilst decomposition of substrate remains unaffected. During energy transfer from low to high trophic levels, energy is lost due to inefficient biomass conversion. Under optimal conditions the total loss of energy will be maximal and the total biomass production will thus be minimal (Ratsak et al, 1996). It is well known that the presence of protozoa and metazoa in aerobic wastewater treatment processes plays an important role in keeping the effluent clear by consuming dispersed bacteria (Wei et al., 2003).

2.2 ENERGY SAVING DURING SLUDGE MANAGEMENT

In the concept of avoidance and minimization during sludge management operations, the idea of minimization of energy requirement must be introduced too. Even if every waste management system requires energy to maintain its efficiency, the minimization of such energy requirements due to optimization of single processes, can contribute to limit the consumption of fossil fuel and consequently the emissions of greenhouse gases. Clearly the concept of minimization of energy requirement must be considered as an optimum value which satisfies in any case the maintenance of the processes and guarantees limited environmental impacts of the whole management system. A paradox that could appear, following the minimization of energy requirement, is “avoid managing the waste”: the energy saving will be maximized but the environmental impacts in such case will be maximized too.

The excess sludge management system could be composed by settling, flotation, thickening, mechanical drying system, thermal drying systems and biological stabilization processes.
The thermal drying system of excess sludge shows possibility of optimization to guarantee the minimization of energy requirement. The thermal drying system has the aim to reduce the volume of sludge to dispose off, due to evaporation of water content of sludge, and the reduction of biological activity connected with the degradation or fermentation of biodegradable organic substances because of the high reduction of moisture content. The lack of sufficient water to maintain bacterial activity stops the biodegradation of organic compounds presents in the excess sludge. The lack of water represents in this case a limiting element for the activity of bacteria as lack of nitrogen, phosphorus or other macro or micro nutrients does in other cases.

The optimization of the thermal drying system aims to characterize the minimum value of total solids content of the sludge, that inhibits or that stops the biological activity of degradation of organic substances in the sludge. It seems not necessary in fact to reach a total dewatering of sludge (Moisture 0%, Total Solid 100%) to avoid biological activity. Even small amounts of moisture can still guarantee the inhibition of biological activity. If that the case, energy can be saved in the characterization of such optimum value of total solid content, because a strong or complete dewatering will be no more necessary.

2.2.1 Materials and Methods

The tests have been realized to evaluate the optimal value of total solid to avoid biological activity of sludge. The tests have been realized both in aerobic and anaerobic condition. For tests

in aerobic condition a respirometer has been used. For the test in anaerobic condition an experimental apparatus has been set up. The experimental apparatus was composed by glass bottles of different sizes and different systems to measure the biogas production.

All tests have the common aim to quantify the biological activity of degradation of the organic substances and identify the maximum value of water content that inhibit the biological activity.

The sludge used in the experiments comes from the mechanical and thermal drying system of excess sludge produced by an industrial wastewater treatment plant, treating wastewater coming from tanneries.

Seven types of sludge have been used during the experiment. Every type of sludge differs from the others only for the percentage of total solid. The seven types of sludge are:

- 30: Tannery sludge at 30% of Total Solids;
- 40: Tannery sludge at 40% of Total Solids;
- 50: Tannery sludge at 50% of Total Solids;
- 60: Tannery sludge at 60% of Total Solids;
- 70: Tannery sludge at 70% of Total Solids;
- 75: Tannery sludge at 75% of Total Solids;
- 80: Tannery sludge at 80% of Total Solids;
- 90: Tannery sludge at 90% of Total Solids.

The sludge “30”, “60”, “75”, ”80”, “90”, have been taken during different phases of the drying system. The sludge “40”, “50”, have been created adding the necessary amount of water to higher percentage of Total Solids to reach the desired percentage of moisture.

Aerobic conditions

The respirometric index represents the amount of oxygen consumed by bacteria to degrade biodegradable organic substances. The respirometric index is commonly used to evaluate the biological activity of solid waste. Higher is the oxygen consumed, higher is the biodegradability of the organic substances in the analyzed waste. The same concept is used to understand the effects of inhibition on biological activity of tannery sludge due to a too low amount of moisture. The respirometer used during the experiment is a Sapromat mod. E (Figure 2.1). This respirometer measure the oxygen consumed during the single test by aerobic degradation of organic substances.

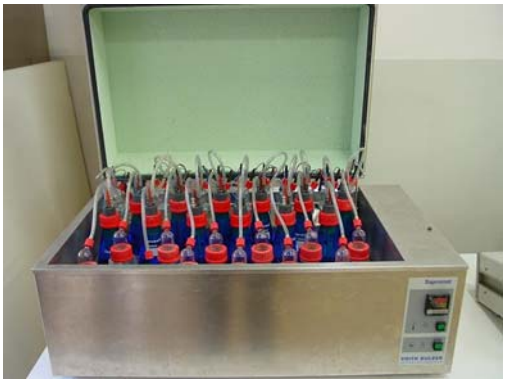

Figure 2.1 Respirometer Sapromat mod E.

The system is composed by a bottle in which the sample is posed, a manometer that measures the pressure or de-pressure in the bottle and an oxygen generator that supply of oxygen the headspace of he bottle when the manometer measures a depression due to the consumption of oxygen.

The test have has a duration of 21 days. An amount of 30 grams have been used in each test.

Anaerobic conditions

The experiments in anaerobic conditions have the aim to evaluate the production of biogas due to degradation of organic substance by anaerobic bacteria. During the experiments external biomass is not used to inoculate the test.

Three types of test have been realized. The first test realized is Black Index, the second and the third tests are fermentative test, to analyse the biogas production from the seven different sludge.

The black index is a simple parameter proposed by Cossu et al. (1999, 2001) that provides an indication of waste biological stability based on the observation of the change of colour of a lead acetate test paper. Lead acetate paper is commercially available as strips made of filter paper impregnated with lead acetate. The test paper is normally used as an indicator for the detection of hydrogen sulfide production by microorganisms in various processes, among others anaerobic digestion of waste (Cossu and Raga, 2008). The lead acetate on the test paper reacts with the hydrogen sulfide yielding black lead sulfide as precipitate on the test paper. The colour of the test paper thus changes from white to brown, gray or black, depending on the concentration of hydrogen sulfide in the atmosphere near the lead acetate paper and on the duration of the test. The test method foresees the utilization of a lead acetate paper strip about 2 cm long, suspended over a sample of waste in a 0.25 l airtight bottle under anaerobic conditions, at a fixed temperature of 35°C. The moisture content of the waste sample has to be adjusted to

approximately 50% and the grain size must be less than 2 cm. Since the result of the test is affected by the head space in the bottle, all measurements have to be carried out with approximately the same waste volume inside the bottles. Observations have to be carried out at fixed time intervals and the changes in colours of the test paper have to be recorded. The test is finished as soon as the entire surface of the test paper is coloured. The black index is calculated as the inverse of the time needed by the test paper for the change of colour, per unit dry mass (BI, $d^{-1}kg\ TS^{-1}$). In the tests carried out for the current research work, the moisture content has not been changed. Glass bottles have been used for the experiments. An amount of 50 grams of Total Solids has been used in each bottle. The bottles have been maintained at a temperature of 35±2°C, in a thermostatic room.

The fermentative experiments have been carried out to analyze the production of biogas in anaerobic condition of sludge without external influence of water content of microbial inoculum. The aim is to evaluate the biological activity of different dry tannery sludge in anaerobic condition, measuring the quantity and the quality of biogas produced during anaerobic degradation of organic substances.

The experiments set up are similar to Biochemical Methane Potential test (BMP), but there is not use of inoculum and water to realize the best condition for the anaerobic degradation of substrate. The aim of that type of tests is to understand the production of biogas in anaerobic condition without external agent.

The experiment on biogas production has been set up in two different scales. In the small scale tests an amount of ten grams of Total Solids are used in each test. In the large scale tests an amount of one kilogram and a half is used in each test. Two different scales have been used to compare and ensure the same answer from such analysis.

The small scale test has been set up using a glass bottle of 120 ml of capacity (Figure 2.2). Different amount of sludge have been put in each bottle, but all the bottle prepared have the same quantity of Total Solids (10 grams). The bottle is closed with a cap that allows taking sample of gas using a syringe. The cap is composed by a silicon part and a metal ring. The bottles are placed in a thermostatic bath at the temperature of 35 ± 0.5 °C (Figure 2.3). Every two or three days the biogas production is measured by a hydraulic system. Another bottle is used to measure the biogas production. That second bottle is full of an acid and high salty solution to avoid that gases pass in the liquid and so a lower amount of biogas produced should be measured (Figure 2.4). The connection between the bottle containing the sample and the bottle containing the liquid have been realized using a plastic pipe and to needle. The over pressure in the bottle containing the sample, move gas into the bottle containing the liquid. The gas moves the same

Figure 2.2 Small scale bottles

Figure 2.3 Thermostatic bath

Figure 2.4 Biogas measuring system

amount in volume of liquid which is dropout in a graduated cylinder. The volume of biogas produced during biological anaerobic degradation is the same volume of liquid dropout in the graduated cylinder. The quality of biogas produced during anaerobic degradation processes is measured by a portable analyzer of landfill gas (LFG20). The analyzer has a pump, and two pipes provided of needle to take samples of gas from the bottle. A pipe is used to suck the gas from the bottle, the second one is used to put in the bottle the gas analysed. In that way, there is no losing of gas.

The experiments at large scale have been set up using a glass bottle of 2 litre of capacity. These bottles are able to contain from 1.3 to 1.5 kilograms of dry sludge. The bottles are closed with a silicon cap. The cap is provided of two glass tubes (Figure 2.5). The biogas produced is collected in a plastic bag. The bag is connected with the head space of the bottle by a plastic pipe.

Figure 2.5 Large scale bottles

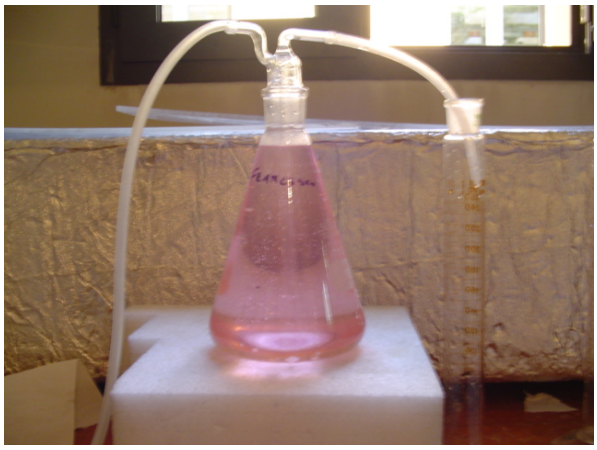

Figure 2.6 Biogas measuring system

The plastic pipe is attached to one of the glass pipe coming out from the silicon top. The bottles are placed in thermostatic room at 35 ± 2 °C. Every two or three days the biogas production is measured by a hydraulic system (Figure 2.6). The volume of the gas contained in the plastic bags is measured moving the same amount of volume of liquid present in a glass bottle full of an acid and high salty solution to avoid that gases pass in the liquid. The amount of liquid moved from the bottle is measured by a graduated cylinder. The total volume of liquid moved from the bottle corresponds to the volume of gas presents in the plastic bag. The quality of biogas produced during anaerobic degradation processes is measured by a portable analyzer of landfill gas (LFG20). The analyzer takes samples of gas from one of two glass pipes present in the silicon cap. The gas pumped out from the bottles and measured is later put in to the bottle from the second glass pipe. In that way, not lose of gas take place.

2.2.2 Results

Aerobic conditions

Te tests realized with seven different types of dry tannery sludge denoted that a value of Total Solid higher that 75%, ensure a limited respiration activity. As shown in Figure 2.7 the consumption of oxygen at the end of 21 days of sludge 75, 80 and 90, is more then ten times lower then the consumption of oxygen of other types of sludge with higher quantity of moisture.
As reported in Table 2.1, after four days the respiration index of sludge 75, 80, and 90 is much lower that the respiration index of other types of sludge. A strange behaviour is denoted for sludge at 40% of Total Solid. The respiration indexes at four and at seven days are low, compared with the sludge at 30% of Total Solid and 50% of Total Solids. This is clearly due to a

lag phase during with the biological activity is inhibited. The lag phase stop at the twelfth day and the consumption of oxygen starts in an exponential way.

A threshold value of 75% of Total Solids seems to be necessary to inhibit the biological activity because the amount of water is too low to allow the degradation processes of organic substances in the sludge.

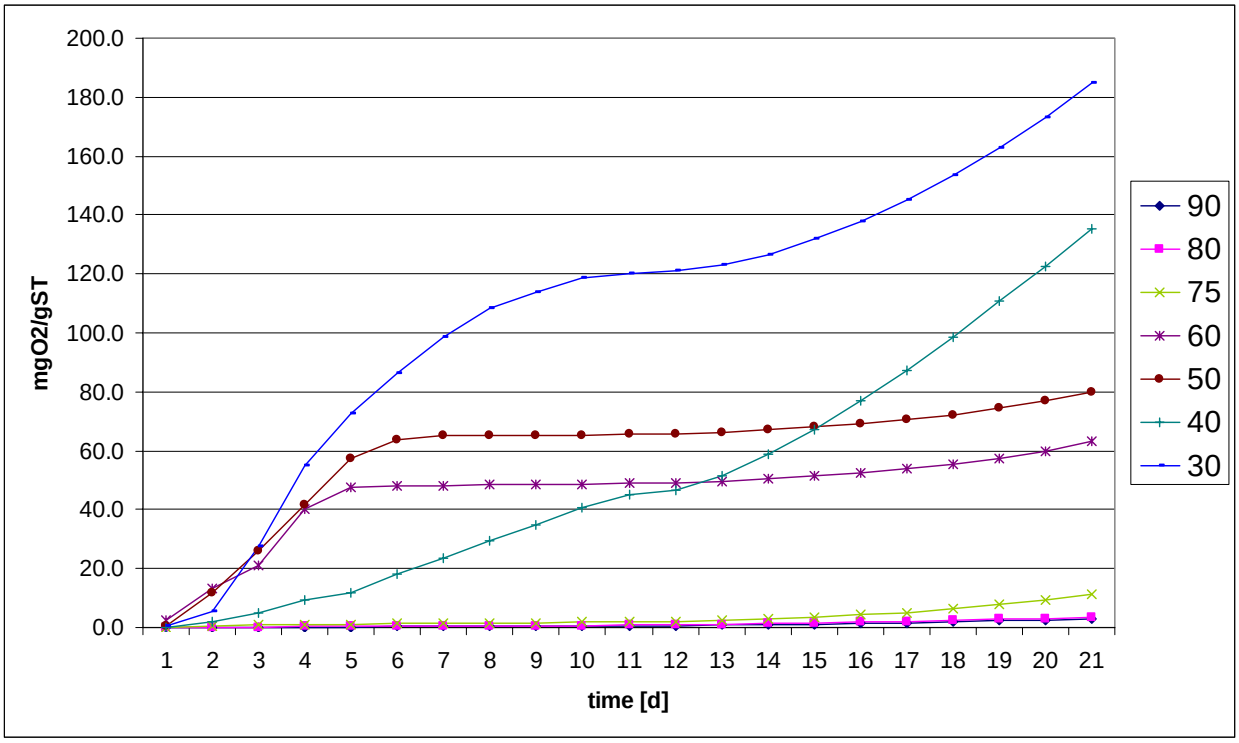

Figure 2.7 Behaviour of Respiration Index of different tannery sludge

Table 2.1 Respiration Index of different tannery sludge

% TS	IR_4 (mgO2/gST)	IR_{21} (mgO2/gST)
30	54,83	184,85
40	9,14	135,52
50	41,52	80,03
60	40,01	80,03
75	1,00	11,09
80	0,28	3,64
90	0,14	3,01

Anaerobic condition

The first experiment realized has been the Black Index. The values of Black Index are reported in Table 2.2. Also in this case the sludge with Total Solid content higher then 70% shows a lower biological activity.

Table 2.2 Black Index values of different tannery sludge

% TS	BI [d^{-1}/KgTs]
90	< 0,1
80	< 0,1
70	< 0,1
60	0,33
50	0,33
40	0,33
30	0,33

Considering the volume of biogas produced during experiments at small scale, similar results have been observed comparing with what already done during aerobic experiment. The production of biogas for sludge at Total Solid of 30% and 40%, starts immediately as it's shown in Figure 2.8. The medium biogas production is of 95 Nml/gTS for sludge at 30% of Total Solids and of 98Nml/gTS for sludge at 40% of Total Solids. The inhibition of fermentative processes seems to start with a Total Solids content of 50%. The production of biogas starts slowly with a lower production compared with the production of biogas from sludge at 40% of Total Solids. In fact the production of biogas after 90 days of test is only 20 Nml/gTS, four times lower then the production of sludge at 30% and 40% of Total Solids. Reducing the moisture content of 10%, the sludge at 60% of Total Solids has a lower production of 10 Nml/gTS after 90 days. Very low biogas productions have been measured for the sludge at 70%, 75%, 80% and 90%. This confirms the results obtained during aerobic experiment. A moisture content of 25%, or lower, is insufficient to maintain a biological process of degradation of organic substances. The desired effect of stabilization of sludge can be reached with a Total Solid content higher then 75%, independently from the biodegradability of organic substances in the sludge. Even from the quality of the biogas produced it is possible to highlight the same result emerged from the biogas production. The biogas quality of sludge at 30% and 40% has the normal behaviour indicating stable anaerobic degradation of organic substances. The concentration of the carbon dioxide increases to a value of 40% during the first week while the concentration of methane grows slowly during the first two weeks. This is due to the initial phase of fermentation of

biodegradable organic substances in the sludge. Hydrolysis and production of Volatile Fatty Acids are the main processes taking place, the production of carbon dioxide is produced by fermentative bacteria, while the production of methane is quite low because small amounts of acetic acid or hydrogen are synthesized. The production of methane increases rapidly after the second week while the concentration of carbon dioxide decreases lightly. The new condition is a stable methanogenic phase; the concentration of methane is about 60% and the concentration of carbon dioxide is about 30%. The sum of the concentrations of methane and carbon dioxide is not 100% because the residual part is composed by nitrogen, which is used at the beginning of the test to remove the oxygen presents in the head space of the bottle. In the bottles containing sludge at 50% and 60% of Total Solids, the behaviour of biogas quality shows as the lower amount of water influences the biological degradation. The concentration of carbon dioxide increases in the first week to a value of 40%, as in the previous tests, and it remains stable around a value of 30%. The concentration of methane increases very slowly in the bottle containing the sludge at 50% of Total Solids reaching a final value of about 30% after 90 days. The concentration of methane remains stable around 2 – 3 % in the bottle containing the sludge at 60% of Total Solids. Analysing the behaviour of bottles containing sludge at concentration of Total Solids higher than 70%, the effects of inhibition emerge clearly. Concentration of methane is not measured in the bottles containing sludge at Total Solid concentration of 75%, 80% and 90%. Higher the concentration of Total Solids is, lower the concentration of carbon dioxide is. The bottles containing the sludge at 75% of Total Solids have an average concentration of 12% of carbon dioxide. The bottles containing the sludge at 80% of Total Solids have an average concentration of 3% of carbon dioxide and the bottles containing the sludge at 90% of Total Solids have an average concentration of 1.5% of carbon dioxide. The quantity and the quality of biogas produced during such experiment clearly show that to avoid fermentative processes of the sludge, a total solid concentration higher to 70% must be reached. In same way it is not necessary to reach a value of 90% of Total Solids because a concentration of 80% of Total Solids can allow the same effects of inhibition of bacterial activity.

Table 2.3 Cumulative biogas production from small scale test

% TS	Cumulative biogas production (ml/gTS)
30	94,5
40	98,0
50	19,9
60	9,8
75	1,5
80	<0.1
90	< 0.1

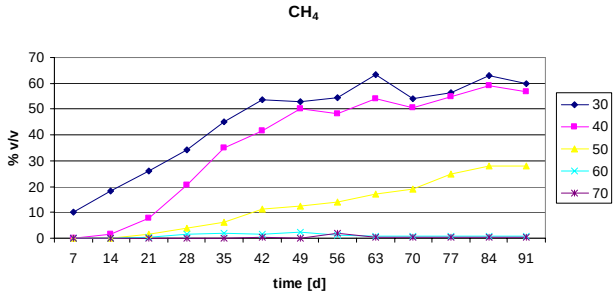

Figure 2.8 Methane concentration in small scale test

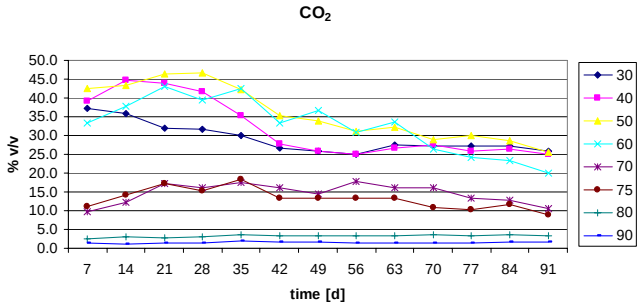

Figure 2.9 Carbon dioxide concentration in small scale test

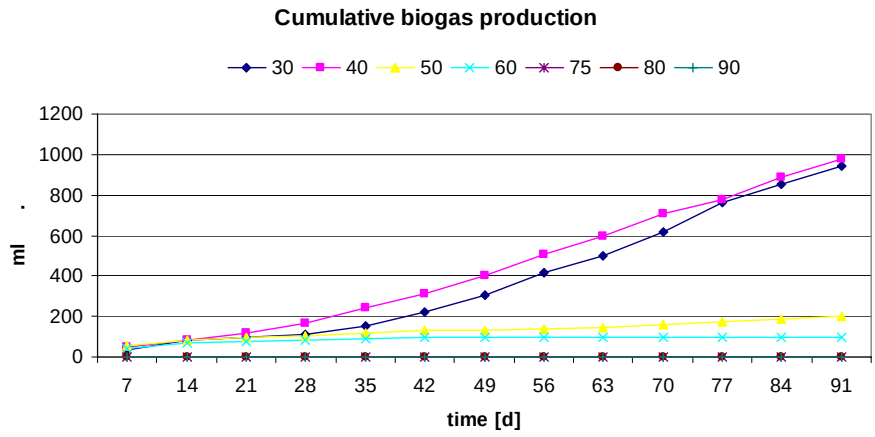

Figure 2.10 Cumulative biogas production in small scale test

The tests realized at large scale have been set up to better understand the threshold value of 75% emerged during experiment in aerobic condition and experiment in anaerobic condition at small scale. The sludge at 30% of Total Solids has hade a high production of biogas. After 90 days of test the total production of biogas has been of 20 litres corresponding to a specific biogas production of 42Nml/gTS. The biogas produced is composed by 60% of methane and 40% of carbon dioxide. This indicates a stable anaerobic condition reached after 15 days of tests. The production of biogas from bottles containing sludge at higher concentration of Total Solids has been strong lower. The specific production of biogas for sludge at 60% of Total Solids has been of 0.2 Nml/gTS. The specific production of biogas for sludge at 75% of Total Solids has been of 0.1 Nml/gTS, while no detectable production of biogas has been measured for sludge at 80% and 90% of Total Solids (Table 2.4). The quality of the biogas produced reflects the same indications (Figures 2.12, 2.13, 2.14, 2.15, 2.16). The concentration of carbon dioxide is high only for sludge at 60% of Total Solids. For sludge at 75% of Total Solids, the concentration of carbon dioxide has been of around 20%. Concentrations of carbon dioxide lower than 5% have been measured for sludge at 80% and 90% of Total Solids. Methane production never reached a stable condition. For all the sludge at Total Solids concentration higher than 60%, the concentration of methane has been lower 1% during the entire period of monitoring. The results obtained with aerobic and anaerobic experiments suggest that a concentration of Total Solids higher than 70% can ensure an inhibition of biological activity, independently by the biodegradability of organic substances contained in the treated sludge. The water content can really play a limiting factor for biological activity. The optimum value of Total Solids for the management of thermal drying system should be selected achieving the two goals of thermal drying system: minimization of density of sludge and minimization of biological activity. The results obtained in the research work can play a role for energy saving because if the density variation of dry sludge is not so high from 60% to 90%, the amount of energy saved and the stability of the process can really increase, just changing the final value of Total Solids from 90% to 75%.

Table 2.4 Cumulative and specific biogas production for large scale test

% TS	Biogas (ml)	ml biogas/ g ST
30	19200	42,6
60	174	0,19
75	64	0,07
80	< 1	< 0.001
90	< 1	< 0.001

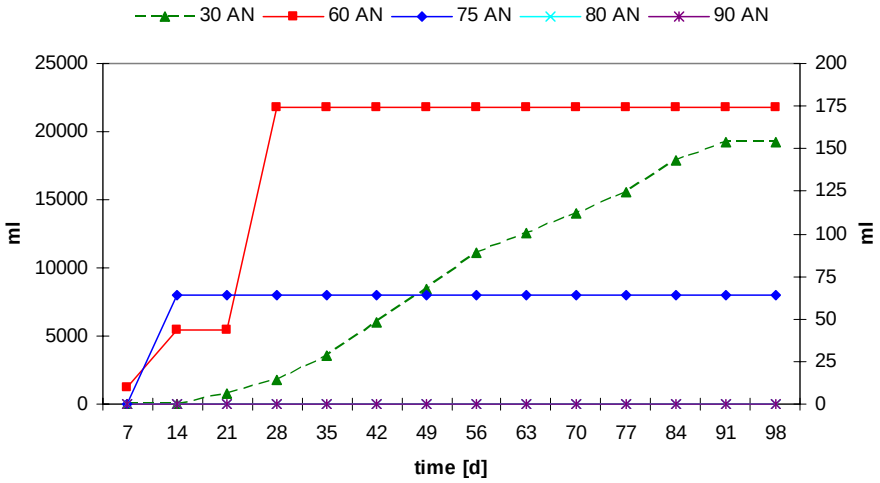

Figure 2.11 Cumulative biogas production for large scale test (Left side axis for 30AN test, right axis for 60AN, 75AN, 80AN, 90AN tests)

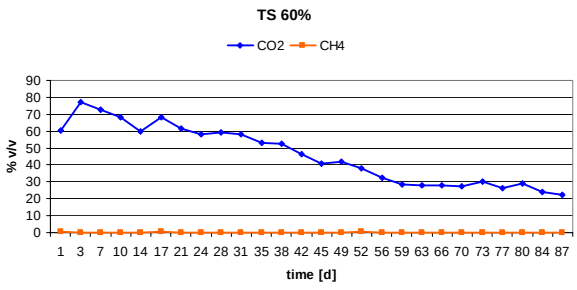

Figure 2.12 Concentration of methane and carbon dioxide in bottle containing sludge at 60% of Total Solids

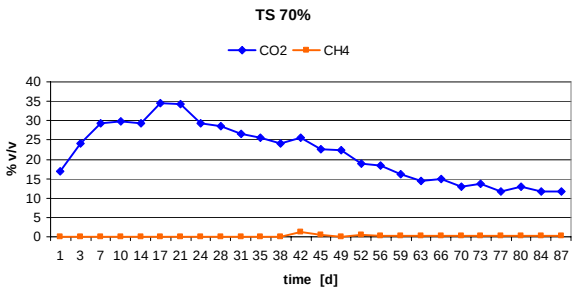

Figure 2.13 Concentration of methane and carbon dioxide in bottle containing sludge at 70% of Total Solids

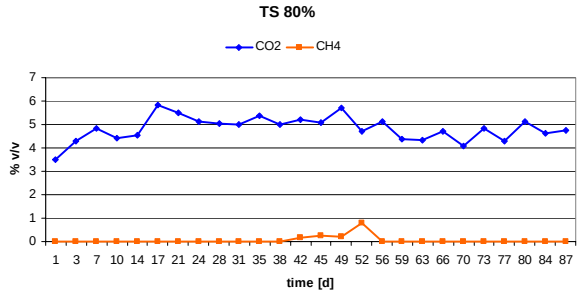

Figure 2.14 Concentration of methane and carbon dioxide in bottle containing sludge at 80% of Total Solids

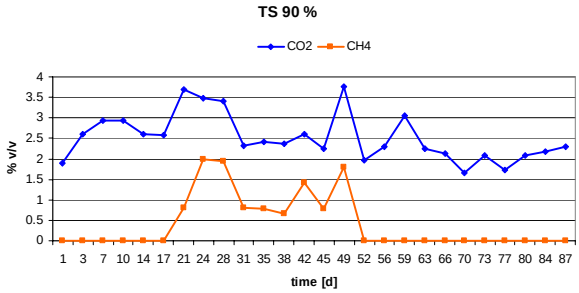

Figure 2.15 Concentration of methane and carbon dioxide in bottle containing sludge at 90% of Total Solids

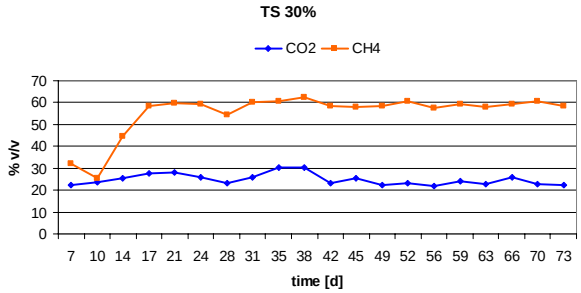

Figure 2.16 Concentration of methane and carbon dioxide in bottle containing sludge at 30% of Total Solids

Chapter 3

BIOLOGICAL HYDROGEN PRODUCTION

Energy is fundamental for life and the development of current society. The global energy request is satisfied from fossil fuels which are currently used as primary energy source and found economic convenience for transport and production of energy for industrial and house requests. Emerging scientific evidences are proving climate change effects from the use of fossil fuels caused by the emissions of COx, NOx, SOx, CxHx, dust and ash, produced during combustion processes and released in atmosphere. Hydrogen is receiving higher interest to avoid fossil fuels consumption and climate changing. It cannot be considered as a primary energy source but it could be transported, stored and used like other primary energy sources. Hydrogen is the most plentiful element in the universe making up about three-quarter of all the matter. The atmosphere contains about 0.07% hydrogen, while the earth's surface contains about 0.14% hydrogen. Hydrogen is the lightest elements. The mass of one litre of hydrogen is 0.09 g, while the mass of one litre of air is about 1.2 g. Due to its clean and high energy yields (122 kJ/g) hydrogen is a promising candidate as an ideal fuel in the future. In addition, hydrogen has great potential for use as primary or secondary energy source for chemical synthesis or for electrical storage and generation with fuel cells. To avoid carbon dioxide emission in atmosphere, hydrogen has to be produced from renewable source.

