DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

MESOPHILIC ANAEROBIC DIGESTIBILITY OF PRE-TREATED SLUDGES

by
Çiğdem COŞKUN

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İZMİR

MESOPHILIC ANAEROBIC DIGESTIBILITY OF PRE-TREATED SLUDGES

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M.Sc THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **"MESOPHILIC ANAEROBIC DIGESTIBILITY OF PRE-TREATED SLUDGES"** completed by **ÇİĞDEM COŞKUN** under supervision of **PROF. DR. AYŞE FİLİBELİ** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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ABSTRACT

Anaerobic digestion has an important role in sludge management as stabilization method. Disintegration methods have taken important role before stabilization to disrupt the sludge flocs and microbial cell walls and improve the stabilization quality. So, these methods improve sludge biodegradability in terms of more biogas production and sludge minimization.

In this thesis, among the pretreatment methods microwave pre-treatment, alkaline pre-treatment and the combination of these methods were investigated with experimental studies to see the effectiveness of biodegradation and biogas production on anaerobic digestion. Sludge sample was taken from the return line of secondary sedimentation tank of the municipal wastewater treatment plant in Izmir.

At the beginning of the studies, disintegration applications have taken part for deciding the most appropriate method. According to the results, application of microwave pre-treatment improved anaerobic digestion performance as more stabilization and biogas production.

At the continuation of the experiments, lab-scale anaerobic reactors were used. Reactors were operated as batch and semi batch system under mesophilic conditions for thirty days. Results showed that volatile solids reductions and biogas productions were higher for the digesters fed with disintegrated sludge than non-disintegrated digesters. All applied method showed a positive effect on anaerobic sludge biodegradability. When comparing the applied methods in terms of sludge digestion performance, batch reactor that include 75 percent microwave pretreated sludge gave higher volatile solids reductions and higher biogas in comparison with 50 percent microwave feeded reactor. But, anaerobic semi-continuous reactors were operated with the 75 percent feeding ratio gave the best results with respect to methane production and volatile solids reduction. 50 percent microwave feeded batch reactor gave lower efficiencies then the other two reactors in terms of methane production. At the same time, disintegration processes did not affect sludge dewatering properties positively.

Keywords : Anaerobic digestion, biological sludge, microwave pre-treatment, floc disintegration, biogas, dewaterability

ÖN ARITILMIŞ ÇAMURLARIN MEZOFİLİK ANAEROBİK ÇÜRÜTÜLEBİLİRLİĞİ

ÖZ

Anaerobik çürütme, stabilizasyon metodu olarak çamur yönetiminde önemli bir role sahiptir. Dezentegrasyon metodları, stabilizasyon öncesi çamur floklarını ve mikrobiyal hücre duvarlarını parçalamada ve stabilizasyon kalitesini arttırma açısından önemli role sahiptir. Yani bu metodlar çamurun biyolojik olarak parçalanabilirliğini arttırarak, daha çok biyogaz üretimi ve çamur miktarının azalmasını sağlamaktadır.

Bu tez kapsamında ön arıtma metodları arasından mikrodalga ön arıtma, alkali ön arıtma ve termokimyasal ön arıtma yöntemi olarak bu iki metodun kombinasyonunun anaerobik çürüme üzerindeki etkileri biyolojik parçalanma ve biyogaz üretimi açısından deneysel çalışmalarla araştırılmıştır. Biyolojik çamur, İzmir'de bulunan bir kentsel atıksu arıtma tesisinin son çökeltim tankı geri devir hattından temin edilmiştir.

En uygun dezentegrasyon metoduna karar vermek için deneysel çalışmalar araştırmanının ilk bölümünde gerçekleştirilmiştir. Sonuçlara göre mikrodalga ön arıtmı anaerobik çürüme performansını daha fazla organic madde indirgemesi ve gaz üretimi açısından arttırmıştır.

