DOKUZ EYLÜL UNIVERSITY GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

ANAEROBIC DIGESTION OF PHOSPHORUS RICH SLUDGE

by Enis TOKAT

> **April 2008 İZMİR**

ANAEROBIC DIGESTION OF PHOSPHORUS RICH SLUDGE

A Thesis Submitted to the

Graduate School of Natural and Applied Sciences of Dokuz Eylül University In Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy in Environmental Engineering, Environmental Technologies Program

> **by Enis TOKAT**

> > **April 2008 İZMİR**

We have read the thesis entitled **"ANAEROBIC DIGESTION OF**

PROF. DR. AYŞEGÜL PALA

Supervisor

PHOSPHORUS RICH SLUDGE" completed by **ENİS TOKAT** under supervision of **PROF. DR. AYŞEGÜL PALA** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Doctor of Philosophy.

Ph.D. THESİS EXAMINATION RESULT FORM

PROF DR. LEMAN TARHAN PROF. DR. SOL ÇELEBİ

Committee Member Committee Member

Jury Member Jury Member

Prof. Dr. Cahit HELVACI Director Graduate School of Natural and Applied Sciences

ACKNOWLEDGEMENTS

I would like to express my appreciation to my advisor, Prof. Dr. Ayşegül PALA, who supported me for everything done in this study, shared her experiences, knowledge and time, and supplied all the materials, for her advises, guidance and patience.

I would also like to thank to the committee members, Prof Dr. Sol ÇELEBİ and Prof. Dr. Leman TARHAN for their advices, guidance and patience for more than four years. I'm very grateful to Prof. Dr. Delya SPONZA and Prof Dr. Lütfi AKÇA for their advices. I am very pleased to Prof. Dr. Osman ÜÇÜNCÜ from Karadeniz Technical University, for sharing his experiences. I would also like to thank to Nuri AZBAR for his advices and sharing his experiences.

I would also like to thank to İZSU General Directorate for letting us use the sludge, laboratory and chemicals. I would like to thank to everybody who supported me in İZSU and İzmir Wastewater Treatment Plant, especially Head of Wastewater Treatment Plants M.Güven AĞAR, former Head of Wastewater Treatment Plants Gürsel ÇALIŞ, Manager of İzmir Wastewater Treatment Plant M. Faruk İŞGENÇ, Cosultant of İZSU General Manager Assoc. Prof. Dr. Vildan GÜNDOĞDU, Environmental Engineers Tolga TUNCAL, Tolga ALPBAZ, Münevver ELELE, Gözde AKGÜN and Onur PİYANCI for their supports, Chemist İlhan ÇİÇEK for his providence in laboratory analysis. I would also like to thank to Gökhan DEMİREL from ASKİ General Directorate Ankara Wastewater Treatment Plant.

This study was financially supported by Dokuz Eylül University Research Fund (Project Code:DEÜ SRPD 03.KB.FEN.022), and I am very grateful for their support.

Finally, I would like to thank to all of my friends for their helps and to my wife Betül Hayriye TOKAT and my family for their moral and financial supports, and their patience.

Enis TOKAT

ANAEROBIC DIGESTION OF PHOSPHORUS RICH SLUDGE

ABSTRACT

In this study, the main purpose was to investigate the behavior of phosphorus during anaerobic digestion process of İzmir Wastewater Treatment Plant's (İzmir W.W.T.P.) sludge, which tends to have higher phosphorus concentrations than conventional activated sludge processes because of the mechanism of biological phosphorus removal.

The stabilization and gas production potential of İzmir W.W.T.P.'s sludge were investigated. The best anaerobic digestion process parameters and the solids and phosphorus balance during the anaerobic digestion process were determined. According to the determined parameters the anaerobic digesters were designed and the energy productions were determined.

The studies were carried out in three stages:

 In the first stage, the characteristics of primary, excess and mixed sludge were determined.

In the second stage the methane production potentials, the COD contents that can be anaerobically converted to methane, of the primary, excess and mixed sludge were determined by using biochemical methane potential (BMP) assay.

In the third stage, an anaerobic digester model with five reactors was used. Three of the reactors were used for primary, excess and mixed sludge. The inoculum sludge was taken from Ankara W.W.T.P. anaerobic digester. The dry solids and volatile solids reductions, gas productions and the behavior of phosphorus were monitored.

When the volatile solids and COD reductions, the gas production and the methane content of the gas are evaluated, the optimum hydraulic retention time was determined as 15 days for İzmir W.W.T.P primary, excess and mixed sludges. At this

HTR the electricity production of the plant would be 112.875 kWh/d which is more than the consumption of the whole treatment plant as 100.000 kWh/d.

It can be concluded that, 25 % of the phosphorus was released from the structure of both the excess and mixed sludges during the anaerobic digestion process which adds a 20 % phosphorus load to the influent phosphorus load.

Keywords: anaerobic digestion, biological phosphorus removal, municipal sewage sludge, biochemical methane potential (BMP)

FOSFORCA ZENGİN ÇAMURLARIN ANAEROBİK OLARAK ÇÜRÜTÜLMESİ

ÖZ

Bu çalışmanın temel hedefi, biyolojik fosfor giderimi mekanizması gereği konvansiyonel aktif çamur prosesine göre daha yüksek miktarlarda fosfor içerme eğilimi gösteren İzmir Atıksu Arıtma Tesisi (İzmir A.A.T) çamurunun anaerobik olarak çürütülmesi sırasında fosforun davranışının araştırılmasıdır.

İzmir A.A.T çamurlarının stabilizasyon ve gaz üretim potansiyeli belirlenmiştir. Optimum anaerobik çürütme proses parametreleri belirlenerek anaerobik çürütme prosesinin kütle ve fosfor dengesi saptanmıştır. Belirlenen parametreler dikkate alınarak anaerobik çürütücülerin tasarımı yapılarak üretilecek enerji miktarları saptanmıştır.

Çalışma üç aşamada yürütülmüştür:

Birinci aşamada, ön, son ve karışık çamurun karakteristikleri belirlenmiştir.

İkinci aşamada, ön, son ve karışık çamurların metan üretim potansiyeli ve anaerobik olarak metana dönüştürülebilecek COD içeriği biyokimyasal metan potansiyeli (BMP) testleri ile belirlenmiştir.

Üçüncü aşamada, beş tane reaktörü olan bir anaerobik çürütme laboratuar modelinin üç reaktörü ön, son ve karışık çamur ile işletilmiştir. Aşı çamuru Ankara Atıksu Arıtma Tesisi anaerobik çürütücüsünden alınmıştır. Kuru madde ve organik madde giderimi, gaz oluşumu ve fosforun davranışı izlenmiştir.

Uçucu katı madde ve KOİ giderimleri, gaz üretimi ve üretilen gazın metan içeriği dikkate alındığında İzmir A.A.T ön, son ve karışık çamur için optimum hidrolik alıkonma süresi 15 gün olarak belirlenmiştir. Bu hidrolik alıkonma süresinde

üretilecek olan elektrik enerjisi 112.875 kWh/gün olarak hesaplanmış olup, bu miktar tesisin toplam enerji tüketimi olan 100.000 kWh/gün'ü karşılayacak miktardadır.

Sonuç olarak son ve karışık çamurun anaerobik olarak çürütülmesi prosesi sırasında çamurun bünyesindeki fosforun % 25'inin salındığı, böylelikle giriş fosfor yükünün % 20 oranında arttığı saptanmıştır.

Anahtar Sözcükler: anaerobik çürütme, biyolojik fosfor giderimi, kentsel arıtma çamuru, biyokimyasal metan potansiyeli (BMP)

CONTENTS

Page

1. CHAPTER ONE INTRODUCTION

In the last decades, concern has arisen over environmental pollution caused by the increase in wastewater quantities and pollution loads with the developing industry and urbanization. To prevent environmental pollution, wastewater is treated by using mechanical, chemical, biological and physicochemical methods.

Only wastewater treatment itself does not mean that the pollution is prevented, because sewage sludge problem is faced. In wastewater treatment processes, settleable suspended solids are separated in primary sedimentation tanks, dissolved solids are settled as biomass in final sedimentation tanks, and this solid material is called "sewage sludge".

One of the leading international pioneers of wastewater technology, the socalled "waste water pope" Dr. Karl Imhoff, commented already in the year 1951:

"All reports regarding treatment and utilization of sludge may not deceive over the fact, that by the waste water disposal we have to get rid off the sludge absolutely and once and for all. A sewage plant, where this could not be managed, is worthless. Even if the sludge will be incinerated or gasified, ashes remain which have to be removed" (Protechnich, 2002).

"The sludge resulting from wastewater treatment operations and processes is usually in the form of a liquid or semisolid liquid that typically contains from 0.25 to 12 percent solids by weight." (Metcalf & Eddy Inc., 1991, p765). Besides this high water content, the organic content of sewage sludge is also high. Therefore, investment and operation costs for the disposal of sludge can be 20-50 % of the treatment plant. Because of this reason for the solution of sludge problem, technically applicable and economical alternatives have been developed.

For sludge treatment various processes can be applied. "Thickening (concentration), conditioning, dewatering, and drying are used primarily to remove moisture from sludge; digestion, composting, incineration, wet-air oxidation, and vertical tube reactors are primarily used to treat or stabilize the organic material in the sludge." (Metcalf $& Eddy$ Inc., 1991, p766).

The applicability of these processes varies mainly depending on simplicity of technology and operation, and investment, maintenance and operation costs. The sludge characteristics of every city may vary; even the same city's sludge may vary by season, weather, sludge withdrawal, etc. Therefore, the process should be selected after the feasibility study for each technology for every city.

If the decrease of the energy sources of the world is taken into consideration, utilization of sludge and energy production by using anaerobic digestion process will be an economical alternative.

The anaerobic sludge digestion (stabilization) process is not a recent development. In the $19th$ century the digestion of domestic wastes and wastewater was accomplished in about eighteen days. The detention time is comparable to that used in the design and operation of current-day anaerobic digestion systems (Eckenfelder et al., 1992).

In the $20th$ century the anaerobic digestion process was studied. Digestion tanks were separated by using heat, related accessories and design parameters of the tanks were improved. "It is interesting to note that the same practice is being followed today, but great progress has been made in the fundamental understanding and control of the process, the sizing of tanks, and the design and application of equipment." Anaerobic digestion is still the most commonly used sludge stabilization process, because of the energy upkeep and recovery, and the alternatives of sludge utilization.

In İzmir W.W.T.P. anaerobic digestion process is one of the sludge treatment alternatives and will most probably be applied in the very near future.

The conventional biological treatment methods that are being used for decades in the world are not effective for the removal of nutrients such as nitrogen and phosphorus. These nutrients cause eutrophication, which is "the pollution of a waterway by heavy organic growth stimulated by inorganic nutrients" (Cinar, 1996, p1). Therefore, with the regulatory and environmental demand for advanced treatment, biological phosphorus removal mechanism was added and applied as a new technology for activated sludge systems.

In İzmir W.W.T.P, a modification of 5-stage Modified Bardenpho Process which is an advanced biological treatment process is applied. In this process nitrogen and phosphorus removal take place besides the treatment of carbonaceous substances. In biological phosphorus removal systems, phosphorus accumulates in the biomass and is removed in the form of excess sludge. Nearly all the enhanced phosphorus removal is due to the storage of poly-phosphates. Because of this mechanism, excess sludge tends to have higher phosphorus concentrations than conventional activated sludge.

The purpose of this thesis is to determine the stabilization and gas production potential of İzmir W.W.T.P's sludge, the optimum process parameters for anaerobic digestion, and the behavior of phosphorus during anaerobic digestion process. It was assumed that one of the problems that must be taken into consideration in the design and operation of the anaerobic digestion system is the expected high phosphorus content of the sludge. The phosphorus in the sludge is expected to be released back to the water from the sludge structure in anaerobic digestion process, as a matter of the mechanism of biological phosphorus removal. In addition, the released phosphorus can be fixed chemically as especially struvite (MAP) and form a precipitate.

In the experimental studies that were carried out in İzmir W.W.T.P. laboratory an anaerobic digester model with five reactors was used. Before the operation of the reactors, the methane production potentials of the sludges were determined by using biochemical methane potential (BMP) assay and the characteristics of the sludges were determined. During the operation of the reactors, the optimum hydraulic retention time was determined according to the VS reductions and gas productions. The formation of struvite was also investigated during 15 and 20 days HRT by the measurement of magnesium in the supernatant of feed and digested sludges.

2. CHAPTER TWO PROCESS DESCRIPTIONS AND LITERATURE SURVEY

2.1 Typical sewage sludge characteristics

"Sludge from primary settling tanks is usually gray and slimy and in most cases, has an extremely offensive odor…. Activated sludge generally has a brownish, flocculent appearance.... Sludge in good condition has an inoffensive earthy odor." The sludge characterization including most of the chemical constituents is important for the selection of dewatering and disposal of sludge. For the process control of anaerobic sludge digestion pH, alkalinity and organic acid content is important. For incineration and land application of sludge, the content of heavy metals, pesticides and hydrocarbons has to be determined. The thermal energy content is also important if a thermal reduction process such as incineration is considered (Metcalf $& Eddy$ Inc., 1991). The composition of untreated primary, excess and mixed sludge is given in (Table 2.1).

	Primary Sludge		Excess Sludge		Mixed Sludge	
Parameter	Range	Typical value	Range	Typical value	Range	Typical value
Dry Solid Content (% DS)	$4.0 - 10.0$	5.0	$0.5 - 1.5$	0.8	$3.0 - 8.0$	4.0
Volatile Solid Content (% LOI)	60-80	65	59-88		60-80	
pH	$5.0 - 8.0$	6.0	$6.5 - 8.0$			
Alkalinity (mg CaCO ₃ /L)	$500 -$ 1500	600	580- 1100			
Organic Acids (mg/L as HAc)	$200 -$ 2000	500	1100- 1700			
Total Nitrogen $(\%$ of DS)	$1.5 - 4.0$	2.5	$2.4 - 5.0$			
Total Phosphorus $\frac{6}{6}$ of DS)	$0.8 - 2.8$	1.6	$2.8 - 11.0$			

Table 2.1 Typical composition of untreated primary excess and mixed sludge (Protechnich, 2002**;** Metcalf & Eddy Inc., 1991).

The typical heavy metal content of wastewater sludge is given in (Table 2.2).

Heavy Metal	Unit	Range	Median
Arsenic	(mg/kg of TS)	1.1-230	10
Cadmium	(mg/kg of TS)	1-3410	10
Total Chromium	(mg/kg of TS)	10-99000	500
Cobalt	$(mg/kg \text{ of } TS)$	11.3-2490	30
Copper	$(mg/kg \text{ of } TS)$	84-17000	800
Iron	$(mg/kg \text{ of } TS)$	1000-154000	17000
Lead	(mg/kg of TS)	13-26000	500
Manganese	(mg/kg of TS)	32-9870	260
Mercury	(mg/kg of TS)	$0.6 - 56$	6
Molybdenum	$(mg/kg \text{ of } TS)$	$0.1 - 214$	$\overline{4}$
Nickel	$(mg/kg \text{ of } TS)$	2-5300	80
Selenium	$(mg/kg \text{ of } TS)$	$1.7 - 17.2$	5
Tin	$(mg/kg \text{ of } TS)$	2.6-329	14
Zinc	$(mg/kg \text{ of } TS)$	101-49000	1700

Table 2.2 Typical heavy metal content of wastewater sludge (Metcalf & Eddy Inc., 1991).

The dry solids content of mixed sludge after aerobic stabilization ranges between 1.5 to 4.0 % DS with a typical value of 2.4 %. After anaerobic digestion the dry solids content can range between 2.5 to 7.0 percent with a typical value of 3.5 %. The organic content of the sludge decreases after stabilization to a range between 30 to 60 % with a typical value of 40 %. By using dewatering processes, the feed sludge can be dewatered up to $20 - 22$ % DS, the aerobically stabilized sludge up to 22 – 25 % DS and the anaerobically stabilize sludge up to 30 – 40 % DS (Metcalf $\&$ Eddy Inc., 1991).

2.2 Sludge Stabilization

"Sludge is stabilized to reduce pathogens, eliminate offensive odor, and inhibit, reduce, or eliminate the potential of putrefaction." These objectives can be achieved by the effectiveness of the applied stabilization process on the degradation of volatile or organic portion of the sludge which is the potential odor producing content. If the microorganisms are allowed to grow in the organic portion of sludge, pathogens are also survived, odor is released and putrefaction occurs. For the elimination of these conditions by stabilization; volatile content can be biologically reduced or chemically oxidized, microorganism activity can be prohibited by the addition of chemicals and the sludge can be disinfected or sterilized by heating (Metcalf & Eddy Inc., 1991).

In addition to the above mentioned objectives, the quantity of solids in the sludge is also reduced and the dewatering property of the sludge is improved. By this manner, the total quantity of the dewatered sludge decreases, which also decreases the polyelectrolyte consumption, transportation and operational cost, the design parameters and investment costs of further units such as storage, land application, solar or thermal drying. During the selection and design of the sludge stabilization process, the sludge quantity, the integration with other treatment units and the regulations should be taken into account. The technologies that are used to stabilize sludge are; lime stabilization, heat treatment, anaerobic digestion, aerobic digestion and composting (Metcalf & Eddy Inc., 1991).

According to the US EPA the sludge can be described as stabilized if there is an at least 38 % reduction in the mass of volatile solids. But it does not mean that the sludge achieves the Class A bio-solids standards which also contains the pathogen reduction (Puchajda et al., 2003).

2.3 Anaerobic Sludge Digestion

"Anaerobic digestion is one of the oldest processes used for the stabilization of sludges. It involves the decomposition of organic and inorganic matter in the absence of molecular oxygen." (Metcalf & Eddy Inc., 1991, p 420).

 "The anaerobic sludge digestion can be defined as a microbial process in which complex organics are broken down in the absence of oxygen to produce a mixture of mainly $CO₂$ and CH₄." (Sanver, 2000, p 3).

The objective of anaerobic sludge digestion is the transformation of wastewater sludge to innocuous and easily dewatered substance. Net reductions in the quantity of solids and volume of sludge requiring disposal also are realized. Destruction of pathogenic organisms also is accomplished during anaerobic digestion. The final product is a stable, innocuous sludge that can be used as a soil conditioner or fertilizer (Eckenfelder et al., 1992).

In anaerobic digestion processes, the sludge can be fed continuously or intermittently and digested for varying retention times. According to the retention times, there are two types of digesters; standard rate and high rate. The retention time for standard rate digesters is 30 to 60 days where the sludge is generally unheated and unmixed. In high rate digestion process, where the sludge is heated and mixed completely, the retention time is typically 15 days or less (Metcalf & Eddy Inc., 1991).

2.3.1 Advantages and Disadvantages of Anaerobic Digestion

The principal advantages of anaerobic digestion compared to the other methods of sludge stabilization include;

• Production of methane gas, which is a useable source of energy. The process is a net energy producer at most treatment facilities in which

anaerobic sludge digestion is used. The energy produced is in excess to that required to maintain the temperature of the digesting sludge and to meet the energy requirements for mixing. The surplus energy may be used to heat buildings, to drive the engines for the aeration blowers, or to generate electricity that can be used to drive the sewage pumps.

- Reduction in the mass and volume of the sludge through the conversion of organic matter in the volatile solids to methane, carbon dioxide and water. Solids destruction usually is approximately $25 - 45$ % of the feed sludge solids and can result in reduction in the cost of sludge disposal.
- Production of a solids residue that may be used as a soil conditioner. The anaerobically digested sludge contains nitrogen and phosphorus and other nutrients as well as organic material that can improve the fertility and texture of soils.
- The odor associated with raw sludge is markedly reduced to a musty odor by anaerobic digestion.
- Pathogens associated with the feed sludge are inactivated during the anaerobic digestion process.

The principal disadvantages of anaerobic sludge digestion are:

- The capital costs are high. Large, covered tanks along with pumps for feeding and circulating sludge, heat exchangers and compressors for gas mixing are required.
- Long hydraulic detention times, in excess of ten days, are required to develop and maintain a population of methane producing bacteria.

The quality characteristics of the supernatant from anaerobic sludge digestion are poor. The supernatants contain suspended solids, dissolved and particulate organic materials (oxygen-consuming compounds), nitrogen and phosphorus. This return flow adds to the solids, oxygen demand and nutrient loads to the treatment system (Eckenfelder et al., 1992, p168).

2.3.2 Mechanism of Anaerobic Digestion

The anaerobic digestion of the organic portion of sludge is a complex process with a consortium of microorganisms, in which these different kinds of microorganisms directly or indirectly share a symbiotic life (Sanver, 2000).

Figure 2.1 Schematic diagram of the patterns of carbon flow in anaerobic digestion. (Metcalf & Eddy Inc., 1991).

The anaerobic digestion, the mechanism is shown in (Figure 2.1), occurs mainly in three sequential processes that are explained in details below. Gavala et.al (2003) describes the anaerobic digestion process in four steps, separating the second step to acidogenesis and acetogenesis phases. Briefly, volatile solids that have higher molecular mass are first hydrolyzed by enzymatic activities into simpler organic compounds that are suitable for use as energy source and cell carbon. These soluble organic compounds are fermented by acid-producing facultative bacteria to lower molecular mass intermediate compounds, volatile acids, carbon dioxide and some hydrogen gas. These intermediate compounds are then converted to methane and carbon dioxide by methane forming bacteria (Eckenfelder et al., 1992; Metcalf & Eddy Inc., 1991).

2.3.2.1 Hydrolysis

"The anaerobic digestion starts with the breakdown of complex polymeric compounds such as polysaccharides, proteins and lipids." (Sanver, 2000).

Particulate material cannot pass through bacteria cell membrane; therefore, the organic solids are hydrolyzed by the specific extra-cellular enzymes of one group of organisms to basic structural building blocks such as monosaccharide, amino acids and etc. By this manner, the energy, organic and inorganic nutrient necessity of the bacterial population is derived (Eckenfelder et al., 1992; Metcalf & Eddy Inc., 1991). The first step of anaerobic digestion is vital for the success of the process, because this step prepares the simpler substrates that will be utilized during the other steps (Sanver, 2000).

2.3.2.2 Acidogenesis

Acid forming bacteria convert the soluble products of the hydrolysis phase such as amino acids, sugars and long chain fatty acids into low molecular weight volatile fatty acids, the most common of which is acetic acid, propionic and butyric acids, and other simple organic compounds (Sanver, 2000).

"During this acid production phase there is almost no change in the quantity of organic material in the system. There is redistribution among the various types of simpler organic compounds and the release of carbon dioxide, hydrogen and hydrogen sulfide gases." The main products of this phase are the volatile acids which will be utilized as substrate by the methane forming bacteria (Eckenfelder et al., 1992).

"The acid forming bacteria are generally facultative, although some are strict anaerobes, and represent a wide variety of microbial genera." The acid forming bacteria is tolerant to the changes in pH and temperature and they grow more rapidly than the methane forming bacteria. If the volatile acids accumulate in the system, the pH may decrease, and the methane forming bacteria can be inhibited (Eckenfelder et al., 1992).

As a sub-phase, acetogenesis is the phase in which all the volatile fatty acids except for acetic acid is converted to acetate, $CO₂$ and $H₂$ by the obligate hydrogen producing acetogenic bacteria. At each reaction an acetate molecule is removed from the volatile fatty acid until all of it is converted to acetate (Sanver, 2000).

2.3.2.3 Methanogenesis

The volatile acids that are produced during acid fermentation are used as substrate by strictly anaerobe methane forming bacteria and converted to methane and carbon dioxide. The methane forming bacteria in anaerobic digestion are similar to the natural saprophytes found in the organic sediments taken from the lakes and rivers or stomachs of ruminant animals (Eckenfelder et al., 1992; Metcalf & Eddy Inc., 1991; Sanver, 2000).