Nearly 90% of hydrogen is actually produced by the reaction of natural gas or light oil fraction with steam at high temperatures (steam reforming). Coal gasification and electrolysis of water are other industrial methods for hydrogen production (Das, 2001).

Hydrogen has various uses, which can be broadly divided into the following categories:

- As a reactant in hydrogenation processes: hydrogen is used to produce lower molecular weight compounds, saturate compounds, crack hydrocarbons or remove sulphur and nitrogen compounds.

- As an O2 scavenger: hydrogen is used to chemically remove trace amount of O2 to prevent oxidation and corrosion.
- As a fuel in rocket engines.
- As a coolant in electrical generators to take advantage of its unique physical properties.

The above stated areas of hydrogen utilization is equivalent to 3% of the energy consumption today, and is expected to grow significantly in the years to come.

At present hydrogen is produced mainly from fossil fuels, biomass and water. The methods of hydrogen production from fossil fuels are:

- Steam reforming of natural gas.
- Thermal cracking of natural gas
- Partial oxidation of heavier than naphtha hydrocarbons.
- Coal gasification.

Methods of hydrogen production from biomass are:

- Pyrolysis or gasification (which produces a mixture of gases, i.e. H_2, CH_4, CO_2, CO, N_2).

Methods of hydrogen production from water are:

- Electrolysis.
- Photolysis.
- Thermochemical process.
- Direct Thermal decomposition or thermolysis.
- Biological production.

The industrial methods for the production of hydrogen mainly consume fossil fuel as energy source, and sometimes hydroelectricity. However, both thermochemical and electrochemical hydrogen generation processes are energy intensive and not always environmental friendly. Hydrogen is strategically important as it has low emission, is environmental-benign, cleaner and more sustainable energy system. Biological Hydrogen Production is an interesting opportunity to produce hydrogen from renewable source, at low costs and sustainable environmental impacts. Biological Hydrogen Production processes also involved the production of CO_2. However, this CO_2 is released from biomass, in which it was recently taken up, which is in contrast to fossil fuels, where the carbon dioxide has taken millions of years to build up, while the release only takes decades. So the duration of the carbon cycle is very important in view of sustainability, which biohydrogen truly is. Biological hydrogen production processes are mostly operated at

ambient temperatures and pressure, thus less energy intensive than the actual production processes. The biological processes are not only environmental friendly, but also they lead to open a new avenue for the utilization of renewable energy sources which are inexhaustible. In addition, they can also use various waste materials, which facilities waste recycling. Biological Hydrogen production can be considered the last, clean and environmental friendly energetic system.

Most biologically produced H_2 in the biosphere is evolved in microbial fermentation process. These organisms decompose organic matter to CO_2 and H_2. The reduction of protons to H_2 serves to dissipate excess electrons within the cell and generally permits additional energy-generating steps in metabolism. The produced H_2 gas is usually taken up directly by H_2 consumers within the same ecosystem. These organisms use the reducing power of H_2 to drive metabolic processes. H_2 bacteria con even grow autotrophically with H_2 gas as the sole reducing power and energy substrate. In these bacteria, oxygen serves as a terminal electron acceptor; thus, water is formed during the biological reaction. It is estimated that around 200 million tons of H_2 are cycled within these ecosystems per year, the atmosphere only harbors some 7.8×10^{-5} % vol% H_2 (Vijayaraghavan et al, 2004). All processes of biological hydrogen production are fundamentally dependent upon the presence of a hydrogen-producing enzyme. It is hypothetically possible that the quantity or inherent activity of these enzymes could limit the overall process. However, even though the catalytic activity of the various enzymes differs enormously, there is no evidence for the quantity of hydrogen-producing enzyme being the limiting factor in any system currently under study. Indeed, in many microbial systems, potential activity far surpasses the amount of hydrogen produced, suggesting that other metabolic factors are limiting. Hydrogen-producing enzymes catalyze what is arguably the simplest chemical reaction: $2H^+ + 2e^- \leftrightarrow H_2$. However, a survey of all presently known enzymes capable of hydrogen evolution shows that they contain complex metallo-clusters as active sites and that the active enzymes units are synthesized in a complex processes involving auxiliary enzymes and protein maturation steps. At present three enzymes out this reaction are know; nitrogenase, Fe-hydrogenas and NiFe hydrogenas.

Biological hydrogen production processes can be calssified as follows:

- Biophotolysis of water using algae and cyanobacteria.
- Photodecomposition of organic compounds by photosynthetic bacteria.
- Fermentative hydrogen production from organic compounds.
- Hybrid systems using photosynthetic and fermentative bacteria.

Table 3.1 Comparison of the synthesis by different technologies.(Levin, 2004)

BioH_2 System	**H_2 synthesis rate (reported units)**	**H_2 synthesis rate (converted units)**	**References**
Direct photolysis	4.67 mmolH_2/l/80h	0.07 mmolH_2/(lxh)	Francou, Vignais, 1984
In direct photlysis	12.6 nmolH_2/ng proteina/h	0.355 mmolH_2/(lxh)	Taguchi, 1996
Photo-fermentation	4.0 ml H_2 /ml/h	0.16 mmolH_2/(lxh)	Melis, 2002
CO-oxidation by *R. gelatinosus*	0.8 mmolH_2/g cdw/min	96.0 mmolH_2/(lxh)	Zhu, 2002
Dark fermentation			
Mesophilic, pure strain	21.0 mmol H_2/l/h	21.0 mmolH_2/(lxh)	Ueno, 1996
Mesophilic, undefined	1600.0 l H_2/m3/h	64.5 mmolH_2/(lxh)	Jouanneau, 1984
mesophilic, undefined	3.0 l H_2/l/h	121.0 mmolH_2/(lxh)	Moran, 1996
Thermophilic, undefined	198.0 mmol H_2/l/24h	8.2 mmolH_2/(lxh)	Lindbald, 2002
Estreme thermophilic, pure strain	8.4 mmol H_2/l/h	8.4 mmolH_2/(lxh)	Kondo, 2002

3.1 DARK FERMENTATION

Hydrogen production by fermentation has been treated with little attention, while hydrogen evolution by photosybthetic microorganism has been extensively studied. The evolution of hydrogen by fermentation has, however, several advantages such as:

- Fermentative bacteria have very high evolution rate of hydrogen.
- They can produce hydrogen constantly through day and night from organic substrates.
- They can have grown rate good for supply of microorganisms to the production systems.

Therefore, the fermentative evolution is more advantageous than photochemical evolution for mass production of hydrogen by microorganisms.

The process of biological hydrogen production that take place independently by the light and in anaerobic condition, is called “dark fermentation”. The hydrogen production by dark fermentation, is part of the anaerobic degradation of organic substances.

The anaerobic digestion is a biochemical process that take place in absence ox oxygen and consist in the demolition of organic biodegradable compounds by means of bacteria with the

production of gas (biogas) composed by 50 – 70 % of methane and with a heating power of 23.000 KJ/Nm^3.

The advantages of anaerobic digestion are well known. The main is that the biogas produced represents a renewable energetic source. Another advantages is that this technology can be utilized in a integrated management system of organic waste with the production of energy which can be converted in electricity or heat (Cossu, 2006).

The anaerobic digestion of organic biodegradable substances is a complex process carried out by different bacteria. Biological hydrogen production shares many common features with methanogenic anaerobic digestion, especially the relative ease with which the two gaseous products can be separated from the treated wastewater. The production of hydrogen take place during the fermentative phase with the production of volatile fatty acids too. These products are converted to acetic acid in the acetogenic phase and then converted to methane and carbon dioxide during the methanogenic phase.

The hydrogen is so converted at the end of the digestion process to methane. The presence of hydrogen in the biogas produced in anaerobic digestion processes for the production of methane is considered as indicator of unbalance conditions between the different phases of the entire process and so an alarm bell.

For the development of the dark fermentation process, the fermentative phase is the one that must be maximized and maintained in stable conditions.

The mixed bacterial communities involved in anaerobic digestion for the production of methane and biological hydrogen production by dark fermentation share some common elements but one important difference: successful biological hydrogen production requires inhibition of hydrogen-using microorganisms such us homoacetogens and methanogens maximized the hydrogen production.

The species *Enterobacter, Bacillus, Clostridium* are knows are hydrogen producing bacteria. Hydrocarbons are the preferred substrates for the production of hydrogen by fermentation. Glucose, isomers of glucose and polymers of starch and cellulose produce different quantity of hydrogen depending on fermentative pathway and final products.

The fermentation can carried out at different temperature: mesophilic conditions (25-40°C), thermophilic conditions (40-65°C), extreme thermophilic conditions (65-80°C) or hyperthermophilic conditions (>80°C).

While direct and indirect photolysis systems produce pure H_2, dark fermentation processes produce a mixed biogas containing primarily H_2 and carbon dioxide (CO_2), but which may also contain lesser amounts of methane (CH_4), CO and/or hydrogen sulphide (H_2S).

The main reactions for the production of hydrogen are the following:

$$C_6H_{12}O_6 \rightarrow CH_3CH_2CH_2COOH + 2CO_2 + 2H_2$$

$$C_6H_{12}O_6 + 6H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2$$

$$CH_3CH_2COOH + 2H_2O \rightarrow CH_3COOH + CO_2 + 3H_2$$

$$CH_3CH_2CH_2COOH + 2H_2O \rightarrow 2CH_3COOH + 2H_2$$

$$CH_3CH_2OH + H_2O \rightarrow CH_3COOH + 2H_2$$

$$CH_3COOH + 2H_2O \rightarrow 2CO_2 + 4H_2$$

The main reactions that consume hydrogen are the following:

$$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$$

$$C_6H_{12}O_6 + 2H_2 \rightarrow 2CH_3CH_2COOH + 2H_2O$$

$$CH_3COOH + H_2 \rightarrow CH_3CH_2OH + H_2O$$

As already said a wide range of bacteria can convert organic substaces to hydrogen and carbon dioxide and other metabolic products as volatile fatty acids and alcohols. Generally these types of bacteria lives in cooperative conditions with other bacteria that consume hydrogen and the other metabolic products to methane and carbon dioxide. That is the reason because no free hydrogen can be found in nature.

To realize a stable production of hydrogen from organic substances, the bacteria that consume hydrogen must be inhibited or killed in the system.

Characteristics of fermentative bacteria and of methanogenic bacteria are used to inhibit the consumption of hydrogen.

The bacterial that belong to species *Clostridium* and *Bacillus* are able to produce spores to resist to environmental unfavourable conditions as lack of nutrients, unfavourable temperatures or long aerobic conditions.

The characteristic to produce spores of fermentative bacteria, is used to inhibit the methanogenic bacteria. The inhibition is usually obtained realising a thermal stress of biomass. The duration and the level of temperature of the stress depend on type of biomass. During this treatment, the methanogenic bacteria are killed because they are not able to produce spore to survive. Another advantages of thermal stress seems the elimination of bacteria producing lactic acids that compete with hydrogen producing bacteria (Noike et al., 2002).

Another method of inhibition of consumption of hydrogen is the pH. The suggested level is between 4.5 to 6. At these pH values the methanogenic bacteria are strongly inhibited instead of

fermentative bacteria that maintain their activity. The optimum value suggested in the international literature is 5.5.

Another possibility to manage the system is hydraulic retention time in the digester. The growth rate of methanogenic bacteria is slower then the growth rate of fermentative bacteria. Realizing short hydraulic retention time in the operation of digester, the methanogenic bacteria are washed out, instead of fermentative bacteria that remain in the system.

From a metabolic point a view, the biological hydrogen production take place during the oxidation of organic substances to produce acetic acid and carbon dioxide in the synthesis of pyruvic acid. The decomposition of pyruvic acid is catalyzed by the two enzymatic system below (Vijayaraghavan et al, 2004):

1. *Pyruvate: Formate Lyase* (PFL)

   (Pyruvate + CoA) → Acetyl-CoA + Formate

2. *Pyruvate*: *Ferrodoxin Oxido Reductase* (PFOR)

   Pyruvate + CoA + 2 Fd(Ox) → Acetyl-CoA + CO_2 + 2Fd(Red)

In both metabolic processes, the pyruvic acid produces during glycolysis is used in absence of oxygen, to produce Acetyl-CoA from which the ATP can be produce. The pyruvic acid is also used to produce Formate or Ferroxidin in reduced state (Fd_{red}) from which hydrogen rises. The facultative bacteria produce hydrogen from Formate while the strictly anaerobes bacteria produce hydrogen from Ferroxidin in reduced state. The overall production of hydrogen from the above processes is of one or two moles of hydrogen per mole of pyruvic acid produced. This is a natural consequence of natural evolution toward the production of new biomass and not hydrogen.

The biological hydrogen processes are fundamentally dependet by the presence of enzymes that catalyze the simply reaction $2H^+ + 2e^- \rightarrow H_2$. Many organisms contain enzymes, known ad *Hydrogenase*, which carry out the oxidation of hydrogen to protons and electrons or reduction of protons and electrons to hydrogen. The physiological roles of such enzymes are various. It is hypothetically possible that the quantity of these enzymes or their activity can limits the entire process. . However, even though the catalytic activity of the various enzymes differs enormously, there is no evidence for the quantity of hydrogen-producing enzyme being the limiting factor in any system currently under study. Indeed, in many microbial systems, potential activity far surpasses the amount of hydrogen produced, suggesting that other metabolic factors are limiting. However, a survey of all presently known enzymes capable of hydrogen evolution shows that they contain complex metallo-clusters as active sites and that the active enzymes units are

synthesized in a complex processes involving auxiliary enzymes and protein maturation steps. At present three enzymes out this reaction are know; nitrogenase, Fe-hydrogenas and NiFe hydrogenas. The research has long investigated and is still investigating on the role of iron during fermentation processes and on the possible optimal concentration of this metals to enhance the biological process of hydrogen production. Many authors suggest that high concentration of iron during batch test can reduce the lag phase of digestion, enhance the production of hydrogen and change the type and concentration of volatile fatty acids produced during fermentative digestion. The optimal concentration seems to be between 10mg/l and 50mg/l of iron in batch test (Alibardi et al. 2007).

The stoichiometry of reactions reported before indicates that 4 moles of hydrogen can be produced from one mole of glucose when acetic acid is the end product and only 2 moles of hydrogen per mole of glucose when butyric acid is the end product. Unfortunately, optimization of biohydrogen production focuses on a relatively small fraction of the total hydrogen equivalents that are presents in biomass. Actual yields are even lower than the four moles of hydrogen that are theoretically possible. The best results reported in the international literature goes from 2 to 2.4 moles of hydrogen per mole of glucose. The difference between the hypothetical production and the real production is due to the contemporary production of different volatile fatty acids as acetic acid, butyric acid, propionic acid, caproic acid and lactic acid (Fang et al., 2002). For example during the production of lactic acids, no production of hydrogen take place:

$$C_6H_{12}O_6 \rightarrow 2CH_3CHOHCOOH$$

The production of lactic acids seems to be favoured by high partial pressure of hydrogen in the system. The partial pressure of H_2 (pH_2) is an extremely important factor for continuous H_2 synthesis. Hydrogen synthesis pathways are sensitive to H_2 concentration and are subject to end-product inhibition. As H_2 concentration increase H_2 synthesis decrease and methabolic pathways shift to producing more reduced substrates such as lactate, ethanol, acetone, butanol or alanine. As the temperature increase, however, conditions that favour hydrogen production are less affected by H_2 concentration. Continuous H_2 Synthesis requires pH_2 of <50 kPa at 60°C, <20kPa at 70°C and <2kPa at 98°C (Levin *et al.,* 2004). Nitrogen spreading is used to avoid high partial pressure of hydrogen in the reactors as the operation at low pressure (Rechtenbach et al., 2006).

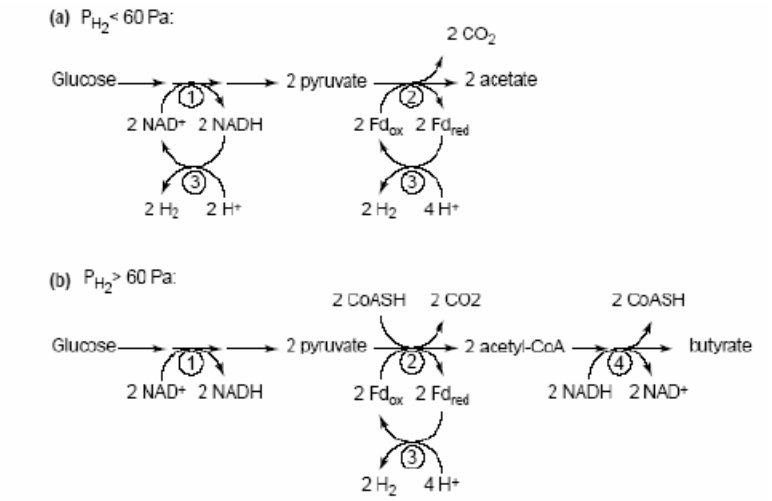

Figure 3.1 Effects of hydrogen partial pressare on metabolic pathway of hydrogen production

The production of volatile fatty acids is also influenced by pH (Fang et al., 2002). The butyric acids is mainly produced in a pH level between 4.0 and 6.0. The concentration of acetic acid and butyric acid is equal at pH level between 6.5 and 7.0. At pH value lower than 5 the production of lactic acid increases. This thwarts the production of acetic acid and butyric acid, consequently the production of hydrogen is inhibited.

The metabolic pathway and mechanisms described are still not clear and they are object of strong research.

Therefore the dark fermentation is non yet a anaerobic digestion process. The dark fermentation process has to optimized to the production of hydrogen an it is not a preliminary step for the production of methane. The production of hydrogen needs the selection of a adequate biomass, the selection of the optimal environmental conditions and the control of important parameters like pH, partial pressure of hydrogen and hydraulic retention time.

The main advantages of dark fermentation are the possibility to produce hydrogen without dependency from a light source, the possibility to digest wastewater, waste or biomass.

It appears that, even under optimized conditions, one cannot expect to recover more than 15% of the electron equivalents in a high-carbohydrate waste or biomass as hydrogen, thus, it is not surprising that several research groups are considering implementing two-steps processes, involving biohydrogen production followed by methanogenic anaerobic digestion to increase the energy yield of the overall process (Angenent et al., 2004). Methanogenic anaerobic digestion is a mature, reliable technology that has been demonstrated in thousands of full-scale facilities worldwide. Therefore, direct biological production of hydrogen through dark fermentation

appears to be restricted to a pre-treatment step in a larger bioenergy or biochemical production concept.

Table 3.2 Maximun hydrogen yields achieved from organic materials by a mixed culture performing dark fermentation durign optimized efforts. (Angenent, 2004)

Optimization effort	**Reactor type**	**Substrate**	**Max. hydrogen yield ($molH_2/molC_6H_{12}O_6$)**	**Reference**
Initial pH ans acetic/butyric acid	Batch	Sucrose/Starch	1.8	Khanal, 2004
Reactor configuration	Fluidizied bed reactor	Sucrose	1.3	Wu, 2003
Hydrogen partila pressure	CSTR	Wheat starch	1.9	Hussy, 2003
Inhibition of acetic/butyric acid	Batch	Glucose	2.0	Chin, 2003
Reactor operation, temperature	Upflow reactor	Wastewater	2.1	Yu, 2002
Immobilized biomass	Batch	Sucrose	2.0	Wu, 2002
Immobilized biomass, granules	Fermentor	Sucrose	2.1	Fang, 2002
pH	Fermentor	Glucose	2.1	Fang, 2002
Hydrogen partial pressure	Batch	Sucrose, Lactate	0.5	Logan, 2002
Hydraulica retention time	CSTR	Glucose, Sucrose	2.2	Chen, 2001
Peptone addition	Batch	Cellulose	2.0	Ueno, 2001
Nitrogen source	Batch	Glucose	2.4	Ueno, 2001
pH and substrate levels	Batch	Sucrose	2.5	Ginkel, 2001
Hydrogen partial pressure	CSTR	Glucose	1.4	Mizuno, 2000

Table 3.3 Merits and demerits of different biological processes for hydrogen production (Das, Veziroglu, 2001)

Type of microorganisms	**Merits**	**Demerits**
Green algae	Can produce hydrogen from water. Solar conversion energy increased by 10 folds as compared to trees, crops.	Requie light for hydrogen production. O_2 can be dangerous for the system.
Cyanobacteria	Can produce hydrogen from water. Nitrogenase enzyme mainly produce H_2. Has the ability to fix N_2 from the atmosphere.	Uptake hydrogenase enzymes are to be removed to stop the degradation of H_2. Require sunlight. About 30% O_2 present in the gas mixture with H_2. O_2 has inhibitory effect on nitrogenise. CO_2 present in the gas.
Photosynthetic bacteria	Can use different waste materials. Can use wide spectrum of light.	Requie light for the hydrogen production. Fermented broth will cause water pollution problem. CO_2 present in the gas.
Fermentative bacteria	It can produce hydrogen all day long without light. It can utilize different carbon sources like, starch, cellobiose, sucrose, xylose, etc. and so different types of raw materials can be used. It produces valuable metabolites such as butyric acid, lactic acid, acetic acid etc. s by products. It is anaerobic process, so there is no oxygen limitation problems.	The fermented broth is required to undergo further treatment before disposal otherwise it will create water pollution problem. CO_2 present in the gas.

3.2 MATERIALS AND METHODS

The substrates used in the research work have been glucose, as model substrate easily degradable, household kitchen waste and tannery sludge. The kitchen waste has been shredded in a kitchen mill before filling the batch tests. The composition of kitchen waste is reported in Figure 3.2. No pre-treatment has been used for enhance the biodegradability of tannery sludge.
Three types of sludge have been used to inoculate the test: granular sludge from an UASB digester treating wastewater from food industry, anaerobic sludge from an anaerobic digester of cow manure and anaerobic sludge from an anaerobic digester of excess sludge from an urban wastewater treatment plant.

All biomasses have been heat pre-treated to inhibit the methanogenic bacteria. The pre-treatment has a different duration dependent by the characteristic of biomass. Granular sludge has been shocked for 4 hours at 100°C, sludge from cow manure digester and sludge from excess sludge digester have been shocked for 30 minutes at 80°C. A thermostatic bath has been used for the thermal shock of biomasses (Figure 3.3).

Laboratory tests have been performed in batch test using one-litre glass bottles (Figure 3.4). The working volume in the bottle has been variable from 300ml to 600ml. These reactors are hermetically closed by means of a silicon plug enabling sampling of the gas and liquid produced in the reactor by a syringe (Figure 3.5).

The bottles have been prepared mixing biomass, substrate and a certain amount of water. Every bottle has been filled with the desired mixture and hermetically closed. The head space of bottles has been saturated of nitrogen to remove the oxygen and to realize perfect anaerobic conditions. Tests have been realized under mesophilic conditions at 35 ± 2°C in a thermostatic bath (Figure 3.6). Bottles have been maintained upside down to realize a hydraulic barrier for biogass.

Each test have had a duration variable from 10 to 50 days, depending on biodegradability of substrate. The test has been stopped when the biogas production was almost zero.

The gas production in terms of volume have been measured by an hydraulic system: the biogas produced during fermentation is directed to a second bottle filled of a saline and acidified solution that avoid biogas dissolution. The over pressure in the second bottle caused by biogas production, move an equal volume of liquid into a cylinder. The volume of the biogas produced is evaluated measuring the liquid volume in the cylinder (Figure 3.7). Gas samples have been taken from top of bottle through silicon top using a syringe. Biogas production and biogas composition in terms of Hydrogen, Carbon Dioxide, Methane have been measured every one or

two days, by a gas chromatograph (GC HP5890) equipped with thermal conductivity detector (TCD) and columns HP- MOLSIV and HP-PLOT U. Nitrogen has been used as carrier gas.
On termination of testing, the composition of the liquid phase have been evaluated to measure the concentration of Volatile Fatty Acids, Alcalinity, Redox potential and Residual Organic Carbon. Volatile Fatty Acids concentrations have been measured by the same gas chromatograph equipped with flame ionization detector (FID) and HP-INNOWAX column.

A nutrient solution have been used during some batch test. The composition of nutrient solution used is reported in Table 3.4. Different quantities of nutrient solution have been chosen for each batch test.

The compositions of each batch test are reported in Table 3.5, Table 3.6 and Table 3.7.

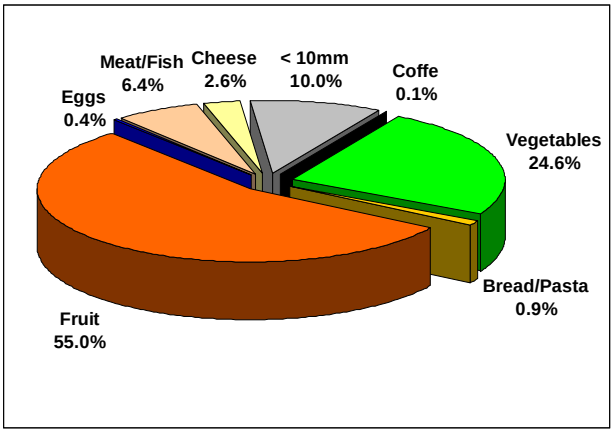

Figure 3.2 Composition of kitchen waste

Figure 3.3 Thermostatic bath used for thermal shock

Figure 3.4 One litre bottles

Figure 3.5 Silicon plug

Figure 3.6 Thermostatic bath

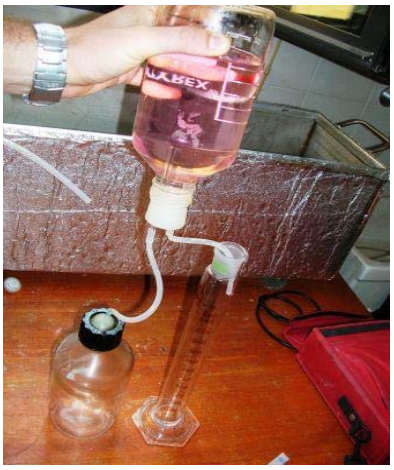

Figure 3.7 Biogas measuring system

Table 3.4. Composition of Nutrient Solution

Compound	Concentration [mg/l]
NH_4Cl	670
KH_2PO_4	500
$NaHCO_3$	63
NaCl	5
$FeSO_47H2O$	2.85
$CaCl_22H2O$	5

Table 3.5. Glucose concentration, type of sludge and nutrient solution for each batch test.