Çalışmanın devamında, laboratuvar ölçekli anaerobik reaktörler kullanılmıştır. Reaktörler kesikli ve yarı kesikli olarak mezofilik ortamda otuz gün süre ile işletilmiştir. Sonuçlara göre, dezentegre edilmiş çamurla beslenen reaktörlerde daha fazla organik madde indirgenmesi ve daha fazla biyogaz oluşumu elde edilmiştir. Uygulanan tüm dezentegrasyon yöntemleri çamurların anaerobik parçalanabilirliği üzerinde olumlu bir etki göstermiştir. Uygulanan yöntemler çamur çürüme performansı açısından karşılaştırıldığında yüzde 75 mikrodalga ile ön arıtılmış çamurla beslenen kesikli reaktör yüzde 50 oranla beslenenden daha fazla biyogaz üretimi ve daha çok organik madde giderimi sağlamıştır. Fakat bu açıdan ele alındığında en iyi sonucu yüzde 75 oranlı yarı kesikli beslemeli reaktör vermiştir. En düşük verim ise yüzde 50 oranlı dezentegre çamurla beslenmiş kesikli reaktörde elde edilmiştir. Diğer yandan, dezentegrasyon yöntemleri anaerobik yöntemle çürütülmüş çamurların su verme özellikleri üzerinde bir etki göstermemiştir.

Anahtar sözcükler : Anaerobik çürüme, biyolojik çamur, mikrodalga ön arıtımı, flok dezentegrasyonu, biyogaz, susuzlaştırabilme

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CHAPTER ONE
INTRODUCTION

Each society generates liquid and solid wastes and also air emissions. The liquid waste, which can be named as wastewater, is the used water in a type of applications by the community. If we look at the sources of wastewater generation, it may be described as a mixing of the liquid and wastes comes from placements, commercial and industrial establishments. Also, it includes groundwater, surface water, and stormwater (Metcalf & Eddy, 2003).

Wastewater treatment, simply, is the eliminating process of contaminants from wastewater. Because of the different kinds of contaminants, the process involves physical, biological and chemical treatment steps. The actual target of these processes is to reduce the contaminants for the environment as a safe fluid waste and solid waste stream. This solid waste, which is often treated as sludge, is suitable for disposal and reuse.

In a wastewater treatment plant, the produced sludge quantity is approximately 1% in comparision of the quantity of treated wastewater. Wastewater treatment takes several hours, but sludge treatment for disposal or reuse takes several days or even several weeks. Also, the use of more complex equipments are needed for sludge processing (Turovskii et al., 2006). The plant’s total cost includes approximately 60% of the excess sludge treatment payments (Chockalingam et al., 2009).

Processing of the sludge depends on the characteristics and quantities of its solid matter content. The core methods used for processing can be classified as thickening, conditioning, stabilization, dewatering, and final disposal methods (incineration and land application) (Spinosa et al., 2001). The treatment processes of sewage sludge follow each other step by step. The water content can decreased in thickening that is chased by a stabilization process with secondary thickening, and/or chemical conditioning and after that a dewatering process may take part in a plant. After those steps the sludge is finally ready for disposal or reuse (Metcalf & Eddy, 1991).

Sludge stabilization takes an important role in sludge management to prevent the adverse effects of sludge on the environment. This method provides reduction of organic matter, removal of pathogens and odor potential. Sludge can be stabilized by using alkaline treatment, aerobic and anaerobic digestion (mesophilic or thermophilic conditions) and composting methods (Metcalf & Eddy, 2003). Among these methods, mesophilic anaerobic digestion is being widely used for its advantages. This process provides the production of biogas, mass and odor reduction, stability and dewaterability of sludge and lower energy requirement in comparision with others. On the other hand, this process has very long retention times (20–50 days) and low efficiency of degradation (20–50%). These features of digestion process are related with the hydrolysis step of the sludge (Kim et al., 2010). Also, low amount of biogas, poor dewaterability, low volatile solids reduction, and high quantities of sludge volume after stabilization are the disadvantages of anaerobic digestion (Vera et al., 2005; Bartholomew, 2002). For these reasons, pretreatment methods have been applied to sludge before stabilization to disrupt the flocs and microbial cell walls and improve the stabilization quality and biogas production. These pre-treatment methods are called as disintegration.