The methanogenesis phase is mainly carried out by two mechanisms. One group of bacteria converts hydrogen and carbon dioxide to methane, meanwhile another group of bacteria converts acetate to methane (Öztürk, 1998). However, each species of methane forming bacteria can ferment only a relatively restricted group of simple

compounds to methane, therefore, several species of methane formers are necessary for the anaerobic stabilization of the organic fraction of sludge. "It has been found that 70 % of the methane production is derived from the acetate and the remaining 30 % come from the reduction of $CO₂$." (Sanver, 2000).

The rate of methane formation controls the overall rate of the digestion because it is generally considered as a slow rate process. For instance, the generation time of methane formers is about ten times longer than that of acid formers. In addition, the methanogenesis phase also determines the efficiency of the system, because the COD is removed in this phase (Sanver, 2000).

"The mechanism of anaerobic digestion of sludge is sequential in nature, however, acid fermentation and methane fermentation takes place simultaneously and synchronously in a well buffered, actively digestion system." The end products of each phase are used as substrate for the next step. The performance of each step directly affects the total performance of the whole process. Therefore, the acid production rate and the conversion rate of volatile acids to methane should be in balance to obtain an effective anaerobic digestion process. As mentioned before, if the pH decreases below 6, methane forming bacteria will be inhibited and the volatile acids will continue to accumulate (Eckenfelder et al., 1992).

The energy flow in the steps of anaerobic digestion is given in (Figure 2.2).

2.3.3 Microbiology and Biochemistry of Anaerobic Digestion

The anaerobic digestion process contains different groups of bacteria living with symbiotic relations. These groups and names of microorganisms are given in (Figure 2.3). Among the given microorganism main acidogens or acid formers and methanogens or methane formers are;

"*Clostridium spp., Peptococcus anaerobus, Bifidobacterium spp., Desulphovibrio spp., Corynebacterium spp., Lactobacillus, Actinomyces,* *Staphilococus, and Escherichia coli.* Other physiological groups present include those producing proteolytic, lipolytic, ureolytic, or cellulytic enzymes…. The principal genera of microorganisms that have been identified include the rods (*Methanobacterium, Methanobacillus*) and spheres (*Methanococus, Methanosacrina*) (Metcalf & Eddy Inc., 1991).

Methane formers can utilize a limited number of substrates that are $CO₂ + H₂$, formate, acetate, methanol, methylamines, and carbon monoxide for methane formation. These compounds are converted to methane by the following equations: (Sanver, 2000).

$4H_2 + CO_2$	$CH_4 + 2H_2O$
$4HCOOH$	$CH_4 + 3CO_2 + 2H_2O$
CH_3COOH	$CH_4 + CO_2$
$4CH_3OH$	$3CH_4 + CO_2 + 2H_2O$
$4CH_3OH$	$9CH_4 + CO_2 + 2H_2O$
$4(CH_3)_3N + H_2O$	$9CH_4 + 3CO_2 + 6H_2O + 4NH_3$

Figure 2.2 Steps in anaerobic digestion with energy flow (Metcalf & Eddy Inc., 1991).

Figure 2.3 Names and groups of anaerobic bacteria (Sanver, 2000).

2.3.4 Important Parameters for Anaerobic Digestion

The anaerobic digestion process can be enhanced or inhibited by the effect of environmental factors. These factors and their optimum operational values are given in (Table 2.3) (Eckenfelder, et al., 1992).

Variable	Optimum	Extreme
pH	$6.8 - 7.4$	$6.4 - 7.8$
Oxidation Reduction Potential (ORP) mV	-520 to -530	-490 to -550
Volatile Acids (mg/L as acetic acid)	50-500	>2000
Alkalinity (mg/L as $CaCO3$)	1500-3000	1000-5000
Temperature $(^{\circ}C)$		
Mesophilic	$30 - 35$	20-40
Thermophilic	50-56	$45 - 60$
Hydraulic Detention Time (days)	$10 - 15$	$7 - 30$
Gas Composition		
Methane $(CH_4)(\%v)$	65-70	60-75
Carbon dioxide $(CO_2)(\%v)$	$30 - 35$	$25 - 40$

Table 2.3 Optimum operation parameters for anaerobic sludge digestion.

2.3.4.1 Anaerobic Conditions

There must be no air inlet to maintain anaerobic conditions. The facultative microorganisms protect the strictly anaerobe bacteria by utilizing the small amounts of dissolved oxygen in the feed sludge during their metabolism. The methane formers are strictly anaerobic bacteria which mean they cannot tolerate even small amounts of oxygen. Another important issue is that, if oxygen is allowed into the digester, an explosive mixture will be formed with methane (Eckenfelder et al., 1992; Zickefoose et al., 1976).

 "It is generally accepted that the oxidation reduction potential (ORP) value is an indirect measure of dissolved oxygen at concentrations that cannot be measured directly with oxygen probes". The ORP values of -500 mV the anaerobic fermentation to methane is accomplished and phosphorus is released into the liquid. If the ORP is – 300 mV the fate of carbon from methane to volatile acids is obtained. It can be understood from these ORP values that there is a clear anaerobic reactor without dissolved oxygen is obtained (Meyer, 2003).

2.3.4.2 Temperature

With the increase of temperature, the growth and activity of the microorganisms also increases which give the chance to decrease the retention time of the reactor.

There is nearly no digestion at approximately 10 $^{\circ}$ C. Most of the digesters are operated in the mesophilic temperature range of $20 - 40$ °C, and the mesophilic bacteria's optimum performance can be achieved at around 35 °C. At lower temperatures and longer contact times, the biomass concentration would be high. In addition, some types of anaerobic bacteria, which can survive in thermophilic temperature ranges of $45 - 80$ °C. However, the number of species that can live in thermophilic conditions is relatively less than the mesophilic range. This case is one of the disadvantages of thermophilic range (Öztürk, 1998; Sanver, 2000; Speece, 1996). The disadvantages of thermophilic anaerobic digestion are the high operational costs, lower process stability and more structural requirements. The advantages are improved sludge dewaterability, increased pathogen destruction and increased scum digestion (De la Rubia et al., 2002).

Sanver (2000) quoted that, Dinsdale et al. (1997) compared the performance of the mesophilic and the thermophilic conditions for coffee production wastewater, and found for all the loading rates that the COD removal efficiency of the mesophilic conditions is higher.

Even $0.6 \degree$ C temperature change per day affects the methane formers. The change of temperature more than 1.2 °C , reduces methane formers activity, but the acid formers are not affected. Therefore, the digester efficiency will be affected (Zickefoose et al., 1976).

Rajeshwari et al. (2000) stated that the hydrolysis and acidogenesis phases of anaerobic digestion are not affected significantly by temperature change. But, the acetogenesis and methanogenesis phases are more sensitive to temperature change. In contrast, the decay rate of anaerobic bacteria is very low under 15° C, which gives the chance to regain the anaerobic sludge activity after a long period. This case can be used as an advantage for seasonal industries and to preserve the inoculum sludge in the refrigerator for laboratory tests for a long time.

2.3.4.3 pH

One of the most important parameters for an effective anaerobic digestion is pH. The optimum pH for all types of bacteria in acidogenesis and methanogenesis differs. "The optimum pH range for methane producing bacteria is $6.8 - 7.2$ while for acidforming bacteria, a more acid pH is desirable." (Rajeshwari et.al., 2000). Experimental studies showed that the maximum volatile fatty acid production is obtained at pH=6 (Sanver, 2000). To prevent volatile fatty acids accumulation in the system, the anaerobic digestion process should be maintained in the pH range of methanogenic limits (Zickefoose et al., 1976).

The measurement and control of pH in anaerobic digestion process is very important for the determination of the signals of acidification and process failure. However, pH measurement may be insensitive to process changes, if the buffering capacity of the fed sludge is high. In this case the bicarbonate alkalinity should be monitored and taken into consideration (Vanrolleghem, 1995).

Anaerobic bacteria also need some nutrients to survive. The macro nutrients that are used by the bacteria are carbon, nitrogen and phosphorus. When compared to aerobic systems, the macro nutrients requirement of anaerobic bacteria is relatively less because of the reduced amount of biomass synthesis of anaerobic digestion process (Sanver, 2000; Speece, 1996).

In addition to the macro nutrients, the anaerobic digestion process also needs micro nutrients and trace elements such as sulphur, potassium, sodium, calcium magnesium, iron, nickel, cobalt, zinc, manganese and copper for optimum growth. These elements are needed in low concentrations, but their absence affects the performance of the anaerobic microorganisms. It was reported that the required optimum $C : N : P$ ratio should be 100 : 2.5 : 0.5 for enhanced yield of methane (Rajeshwari et.al., 2000). Whereas, it was stated by Sanver (2000) that anaerobic systems can perform well with 1000 : 5 : 1 ratio.

2.3.4.5 Digester Feeding

Feeding is one of the parameters that should be controlled by the operators, because uniformity and consistency are very important for anaerobic processes. The concentration of incoming sludge, amount of volatile solids, organic loading rate just like food to microorganism ratio used in activated sludge systems, and hydraulic retention time related to the hydraulic loading, are the parameters that should be taken into consideration (Zickefoose et al., 1976). These parameters determine the available reaction time for the microorganisms to stabilize the food as volatile solids. The digesters are generally operated at solids concentrations more than 4 %. The volatile solids content of the municipal sludge is generally above 70 %. The organic loading ranges between $1.5 - 6.2$ kg VS/m³.day (Öztürk, 1998).

According to Metcalf & Eddy Inc. (1991) the volatile solids loading rate ranges between 1.6 to 4.8 kg VS/m^3 day, and the hydraulic retention time ranges between 10 to 20 days. The effect of sludge concentration and hydraulic retention time on the volatile solids loading rate is given in (Table 2.4). It was determined by Eastman et al. (1981) that the sludge digestion and the gas production in anaerobic processes decreases significantly after 14 days retention time and after 20 days it nearly stops.

Sludge	Volatile solids loading rate kg VS/m ³ .day				
Concentration, $\frac{0}{0}$	10d	12d	15d	20d	
4	2.9	2.4	1.9	1.4	
5	3.6	3.0	2.4	1.8	
6	4.3	3.6	2.9	2.1	
7	5.0	4.2	3.3	2.6	
8	5.7	4.8	3.8	2.9	

Table 2.4 Effect of sludge concentration hydraulic retention time on volatile solids loading rate.

The sludge concentration is reported to be very important for methanogenic activity by Lay et al. (1997). It was determined that with the increase of solids concentration from 4 % to 10 % the methanogenic activity decreases approximately 50 %.

2.3.4.6 Alkalinity & Volatile Acids

Alkalinity is the acid neutralizing, buffering capacity. "Properly operating anaerobic digesters typically have supernatant alkalinities in the range of 2000 to 4000 mg calcium carbonate $(CaCO₃)/L$." (APHA, AWWA, WEF 1992).

The pH can decreases with the two sources of acidity, H_2CO_3 and volatile fatty acids which are generated as the intermediate digestion products. These acids should be buffered by the alkalinity that is already present in the incoming sludge and produced by the methane formers as part of the digestion process. The amount of produced buffer is generally enough to neutralize the acids produced by the acid formers (Zickefoose et al. 1976).

The volatile fatty acids/Total alkalinity (VFA/TA) Ratio is a commonly used operation control parameter for anaerobic digesters. It was advised by Zickefooser et al (1976) that the digesters operate well if the ratio is less than 0.25, and many operators prefer to keep it less than 0.15. It was also stated that the first indications of reactor's becoming sour is the increase of volatile fatty acids. After a period the alkalinity starts decreasing. At this point the VFA/TA ratio exceeds 0.3. The pH begins to decrease when the reactor becomes sour, and it will be too late (Zickefoose et al. 1976).

Although VFA/TA ratio was recommended by EPA in the last decades, it contains many assumptions. "Total alkalinity includes the bicarbonate alkalinity plus the alkalinity of the salts of VFA, with only the bicarbonate alkalinity available to neutralize additional VFA. A very significant fraction of the bicarbonate alkalinity may be allocated to neutralize the $CO₂/H₂CO₃$ with only the excess available for neutralizing an increase in VFA." Speece (1996) stated that the reserve bicarbonate alkalinity is a more accurate parameter than VFA/TA. "Reserve bicarbonate alkalinity is defined as the concentration of bicarbonate alkalinity available to neutralize additional free VFA." The reserve bicarbonate alkalinity indicates the problem in the digester before the pH drops, which can be explained as the VFA concentration increase before the pH is depressed (Speece,1996).

2.3.4.7 Mixing

Especially high rate anaerobic digestion process requires the maximum contact of bacteria and food which can be achieved by mixing. By mixing the digesters uniformity is maintained which means the substrate and heat is distributed in the digester, the scum formation and accumulation can be prevented (Öztürk, 1998). In addition, by agitation the particle size is reduced and the biogas is released form the mixture. It was stated by Karim et al. (2005) that the mixing is researched many

times, but its pattern is a subject of much debate. For substrate utilization optimum condition is intermediate degree of mixing.

Homogenous mixing can be applied by gas recirculation, mechanical mixers or slurry recirculation. The most effective mixing type is mechanical mixing in terms of power consumed per reactor volume mixed. Its disadvantages are; the internal fittings and equipment cannot be accessed and maintained during digesters are in operation and long term reliability. Whereas the long term reliability can be obtained by using gas or slurry recirculation types, because there is no moving parts inside the digester (Karim et al., 2005).

It was stated by Krishna et al. (1997) that reactors mixed by gas recirculation are much more affected by foam formation than that is mixed mechanically. The scum layer formation of gas re-circulated reactor was 1.3 m while the mechanically mixed reactor was 2.4 m.

2.3.4.8 Gas production

The gas production of anaerobic digestion process varies from $0.75 - 1.12 \text{ m}^3/\text{kg}$ VSS_{removed}. The produced gas consists of $65 - 70$ % methane, $25 - 30$ % carbon dioxide and small amounts of N_2 , H_2 , H_2S , water vapor and other gases. The gas production is effected by volatile solids concentration of the influent sludge and biological activity in the digester. During the start up period the gas production may be high which causes foaming and escape of foam and gas from the cover of the digester. When the digester comes to stable operation and the estimated gas production is achieved the sludge digestion will be efficient (Metcalf & Eddy Inc. 1991).

Methane gas has a net heating value of $35,800 \text{ kJ/m}^3$ at standard conditions. The biogas contains 65 % methane; therefore the low heating value of biogas is approximately 22,400 kJ/m³, whereas the natural gas is 37,300 kJ/m³. The biogas can be used as fuel for boiler or internal combustion engines and electricity is produced

(Metcalf & Eddy Inc., 1991). The produced heat energy is used to heat the sludge fed to the anaerobic digester and the operational buildings. The electricity produced can hold the electricity consumption of the whole wastewater treatment plant.

2.3.4.9 Heavy Metals

The heavy metals that can be effective on the efficiency of anaerobic digestion process, and their levels of inhibition and toxicity are given in (Table 2.5).

Chemical	mg metal/L	Observations		
Ni(NO ₃) ₂	10, 50, 250	10 mg/L inhibiting, 30 mg/L toxic limit		
Cu(NO ₃) ₂	20, 100, 500	40mg/L inhibiting, 70 mg/L toxic limit		
Cd(NO ₃) ₂	20, 50, 100	No inhibiting level or toxic limit		
Pb(NO ₃) ₂	80, 400, 2000	340 mg/L inhibiting, >250 mg/L toxic limit		
Zn(NO ₃) ₂	400, 200, 15000	400 mg/L inhibiting, >600 mg/L toxic limit		
NiSO ₄	10, 40, 200	No inhibition with 277 mg/L Ni in digested primary sludge		
NiSO ₄	367, 734	%50 inhibition at 134 mg/L		
ZnSO ₄	2.5, 20	Normal digestion at 10 to 20 mg/L Zn		
ZnSO ₄	409, 817	%50 inhibition at 136 mg/L		
Zn(CN) ₂	16	20 mg/L Zn caused inhibition		
Cr(VI)	0.5, 2.0, 5.0	No inhibition due to wastewater loadings up to 50 mg/ L		
CuSO ₄	367, 794	%50 inhibition at 211 mg/L		
FeSO ₄	349, 698	No inhibition		

Table 2.5 Effect of heavy metals on anaerobic digestion process efficiency. (Eckenfelder et al., 1992).

Pahl et al. (2008) stated that the relative toxicities for anaerobic digestion are $Zn > Cr > Cu > Cd > Ni > Pb$. Absolute EC_{50} values, which is the inhibition of microbiological activity by 50 %, are 50, 50, 100, 200, and 350 mg /L, respectively (Pb not reported).
2.3.5 Researches on Anaerobic Digestion

The digestion process can be accomplished in two serial operating reactors as well as one reactor. These types of reactors are called two stage digesters. In the first reactor, the retention time of which is relatively low, the acidogenesis phase takes place. In the second reactor the methanogenesis phase is accomplished. It was stated by Ghosh et al.(2000) that by using two stage reactors the gas production and methane content of the gas can be increased.

In two stage anaerobic digestion, the stages can be operated in different conditions. For instance, the first reactor can be thermophilic and the second reactor can be mesophilic. It was found by Oles et al. (1997) that the best results for sludge digestion are obtained by using these types of reactors (Oles et al., 1997).

Puchajda et al. (2003) compared the single stage and two stage anaerobic reactors. In their research, a two stage system with a thermophilic reactor followed by a mesophilic reactor was compared to a single stage mesophilic reactor and a single stage thermophilic reactor. They concluded that there was no significant difference between digestion systems in gas production. But while the end product of both the single stage thermophilic reactor and two stage reactors achieved the Class A biosolids standards, the mesophilic reactor's end product often failed to produce Class B bio-solids. The digesters were fed with primary and excess sludge mixture which was sieved through a sieve with opening size of 4 mm and stored at 4° C, once a day. The mesophilic reactor was operated at 36 $^{\circ}$ C with 15, 13 and 11 days sludge retention times. The volatile sludge reductions of mesophilic reactor were found as 46.6 ± 11.6 %, 53.1 ± 4.0 % and 42.2 ± 9.0 %, respectively. The methane production was found to decrease with the increase of sludge retention time and decrease of organic loading rate while the methane content of the produced gas increased.

Cheunbarn et al. (2000) determined the volatile solids reduction of a mesophilic digester operated by mixture of primary and excess sludge as 50 %. The methane

production was determined as 0.52 ± 0.03 m³/kg VS_{destroyed}, supernatant COD was $14,100 \pm 350$ mg/l and the capillary suction time was found as 364 s.

Gavala et al. (2003) operated a mesophilic digester with mixed sludge and obtained a volatile solids reduction of 47 %, with a biogas production of 406 ml/d having 61.6 % methane. The COD of the supernatant was found as 21,260 mg/L.

De la Rubia et al. (2002) studied on a mesophilic digester having 27 days retention time, which is the retention time of the full scale plant, with mixed sludge. The influent sludge has a solids concentration of about 5 % and a volatile solids concentration of 68 %. At this conditions 53 % volatile solids reduction was accomplished while the COD is decreased by 52.8 %. Gas production of the reactor was 0.36 m³/m³d while the methane content of the gas ranges from 57.7 to 64.5 %. During the operation period, the bicarbonate alkalinity was $12,500$ mg CaCO₃/L, in average. The VFA/TA ratio was very low, 0.065 in average.

Atilla et al. (2002) studied on the mesophilic anaerobic digestion of primary, excess and mixed sludge taken from İstanbul Tuzla W.W.T.P. The volatile solids reduction of primary sludge was found as 30 %, excess sludge as 44 % and the mixed sludge as 39 %, in average. The biogas production per volatile solids removed for primary sludge was 1.06 L/g VS $_{\text{removed}}$, excess sludge was 0.504 L/g VS $_{\text{removed}}$ and mixed sludge was 0.698 L/g VS_{removed}.

Lanting (2003) operated a pilot anaerobic digester with a mixture of primary and excess sludge in a 40/60 dry solids mass ratio and a starting solids retention time of 10 days. The measured bicarbonate alkalinity in the reactor was $4500 \text{ mgCaCO}_{3}/L$ at 4 % solids concentration and 2500 mg CaCO₃/L at 2 %. "In order to keep power consumption reasonable our recommendation is to keep the design SUR for municipal sludge digesters below a maximum 1.5 kg VS destroyed per kg biomass VS per day."

Witzgall et al. (2003) compared the operation and maintenance experience of three plants in the west of U.S.A; Los Angeles Hyperion Treatment Plant, the Greater Vancouver Regional District's Annacis Island W.W.T.P. and the Sacramento Regional W.W.T.P.. Hyperion plant was operated as two stage mesophilic digester, before it was taken into thermophilic operation. In mesophilic operation the average solids retention time was 20 days with a volatile solids loading rate of $2.40 - 2.72$ for one stage and $1.60 - 1.92$ kg/m³.d for two stage operation. The average volatile solids reduction was 62.5 % with a gas production rate of 0.936 m³/kg VS_{removed}, having 65 % methane. The volatile acids range between $80 - 120$ mg/L while the average alkalinity was 3,600 mg/L. Sacramento plant was also operated in mesophilic conditions. The plant was operated with the following parameters; solids retention time 20 days, volatile solids loading rate 2.08 kg/m³.d, volatile solids reduction 58 %, gas production 1.08 m³/kg VS_{removed} with 59 – 61 % methane content, volatile acids $110 - 135$ mg/L and alkalinity $2,900 - 3,500$ mg/L.

Üçüncü (1994) operated three pilot reactors with primary, excess and mixed sludge of an advanced wastewater treatment plant. The reactors were operated at 20 days retention time. The volatile solids reductions were found as; 42 % for primary sludge, and 38.5 % for excess sludge and % 39 for mixed sludge. The gas production and was determined as; 1.310 m³/kg VS_{removed}, for primary sludge, 0.609 m³/kg $VS_{\rm removed}$ for excess sludge and 1.085 m³/kg $VS_{\rm removed}$ for mixed sludge. The methane content of the gas was $68 - 70\%$.

To improve the digestion performance pretreatment of sludge can be applied by using ultrasonic or ozone disintegration, thermal treatment and freezing. Wang et al. (1999) studied on the anaerobic digestion of excess sludge having a solids concentration of 3.3 – 4.0 %, and volatile solids concentration of $77 - 79$ % in a mesophilic reactor. It was determined that the daily methane production changed from 350 to 100 ml in 7 days period. The pretreatment methods increased the methane production in the second and third days of operation period significantly (Wang et al., 1999).

2.4 Biological Phosphorus Removal

The biological phosphorus removal was first discovered by chance in wastewater treatment plants at the end of 50's. At the end of 60's and early years of 70's, many researches were conducted on the reasons of phosphorus luxury uptake without the microbiological examinations. The first findings of the Acinetobacter genus were found in the late 70's. And the mechanism of biological phosphorus removal took its shape in the 80's and 90's. After these researches, many process configurations for biological phosphorus removal were proposed and applied such as Bardenpho, Phoredox, UCT, JHB, etc (Janssen et al., 2002).

With the strict regulations or requirements to eliminate eutrophication in receiving media such as rivers, lakes and gulfs, today there are many advanced biological wastewater treatment plants in operation including biological phosphorus removal process.

2.4.1 Mechanism of Biological Phosphorus Removal

The typical phosphorus content of microbial solids is $1.5 - 2.0$ % of dry weight. In conventional systems the phosphorus can be removed by 10 to 30 % by excess sludge withdrawal. According to Bowker et al. (1987) it has been shown that exposing the mixed liquor to an anaerobic/aerobic sequence in the biological reactor selects microorganisms that accumulate higher levels of intracellular phosphorus than other conventional treatment microorganisms. It has also been concluded that these microorganisms belongs to the Acinetobacter genus. These phosphorusremoving microorganisms are able to rapidly assimilate and store volatile fatty acids (VFAs) and other fermentation products under anaerobic conditions. Aeromonas and pseudomonas bacteria were also found to serve the important function of producing fermentation products in the anaerobic phase for Acinetobacter. "Various investigators have observed a decrease in soluble substrate and an increase in orthophosphate concentrations in the anaerobic zone of anaerobic-aerobic sequenced biological phosphorus removal systems." As fermentation products mainly acetate as

VFA, is produced and VFA concentration decreases with the increase of orthophosphate concentration as a function of the anaerobic time. (Figure 2.4) (Bowker et al., 1987).