Test Name	Glucose Concentration [g/l]	Type of Sludge	Nutrient Solution [ml/300ml]
FGG 5g/l 25ml	5	Granular	25
FGG 10 g/l 25ml	10	Granular	25
FGG 10 g/l 50ml	10	Granular	50
FGG 10 g/l 75ml	10	Granular	75
FGG 10 g/l 100ml	10	Granular	100
FGG 20 g/l 25ml	20	Granular	25
FGG 20 g/l 50ml	20	Granular	50
FGG 20 g/l 75ml	20	Granular	75
FGG 20 g/l 100ml	20	Granular	100
FZG 5 g/l 25ml	5	Anaerobic	25
FZG 10 g/l 25ml	10	Anaerobic	25
FZG 20 g/l 25ml	20	Anaerobic	25

Table 3.6 Kitchen Waste concentration, type of sludge and nutrient solution for each batch test.

Test Name	Kitchen Wate Concentration [g/l]	Type of Sludge	Nutrient Solution [ml/300ml]
FGFOP 5 g/l	5	Granular	-
FGFOP 10 g/l	10	Granular	-
FGFOP 20 g/l	20	Granular	-
FZFOP 5 g/l	5	Anaerobic	-
FZFOP 10 g/l	10	Anaerobic	-
FZFOP 20 g/l	20	Anaerobic	-

Table 3.7 Tannery Sludge concentration, type of sludge and nutrient solution for each batch test.

Test Name	Tannery Sludge Concentration [gTS/l]	Type of Sludge	Nutrient Solution [ml/300ml]
FGFC 10 g/l	10	Granular	-
FCNFC 10 g/l	10	Anaerobic Excess Sludge	-
FZFC 5 g/l	5	Anaerobic Cow Manure	-
FZFC 10 g/l	10	Anaerobic Cow Manure	-
FZFC 20 g/l	20	Anaerobic Cow Manure	-

3.3 RESULTS

3.3.1 Glucose

Observing the experimental results, the production of hydrogen take place quickly. The higher production rate is within the first 24 or 36 hours for the test at concentration of 5 and 10 g/l of glucose. The production continues with a lower rate to reach the total biogas production from the fourth and the ninth day. The best results have been obtained with concentration of 5g/l and 10 g/l of glucose. The results are comparable with results reported in the international literature about fermentative test using glucose as substrate. It is important to underline that the biogas production do not double, doubling the concentration of glucose. High concentration of substrate can represtent an overloading of the system with high production of volatile fatty acids and consequently a decreasing of pH. The concentration of 20g/l of glucose seems be to high and the pH level decrease quickly to values under the optimal value of 5.5. The fermentative bacteria can survive at pH level under 5.5 but their activity is strongly slowed down. No buffer compounds have in fact been used to stabilize to pH level. The natural buffer capacity of the system can be therefore observed without using buffer compounds. The effects of pH on the production of hydrogen can be observed comparing the tests at different concentration of pH. Doubling the concentration of glucose, the biogas and hydrogen productions do not double. Probably this is due to high production of volatile fatty acids during fermentative processes. When pH decreases to values under 4.5, the bacterial activity is inhibited and the hydrogen production stops even if organic substrate is still available for the degradation.

Comparing the cumulative biogas and hydrogen productions and the behaviour of pH during test inoculated with granular sludge it is possible to underline that the production of hydrogen take place even at pH lower then 5 and it stops at a pH value of 4. Tests inoculated with anaerobic sludge from cow manure digester show that the hydrogen production slows down at pH values under 6 and it stops at pH 5. The optimal pH value depend therefore from the type of biomass and it is not equal for all type of test. The importance of pH level can be observed for the inhibition of methanogenic bacteria instead of enhancement of hydrogen production. It is possible to think that hydrogen production can take place even at neutral pH if the biomass is free of methanogenic bacteria and if the metabolic pathways of hydrogen producing bacteria are forced to hydrogen production with other parameters different from pH. pH remains in any case one of the most important parameters for anaerobic digestion and for hydrogen production too, but if it is possible to realize a stable hydrogen production at neutral pH, the realization of a

double step digestion processes could be easier. The second step of production of methane from residues of hydrogen production phase can be more stable and more reliable if the pH remains neutral in all the degradation processes.

Even the biogas composition seems to be influenced by the pH level and therefore by the buffer capacity of the system. The biogas composition of tests with concentration of glucose of 5g/l and 10g/l, has been of 50% v/v of hydrogen and 50% v/v of carbon dioxide. The biogas composition of tests with concentration of glucose of 20g/l has been higher in carbon dioxide instead of hydrogen. This is probably due to lower hydrogen production due to low pH level and also higher release of carbon dioxide from liquid phase. The carbon dioxide produced could remain in liquid phase as carbon acid for pH level higher than 4.3. At lower pH level then 4.3 the carbon dioxide is completely in gas phase due to the following balance equation.

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$

The productions of hydrogen from glucose inoculated with granular sludge are reported in Figure 3.8 to Figure 3.16. The production of Hydrogen was varying from 25 to 250 Nml H_2/gTS. Converting the volume of Hydrogen in moles the production was varying from 0.25 to 2.1 mole H_2/mole glucose. Similar results have been obtained from glucose inoculated with anaerobic sludge from cow manure digester. The Hydrogen production was varying from 100 to 250 NmlH_2/gTS and from 1.15 to 2.18 mole H_2/mole gluocose (Figure 3.21 and Figure 3.22). Two production rate can be denoted from batch test inoculated with anaerobic sludge from cow manure digester; 50Nml H_2/gTS*d at concentration of 10g/l of glucose and 30NmlH_2/gTS*d at concentration of 5 and 20 g/l of glucose. The same effects can be denoted in batch test inoculated with granular sludge; two production rate can be denoted from Figure 4. Production from 100 to 140 NmlH_2/gTS*d (1.0 mole H_2/mole glucose*d) have been realized in the batch test with lower concentration of glucose or high concentration of nutrient solution. Production around 22 NmlH_2/gTS*d (0.1 mole H_2/mole glucose*d) have been realized in the batch test with higher concentration of glucose or lower concentration of nutrient solution. The higher production rate of Hydrogen can be correlated with a lower production and concentration of volatile fatty acids due to lower concentration of glucose; moreover the higher concentration of ammonia and carbonates in the nutrient solution can limit the crash of pH to values not compatibles with bacterial activity. The concentration of biomass seems do not have influence in hydrogen production and seems do not have higher buffer capacity if higher the concentration is.

Black tests have been carried out to evaluate the potential hydrogen production from biomass. The biomass used has been treated with the same thermal shock used for fermentative test. All

the other conditions have been the same of fermentative test. This test has the aim to verify if the hydrogen production measured during fermentative test comes from substrate or biomass. If the production in this test has the same order of magnitude of the production in fermentative test, the hydrogen produced by biomass has to be subtract from the hole production. The results obtained are reported in Figure 3.23 and Figure 3.24. The production of hydrogen due to endogenous respiration is of 2 or 3 millilitres with a concentration of biomass of 20gTS/l. It possible to conclude that the contribution of endogenous respiration on hydrogen production is negligible and of the same order of magnitude of the errors committed during measurements of quantity and quality of biogas produced.

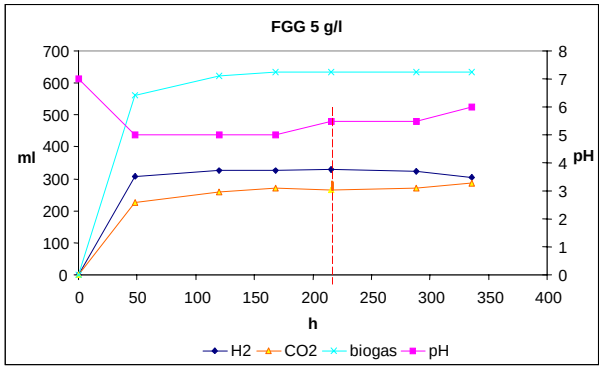

Figure 3.8 Biogas production, composition and pH of glucose 5g/l inoculated with granular sludge

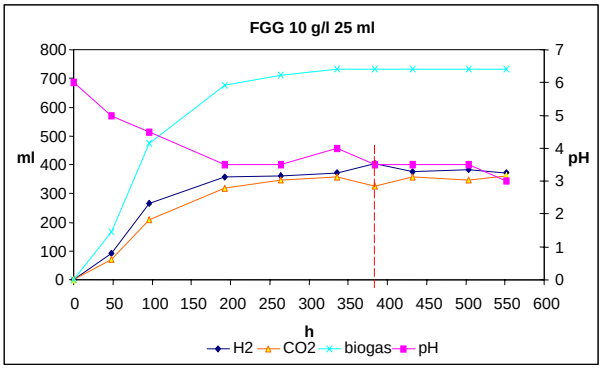

Figure 3.9 Biogas production, composition and pH of glucose 10g/l inoculated with granular sludge

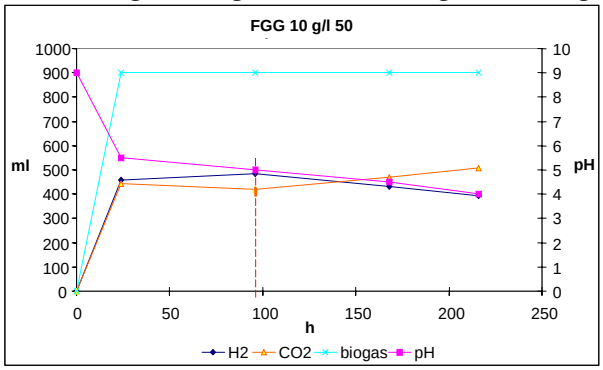

Figure 3.10 Biogas production, composition and pH of glucose 10g/l inoculated with granular sludge

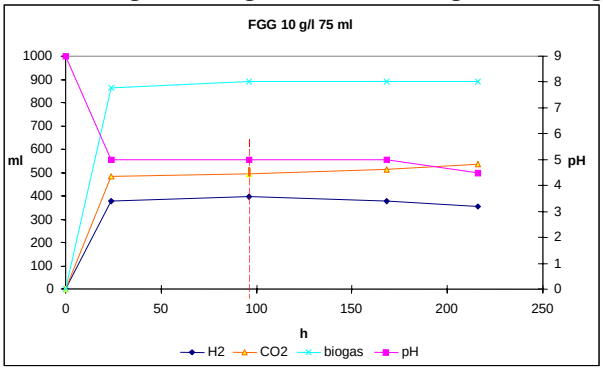

Figure 3.11 Biogas production, composition and pH of glucose 10g/l inoculated with granular sludge

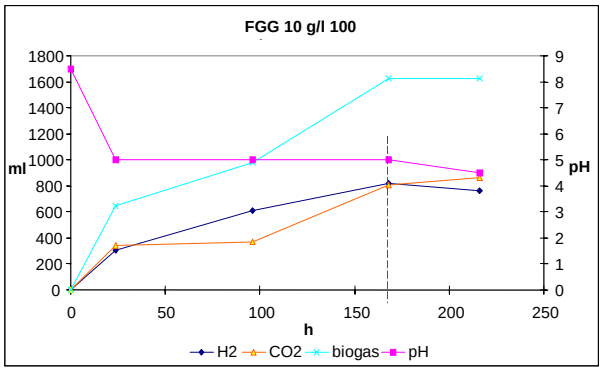

Figure 3.12 Biogas production, composition and pH of glucose 10g/l inoculated with granular sludge

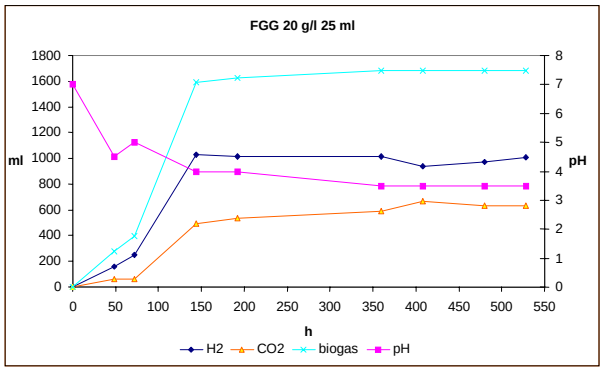

Figure 3.13 Biogas production, composition and pH of glucose 20g/l inoculated with granular sludge

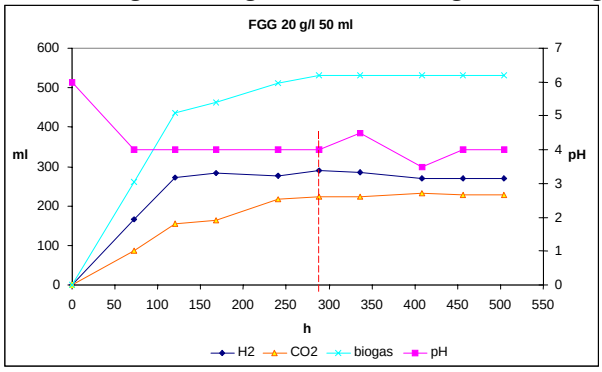

Figure 3.14 Biogas production, composition and pH of glucose 20g/l inoculated with granular sludge

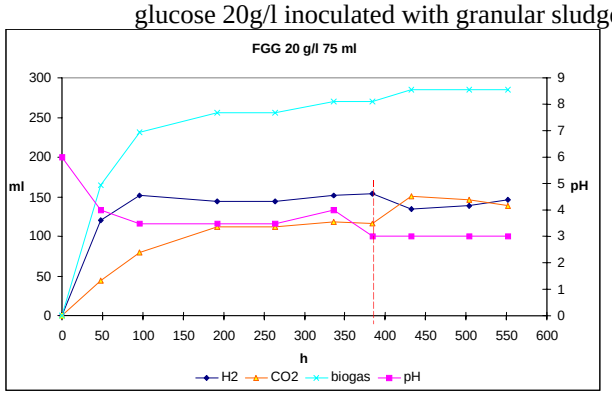

Figure 3.15 Biogas production, composition and pH of glucose 20g/l inoculated with granular sludge

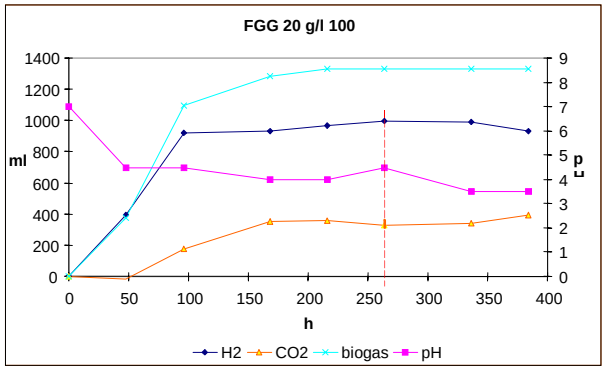

Figure 3.16 Biogas production, composition and pH of glucose 20g/l inoculated with granular sludge

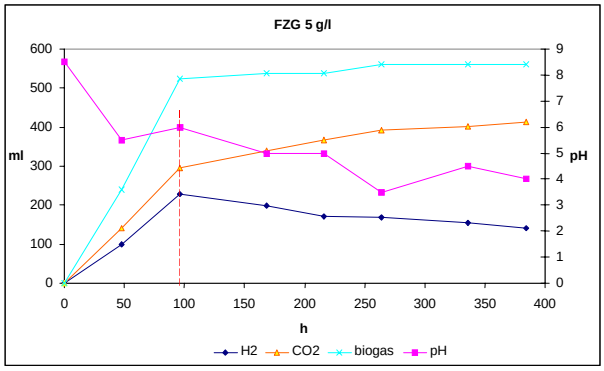

Figure 3.17 Biogas production, composition and pH of glucose 5g/l inoculated with anaerobic sludge

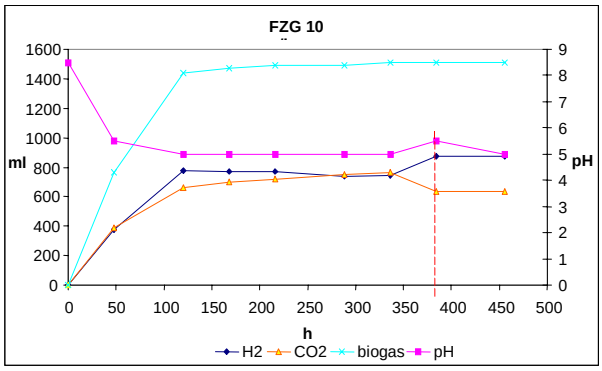

Figure 3.18 Biogas production, composition and pH of glucose 10g/l inoculated with granular sludge

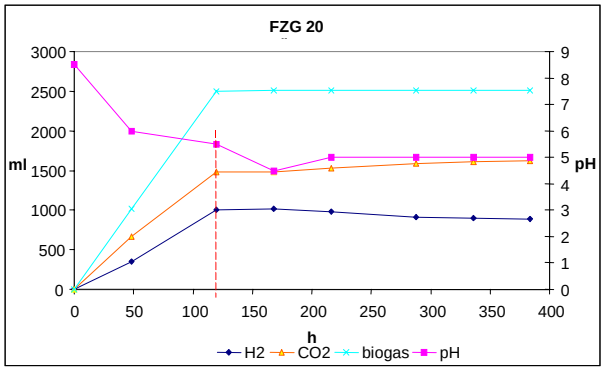

Figure 3.19 Biogas production, composition and pH of glucose 20g/l inoculated with granular sludge

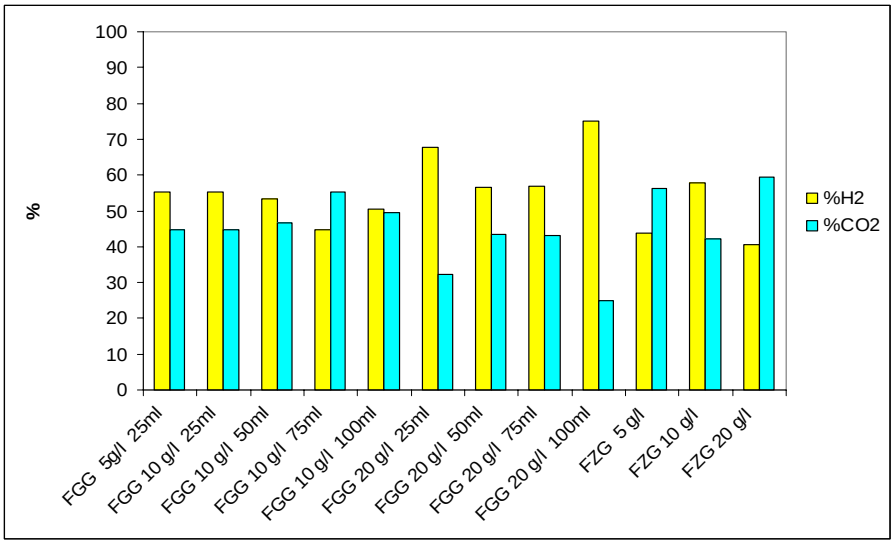

Figure 3.20 Biogas composition of fermentative test with glucose

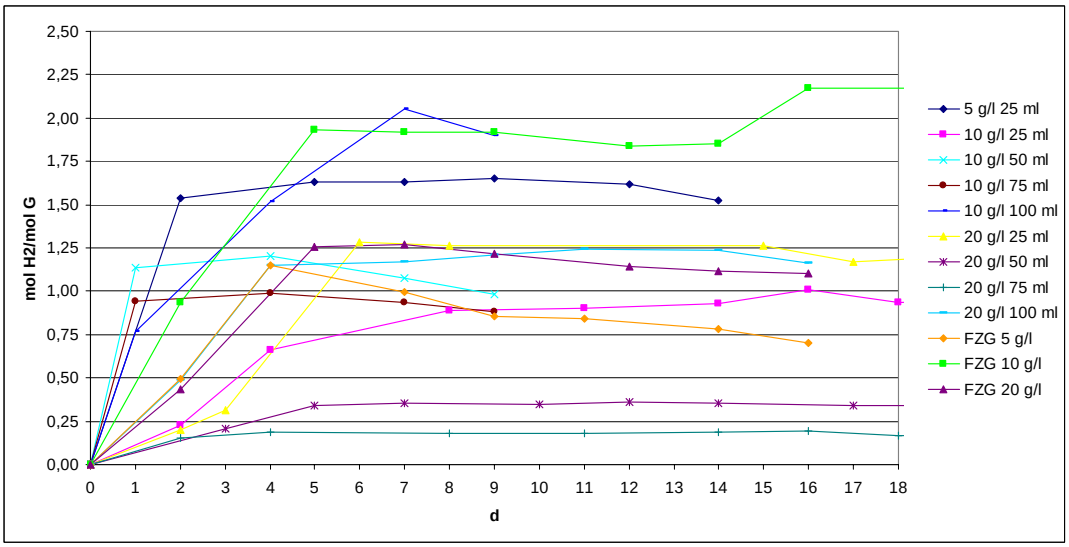

Figure 3.21 Specific cumulative hydrogen production (mole H_2/mole glucose)

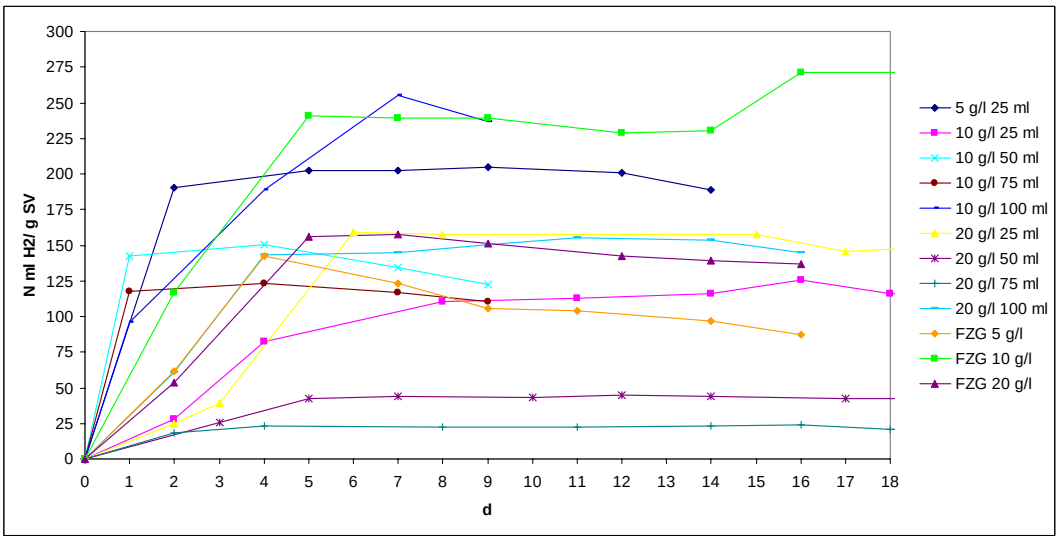

Figure 3.22 Specific cumulative hydrogen production (Nml H_2/g glucose)

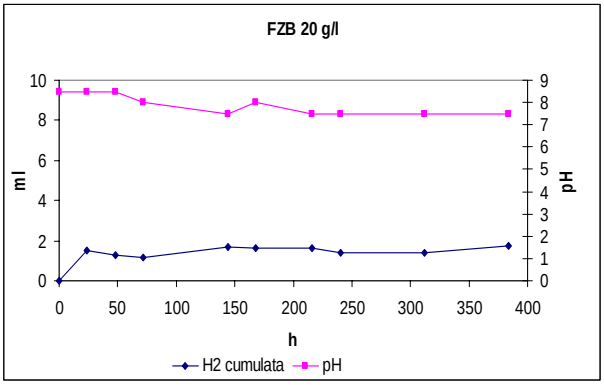

Figure 3.23 Hydrogen production from blank test with anaerobic sludge from cow manure digester

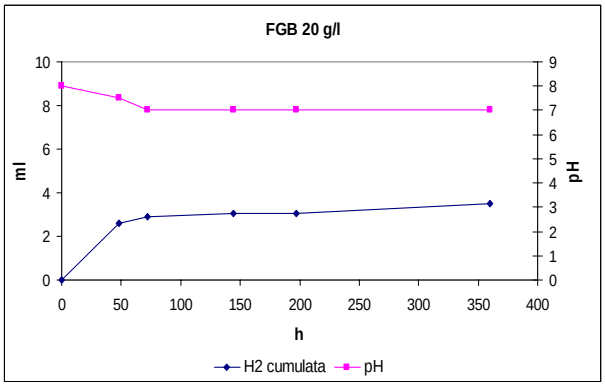

Figure 3.24 Hydrogen production from blank test with granular sludge

Carbon balance

The carbon balance can be a useful tool to analyse the fermentative process and to evaluate the use of available substrate and the production yields.

The production of hydrogen by dark fermentation and in general all biological hydrogen processes, is not correlated to the amount of carbon leaded in the system but with the amount of hydrogen loaded in the system. The hydrogen produced by bacteria derives part from the hydrogen content of organic substrate and part from the hydrogen content of water. Even so the transformations of carbon are useful to understand the carbon dioxide emissions during fermentative phase and the amount of carbon still available to a second phase of anaerobic digestion finalized to produce methane and the characteristics of fermentation products.

The carbon balance for the fermentation test with glucose is reported below.

$$TOC_{start} \rightarrow CO_2 + DOC + Uptake_{biomass} + Err$$

$$DOC = VFA + Other$$

Where:

- TOC_{start} is the amount of carbon in the initial substrate loaded in the system [g].
- CO_2 is the amount of carbon transformed to carbon dioxide at the end of the process [g] .
- DOC is the total amount of dissolved carbon measured in the liquid phase at the end of the fermentative test. It is composed by the total carbon in the volatile fatty acids and the amount of carbon in other dissolved organic compounds.

- *VFA* is the total amount of carbon present in the volatile fatty acids produced during the fermentation test and measured at the end of the process.
- *Other* is the term used to indicate the amount of dissolved ordanic carbon composed by organic compounds different than volatile fatty acids.
- $Uptake_{biomass}$ is the amount of carbon used by biomass to produce new cells. This term is negligible due to low metabolic activity of anaerobic bacteria and due to the shortness of test.
- *Err* is the amount of carbon missing the closure of the balance.

The term *Err* that indicate the missing carbon in the balance is due to mistakes in the measuring system and it is also due to different sensitivity of machines used to measure single terms.

Figure 3.25 reports the graphs of different carbon balance realize for different fermentative tests.

The left column report the initial amount of carbon introduced as glucose. The right column indicate the final condition of carbon after fermentation. The single parts are indicate in percentage.

The experiments shows comparable results for concentration of glucose at 5 g/l and 10g/l. About 30% of carbon is converted to carbon dioxide, about 30% is transformed to volatile fatty acids and the last part is transformed to other dissolved organic compounds. About 60 – 70 % of initial amount of organic carbon remains available at the end of the fermentation process to a second phase of anaerobic digestion to produce methane.

It is possible to suppose that the quality of the biogas produced in a second phase should vary, because a certain amount of carbon dioxide is emitted in the first step. The percentage of methane in the biogas produce in a second phase, after hydrogen production, should be higher.

The fermentative test with 20g/l of glucose and granular sludge, shows low amount of carbon transformed to carbon dioxide. This confirms what already said in biogas production. The low pH level has stopped the process and part of the glucose has not been transformed and it is still present in the liquid phase.

Different results has been obtained from fermentation test with 20g/l of glucose and anaerobic sludge from cow manure digester as inoculum. The carbon transformed to carbon dioxide is high instead of low emission of hydrogen. This is probably due to influence on metabolic pathway of biomass by the pH behaviour.