Disintegration of sludge means that solubilization and convertion of macro-biodegradable and particulate organic materials into low weighted molecules and microparticules (Park et al., 2009). The macro substances that include in sludge are microorganisms, cell walls, intracellular materials and macro molecules like lipids, peptids, etc. These are converted into bioavailable substrate for microorganisms that will be used in stabilization (Müller et al., 2004, Weemaes et al., 1998).

The kinds of pretreatment methods for disruption of sludge can be classified as mechanical, physical, biological, chemical, and the combined methods. Thermal treatment, microwave, freezing and thawing are some examples of physical pre-treatment. Chemical pre-treatment can be applied by using ozone, acids, alkali or other chemicals. Ultrasound, high pressure homogenizers, impact grinding, the Lysat-centrifugal technique, high performance pulse technique, stirred ball mills, are some of mechanical pre-treatment methods. Hydrolysis step can be accelerated by addition for biological pretreatment methods. Also, combination of these (like thermochemical) methods improves the effect of disintegration (Müller, 2001; Perez-Elvira et al., 2006).

The scope of the thesis is to research the improvement of anaerobic sludge digestion with thermal, chemical and thermochemical pretreatment techniques usage. The objectives are therefore:

- To investigate the feasibility of alkaline and microwave treatment for biological sludge disruption purpose,
- To optimize the disintegration processes in terms of sludge and sludge's supernatant properties,
- To compare the effects of applied disintegration processes on biological sludge,
- To search the effects of applied disintegration methods on accelerated hydrolysis of the organic matter content of sludge,
- To determine whether pre-treatment methods enhance dewaterability capacity of sludge.

CHAPTER TWO
LITERATURE REVIEW

2.1 General Sludge Processing

Sludge cumulates as a remnant in all kinds of wastewater treatment plants and includes the solids and colloids separated from wastewater. Some sludge are produced during wastewater treatment, including primary sludge which comprises settleable solids removed from the primary clarifier, and secondary sludge, which comprises biological solids generated in secondary wastewater treatment plant (Lee et al., 2005).

Sludges have very complicated materials for characterization and they should be treated by using appropriate environmental procedures.

The problem of dealing with sludge is complicated because;

i. they largely include the materials of untreated wastewater,
ii. the part of sludge that comes from biological wastewater treatment includes the organic matter contained in the wastewater and will decompose and become more offensive,
iii. it contains only a small portion of solid matter (Metcalf & Eddy, 2003).

Sludge management aims to minimize the water and organic content of sludge and to get the processed solids suitable for reuse or final disposal. Therefore, sludges should be processed and disposed of with respect to the environmental health criteria. The efficient sludge management is still a big challenge since the investment and operational payments of sludge handling have an important significant part of overall treatment plant’s costs (Metcalf & Eddy, 2003).

2.2 Sludge Treatment

"Sludge treatment" term describes the whole processes that are used to manage and dispose of the sludges. The goals of sludge treatment are:

i. Stabilisation for a controlled degradation of organic ingredients and odour removal
ii. Volume and weight reduction
iii. Hygiene – the deadening of pathogen organisms
iv. Ameliorating of sewage sludge characteristics for the further utilization or disposal (Metcalf & Eddy, 2003).

These goals are served to increase the concentration of solids in order to reduce the excess sludge volume to be disposed off, and to reduce the fraction of biodegradable matter and the pathogen concentration in order to obtain a stable and safe end product that does not constitute a public health risk (van Haandel et al., 2007).