Figure 2.4 Behavior of VFA and P during biological phosphorus removal systems (Janssen et al., 2002)

The mechanism of biological phosphorus removal is given in (Figure 2.5). Polyphosphate in the cell structure of the microorganism is hydrolyzed and phosphorus is released in the anaerobic zone to produce the energy needed to take up the fermentation products, which are stored as poly-ß-hydroxybutyrate. Phosphorusremoving microorganisms produce energy by oxidizing the stored fermentation products in the aerobic/anoxic zone while simultaneously accumulating intracellular phosphate. For the formation of ATP in aerobic zone oxygen is used, whereas in anoxic zone nitrate is used. The ability of phosphorus-removing microorganisms to rapidly assimilate the fermentation products under anaerobic conditions gives them a competitive advantage over other microorganisms and results in their preferential growth in the wastewater treatment system. Thus, the anaerobic-aerobic sequence

allows the selection of a large population of phosphorus-removing microorganisms (Bowker et al., 1987; Janssen et al., 2002).

Figure 2.5 Mechanism of biological phosphorus removal

In biological phosphorus removal systems, phosphorus accumulates in the biomass and is removed in the form of waste-activated sludge. A recent study showed that nearly all the enhanced phosphorus removal is due to the storage of poly-phosphates. Therefore the waste activated sludge is expected to have higher phosphorus concentrations than conventional treatment systems. "Typical phosphorus concentrations in waste activated sludge from the Bardenpho and A/O processes are $4 - 6\%$ by weight..." (Bowker et al., 1987).

2.4.2 Advantages and Disadvantages of Biological Phosphorus Removal

The most important advantage of biological phosphorus removal is that no chemicals are used and no chemical sludge is produced which decreases the total sludge production. In addition, the surplus sludge dewateability does not decrease, the effluents salinity is lower, nitrification process inhibition is decreased, total nitrogen removal is not affected and the sludge quality increases (Janssen et al., 2002).

The most important disadvantages of biological phosphorus removal are; the dependence on wastewater composition, lower stability and flexibility, negative effect on sludge settleability and phosphorus release in sludge treatment (Janssen et al., 2002).

2.5 The Biological Phosphorus Removal and Sludge Treatment

The only difference of excess sludge withdrawn from the biological phosphorus removal systems is the higher phosphorus content, because of the mechanism of excess phosphorus uptake. As mentioned before the excess sludge can be treated by several methods. The phosphate can be released back from the cell structure if the anaerobic conditions occur. The phosphate release can be not only the biologically up taken excess sludge but also the decay of cells due to the mechanism of stabilization and long sludge ages. By the release of phosphate, the supernatant with

high phosphorus content, which is directed through the inlet of the treatment plant, increases the phosphorus load of the plant (Bowker et al., 1987: Janssen et al., 2002).

It was stated by Janssen et al. (2002) that the gravitational sludge thickener supernatant can also contain $2 - 30$ % of the influent phosphate load. It was also reported that in Germany, the phosphorus recycle in the supernatant of digesters is approximately 15 % of the influent phosphorus load.

It was also quoted by Carliell-Marquet et al. (2001) that during the anaerobic digestion of the biological phosphorus removal sludge, $20 - 50$ % of phosphorus is released. They studied on three anaerobic reactors with biological phosphorus removal sludge, chemical phosphorus removal sludge and a control excess sludge without biological phosphorus removal. It was determined that the phosphorus content of the sludges were 31 g/kg (dried sludge) in CPR, 26 g/kg for BPR and 16 g/kg for control digester sludges. It was found that 10 % of magnesium and 20 % of phosphate remains soluble which indicates precipitation.

In another paper of Carliell et al. (1997) the phosphorus contents were determined as 9 g/kg (dried sludge) for control digester, 11 g/kg for BPR and 36 g/kg for CPR. The low phosphorus content of biological phosphorus removal sludge was because the plant was not in full operation.

Janssen et al. (2002) investigated some treatment plants with biological phosphorus removal and determine the phosphorus recycle by the supernatant of various sludge treatment processes. Among them Goor treatment plant has anaerobic digestion of primary and excess sludge and it was determined that 3% of influent phosphorus load is recycled with the anaerobic digester's supernatant. The low phosphorus recycle is due to the calcium dosage.

According to Jardin et. al. (1994) that for the enhanced biological phosphorus removal process, the phosphorus content of the activated sludge can reach values up to 7 % of DS. "During wastewater treatment, phosphorus can be bound in the excess

sludge by (i) enhanced removal in form of stored polyphosphate, (ii) by a conventional biological mechanism (part of the organic matter of the microorganism), and (iii) by chemical fixation to metal ions." It was proved by the first set of experiments in the study that the phosphorus was fixed due to the enhanced biological phosphorus removal process and stored in the cell structure as polyphosphates.

Theoretically "most of the phosphorus eliminated as polyphosphate should be released during the anaerobic treatment of excess sludge". The reason could be the chemical fixation of some part of the released phosphorus as metal phosphate precipitates. Jardin et al. (1994) tired to apply anaerobic digestion to phosphorus rich excess sludge and a mixture of primary and excess sludge with a retention time of 20 days at mesophilic conditions. It was determined that 38 % of the Total-P of the raw excess sludge and 42 % of the Total-P of the raw mixed sludge was reduced. It was concluded that during the digestion of excess sludge, all of the phosphorus stored in the cell structure as polyphosphate was released, but only a part of it remained in soluble form. The chemically fixed phosphorus can be calculated as the difference of released and remaining phosphorus. It was also concluded that all of the released magnesium and 20 % of the total phosphorus could be fixed in the particular digester as struvite.

The phenomenon given by Jardin et al (1994) was defined by Janssen et al. (2002) as follows: In addition to the release of phosphorus metals such as iron, aluminum, magnesium and calcium can bind phosphate. These metals are present in the wastewater sludge. In addition, as an anti-ion of phosphate additional magnesium is utilized during the biological phosphorus removal. These metals bind phosphates spontaneously during the digestion process. With the spontaneous binding, the phosphate that is recycled to the inlet of the treatment plant may be reduced. The phosphates can be separated as magnesium ammonium phosphate hexahydrate (MAP, struvite, $MgNH_4PO_4*6H_2O$) and aluminum salts.

It was stated by Doyle et al. (2002) that the two components of struvite formation, phosphorus and ammonium can be found in high amounts naturally in wastewater. Magnesium has various sources such as hard potable water in the region of the W.W.T.P, sea water infiltration to the pipe line, industrial discharge and support material for anaerobic digestion.

Struvite is a crystalline mineral that often accumulates on equipment surfaces of anaerobic digestion and post-digestion processes within the wastewater treatment industry. This scenario plagues the industry commercially through major downtime, loss of hydraulic capacity, and increasing pumping and maintenance costs. A novel solution to this problem is to recover phosphate as struvite before it forms-accumulates on wastewater treatment equipment (Adnan et al., 2003).

2.6 İzmir Wastewater Treatment Plant

İzmir W.W.T.P. is an advanced biological treatment plant which was taken into operation in the beginning of year 2000. The plant is designed to treat 7 m^3 /s average dry weather flow, 9 m^3/s maximum dry weather flow and 12 m^3/s maximum wet weather flow. The influent and effluent design characteristics of the plant are given in (Table 2.6).

Parameter	Influent		Effluent	
	Conc. (mg/L)	Load (t/d)	Conc. (mg/L)	Load (kg/d)
BOD ₅	400	242	20	12
COD	600	363	100	60
TSS	500	302	30	18
Total-N	60	36	12	7.3
NH_4-N		-	10	6
Total-P	6	3.6		
$PO4-P$				0.6

Table 2.6 Design characteristics of İzmir W.W.T.P. influent and effluent

The plant consists of mechanical and physical treatment by fine screens, aerated girt chambers, primary sedimentation tanks, biological treatment by bio-p tanks, aeration tanks and final sedimentation tanks, and sludge treatment by mechanical thickening and belt presses. The plant is consisted of three parallel lines. The flow scheme of the plant is given in (Figure 2.6).

Figure 2.6 Flow Scheme of İzmir W.W.T.P.

In İzmir W.W.T.P. a modification of 5-Stage Modified Bardenpho process is us ed. In this process, the influent and return sludge are contacted in an anaerobic tank to promote fermentation reactions and phosphorus release prior to passing the mixed liquor through the four stages Bardenpho System. In the first anoxic zone nitrate nitrogen contained in the internal recycle from the nitrification zone is reduced to nitrogen gas (denitrification) by metabolizing influent BOD using nitrate oxygen instead of DO. About 70 percent of nitrate nitrogen produced in the system is removed in the first anoxic stage. In the first aerobic zone (nitrification) BOD removal, ammonium nitrogen oxidation, and phosphorus uptake occurs. The

second anoxic zone provides sufficient detention time for additional denitrification by mixed liquor endogenous respiration, again using nitrate oxygen instead of DO. The final aerobic stage provides a short period of mixed liquor aeration prior to clarification to minimize anaerobic conditions and phosphorus release in the secondary clarifier (Bowker et al., 1987).

In İzmir W.W.T.P primary sludge and excess sludge is processed mechanically by us ing sludge dewatering tables and belt presses. Primary sludge is pumped automatically from the primary settling tanks to sludge holding tank -1 according to obtain a dry solids content of $2 - 3$ %. The tank has a volume of 2,860 m3 and settling of the sludge is prevented by mixing homogenously. Excess sludge is pumped from the return sludge pumping stations continuously to the sludge holding $tank - 2$. Withdrawn excess sludge has a dry solids content of 1 %. The primary sludge is also pumped from tank -1 to tank -2 continuously in a constant flow rate and mixed with excess sludge at 1:1 ratio in dry solids content. The mixed sludge was designed to have a dry solids content of 1.46 %. The sludge holding tank -2 is mixed by giving air from bottom of the tank by diffusers which is designed to prevent anaerobic conditions and phosphate release from the cell structure.

The sludge is thickened by using belt type mechanical dewatering tables after the ad dition of 0.5 % polyelectrolyte and mixing. The dry solids content is increased from 1.46 % to $6 - 8$ %. Thickened sludge is fed to belt presses and dewatered to 20 – 25 % dry solids content. Sludge cake is mixed with lime for stabilization on transported to sludge landfill areas for disposal. The filtrate is used for washing the belts of both mechanical dewatering tables and belt presses. The remaining part of the filtrate is returned to the inlet of the treatment plant.

Because of the mechanical problems and inefficiency faced in the dewatering sy stem by using belt presses, a new dewatering plant was constructed in the plant. The new plant, which consists of 7 high capacity and newest technology centrifuge machines, has been completed and taken into operation in the first week of July 2007. The centrifuges were designed to be operated in two modes. In the first

operation mode all machines are used for dewatering the existing sludge more than 20 % DS. In the second operation mode, which will be applied after the construction of the anaerobic digesters, 4 centrifuge machines will be used to thicken the sludge before anaerobic digesters to $4 - 6$ % DS and 3 centrifuge machines will be used to dewater the digested sludge up to 30 % DS. The plant was designed according to the increases in the sludge quantities with the construction of a new treatment line, since the project tender of the new treatment line was conducted.

3. CHAPTER THREE MATERIALS AND METHODS

3.1 Materials

The materials used during the experimental studies that were carried out in İzmir W.W.T.P. laboratory are as follows;

- An anaerobic digestion laboratory model.
- A pH meter which can also measure the conductivity, salinity and ORP with electrodes.
- An oven for dry solids measurements.
- A furnace for volatile solids measurements.
- A heater for the chemical analysis.
- A spectrophotometer and appropriate cell tests for different kinds of experiments.
- An analytical balance.
- A shaker.
- An incubator oven suitable for incubation at 35° C.
- A laboratory digestion unit
- A gas detector having methane and $CO₂$ sensors.
- A N_2 and a CO_2 gas tube
- Sealed serum bottles and hypodermic glass needles
- Membrane filter papers.
- Several laboratory equipment and chemicals.
- Sludge taken as inoculum from Ankara W.W.T.P.
- Primary, excess and mixed sludge of İzmir W.W.T.P. (the characteristics of the sludges will be given as a separate chapter.)

3.1.1 Anaerobic Digestion Laboratory Model

In the experimental studies a laboratory model which was made of plexi-glass and stainless steel having five reactors was used. The Section of one digestion reactor is given in Figure 3.1 and the photo of the system is given in (Figure 3.2).

Figure 3.1 Section of one anaerobic digestion reactor

As it can be seen from Figure 3.1 there are three pipes on each reactor; sludge feeding, sludge withdrawal and gas collection. There is a valve on each pipe. In the sludge feeding and mixing parts, the pipes are plunged into the sludge more than half of the reactor sludge volume. The reason of this design is to prevent possible gas leakage from the sludge feeding pipe during the sludge feeding and from the bearings of the mixers.

Each reactor has 7 L capacity, but operation volume in this study was selected as 6 L to obtain enough space for the gas production and foam formation. The reactors were operated at 10, 12, 15 and 20 days hydraulic retention times by withdrawing and feeding 600, 500, 400 and 300 ml's of sludge daily from the reactors, respectively.

Reactors were operated in the mesophilic conditions; therefore the temperature was kept constant at $35 \pm 0.5^{\circ}$ C. For this purpose, the reactors were heated by a hot water jacket surrounding the reactors. There is a temperature sensor in the middle reactor and the heaters automatically start and stop heating the water jacket according to the temperature in the reactors. The heater surrounds all the reactors and there are two mixers for mixing the water jacket, therefore the water and reactors were heated homogenously.

Figure 3.2 Anaerobic digestion laboratory model

The gas taken from each reactor was stored and the volume is measured by using a simple system (Figure 3.3). The produced gas is given to plexi-glass caps that are filled with water. With the gas inlet the caps begins to rise and from the amount of rising, the amount of gas is calculated. The content of stored gas was determined by

using a gas detector having methane and carbon dioxide sensors and with the same method used in BMP test.

Figure 3.3 Gas measuring and storage

.2 Analytical Methods 3

The parameters that were measured during the experimental studies are given as fol lows (R: Feed Sludge, D: Digested Sludge, Reactor, S: Supernatant, G: Gas)

.2.1 BMP Test 3

Just as the BOD assay indicates how much organic pollution can be degraded in " an aerobic process, the BMP is the correlative measure in the anaerobic process. By applying BMP test the amount of organic pollutants that can anaerobically be converted to methane can be measured. In addition, the efficiency of the anaerobic digestion process can be evaluated (Speece, 1996).

MP test was conducted by using 150 and 250 ml serum bottles with a selected B qu antity of sludge samples, inoculum and substrate solution. In the experiments the sample volume was selected as 40 ml after many trials. In the test an acclimated inoculum (approximately $20 - 50$ ml) can be taken directly from the anaerobic reactor. However, the inoculum taken from Ankara W.W.T.P. was dewatered sludge. Therefore, the volume of inoculum was chosen as 10 ml. In the experiments 40 ml's of substrate solution, constituents of which are given in Table 3.1, was also added into the serum bottles (Speece, 1996).

The head space in the serum bottle was purged with $CO₂$ for pH control, and $N₂$ to ob tain anaerobic conditions shown in Figure 3.4 and (Figure 3.5). The serum bottles were then incubated at 35 $\mathrm{^{\circ}C}$ in an incubator with a shaker shown in Figure 3.6, and the daily gas productions were measured (Speece, 1996). The gas production is first tried to be measured by inserting a hypodermic needle connected to a calibrated fluid reservoir, through the serum cab (Haskök, 2005). But because of clogging problem

the gas quantity was measured by using a hypodermic glass needle through the serum cab shown in Figure 3.7 that was advised by Assoc. Prof. Dr. Nuri AZBAR.

Figure 3.4 $CO₂$ and $N₂$ tubes.

Figure 3.5 $CO₂$ and N₂ purging.

Figure 3.6 BMP test equipment.

Figure 3.7 Gas volume measurement by using a glass hypodermic needle.

The COD reduction can be calculated from the stoichiometric relationship accepting that 395 ml of CH₄ production is equivalent to 1 g COD reduction at 35° C temperature (Speece, 1996). The $CO₂$ produced should not be evaluated for the calculation of COD reduction, because CO2 does not represent COD reduction under

anaerobic conditions (Speece, 1996). Therefore, the gas produced was syringed out by the needle and injected to another serum bottle containing 20 g/L of KOH solution. The bottle was shaken for $3 - 4$ minutes and CO_2 and H_2S was absorbed in the concentrated KOH solution. The volume of the remaining gas, which was 99.9 % methane, in the serum bottle was also determined by the hypodermic glass needle (Ergüder et al., 2000).

According to the results of the BMP tests the methane yields were calculated as mlCH4/gVSadded and the amount of COD converted to methane were calculated as and g $\text{COD}_{\text{converted}}/\text{g}$ VS $*d$.

Constituents	Conc. (mg/L)	Constituents	Conc. (mg/L)
NH ₄ Cl	400	NH ₄ VO ₃	0.5
$MgSO_4*7H_2O$	400	$CuCl2*2H2O$	0.5
KCl	400	ZnCl ₂	0.5
$Na2S*9H2O$	300	$AICl_3*6H_2O$	0.5
$CaCl2*2H2O(NH4)2HPO4$	50	$NaMoO4*2H2O$	0.5
$(NH_4)_2HPO_4$	80	H_3BO_3	0.5
$FeCl2*4H2O$	40	$NiCl2*6H2O$	0.5
$CoCl2*6H2O$	10	$NaWO4*2H2O$	0.5
KI	10	Na ₂ SeO ₃	0.5
(NaPO ₃) ₆	10	Cysteine	10
$MnCl2*4H2O$	0.5	NaHCO ₃	6000

Table 3.1 Constituents of substrate solution used in BMP tests.

3.2.2 Total Dry Solids and Total Volatile Solids

The Total Dry Solids and Total Volatile Solids measurements were carried out according to the Standard Methods, method 2540 G "Total, fixed, and volatile solids in semisolid samples" (APHA, AWWA, WEF, 1992).

The evaporating dishes are ignited at 550 $\mathrm{^{\circ}C}$ for 1 h in a muffle furnace, stored and cooled in desiccator, and weighed immediately before use. The samples are mixed carefully to obtain a homogenous mixture, and a chosen volume is taken into the dishes. The samples are dried at least 1 h in the oven at $103 - 105$ °C. The dishes are cooled in desiccator to balance temperature and weight. The dishes are weighted again and Total Dry Solids contents are calculated from the difference between initial and final weights.

The residues produced in Total Dry Solids measurement are ignited to constant weight in a muffle furnace at a temperature of 550 °C. The dishes are cooled in desiccator to balance temperature and weight. They are weighted again and Total Volatile Solids contents are calculated from the difference between initial and final weights as follows:

 $(A - B) * 1000$ mg total dry solids/ $L =$ $C - B$ $(A - D) * 1000$ mg total volatile solids/ $L =$ $A - B$

Where;

- A : weight of dried residue + dish, mg,
- B : weight of dish, mg,
- C : weight of wet sample $+$ dish, mg, and
- D : weight of residue + dish after ignition, mg

The materials and equipment that were used in this experiment are: Oven $(NÜVE - FN - 500)$ Muffle Furnace (NÜVE – MF – 100) Analytical Balance (Scaltec – SPB31, Sartorius Minisart RC 25) Desiccator Porcelain dish

3.2.3 pH, Conductivity, Salinity, Oxidation Reduction Potential

The pH, Conductivity, Salinity, Oxidation Reduction Potential measurements were carried out by using a portable multi-parameter water quality analyzer and electrodes (WTW Multiline P3).

3.2.4 Alkalinity

The Alkalinity measurements were carried out according to the Standard Methods, method 2320 B (APHA, AWWA, WEF,1992).

3.2.4.1 Reagents

Sulfuric acid, 0.1 N: which is sufficient for alkalinities ranging from $500 - 6000$ mg/L. 2.8 ml of concentrated sulfuric acid (H₂SO₄) is cautiously added to 300 ml of distilled water. With boiled and cooled distilled water it is diluted to one liter. Standardized against 0.10 N sodium carbonate.

Sodium Carbonate, 0.10 N: Dried in oven before weighting. 5.3 g of anhydrous sodium carbonate (Na_2CO_3) is dissolved in boiled and cooled distilled water and diluted to one liter with distilled water.

Methyl orange chemical color indicator: 0.05 g of methyl orange is dissolved in 100 milliliters of distilled water.

3.2.4.2 Procedure

A clean 250 ml beaker is taken and 100 ml or less of clear supernatant is added. The liquid is separated from the sludge by filtration. If digester alkalinity tends to be above 3000 mg/L, the sample size is adjusted between 20 and 50 ml (Zickefoose et al., 1976).

The electrodes of pH meter are placed into the 250 ml beaker containing the sample. The sample is titrated to a pH of 4.5 with 0.10 N sulfuric acid. Five drops of methyl orange indicator is added. In this case, the sample is titrated to the first permanent change of color to a red – orange color.

The alkalinity is calculated as mg $CaCO₃/L$

 B * N * 50000 Alkalinity mg CaCO₃/L = $$ ml sample

where:

B : ml's of H_2SO_4 required to titrate sample to pH 4.5

N : normality of H_2SO_4

The materials and equipment that were used in this experiment are: WTW Multiline P3 for pH Beaker Automatic burette

3.2.5 Total Nitrogen

The Total Nitrogen measurements were carried out using Merck® 14537 cell tests.

3.2.6 Total Phosphorus and PO4-P

The Total Phosphorus and PO₄-P measurements were carried out using Merck[®] 14729 and 14848 cell tests.

To measure the total P content of the sludge two separate samples were taken. The first sludge sample was filtered by using 0.45 µm syringe filter. The other sludge sample was diluted with distilled water. 5 ml of diluted sludge were digested after addition of required digestion reagents. For the digestion process, Merck[®] MW 520 digestion unit was used. Phosphate concentrations of both samples were measured by using above mentioned cell tests. Total-P content of the sludge was calculated by subtracting the phosphate concentration of the filtrated sample from the phosphorus concentration of the diluted sludge sample.

3.2.7 Magnesium

According to APHA, AWWA, WEF, (2005) that "magnesium may be estimated as the difference between hardness and calcium as $CaCO₃$ if interfering concentrations in the calcium titration (Section 3500-Ca.B) and suitable inhibitors are used in the hardness titration (Section 2340C). Total hardness and calcium analysis methods were both EDTA titrimetric methods.

mg Mg/L =
$$
\begin{bmatrix} \text{total hardness} \\ \text{(as mg CaCO3/L)} \end{bmatrix}
$$
 =
$$
\begin{bmatrix} \text{calcium hardness} \\ \text{(as mg CaCO3/L)} \end{bmatrix}
$$
 * 0.243

3.2.7.1 Hardness

The Hardness measurements were carried out according to the Standard Methods, method 2340 C (APHA, AWWA, WEF,2005).

3.2.7.1.1. Reagents

Buffer solution: 16.9 g of ammonium chloride is dissolved in 143 mL conc. ammonium hydroxide. 1.25 g magnesium salt of EDTA is added and diluted to 250 mL with distilled water.

EDTA solution, 0.01 M: 3.723 g of disodium ethylenediaminetetraacetate dehydrate is dissolved in distilled water and dilute to 1.0 liter.

Eriochrome Black T indicator: 0.5 g of dye is dissolve in 100 g of triethanolamine or 2-methoxymethanol. 2 drops is added per 50 mL to be titrated.

25-ml of the water sample is pipetted into an erlenmeyer flask and diluted to a total volume of approximately 50 ml. 1-2 ml of pH 10 buffer solution is added to the sample. The pH should be 10.0- 10.1. To check pH, pH meter is standardized. 1-2 drops of indicator solution is added. The standard EDTA titrant is added slowly, with continuous stirring, until the last reddish tinge disappears. At the end point the solution is blue.