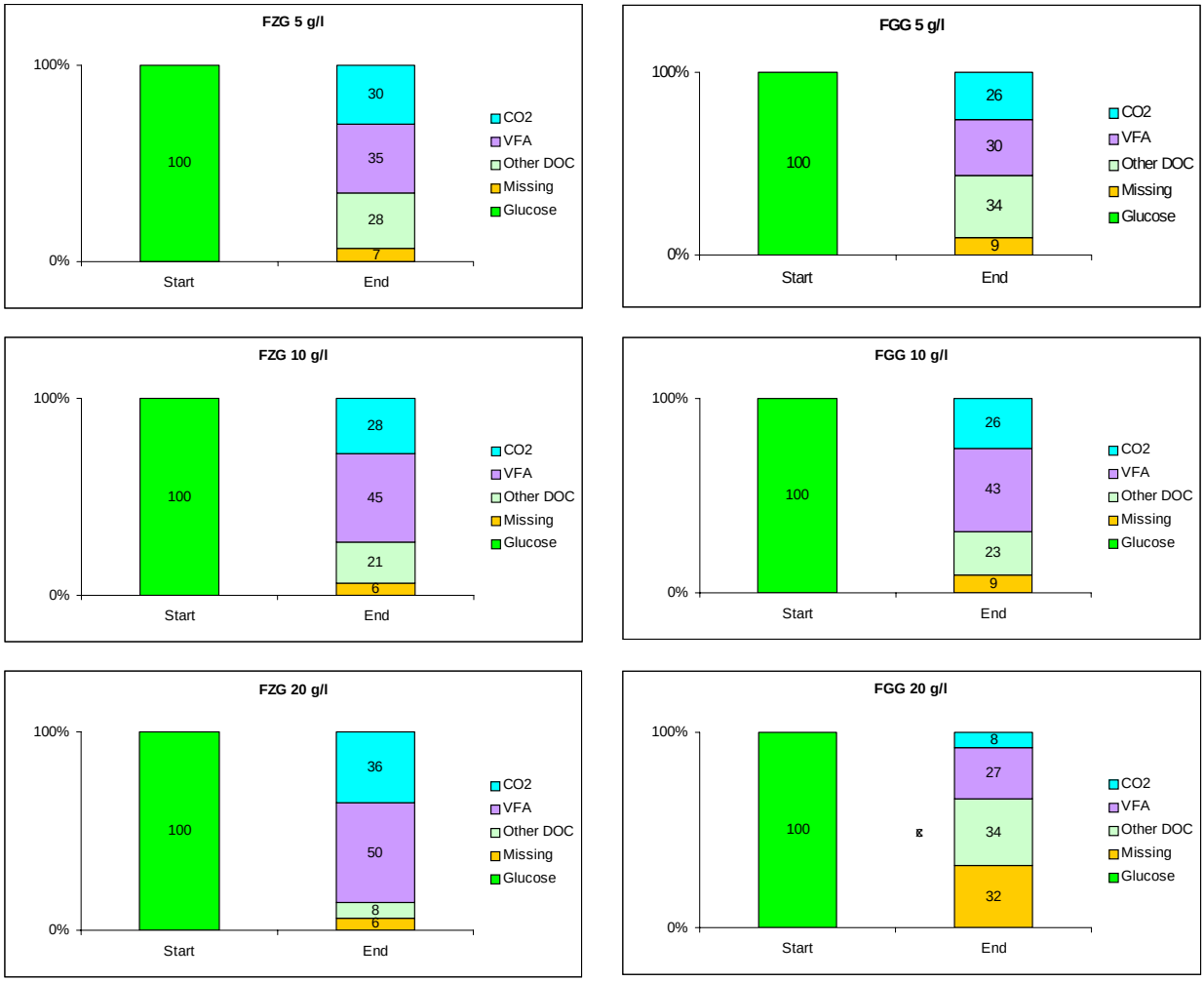

Figure 3.25 Carbon balance of fermentative test inoculated with anaerobic sludge from cow manure digester (left) and granular sludge (right)

3.3.2 Effects of iron on dark fermentation

Hydrogenase is the name given to the family of enzymes that catalyze what is seemingly one of the simplest possible chemical reactions, the interconversion of the smallest molecule, hydrogen gas (H_2), and its elementary particle constituents, two protons and two electrons: $2H^+ + 2e^- <> H_2$. Representatives of most prokaryotic genera, as well as a few eukaryotes, metabolize hydrogen gas and contain hydrogenase. The enzyme was discovered in the 1930s, its requirement for iron was established in the 1950s, and, in the 1980s, many, but not all, hydrogenases were shown to contain nickel as well as iron. Nickel-iron varieties are usually found in microorganisms that consume hydrogen, whereas those that typically produce hydrogen contain iron-only enzymes (Adams and Stiefel, 1998).

In order to analyse the effects of different iron concentration during dark fermentation for biological hydrogen production, some lab scale tests have been set up using glucose as substrate

and granular sludge and anaerobic sludge as inoculum. The concentration of biomass has been constant for all tests at 10gTS/l. Two concentrations of glucose have been tested: 5g/l and 10 g/l. The concentrations of iron in the liquid phase have been: 0 mg/l, 1 mg/l, 10 mg/l and 50 mg/l. The tests have been carried out using bottles and method already presented in Paragraph 3.2. No buffers have been used to stabilize the pH level in the reactors. As reported in Figure 3.26 to Figure 3.29, the production of hydrogen have been positively influenced by higher concentration of iron. The presence of iron in the liquid phase allow a faster production of hydrogen if compared with batch tests where no iron was added. A production of 1.92 mole H_2/mole glucose have been reached with glucose at 5g/l and granular sludge with an iron concentration of 10mg/l. All batch tests was not buffered and the pH decreased quickly in all tests. As shown in Figure 3.27 and Figure 3.29, not always doubling the concentration of glucose, the production of hydrogen was doubling. The pH was crashing too rapidly at high concentration of glucose and the production of hydrogen have been stopped before reaching the maximum level. Despite the maximum hydrogen production have not been reached, the tests have shown as higher concentration of iron have positive effects on dark fermentation. Higher production of acetic acid (CH_3COOH) have been measured in bath test with higher concentration of iron, so high concentration of iron seems to favour metabolic pathway producing acetic acid despite of other volatile fatty acids (Table 3.9). As reported in Paragraph 3.1, acetic acid production is related with the production of 4 mole of hydrogen per mole of glucose.

Table 3.8 Glucose concentration, type of sludge and iron concentration for each batch test.

Test Name	Glucose Concentration [g/l]	Type of Sludge	Iron Concentration [mgFe/l]
FGG 5 0mgFe/l	5	Granular	0
FGG 5 1mgFe/l	5	Granular	1
FGG 5 10mgFe/l	5	Granular	10
FGG 5 50mgFe/l	5	Granular	50
FGG 10 0mgFe/l	10	Granular	0
FGG 10 1mgFe/l	10	Granular	1
FGG 10 10mgFe/l	10	Granular	10
FGG 10 50mgFe/l	10	Granular	50
FZG 5 0mgFe/l	5	Anaerobic	0
FZG 5 1mgFe/l	5	Anaerobic	1
FZG 5 10mgFe/l	5	Anaerobic	10
FZG 5 50mgFe/l	5	Anaerobic	50
FZG 10 0mgFe/l	10	Anaerobic	0
FZG 10 1mgFe/l	10	Anaerobic	1
FZG 10 10mgFe/l	10	Anaerobic	10
FZG 10 50mgFe/l	10	Anaerobic	50

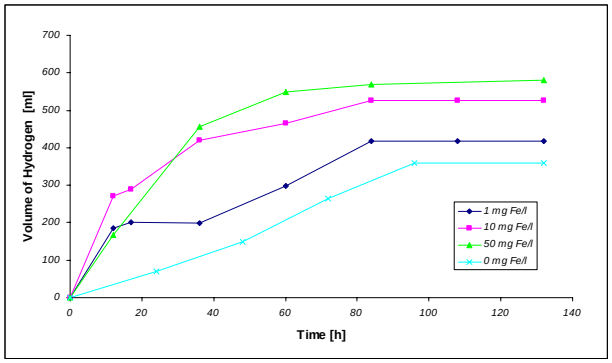

Figure 3.26 Hydrogen production from glucose at 10g/l and granular sludge

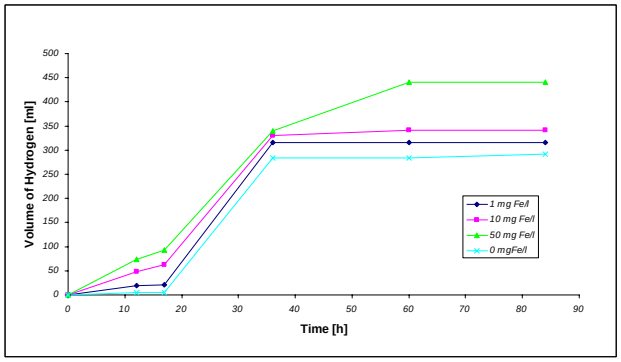

Figure 3.27 Hydrogen production from glucose at 10g/l and anaerobic sludge

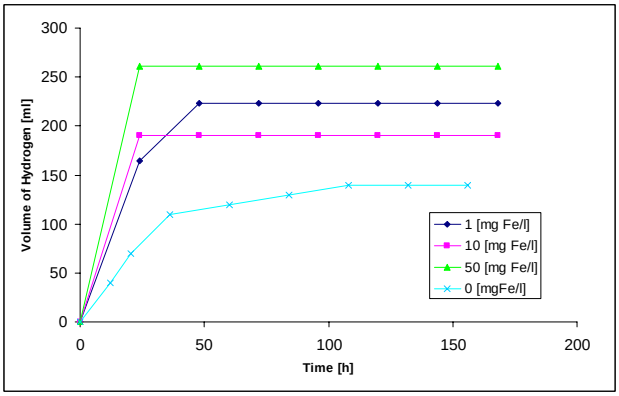

Figure 3.28 Hydrogen production from glucose at 5g/l and granular sludge

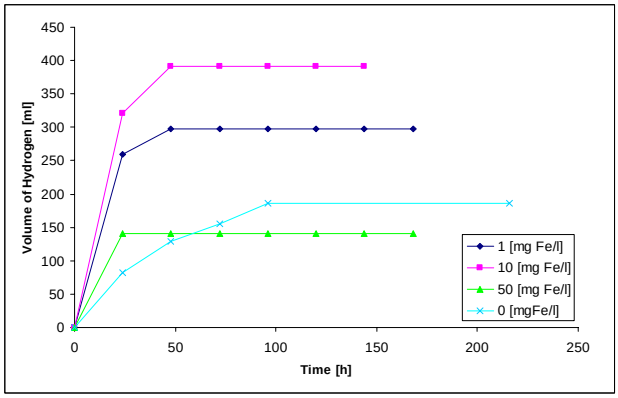

Figure 3.29 Hydrogen production from glucose at 5g/l and anaerobic sludge

Table 3.9 Percentage of contribution on total hydrogen production from some volatile fatty acids depending on iron concentrations

TEST	Iron Concentration [mg/l]	VFA type	VFA [mole]	Theoric moleH_2/mol	H_2 [mole]	Total H_2 [mole]	% of production
FGG 5	1	Acetic	0.000505	4	0.00202	*0.0122*	17
		Propionic	0.000358	2	0.000716	*0.0122*	6
		Butyric	0.000386	2	0.000772	*0.0122*	6
		Valeric	0.000419	3	0.001257	*0.0122*	10
	10	Acetic	0.000512	4	0.002048	*0.0160*	13
		Propionic	0.000331	2	0.000662	*0.0160*	4
		Butyric	0.00045	2	0.0009	*0.0160*	6
		Valeric	0.000381	3	0.001143	*0.0160*	7
	50	Acetic	0.000605	4	0.00242	*0.0057*	42
		Propionic	0.000387	2	0.000774	*0.0057*	13
		Butyric	0.000603	2	0.001206	*0.0057*	21
		Valeric	0.000444	3	0.001332	*0.0057*	23
FGG 10	1	Acetic	0.001487	4	0.005948	*0.0171*	35
		Propionic	0.001385	2	0.00277	*0.0171*	16
		Butyric	0.001349	2	0.002698	*0.0171*	16
		Valeric	0.001122	3	0.003366	*0.0171*	20
	10	Acetic	0.001348	4	0.005392	*0.0215*	25
		Propionic	0.000937	2	0.001874	*0.0215*	9
		Butyric	0.001041	2	0.002082	*0.0215*	10
		Valeric	0.000792	3	0.002376	*0.0215*	11
	50	Acetic	0.002569	4	0.010276	*0.0238*	43
		Propionic	0.00318	2	0.00636	*0.0238*	27
		Butyric	0.001831	2	0.003662	*0.0238*	15
		Valeric	0.001094	3	0.003282	*0.0238*	14
FZG 5	1	Acetic	0.000581	4	0.002324	*0.0091*	25
		Propionic	0.000284	2	0.000568	*0.0091*	6
		Butyric	0.000565	2	0.00113	*0.0091*	12
		Valeric	0.00034	3	0.00102	*0.0091*	11
	10	Acetic	0.000719	4	0.002876	*0.0078*	37
		Propionic	0.000348	2	0.000696	*0.0078*	9
		Butyric	0.000471	2	0.000942	*0.0078*	12
		Valeric	0.000349	3	0.001047	*0.0078*	13
	50	Acetic	0.000713	4	0.002852	*0.0107*	27
		Propionic	0.000325	2	0.00065	*0.0107*	6
		Butyric	0.000442	2	0.000884	*0.0107*	8
		Valeric	0.000294	3	0.000882	*0.0107*	8
FZG 10	1	Acetic	0.001329	4	0.005316	*0.0172*	31
		Propionic	0.006589	2	0.013178	*0.0172*	77
		Butyric	0.001106	2	0.002212	*0.0172*	13
		Valeric	0.000717	3	0.002151	*0.0172*	13
	10	Acetic	0.001373	4	0.005492	*0.0130*	42
		Propionic	0.007663	2	0.015326	*0.0130*	118
		Butyric	0.000966	2	0.001932	*0.0130*	15
		Valeric	0.000785	3	0.002355	*0.0130*	18
	50	Acetic	0.001263	4	0.005052	*0.0171*	29
		Propionic	0.004658	2	0.009316	*0.0171*	54
		Butyric	0.000938	2	0.001876	*0.0171*	11
		Valeric	0.000683	3	0.002049	*0.0171*	12

3.3.3 Kitchen waste

The hydrogen production during fermentative test of kitchen waste are lower to the productions obtained by experiments with glucose. The fermentation in this case is slower due to the lower biodegradability of the substrate and the necessity of a hydrolytic phase to make organic substances available to bacteria. The hydrolytic phase take place in the first part of digestion, during this phase low or no production of biogas can be observed. The hydrogen production is slackened if compared to test with glucose. The hydrogen production take place within the first 50 or 70 hours from the beginning of the experiment for fermentative test of kitchen waste at concentration of 5gTs/l, 10gTS/l and 20gTS/l.

During all the tests, no production of methane has been measured. This indicate that the thermal shock of biomass has a good effect of inhibition of methanogenic bacteria.
Figure 3.30 and Figure 3.31 report the cumulative hydrogen production of experiments per gram of Total Solids, and the final pH value.

The pH during fermentative test of kitchen waste has been always stable between a value of 5 and 6. Only during fermentative test at high concentration of kitchen waste (25 gTS/l and 50 gTS/l) the pH decreased to a value of 4.5, but far from the beginning of the test. This is due to high buffer capacity of kitchen waste. Salts and carbonates present in the kitchen waste can contribute to maintain the pH level around 5.5, the optimal value suggested in the international literature.

The results of hydrogen production from kitchen waste are reported in Figure 3.32 to Figure 3.40. The production of hydrogen was varying from 25 to 45 NmlH_2/gVS from test inoculated with granular sludge. Better results have been reached with anaerobic sludge; the hydrogen production was varying from 60 to 65 NmlH_2/gVS. The final pH value was of 5-5.5 for granular sludge tests and 5.5-6 for anaerobic sludge.

Considering that not all the substrate loaded in the system is biodegradable, and considering that part of the biodegradable substrate could not be assimilated by bacteria, the production of hydrogen per gram of fermented volatile solid can be calculated. From the carbon balance reported in following paragraphs it is possible to calculate the amount of solids fermented in the fermentation test. The results are reported in Table 3.10. The productions of hydrogen are about two times higher than the production calculated per gram of volatile solids loaded in the batch test. The obtained results are perfectly comparable with what is present in the international literature. Not so many results are reported in the international literature on biological hydrogen

production from kitchen waste. The results reported in the literature indicate the total production of hydrogen per gram of fermented volatile solids.

Muntoni ed al. (2005) has reached a production of 75 Nml/g $SV_{fermented}$ using the organic fraction of municipal solid waste mixed with wastewater from olive mill. Lay at al (1999) has reported production of 140 Nml/$gTS_{fermented}$ at concentrations of 5g/l of organic fraction of municipal solid waste. Boni et al (2006) reported production of 186 Nml/gVS with a pre-treatment of chemical hydrolysis.

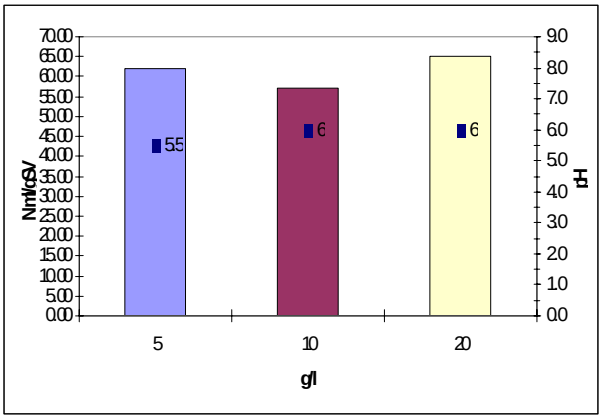

Figure 3.30 Volume of hydrogen produced per gram of volatile solid in batch tests with kitchen waste and anaerobic sludge

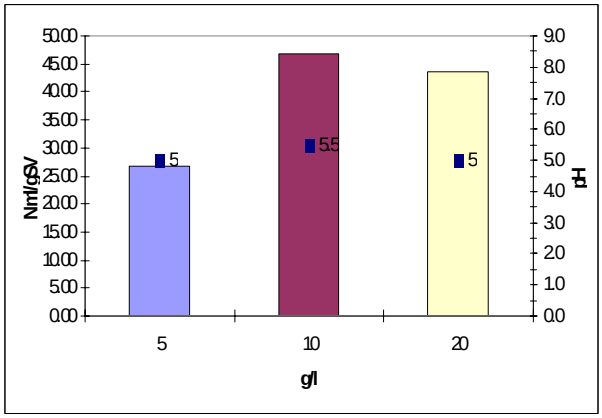

Figure 3.31 Volume of hydrogen produced per gram of volatile solid in batch tests with kitchen waste and granular sludge

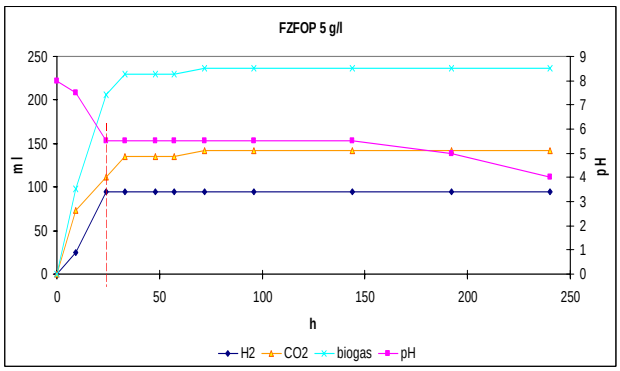

Figure 3.32 Biogas production, composition and pH of kitchen waste 5gTS/l inoculated with anaerobic sludge

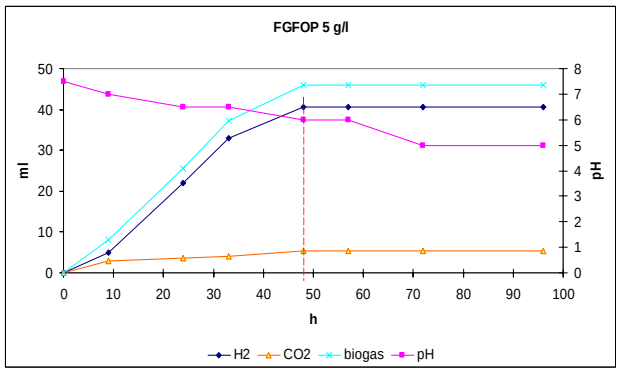

Figure 3.33 Biogas production, composition and pH of kitchen waste 5gTS/l inoculated with granulare sludge

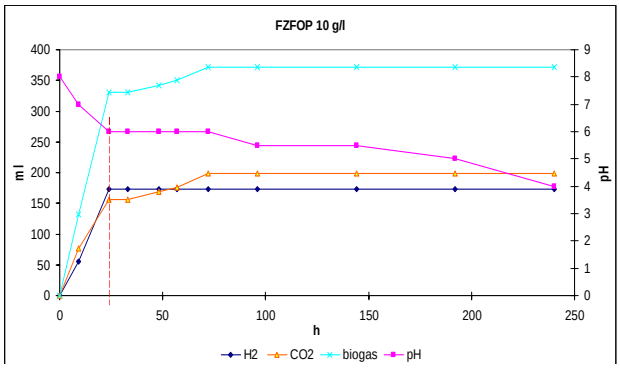

Figure 3.34 Biogas production, composition and pH of kitchen waste 10gTS/l inoculated with anaerobic sludge

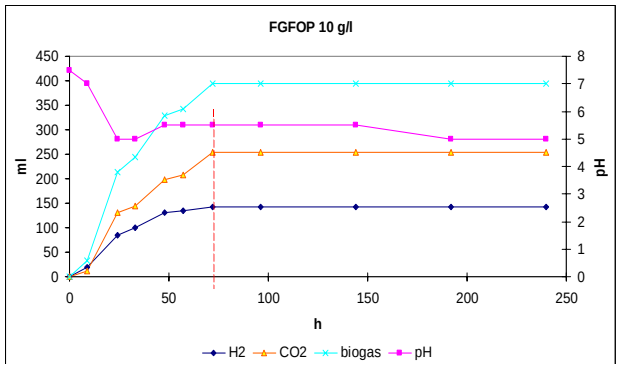

Figure 3.35 Biogas production, composition and pH of kitchen waste 10g/l inoculated with granulare sludge

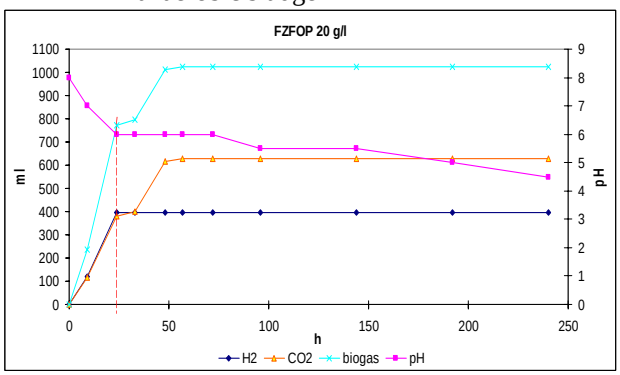

Figure 3.35 Biogas production, composition and pH of kitchen waste 20gTS/l inoculated with anaerobic sludge

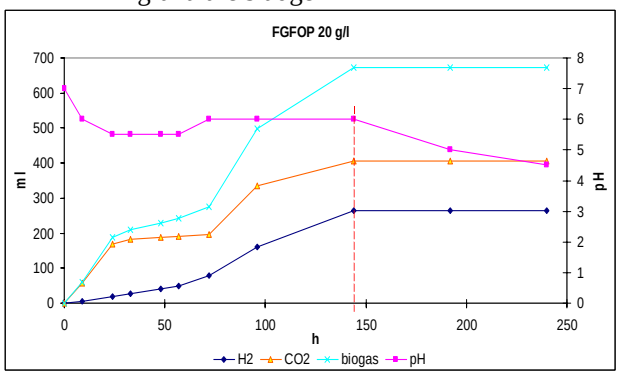

Figure 3.36 Biogas production, composition and pH of kitchen waste 20gTS/l inoculated with granular sludge

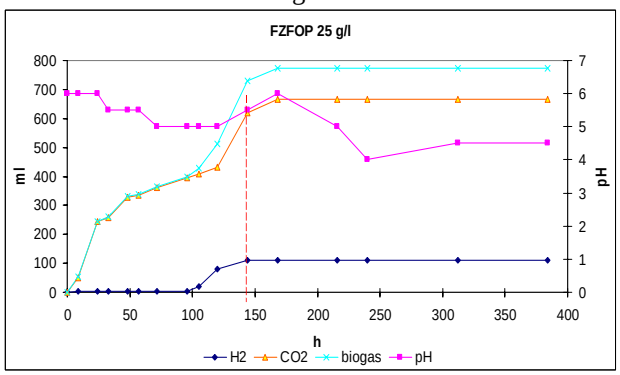

Figure 3.37 Biogas production, composition and pH of kitchen waste 25gTS/l inoculated with anaerobic sludge

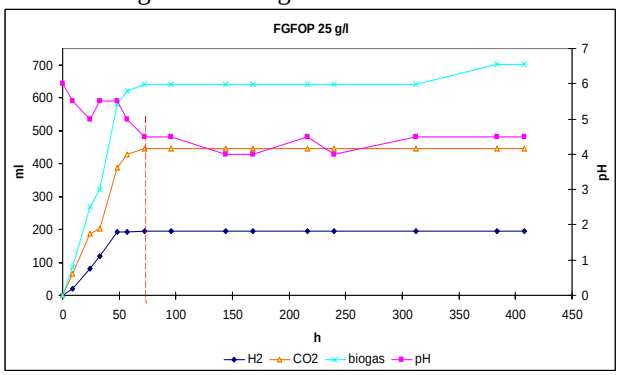

Figure 3.38 Biogas production, composition and pH of kitchen waste 25gTS/l inoculated with granular sludge

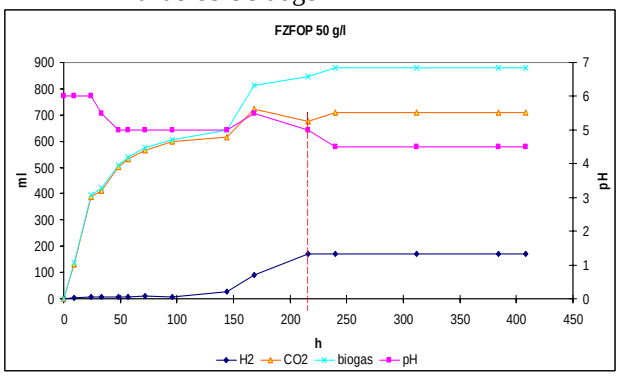

Figure 3.39 Biogas production, composition and pH of kitchen waste 50gTS/l inoculated with anaerobic sludge

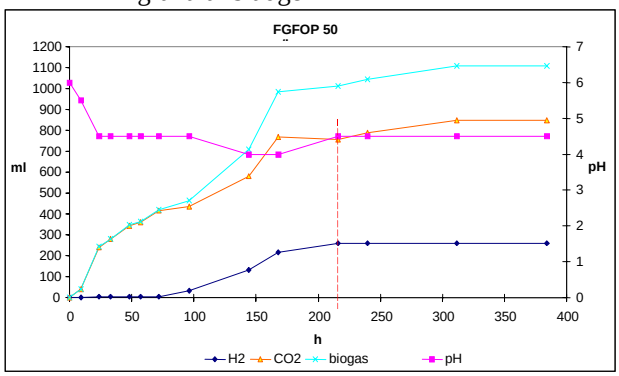

Figure 3.40 Biogas production, composition and pH of kitchen waste 50gTS/l inoculated with granular sludge

Table 3.10 Cumulative hydrogen production from kitchen waste.

	Concentration	Hydrogen Production	
Granular Sludge & Kitchen Waste	5 gTS/l	26.80 Nml/g VS	67.03 Nml/g $VS_{fermented}$
	10 gTS/l	46.71 Nml/g VS	74.13 Nml/g $VS_{fermented}$
	20 gTS/l	43.65 Nml/g VS	89.08 Nml/g $VS_{fermented}$
Anaerobic Sludge & Kitchen Waste	5 g TS/l	58.61 Nml/g VS	80.62 Nml/g $VS_{fermented}$
	10 gTS/l	57.22 Nml/g VS	74.20 Nml/g $VS_{fermented}$
	20 gTS/l	64.93 Nml/g VS	141.15 Nml/g $VS_{fermented}$

Carbon balance

The carbon balance for fermentative experiments with kitchen waste can be realized as reported below.

$$TOC_{start} \rightarrow TOC_{residual} + CO_2 + DOC + Err$$

$$DOC = VFA + Other$$

$$TOC_{start} = TOC_{biomass} + TOC_{KW}$$

$$TOC_{residual} = TOC_{biomass} + TOC_{KW,residual}$$

Where:

- TOC_{start} is the total amount of carbon at the begininnig of test and it is composed by the amount of carbon in the kitchen waste (TOCkw) and the amount of carbon in the biomass. [g]
- $TOC_{residual}$ is the residual amount of carbon in the solid fraction of mixture. [g].
- $TOC_{biomass}$ is the amount of carbon in the biomass. It is suppose to be constant during the fermentation test due to low metabolic activity of anaerobic bacteria and due to the shortness of test.

- CO_2 is the amount of carbon transformed to carbon dioxide at the end of the process [g].
- *DOC* is the total amount of dissolved carbon measured in the liquid phase at the end of the fermentative test. It is composed by the total carbon in the volatile fatty acids and the amount of carbon in other dissolved organic compounds.
- *VFA* is the total amount of carbon present in the volatile fatty acids produced during the fermentation test and measured at the end of the process.
- *Other* is the term used to indicate the amount of dissolved ordanic carbon composed by organic compounds different than volatile fatty acids.
- *Err* is the amount of carbon missing the closure of the balance.