A typical sludge treatment system includes four stages such as;

1) Pre-treatment, during sludge characteristics are altered to enhance subsequent process performance;
2) Dewatering, for separating moisture from the sludge body;
3) Post-treatment, for stabilizing or detoxicizing the sludge, and
4) Final disposal, which aims to achieve safe and economically feasible disposal (Lee et al., 2005).

An example of sludge treatment network that includes these stages is shown in Figure 2.1 (Lee et al., 2005).

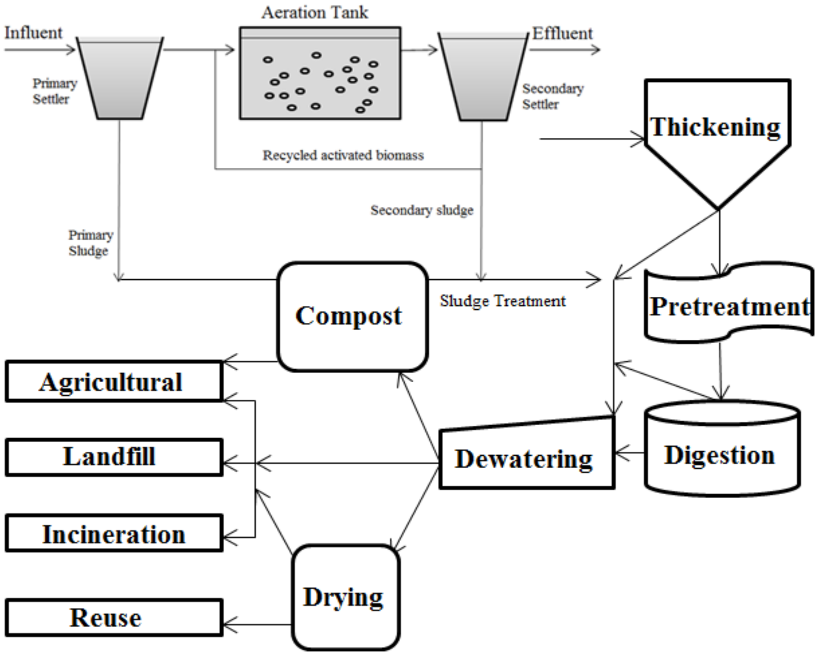


Figure 2.1 A sludge treatment network (Lee et al., 2005).

2.3 Sludge Stabilization

From all steps of wastewater treatment, sludge is produced which has high quantities of organics, pathogens, lots of water and nutrients. Therefore sludge should be further treated for an environmentally safe disposal in a way that stabilized sludge should not have an undesirable rate of degradation and adverse effects on the existing ecology (Vesilind, 1979). Sludge stabilization process means that treating wastes has a high amount of biodegradable colloidal and suspended matter.

The aim of the stabilization is;

i. Destruction of most pathogens,
ii. Reduction in the organic content of the sludge
iii. And preventing unwanted odor (Lee et al., 2005).

Sludge may be stabilized using chemical, physical and biological methods. The methods that are used for stabilization summarized as follows:

- Biological sludge digestion: aerobic digestion, anaerobic digestion, compositing,
- Alkaline stabilization: usually with lime,
- Thermal stabilization: pasteurization, thermal drying (Metcalf & Eddy, 2003; Weiner et al., 2003).

2.3.1 Aerobic Digestion

Sludge stabilization can be achived by using an aerobic process. They are sustained in aerobic circumstances by suppling aeration, through which organic material is oxidised (Scholz, 2006). The main target of aerobic digestion is to produce a biologically stable sludge, and also to decrease its mass and volume. The final product should have good settleability characteristics that can be easily thickened and dewatered.