The hardness is calculated as mg $CaCO₃/L$:

 $A * B * 1000$ Hardness (EDTA) as mg CaCO₃/L = $$ ml sample

where:

A : mL titration for sample

 B : mg CaCO₃ equivalent to 1.00 ml EDTA titrant.

3.2.7.2 Calcium

The Calcium measurements were carried out according to the Standard Methods, method 3500 B (APHA, AWWA, WEF,2005).

3.2.7.2.1. Reagents

Sodium hydroxide, NaOH, 1N

Murexide indicator: This indicator changes the color from pink to purple at the end point. 150 mg of dye is dissolved in 100 g of absolute ethylene glycol.

EDTA solution, 0.01 M: 3.723 g of disodium ethylenediaminetetraacetate dehydrate is dissolved in distilled water and dilute to 1.0 liter.

2.0 mL or a volume sufficient to produce a pH of 12 to 13 of NaOH solution is added to the sample. 1 - 2 drops of murexide is added ad stirred. The EDTA titrant is added slowly with continuous stirring to the proper end point. 1 to 2 drops of titrant is added in excess to make certain that no further color change occurs.

The calcium is calculated as mg $CaCO₃/L$:

 $A * B * 1000$ Calcium hardness as mg CaCO₃/L = $$ ml sample

where:

A : mL titration for sample

 B : mg CaCO₃ equivalent to 1.00 mL EDTA titrant at the calcium indicator end point.

3.2.8 Chemical Oxygen Demand (COD)

The Chemical Oxygen Demand (COD) measurements were carried out using Merck[®] 14541 cell tests and Standard Methods, method 5220 C "Closed Reflux, Titrimetric Method".

3.2.8.1 Reagents

Standard potassium dichromate solution, 0.0167 M: 4.913g of $K_2Cr_2O_7$, primary standard grade, which is previously dried at 103 °C for 2 h, 167 ml of conc. H₂SO₄, and 33.3 g of HgSO₄ is added to about 500 ml distilled water. It is waited to dissolve and cool to room temperature, and diluted to 1000 ml.

Sulfuric acid reagent: Ag_2SO_4 reagent in powdered form is added to conc. $H₂SO₄$ at a rate of 5.5 g Ag₂SO₄ / kg $H₂SO₄$. It is wait to dissolve for 1 to 2 days.

Ferroin indicator solution: This indicator is bought in commercial form.

Standard ferrous ammonium sulfate titrant (FAS), approximately 0.10 M: 39.2 g of $Fe(NH_4)_2(SO_4)_2.6H_2O$ is dissolved in distilled water and 20 ml of conc. H2SO4 is added. Before diluting to 1000 ml the solution is cooled.

The molarity of FAS solution is adjusted according to the volume of FAS used for blank titration:

Volume of $0.0167M K_2Cr_2O_7$ Solution titrated, ml M = * 0.10 Volume of FAS used in titration, ml

3.2.8.2 Procedure

In COD measurement 10 ml round cells are used. The volumes of the sample and the reagents are: 2.5 ml sample, 1.5 ml standard potassium dichromate digestion solution and 3.5 ml sulfuric acid reagent. Before addition of sample and reagents, the cells are washed with 20% H₂SO₄ to prevent contamination. The cells are placed into heater, which is preheated to 148 °C , and heated for 2 hours. The cells are waited to cool to room temperature; 1-2 drops of ferroin indicator is added and titrated with FAS solution. After ferroin addition the color turns from yellow to green. With the addition of FAS the color changes from green to blue and the end point is a sharp color change from blue to reddish brown. The COD is calculated from the equation given below:

 $(A - B) * M * 8000$ COD as mg O_2/L = ml sample

where:

A : ml FAS used for blank,

B : ml FAS used for sample, and

M : Molarity of FAS

The materials and equipment that were used in this experiment are: Heater (Velp Scientifica Eco-16) 10 ml cells Automatic burette

3.2.9 Capillary Suction Time (CST) Test

The Capillary Suction Time measurements were carried out according to the Standard Methods, method 2710 G (APHA, AWWA, WEF, 1992).

3.2.9.1 Principle

The capillary suction time (CST) test determines rate of water release from sludge. It provides a quantitative measure, reported in seconds, of how readily sludge releases its water…. The test consists of placing a sludge sample in a small cylinder on a sheet of chromatography paper. The paper extracts liquid from the sludge by capillary action. The time required for the liquid to travel a specified distance is recorded automatically by monitoring the conductivity change occurring at two contact points appropriately spaced and in contact with the chromatography paper (APHA, AWWA, WEF, 1992).

3.2.9.2 Procedure

6.4 mL of sludge sample is pippetted into test cell reservoir; if pipetting is difficult because of sludge consistency, a representative sludge sample is poured into the test cell until it is full. The CST device begins time measurement as liquid being drawn into the paper reaches the inner pair of electrical contacts. Timing ends when the outer contact is reached. CST is shown on digital display. The remaining sludge is emptied from the reservoir and the used CST paper is removed and discarded. The test block and the reservoir is rinsed and dried. The procedure is repeated for a minimum of five determinations per sample to account for measurement variation and to allow identification of any faulty readings due to leaks or spills.

3.3 Statistical Methods

In the statistical analysis of the data, Microsoft Office Excel 2003 and SPSS 13.0 for Windows software were used. The mean, maximum and minimum values, variance, standard deviation and the coefficient of variance (CV) are given as the summary statistics for scale variables. The other methods selected were Kruskal-Wallis H test and Mann-Whitney U test which are non-parametric tests.

3.3.1 Summary Statistics

Mean: Arithmetic average; the sum divided by the number of cases.

$$
M = \frac{\sum_{s=1}^{m} \sum_{i=1}^{n} y_{is}}{n_y}
$$

where;

s : number of series

i : number of points in s series

- m : number of series for y point
- n : number of points in each series
- yis : data value of s series and I point of this
- n_v : total number of data values in every series

Minimum: Smallest (lowest) value.

Maximum: Largest (highest) value.

Variance: A measure of dispersion around the mean, equal to the sum of squared deviations from the mean divided by one less than the number of cases. The variance is measured in units that are the square of those of the variable itself (the square of the standard deviation).

Standard deviation: A measure of dispersion around the mean. In a normal distribution, 68% of the cases fall within one standard deviation of the mean and 95% of the cases fall within two standard deviations. For example, if the mean age is 45, with a standard deviation of 10, 95% of the cases would be between 25 and 65 in a normal distribution (the square root of the variance).

$$
SD = \sqrt{\sum_{s=1}^{m} \sum_{i=1}^{n} (y_{is} - M)^{2} \over (n_{y} - 1)}
$$

where;

- s : number of series
- i : number of points in s series
- m : number of series for y point
- n : number of points in each series
- yis : data value of s series and I point of this
- n_v : total number of data values in every series
- M : mean

Coefficient of variation: The ratio of the standard deviation of the estimate to the mean of the estimate. The relative variation would be smaller if the coefficient of variation is smaller. If the CV value exceeds 10, it can be understood that there is a significant variation in the data series.

 Standard Deviation CV = * 100 Mean

3.3.2 Non-parametric Tests

Kruskal-Wallis H test and Mann-Whitney U test were selected from nonparametric tests (also known as distribution-free model), "because their validity does not depend on the data being drawn from any particular distribution. The estimates obtained by these methods are not as precise as we could obtain with parametric method. The advantage of the non-parametric method is that they can be used with any data set. The non-parametric method should be used only when the underlying distribution is unknown or can not be transformed to make it become normal" (Berthouex et al., 1994). In this study every group of data has different numbers of data and the number of data for all groups were under which is another reason to use non-parametric tests (Ergün, 1995).

3.3.2.1 Mann-Whitney U Test

If parametric test hypothesis can not be proved, the significance of the differences between two means can be determined with Mann-Whitney U Test, which is also known as "Wilcoxon Test". On the other hand, if the variables are both numerical and intermittent, and the number of data is less than 30, Mann-Whitney U Test must be used. According to the 2 tailed P value obtained from the SPSS program, if 2 tailed P value is less than 0.05 significance level, we can declare that there is a significant difference between the 2 groups. In this test U is the number of times a value in the first group precedes a value in the second group, when values are sorted in ascending order and Z is often the ration of an estimate to its standard error (Ergün, 1995).

3.3.2.2 Kruskal-Wallis H Test

Kruskal-Wallis H Test is a one-way ANOVA variance analysis test which is used to determine whether k independent samples are in the same space or not. Kruskal-Wallis H Test is used for the comparison of three or more different groups and is an extension of Mann-Whitney U Test, which is used for the comparison of two

different groups. According to the significance obtained from the SPSS program, if significance is less than 0.05 we can declare that there is a difference between the data groups (Ergün, 1995)

4. CHAPTER FOUR CHARACTERISTICS OF İZMİR W.W.T.P. SLUDGES

In the first period of the study, the characteristics of the raw primary, excess and mixed sludge of İzmir W.W.T.P. were determined. The experiments that were carried out in İzmir W.W.T.P. laboratory are explained in Section 3.2. Some of the experiments that can not be analyzed in İzmir W.W.T.P. laboratory, the sludge samples were analyzed by İzmir Hıfzıssıhha Institute Laboratory.

The pH, conductivity, salinity, dry solid content, volatile solids content, capillary suction time, total nitrogen, total phosphorus, ortho-phosphate, nitrate nitrogen and alkalinity are the main parameters that were monitored.

4.1 Sludge Quantity, Dry and Volatile Solids Contents

The amount of primary, excess and mixed sludge that were processed in İzmir W.W.T.P. from March 2003 to September 2005 was monitored. The primary sludge quantity was $2,596 \pm 619$ m³/day, the minimum was 754 m³/day, and the maximum was $3,646$ m³/day in the operation period of the primary sedimentation tanks. The excess sludge quantity was $7,059 \pm 2,336$ m³/day, the minimum was 277 m³/day, and the maximum was 12,759 m³/day. The mixed sludge quantity was $8,837 \pm 2,247$ m^3/day , the minimum was 277 m³/day, and the maximum was 13,233 m³/day. The sludge quantities are lower when compared to the design values of the former sludge dewatering system, because of the lower suspended solids and COD loads of the influent wastewater. The new dewatering system is designed to process 14.000 m^3 sludge per day assuming that the plant will be expanded by the addition of the fourth phase with a capacity of $3 - 4$ m³/s wastewater treatment.

The dry solids content and the volatile solids content of the sludge was also measured from March 2003 to September 2005. The results are given in (Figure 4.1, 4.2 and 4.3). The missing data seen in Figure 4.1 and 4.3 (a and b) represents the periods that the primary settling tanks were out of operation. The two periods were

between 17.10.03 – 19.03.04 and 05.11.04 - 23.01.05. During these periods there was no primary and mixed sludge formation.

Figure 4.1 The variation of dry solids (a) and volatile solids (a) content of **primary sludge** from March 2003 to September 2005.

The dry solids content of the primary sludge was $2.24 \% \pm 0.47$, with a minimum and a maximum value of 1.51 % and 4.44 %. These values are lower than the range and the typical value given by Metcalf & Eddy Inc, (1991) in (Table 2.1). İstanbul Tuzla W.W.T.P primary sludge was reported to have 4.7 % DS by Atilla et al.(2002). Johannesburg W.W.T.P primary sludge was also reported to have 4.0 % DS by Banister et al. (1998). The low dry solids content of the primary sludge is due to the operation of the primary settling tanks according to the operational instructions given by the constructor of İzmir W.W.T.P. To avoid clogging of the sludge pipeline, the dry solids content of primary sludge should be lower than 3 % and the PLC system is adjusted to obtain these conditions. The peak values (4.09, 4.44) were obtained during the rainy period (23.04.04, 08.10.04) with the increase of inorganic material in the structure of the primary sludge.

The volatile solids content of the primary sludge was $66.85 \% \pm 8.72$ with a minimum and a maximum value of 38.99 % and 84.93 %. The volatile solids content of primary sludge is very close to the typical values given in (Table 2.1) while it was 47 % for İstanbul Tuzla W.W.T.P. primary sludge (Atilla et. al., 2002) and 45 % for Athens W.W.T.P. primary sludge (Zorpas et. al., 2003). It was observed that during the rainy periods with the increase of inorganic material in the structure of the primary sludge the volatile solids content decreased. The lowest values (40.34, 44.13, 38.99, 43.32) were obtained (25.04.03, 06.02.05, 20.02.05, 13.03.05) in this period.

The dry solids content of the excess sludge was $1.27 \% \pm 0.18$, with minimum and maximum values of 0.84 % and 1.89 %. These values are in the range but higher than the typical value given in (Table 2.1). The values were also higher than the design value of İzmir W.W.T.P. given as 0.88 %. As it can be seen from Figure 4.2 (b) that during the primary settling tanks were out of operation from 31.10.03 to 30.04.04, the DS of excess sludge decreased from $1.55 - 1.65$ % to $0.9 - 1.0$ %. This can be explained by the increase of the quantity of the excess sludge withdrawn from 6,000 m³/d to 11,000 m³/d. In contrast, İstanbul Tuzla W.W.T.P excess sludge was reported to have 2.2 % DS by Atilla et al.(2002), which is a very high concentration for biological treatment excess sludge.

Figure 4.2 The variation of dry solids (a) and volatile solids (b) content of **excess sludge** from March 2003 to September 2005.

The volatile solids content of the excess sludge was $74.45 \% \pm 3.53$ with minimum and maximum values of 64.94 % and 84.90 %. The volatile solids content of excess sludge is in the range given in (Table 2.1). The volatile solids content of İstanbul Tuzla W.W.T.P was reported by Atilla et. al. (2002) as 55.0 % and 62.2 % by Alp et al. (2007) which are very low volatile solid contents for excess sludge.

Park et al. (2007) reported 73 % volatile solids content for a municipal W.W.T.P. in Korea. Wang et. al.(1999) determined the volatile solids content of excess sludge as 77 – 79 % which is higher than the values observed in İzmir W.W.T.P.

Figure 4.3 The variation of dry solids (a) and volatile solids (b) content of **mixed sludge** from March 2003 to September 2005.

The dry solids content of the mixed sludge was $1.47 \% \pm 0.24$, with minimum and maximum values of 0.95 % and 2.12 %, which complies the design value of İzmir W.W.T.P. But it was lower than the range and the typical value given in (Table 2.1). İstanbul Tuzla W.W.T.P. mixed sludge was reported to have 3.7 % DS by Atilla et al.(2002), Spain, Guadalete W.W.T.P. mixed sludge was reported to have 5.14 % DS by De la Rubia et al. (2002), and Texas, Village Creek W.W.T.P. mixed sludge was reported to have 3.56 % DS by Sosnowski et al. (2003). The dry solids content of İzmir W.W.T.P. mixed sludge is lower than all the values reported. The reason of the low dry solids content of the mixed sludge is the low dry solids content of the primary sludge.

The volatile solids content of the mixed sludge was $72.61 \% \pm 3.62$ with minimum and maximum values of 61.23 % and 81.02 %, which is the range given in (Table 2.1). İstanbul Tuzla W.W.T.P. mixed sludge was reported to have 48.6 % VS by Atilla et al.(2002), Spain, Guadalete W.W.T.P. mixed sludge was reported to have 67.81 % VS by De la Rubia et al. (2002), Greece, Crete W.W.T.P. mixed sludge was reported to have 60.8 % VS by Manios (2004) and Texas, Village Creek W.W.T.P. mixed sludge was reported to have 74.7 % VS by Sosnowski et al. (2003).

4.2 Chemical – Physical Characteristics and Heavy Metal Contents

Chemical and physical characteristics of the primary, excess and mixed sludge were also analyzed from March 2003 to September 2005. The results are given in (Table 4.1).

The pH of all sludges was in the range given as the typical composition of untreated primary, excess and mixed sludges in (Table 2.1). The conductivity and salinity of İzmir W.W.T.P sludges are relatively high because of the characteristics of the influent wastewater as $7,782 \pm 902$ mS/cm conductivity and 4.43 ± 0.61 ‰ salinity. Capillary suction time, which is one of the indications of sludge dewaterability, mixed sludge was found as 364 s by Cheunbarn et. al.(2000) which is higher than İzmir W.W.T.P mixed sludge. The values found by Üçüncü (1994) for

primary, excess and mixed sludge of Chemnitz-Heinersdorf Central W.W.T.P was 68, 58 and 34 s respectively, which are relatively lower than İzmir W.W.T.P sludges. The alkalinity of primary and excess sludge was in the range given in (Table 2.1). Total – N, NH₄ – N, Total – P and PO₄ – P values were given as mg/kg of total solids.

Parameter	Unit	Primary Sludge	Excess Sludge	Mixed Sludge	
pH		7.83 ± 0.33	7.52 ± 0.26	7.67 ± 0.28	
Conductivity	mS/cm		5.51 ± 1.59	6.02 ± 1.61	
Salinity	$\%$	3.9 ± 1.0	3.2 ± 0.8	3.6 ± 0.9	
Capillary Suction	Second		213 ± 36	255 ± 32	
$mg \text{CaCO}_3/\text{L}$ Alkalinity		865 ± 576	926 ± 689	912 ± 532	
Total Nitrogen	mg/kg of TS	$4,133 \pm 607$	$20,880 \pm 22,369$	$5,875 \pm 1,327$	
Ammonia Nitrogen	mg/kg of TS	343 ± 60	$2,942 \pm 1,172$	$1,389 \pm 966$	
Total mg/kg of TS Phosphorus		$2,092 \pm 857$	$10,713 \pm 2,982$	$5,255 \pm 1,931$	
Ortho Phosphate	mg/kg of TS	$1,757 \pm 1,542$	$7,361 \pm 3,355$	$4,133 \pm 1,586$	

Table 4.1 Characteristics of İzmir W.W.T.P. primary, excess and mixed sludge.

The heavy metal and metals contents of primary, excess and mixed sludges are given in comparison to the "Turkish Soil Pollution Control Regulation" (T.S.P.C.R) (31.05.2005, 25831), the EU Directive 86/278/EEC values (Jensen et. al., 2005) and the other treatment plant sludge heavy metal contents in (Table 4.2). The heavy metal and metal contents of Ankara W.W.T.P. were given by Arcak et al. (2000). The heavy metal and metal contents of Athens W.W.T.P. were given by Zorpas et al. (2003). The heavy metal and metal contents of Crete W.W.T.P. were given by Manios (2004). The heavy metal and metal contents of Beijing W.W.T.P. were given by Dai et al. (2007).

Heavy Metals/ Metals (mg/kg TS)	T.S.P C.R	EU	Primary Sludge	Excess Sludge	Mixed Sludge	Ankara	Athens	Crete	Beijing
Aluminum	\overline{a}		$3,676 \pm$ 4,250	$5,089 \pm$ 3,369	$10,771 \pm$ 9,174	\overline{a}	\overline{a}	\overline{a}	
Arsenic	20		$17.55 \pm$ 2.19	$18.60 \pm$ 4.37	$23.31 \pm$ 17.35				$16.7 \pm$ 4.0
Beryllium	\overline{a}	$\overline{}$	1.00	1.00	1.90	\blacksquare	$\qquad \qquad \blacksquare$	$\overline{}$	
Boron	$\overline{}$		1.30	$42.03 \pm$ 28.46	$714.80 +$ 155.29				
Cadmium	40	20-40	1.20	$1.58 \pm$ 0.21	$2.47 +$ 2.23	0.12	2.0		$7.0 \pm$ 1.2
Total Chromium	1,500	\overline{a}	$81.00 \pm$ 21.78	$124 \pm$ 33.44	$140.50 \pm$ 95.96	$\overline{}$	552	\blacksquare	$57.8 \pm$ 22.3
Hexavalent Chromium	\overline{a}	\overline{a}	< 0.05	< 0.05	123.90	\overline{a}	$\overline{}$	$\overline{}$	
Cobalt	20		2.60	$2.93 +$ 1.72	$4.70 \pm$ 4.95	0.53	\overline{a}	\blacksquare	
Copper	1,200	1000- 1750	$119 \pm$ 2.19	$191.45 \pm$ 71.75	$178.68 \pm$ 101.75	14.4	258	230	229 ±70.4
Iron	\overline{a}		$8,886 \pm$ 6,625	$8,235 \pm$ 6,129	$17,841 \pm$ 30,608	28.8	5,098		
Lead	1,200	750- 1200	$72.65 \pm$ 14,92	$76.00 \pm$ 15.99	$116.41 \pm$ 126.50	$\qquad \qquad \blacksquare$	326	\overline{a}	$57.5 +$ 10.4
Lithium	\overline{a}	\overline{a}	$8.35 \pm$ 5.15	$6.00 \pm$ 5.08	$12.30 \pm$ 16.76	\blacksquare	$\overline{}$	\overline{a}	
Manganese	$\frac{1}{2}$	\overline{a}	$125 +$ 28.43	$790.85 \pm$ 516.30	$469 \pm$ 126.5	72.5	150	168	
Mercury	10	16-25	< 1.00	1.30	10.00				$21.8 +$ 2.9
Molybdenum	110	\overline{a}	2.90	$2.13 +$ 1.29	$4.66 \pm$ 3.79	$\overline{}$	$\qquad \qquad \blacksquare$	$\overline{}$	
Nickel	300	300- 400	$36.15 \pm$ 28.64	$40.15 \pm$ 21.60	$38.06 \pm$ 32.76	1.47	41		49.9 ±12.8
Selenium	$\overline{5}$	\overline{a}	n.m.	n.m.	n.m.	\overline{a}	\overline{a}	\blacksquare	
Tin	20	$\overline{}$	n.m.	n.m.	n.m.	\blacksquare	$\overline{}$	\blacksquare	
Vanadium	\overline{a}	$\qquad \qquad \blacksquare$	$31.45 \pm$ 10.25	$19.70 \pm$ 9.78	$27.63 \pm$ 25.84	\blacksquare	$\overline{}$	\overline{a}	
Zinc	3,000	2500- 4000	$423.80 \pm$ 72.69	$500.25 \pm$ 234.85	$759.56 \pm$ 410.87	109	1,739	1,217	1,431.4 ± 395.1

Table 4.2 Heavy metals and metals content of primary, excess and mixed sludge. (Arcak et. al.,2000, Zorpas et. al. 2003, Manios, 2004, Dai et. al., 2007)

Arsenic: The arsenic contents of İzmir W.W.T.P. primary and mixed sludge were lower than the value given in T.S.P.C.R. while the mixed sludge arsenic content exceeded the value. The arsenic contents of İzmir W.W.T.P. sludges were higher than the median given as the typical arsenic content of wastewater sludge in (Table 2.2). Similar arsenic contents were also reported for Beijing W.W.T.P.

Cadmium: The cadmium contents of İzmir W.W.T.P. sludges were extremely lower than the limits values given in the T.S.P.C.R. and the E.U. Directive. Athens W.W.T.P sludge was reported to have similar cadmium content while Ankara W.W.T.P. sludge was reported as 1/10 of İzmir W.W.T.P. sludge. Beijing W.W.T.P. sludge cadmium content was $2.8 - 5.8$ times higher than \overline{l} zmir W.W.T.P. sludges.

Total Chromium: The total chromium contents of İzmir W.W.T.P. sludges were extremely lower than the limit given in the T.S.P.C.R. while there was no limit given in the E.U. Directive. The total chromium content of Athens W.W.T.P. sludge was 4 to 7 times higher than the total chromium content of İzmir W.W.T.P sludges. Beijing W.W.T.P. sludge was reported to have lower total chromium content than İzmir W.W.T.P sludges.

Cobalt: The cobalt contents of İzmir W.W.T.P. sludges were extremely lower than the limit given in the T.S.P.C.R. The cobalt content of Ankara W.W.T.P. sludge reported to be lower than İzmir W.W.T.P sludges.