The amount of carbon gasified to carbon dioxide in these fermentative tests is less than the amount of carbon transformed to carbon dioxide in fermentative test with glucose. This is mainly due to a smaller assimilation capacity of bacteria. At the end of test in fact not all the organic substrate has been hydrolysed to dissolved organic compounds.

The amount of organic substrate transformed to volatile fatty acids is comparable to what reported for glucose considering that the amount of organic substrate non hydrolyzed must be erased from the calculation. The best results has been obtained with concentration of 5 and 10 gTS/l inoculated with anaerobic sludge from cow manure digester. This is due to a better distribution of biomass in the mixture that allows a better degradation of substrate. The granular sludge seems to shows a lower activity of degradation. The granules has a defined surface of contact with substrate smaller than the contact surface of anaerobic sludge. The hydrolytic activity and degradation should be lower because the amount of substrate available to granules is the only the one in the around of single granules.

Table 3.11 Carbon balance for batch test with kitchen waste as substrate.

	Starting Carbon Quantity [g]	Carbon Gassified [g]	Carbon Gassified [%]	Dissolved Carbon [g]	Carbon Dissolved [%]	Residual Carbon [g]	Residual Carbon [%]
FGFOP 5 g/l	0.75	0.005	0.62	0.30	39.82	0.34	45.63
FGFOP 10 g/l	1.51	0.17	11.59	0.78	51.76	0.34	22.71
FGFOP 20 g/l	3.01	0.30	9.85	1.18	39.12	1.12	37.09
FZFOP 5 g/l	0.75	0.12	15.64	0.51	67.29	0.02	3.14
FZFOP 10 g/l	1.51	0.18	11.65	0.98	65.30	0.14	9.12
FZFOP 20 g/l	3.01	0.42	13.89	0.96	31.95	1.21	40.22

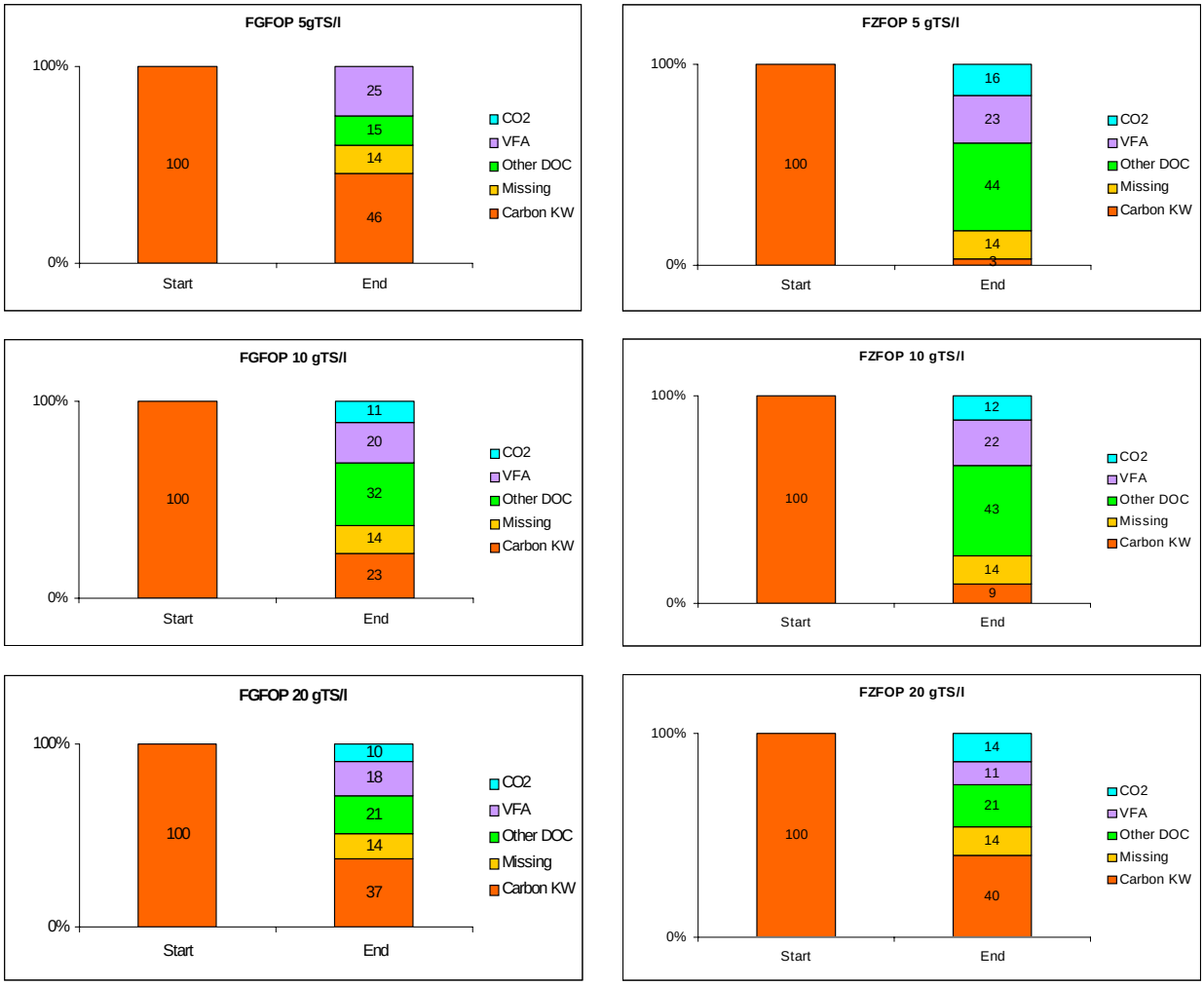

Figure 3.41 Carbon balance of fermentative test inoculated with granular sludge (left) and anaerobic sludge from cow manure digester (right)

3.3.4 Tannery sludge

The results of fermentative test for the biological hydrogen production from tannery sludge reflect the intrinsic problems of such substrate. The sludge is mainly composed by complex organic substances and the biodegradability is slow. A strong hydrolytic phase is request to enhance the availability of substrate to bacteria. The effects of a hydrolytic phase are a low biogas production in the first 100 hours of digestion. After that the biogas production of biogas start and it has gone on for a period of about 35 – 45 days. The pH behaviour is the first parameter to underline. The pH has never reach values lower than 7. The average value during all experiments has been of 7.5. At the same concentration of glucose and kitchen waste, the pH never crashed down. This could be due to the presence of buffer compounds, used during tanning activity and present in the sludge. Also the ammonia buffer effects can be a reason of stability of pH.

Even if the pH never reached the optimal value of 5.5 as indicated in the international literature for hydrogen production, the fermentative tests have produce different amount of hydrogen.

The thermal shock used to inhibit the methanogenic bacteria has had different results. The first test has been realized pre-treating only the biomass used to inoculate the test. The treatment has been the same of what already done with success for test with glucose or kitchen waste. Hydrogen has been produced in this conditions but methane has been produced too. The percentage of hydrogen on the total biogas production has been of 12%. The percentage of methane in the biogas has been of 67%. The residual part is carbon dioxide. Even if the biomass used to inoculate the test has been treated to kill or strongly inhibit the methanogenic bacteria, methane has been still present in the biogas, at higher concentration then hydrogen. This is probably due to the fact that the sludge used contains biomass and so mathanogenic bacteria can be present. The thermal shock has been apply only to the biomass used to inoculate the test. Due to the low biodegradability of substrate, the biogas production started after about ten days. During this phase the methanogenic bacteria could had the possibility to develop and maintain their activity. The hydrogen production started at the same time of methane production but stopped around the twentieth days, while the methane production was still in the exponential phase. The biogas production stopped after forty days of test. The total biogas production has been of 400 Nml/gVS.

The second test realized to enhance the hydrogen production has been realized shocking the mixture of biomass and substrate instead off only biomass used as inoculum. The thermal

treatment has been the same already used in the test with glucose and kitchen waste. The tests inoculated with granular sludge have been shocked for four hours at 105°C. The tests inoculated with anaerobic sludge from a digester of excess sludge have been shocked for thirty minutes at 80°C.

The results show an enhancement of hydrogen production for all the experiments. The production of hydrogen has been variable from 140 to 165 Nml/gVS. These values are about two or three times higher than the productions obtained in the previous test. The thermal treatment of mixture instead of only inoculum has demonstrated good effects. The methane production has take place in any case. The amount of methane produced in these test has been variable from 165 to 220 Nml/gVS. These values are 20% to 40% lower that the production obtained in the first experiments. The percentage of hydrogen in current experiment has been of 37%.

The main difficulty to avoid the methane production could be the low biodegradability of tannery sludge. Even observing the results obtained from the modelling of fermentative processes by Gompertz equation reported in the following paragraph, the lag phase is longer then in case of the organic fraction of municipal solid waste and the biogas production rate and the hydrogen production rate are lower that what obtained in the previous experiments. Probably the low biodegradability of tannery sludge and the fact that this substrate contents different types of biomass allows methanogenic bacterial to maintain or establish again their activity. In case of kitchen waste the production of hydrogen takes place in the first days of experiment instead of tannery sludge where the hydrogen production takes place after a long period of hydrolytic phase. In this long phase probably the methanogenic bacteria, inhibited by thermal shock, establish again their activity.

Methods to enhance to biological activity can be tried to realize a shorter hydrolytic phase. Chemical oxidation of chemical pre-treatments as acidification of basification could breaks the long chain of organic substances in the sludge. The production of undesirable substances must be however checked. Another possibility could be low level of pH, dosing acids to overcome the intrinsic buffer capacity of tannery sludge and inhibit the methanogenic activity.

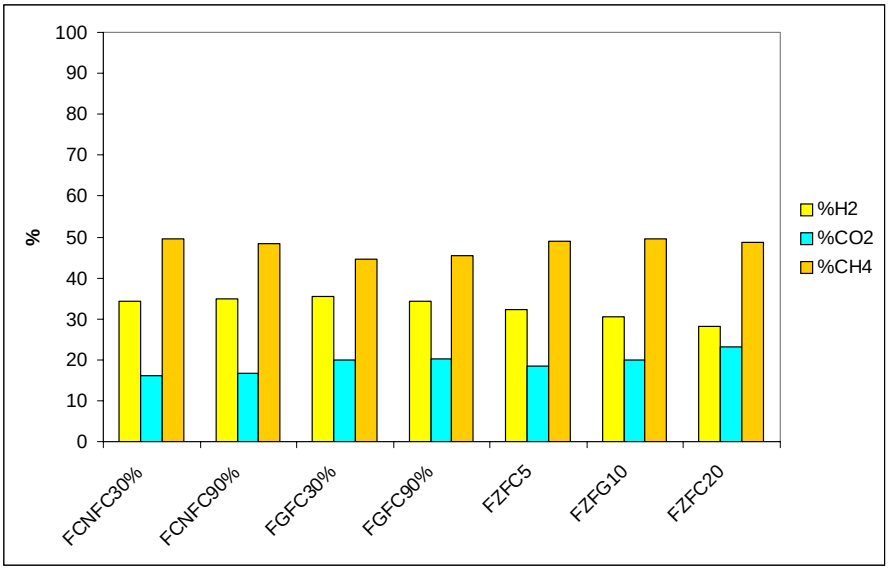

Figure 3.42 Biogas composition of fermentative test with tannery sludge

Table 3.12 Cumulative hydrogen production from tannery sludge and final pH value

	Concentration	Cumulative hydrogen production	Final pH value
Tannery sludge & Granular sludge	10 gSV/l	165 Nml/g VS	7
Tannery sludge & Anaerobic sludge from excess sludge digester	10 gSV/l	140 Nml/g SV	7
Tannery sludge & Anaerobic sludge from cow manure digester	5 gSV/l	80 Nml/g VS	7.5
	10 gSV/l	90 Nml/g VS	7.5
	20 gSV/l	103 Nml/g VS	7.5

3.4 GOMPERTZ EQUATION

The data collected in the experiments have been evaluated by the Gompertz Equation. The aim is to determine the three main parameters that can be taken from the batch test: the duration of lag phase, the specific rate of production and the maximum specific potential production.

The Gompertz equation has been developed to predict the potential production of methane from biodegradable substrates. The same model has been used to evaluate the hydrogen production due to its reliability.

The model proposed that the growth rate of a population of bacteria is not constant but it is dependent by a decreasing exponential rate:

$$\begin{cases} r_g = \dfrac{dP}{dt} = k(t) \cdot P(t) \\ \dfrac{dk}{dt} = -\alpha \cdot k(t) \end{cases}$$

Where:

- P is the growth rate of population
- $k(t)$ is the exponental growth rate
- α is the growth rate

Following:

$$k(t) = k_0 \cdot e^{-\alpha \cdot t}$$

Where k_0 is the initial specific growth rate that decreases exponentially depending of rate α.

The system became:

$$\frac{dP}{dt} = k_0 \cdot e^{-\alpha \cdot t} \cdot P(t)$$

The integral solution is:

$$\int_{P_0}^{P(t)} \frac{dP}{P} = k_0 \cdot \int_0^t e^{-\alpha \cdot t} \cdot dt$$

The result is:

$$P(t) = P_0 \cdot \exp\left[\frac{k_0}{\alpha} \cdot \left(1 - e^{-\alpha \cdot t}\right)\right]$$

Using the above condition, it is possible to obtain the Gompertz equation:

$$N = \int_0^t r_g dt = A \cdot \exp\left\{-\exp\left[\frac{\mu_m \cdot e}{A}(\lambda - t) + 1\right]\right\}$$

Where:

- r_g is the growth rate of bacteria
- A is the maximum growth of bacterial population
- μ_m is the maximum growht rate of the population
- λ is the duration of lag phase

The relation between the growth rate of bacterial population and the consumption rate of substrate can be defined as:

$$r_g = Y_1 \cdot (-r_{su})$$

Where r_{su} is the consumption rate of substrate.

On the other hand the relation between the consumption rate of substrate and the production of methane can be defined as:

$$-r_{su} = Y_2 \cdot r_m$$

Using the last to relations, the methane production rate began:

$$r_m = \frac{r_g}{Y_1 \cdot Y_2}$$

The cumulative methane production can be written as:

$$M = \int_0^t r_m dt = \int_0^t \frac{r_g}{Y_1 \cdot Y_2} dt = \frac{1}{Y_1 \cdot Y_2} \int_0^t r_g dt$$

Substituting in the above formula the integral $\int_0^t r_g dt$, the relation began:

$$M = \frac{A}{Y_1 \cdot Y_2} \cdot \exp\left\{-\exp\left[\frac{(\mu_m / Y_1 \cdot Y_2) \cdot e}{(A / Y_1 \cdot Y_2)}(\lambda - t) + 1\right]\right\}$$

The term $\frac{A}{Y_1 \cdot Y_2}$ can be substetuded by the term P, while the term $\mu_m / Y_1 \cdot Y_2$ can be substituted by the term R_m. The relation began:

$$M = P \cdot \exp\left\{-\exp\left[\frac{R_m \cdot e}{P}(\lambda - t) + 1\right]\right\}$$

The model contains three fundamental parameters:

- M is the cumulative methane production in volume [ml] in a certain time T [h]
- R_m is the production rate of methane, [ml/h]
- λ *[h]* is the duration of lag phase during which no production is expected.
- e = 2.71828

The model can be used to analyze the production of hydrogen during dark fermentation (Oh et al., 2003).

The model began:

$$H(t) = H_{\max} \exp\left\{-\exp\left[\frac{R \times e}{H_{\max}}(\lambda - t) + 1\right]\right\}$$

Where:

- $H(t)$ is the cumulative hydrogen production in volume [ml] in a certain time T [h]
- H_{max} is the total potential production [ml]
- R is the production rate of hydrogen, [ml/h]
- λ is the duration of lag phase during which no production is expected [h].
- e = 2.71828

The terms H_{max}, R and λ are obtained interpolating the experimental results of hydrogen production and minimizing the sum of square errors.

$$\sum_{i=0}^{t}\left(H_{i,teorica} - H_{i,sperimentale}\right)^2$$

The function Solver in Microsoft Excell has been used to obtain the values of H_{max}, R and λ, which minimizes the sum of square errors.

The results obtained in the data analysis are reported in Table 3.13.

	Concentration [g ST/l]	Hmax [ml]	R [ml/h]	λ [h]	Hs [ml/g SV]	Rs [ml/h*g SV]
Kitchen waste & Granular sludge	**5 g/l**	41,49	1,47	7,85	29,64	1,05
	10 g/l	141,65	4,18	4,82	50,59	1,49
	20 g/l	273,08	3,54	45,84	47,89	0,62
	25 g/l	194,87	9,59	17,01	29,13	1,43
	50 g/l	258,00	3,50	96,67	19,29	0,26
Kitchen waste & Anaerobic sludge (Cow)	**5 g/l**	94,35	20,05	7,76	67,39	14,32
	10 g/l	173,63	38,34	7,57	62,01	13,69
	20 g/l	394,06	93,06	7,71	69,14	16,33
	25 g/l	109,35	4,74	101,14	16,35	0,71
	50 g/l	172,23	3,82	141,37	12,87	0,29
Tannery sludge & Granular sludge	**10 g/l**	1312.18	3.25	200	170	0.49
Tannery sludge & Granular sludge	**10 g/l**	1329.69	3.14	180	170	0.42
Tannery sludge & Anaerobic sludge (Excess sludge digester)	**10 g/l**	1034.34	2.98	20	110	0.35
Tannery sludge & Anaerobic sludge (Excess sludge digester)	**10 g/l**	1264.82	3.38	10	135	0.41
Tannery sludge & Anaerobic sludge (Cow)	**5 g/l**	474.51	1.02	197	83	0.24
	10 g/l	907.29	1.90	186	87	0.28
	20 g/l	1838.32	4.47	176	99	0.33

Comparing the results obtained in the modelling of data with Gompertz equation the slow biodegradability of tannery sludge emerges. The lag phase, during which the biogas production is low, is of about 200 hours for tannery sludge inoculated with granular sludge and anaerobic sludge from an anaerobic digester of cow manure. This time is about 8 times higher then the lag phase of kitchen waste. Also the hydrogen production rate of tannery sludge is lower than the production rate of kitchen waste. The values of the production rate have been from 0.35 to 0.49 $NmlH_2/gVSh$. The production rate for kitchen waste has had an average value of 1.05 $NmlH_2/gVSh$ for experiments inoculated with granular sludge while it has had an average value of 14.8 Nml/gVSh for experiments inoculated with anaerobic sludge from anaerobic digester of cow manure.

On the other hand the potential specific hydrogen production from tannery sludge is two or three times higher than the hydrogen production from kitchen waste.

The analysis obtained with the support of Gompertz equation, can confirm the results and discussion reported on previous paragraph. The methane during the fermentative test is produced by methanogenic bacteria that are present in the mixture. The thermal pre-treatment that is used to kill or inhibit the methanogenic bacteria has had good results for glucose and kitchen waste, but it seems not be sufficient for tannery sludge. The long period of digestion probably permit to methanogenic bacteria to resume their activity. Other type of pre-treatment should be useful to divide the anaerobic digestion in two different phases. The first phase of fermentation for the production of hydrogen, with short retention time and lower value of pH, and a second phase of digestion during which methane is produced from volatile fatty acids and other dissolved compounds produced in the fermentative phase.

Chapter 4

AEROBIC STABILIZATION

When solid waste is landfilled without pretreatment, emissions occur during and after the landfill operation in the form of biogas and polluted leachate. The amount of such fluxes depend on composition of waste and climatic conditions of landfill site. The chemistry of landfilled municipal waste is dominated by decomposition processes. Decomposition processes in landfills usually take place under anaerobic conditions and are therefore fairly long-term (up to several decades). Landfill gas and long-term leachate emissions cannot be prevented in case of reactor landfills.

Uncontrolled escape of landfill gas contributes to the greenhouse effect, mainly due to CH4, which has a 21-time greater impact on the environment than CO2. Estimates have put total global annual methane emissions from all sources at about 500 - 600 Tg, of which only less than 200 Tg are natural. Thus methane emissions due to human activity, mainly agriculture, biomass burning and landfilling, are up to three times higher than emissions due to natural producers (e.g., wetlands, termites). Although today's sanitary landfills are usually operated with a gas extraction system by which landfill gas is collected and burned in flares or used as an energy source, a high amount of gas still escapes into the atmosphere. Methane is also emitted from older and smaller landfill sites, where retrofitting with a gas collection system is too costly, as well as from open, unauthorized dumps. Landfills contribute about 20 – 70 Tg to global methane emissions each year (Lechner, 2004)

The objective of biological waste treatment is to minimize the reactivity of the waste and thus prevent subsequent unchecked emissions, and to match the chemical conversions to those in nature in terms of quantity and speed. By the biological waste pretreatment, processes taking place in the landfill over long periods of time will be shortened to a few years. The emission potential contained in the waste is reduced to a large extent during pretreatment so that, compared to unpretreated wastes, only minor emissions occur, which can be controlled and treated with little expenditure.

In general the mechanical-biological pretreatment of solid waste can be applied within in general a waste management concept as a sole process or in combination with thermal pretreatment:

1. mechanical-biological pretreatment as an alternative to thermal waste pre-treatment;
2. mechanical-biological pretreatment as an equivalent process in combination with thermal pretreatment after separation of the waste streams into one of high calorific value (Refuse Derived Fuel - RDF) and one predominantly biologically degradable;
3. mechanical-biological pretreatment as a pretreatment step before thermal waste treatment to reduce the quantity of waste to be incinerated.

When variant 1 is applied a relatively large landfill volume is needed. During mechanical pretreatment using variant 2, the waste is separated according to its material-specific properties and prepared for the subsequent treatment steps. The waste of high organic content is aerobically treated in the biological process step or in combination of anaerobic/aerobic processes where it is largely biologically degraded. The RDF stream with high amounts of plastic materials, which are not biodegradable within a predictable period of time but are of high calorific value, and paper could be thermally treated with the aim of energy recovery.

During the aerobic biological treatment the organic matter is degraded under heat release to carbon dioxide, water and biomass.

During anaerobic pretreatment the organic waste residues are converted into biogas and a digestion residue. The anaerobic pretreatment has several advantages compared to aerobic treatment, e.g. minor space requirements, modular construction, a net gain in energy from biogas production as well as minor odour problems due to closed construction. Anaerobic fermentation should always be run in combination with an after composting step, since not all organic substances (e.g. lignin containing components) can be degraded under anaerobic milieu conditions; in addition, the compounds are in a reduced stage and should be converted into the oxidised form.

In addition to the mineralization of organic substances (CO_2, water, NH_4, metals, ...), synthesis processes also occur. An important product of the synthesis is humic matter, which functions as a sink for carbon and nitrogen. Even though it has not been exactly defined chemically, the role played by humic matter as a sink for carbon and nitrogen and in immobilizing organic contaminants and heavy metals is undeniable. Soil science has provided us with numerous studies of humic matter and its function in soils. To a certain extent, this information is also applicable to compost and landfilled materials. Humic matter is characterized by an amorphous structure of brown-colored substances of high molecular weight. A prerequisite

for the formation of humic matter is the presence of molecular fragments. These “building blocks” originate from diverse compounds (lignin, dies and tanning substances, aliphatic structures, etc.) The synthesis mechanism is not yet fully clarified. As humic acids age, its characteristics also change. Due to the favorable characteristics, biological waste treatment aims to maintain as high a content in stable humic matter as possible. When mineralization occurs too rapidly, the development of humic matter is reduced and waste is inadequately degraded. Even though microbial breakdown and synthesis are primarily responsible for the production of humic matter, chemical reactions occurring during radical and condensation steps are also included in the synthesis process. Clay minerals have, on the one hand, a catalytic effect on humus production, and on the other, they also act as electron receptors in radical reactions and contribute to humic matter stabilization. Biologically stabilized organic matter locks a significant part of the initial organic carbon in form of stable humic substances. The decomposition rate of humic substances is very slow (1 –2% per year, like humus in soil) under aerobic conditions; under anaerobic conditions in a landfill, this occurs much more slowly. CO_2 is released over a long period of time in a natural cycle and therefore does not negatively impact the greenhouse effect.

Brown humic acids already start forming during the hot decomposition phase, at the beginning of the decomposition process. During this thermophilic phase, microorganisms excrete exoenzymes to break the macromolecules into smaller fragments. Because of the high activity, an excess of these metabolites is produced, which in turn is available as the starter for the humification process. Generation of humic acid could be fostered in an only partially aerobic environment or when environmental conditions fluctuate (aerobic – anaerobic),

Humic matter generation in the course of a biological process also induces the long-term stabilization of nitrogen. The way in which nitrogen-containing molecules or polymers are bound to humic substances, however, is for the most part unknown. The amount of nitrogen that can be fixed depends on the availability of nitrogen in the starting material, on the shape and distribution of the different nitrogen compounds, the conditions under which humic substances are produced, and the speed of the mineralization process (Heimovaara et al., 2007).

The content of stable organic carbon compounds in MBP materials lies between 18 and 25% of dry matter. An mechanical and biological pretreated landfill is therefore a significant carbon sink.

In conclusion a low-emission landfill is characterized by no or only a very minimal amount of gas generation, a small quantity of low-load leachate, good geotechnical behavior, and least possible contaminant transfer via the surface. These characteristics must be present over the long

term. Biological pretreatment processes reduce the amount of gas generated to a level that is deemed no longer critical for the environment. It can be further expected that the leachate burden will approach negligible values in the mid-term.

The targets of the aerobic stabilization treatment are the stabilization of organic substances and the reduction of water content, differently by a composting process the target of which is the production of an agricultural fertilizer. The advantages of a preliminary aerobic treatment are the reduction of environmental impacts of landfilling, better disposal conditions and lower costs for treating plant investment and management when compared, for example, to a thermal treatment plant.

This research work has verified the possibilities and the limits of a treatment process for aerobic stabilization by forced aeration. Furthermore the research work has verified the variation of the mobility of some metals in leaching test and the variation of Dissolved Organic Carbon content, during the process of stabilization.

4.1 MATERIALS AND METHODS

The work has regarded the stabilization of tannery sludges originating from a drying system and the stabilization of tannery sludge mixed with compost. The mixture of materials with different characteristics has the main function to positively influencing the general conditions of the degradation process of the organic compounds and to give the adequate porosity for the air inflow. Moreover the compost can be used as chelant for the metals in the sludge with the aim to limit their mobility. The tannery sludge comes from a tannery wastewater treatment plant and the compost comes from a composting plant treating garden waste.

The experimentation has regarded the aerobic stabilization of the following materials:

- Tannery sludge.
- Tannery sludge mixed with Compost (20% in weight of compost in the mixture).
- Tannery sludge mixed with Compost (10% in weight of compost in the mixture).

The low ratios between tannery sludge and compost have been decided to avoid high compost supply for the realization of a real plant. The utilization of compost could be in some cases a material to by bough from an external company, and so a cost. The evaluation of the effects of small amount of compost in the mixture with tannery sludge could be a solution not only environmental friendly but also economically friendly.

Two aeration rate have been chosen to analyse the effects of different flow. The two rates are 1 and 10 Nm3/kgh. The two value have been selected among the values suggested for the composting plant realized by biocell.

For the treatment process, small lab-scale reactors have been used. The reactors are completely made of glass. The reactor consists in two parts, one over the other. The air diffusing system is located in the part below; the materials to treat is disposed on the upper part. The two parts are connected to each other by a metal disc which is perforated to let the air flow from the bottom to the top. The aeration is realized by small pumps and the flow is controlled by flowmeters. The outgoing gases are collected and treated in an air treating system which is composed by an activated carbon section and a biofilter.

The reactors are simply built but this is sufficient for a good control on the degradation processes. The reactors are shown in Figure 4.1 and Figure 4.2.

About 6 Kg of materials have been put in every reactor. The forced aeration has been realized by a small air-pump.

Prior to filling the reactors, the material have been analyzed as reported in Table 4.2 and Table 4.3. The parameters monitored during the tests are:

- Total Solids;
- Total Volatile Solids;
- Total Organic Carbon;
- Total Kjeldhal Nitrogen;
- Ammonia;
- Nitrate;
- Sulphate;
- Sulphide;
- Dissolved Organic Carbon content;
- Metals content (Cr, Cu, Fe, Mn, Ni, Pb, Zn);
- Respiration Index at 7 days;
- Biochemical Methane Potential (BMP);

The respiration index for seven days has been measured using a Sapromat respirometer (Sapromat E). The other parameters have been measured according to Italian standard methods. The outgoing gas composition has been measured by an infrared analyzer (mod. LFG 20). The temperature of the materials in the reactors has been measured by a thermometer.

The tests have had a duration of 8 weeks. Every three days the materials have been turned. Before every turning the material in the reactor has been weighed and every week a sample has been taken for the analyses.