Aerobic digestion is commonly chosen at smaller treatment plants. But it does not provide energy recovery for operational costs like aeration and mixing. Despite this disadvantage aerobic digestion is comperatively cheap and easy to manage for small plants and it has low odour and largely oxidized supernatant. Because it often has a high suspended solids concentration, that is returned to the inlet of the plant. In process, a pH decrease during the digestion exists because of nitrification. That may inhibit process so that pH control near to 6.5should be done. The performance of process is directly associated with microbial activity which is largely sensitive on temperature. Therefore, digester heating should be provided in winter due to not to let the oxidation rate fall dramatically (Gray, 2005; Metcalf & Eddy, 2003; Scholz, 2006; Whiteley et al., 2006). Figure 2.2 summarized the mechanism of aerobic digestion process.

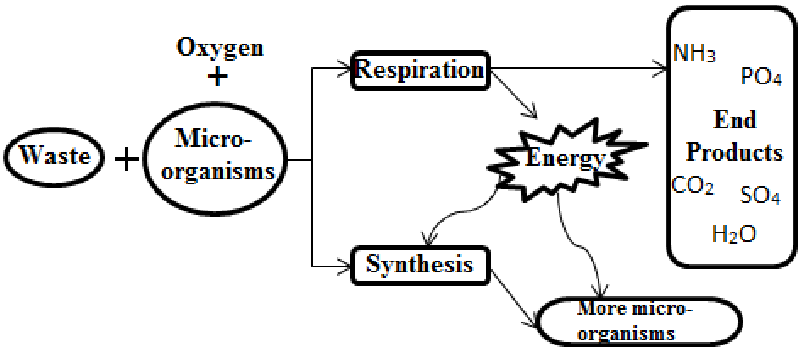


Figure 2.2 Path of Aerobic Digestion (Long, 2011).

2.3.2 Anaerobic Digestion

Anaerobic digestion process allows to the solubilization and acetification of complicated organic substances by the usage of microorganisms in the absence of oxygen. Methane, carbon dioxide, other trace gases, and the stabilized sludge are the products of anaerobic digestion. The pathogenic microorganisms can be effectively inactivated in the sludge by the digestion process (Lee et al., 2005). Anaerobic digestion is described with more detail in Section 2.4 such as digestion stages, advantages and disadvantages, the effect of environmental factors.

2.3.3 Alkaline Stabilization

Alkaline stabilization is used to eliminate the unwanted conditions in sludge by using an alkaline material. Generally, lime is used at alkaline stabilization. To create an unsuitable environment for micro-organisms, pH value is raised above 11 by adding lime to the untreated sludge. Appliying this process during 3 hours allows the elimination of pathogens from sludge before anaerobic digestion with higher reduction rates. When the high pH is provided, lime stabilization avoids putrefaction but it does not decrease the organic matter or maintain permanent stabilization. On the other hand, while the high pH prevents the emission of volatile sulphides and fatty acids, the emission of amines and ammonia is improved making lime-treated sludge less offensive than raw sludge but certainly not odourless. The elevated pH is normally ensured for several days or until added into the soil.

Lime addition can also help in the dewatering process and it is beneficial for the sludge disposal into agricultural land applications. In lime addition, two types are used, the addition of quicklime to dewatered sludge and the incorporation of hydrated lime into non-dewatered sludge. The dosage is explained as grams of lime per kg dry sludge solids (g $kgDS^{-1}$). The mass of solids can raises seriously after treatment so the average dosage for a primary sludge should be between 100 and 200 $gCa(OH)_2kgDS^{-1}$. The treated sludges' pH decreases with time, when the preliminary dosage is not enough. So the most important part of this process is sufficient lime addition for keeping the pH for the necessary period (Gray, 2005).

2.3.4 Thermal Stabilization

Thermal stabilization has been suggested as the most proper technique to inactivate the microorganisms in wastewater and sludge. Total coliform falls to very low levels. The soluable chemical oxygen demand (*SCOD*) also rises clearly after heating. However, treated sludge still indicates good dewaterability while the global floc structure is not significantly dispersed. Heating time is important on the hydrolysis performance. Thermal treatment requires more energy in comparison with other mechanical processes, but cheaper thermal energy (such as waste steam, if available) may be operated rather than the electrical energy that is provided for mechanical processes (Lee et al., 2005).