Copper: The copper contents of İzmir W.W.T.P. sludges were extremely lower than the limits given in the T.S.P.C.R. and the E.U. Directive. Similar results were reported for Athens, Crete and Beijing W.W.T.P's sludges while the copper content of Ankara W.W.T.P. sludge was lower than all sludges.

Lead: The lead contents of İzmir W.W.T.P. sludges were extremely lower than the limits given in the T.S.P.C.R. and the E.U. Directive. Similar lead contents were also reported for Beijing W.W.T.P. while the lead content of Athens W.W.T.P was 2 times higher than the lead content İzmir W.W.T.P. sludges.

Manganese: The manganese content of the excess sludge was 3.7 times higher than the manganese content of the mixed sludge and 6.3 times higher than the manganese content of the primary sludge. Ankara, Athens and Crete W.W.T.P.'s sludges were reported to have similar manganese contents with the primary sludge of İzmir W.W.T.P.

Mercury: The mercury content of Izmir W.W.T.P. primary and excess sludges were lower than the limits given in the T.S.P.C.R. and the E.U. Directive. The mercury content of İzmir W.W.T.P. mixed sludge was at the limit value given in the T.S.P.C.R. as 10 mg/kg TS but it was lower than the limit given in the E.U. Directive. Higher lead contents were reported for Beijing W.W.T.P.

Molybdenum: The molybdenum contents of İzmir W.W.T.P. sludges were extremely lower than the limit given in the T.S.P.C.R. while there was no limit given in the E.U. Directive.

Nickel: The nickel contents of İzmir W.W.T.P. sludges were extremely lower than the limits given in the T.S.P.C.R. and the E.U. Directive. Similar results were reported for Athens and Beijing W.W.T.P's sludges while the copper content of Ankara W.W.T.P. sludge was the lower than all sludges.

Zinc: The zinc contents of İzmir W.W.T.P. sludges were lower than the limits given in the T.S.P.C.R. and the E.U. Directive. The zinc contents of Athens, Crete and Beijing W.W.T.P's sludges were 2 to 3 times higher than İzmir W.W.T.P. sludges. The copper content of Ankara W.W.T.P. sludge was lower than all sludges.

5. CHAPTER FIVE

DETERMINATION OF METHANE POTENTIAL OF THE SLUDGES

In the second period of the study Biochemical Methane Potential (BMP) and methane yields were investigated to determine the methane potential of İzmir W.W.T.P. sludges.

5.1 BMP Test

During the BMP tests, all the sludge samples were taken from site before thickening or dewatering processes for the period of 01.11.2005 and 15.08.2005. Sludge samples were taken weekly and analyzed for DS % and VS % contents. Since the required DS content of the sludge for anaerobic digestion was $4 - 6\%$, the sludge samples were processed in the laboratory in order to achieve 6 % DS. The DS content was adjusted to 6 % to obtain the minimum digestion volume with the decrease of sludge volume. In the thickening process polyelectrolyte was added to each sample. After a time for settling, the supernatant was taken and the samples were sieved by using the belts of the mechanical dewatering tables.

The BMP tests were carried out according to the procedure given in Chapter 3. The gas produced from each sludge sample was measured by using hypodermic glass needle. The amount of gas produced from only inoculum bottle was subtracted from these values and the net gas production of the sludge is calculated. The methane content of the produced gas was measured by the method described in the BMP test procedure, by using KOH. By using the acceptation of 395 ml of $CH₄$ production is equivalent to 1 g COD reduction the BMP is calculated as g COD converted to methane/gVS*d.

Figure 5.1 The variation of (a) dry solids (%) and volatile solids (%) contents (b) BMP (g CODconverted/ g VS*d) of thickened **primary** sludge

Dry solids and volatile solids content of the thickened primary sludge used in the BMP experiments are given in Figure 5.1 (a). The DS content of the primary sludge was 7.50 ± 1.38 % with minimum and maximum values of 6.11 and 11.38 %. The VS content of the primary sludge was 64.71 ± 5.90 % with minimum and maximum values of 41.63 and 72.86 %. During the summer months, the DS content was 6.41 \pm 0.34 % and the VS content was 67.26 \pm 1.59 %. The coefficient of variation for the whole experimental period for DS content was 18.4 and for VS content was 9.1. The coefficient of variation decreases to 5.3 for DS content and 2.4 for VS content during the summer months. Although the thickening process was applied up to 6 % DS, some uncontrolled conditions occurred due to the rainy periods which increased the dry solids content and decrease the volatile solids content of the sludge. It may be thought due to the increase of the inorganic material of sludge content.

The variation of BMP during the experiment period is shown in Figure 5.1 (b) for primary sludge. The COD content that can anaerobically be converted to methane gas, BMP, of primary sludge was 0.063 ± 0.023 g COD_{converted}/gVS^{*}d with minimum and maximum values of 0.014 and 0.113 g $\text{COD}_{\text{converted}}/\text{gVS}^*$ d. The BMP of the sludge changed significantly which can also be understood from the high standard deviation and coefficient of variation as 0.023 and 36.5, respectively. It can be seen from Figure 5.1 (b) that after the $8th$ week when both the VS content and BMP decreased with the affect of the rainy period, the BMP was stabilized at approximately $0.060 \text{ gCOD}_{\text{converted}}/\text{gVS}^*d$. The BMP values were measured approximately at 0.100 gCOD_{converted}/gVS*d after the $28th$ week which was after a break in June. As mentioned before, the required DS content of the sludge for best anaerobic digestion was reported as $4 - 6$ %. The increase of BMP can be explained by the stabilized DS content of the sludge at 6 %.

Volatile solids quantity (gVS) was plotted against to methane content $\frac{1}{2}$ and the total gas and methane production rate (ml/d) in Figure 5.2 for primary sludge. It was observed that with the increase of volatile solids, the total gas and methane production increases. The methane content of the gas was minimum when 1.0 g VS was added. The total gas production increased from 25 ml/d for 1.0 g VS to 60 ml/d for 1.7 g VS and it stayed constant up to 2.7 g VS. The total gas production increased to 90 ml/d at over a value of 2.8 g VS. The methane content increased over 70 % for 2.0 g VS and began to decrease over a value of 2.5 g VS. It can be concluded from

these results that it would be better to feed the anaerobic digestion system with a VS content of 1.7 g for primary sludge.

Figure 5.2 The total gas and methane production rates and methane content of the **primary** sludge per gVS.

5.1.2 Excess Sludge

The dry solids and volatile solids content of the thickened excess sludge during the BMP experiments are given in Figure 5.3 (a). The DS content of the excess sludge was 5.50 ± 0.26 % with minimum and maximum values of 4.92 and 5.99 %. The VS content of the excess sludge was 71.78 ± 3.51 % with minimum and maximum values of 64.58 and 78.45 %. The DS and VS content of the excess sludge did not change significantly which can also be understood from the low standard deviations as 0.26 and 3.51 and coefficient of variations as 4.73 and 4.89, respectively.

The variation of BMP during the experiment period is shown in Figure 5.3 (b) for excess sludge. The COD content that can anaerobically be converted to methane gas, BMP, of excess sludge was 0.067 ± 0.006 g COD_{converted}/gVS^{*}d with minimum and maximum values of 0.054 and 0.079 g COD_{converted}/gVS^{*}d. It can be seen from Figure 5.3 (b) that the BMP of excess sludge did not change significantly, and remained steady during the experimental period which can also be understood from the low standard deviation as 0.006 and coefficient of variation as 8.96.

Figure 5.3 The variation of (a) dry solids (%) and volatile solids (%) contents

(b) BMP (g CODconverted/ g VS*d) of thickened **excess** sludge

Figure 5.4 The total gas and methane production rates and methane content of the **excess** sludge per gVS.

Volatile solids quantity (gVS) was plotted against to methane content (%) and the total gas and methane production rate (m/d) in Figure 5.4 for excess sludge. 1.0 to 2.0 g VS was observed for the excess sludge, which is because of the low DS content of the excess sludge when compared to the primary sludge. The total gas production increased from 54 ml/d for 1.0 g VS to 75 ml/d for 2.0 g VS. The methane content of the gas increased to a maximum value of more than 71.5 % for 1.4 g VS. But it decreased to 67.3 % for 2 g VS.

5.1.3 Mixed Sludge

The dry solids and volatile solids content of the thickened mixed sludge during the BMP experiments are given in Figure 5.5 (a). The DS content of the mixed sludge was 6.26 ± 0.43 % with minimum and maximum values of 5.56 and 7.27 %. The VS content of the mixed sludge was 68.28 ± 3.34 % with minimum and maximum values of 61.52 and 75.57 %. The DS and VS content of the excess sludge did not change significantly which can also be understood from the low standard

deviations as 0.43 and 3.34 and coefficient of variations as 6.87 and 4.95, respectively.

Figure 5.5 The variation of (a) dry solids (%) and volatile solids (%) contents (b) BMP (g CODconverted/ g VS*d) of thickened **mixed** sludge

The variation of BMP during the experiment period is shown in Figure 5.5 (b) for mixed sludge. The COD content that can anaerobically be converted to methane gas, BMP, of mixed sludge was 0.070 ± 0.012 g COD_{converted}/gVS^{*}d with minimum and maximum values of 0.053 and 0.102 g $\text{COD}_{\text{converted}}/\text{gVS}^*$ d. It can be seen from Figure 5.5 (b) that the BMP of mixed sludge changed during the experimental period which can also be understood from the standard deviation as 0.012 and coefficient of variation as 17.14.

Figure 5.6 The total gas and methane production rates and methane content of the **mixed** sludge per gVS.

Volatile solids quantity (gVS) was plotted against to methane content (%) and the total gas and methane production rate (ml/d) in Figure 5.6 for mixed sludge. It was observed that the increase of VS did not significantly affect the total gas and methane production. The total gas production increased from 58 ml/d for 1.0 g VS to 67 ml/d for 2.0 g VS. The methane content of the gas increased to 69.0 % for 1.4 g VS added and remained nearly constant for more than 1.4 g VS added.

If the total gas and methane productions of primary, excess and mixed sludges are compared from figures 5.2, 5.4 and 5.6, the total gas and methane production of the mixed sludge for 1 g VS was higher than that of the primary and excess sludge. The total gas and methane production of the mixed and excess sludge was two times higher than the total gas and methane production of the primary sludge for 1 g VS. The total gas and methane production of the excess sludge for 2 g VS was higher than that of the primary and mixed sludge.

5.2 Determination of Methane Yield

For the determination of the methane yields 40 ml's of sludge samples taken from the primary, excess and mixed sludge of İzmir W.W.T.P. were filled into the bottles with the addition of 10 ml's of inoculum and 20 ml's of substrate solution. The gas formation and the methane content of the gas were monitored for 25 days without sludge addition or withdrawal. The dry solids content of the primary, excess and mixed sludges were 6.80 %, 5.47 % and 6.35 %, respectively, while the volatile solids contents were 64.64 %, 72.57 % and 68.88 %, respectively. The gas production and the methane content were measured daily or in every two days. The methane yields were calculated as mlCH₄/gVS_{added}. The cumulative methane production (a) and methane contents (b) of primary, excess and mixed sludges are given in (Figure 5.7).

The methane yield of primary sludge was calculated as $382.90 \text{ mlCH}_4/\text{gVS}_\text{added}$ and the methane content was found as 64.00 %. The methane yield of excess sludge was calculated as 528.55 mlCH₄/gVS_{added} and the average methane content was found as 66.42 %. The methane yield of mixed sludge was calculated as 496.16 mlCH₄/gVS_{added} and the methane content was found as 65.33 %. The methane yields found and quoted by Cho et. al. (1995) were 482 for cooked meat, 356 for cellulose, 294 for boiled rice, 277 for fresh cabbage, 472 for mixed food waste, $186 - 222$ for municipal solid waste and 590 for primary sludge as mlCH₄/gVS_{added}. The methane yield was found lower than the reported value as 590 mlCH₄/gVS_{added} found for the primary sludge, but it is acceptable when compared to the value given by Protechnich (2002) as $400 - 450$ mlgas/gVS_{added}. The methane yields that were found for excess and mixed sludge were higher than that of the primary sludge.

Figure 5.7 (a) The cumulative methane yield of **primary, excess and mixed** sludge

(b) Methane content of **primary, excess and mixed** sludge.

The methane yield of the primary sludge increased rapidly than the methane yields of excess and mixed sludge and reached to 80 % of the total methane production in 7 days. However, the methane yield of the excess and mixed sludge increased to 80 % of the total methane production in the $10th$ day. This can be explained by the available easily biodegradable substances in the primary sludge.

Whereas, the excess sludge is completely consists of microorganisms which is difficult to biodegrade. After 10 days the methane production of all sludges was nearly the same and the quantity of the methane production was very low when compared to the first 10 days. The methane contents of the sludges were lower in the first two days, but it was stabilized after the third day.

The low methane yield of the primary sludge when compared to the excess and mixed sludges may be due to the inconvenient $C : N : P$ ratio of the primary sludge which can be seen from Table 4.1. The required optimum $C : N : P$ ratio for enhanced yield of methane was given as 100 : 2.5 : 0.5 by Rajeshwari et.al., 2000. Whereas, it was stated by Sanver (2000) that anaerobic systems can perform well with $1000 : 5 : 1$ ratio.

6. CHAPTER SIX OPERATION OF THE REACTORS

After the characterization and determination of the methane potential of the sludge both by batch tests and BMP tests, continuous operation of the reactors, each of having the same operation volume were taken into operation. The reason of the continuous operation of the reactors was to determine the best process operation conditions for the anaerobic digestion of İzmir W.W.T.P. sludges which is and advanced biological treatment plant consisting of biological nitrogen and phosphorus removal. Continuous reactor operation was between 06.05.2006 and 29.04.2007.

The sludge that was previously processed in order to obtain 6 % DS and inoculum taken from Ankara W.W.T.P. were mixed by using a homogenization device and filled into the reactors. 6 L's of sludge and inoculum mixture was filled into the reactors. Before the reactors were taken into operation, N_2 and CO_2 gases were introduced into the reactors to obtain anaerobic conditions. Everyday 600 and 500 ml's of sludge was withdrawn and the same amount of sludge was added to maintain a hydraulic retention time of 10 and 12 days for primary, excess and mixed sludges. For the excess and mixed sludge, 15 and 20 days hydraulic retention time was also obtained by the withdrawal of 400 and 300 ml's of sludge from the reactor, and addition of the same amount of feed sludge into the reactors.

After the reactors have been taken into operation, pH, conductivity, salinity, dry solid content, volatile solids content, COD, T-P of feed sludge, COD, T-N, T-P and PO4-P of feed sludge supernatant, pH, ORP, conductivity, salinity, dry solid content, volatile solid content, COD, T-P and PO_4 -P of the digested sludge, COD, T-P, PO_4 -P and Total Magnesium of digested sludge supernatant were measured. The results of phosphorus measurements were not evaluated in this chapter, since the phosphorus balance is given as a separate chapter.

6.1 Sludge Properties

6.1.1 Temperature

The temperature values of the feed primary, excess and mixed sludges observed during the operation period of the reactors in different hydraulic retention times (HRTs) are given in (Table 6.1). The reason of feed sludge temperature monitoring was to determine the additional heat requirement in the design of the anaerobic digestion system. The temperature of the feed sludge was completely dependent on the season. However, the temperature of the reactor was kept constant at 35 $^{\circ}$ C \pm 0.5 (mesophilic conditions) with an automatically controlled heating system and observed by a digital indicator.

HRT (days)	Sludge	Temperature °C				
		Mean \pm Std. Dev.	Minimum	Maximum		
10	Primary	22.7 ± 0.5	21.6	23.6		
	Excess	22.5 ± 0.4	21.5	23.0		
	Mixed	22.3 ± 1.0	19.0	23.3		
12	Primary	26.0 ± 0.8	25.0	27.0		
	Excess	27.1 ± 0.6	26.5	28.1		
	Mixed	26.9 ± 0.5	26.4	27.6		
15	Primary					
	Excess	17.0 ± 1.6	14.8	19.7		
	Mixed	16.8 ± 1.7	15.2	22.4		
20	Primary		$\overline{}$			
	Excess	18.5 ± 2.3	15.2	22.4		
	Mixed	18.3 ± 2.2	16.8	18.3		

Table 6.1 Temperature of feed primary, excess and mixed sludge in different reactor HRTs

6.1.2 pH

The pH variation of the feed and digested primary, excess and mixed sludges is given in (Figure 6.1).

In Figure 6.1 (a), the pH of the feed primary sludge and the pH of the digested primary sludge are shown. The pH of the feed primary sludge was measured as 7.52 ± 0.18 and the digested primary sludge was measured as 6.96 ± 0.26 . After the primary sludge reactor has been taken into operation for 10 days retention times, the pH in the reactor decreased from 7.5 to 6.6. Then it started to increase to neutral pH. This case was due to the methanogenic activity sensitivity compared to the acid production microorganisms. The methane formers were affected by the unsuitable conditions of the primary sludge than the acid formers. Because of this reason, the methane formers could not convert enough volatile acids to methane and the pH started to decrease.

In Figure 6.1 (b), the pH of the feed excess sludge and the pH of the digested excess sludge are shown. The pH of the feed excess sludge was measured as 7.42 \pm 0.23 and the digested excess sludge was measured as 7.18 \pm 0.19. It can be seen from Figure 6.1 (b) that the pH of feed and digested excess sludge did not change significantly during the operation of the reactors which can also be understood from the coefficient of variation as 3.1 and 2.6, respectively.

In Figure 6.1 (c), the pH of the feed mixed sludge and the pH of the digested mixed sludge are shown. The pH of the feed mixed sludge was measured as 7.51 ± 0.21 and the digested mixed sludge was measured as 7.08 ± 0.20 . It can be seen from Figure 6.1 (c) that the pH of feed and digested mixed sludge did not change significantly during the operation of the reactors which can also be understood from the coefficient of variation as 3.8 and 2.8, respectively.

For both the excess and mixed sludges the pH of the raw sludge was approximately 7.5. In contrast to the primary sludge, the pH of the excess sludge and mixed sludge did not show strict decreases. But it can be seen from the figures that for all retention times the average pH decreases slightly to a nearly neutral pH.

Figure 6.1 The pH of (a) **primary** sludge, (b) **excess** sludge (c) **mixed** sludge.

6.1.3 Conductivity and Salinity

The conductivity and salinity of feed and digested primary, excess and mixed sludges during the operation of the reactors are given in (Figure 6.2).

The conductivity and salinity of all sludges were high for a wastewater sludge which can be explained by the infiltration of salty ground water and sea water into the sewage pipelines especially that are near the seashore. It was determined by Özalp et. al (2002) for the anaerobic digestion process that there was "no significant inhibition due to high salinity contents up to 1.5 % and the system could well tolerate such salt concentrations." It was also found that the volatile solids reduction and the gas and methane formation of the system were not affected by high salt concentrations. The only serious effect of high conductivity and salinity would be the corrosion risk of the mechanical equipment of the whole plant.

During the operation of the reactors the highest conductivity and salinity levels were observed as 9.35 mS/cm and 5.1 ‰.

Figure 6.2 The conductivity and salinity of feed and digested (a) **primary** sludge, (b) **excess** sludge

6.1.4 Capillary Suction Time (CST)

The capillary suction time (CST), the procedure of which is given in Chapter 3, of feed and digested primary, excess and mixed sludge is given in (Table 6.2). The CST of the digested sludge was measured for the excess and mixed sludges at the operation of reactors in 15 and 20 days hydraulic retention times.

HRT (days)	Sludge		Capillary Suction Time (CST) (second)
		Primary	119 ± 23
	Feed	Excess	213 ± 36
		Mixed	255 ± 32
15	Digested	Primary	n.m
		Excess	140 ± 23
		Mixed	176 ± 18
20		Primary	n.m.
	Digested	Excess	132 ± 18
		Mixed	173 ± 26

Table 6.2 Capillary Suction Time (CST) of feed and digested primary, excess and mixed sludge during the operation of the reactors.

* n.m : not measured

 ⁽c) **mixed** sludge.

The CST of the feed primary sludge was the minimum which shows the best performance for dewatering. The excess sludge and mixed sludge contains microorganisms and the water in cell structure of the microorganisms makes it difficult to dewater. Therefore, the CST values measured for the excess and mixed sludge are higher than the primary sludge. After the digestion process, $30 - 35$ % reduction of the CST was observed for both excess and mixed sludges which show the enhanced dewatering properties of digested sludge. The increasing dewatering properties were also stated by Lin et.al. (1998). The capillary suction of digested sludges was in the range $148 - 389$ s compared with $309 - 735$ s for undigested sludges.

With the selection of appropriate polyelectrolyte, the best dewatering performance can be obtained for the mixed sludge, because the polyelectrolyte is purchased according to the dewatering performance of the mixed sludge.

6.1.5 Oxidation Reduction Potential (ORP)

The oxidation reduction potential (ORP) was determined by using an electrode as mV. The ORP values for primary, excess and mixed sludge reactors, during the operation are given in (Table 6.3). Nearly all of the ORP values were in the optimum range given in Table 2.3 for the best digestion. It can be concluded that the anaerobic conditions was not broken down for the whole operation period and N_2 and CO_2 gas application to the reactors at start-up was successful.

6.1.6 Dry Solids and Volatile Solids Contents

6.1.6.1 Primary Sludge

The dry solids contents of feed and digested primary sludge and the dry solid reductions (%) of primary sludge are illustrated in (Figure 6.3 a) and (Figure 6.3 b). The volatile solids contents of feed and digested primary sludge and volatile solids reductions (%) of primary sludge are illustrated in (Figure 6.4 a) and (Figure 6.4 b).

As it can be seen from (Figure 6.3 a) that the DS content of the feed primary sludge was higher at the beginning of the operation period for the reactor operated with 10 days HRT. Therefore the DS content of the digested sludge was also higher at the beginning. Then the DS content of the sludge decreased slightly. It may be thought that the manual thickening process to adjust the DS content to a given percent (6 %) was not successful because of seasonal variations of sludge DS characteristics. It can be seen from (Figure 6.3 b) that the feed sludge DS was 7.25 \pm 0.55 %, while the digested sludge DS was stabilized at 5.31 ± 0.46 %. For 12 days HRT operation, the feed primary sludge DS was 6.41 ± 0.34 %, while the digested sludge was 4.86 ± 0.18 %. The DS reduction was 26.36 ± 8.21 % for 10 days HRT operation and 24.01 ± 3.29 % for 12 days HRT operation. The variation of DS reduction fluctuated with a minimum value of 17.32 % and a maximum value of 33.67 % for 10 days HRT operation. But the variation of the DS content was significant which can be proved by the coefficient of variation as 7,6 and 5,3 for 10 and 12 days HRT operation, which are also lower when compared to that of the BMP test period.

Figure 6.3 (a) The DS variation of feed and digested **primary** sludge – DS reduction (b) The DS of feed and digested **primary** sludge – DS reduction

The volatile solids contents of feed primary sludge and digested primary sludge were nearly constant for both 10 and 12 HRT operation. The feed sludge VS was 66.23 \pm 4.82 % for 10 days HRT operation and 67.26 \pm 1.59 for 12 days HRT operation, while the digested sludge VS was 44.97 ± 1.75 % for 10 days HRT operation and 43.84 ± 1.92 % for 12 days HRT operation. It can be seen from Figure 6.4 (a) that the VS content of feed and digested primary sludge did not change significantly during the operation of the reactors which can also be understood from the coefficient of variation as 7.3 and 3.9, 2,4 and 4,4 for 10 and 12 days HRT operation respectively.

Figure 6.4 (a) The VS variation of feed and digested **primary** sludge – VS reduction (b) The VS of feed and digested **primary** sludge – VS reduction

The volatile solids reduction was 31.76 ± 5.54 % for 10 days and 34.81 ± 2.71 % for 12 days HRT operations. Both of them are under the value given as 38 % volatile solids reduction by EPA (Puchajda et al., 2003) but most probably would be higher for 15 days HRT operation. The volatile solids reduction of primary sludge was found as 30 % by Atilla et.al.(2002) and 42 % by Üçüncü (1994) which were similar to the results obtained from the operation of the reactors. While the variation of volatile solids reduction for 10 days HRT operation was significant with a coefficient of variation value of 17.4, it was not significant for 12 days HRT operation with a coefficient of variation value of 7.8.