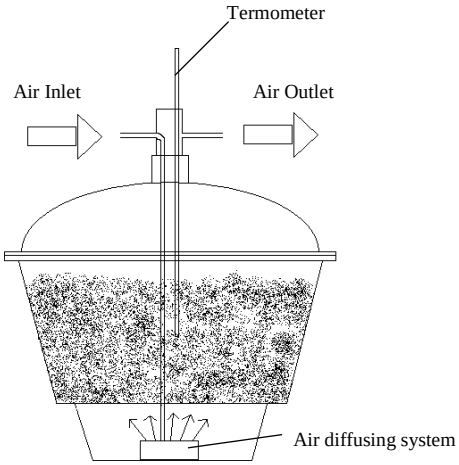

Figure 4.1 Scheme of a single reactor

Figure 4.2 Picture of some reactors

Table 4.1 Flow rates of single reactors.

Material	Flow rate [Nl/Kg*h]
Tannery Sludge at high flow rate	10
Tannery Sludge at low flow rate	1
Tannery sludge and Compost (20%)	10
Tannery sludge and Compost (20%)	1
Tannery Sludge and Compost (10%)	10

Table 4.2 Characterization of materials (Solids, Biological stability)

	Moisture	Total Solids	Total Volatile Solids	Respiration Index (7days)
Material	[%]	[%]	[% of TS]	[mgO_2/gTS]
Tannery sludge	73	27	72	175
Compost	28	72	60	7
Tannery Sludge and Compost (20%)	61	39	61	97
Tannery Sludge and Compost (10%)	66	34	64	130

Table 4.3 Characterization of Tannery Sludge (Metals)

	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Material	[mg/KgTS]	[mg/KgTS]	[mg/KgTS]	[mg/KgTS]	[mg/KgTS]	[mg/KgTS]	[mg/KgTS]
Tannery sludge	38150	64	13193	150	18	82	3047

4.2 RESULTS

4.2.1 Tannery sludge

Two reactors have been prepared for Tannery Sludge. The aim is to analyse the effects of different aeration rate for the same material. The two aeration rate was 10Nl/Kgh (high aeration rate) and 1 Nl/Kgh (low aeration rate).

The temperature of the sludge at high aeration rate fast increased up to a value of about 58°C in the first two days of experiment,. After the third day, the temperature rapidly decreased to a value of 38°C. After the first turning, at the fourth day, the temperature has increased again to 43°C and the following days the temperature was stable around 32-33°C without being influenced by the subsequent turning. (See Figure 4.7). After the first month the temperature slowly decreased to a final value of 25°C. The high temperatures of first phase are main due to the biological activity for the degradation of the readily biodegradable organic matter. The degradation of organic matter in the sludge can also be seen in Figure 4.3. The 20% of Volatile Solids are degraded to Carbon Dioxide and Water in the first two weeks. As shown in Figure 4.9

the high Oxygen consumption is in the first two weeks as the higher emission of Carbon Dioxide. Two different phases can be considered: the first phase at high temperature can be considered the thermophilic phase and the second and final phase can be considered the maturation phase, at mesophilic condition. In the first phase the readily biodegradable organic substances are consumed by bacteria with production of heat and high emission of Carbon Dioxide. During the second phase the slowly biodegradable substances are degraded and the production of humic substances starts.

The higher reduction of weigh is during the first week and the second week. The percentage of reduction of Volatile Solids is 17% at the end of the first week and 24% at the end of second week. The percentage of total reduction of Volatile Solids is 44% at the end of eighth week. The reduction of moisture content can be considered constant during the first six week with a final increase during the last two weeks. The final reduction of moisture is of 61%. The total reduction of weigh of the material is of 53%. The weight goes from 6 Kg at the beginning of the treatment to 2.80 Kg at the end of the treatment.

The biological stability of treated sludge have been evaluated by Respirometric Index at 7 days (RI_7) and by anaerobic test of fermentation (B21). The RI_7 starts from a value of 175 mgO_2/gTS and it reach a value of 8.5 mgO_2/gTS after eight weeks, with a fast decreasing phase in the first month and a stable phase in the second month (Figure 4.11). The potential biogas production of the material is 57.5 Nl/KgTS at the beginning of the treatment. During the stabilization of the material the value of potential biogas production has been reduced to 20 Nl/KgTS at the fourth week and to 5 Nl/KgTS at the end of experiment.

The temperature of the sludge at low aeration rate remained stable around 37°C in the first 15 days. After the fifth turning, at the fifteenth day, the temperature slowly decreased to a final value of 27°C. The lower aeration rate does not permit a high increase of temperature of the material. The amount of air supply per hours is lower the total request of oxygen for the degradation of biodegradable organic substances. The activity of bacteria is controlled by the amount of oxygen available. Comparing the quality of outgoing gas the longer consumption of oxygen can be notice for material at low aeration rate.

The degradation of organic matter in the sludge can be seen in Figure 4.5. and 4.6. As for reactor at high aeration rate, the Volatile Solids have had a reduction of 20% in the first two weeks and a final reduction of 32% in the end of the treatment. The Moisture content reduction was lower then in the reactor at high aeration rate. This is because the high aeration rate demonstrate a drying effects of the sludge not seen in the slow aeration rate. The Oxygen in the reactor at low aeration rate is sufficient for aerobic stabilization (Figure 4.10), but the air flow is

not sufficient to realize a drying effect of the Tannery Sludge. In fact the reduction of Moisture content is of 10% in the reactor at low aeration rate instead of 60% in the reactors at high aeration rate. The lower reduction of the moisture content is also due to the lower temperature during the first two weeks of the experiment.

The biological stability of sludge treated at low aeration rate is similar to the one at high aeration rate. The Respirometric Index reaches a value of 10 mgO_2/gTS after eight weeks, with a fast decreasing phase in the first month and a stable phase in the second month. During the stabilization of the material the value of potential biogas production has been reduced to 35 Nl/KgTS at the fourth week and to 9 Nl/KgTS at the end of experiment.

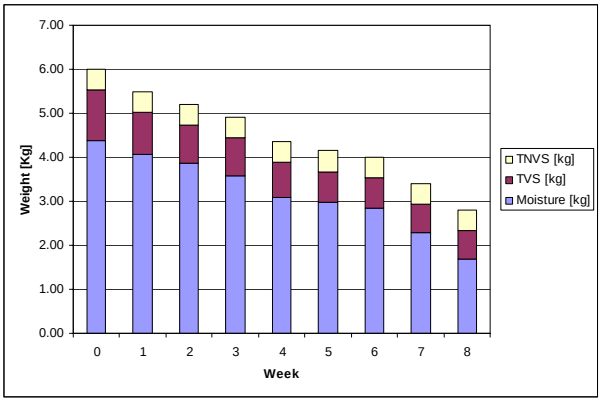

Figure 4.3 Total Volatile Solids, Total Non Volatile Solids and Water content in the Tannery sludge at 10 Nl/Kg*h of aeration

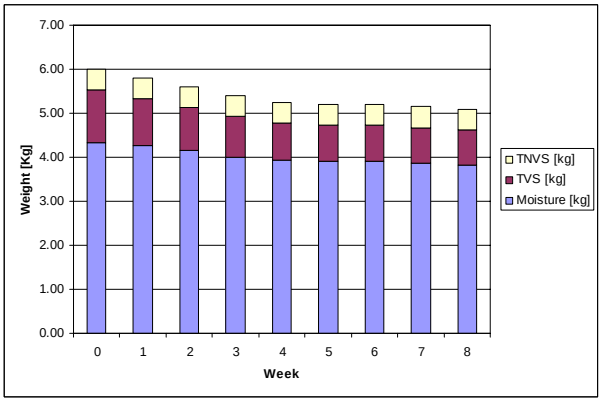

Figure 4.4 Total Volatile Solids, Total Non Volatile Solids and Water content in the Tannery sludge at 1 Nl/Kg*h of aeration

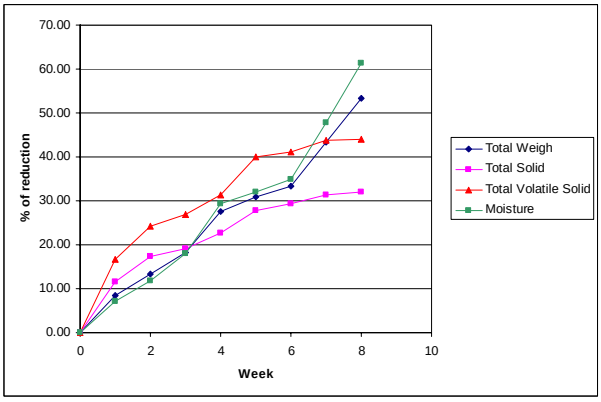

Figure 4.5 Percentage of reduction of Total Weight, Total Solids, Total Volatile Solids and Water content in the Tannery sludge at 10 Nl/Kg*h of aeration

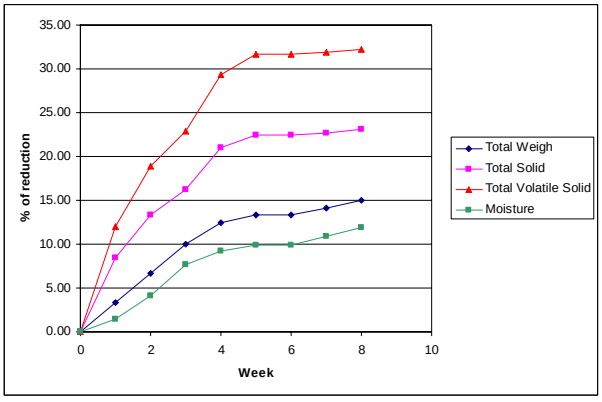

Figure 4.6 Percentage of reduction of Total Weight, Total Solids, Total Volatile Solids and Water content in the Tannery sludge at 1 Nl/Kg*h of aeration

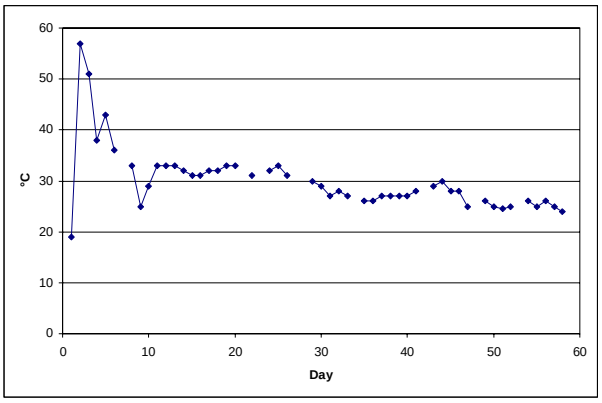

Figure 4.7 Temperature of the sludge at 10 Nl/Kg*h of aeration

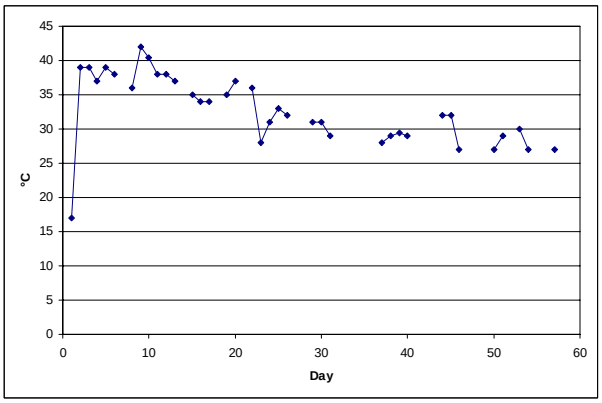

Figure 4.8 Temperature of the sludge at 1 Nl/Kg*h of aeration

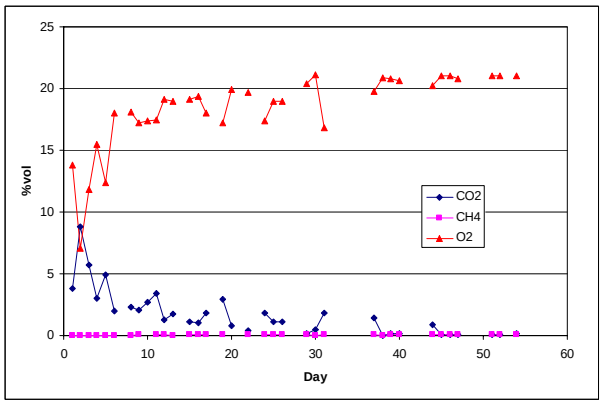

Figure 4.9 Composition of outlet gas of sludge reactor at 10 Nl/Kg*h of aeration

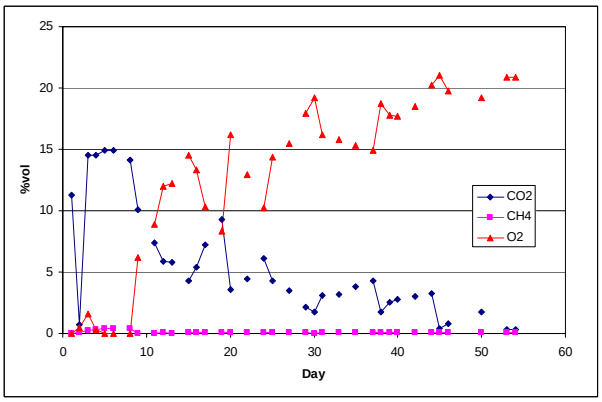

Figure 4.10 Composition of outlet gas of sludge reactor at 1 Nl/Kg*h of aeration

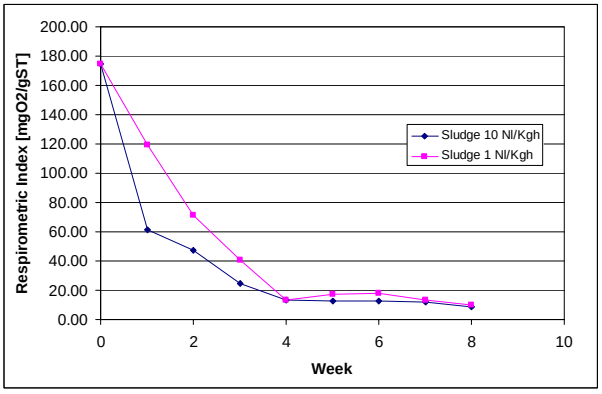

Figure 4.11 Respiration Index of treated materials

4.2.2 Tannery sludge and Compost

The aim of adding Compost to Tannery Sludge before an aerobic treatment is to realize better condition for the reaction process and to analyze the effect on mobility of metals in leaching test. Two rate of mixtures have been prepared at 20% and 10% of Compost in weight in the mixture. The rate are not high because the idea is do not change too much the structure of Tannery Sludge and evaluate if small amount of Compost can improve the effects of aerobic treatment.
The two mixtures (10% and 20%) at the aeration rate of 10Nl/Kgh have had a similar degradation process. The temperatures for both reactors increased to values higher then 50°C for the first two days (Figure 4.15 and 4.16). This demonstrates a high bacterial activity due to the degradation of readily biodegradable organic substances especially in the first phase. The temperature maintained a value around 32°C during the first month without being influenced by the turning. In the second month the temperature decreased to a stable value of 26°C.

The percentage of reduction of Volatile Solids is 30% at the end of the experiment for both the mixtures. Also the reduction of moisture content is of 50% for both the mixtures.

The behaviour of the two mixtures is similar to that of tannery sludge at the same aeration rate even for the biological stability. The high biological activity of the first days, highlighted to the temperature value of about 45°C, caused a high reduction of Respirometric Index value. As shown in Figure 4.19, after two weeks of treatment, the Respiromentric Index is decreased to 20 mgO_2/gTS and less then 4 mgO_2/gTS after eight weeks. Even the potential biogas production decreased to a final value of 6 for the mixture of 20% of compost and 5.5 for the mixture of 10% of compost.

The lower reduction in weight, in comparison with Tannery Sludge, are doe to the mixing with compost, a material already biologically stable. Good results are reached on biological stability, because the simple reaction with the addition of compost, have had as result the halving of final value of Respirometric Index.

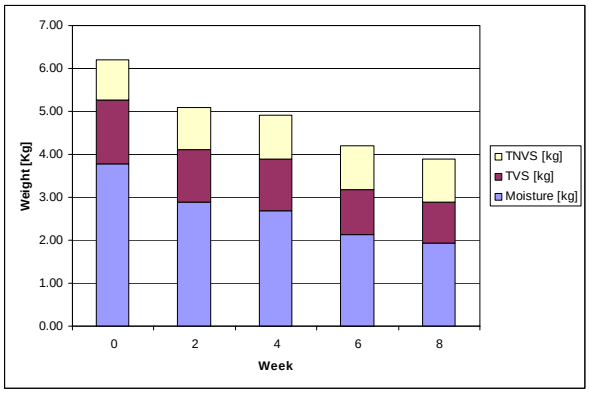

Figure 4.12 Total Volatile Solids, Total Non Volatile Solids and Water content in the Tannery sludge and Compost (20%) at 10 Nl/Kg*h of aeration

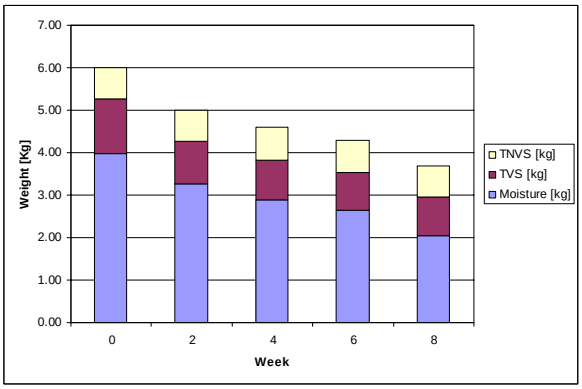

Figure 4.13 Total Volatile Solids, Total Non Volatile Solids and Water content in the Tannery sludge and Composto (10%) at 10 Nl/Kg*h of aeration

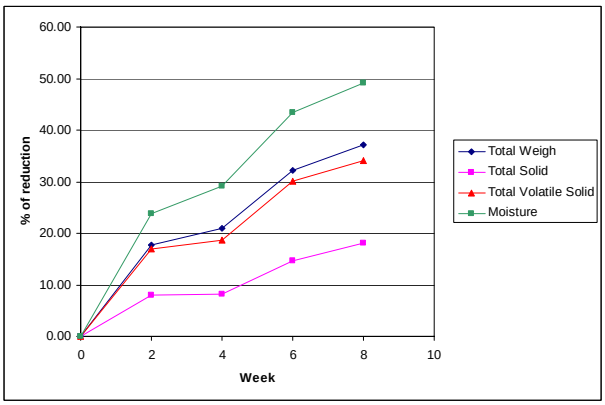

Figure 4.14 Percentage of reduction of Total Weight, Total Solids, Total Volatile Solids and Water content in the Tannery sludge and Compost (20%) at 10 Nl/Kg*h of aeration

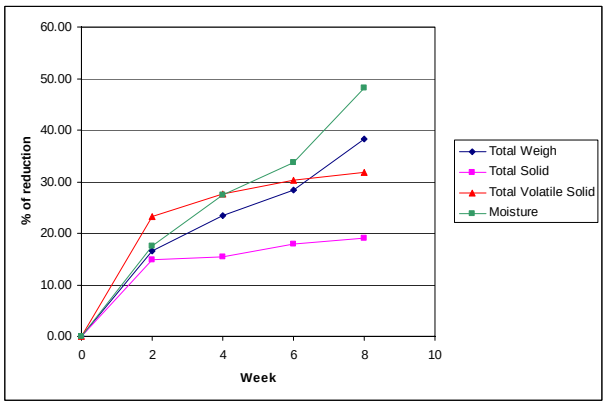

Figure 4.15 Percentage of reduction of Total Weight, Total Solids, Total Volatile Solids and Water content in the Tannery sludge and Compost (10%) at 10 Nl/Kg*h of aeration

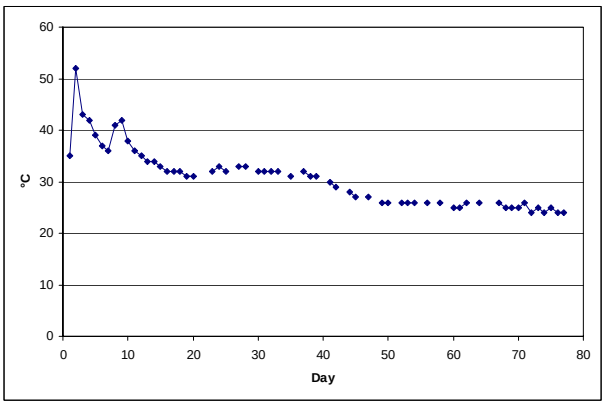

Figure 4.15 Temperature of the Tannery sludge and Compost (20%) at 10 Nl/Kg*h of aeration

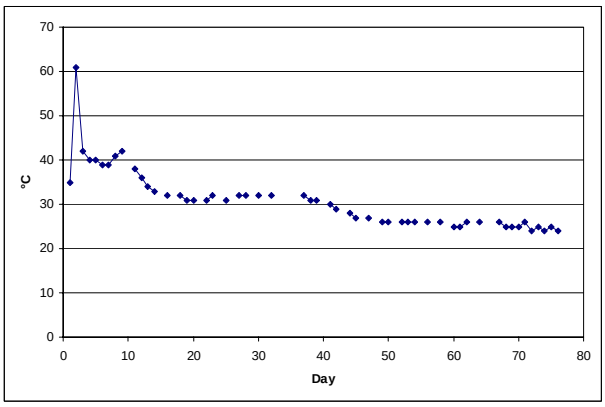

Figure 4.16 Temperature of the Tannery sludge and Compost (10%) at 10 Nl/Kg*h of aeration

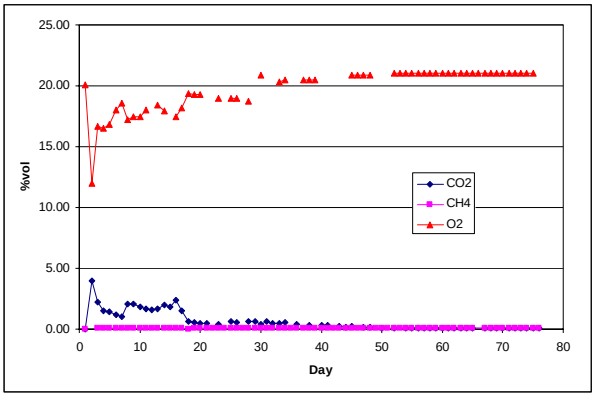

Figure 4.17 Composition of outlet gas of Tannery sludge and Compost (20%) reactor at 10 Nl/Kg*h of aeration

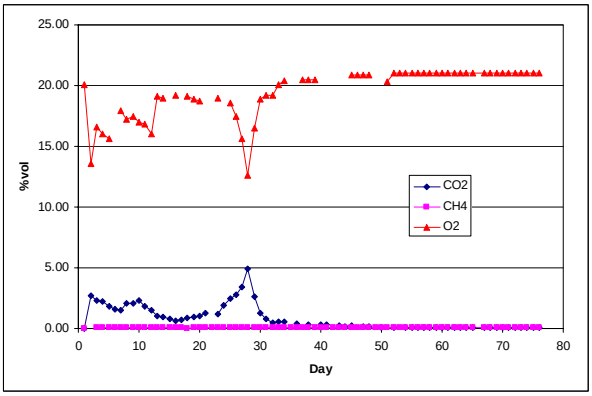

Figure 4.18 Composition of outlet gas of Tannery sludge and Compost (10%) reactor at 10 Nl/Kg*h of aeration

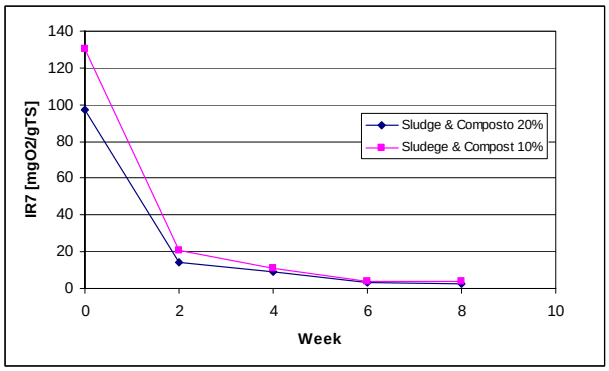

Figure 4.19 Respiration Index of treated materials

The mixture of 20% of Compost at low aeration rate has had a good degradation process. The temperatures during the reaction period have been similar to the temperature of Tannery sludge and low aeration rate. Total Volatile Solids decreased of 25% in four weeks and more then 35% in eight weeks. This results are similar to the results obtained with Tannery sludge at low aeration. Moisture content decreased of 25% after eight week of aeration showing better results then Tannery Sludge at low aeration. As shown in Figure 4.24, the Respiromentric Index is around 20 mgO_2/gTS after two weeks of treatment and less then 4 mgO_2/gTS after eight weeks.

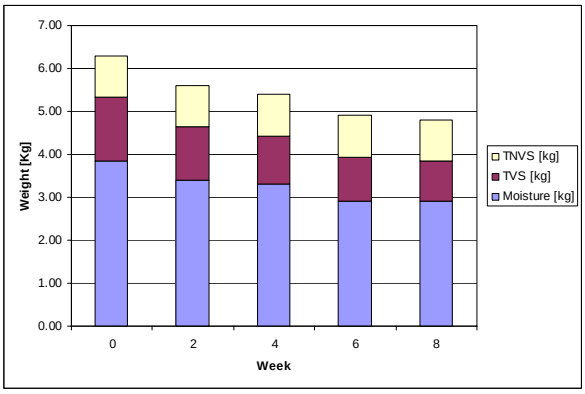

Figure 4.20 Total Volatile Solids, Total Non Volatile Solids and Water content in the Tannery sludge and Compost (20%) at 1 Nl/Kg*h of aeration

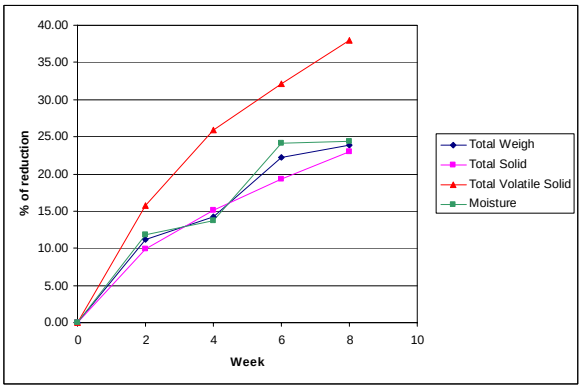

Figure 4.21 Percentage of reduction of Total Weight, Total Solids, Total Volatile Solids and Water content in the Tannery sludge and Compost (20%) at 1 Nl/Kg*h of aeration

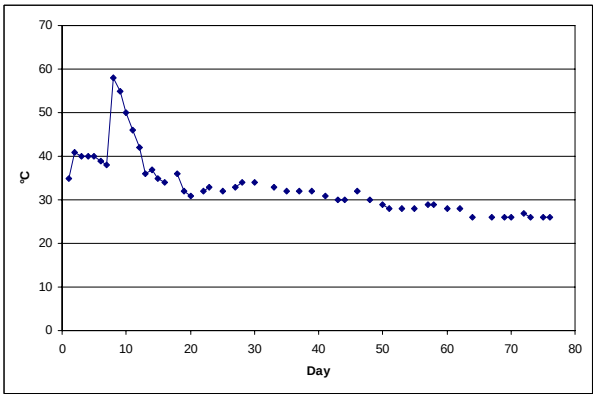

Figure 4.22 Temperature of the Tannery sludge and Compost (20%) at 1 Nl/Kg*h of aeration

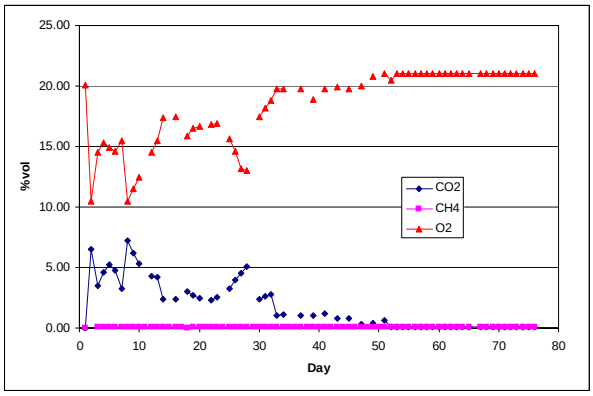

Figure 4.23 Composition of outlet gas of Tannery sludge and Compost (20%) reactor at 1 Nl/Kg*h of aeration

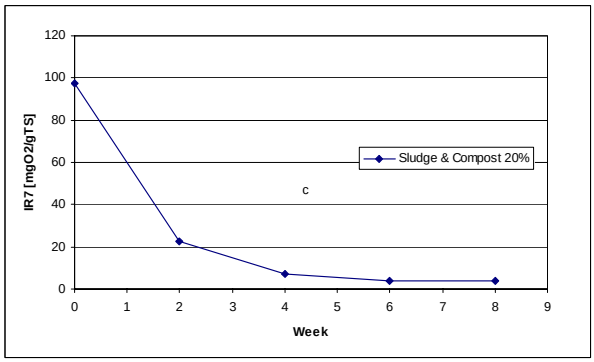

Figure 4.24 Respiration Index of treated materials

The compost used in the experiment is a material already biologically stabilized. The amount of Volatile Solids present in the compost can be considered constant during the treatment with the tannery sludge. It is possible to evaluate the real reduction of Total Solids and Total Volatile Solids of the tannery sludge in the mixture considering that the variation of weigh of the mixture during the experiment is only due to consumption of volatile substances present in the tannery sludge and not in the compost.