6.1.6.2 Excess Sludge

The dry solids contents of the feed and the digested excess sludge and the dry solid reductions $(\%)$ of excess sludge are shown in (Figure 6.5 a). The volatile solids contents of the feed and the digested excess sludge and the volatile solids reductions $(\%)$ of excess sludge are given in (Figure 6.5 b).

As it can be seen from (Figure 6.5 a) that the dry solids content of the feed excess sludge for 10, 12, 15 and 20 days HRT operation was nearly constant (coefficient of variation was 5.9) and ranged between $5.5 - 5.7$ %. The DS content of the digested sludge ranged between $4.07 - 4.32$ %. The maximum DS reduction was obtained for 15 d HRT as 25.95 %.

The volatile solids content of feed excess sludge was nearly constant ranging between 70.42 and 71.88 % with a coefficient of variation as 2.6. For the digested sludge, the volatile solids of excess sludge for 10, 12, 15 and 20 days HRT operation ranged between 37.23 and 41.42 % with the lowest value at 15 days HRT operation. The maximum VS reduction was observed for 15 d HRT operation as 47.91. All of the values were higher than the value given as 38.0 % by EPA (Puchajda et al., 2003) which is one of the indicators of the degree of sludge stabilization. The volatile solids reduction of excess sludge was found as 44.0 % by Atilla et.al.(2002) and 38.5 % by Üçüncü (1994) which were similar to the results obtained during the operation of the reactors.

Figure 6.5 (a) The DS of feed and digested **excess** sludge – DS reduction (b) The VS of feed and digested **excess** sludge – VS reduction

6.1.6.3 Mixed Sludge

The dry solids contents of feed and digested mixed sludge and the dry solid reductions (%) of mixed sludge are shown in (Figure 6.6 a). The volatile solids contents of feed and digested mixed sludge and the volatile solids reductions (%) of mixed sludge are shown in (Figure 6.6 b).

Figure 6.6 (a) The DS of feed and digested **mixed** sludge – DS reduction (b) The VS of feed and digested **mixed** sludge –VS reduction

As it can be seen from (Figure 6.6 a) that the DS content of the feed mixed sludge ranged between 5.90 – 6.43 % The DS content of the digested sludge ranged between 4.32 – 4.83 %. There was no significant variation both for the feed and digested mixed sludge since the coefficient of variation was 6.1 and 7.5, respectively. The maximum DS reduction was obtained for 20 d HRT operation as 28.21 %.

The volatile solids content of feed mixed sludge was nearly constant (coefficient of variation was 3.4) ranging between 67.28 and 69.21 %. For the digested sludge, the volatile solids decreased significantly (coefficient of variation was 11.4) from 44.35 to 36.15 % with the increase of HRT. Therefore, the VS reduction increased with the increase of HRT. The maximum reduction was obtained at 20 days HRT operation as 46.27 %, but 15 days HRT operation was also resulted with a high VS reduction as 45.76 %. The volatile solids reduction for 10 days HRT operation was not higher than the value given as 38 % by EPA (Puchajda et al., 2003), but at the other HRT's the volatile solids reductions were higher than the value given as 38 % by EPA. The volatile solids reduction of mixed sludge was found as 39 % by Atilla et al.(2002), 39 % by Üçüncü (1994), 46.6 \pm 11.6, 53.1 \pm 4.0 and 42.2 \pm 9.0 % at 15, 13 and 11 days HRT by Puchajda et al. (2003), 50 % by Cheunbarn et al.(2000), 47 % by Gavala et al. (2003), 53 % by De la Rubia et al. (2002), 62,5 % for Los Angeles Hyperion W.W.T.P at 20 days HRT and 58 % for Sacramento Regional W.W.T.P. at 20 days HRT by Witzgall et al. (2003) which were similar to the results obtained in the operation of the reactors.

6.1.7 Volatile Solids Loading Rate

The volatile solids loading rate, which is just like food to microorganism ratio used in activated sludge systems, is one of the important parameters in the design and operation of anaerobic processes (Zickefoose et al., 1976). The volatile solids loading ranges between $1.5 - 6.2$ kg VS/m³.day (Öztürk, 1998). According to Metcalf $&$ Eddy Inc. (1991) the volatile solids loading rate ranges between 1.6 to 4.8 kgVS/m³.day.

The volatile solids loading rates (kg VS / $m³$ * d) calculated according to formula given below by using the feed sludge dry solids and volatile solid contents are introduced in Figure 6.7 together with the volatile solids loading rates given in (Table 2.4) as a function of the dry solids content of the feed sludge and the hydraulic retention times.

$$
V_{\text{olating Rate}} = \frac{V_{\text{f}} \cdot (DS / 100) \cdot (VS / 100)}{V_{\text{d}}}
$$
\n
$$
V_{\text{d}}
$$

where:

 V_f : volume of sludge fed into the reactor per day (ml/d)

 V_d : volume of reactor (L)

- DS : Dry solids content of sludge $(\%)$
- VS : Volatile solids content of the sludge $(\%)$

Figure 6.7 Volatile solids loading rates of **primary, excess** and **mixed** sludges.

The volatile solids loading rate of primary sludge was 4.79 ± 0.5 kg VS / m³ $*d$ for 10 days HRT operation and 3.59 ± 0.2 kg VS / m³ $*$ d for 12 days HRT operation. When these values were plotted into Figure 6.7 together with the dry solids content of the primary sludge, it was found that the volatile solids loading rates did not fit the lines given for 10 and 12 days HRT.

The volatile solids loading rate of excess sludge was 4.01 ± 0.28 kg VS / m³ *d for 10 days HRT operation, 3.34 ± 0.24 kg VS / m³ $*$ d for 12 days HRT operation, 2.36 ± 0.17 kg VS / m³ * d for 15 days HRT operation and 1.99 ± 0.11 kg VS / m³ * d for 20 days HRT operation. When these values were plotted into Figure 6.7 together with the dry solids content of the excess sludge, it was observed that the volatile solids loading rates fitted with the given lines exactly.

The volatile solids loading rate of mixed sludge was 4.45 ± 0.35 kg VS / m³ $*$ d for 10 days HRT operation, 3.37 ± 0.25 kg VS / m³ $*$ d for 12 days HRT operation, 2.74 \pm 0.08 kg VS / m³ \star d for 15 days HRT operation and 2.03 \pm 0.09 kg VS / m³ \star d for 20 days HRT operation. When these values were plotted into Figure 6.7 together with the dry solids content of the mixed sludge, it was observed that the volatile solids loading rates fitted the given lines with very small differences. The volatile solids loading rate was determined by Witzgal et al. (2003) as $2.40 - 2.72$ kgVS/m^{3*}d for Los Angeles Hyperion W.W.T.P and 2.08 kg VS $/m³$ * d Sacramento Regional W.W.T.P mixed sludge which were operated at 20 days HRT.

6.1.8 COD

The COD of the feed and digested primary, excess and mixed sludge was monitored during the reactor operation period.

6.1.8.1 Primary Sludge

The COD values of feed and digested primary sludge and the COD reductions (%) are given in (Figure 6.8).

The COD of the feed primary sludge was 26.47 ± 1.75 g COD/L with minimum and maximum values of 23.1 and 29.2 g COD/L for 10 days HRT operation, while it was 29.36 ± 2.16 g COD/L with minimum and maximum values of 26.3 and 32.6 g COD/L for 12 days HRT operation. The COD of digested sludge was 17.99 ± 1.40 g COD/L with minimum and maximum values of 15.6 and 21.6 g COD/L for 10 days HRT operation, while it was 19.00 ± 1.61 g COD/L with minimum and maximum values of 16.50 and 21.6 g COD/L for 12 days HRT operation. The COD values did not change significantly both for the feed and digested primary sludge with coefficients of variation as 6.8 and 7.8, 7.8 and 8.5 in 10 and 12 days HRT operation, respectively. The COD reduction was 31.97 % for 10 days and 35.28 % for 12 days HRT operation.

Figure 6.8 The COD of feed and digested **primary** sludge – COD reduction.

6.1.8.2 Excess Sludge

The COD values of feed and digested excess sludge and the COD reductions (%) are given in (Figure 6.9).

The COD of the feed excess sludge was nearly constant for all the HRT operation periods ranging between 22.17 – 23.28 g COD/L with a coefficient of variation of 5.0. The COD of the digested excess sludge decreased with the increase of HRT ranging between $11.69 - 13.68$ g COD/L with a coefficient of variation of 9.8. The maximum COD reduction of the excess sludge was obtained at 15 days HRT operation as 48.55 %. The COD reduction changed significantly which can be understood from the high coefficient of variation as 11.4.

Figure 6.9 The COD of feed and digested **excess** sludge – COD reduction.

6.1.8.3 Mixed Sludge

The COD values of feed and digested mixed sludge and the COD reductions (%) are given in (Figure 6.10).

The COD of the feed mixed sludge ranged between $22.39 - 25.10$ g COD/L with a coefficient of variation of 6.1. The COD of the digested mixed sludge decreased with the increase of HRT ranging between $11.95 - 15.19$ g COD/L with a coefficient of variation of 11.3 which indicates a significant variation. The COD reduction of the mixed sludge increased and changed significantly with a coefficient of variation of 13.0 up to 46 % with the increase of the HRT to 20 days. It was lower in the comparison with the COD reduction determined by De la Rubia et al. (2002) as 52.8 % for 27 days HRT.

Figure 6.10 The COD of feed and digested **mixed** sludge – COD reduction.

6.2 Gas Production

The gas produced during the operation of the reactors was stored and the volume was measured by the device shown in (Figure 3.2). The gas production was compared with the values given in the literature as $0.40 - 0.45$ m³ gas / kg VS _{fed} to the reactor by Protechnich (2002), or $0.75 - 0.95$ m³ gas / kg VS _{removed} by Speece (1996) and $0.75 - 1.12$ m³/kg VS removed by Metcalf & Eddy Inc. (1991). The content of the gas was determined by using KOH solution as used in BMP tests.

6.2.1 Primary Sludge

The gas production values of the primary sludge are given in (Figure 6.11) as $m³$ gas / VS _{fed} to the reactor and $m³$ gas / VS _{removed}.

The gas production of primary sludge reactor for 10 d HRT operation was 4.88 \pm 1.21 L, while it was 6.18 \pm 0.29 L for 12 days HRT operation. The gas production per volatile solids fed to the reactor and volatile solids removed from the reactor were determined as 0.17 ± 0.03 m³ gas / kg VS _{fed} and 0.53 ± 0.08 m³ gas / kg VS removed for 10 days HRT operation, and 0.29 ± 0.02 m³ gas/kg VS _{fed} and $0.69 \pm$ 0.06 $m³$ gas/ kg VS $_{\text{removed}}$ for 12 days HRT operation. The variation of gas production was significant for 10 days HRT operation with 14.1 and 16.3 coefficients of variation values, while it was not significant for 12 days HRT operation with 8.6 and 6.7 coefficients of variation values. The methane content of the gas was measured for 12 days retention time as 66.55 ± 2.18 %.

The produced gas for primary sludge was lower than the above mentioned typical ranges but most probably would be higher for 15 days HRT operation. The gas production of primary sludge was determined by Atilla et al. (2002) as 1.06 $m³$ gas/kg VS $_{\text{removed}}$ and by Üçüncü (1994) as 1.310 m^3 gas/kg VS $_{\text{removed}}$. These two values are higher than that of both the primary sludge of İzmir W.W.T.P and the typical ranges.

Figure 6.11 The variation of the gas production of **primary** sludge.

6.2.2 Excess Sludge

The gas and methane productions and the methane content of the excess sludge are given as m³ gas-CH₄ / VS _{fed} in (Figure 6.12 a) and as m³ gas-CH₄ / VS _{removed} in (Figure 6.12 b).

⁽b) m^3 gas-CH₄ / VS removed

It can be seen from (Figure 6.12) that the highest gas production was obtained at 15 days HRT operation as 0.79 ± 0.09 m³ gas/kg VS removed and 0.45 ± 0.04 m³ gas/kg VS _{fed} which are in the limit values given in the above mentioned literatures. The gas productions for 10 and 12 days HRT operation were lower than the typical ranges. The gas production values significantly changed with the increase of HRT with a coefficient of variation value of 23.1. The methane content was also maximum for 15 days HRT operation as 70.75 ± 1.27 % but did not change significantly as the coefficient of variation was 1.7. The gas production of the excess sludge was determined as 0.504 m^3 gas/kg VS removed by Atilla et al. (2002) and 0.609 m³ gas/kg VS _{removed} by Üçüncü et al. (1994). The gas production of ℓ zmir W.W.T.P. was higher than the quoted values which can be explained by the higher volatile solids content of İzmir W.W.T.P excess sludge.

6.2.3 Mixed Sludge

The gas and methane productions and the methane content of the mixed sludge are given as m³ gas-CH₄/kg VS _{fed} in (Figure 6.13 a) and as m³ gas-CH₄/kg VS _{removed} in (Figure 6.13 b). The mixed sludge gas production was similar to the excess sludge gas production.

It can be seen from (Figure 6.13) that the highest gas production was obtained at 15 days HRT operation as 0.74 ± 0.08 m³ gas /kg VS removed and 0.51 ± 0.06 m³ gas / VS _{fed} which were also in the limit values given in the above mentioned literatures. The gas productions for 10 and 12 days HRT operation were also lower than the typical ranges. The gas production values significantly changed with the increase of HRT with a coefficient of variation value of 19.7.

The gas production of the mixed sludge was determined as 0.52 ± 0.03 m^3 CH₄ / kg VS _{removed} by Cheunbarn et al. (2000), 0.698 m^3 gas / kg VS _{removed} by Atilla et al. (2002), 1.085 m^3 gas /kg VS removed by Üçüncü (1994), 0.936 m³ gas / kg VS removed for Los Angeles Hyperion W.W.T.P and 1.08 m^3 gas /kg VS removed for Sacramento Regional W.W.T.P by Witzgall et al. (2003). It can be said that the gas

production was at a high level for 15 days HRT operation in İzmir W.W.T.P mixed sludge in comparison to the other treatment plants' mixed sludges which were operated in 20 days HRT.

(b) m^3 gas-CH₄ / VS removed

The methane content of İzmir W.W.T.P mixed sludge gas was also maximum for 15 days HRT as 68.94 ± 0.99 % and did not change significantly with a coefficient of variation of 1.4. When it is compared to the methane contents determined by Gavala et al. (2003) as 61.6 %, De la Rubia et al. (2002) as 57.7 – 64.5 %, Üçüncü (1994) as $68.0 - 70.0$ %, Witzgall et al. (2003) for Los Angeles Hyperion W.W.T.P as 65 % and Sacramento Regional W.W.T.P as $59 - 61$ %, the methane content of İzmir W.W.T.P mixed sludge gas contains more methane than the quoted sludges except for Üçüncü (1994).

6.3 Supernatant Properties

During the operation of the reactors, the COD, T-N, T-P and $PO₄-P$ of the feed sludge supernatant were monitored. The supernatant of the feed sludge was easily sieved by using the belts of the İzmir W.W.T.P.'s belt-presses. The COD, T-P, PO4-P and alkalinity of the filtrate was analyzed. The results are given in Table 6.5. The phosphorus measurements' results are given and evaluated in the next Chapter.

Sludge supernatant		COD (mg/L)	$T-N$ (mg/L)	Alkalinity (mg CaCO ₃ /L)	
Primary	Feed	256 ± 61	24.72 ± 5.63		
	Digested	1885		1450	
Excess	Feed	62 ± 17	9.60 ± 1.30		
	Digested	1650		1753	
Mixed	Feed	128 ± 18	13.74 ± 1.92		
	Digested	1845		1845	

Table 6.5 The properties of **feed** and **digested** sludge supernatants

7. CHAPTER SEVEN PHOSPHORUS BALANCE DURING ANAEROBIC DIGESTION OF PHOSPHORUS RICH SLUDGE

The phosphorus contents of the excess and mixed sludge are taken into consideration during anaerobic digestion. According to the mechanism of the biological phosphorus removal, the phosphorus of the digested sludge should reduce both with the metabolic demand of the anaerobic bacteria and the release of the phosphorus in the cell structure.

The Total-P content of the feed and digested excess sludge (g P/L) are shown in (Figure 7.1 a). The Total-P content of the feed and digested excess sludge (% of DS) and the reduction of the phosphorus content $(\%)$ are shown in (Figure 7.1 b).

As it can be seen from (Figure 7.1), the phosphorus content of the feed excess sludge for 10 days HRT operation was lower than the phosphorus content of the feed excess sludge for the other HRT operations. In the period that the reactor was operated with 10 days HRT operation, the efficiency of the biological phosphorus removal system of the İzmir W.W.T.P. was low and the Total-P of the feed excess sludge was measured as 2.05 ± 0.45 g/L which was equal to 3.65 ± 0.71 % of DS. The maximum Total-P content of feed sludge was measured as 3.36 ± 0.30 g/L which corresponds to 6.04 ± 0.63 % of DS in the operation of the reactor with 20 days HRT. It was found that the maximum Total-P reductions 25.96 % in the operation of the reactor with 10 d HRT. There was a significant change of phosphorus content of both the feed and digested excess sludge and Total-P reductions which can be observed by the coefficients of variation as 23.5, 25.6 and 30.0, respectively.

Figure 7.1 (a) The phosphorus content of the feed **excess** sludge and digested sludge (g/L) (b) The phosphorus content of the feed **excess** sludge and digested sludge (% of DS) and reduction total phosphorus (%)

The Total-P content of the feed and digested mixed sludge (g P/L) are shown in (Figure 7.2 a). The Total-P content of the feed and digested excess sludge (% of DS) and the reduction of the phosphorus content $(\%)$ are shown in (Figure 7.2 b).

Figure 7.2 (a) The phosphorus content of the feed **mixed** sludge and digested sludge (g/L) (b) The phosphorus content of the feed **mixed** sludge and digested sludge (% of DS) and reduction total phosphorus (%)

As it can be seen from (Figure 7.2), the phosphorus content of the feed mixed sludge was in the range of $1.50 - 1.55$ g/L which corresponds to $2.5 - 2.6$ % of DS in the operation of the reactor with 10, 15 and 20 days HRT, but 2.46 g/L which is equal to 4.16 % of DS for 12 days HRT operation. The Total-P reduction of the mixed sludge was maximum 25.41 % which was very similar to the phosphorus reduction of excess sludge.

It was stated by Carliell-Marquet et al. (2001) that $20 - 50$ % of the phosphorus is released during the anaerobic digestion of phosphorus rich sludge. In this study the Total-P content of both the excess and mixed sludges decreased approximately 25 % which was between the given values.

In Table 7.1 the Total-P and PO_4 -P content of the feed primary, excess and mixed sludge supernatants are given as mg/L. It can be seen from Table 7.1 that the phosphorus content of the feed primary sludge supernatant was higher than the phosphorus content of the excess and mixed sludge supernatant. This was because the primary sludge was taken from the wastewater before the phosphorus is removed by the enhanced biological phosphorus removal system.

HRT (days)	Sludge	Total-P (mg/L)	$PO4-P$ (mg/L)
10 12	Primary	7.00 ± 1.31	4.80 ± 0.96
	Excess	4.59 ± 1.63	3.33 ± 1.05
	Mixed	5.35 ± 1.17	3.79 ± 0.80
	Primary	7.41 ± 0.74	5.19 ± 0.52
	Excess	3.70 ± 0.32	2.67 ± 0.32
	Mixed	4.76 ± 0.29	3.39 ± 0.20
	Primary		
15	Excess	5.38 ± 0.57	3.76 ± 0.40
	Mixed	5.88 ± 0.53	4.12 ± 0.37
20	Primary		
	Excess	4.53 ± 0.92	3.08 ± 0.63
	Mixed	3.97 ± 0.30	3.97 ± 0.30

Table7.1 The Total-P and PO4-P content of **feed** primary, excess and mixed sludge supernatants as mg/L.

The Total-P of the digested excess and mixed sludge supernatants were measured in the operation of the reactors with 15 and 20 days HRT en the results are given in (Table 7.2).

Table 7.2 The Total-P content of **digested** excess and mixed sludge supernatant for 15 and 20 d HRT as mg/L

HRT (days)	Sludge	Total-P (mg/L)		
15	Excess	407.20 ± 32.40		
	Mixed	443.80 ± 23.00		
20	Excess	362.20 ± 53.00		
	Mixed	384.20 ± 38.40		

The total magnesium content for the feed and digested sludge supernatant during the operation of the reactors at 15 and 20 days HRT were measured and the results are given in (Table 7.3).

Table 7.3 The Total Mg content of **feed and digested** excess and mixed sludge supernatant for 15 and 20 d HRT as mg/L

HRT (days)		Sludge	Total Mg			
	Excess	Feed	128.30 ± 10.30			
15		Digested	93.60 ± 7.20			
	Mixed	Feed	154.30 ± 9.30			
		108.40 ± 10.60 Digested				
	Excess	142.70 ± 12.80 Feed				
20		110.50 ± 9.30 Digested				
	Mixed	Feed	113.50 ± 8.20			
		Digested	95.20 ± 8.30			

It was stated by Suschka et al (2000) that a part of the phosphorus is chemically fixed as struvite and according to the molar rates the difference of 2.0 mg Mg/L can mean a removal of about 8.0 mg PO₄/L. This case was also proved by Doyle et al. (2002) that magnesium released and taken during the polyphosphate hydrolysis and formation was 0.25 and 0.26 g magnesium per gram of phosphorus. If this ratio is taken into consideration, the decrease of magnesium content for excess and mixed sludge, decrease of phosphate release by the formation of struvite was calculated and given in (Table 7.4). The amount calculated as the phosphorus forming struvite should be added to the phosphorus content of the digested sludge supernatant to obtain the real released phosphorus value in anaerobic digestion of phosphorus rich sludge.

HRT (days)	Sludge	Magnesium reduction (mg/L)	Total-P supernatant of digested sludge (mg/L)	P fixed as struvite (mg/L)	Total-P released (mg/L)
15	Excess	34.70	407.20	138.80	546.00
	Mixed	45.90	443.80	183.60	627.40
20	Excess	32.20	362.20	128.80	491.00
	Mixed	18.30	384.20	73.20	457.40

Table 7.4 The real total amount of Total-P released

8. CHAPTER EIGHT EVALUATION OF DATA WITH STATISTICAL ANALYSIS

The aim of the statistical analysis was to determine whether there was a significant difference between the operation of the rectors at different hydraulic retention times and the results of primary, excess and mixed sludge. The parameters that were investigated are; DS and VS content $(\%)$, COD and Total-P (g/L) of feed and digested sludge, DS and VS reduction (%), total gas production $(m^3$ gas/kgVS_{removed} and m^3 gas/kgVS_{fed}), methane content and Total-P reduction (%). For this purpose SPSS 13.0 for Windows software was used. The groups of data that were used in this program were as follows:

- For HRT:
	- \circ 1 = 10 days HRT operation
	- \circ 2 = 12 days HRT operation
	- \circ 3 = 15 days HRT operation
	- \circ 4 = 20 days HRT operation
- For sludge type:
	- \circ 1 = primary sludge
	- \circ 2 = excess sludge
	- \circ 3 = mixed sludge

Kruskal-Wallis H test was conducted to determine whether there is a significant difference between all groups. Typically, a significance level value, which show whether there is a difference between the groups or not, less than 0.05 is considered significant.

To determine the differences between each group, the groups were analyzed two by two with Mann-Whitney U test. According to the 2-tailed P value, it can be said whether there is a significant difference between the groups, or not. If 2-tailed P value is less than 0.05, it can be said that the analyzed groups are different from each other. If it is higher, the groups are similar.

8.1 The Results Obtained for Different Sludge Types

8.1.1 Primary Sludge

The primary sludge reactors were only operated at 10 and 12 days HRT. Therefore, Kruskal-Wallis H test, which is used for the comparison of three or more different groups, was not applied to the primary sludge data group. According to the 2-tailed P values obtained from Mann-Whitney U test, it can be said that only the VS content $(\%)$ of the feed sludge (2-tailed P 0.689>0.05) and the DS reduction $(\%)$ (2-tailed P 0.626>0.05) parameters were similar for 10 days and 12 days HRT operation. It can be concluded that although the reactors were fed with sludges having similar VS contents (%), there was a significant increase in the VS reduction (%) and gas production with the increase of HRT from 10 to 12 days.

8.1.2 Excess Sludge

For excess sludge reactors operated at 10, 12, 15 and 20 days HRT, the significance levels obtained from Kruskal-Wallis H test for the DS and VS contents $(\%)$ and COD (g/L) of the feed sludge were higher than 0.05, which indicates that the feed sludge properties did not change significantly during the whole experimental period except for the Total-P content. The digested sludge properties, total gas productions and VS reductions (%) were significantly different for each HRT operation group as the significant levels were obtained as 0. As the significance level for the DS reduction and Total-P reduction (%) were higher than 0.05, there was a significant difference between the HRT operation groups. The methane content did not change significantly during the operation of the reactors with excess sludge as the significance level was higher than 0.05.

When the groups are analyzed by Mann-Whitney U test;

- It can be concluded that the feed excess sludge properties including the DS and VS contents $\frac{6}{90}$ and COD $\left(\frac{g}{L}\right)$ except for the Total-P content (%), did not change significantly as the 2-tailed P values for each comparison were higher than 0.05.
- In contrast, the digested sludge properties differed significantly between all HRT operation groups except for the comparison of 10 days HRT operation with 12 days HRT operation (2-tailed $P > 0.05$).
- The 2 tailed P values were higher than 0.05 for the DS reductions (%) of all the groups compared, which indicates that the increase of HRT did not significantly effect the DS reductions.
- The VS reduction $\frac{9}{6}$ differed significantly (2-tailed P<0.05) except for the comparison between 10 days HRT operation and 12 days HRT operation (2-tailed P=0.287>0.05).
- It can be concluded that the total gas production significantly differed and increased with the increase of HRT. However, it was similar for 15 days HRT operation and 20 days HRT operation (2-tailed P=0.113>0.05).
- The methane content did not change significantly as the 2-tailed P values were always higher than 0.05.
- The Total-P reduction $(\%)$ did not change significantly as the 2-tailed P values were always higher than 0.05 which proves that the release of phosphorus is completed rapidly and no increase in the released phosphorus can be observed with the increase of HRT.

8.1.3 Mixed Sludge

For mixed sludge reactors operated at 10, 12, 15 and 20 days HRT, the significance levels obtained from Kruskal-Wallis H test for the parameters of both the feed sludge and the digested sludge were 0, which indicates that the feed sludge properties changed significantly during the whole experimental period which can be due to the properties of the primary sludge. DS reduction (%), VS reduction (%) and gas productions also differed significantly. The only similar parameters were the methane contents (%) and the Total-P reductions (%) with significance levels of 0.690 and 0.593 which are higher than 0.05.

When the groups are analyzed by Mann-Whitney U test;

- The DS content (%) of the feed mixed sludge differed significantly at 10 days HRT operation from the other HRT's with 2-tailed P values of 0. The DS contents (%) of the other groups were similar. The VS content (%) of the feed mixed sludge differed significantly at 12 days HRT operation from the other HRT's with 2-tailed P values lower than 0.05. The VS content (%) of the other groups were similar with 2 tailed P values higher than 0.05. There was a significant difference between the COD (g/L) of the feed mixed sludges except for the comparison of 15 days HRT operation with 10 days HRT operation $(2$ -tailed P=0.107>0.05) and 20 days HRT operation (2-tailed P=0.393>0.05).
- The digested sludge properties differed significantly between all HRT operation groups except for the comparison of 10 days HRT operation with 12 days HRT operation and 15 days HRT operation with 20 days HRT operation (2-tailed P>0.05).
- The 2 tailed P values were higher than 0.05 for the DS reductions (%) of the groups compared except for the comparison of 12 days HRT operation with 15 days HRT operation and 20 days HRT operation.
- The VS reduction $\frac{9}{6}$ differed significantly (2-tailed P<0.05) except for the comparison of 10 days HRT operation with 12 days HRT operation $(2$ -tailed P=0.202>0.05) and 15 days HRT operation with 20 days HRT operation (2-tailed $P=0.272>0.05$)
- It can be concluded that the total gas production significantly differed and increased with the increase of HRT. However, it was similar for 15 days HRT operation and 20 days HRT operation (2-tailed P=0.359>0.05).
- The methane content did not change significantly as the 2-tailed P values were always higher than 0.05.
- The Total-P reduction (%) did not change significantly as the 2-tailed P values were higher than 0.05.

9. CHAPTER NINE SCALE-UP OF ANAEROBİC DIGESTION IN İZMİR W.W.T.P

9.1 Solids Balance

In Izmir W.W.T.P the sludge quantity is estimated to be $14.000 \text{ m}^3/\text{d}$ having 1.46 % DS for mixed sludge and the new dewatering plant was designed and constructed to dewater this amount of sludge to more than 20 % DS in the first operation mode which was explained in Chapter II. After the construction of the anaerobic digestion system the dewatering plant will be used to thicken the sludge up to 6 % to feed the digesters. The solids balance was calculated by using these conditions and given in (Figure 8.1).

Figure 8.1 The solids balance of İzmir W.W.T.P. mixed sludge.

- **Phosphorus in liquid phase**
- **Phosphorus in sludge phase**
- * Calculated values

Figure 8.2 The phosphorus balance of İzmir W.W.T.P. mixed sludge for 15 d HRT operation period.

The phosphorus load to the influent is calculated as 20 % of the influent phosphorus load. It was reported by Janssen et al. (2002) that in Germany, the phosphorus recycle in the supernatant of digesters is approximately 15 % of the influent phosphorus load. It was determined for Goor treatment plant sludge that 3% of influent phosphorus load is recycled with the anaerobic digester's supernatant.

9.3 Design of Anaerobic Digestion Plant

9.3.1 Determination of digester volume

The volume of the reactors were calculated according to the organic loading rates given in Figure 6.6 as $4.45 \text{ kg } VS/m^3$ day for 10 d HRT operation, 3.37 kg VS/m³ day for 12 d HRT operation, 2.74 kg VS/m³ day for 15 d HRT operation and 2.03 kg VS/m^3*d for 20 d HRT operation. The height of the reactors could not be selected more than 30 m because of Çiğli Air Base and most probably the reactors would be half buried during the construction. According to these values; the total volume, unit dimensions, the number of units and the volume of one reactor in anaerobic digestion system were calculated and given in (Table 8.1).

Dimension	Unit	HRT(d)				
		10	12	15	20	
V_{total}	m ³	34.067	40.880	51.100	68.133	
Height (H)	m	30	30	30	30	
Diameter (D)	m	25	24	26	25	
$\mathbf{V}_{\text{reactor}}$	m ³	11.400	10.300	12.775	11.400	
Number of units						

Table 8.1 The dimensions of anaerobic digestion reactors for different HRT's.

9.3.2 Gas production

The total gas and methane production of the anaerobic digestion system was calculated according to the gas production rates given in Figure 6.12 as $m³$ gas per kg VS removed. The gas and energy productions of anaerobic digestion reactors for different HRT's are given in (Table 8.2). The net heating value of methane is 35,800 kJ/m³ CH₄ and the low heating value of biogas is given as 22,400 kJ/m³ gas Protechnich (2002).

Parameter	Unit	HRT(d)				
		10	12	15	20	
VS reduced	kg VS/d	50.300	55.000	63.600	63.600	
Gas production kg VS / $m^3 * d$ rate		0,51	0,63	0,74	0,73	
Total gas production	m^3/d	25.652	34.635	47.028	46.449	
Methane content	$\frac{0}{0}$	68,50	68,52	68,94	68,85	
Total methane production	m^3/d	17.571	23.732	32.421	31.980	
Total energy	kJ/d	$0.58 * 10^9$	$0.78 * 10^9$	$1.05 * 10^9$	$1.04 * 10^9$	
content of the	kWh/m^3	159,610	215,500	292,617	289,017	
sludge	ton fuel-oil/d	14.5	19.5	26.5	26.0	

Table 8.2 The gas and energy productions of anaerobic digestion reactors for different HRT's.

9.3.3 Heating of the reactors

The total wall floor and frame area, the heat losses and the heat requirement of the anaerobic digestion system are given in (Table 8.3). During the calculation of the heat losses the heat transfer coefficients were selected as 0.68 W/m^2 . ^oC for concrete floor, 0.60 W/m². °C for concrete walls and 1.12 W/m². °C for fixed concrete frame. The minimum temperatures were used to obtain extreme conditions for the anaerobic digesters as; 10 $\rm{^{\circ}C}$ for air temperature, 10 $\rm{^{\circ}C}$ for soil temperature, feed sludge temperature 15 $^{\circ}$ C, digester temperature 35 $^{\circ}$ C. Heat requirement of the sludge was calculated by using 3.406,7 t/d sludge feeding and specific heat value of the sludge as 4.200 J/kg.^oC.

9.3.4 Gas Storage Tanks

The gas storage tanks can hold methane gas in $1/5 - 1/10$ ratios. The gas storage tank capacities and dimensions for different HRT's are given as follows:

- For 10 d HRT gas storage tank capacity = 2.600 m^3 (D=15,0 m, H=15 m)
- For 12 d HRT gas storage tank capacity = 3.500 m^3 (D=17.3 m, H=15 m)
- For 15 d HRT gas storage tank capacity = 4.700 m^3 (D=20,0 m, H=15 m)
- For 20 d HRT gas storage tank capacity = 4.700 m^3 (D=20,0 m, H=15 m)

Parameter	Unit		HRT (d)		
		10	12	15	20
Heat loss of one reactor (walls)	J/d	$2.03 * 10^9$	$1.95 * 10^9$	$2.12 * 10^9$	$2.03 * 10^9$
Heat loss of one reactor (floor)	J/d	$0.78 * 10^9$	$0.72 * 10^9$	$0.84 * 10^9$	$0.78 * 10^9$
Heat loss of one reactor (frame)	J/d	$1.37 * 10^9$	$1.27 * 10^9$	$1.47 * 10^{9}$	$1.37 * 10^9$
Total heat loss of one reactor	J/d	$4.19 * 10^{9}$	$3.94 * 10^{9}$	$4.43 * 10^{9}$	$4.19 * 10^{9}$
Number of Units		3	$\overline{4}$	$\overline{4}$	6
Total heat loss of the system	J/d	$12.6 * 10^9$	$15.8 * 10^9$	$17.7 * 10^9$	$25.1 * 10^9$
Heat requirement for sludge heating	J/d	$286 * 10^9$			
Total heat requirement for digester heating (heat exchanger capacity)	J/d	$298.6 * 10^9$	$301.8 * 10^{9}$	$303.7 * 10^{9}$	$311.0 * 10^{9}$

Table 8.3 The heat losses and heat requirements of anaerobic digestion reactors for different HRT's.

9.3.5 Electricity production

The electricity production will be made by using gas engines which have 38,7 % electricity production efficiency and 46,7 % thermal energy production efficiency according to the report prepared by Protechnich, 2002 for İzmir W.W.T.P. It was stated in "Cogeneration with gas engines" report by Anonymus, 2007 that "the total efficiency of gas engine cogeneration plants attains up to over 90 $\%$ (30 – 40 $\%$) electrical and 50 % thermal)". Fischer et al. 2002 also stated electrical efficiencies over 34 % for gas engines. The electricity production, heat production and number and capacity of the gas engines are given in (Table 8.4). It can be seen from the table the heat production of the gas engines will be more than the heat requirement to heat the reactors which consists of heat losses and heat required for sludge heating for 12, 15 and 20 days HRT operation. However, when the reactors are operated for 10 days

HRT operation extra heat should be supplied. The electricity consumption of İzmir W.W.T. P is approximately 100.000 kWh/day which can also be supplied by anaerobic digestion in the operation of the anaerobic digesters for 15 or 20 days HRT operation.

Parameter	Unit				
		10	12	15	20
Total energy content of the sludge	kJ/d	$0.58 * 10^9$	$0.78 * 10^9$	$1.05 * 10^9$	$1.04 * 10^9$
Total electricity production $(38.7 %$ efficiency)	kWh/d	62,350	83,850	112,875	111,800
Total gas engine capacity	kW	2,600	3,500	4,700	4,660
Number of gas engines		$\overline{2}$	3	$\overline{4}$	$\overline{4}$
One gas engine capacity	kW	1,300	1,170	1,170	1,170
Total heat production $(46.7\%$ efficiency)	kWh/d	75,238	101,183	136,208	134,911
Total heat requirement to heat digesters	kWh/d	82,944	83,833	84,361	86,388

Table 8.4 The electricity and heat production of anaerobic digestion reactors for different HRT's.

10. CHAPTER TEN CONCLUSIONS

In this study, the primary, excess and mixes sludge of İzmir W.W.T.P., which is an advanced biological treatment plant including nitrogen and phosphorus removal, was tried to be anaerobically digested and various parameters were monitored.

In the first stage of the thesis, the characteristics of the feed primary excess and mixed sludge were determined as follows:

The dry solids content of primary sludge was found as 2.24 %, excess sludge was found as 1.27 and mixed sludge was found as 1.47 %. The value determined for the primary sludge was lower than the typical ranges, which can be due to prevent clogging of the pipelines of the primary settling tanks. The value determined for the excess sludge was higher than the plant design value. The value determined for the mixed sludge fits the design value of the treatment plant. The volatile solids content of primary sludge was found as 66.85 %, excess sludge was found as 74.45 and mixed sludge was found as 72.61. All the volatile solids content values are in the typical ranges and similar to the other treatment plants quoted in the thesis.

The heavy metal contents of İzmir W.W.T.P sludges were found more than Ankara W.W.T.P. mixed sludge. Nearly all of the heavy metal values of Athens W.W.T.P primary sludge are higher than İzmir W.W.T.P. When compared to Beijing W.W.T.P. mixed sludge heavy metal contents, while As, T-Cr, Pb were lower, Cd, Cu, Ni, Zn and Hg were higher than other treatment plants. On the other hand all of the values were under the values given in S.P.C.R and EU Directive 86/278/EEC except for arsenic value of the mixed sludge.

In the second of the thesis, biochemical methane potential (BMP) tests were conducted and the methane yields of the sludges were determined.

During the BMP test period, it was determined that 0.063 g COD for primary sludge, 0.067 g COD for excess sludge and 0.070 g COD of mixed sludge, can be anaerobically converted to methane per g VS added per day. It can be concluded from the BMP tests that;

- for primary sludge, it would be better to feed at a VS of 1.7 g instead of feeding 1.8 g up to 2.8 g and not to feed more than 2.8 g because the maximum methane production rate was obtained for 2.8 g VS added.
- for excess sludge, the gas and methane production of the excess sludge was more than two times higher than the gas and methane production of the primary sludge for 1 g VS added. But the increase of the total gas and methane production was not as much as the primary sludge.
- for mixed sludge, the maximum total gas and methane production was observed for 1.0 g VS added.
- the gas production of primary sludge is 15 % lower than the excess and mixed sludges. This is due to the low gas production rates of primary sludge during the rainy period. In contrast, after the rainy period, the gas production of primary sludge is 12 % higher than mixed sludge and 30 % higher than the excess sludge.

The methane yield of primary sludge was calculated as 382.90 ml CH₄ / g VS added and the methane content was found as 64.00 %. The methane yield of excess sludge was calculated as 528.55 ml CH₄ / g VS added and the methane content was found as 66.42 % The methane yield of mixed sludge was calculated as 496.16 ml $CH₄$ / g VS added and the methane content was found as 65.33 %. It can be concluded that the low methane yield of the primary sludge when compared to the excess and mixed sludges may be due to the inconvenient $C : N : P$ ratio of the primary sludge

In the third stage of the thesis, the reactors were taken into operation and were operated at 10, 12, 15 and 20 days retention times. During the operation period, it can be concluded that;

- the pH in the reactor decreased from 7.5 slightly to a nearly neutral pH for all the reactors which may be due to the methanogenic activity sensitivity compared to the acid production microorganisms.
- the volatile solids reduction and the gas and methane formation of the system were not affected by high salt concentrations
- the capillary suction time values measured for the excess and mixed sludge were higher than the primary sludge. After the digestion process, 30 – 35 % reduction of the CST was observed for both excess and mixed sludges which show the enhanced dewatering properties of digested sludge.
- the oxidation reduction potentials were in the optimum range which indicates that the anaerobic conditions was not broken down for the whole operation period and N_2 and CO_2 gas application to the reactors at start-up was successful

It can be concluded that the primary sludge was not stabilized for 10 and 12 days HRT operation while the VS reductions were fewer than 38 %. For excess sludge the maximum DS reduction was obtained for 15 d HRT operation as 25.95 % while it was not so different for the other HRT's. For mixed sludge, the maximum DS reduction was obtained for 20 d HRT operation as 28.21%. The VS reduction increased with the increase of HRT for both the excess and mixed sludges. The volatile solids reductions for 10 days HRT operation was not higher than the value given as 38 % by EPA, but at the other HRT operations the volatile solids reductions were higher than the value given as 38 % by EPA.

The COD reductions for primary sludge were 32.0 % for 10 days HRT operation and 35.3 % for 12 days operation. The COD of the digested excess sludge decreases with the increase of HRT ranging between $11.69 - 13.68$ g/L. The maximum COD reduction of the excess sludge was obtained at 15 days HRT operation as 48.55 %. The COD of the digested mixed sludge decreases with the increase of HRT ranging between 11.95 – 15.19 g/L. The COD reduction of the mixed sludge increased to 46 % with the increase of the HRT to 20 days.

The gas production of primary sludge was determined as $0.17 \text{ m}^3/\text{kg VS}_{\text{fed}}$ and 0.53 m³/ kg VS_{removed} for 10 days, and 0.29 m³/kg VS_{fed} and 0.69 m³/ kg VS_{removed} for 12 days HRT operation. The produced gas for primary sludge was lower than the typical ranges but most probably would be higher for 15 days HRT operation. For the excess sludge, the highest gas production was obtained at 15 days HRT as 0.79 m^3 gas /kg $VS_{\rm removed}$ and 0.45 m³ gas / $VS_{\rm fed}$ which are between the limit values. The gas production for 10 and 12 days HRT operation was lower than the typical ranges. The methane content was also maximum for 15 days HRT operation as 70.75 %. For mixed sludge the highest gas production was obtained at 15 days HRT operation as 0.74 m³ gas /kg $VS_{\rm removed}$ and 0.41 m³ gas / $VS_{\rm fed}$ which were also between the limit values. The methane content of İzmir W.W.T.P mixed sludge gas was also maximum for 15 days HRT operation as 68.94 %.

The reduction of the phosphorus content of the excess sludge was maximum 25.96 % which was observed for 10 d HRT. For mixed sludge the reduction of the phosphorus content of the excess sludge maximum 25.41 % which was observed for 20 d HRT. The Total-P content of both the excess and mixed sludges decreased approximately 25 % which was not the real phosphorus release. The decrease of magnesium content of the excess and mixed sludge was 33.5 mg/L which causes struvite formation and decreases the phosphorus release approximately 134 mg/L. When the real released phosphorus is calculated, it can be seen that it can reach up to 45 % of the Total-P load entering the digesters.

It can be concluded from the phosphorus balance that the phosphorus load added to the influent was 20 % of the influent phosphorus load.

When the volatile solids and COD reductions, the gas production and the methane content of the gas are evaluated, it can be concluded that the optimum hydraulic retention time was **15 days** for İzmir W.W.T.P primary, excess and mixed sludges.

- The designed digesters for 15 days HRT:
	- 4 reactors
	- 26 m diameter
	- 30 m height
	- -12.775 m^3 volume/reactor
	- -51.100 m^3 total reactor volume
	- $-$ 47.028 m³ gas production with 68.94 % methane content
	- 112.875 kWh/d electricity production which is more than the consumption of the whole treatment plant as 100.000 kWh/d.
	- the heat production of the gas engines will be more than the heat requirement to heat the reactors which consists of heat losses and heat required for sludge heating for 12, 15 and 20 days HRT operation. However, when the reactors are operated for 10 days HRT operation extra heat should be supplied