Considering this hypothesis, it is possible to calculate the percentage reduction of Total Solid weight and of Total Volatile Solid weight of only the amount of tannery sludge presents in the mixtures. The percentage of reduction of total volatile solids for the mixture at 20% of compost both at high and low aeration rate, reached a final value of more then 50% while in the mixture of 10% of compost the percentage of reduction of total volatile solids reached a final value of 35% (Figure 4.25, Figure 4.26 and Figure 4.27).

The positive effects of mixing the tannery sludge with compost can be seen also on the reduction of the Respirometric Index. The Respiration Index of compost is 7 mgO_2/gTS, more then twenty times lower that the initial valua of Respiration Index of tannery sludge (180 mgO_2/gTS). Considering that the compost is a stable material and that the Respiration Index can be considered stable during the treatment process, the variation of the Respirometric Index of the tannery sludge in the mixture can still be calculated.

As reported in Figure 4.28 and Figure 4.29, the Respirometric Index of tannery sludge in the mixture reach a final value of about 6 mgO_2/gTS for both mixtures at high aeration rate and of about 9 mgO_2/gTS for the mixture at low aeration rate. All the three mixtures reach a value lower that 10 mgO_2/gTS at the sixth week of treatment instead of the eighth week in case of no mixing with compost. A value of 10 mgO_2/gTS of the Respiration Index is considerate in the international scientific literature as indicative of biological stable state of the waste materials.

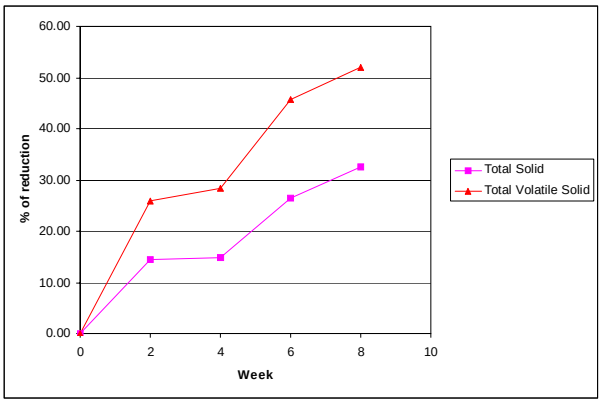

Figure 4.25 Percentage of reduction of Total Solids and Total Volatile Solids content of Tannery sludge (in the mixture with 20% of Compost) at 10 Nl/Kg*h of aeration.

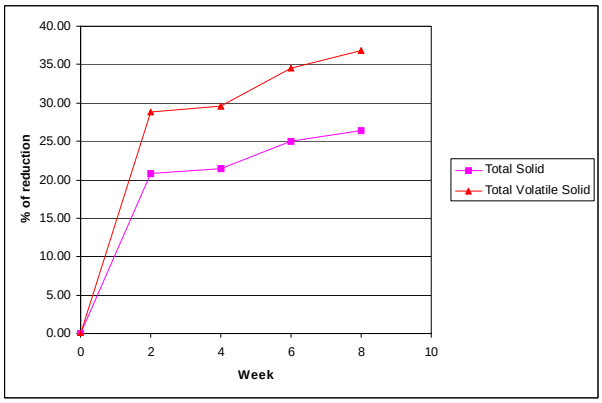

Figure 4.26 Percentage of reduction of Total Solids and Total Volatile Solids content of Tannery sludge (in the mixture with 10% of Compost) at 10 Nl/Kg*h of aeration.

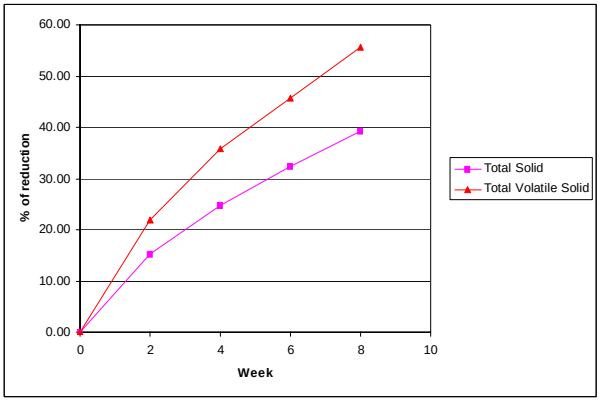

Figure 4.27 Percentage of reduction of Total Solids and Total Volatile Solids content of Tannery sludge (in the mixture with 20% of Compost) at 1 Nl/Kg*h of aeration.

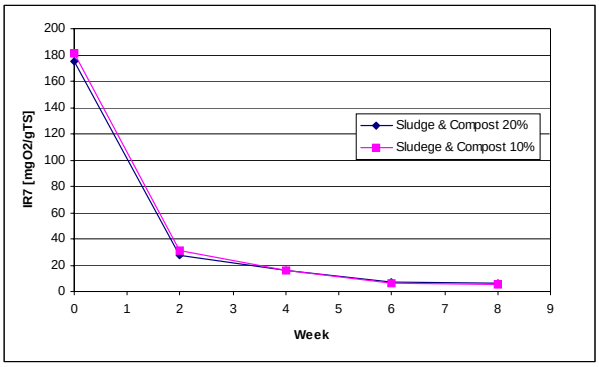

Figure 4.28 Respiration Index of Tannery Sludge at 10Nl/Kh*h.

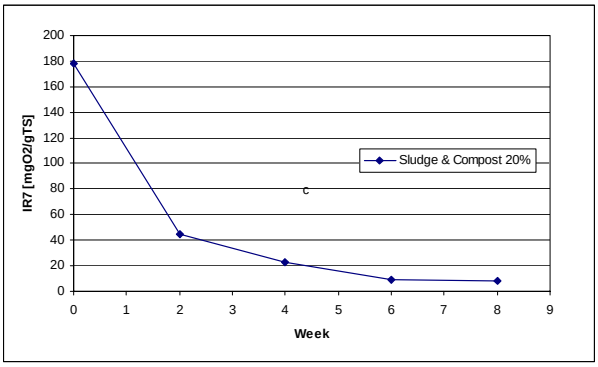

Figure 4.29 Respiration Index of Tannery Sludge at 1Nl/Kh*h.

4.2.3 Dissolved Organic Carbon as parameter for biological stability

The dissolved organic carbon (DOC) or water soluble carbon has been proposed by a number of researcher as a parameter which consistently decreased during composting processes. DOC was shown to be highly correlated to respiration (Chica et al.,2003) and suggested as a maturity parameter (Helfrich et al., 1998). Several DOC cutoff values have been suggested as indicators of maturity for compost: Hue and Liu (1995) suggested 10gDOC/KgST, Bernal et al. (1998) suggested 17 gDOC/KgTS, Zmora-Nahum et al. 4 gDOC/KgTS.

The aerobic stabilization process applied to Tannery Sludge or Tannery Sludge mixed with Compost, presented in this research work, is not finalized to the production of an agricultural fertilizer because of the high content of heavy metals. The comparison between DOC content of compost and DOC content of treated tannery sludge, can be useful for the evaluation of biological stability of treated material for landfill disposal. Italian legislation posed a limit of 0.8 gDOC/KgTS content for non dangerous waste. This limit is extremely difficult to be reached for organic waste that also a compost could be considered an instable and dangerous waste.

In this research work the variation of DOC content in treated material have been analyzed and compared with values proposed in the international literature. DOC content have been measured with water extraction method. Water extracts were prepared by shaking dry material with deionized water in a 1:10 material:water weight ratio for 24 h. The suspension was then centrifuged and filtered through a 0.45 membrane filter. The concentration of DOC was determined after acidification to pH 5, on a Shimadzu Total Carbon Analyzer.

The initial DOC content of Tannery Sludge is 24gDOC/KgTS, 18 gDOC/KgTS for Tannery Sludge mixed with 20% of Compost, and 23 gDOC/KgTS for Tannery Sludge mixed with 10% of Compost. The content of DOC decreased for all the experiment under a value of 4 gDOC/KgTS in four weeks and reached a final value of 3gDOC/KgTS for Tannery Sludge at low aeration rate and Sludge and Compost (10%), 2.5 gDOC/KgTS for Sludge and Compost (20%) at high aeration rate, and only 1 gDOC/KgTS for Sludge and Compost (20%) at low aeration rate. The treatment reached a reduction of DOC content of more then 90% for all treated material (Figure 4.30 and Figure 4.31).

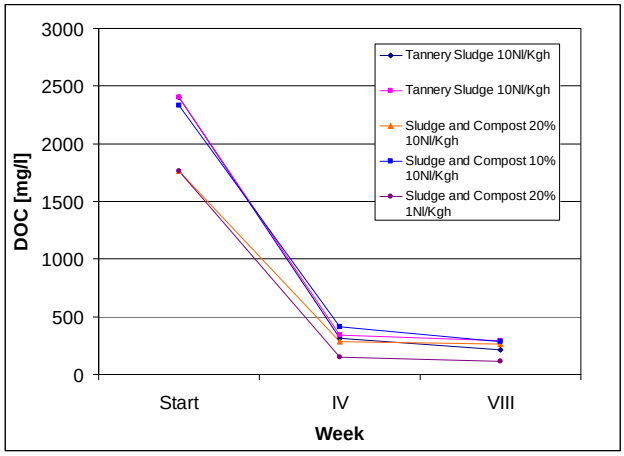

Figure 4.30 Dissolved Organic Carbon concentrations in leaching tests.

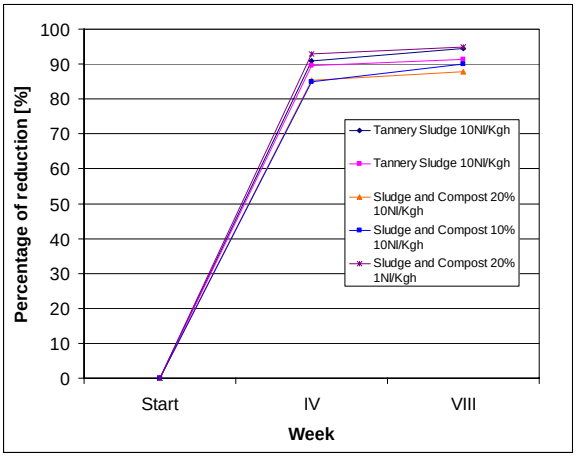

Figure 4.31 Percentage of reduction of Dissolved Organic Carbon content during aerobic stabilization tests.

4.2.4 Metals

One of the aim of the research work was to investigate the effects the aerobic stabilization and of the co-treatment with compost on metals fate. The mixture of Tannery Sludge and Compost and the aerobic treatment was supposed to develop good condition for limiting the concentration of metals in the liquid phase during leaching tests and consequently the mobility of metals in the environment. The mobility of metals have been measured with water extraction method. Water extracts were prepared by shaking dry material with deionized water in a 1:10 material:water weight ratio for 24 h. The suspension was then centrifuged and filtered through a 0.45 membrane filter. The concentration of metals was determined by an Inductively Coupled Plasma (ICP) analyzer.

The concentration of metals during the stabilization process increases caused by the reduction of mass due to the gasification of biodegradable organic substances to Carbon Dioxide. Considering that fact, it is important to evaluate the mobility of metals. If the concentration of metals in the dry mass increases, but the mobility of metals decreases due to aerobic stabilization process and due to the mixing with compost, the final storage in the landfill will represent a metal sink deposition that can contribute to the limitation of pollution of the environment even for the future generations when the barrier systems of the landfill will fail (Cossu et al. 2007).

The results are shown in Table 4.5 Concentrations of Chrome, Nickel and Iron in leaching tests, are decreasing in all case during treatment, but better results are given in presence of Compost. The concentrations in leaching tests of Zinc and Selenium are increasing during the

aerobic treatment phases for all types of materials but the presence of Compost is limiting the increasing trend.

The percentage of reduction of Concentration of metals in leaching test are presented in Table 4.6. A negative value means increasing of concentration. The best results are given by a mixture of Tannery Sludge and Compost at 20% in weight with aeration at 1 Nl/Kg/h.

Table 4.4 Composition of single tests, aeration rate and time of sampling.

	Materials	**Aeration rate [Nl/Kgh]**	**Timing of sample [week]**
SC2010 start	Tannery Sludge and Compost at 20%	10	Start
SC2010 IV	Tannery Sludge and Compost at 20%	10	IV
SC2010 VIII	Tannery Sludge and Compost at 20%	10	VIII
SC1010 start	Tannery Sludge and Compost at 10%	10	Start
SC1010 IV	Tannery Sludge and Compost at 10%	10	IV
SC1010 VIII	Tannery Sludge and Compost at 10%	10	VIII
SC201 start	Tannery Sludge and Compost at 20%	1	Start
SC201 IV	Tannery Sludge and Compost at 20%	1	IV
SC201 VIII	Tannery Sludge and Compost at 20%	1	VIII
TS Start	Tannery Sludge	10	Start
TS 10 IV	Tannery Sludge	10	IV
TS 10 VIII	Tannery Sludge	10	VIII
TS Start	Tannery Sludge	1	Start
TS 1 IV	Tannery Sludge	1	IV
TS 1 VIII	Tannery Sludge	1	VIII

Table 4.5 Concentration of Metals in leaching test.

	Cr	Cu	Ni	Zn	Fe
	microg/l	microg/l	microg/l	microg/l	microg/l
FC2050 start	726	38	92	130	996
FC2050 IV	304	106	44	191	198
FC2050 VIII	195	82	31	197	115
FC1050 start	1270	62	145	73	1490
FC1050 IV	746	157	92	325	631
FC1050 VIII	204	72	46	221	131
FC205 start	726	38	92	130	996
FC205 IV	125	50	24	92	94.3
FC205 VIII	87	29	20	140	70
FTQ 29/6/06	1400	44	184	84	1500
FTQ1/50 4	276	8	130	363	193
FTQ 1/50 8	199	3	109	352	183
FTQ 29/6/06	1400	44	184	84	1500
FTQ2/5 4	329	20	140	468	470
FTQ2/5 8	289	1	133	524	328

Table 4.6 Percentage of reduction of concentration of Metals in leaching test.

	Cr	Cu	Ni	Zn	Fe
	%	%	%	%	%
FC2050 start	0	0	0	0	0
FC2050 IV	62	-158	56	-35	82
FC2050 VIII	78	-77	73	-24	91
FC1050 start	0	0	0	0	0
FC1050 IV	50	-115	47	-274	64
FC1050 VIII	87	6	74	-144	93
FC205 start	0	0	0	0	0
FC205 IV	85	-12	78	40	92
FC205 VIII	92	10	86	-121	94
FTQ 29/6/06	0	0	0	0	0
FTQ1/50 4	86	87	49	-214	91
FTQ 1/50 8	91	95	62	-173	92
FTQ 29/6/06	0	0	0	0	0
FTQ2/5 4	83	66	45	-304	77
FTQ2/5 8	86	98	50	-329	85

The results seem to be encouraging for the development of an aerobic treatment technology for the stabilization of tannery sludge. The treatment seems to work though the negative characteristics of the tannery sludge, as the high heavy metals content. The addition of small amount of compost allow good condition for aerobic stabilization process and seems to realize better condition to limit the mobility of metals. The best results are given by a mixture of Tannery Sludge and 20% in weight of Compost with a treatment of eight week at 1Nl/Kgh of aeration rate.

The experimental results indicate also the following: the high reduction of weight and volume of the sludge, allows longer duration of the landfill site; the lower biological activity avoids a high biogas production in landfill and reduces the organic content in the landfill leachate. The different flow rates indicate that a high aeration has high drying effects on the sludge, reducing the moisture content; the low aeration rate seems to maintain a high temperature and biological activity for a longer period. The advantages of a lower flow rate are also economical. Lower flow rates require lower energetic and installation costs. Mixing with Compost seems to allow better condition especially for the reduction of mobility of metals.

Chapter 5

SUSTAINABLE LANDFILL

The technical-scientific community for many years has been engaged in the identification of waste management ways coherent with the concept of Integrated System, thus finalized to waste avoidance, materials and energy recovery, final disposal in environmentally sustainable landfills (Stegmann, 1995; Driessen et al., 1995). “Sustainability” idea is present in the history of the humanity since its origin. In 1987 World Commission on Environment and Development defined “Sustainable Development” as a development “which meets the needs of the present without compromising the ability of future generations to meet their own needs” (WCED, 1987). Waste and landfill problems should be managed keeping in mind this concept.

Current regulations in Europe set the duration of the aftercare of a municipal solid waste landfill in at least 30 years. But actual sequences of operative management of a landfill and waterproof coverage commanded by the same regulations do not guarantee to reach limits fixed by the law regarding environmental emissions within this period of time. The current approach to landfilling may lead to creation of future contaminated sites instead of safe disposal sites (Cossu et al., 2005). Concept of “sustainability” of a landfill concerns exactly this subject: it’s not morally acceptable to leave to future generations a high pollution potential site, without economic coverage to manage it.

Acceptable impact is need to be reached within the period of assured economic coverage. A landfill has an acceptable impact if emissions that come from it do not change in a considerable way quality of the surrounding air, ground and groundwater; therefore emissions that do not cause significant modifications to the surrounding environment can be considered as negligible.

Several approaches to the environmental sustainability have been proposed, based either on the modification of the characteristics of the waste to be landfilled such as mechanical and biological pretreatments, or on the modification of the landfill construction and operation procedures such as aerobic or semi-aerobic landfill, flushing, leachate recirculation. All these strategies come together in the more general idea of multi-barrier landfill which provides the

extension of the concept of barrier from the simple physical control of the emission to the waste characteristics and the landfill operation (Cossu, 1995).

Consequently landfill science has shown a significant shift from a strong emphasis on isolation technologies towards obtaining a fundamental understanding of processes occurring in landfill bodies. One of the main reasons for this shift in thinking is the realization that isolation technologies alone cannot guarantee long-term protection of the environment.

The main reason lies with the so-called contaminating life span of a landfill body (Rowe, 2005). The contaminating lifespan of a landfill body is defined as the period a landfill body is capable of producing emissions (both gas and liquid) in which substances are present at levels that could have an unacceptable impact on the surrounding environment. Now we realize that the contaminating lifespan of modern landfills may last for centuries (Gronow et al, 2007; Ehrig and Kruempelbeck, 2007). This is not clearly sustainable as future generations are burdened with more or less eternal aftercare of modern landfills.

In order to obtain a sustainable landfill, processes that occur naturally are controlled with special technology in order to optimize the processes so that the landfill body will be stabilized as fast as possible. The aim of these treatments is to enhance the utilisation of natural processes so that after a period of active control and active after-care we can safely release the landfill from after-care because the landfill is completely stabilized. It is important to realize that reaching a sustainable situation can only be reached by implementing the correct measures for pretreatment.

The major step before landfilling is pretreatment in order to stabilize and reduce the volume of the waste before landfilling. This step includes for the management of tannery sludge biological degradation, incineration, chemical solidification.

The biological degradation processes are composed by aerobic stabilization and or anaerobic digestion in order to rapidly stabilize the organic fraction. Aerobic stabilization is suitable for all kinds of organic waste, the purpose is to reduce waste volume, avoid future methane emissions and to stabilize the waste. Contrary to anaerobic stabilization, lignine will also be degraded by fungi (Bramryd and Binder, 2007). Nitrogen species will be oxidized to nitrate which may be further transformed to nitrogen by denitrification or which can be leached. Anaerobic stabilization will also reduce the amount of organic waste, however methane is produced. This methane can be used as a fuel for electricity and heat production. In addition to recovery of energy the anaerobic residue is also enriched in nutrients which can be recovered. The residue is high in lignine content, and as a high water retention capacity and a high sorption capacity for heavy metals. This last property is beneficial in keeping a landfill anaerobic for a very long

period. The residues after biological degradation will have a very low production of landfill gas after landfilling (Stegmann, 2005a). As a result of both cases, carbon is efficiently sequestered.

In fact another important issue to consider for the sustainability of landfills, is the emission of greenhouse gases. Much of the current regulation on landfilling focuses on reducing the amount of organic matter in the waste in order to reduce methane emissions or on technology for capturing and treating the methane emissions. The aim is to have zero emissions (Morcet et al., 2007; Humer and Lechner, 2007). However, stabilized organic matter in a landfill may prove to be an interesting carbon sink, if it can be shown that the stability is guaranteed for a long period of time.

In view of the fact that, as in any cycle of individual elements (carbon, nitrogen, etc.), we mobilize geological resources (ore, fossil fuels) to obtain a supply of energy and materials, after sequential transformation (production, use, recycling), in order to avoid dystrophic accumulation of elements and their uncontrolled mobilization in the environment, a sink returning the elements to a geological like deposit in which they are permanently immobilized (mineralized to rock quality or transformed into a stable form), is mandatory. In general terms the landfilled material (both organic and inorganic) is made up of four fractions: gasifiable, leachable, stable, mineralizable. Once the degradable fractions have degraded by aerobic stabilization or by anaerobic digestion and the leachables have been washed out, stable and mineralized matter – roughly accounting for as much as 50 % (Bogner, 2007) - represents a potential geological sink. Modern landfill design should adopt the best available strategy to deal with the mobile fraction capable of harming the environment in both the short and long term, in a sustainable manner (multibarrier system, pretreatment, biodegradation enhancement, methane capture and oxidation, in situ-aeration, flushing, etc), achieving a final storage quality in equilibrium with the environment within the span of one generation. Subsequently, geological processes will gradually establish rock quality conditions (Cossu et al. 2007).

5.1 SUSTAINABLE LANDFILLING OF TANNERY SLUDGE

The last phase of management of tannery sludge is landfill. The tannery sludge could be dispose off in sanitary landfills realized as reported in the European Landfill Directive (EC/99/31). The tannery can be dispose off at different dry conditions. The thermal drying treatment has the important role of reduce the volume of sludge due to evaporation of the most part of moisture content in the sludge. As already reported in Chapter 2 the thermal drying treatment has also the

effect of inhibition of biological activity due to a too low level of water. Also the biological pre-treatment, especially the aerobic stabilization of sludge, can play an important role before the landfill. The reduction of biodegradability of organic substances contained in the sludge and the evaporation of water due to biological drying effects, can contribute to reduce the long term impacts of landfills.

The current research work has been set up to evaluate the sustainability of landfills in which different type of sludge are dispose off.

As already reported in Chapter 4 the main long term impacts of landfills are the uncontrolled biogas production and the uncontrolled leachate emissions.

The research work has been set up to understand the behaviour of landfill, especially when the barrier systems will fail. The actual landfill regulation imposes clay liners on the bottom and on the top of landfill, to avoid infiltration of water and uncontrolled leachate emissions. It is well known that these systems have a life time of some decades (Cossu et al., 2005) and they do not guarantee the perfect isolation of landfill from the environment to the eternity. Before or later a certain amount of water will enter in the landfill and uncontrolled emissions of biogas and leachate will escape.

Experiments have been set up to simulate the landfilling of tannery sludge under different conditions. Some tests have the aim to evaluate the emissions of biogas and leachate from landfill containing dry sludge perfectly isolated from the environment, without water infiltration. Other tests are finalized to characterize the long terms emissions from landfill of dry tannery sludge and of biological pre-treated tannery sludge.

The comparison between the different results obtained from experiments permits to understand what is the best management system that minimize the long term impacts of such landfill and establish the sustainable options for landfilling.

5.2 MATERIALS AND METHODS

The first experiment set up has been realized using column test. The materials used are tannery sludge at different concentration of Total Solids. Four type of sludge have been used:

- Dry tannery sludge at 60% of Total Solids.
- Dry tannery sludge at 70% of Total Solids.
- Dry tannery sludge at 80% of Total Solids.
- Dry tannery sludge at 90% of Total Solids.

The sludge has been taken from a thermal drying system treating the same excess sludge produced in an industrial wastewater treatment plant treating tannery wastewater. The lysimeters used for dry tannery sludge are represented in Figure 5.1.

The aerobically stabilized sludge comes from the experiments already presented in Chapter 4. Lysimeters have been use to simulate the landfilling of tannery sludge. The lysimeter is composed by a Plexiglas pipe close in the bottom and on the top by two black flanges. The flanges have different sampling point to take samples of gas from the top and leachate from the bottom.

The lysimeters have been placed in a thermostatic room at 35±2°C. The biogas produced is collected in a plastic bag. The bag is connected with the head space of the lysimeter by a plastic pipe. The volume of the gas contained in the plastic bags is measured moving the same amount of volume of liquid present in a glass bottle full of an acid and high salty solution to avoid that gases pass in the liquid. The amount of liquid moved from the bottle is measured by a graduated cylinder. The total volume of liquid moved from the bottle corresponds to the volume of gas presents in the plastic bag. The quality of biogas produced during anaerobic degradation processes is measured by a portable analyzer of landfill gas (LFG20). The analyzer takes samples of gas from one of the sampling point presents in top flange. The gas pumped out from the lysimeter and measured is later put in to the head space of lysimiter again by another sampling point. In that way, not lose of gas take place.

Leachate is collected in the bottom of lysimeter and samples are taken from a sampling point. All sampling points are close by valves.

The lysimeters used for aerobically stabilized tannery sludge are represented in Figure 5.2. The lysimeter is smaller that the lysimeters used for dry tannery sludge. The lysimeter is made of glass and it is closed on the top by a silicon cap. The cap is provided of two glass tubes to take samples of gas from the head space of the lysimeter. The biogas produced is collected in a plastic bag. The bag is connected with one of the sampling points by a plastic pipe. The volume of the gas contained in the plastic bags is measured moving the same amount of volume of liquid present in a glass bottle full of an acid and high salty solution to avoid that gases pass in the liquid. The amount of liquid moved from the bottle is measured by a graduated cylinder. The total volume of liquid moved from the bottle corresponds to the volume of gas presents in the plastic bag. Another sampling point is present in the bottom of the lysimeter. All sampling points are closed by valves. The lysimeters have been placed in a thermostatic room at 35±2°C. The lysimeters have been filled with 0.5 Kg of aerobically stabilized tannery sludge.

Figure 5.1 Lysimeters used for dry tannery sludge

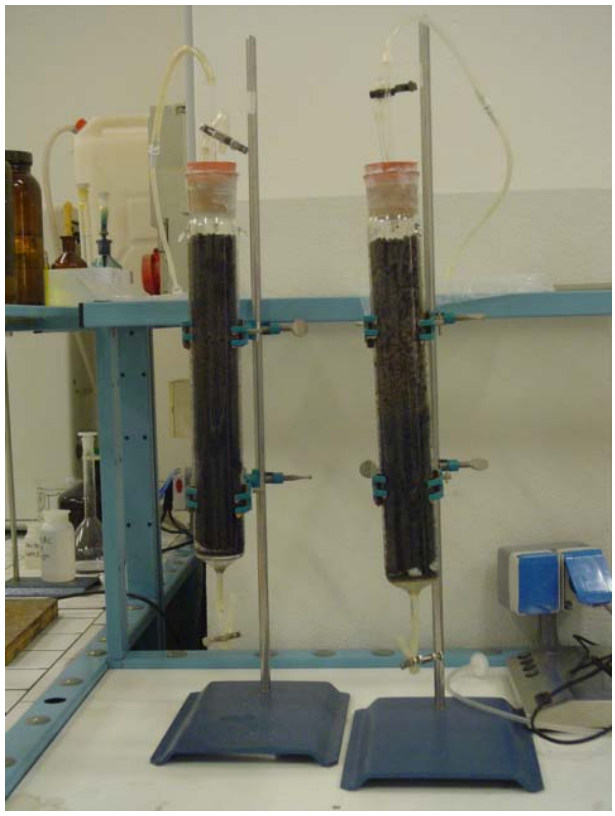

Figure 5.2 Lysimeters used for aerobically stabilized tannery sludge

The two sludges used for the experiments are:

- Tannery sludge stabilized for eight weeks at an aeration rate of 10 Nl/h
- Tannery sludge stabilized for eight weeks at an aeration rate of 1 Nl/h

The leachate samples taken from the bottom of the lysimeters have been analyzed according to Italian standard methods. The parameters analyzed have been:

- TS (Total Solids mg/l);
- TVS (Total Volatile Solids);
- COD (mg O2/l);
- BOD_5 (mg O2/l);
- DOC (Dissolved Organic Carbon, mg C/l);
- TKN (Total Kjeldhal Nitrogen, mg N/l);
- Nitrite (mg N/l);
- Sulfide (mg S=/l);
- Sulfate (mg SO42-/l);
- Clorite (mg Cl-/l);
- pH;

- Metals (Cd, Cr, Cu, Fe, Mn, Ni, Pb) (mg/l);

The experiments for dry tannery sludge have been divided in two phases: the first phase simulate the behaviour of sludge in a sanitary landfill, without infiltration of water and perfectly isolated from the environment. The aim of the experiments is to confirm the previous results presented in the Chapter 2. The first part has had a duration of one year. The biogas production and the quality have been measured constantly. The second part of the experiments has the aim to evaluate the behaviour of dry tannery sludge when the barrier systems of landfill should fail. Infiltrations of rain have been simulated adding water from the top of lysimeter. The production and the quality of biogas have been measured as well as the production and the quality of leachate. The second part of experiments has had a duration of four month.