REFERENCES

- Alp, K, Akça, L. & Gömeç C.Y. (2007). Drying characteristics of sewage sludge. *Proceedings of Facing Sludge Diversities: Challenges, Risks and Opportunities, Antalya, Turkey, 28 – 30 March 2007, 825 – 829.*
- Arcak, S., Karaca, A., Erdoğan, E., & Türkmen, C. (2000). A study on the potential agricultural use of sewage sludge of Ankara Wastewater Treatment Plant. *Proceedings of International Symposium on Desertification (ISD),* Konya, Turkey, June 13-17.
- Atilla, B., Gomec, C.Y., Altinbas, M. & Ozturk, I. (2002). Anaerobic digestion of municipal sludges wit high silt content using granular seed. *Proceedings of 5th Specialized Conference on Small Water and Wastewater Treatment Systems,* İstanbul, Turkey, September 24-26.
- Banister, S.S., & Pretorius, W.A. (1998). Optimisation of primary sludge acidogenic fermentation for biological nutrient removal. *Water SA, 24* (1), 35-41.
- Berthouex, P.C., & Brown, L.C. (Eds) (1994) *Statistics for environmental engineers.* Florida,CRC Press Inc..
- Bowker, R.P.G., Stensel, H.D., Hartmann, G.L., & Smith, J.M. (1987) *Design manual, phosphorus removal.* Cincinnati, U.S.A.: Environmental Protection Agency.
- Brdanovic, D. (1998) *Modeling biological phosphorus removal in activated sludge systems.* Rotterdam, Netherlands: A.A.Balkema.
- Carliell, C.M., & Wheatley, A.D. (1997). Metal and phosphate speciation during anaerobic digestion of phosphorus rich sludge. *Water Science and Technology, 36* (6-7), 191-200.
- Carliell-Marquet, C.M., Wheatley, A.D., & Churchley, J. (2001). Anaerobic digestion of phosphorus rich sludge. *Proceedings of the 2nd International Conference on the Recovery of Phosphorus from Sewage and Animal Wastes.* The Netherlands, March 12 -13.
- Cheunbarn, T., Pagilla, K.R. (2000) Anaerobic thermophilic/mesophilic dual-stage sludge treatment. *Journal of Environmental Engineering, 126* (9), 796-801.
- Cho, J.K., Park, S.C. & Chang, H. N. (1995). Biochemical methane potential and solid state anaerobic digestion of Korean food wastes. *Bioresource Technology. 52,* 245-253.
- *Cogeneration with gas engines.* (n.d.) retrieved June 20, 2007 from http://www.clarke-energy.co.uk/clarke_energy/downloads/chp_brochure.pdf
- Çınar, Ö. (1996). *Thesis of Master of Science: Evaluation of IAWQ activated sludge model no.2 using four full-scale wastewater treatment plants.* U.S.A : Clemson University.
- Dai, J., Xu, M., Chen, J., Yang, X. & Ke,Z. (2007). PCDD/F, PAH and heavy metals in sewage sludge from six wastewater treatment plants in Beijing, China. *Chemosphere.66,* 353-361.
- De la Rubia, M.A., Perez, M., Romero, L.I., & Sales, D. (2002). Anaerobic mesophilic and thermophilic municipal sludge digestion. *Chem. Biochem. Eng. Q. 16* (3), 119-124.
- Doyle, J.D. & Parsons, S.A. (2002). Struvite formation, control end recovery. *Water Research..36*, 3925-3940.
- Eastman, J.A., & Fergusaon,J.F (1981). Solubilization of particulate organic carbon during the acid phase of anaerobic digestion. *Journal WPCF,* 53 (3), 352-366.
- Eckenfelder, W.W., Malina, Jr.J.F., & Patterson, J.W. (1992) *Design of anaerobic processes for the treatment of industrial and municipal wastes.* Pennsylvania, U.S.A.: Technomic Publishing Company Inc.
- Ergüder, T.H., Güven, E. & Demirer G.N. (2000). Anaerobic treatment of olive mill wastes in batch reactors. *Process Biochemistry,* 36 (3), 243-248.
- Ergün, M. (1995) *Bilimsel Araştırmalarda Bilgisayarla İstatistik Uygulamaları, SPSS for Windows.* Ankara. Ocak Yayınları.
- Ersöz, E. (2002). *Final Project: İzmir Çiğli Kentsel Atıksu Arıtma Tesisi örneğinde anaerobik çürütücü tasarım*. İzmir, Dokuz Eylül University.
- Fischer, T. & Kreig, A. (December 2002). *Planning and costruction of biogas plants for solid waste digestion in agriculture.* 20. June 2007, http://www.kriegfischer.de/texte/BioCycle_12_2002.pdf
- Gavala, H.N., Yenal, U.,Skiadas, I.V.,Westermann, P., Ahring, B.K. (2003). Mesophilic and thermophilic anaerobic digestion of primary and secondary sludge. Effect of pre-treatment at elevated temperatures. *Water Research, 37,* 4561-4572
- Ghosh, S., Henry, M.P., Sajjad, A., Mesinger, M.C., & Arora, J.L. (2000). Pilot-scale gasification of municipal solid waste by high-rate and two-phase anaerobic digestion (TPAD). *Science and Technology*, 41(3), 101-110.
- Greenberg, A.E., Clesceri, L. S., & Eaton, A.D. (EdS).(1992). *Standard methods for the examination of water and wastewater.* $(18th$ ed.). Washington D.C., U.S.A.: APHA, AWWA, WEF.
- Greenberg, A.E., Clesceri, L. S., & Eaton, A.D. (EdS).(2005). *Standard methods for the examination of water and wastewater.* (21st ed.). Washington D.C.,U.S.A.: APHA, AWWA, WEF.
- Haskök, S.H. (2005). *Thesis of master of science: Zeytin karasuyunun arıtılmasında kullanılacak paket arıtma sistemi için tasarım parametrelerinin araştırılması*. İzmir, Ege University.
- Janssen, P.M.J., Meinema, K., & Van der Roest, H.F. (2002) *Biological phosphorus removal, manual for design and operation.* Cornwall, UK: TJ International Ltd.
- Jardin, N. & Pöpel, H.J. (1994) Phosphate release from enhanced biological P-removal during digestion. *Water Science and Technology.* 30 (6), 281-292.
- Karim, K., Klasson, K.T., Hoffmann, R., Drescher, S.R.,Depaoli, D.W., & Al-Dahhan, M.H. (2005). Anaerobic digestion of animal waste: Effect of mixing. *Bioresource Technology, 96,* 1607-1612.
- Kocasoy, G. (1996). *Atıksu Arıtma Çamuru ve Katı Atık ve Kompost Örneklerinin Analiz Yöntemleri* . (2nd ed.), İstanbul, Boğaziçi University.
- Krishna, R.P., Craney, K.C., & Wendell, H.K. (1997). Causes and effects of foaming in anaerobic sludge digesters. *Water Science and Technology.* 36 (6-7), 463-470.
- Lanting, J. (2003). Optimization of biological activity for anaerobic sludge digestion. *Proceedings of WEFTEC 2003, U.S.A., Water Environment Federation.*
- Lay, J.J., Li, Y.Y., & Nokie,T. (1997). Influences of pH and moisture content on the methane production in high-solids sludge digestion. *Water Research,* 31 (6), 1518-1524
- Lin, J.G., Chang, C.N., & Chang, S.C. (1997). Enhancement of anaerobic digestion of waste activated sludge by alkaline solubilization. *Bioresource Technology*, 62 (3), 85-90
- Manios, T. (2004). The composting potential of different organic solid wastes: experience from the island of Crete. *Environmental International.* 29 (8) 1079-1089
- Metcalf & Eddy Inc. (1991) *Wastewater engineering treatment, disposal, reuse)*. (3rd ed.) Singapore: McGraw-Hill International Editions.
- Meyer, D. (2003). Manure technologies for today and tomorrow. *Proceedings of the 6th Western Dairy Management Conference.* U.S.A., March 12-14.
- Oles, J., Dichtl, N., & Niehoff, H. (1997) Full stage experience of two stage thermophilic sludge digestion. *Water Science and Technology.* 36 (6-7), 449-456.
- Özalp, G., Gomec, C.Y., Öztürk, S., Gönüldinç, S. & Altınbaş, M. (2002) Effect of high salinity on anaerobic treatment of low strength effluents. *Proceedings of 5th Specialized Conference on Small Water and Wastewater Treatment Systems,* İstanbul, Turkey, September 24-26. 645-650
- Öztürk, N. (1998) *Thesis of Master of Science: Biogas production by anaerobic cofermentation of organic wastes.* İzmir: Dokuz Eylül University
- Pahl, O., Firth, A., MacLeod, I., & Baird, J. (2008). Anaerobic co-digestion of mechanically treated municipal waste with primary sewage sludge $- A$ feasibility study. *Bioresource Technology,* 99*,* 3354-3364.
- Park, K.Y., Maeng, S.K., Song, K.G. & Ahn, K.H. (2007). Ozone treatment of wastewater sludge for reduction and stabilization. *Proceedings of Facing Sludge Diversities: Challenges, Risks and Opportunities, Antalya, Turkey, 28 – 30 March 200, 793 – 798.*
- Puchajda, B., & Oleszkiewicz, J. (2003). Single and two-stage anaerobic digestion: hydrolysis, acidification and pathogen inactivation. *Proceedings of WEFTEC 2003, U.S.A., Water Environment Federation.*
- Protechnich Engineering Gmbh. (2002). İzmir Wastewater Treatment Plant, Report on Possibilities for the Sludge Treatment. *A report submitted the İZSU General Directorate.*
- Rajeshwari, K.V., Balakrishnan, M., Kansal, A., Lata, K., & Kishore, V.V.N. (2000). State-of-the art of anaerobic digestion technology for industrial wastewater treatment. *Renewable & Sustainable Energy Reviews.* 4, 135-156
- Sanver, H.S. (2000) *Thesis of Master of Science: Anaerobic digestion of a chemical synthesis based pharmaceutical wastewater.* İstanbul: Boğaziçi University.
- Sosnowski, P., Wieczorek, A., & Ledakowicz, S. (2003). Anaerobic co-digestion of sewage sludge and organic fraction of municipal solid wastes. *Advances in Environmental Research.* 7, 609-616.
- Suschka, J. & Poplawski, S. (2000). Phosphorus recovery laboratory scale experiments. *Proceedings of Polish – Sweedish Seminar May 2000* 97-103*.*
- Speece, R.E. (1996) *Anaerobic Biotechnology for industrial wastewaters.* Tennessee, U.S.A.: Archae Press.
- Üçüncü, O. (1994). *Thesis of Doctor of Philosophy: İleri biyolojik arıtma tesisi çamurlarının mezofilik anaerobik çürütülmesi üzerine bir araştırma.* Trabzon: Karadeniz Technical University.
- Vanrolleghem, P.A. (1995). Sensors for anaerobic digestion: an overview. *Int. Workshop on Monitoring and Control of Anaerobic Digestion Process.* France, December 6-7.
- Wang, Q., Kuninobu, M., Ogawa, H.I., & Kato, Y. (1999). Degradation of volatile fatty acids in highly efficient anaerobic digestion. *Biomass and Bioenergy, 16,* 407-416.
- Witzgall, R.A., Schafer, P.L., Haug, R.T., Mundine, J., Kido, W.H., Mulkerin, M. et al. (2003). Performance evaluation and O&M comparison following five years of operation of three anaerobic digester projects. *Proceedings of WEFTEC 2003, U.S.A., Water Environment Federation.*
- Zickefoose, C., & Hayes, R.B.J. (1976) *Anaerobic sludge digestion, operations manual.* Washington D.C., U.S.A.: Environmental Protection Agency.
- Zorpas, A.A., Arapoglou, D., Panagiotis, K. (2003) Waste paper and clinoptilolite as a bulking material with dewatered anaerobically stabilized primary sewage sludge (DASPSS) for compost production. *Waste Management. 23*, 27- 35.
APPENDICES

Parameter (mg/kg)	19.03.03	09.04.03	07.05.03	05.06.03	27.08.03	MIN	AVR	MAX
NH ₄ -N				385	300	300	343	385
Total-N	4.352	4.267	4.647	3.080	4.322	3.080	4.133	4.647
Total-P			2.300	2.825	1.150	1.150	2.092	2.825
$PO4-P$			1.100	652	3.519	652	1.757	3.519
T-Al	670	6.681	\overline{a}	\overline{a}	$\frac{1}{2}$	670	3.676	6.681
T-As	19,10	16,00	\blacksquare	$\frac{1}{2}$	$\overline{}$	16,00	17,55	19,10
T-Be	\blacksquare	$\overline{}$	$\qquad \qquad \blacksquare$	\overline{a}	$\overline{}$	\blacksquare	\blacksquare	\blacksquare
T-B	1,30		$\overline{}$	\overline{a}	$\overline{}$	1,30	1,30	1,30
T-Cd	1,20	\overline{a}			\overline{a}	1,20	1,20	1,20
T-Cr	96,40	65,60				65,60	81,00	96,40
$Cr + 6$	\blacksquare	$\overline{}$	$\qquad \qquad \blacksquare$		$\overline{}$	\blacksquare	\blacksquare	\blacksquare
T-Co	2,60	$\frac{1}{2}$	$\qquad \qquad \blacksquare$			2,60	2,60	2,60
T-Cu	120	117			$\overline{}$	117	119	120
T-Fe	13.570	4.202	$\qquad \qquad \blacksquare$	\overline{a}	$\qquad \qquad \blacksquare$	4.202	8.886	13.570
T-Pb	62,10	83,20	$\overline{}$	$\overline{}$	$\overline{}$	62,10	72,65	83,20
T-Li	12,70	4,00	\overline{a}		\overline{a}	4,00	8,35	12,70
T-Mn	145	105				105	125	145
T-Hg	\blacksquare	\blacksquare			$\frac{1}{2}$	\blacksquare	\blacksquare	\blacksquare
T-Mo	2,90	$\overline{}$				2,90	2,90	2,90
T-Ni	56,40	15,90	$\qquad \qquad \blacksquare$		$\overline{}$	15,90	36,15	56,40
$T -$ Vanadium	38,70	24,20				24,20	31,45	38,70
$T-Zn$	372,40	475,20				372,40	423,80	475,20

Table 1 Heavy metal content of primary sludge

Parameter (mg/kg)	19.03.03	09.04.03	07.05.03	28.05.03	05.06.03	27.08.03	10.02.04	03.03.04	MIN	AVR	MAX
NH ₄ -N	\overline{a}	\blacksquare	\sim	1.595	3.730	3.500	\blacksquare	\sim	1.595	2.942	3.730
Total-N	9.248	8.355	9.608	7.858	9.868	8.581	51.015	62.511	7.858	20.880	62.511
Total-P	\blacksquare	\blacksquare	10.050	11.000	14.400	7.400			7.400	10.713	14.400
$PO4-P$	\sim	\blacksquare	8.500	9.882	10.747	\blacksquare	3.100	4.575	3.100	7.361	10.747
$T-A1$	859,00	5.323,90	\blacksquare			\blacksquare	9.102,00	5.072,80	859,00	5.089,43	9.102,00
T-As	20,30	15,30	\blacksquare		\blacksquare	\overline{a}	24,00	14,80	14,80	18,60	24,00
T-Be	\mathbf{r}	\blacksquare			\overline{a}	\overline{a}	\blacksquare				\mathbf{r}
$T-B$	11,80						46,00	68,30	11,80	42,03	68,30
T-Cd	1,80	1,40				\overline{a}	1,70	1,40	1,40	1,58	1,80
T-Cr	130,90	80,50	$\overline{}$	\blacksquare	\overline{a}	\blacksquare	123,00	161,60	80,50	124,00	161,60
$Cr + 6$	\sim	$\overline{}$	$\qquad \qquad \blacksquare$	\blacksquare	\blacksquare	\overline{a}	\blacksquare			\blacksquare	
T-Co	4,80	\blacksquare		\blacksquare			1,40	2,60	1,40	2,93	4,80
T-Cu	162,00	112,80	\blacksquare	\blacksquare	\blacksquare	\blacksquare	209,80	281,20	112,80	191,45	281,20
T-Fe	17.070	3.369					7.491	5.010	3.369	8.235	17.070
T-Pb	71,00	55,60					87,50	89,90	55,60	76,00	89,90
T-Li	13,60	3,10	\overline{a}	\blacksquare			3,40	3,90	3,10	6,00	13,60
T-Mn	624,30	169,00	\blacksquare	\blacksquare	$\overline{}$	\blacksquare	1.378,00	992,10	169,00	790,85	1.378,00
T-Hg	\blacksquare	\blacksquare	$\qquad \qquad \blacksquare$	\blacksquare	\blacksquare	\overline{a}	\blacksquare	1,30	1,30	1,30	1,30
T-Mo	3,60	\blacksquare	$\overline{}$	\blacksquare	\blacksquare	\blacksquare	1,20	1,60	1,20	2,13	3,60
T-Ni	57,50	15,40	\overline{a}	\blacksquare	\blacksquare	\overline{a}	59,00	28,70	15,40	40,15	59,00
T-Vanadium	33,70	14,00	\overline{a}				19,00	12,10	12,10	19,70	33,70
$T-Zn$	322,10	387,00					844,00	447,90	322,10	500,25	844,00

Table 2 Heavy metal content of excess sludge

Table 3 Heavy metal content of mixed sludge

 Γ

ㄱ

	Çiğli W.W.T.P Primary Sludge Results												
Date	$T(^{\circ}C)$	pH	conductivity (mS/cm)	Salinity $(\%o)$	DS (%)	LOI (%)	Daily Gas Production (mI/40 ml)	Net Gas Production (ml gas / L sludge)	BMP (gCOD converted/gVSS*d)	g VSS/ 40 ml	g VSS/L	ml gas produced /g VSS* d	Methane content (%)
01.11.2005	21,5	7,72	7,55	4,1	8,23	73,23	64	8000	0,047	2,41	60,27	26,55	\blacksquare
02.11.2005	21,0	7,54	7,55	4,1	6,35	72,21	57	7125	0,055	1,83	45,85	31,08	$\overline{}$
07.11.2005	20,9	7,54	7,02	3,8	7,76	71,56	61	7625	0,049	2,22	55,53	27,46	
08.11.2005	20,8	7,61	7,21	3,9	9,93	73,26	67	8375	0,041	2,91	72,75	23,02	\blacksquare
09.11.2005	20,3	7,54	7,21	3,9	5,87	75,65	55	6875	0,055	1,78	44,41	30,96	
10.11.2005	20,8	7,25	7,01	3,8	9,18	70,23	63	7875	0,043	2,58	64,47	24,43	\blacksquare
12.11.2005	20,0	7,49	7,15	3,9	8,88	69,60	60	7500	0,043	2,47	61,80	24,27	
13.11.2005	20,9	7,10	5,48	2,9	8,98	76,87	65	8125	0,042	2,76	69,03	23,54	\blacksquare
16.11.2005	20,5	7,05	7,50	4,0	10,04	71,52	97	12125	0,060	2,87	71,81	33,77	-
17.11.2005	20,4	7,60	7,17	3,9	6,99	66,56	58	7250	0,055	1,86	46,53	31,17	
18.11.2005	17,3	7,10	5,15	2,9	16,60	48,95	6	750	0,003	3,25	81,26	1,85	
29.11.2005	19,2	7,75	9,33	6,0	13,25	50,88	27	3375	0,018	2,70	67,42	10,01	
30.11.2005	19,3	7,81	7,20	3,9	8,95	60,23	62	7750	0,051	2,16	53,91	28,75	٠
01.12.2005	19,3	7,80	9,11	5,8	6,30	67,03	54	6750	0,057	1,69	42,23	31,97	-
02.12.2005	19,4	7,73	9,35	6,0	5,64	70,73	51	6375	0,057	1,60	39,89	31,96	\blacksquare
03.12.2005	19,6	7,67	7,62	4,8	7,02	65,63	56	7000	0,054	1,84	46,07	30,39	-
05.12.2005	20,0	7,69	9,11	5,8	6,53	63,81	50	6250	0,053	1,67	41,67	30,00	
07.12.2005	19,7	7,69	8,59	5,4	6,03	61,46	49	6125	0,059	1,48	37,06	33,05	
08.12.2005	19,7	7,69	8,56	5,4	13,56	38,38			0,000	2,08	52,04	0,00	-
10.12.2005	19,5	7,78	6,94	4,3	9,60	57,98	41	5125	0,033	2,23	55,66	18,42	
11.12.2005	19,4	7,73	6,20	3,8	6,42	75,27	56	7000	0,051	1,93	48,32	28,97	\blacksquare
13.12.2005	19,0	7,74	6,71	4,2	8,88	48,74	4	500	0,004	1,73	43,28	2,31	\blacksquare
14.12.2005	18,6	7,75	5,42	3,8	5,87	70,32	52	6500	0,056	1,65	41,28	31,49	
16.12.2005	17,0	7,82	8,06	5,2	6,59	59,28	54	6750	0,061	1,56	39,07	34,56	

Table 4 BMP Tests Primary Sludge

	Çiğli W.W.T.P Excess Sludge Results												
Date	$T(^{\circ}C)$	pH	conductivity (mS/cm)	Salinity $(\%0)$	DS (%)	LOI (%)	Daily Gas Production (mI/40 ml)	Net Gas Production (ml gas / L sludge)	BMP (gCOD converted/gVSS*d)	g VSS/ 40 ml	g VSS/L	ml gas produced /g VSS	Methane content $(\%)$
01.11.2005	21,2	7,31	5,76	3,0	4,23	77,44	56	7000	0,076	1,31	32,76	42,74	\blacksquare
02.11.2005	21,4	7,34	6,33	3,4	5,60	78,23	65	8125	0,066	1,75	43,81	37,09	
07.11.2005	20,5	7,09	6,55	3,4	6,30	73,25	65	8125	0,062	1,85	46,15	35,21	۰
08.11.2005	20,7	7,12	6,18	3,3	4,77	73,48	54	6750	0,068	1,40	35,04	38,52	٠
09.11.2005	20,2	7,14	6,05	3,2	5,60	75,67	63	7875	0,066	1,70	42,38	37,17	٠
10.11.2005	20,5	7,32	6,50	3,4	5,02	72,32	55	6875	0,067	1,45	36,30	37,87	\blacksquare
12.11.2005	20,3	7,39	6,06	3,2	4,41	73,41	58	7250	0,079	1,29	32,37	44,79	
13.11.2005	20,6	7,14	4,82	2,5	5,25	76,74	58	7250	0,064	1,61	40,29	35,99	۰
16.11.2005	20,0	6,98	6,20	3,3	4,94	74,58	46	5750	0,055	1,47	36,84	31,21	$\overline{}$
17.11.2005	19,4	7,31	5,60	3,0	5,60	74,13	62	7750	0,066	1,66	41,51	37,34	\blacksquare
18.11.2005	18,7	6,85	3,36	1,8	5,19	56,81	36	4500	0,054	1,18	29,48	30,52	$\overline{}$
29.11.2005	19,5	7,26	5,45	2,9	4,56	72,72	57	7125	0,076	1,33	33,16	42,97	۰
30.11.2005	18,4	7,39	5,76	3,0	5,65	79,50	64	8000	0,063	1,80	44,92	35,62	\blacksquare
01.12.2005	19,1	7,29	5,57	3,4	5,82	73,91	62	7750	0,064	1,72	43,02	36,03	۰
02.12.2005	20,9	7,33	6,18	3,7	6,02	73,06	69	8625	0,070	1,76	43,98	39,22	\blacksquare
03.12.2005	18,9	7,29	6,53	4,0	5,20	79,92	69	8625	0,074	1,66	41,56	41,51	
05.12.2005	21,0	7,41	7,47	4,5	4,36	78,30	59	7375	0,077	1,37	34,14	43,21	\blacksquare
07.12.2005	19,1	7,31	6,69	4,2	4,56	77,60	61	7625	0,076	1,42	35,39	43,10	\blacksquare
08.12.2005	18,3	7,45	6,39	4,1	5,23	78,33	65	8125	0,070	1,64	40,97	39,67	\blacksquare
10.12.2005	18,0	7,36	5,72	3,6	5,98	76,30	75	9375	0,073	1,83	45,63	41,09	\blacksquare
11.12.2005	18,3	7,25	5,47	3,4	5,20	75,60	69	8625	0,078	1,57	39,31	43,88	\blacksquare
13.12.2005	19,6	7,24	5,43	3,2	4,80	75,23	61	7625	0,075	1,44	36,11	42,23	۰
14.12.2005	19,3	7,24	4,93	3,0	5,06	79,02	64	8000	0,071	1,60	39,98	40,02	
16.12.2005	18,5	6,97	5,00	3,2	5,68	76,36	69	8625	0,070	1,73	43,37	39,77	

Table 5 BMP Tests Excess Sludge

Table 6 BMP Tests Mixed Sludge

Çiğli W.W.T.P Primary Sludge Results

Table 7 Reactor Operation Primary Sludge

Table 7 Reactor Operation Primary Sludge (cont.)

			Gas	Efficiency									
10	Date	Volume	Methane Content (%)	DS reduction (%)	VS reduction $(\%)$	VS reduction (gr)	$m3$ Gas / kg VS reduction	VS fed (gr)	m^3 Gas / kg VS fed	VS loading rate (kg VS/m ³ d)	COD Reduction (%)		
	AVE	4,88	#SAYI/0!	26,36	31,76	9,22	0,53	28,76	0,17	4,79	31,97		
10	MIN	2,67	0,00	5,84	20,50	4,64	0,41	22,58	0,10	3,76	24,48		
	MAX	6,71	0,00	33,67	40,47	12,82	0,71	34,03	0,21	5,67	36,96		
	STD. DEV.	1,21	#SAYI/0!	8,21	5,54	2,22	0,08	3,02	0,03	0,50	4,00		
	AVE	6,18	66,55	24,01	34,81	9,00	0,69	21,54	0,29	3,59	35,28		
12	MIN	5,40	63,20	18,02	28,30	6,88	0,63	19,62	0,25	3,27	29,18		
	MAX	6,50	69,40	28,35	38,82	10,05	0,80	23,71	0,33	3,95	40,00		
	STD. DEV.	0,29	2,16	3,29	2,71	0,91	0,06	1,23	0,02	0,20	3,19		
	AVE	5,26	66,55	23,95	32,65	9,15	0,58	26,64	0,20	4,56	33,29		
AVE.	MIN	2,67	63,20	5,84	20,50	4,64	0,41	19,62	0, 10	3,27	24,48		
	MAX	6,71	69,40	33,67	40,47	12,82	0,80	34,03	0,33	6,08	40,00		
	STD. DEV.	1,18	2,16	7,08	5,05	1,92	0, 10	4,22	0,06	0,76	3,99		

Çiğli W.W.T.P Primary Sludge Results

Table 8 Reactor Operation Excess Sludge

Table 8 Reactor Operation Excess Sludge (cont.)

Çiğli W.W.T.P Excess Sludge Results

Çiğli W.W.T.P Mixed Sludge Results

Table 9 Reactor Operation Mixed Sludge

Table 9 Reactor Operation Mixed Sludge (cont.)

Çiğli W.W.T.P Mixed Sludge Results