5.3 RESULTS

5.3.1 Lysimeters of dry sludge

The first part of the experiments has simulated a sanitary landfill with barrier system perfectly working. No water has been added to the sludge in the lysimeters. The lysimeter containing dry sludge at 60% has shown a modest biological activity. The total biogas production after one year has been of 0.8 litres. The composition of biogas has been of an average carbon dioxide concentration of 30% and an average methane concentration of 1.5%. The average ratio between the concentration of methane and the concentration of carbon dioxide is 0.06. The average ratio between concentration of methane and concentration of carbon dioxide in landfill in unstable anaerobic condition is 0.7 and in stable anaerobic condition is 1.5. Considering that, the biological activity of landfill containing sludge at 60% of Total Solids, is far away from a stable anaerobic condition and is far away from unstable anaerobic condition too (Table 5.1).

The lysimeters that contain sludge at higher Total Solid concentration (70%, 80% and 90%), do not produced measurable biogas production during all the first year of monitoring. The production has been lower then the minimum measurable value of 0.1 litres.

For the lysimeter that contains dry tannery sludge at 70% of Total Solids, the average concentration of carbon dioxide have been of 21% and the average concentration of methane have been of 0.7. The average ratio between concentration of carbon dioxide and concentration of methane has been of 0.03.

For the lysimeter that contains dry tannery sludge at 80% of Total Solids, the average concentration of carbon dioxide have been of 15% and the average concentration of methane have been of 0.6. The average ratio between concentration of carbon dioxide and concentration of methane has been of 0.03.

For the lysimeter that contains dry tannery sludge at 90% of Total Solids, the average concentration of carbon dioxide have been of 2.7% and the average concentration of methane have been of 0.7. The average ratio between concentration of carbon dioxide and concentration of methane has been of 0.08.

Table 5.1 Biogas composition of different lysimeters and CH_4/CO_2 ratio, compared with average values of a landfill (bottom-right)

90A	CO2 [%v/v]	CH4 [%v/v]	CH4/CO2
12/05	2,5	0	0,00
4/06	3,09	0,05	0,02
9/06	3,5	0,1	0,03
1/07	5	0,2	0,04

90B	CO2 [%v/v]	CH4 [%v/v]	CH4/CO2
12/05	2,3	0	0,00
4/06	1,6	0,02	0,01
9/06	1,7	0,08	0,05
1/07	1,8	0,15	0,08

80A	CO2 [%v/v]	CH4 [%v/v]	CH4/CO2
12/05	6,3	0	0,00
4/06	19,7	1,24	0,06
9/06	17	0,8	0,05
1/07	18	0,2	0,01

70A	CO2 [%v/v]	CH4 [%v/v]	CH4/CO2
12/05	16,9	0	0,00
4/06	36,5	1,40	0,04
9/06	17	0,85	0,05
1/07	13	0,4	0,03

60A	CO2 [%v/v]	CH4 [%v/v]	CH4/CO2
12/05	35,7	0,46	0,01
4/06	36,9	2,50	0,07
9/06	23	1,8	0,08
1/07	15,5	1,5	0,10

60B	CO2 [%v/v]	CH4 [%v/v]	CH4/CO2
12/05	33	0,55	0,02
4/06	36,5	1,55	0,04
9/06	25	1,3	0,05
1/07	17,5	0,5	0,03

60C	CO2 [%v/v]	CH4 [%v/v]	CH4/CO2
12/05	29	0,26	0,01
4/06	33,7	4,90	0,15
9/06	29	2,3	0,08
1/07	30	0,3	0,01

	CO2 [%v/v]	**CH4 [%v/v]**	**CH4/CO2**
Stable	**40**	**60**	**1,50**
Unstable	**60**	**40**	**0,67**

Such results confirm the conclusions of Chapter 2. If the sludge are maintained in perfect isolated conditions, the biological activity of degradation of organic substances in the sludge are very slow, due to an insufficient amount of water available for bacteria. The amount of carbon dioxide results higher than the emission of methane; that indicates that only very slow fermentative degradation processes are present and the anaerobic condition never reaches a stable state.

The second part of the experiment has simulated the infiltration of rain in the body of landfill. The water added from the top of lysimeters has restarted the biological activity of sludge. Not all the water added has produced leachate. Figure 5.3 reports the hydraulic balance between the amount of water added form the top of lysimeters and the leachate extracted from the bottom. About 17% of water added in the lysimeter containing sludge at 60% of Total Solids has been adsorbed while 83% produced leachate extracted from the bottom. About 28% of water added in the lysimeter containing sludge at 70% of Total Solids has been adsorbed while 72% produced leachate extracted from the bottom. About 47% of water added in the lysimeter containing sludge at 60% of Total Solids has been adsorbed while 53% produced leachate extracted from the bottom. All the water added in the lysimeter containing sludge at 90% of Total Solids has been adsorbed by sludge and no production of leachate took place in four month of experiment.

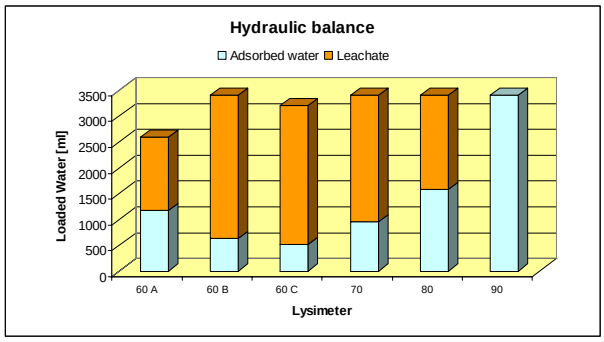

Figure 5.3 Hydraulic balance for lysimeters containing dry tannery sludge

% TS	Cumulative biogas production (ml)	Specific biogas production [Nml/ gTS]
60	48314	26,84
70	5504	2,62
80	26233	10,93
90	99178	36,73

Table 5.2 Biogas production from lysimeters containing dry tannery sludge

The biogas production started about after one month from the first water added. The production rate has been of 150Nml/d for lysimeter 60, 10 Nml/d for lysimeter 70, 60 Nml/d for lysimeter 80 and 400 for lysimeter 90. Around the third month the production of biogas increased. The biogas production rates increased for all lysimeters of about ten times. The production rate of last month has been of 1250Nml/d for lysimeter 60, 100 Nml/d for lysimeter 70, 1400 Nml/d for lysimeter 80 and 2850 for lysimeter 90.

The specific total biogas production after four month has been of 23Nl/KgTS for sludge at 60% of Total Solids, 3Nl/kgTS for sludge at 70% of Total Solids, 10Nl/KgTS for sludge at 80% of Total Solids and 31Nl/KgTS for sludge at 90% of Total Solids.

The biogas composition is shown on Figures 5.4 and Figure 5.5. The concentration of carbon dioxide increase during the fist 80 days of experiment to a value of 40%. In this phase the main processes carrying out are hydrolysis and fermentation; the long chain of organic substances are hydrolyzed to monomers by bacterial enzymes and the fermentative bacteria consume such monomers to produce volatile fatty acids, carbon dioxide and hydrogen. In this phase the production of methane is low because the concentration of acetic acids in low. The concentration of methane start to increase after about eighty days for lysimeters containing sludge at 80% and 90% of sludge and it reach a stable value of about 50% after about one hundred days. The concentration of carbon dioxide decrease lightly in this phase because part of its is consumed to produced to produce methane from hydrogen.

The conditions remain stable and the production of biogas carries on in a faster way.

The lysimeter containing sludge at 70% of Total Solids follows the same behaviour but with one month of delay. The concentration of methane increase slowly but constantly and it reaches a value of 40% in the end of the test.

The lysimeter containing sludge at 60% has had a behaviour similar to the lysimeters containing sludge at 80% and 90% of Total Solids. The concentration of carbon dioxide remained stable during the four month at an average value of 20%. The methane production started around the first month to reach an exponential grown at the second month. The final value of 60% have been reached after three month.

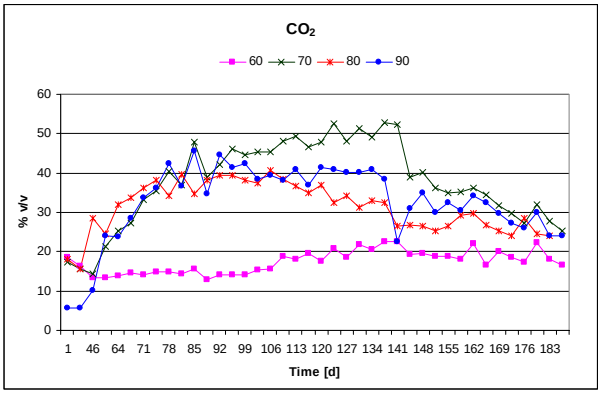

Figure 5.4 Carbon dioxide concentration in biogas from different lysimeters

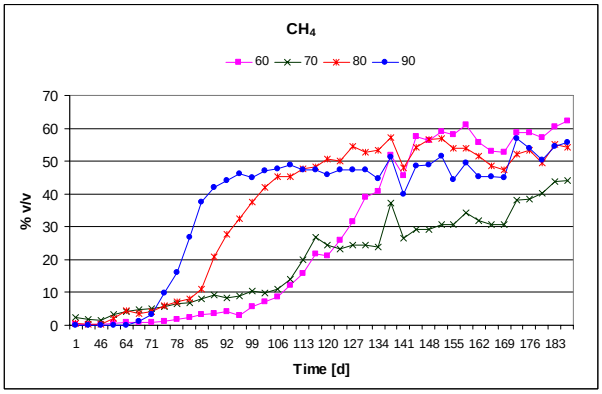

Figure 5.5 Methane concentration in biogas from different lysimeters

The quality of the leachate produced during the experiments is reported in Table 5.3 and it shows high polluting features. The pH of leachate produced in all the lysimeters has an average value of 7.7 for lysimeter at 60% of Total Solids, 7.3 for lysimeter at 70% of Total Solids and 7.74 for lysimeter at 80% of Total Solids. This is due to the buffer compounds used during the tanning processes and presents in the tannery sludge. The average pH of a landfill during the first phase of anaerobic degradation should be around 6, due to the high production of volatile acids. In this case the production of volatile acids is buffers by such buffer compounds.

The concentration of organic compounds is one or two times higher then the concentration of organic compounds normally presents in a landfill in the first phase of anaerobic condition. The concentration of COD has an average value of 89300 mgO_2/l for lysimeter at 60% of Total Solids, of 36700 mgO_2/l for lysimeter at 70% of Total Solids and 26000 mgO_2/l for lysimeter at 80% of Total Solids. The average concentration of COD reported by Ehrig, (1990) measured in different landfill is 22000 mgO_2/l during the first phase of anaerobic degradation and 3000 mgO_2/l during the longer phase of stable methane production. Comparing the values the high concentration of organic substances can be understood and consequently the high polluting feature of such leachate.

Table 5.3 Quality of leachate from lysimeters containing dry tannery sludge

		60		70		80		Leachate quality of a landfill in acids conditions		Leachate quality of a landfill methanogenic conditions	
		range	average	range	average	range	average	range	average	range	average
pH		7.11 - 8.03	7.71	6.98 - 7.49	7.33	7.55 - 8.04	7.74	4,5 - 7	6	7,5 - 9	8
COD	mgO_2/l	35681 - 142542	89319	13333 - 58032	36709	13146 - 43430	25994	6.000 - 60.000	22000	500 - 4.500	3000
BOD_5	mgO_2/l	0 - 300	80	60 - 300	200	0 - 500	215	4000 - 40000	13000	20 - 550	180
DOC	mgC/l	12250 - 69200	42873	12000 - 30500	17554	7209 - 22600	11889	-	-	-	-
TKN	mgN/l	6188 - 18060	11968	4620 - 9884	6288	5152 - 6496	5626	40 - 3425	1350	40 - 3425	1350
NH_4^+	mgN/l	3051 - 16862	10041	4311 - 8792	5887	3827 - 5712	4888	30 - 3000	750	30 - 3000	750
SO_4^{2-}	mgS/l	104 - 4992	1712	5- 5057	1838	5 - 997	614	70 - 1750	500	10 - 420	80
S^{2-}	mgS/l	24 - 112	60	32 - 128	59	24 - 128	66	-	-	-	-
Cl^-	mgCl/l	2411 - 13474	6979	3616 - 10424	6068	4751 - 10708	7476	100 - 5000	2100	100 - 5000	2100
Cd	mg/l	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	-	-	-	-
Cr	mg/l	10.0 - 16.9	11.37	25 - 73.8	39.18	32.6 - 46.7	38.93	0.03 - 1.6	0.3	0.03 - 1.6	0.3
Cu	mg/l	7.73 - 18.20	10.41	0.46 - 2.76	1.19	0.349 - 5.75	2.23	0.004 - 1.4	0.08	0.004 - 1.4	0.08
Fe	mg/l	2.45 - 6.61	3.97	2.16 - 25.70	9.34	6.86 - 14.7	10.04	20 - 2100	780	3 - 280	15
Mn	mg/l	0.106 - 0.994	0.38	0.064 - 1.07	0.48	0.141 - 0.528	0.37	-	-	-	-
Ni	mg/l	0.82 - 3.21	1.48	0.166 - 0.422	0.27	0.731 - 0.888	0.81	0.02 - 2.05	0.2	0.02 - 2.05	0.2
Pb	mg/l	0.145 - 1.08	0.48	<0.05	<0.05	<0.05	<0.05	-	-	-	-
Zn	mg/l	3.12 - 16.00	8.36	0.01 - 1.22	0.31	1.23 - 4.63	2.78	0.1 - 120	5	0.03 - 4	0.6

The BOD_5/COD ratio is very low for all the leachate produced in the lysimeters. The average value of BOD_5 is 165 mgO_2/l and the average BOD_5/COD ratio is 0.003. The BOD_5/COD ratio generally indicates the biodegradability of a wastewater. A low value indicate that the most part of organic substances in the wastewater are not biodegradable. In this case could not be true this sentence because the biological degradation of organic substances can be inhibited by the high ammonia concentration and the high chloride concentration.

Even the nitrogen compounds are times higher than the average value in landfills. Ammonia is the main nitrogen compound presents in the leachate. The Total Kjeldahl is composed more then 80% by ammonia. The average concentration of ammonia in lysimeter containing tannery sludge at 60% of Total Solids is 10050 mgN/l, the average concentration in lysimeter containing tannery sludge at 70% of Total Solids is 5887 mgN/l and the average concentration in lysimeter containing tannery sludge at 80% of Total Solids is 4888mgN/l. The average concentration of ammonia in a landfill is of 750mgN/l and that value remains stable due to anaerobic conditions. No degradation of ammonia can be observed because bacteria can not oxidize it due to the lack of oxygen.

The other compounds that are present in the leachate at higher concentration than average value of landfill are chloride, chrome and cupper. These compounds are present in the tannery sludge due to the high concentration in tannery wastewater. Chloride is largely discharged in tanning processes while chrome and cupper are used during tanning process.

The average concentration of chloride is three times higher than the average concentration in a normal landfill.

The average chrome concentration in lysimeter containing tannery sludge at 60% of Total Solids is 11.37 mg/l, the average concentration in lysimeter containing tannery sludge at 70% of Total Solids is 39.18 mg/l and the average concentration in lysimeter containing tannery sludge at 80% of Tannery Sludge is 38.93mg/l. These values are one hundred times higher than the concentration of chrome in a landfill.

Even the concentration of copper is higher than the average concentration in a landfill as reported in Table 5.3.

The results indicate that the landfilling of dry tannery sludge, without pre-treatment, represent a potential environmental problem, when the barrier system of the landfill will fails. Even if the moisture content of sludge in not sufficient to support biological activity, this situation is limited during the life of the landfill. When the impermeable layers will reach they end of life, rain will enter in the body of landfill and the biological degradation of organic substances will start again.

The dry tannery sludge landfilled without pre-treatment are mummified and the biodegradability is organic substances conserved during the years.

5.3.2 Lysimeters of aerobically pre-treated sludge

The lysimeters containing aerobically pre-treated tannery sludge have shown a different behaviour. The sludge has not been dry after the biological stabilization process and the concentration of Total Solids is 27%. The amount of water added to the lysimeter has been proportionally equal to the amount of water added to the lysimeters containing dry and not pre-treated tannery sludge.

The biogas production has been very low. The total production of biogas, after two month of experiments has been of been lower than 0.05 litres that lower that the detectable limit of the measuring system. The quality of the biogas of the two lysimeters is reported in Figure 5.6 and Figure 5.7. The average concentration of carbon dioxide has been of 10% while the average concentration of methane has been always lower than 1%.

The average value of leachate quality is reported in Table 5.4. The concentration of COD is 3250 mgO2/l for tannery sludge treated with 10Nl/kgh of aeration and the concentration of COD is 1400 mgO2/l for tannery sludge treated with 1Nl/kg/h. These values are ten times lower than the average concentration of COD for dry tannery sludge not pre-treated. The concentration of BOD_5 is lower than 0.01 mg/l. The ammonia concentration is about one hundred times lower than the average concentration of lysimeter containing not pre-treated sludge.

The concentration of metals is always lower than 0.8 mg/l except for Iron. The aerobic stabilization has influenced the mobility of metals as reported in Chapter 4. Even if the concentration in the treated sludge of metals increased, due the reduction of weigh during the treatment, the mobility has been really decreased. Comparing the concentration of metals of lysimeters containing pre-treated sludge and not pre-treated sludge, it is possible to understand the effects of biological stabilization of sludge and the advantages to reach the environmental sustainability of landfill.

Only chlorides maintain the same concentration between lysimeters containing pre-treated sludge and not pre-treated sludge. The concentration of sulphate increased in lysimeters containing sludge pre-treated. This is due to the aerobic stabilization process during which the sulphide has been oxidized to sulphate in presence of oxygen.

The results obtained from the research work show the main role played by aerobic pre-tretment for the realization of a sustainable landfill. The impacts of uncontrolled emissions have been

measured in the first part of the research work. The emission of biogas and the quality of leachate can not be considered sustainable for the future generation. Analysing the emissions of lysimeters containing pre-treated sludge, the possibility to realized a sustainable systems emerges.

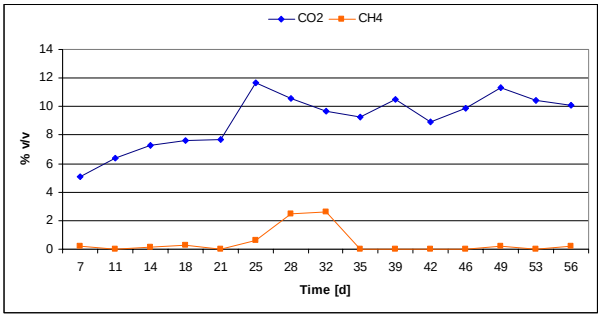

Figure 5.6 Biogas composition of aerobically stabilized tannery sludge at 10Nl/kg*h

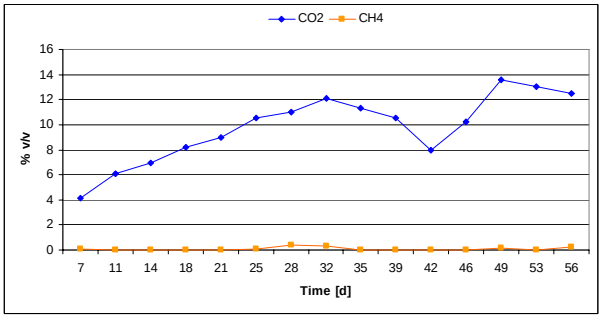

Figure 5.7 Biogas composition of aerobically stabilized tannery sludge at 1Nl/kg*h

Table 5.4 Leachate quality of lysimeter containing aerobically stabilized tannery sludge

		Aerobic stabilized tannery sludge at 10 Nl/Kgh	**Aerobic stabilized tannery sludge at 1 Nl/Kgh**	**Average leachate quality of untreated dry tannery sludge**
pH		7.5	7.6	7.6
COD	mgO_2/l	3250	1400	50674
BOD_5	mgO_2/l	-	-	165
DOC	mgC/l	1280	1000	24105
TKN	mgN/l	800	360	7961
NH_4^+	mgN/l	620	280	6939
SO_4^{2-}	mgS/l	4800	2700	1388
S^{2-}	mgS/l	16	24	62
Cl^-	mgCl/l	5600	2650	6841
Cd	mg/l	<0,01	<0,01	<0.01
Cr	mg/l	0.71	0.35	29.83
Cu	mg/l	<0,01	<0,01	4.61
Fe	mg/l	35.90	14.50	7.78
Mn	mg/l	0.40	0.23	0.41
Ni	mg/l	0.22	0.10	0.85
Pb	mg/l	<0,05	<0,05	<0.05
Zn	mg/l	<0,05	<0,05	3.82

Chapter 6

CONCLUSIONS

The treatment of municipal and industrial wastewater is a field of environmental and sanitary engineering characterized by a long tradition, if compared to other fields, and the developments of the research are providing interesting and fascinating opportunities. On the other hand the wastewater treatment processes produce residues, frequently in solid state, that are a waste to treat and dispose off. In this case the wastewater treatment theory and processes meet the solid waste theory and processes. The management of excess sludge from biological wastewater treatment plants is one of the main problems connected with such treatment processes because excess sludge is a waste to treat and dispose off. The excess sludge can be considered the ring of connection between the treatment of wastewater and the treatment of solid waste.

To limit the growing impacts of human society to environment, sustainable management systems of waste must be find out. A management system can be composed by different phases and treatments. Common aim of all possible processes must be not only economical convenience but environmental sustainability.

The present research work has been carried out to evaluate some possible treatments with the aim to reach sustainability of tannery sludge management systems.

In relation to the overall approach the main findings are the followings.

Experimental tests have been set up to evaluate the effects of thermal drying system of the biological activity of sludge. The optimization of this process has the target of evaluate the minimum total solid content in the sludge that allow an inhibition of microbial activity due to lack of water. The experiments have been set up both in aerobic and anaerobic conditions. The minimum total solid content emerged in the research work seems to be 75%. Consequently an amount of moisture of 25% is not sufficient to support microbial activity, and the dry sludge does not show appreciable biological degradation processes, independently by he biodegradability of organic substances in the sludge. The thermal drying system can be set to a

final target value of 75% of Total Solid content of treated sludge. Energy saving can be obtained avoiding lower moisture content than 25%.

The research work regarding the aerobic stabilization of tannery sludge has verified the possibilities and the limits of a treatment to stabilize the sludge by forced aeration previous landfill disposal. The targets have been the stabilization of organic substances and the reduction of water content, limiting the negative effects on the quality of landfill biogas and leachate. Furthermore the research work has verified the variation of the mobility of some metals during leaching test and the variation of Dissolved Organic Carbon content, during the process of stabilization. The work has regarded the stabilization of tannery sludges originating from a drying system and a mixture of tannery sludge and compost. The mixture of materials with different characteristics has the main function to positively influencing the general conditions of the degradation process of the organic compounds and to give the adequate porosity for the air inflow. Moreover the compost can be used as chelant for the metals in the sludge. The results seem to be encouraging for the development of an aerobic treatment technology for the stabilization of tannery sludge. The treatment seems to work though the negative characteristics of the tannery sludge. The reduction of total volatile solid content have been of 35% in all the experiments set up. The reduction of moisture content goes from 10%, for low aeration rate, to 60% fro high aeration rate. Even the biological activity, measured by respiromentric test and fermentative test, has reach the values suggested in the international literature as stable waste conditions. The mixing with compost has demonstrated good results too. The reduction of moisture and total volatile solids contents have been comparable with test without compost. Analyzing the reduction of volatile solids and biological stability of tannery sludge in the mixture, better results emerged compared to experiments without compost. The reduction of volatile solids has been from 35% to 50%. The respiromentric index reach values indicating stable conditions after four weeks, instead of eight weeks in the experiments without compost.

Good results have been obtained also for metal leachability. The aerobic stabilization has reduced the mobility of metal during leaching test of about 80% in most cases. Similar results have been obtain in lysimeter test, comparing the leachate quality of untreated sludge and aerobically stabilized sludge.

For the investigation of the biological production of hydrogen by dark fermentation, laboratory tests have been conducted at a mesophilic process temperature of 35°C in batch operation. The biomass used as inoculum have been subjected to thermal pre-treatment to inhibit the methanogenic acivity and to enhance the hydrogen production. The results show a good production of hydrogen from glucose. This indicate the good effects of heat pre-treatment on

inhibition of methanogenic bacteria. Good production of Hydrogen have been realized also from Kitchen Waste. Iron positively influences the fermentation process. The presence of higher concentration of iron in the liquid phase allow a faster production of hydrogen if compared with batch tests where no iron was added. Moreover iron seems to influence the metabolic pathways of bacteria favouring the production of Acetic Acids as final product of fermentation and so improving the production of Hydrogen due to high theoretical hydrogen production correlated with Acetic Acid production. The hydrogen production from tannery sludge has been comparable with the results from kitchen waste but with slower production rate and long lag phase. The methane production has not been avoided. Probably the low biodegradability of tannery sludge and the fact that this substrate contents different types of biomass allows methanogenic bacterial to maintain or establish again their activity.

The last part of present research work has been set up to understand the behaviour of tannery sludge dispose of in sanitary landfill, especially when the barrier systems will fail. The actual landfill regulation imposes clay liners on the bottom and on the top of landfill, to avoid infiltration of water and uncontrolled leachate emissions. It is well known that these systems have a life time of some decades and they do not guarantee the perfect isolation of landfill from the environment to the eternity. Before or later a certain amount of water will enter in the landfill and uncontrolled emissions of biogas and leachate will escape. Some tests have the aim to evaluate the emissions of biogas and leachate from landfill containing dry sludge perfectly isolated from the environment, without water infiltration. Other tests are finalized to characterize the long terms emissions from landfill of dry tannery sludge and of biological pre-treated tannery sludge.

The monitoring of lysimeter has confirmed what already emerged in the first part of present research work. Moisture content of 25% is not sufficient to support biological activity and the tannery sludge remains in stable condition until water do not reach the body of landfill. The second part of experimentation has analyze the emissions from landfill containing untreated dry sludge when water reach the sludge due to failing of barrier system. The emission of biogas and quality of leachate indicate that the degradation of organic substances start quickly and the thermal drying treatment does not sterilize the sludge. The biogas emissions and the leachate quality do not indicate a sustainable condition. Comparing these conditions with lysimeters contatining aerobically stabilize tannery sludge, the good effects of pre-treatment can be observed. The biogas production has been very low. The average concentration of carbon dioxide has been of 10% while the average concentration of methane has been always lower than 1%. The aerobic stabilization has positively influenced the mobility of metals as reported in

Chapter 3 and Chapter 6. Even if the concentration in the treated sludge of metals increased, due the reduction of weigh during the treatment, the mobility has been really decreased. Comparing the concentration of metals of lysimeters containing pre-treated sludge and not pre-treated sludge, it is possible to understand the effects of biological stabilization of sludge and the advantages to reach the environmental sustainability of landfill.

The presented research work and to final conclusions and consideration should be useful to analyse and evaluate different possibilities for the realization and management of a complete treatment system form tannery sludge and also in general for the entire strategy of a wastewater treatment plant, analysing costs and return, environmental impacts and benefits.

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