2.4 Anaerobic Digestion

Anaerobic digestion takes place in a heated reactor with the absence of molecular oxygen that ends up with methane and carbon dioxide gas production (Metcalf & Eddy, 2003). Heated anaerobic digesters are mostly used as stabilization method in medium and also large-sized treatment plants. In small treatment plants cold anaerobic digesters are used in tanks or lagoons (Scholz, 2006).

Produced gas during anaerobic digestion process is called as biogas which contains in trace amounts of water vapor, hydrogen, nitrogen, hydrogen sulphide, unsaturated hydrocarbons and other gases. In the biogas methane and carbon dioxide present in large measure with typically 65%-70% and 30%-35% by volumes, respectively (Gray, 2005). Methane is the major advantage of anaerobic digestion processes for energy production.

This degredation process includes the conversion of complex organic materials into methane and carbon dioxide and has four steps (Gray, 2005), which is also shown in Figure 2.3: hydrolysis phase, acidification phase, acetogenesis phase and methanogenesis phase.

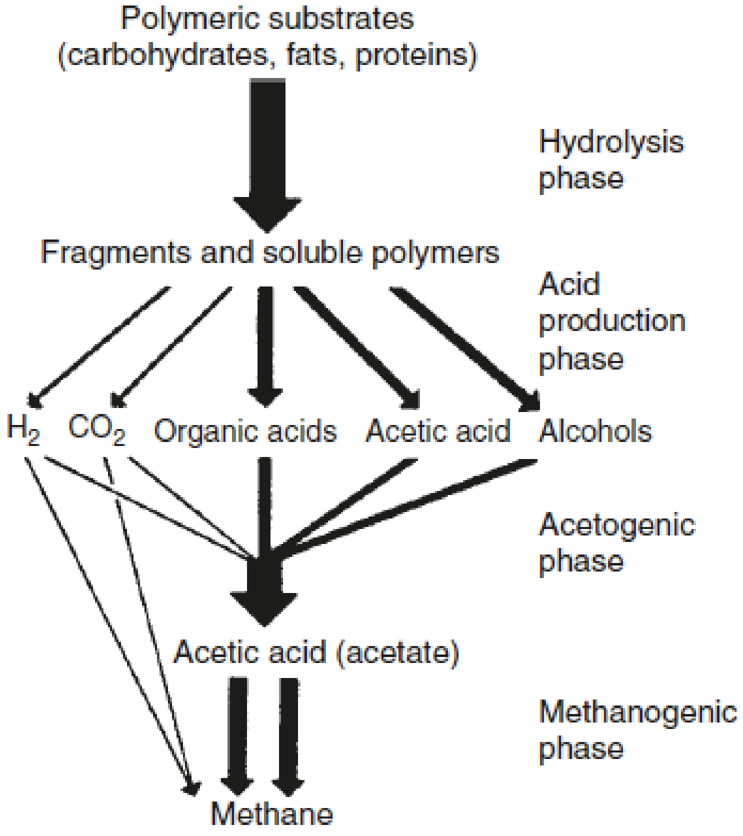


Figure 2.3 Major steps in anaerobic decomposition (Gray, 2005).

2.4.1 Anaerobic Digestion Phases

2.4.1.1 Hydrolysis Phase

It is hard to directly treat wastes which contain complex and insoluble organic compounds by microorganisms. Therefore, decomposition of these complex and insoluble organics into simple soluble organic materials is very important for using as an energy and nutrient source by bacterias. Organic matter stabilization is not possible during the rate limiting step hydrolysis phase. At this phase, conversion of the organic matter into a structure is carried out by enzymes (glucosidases, lipases, proteases, sulphatases, phosphatases) that supported by bacteria groups (Metcalf & Eddy, 2003; Whitely et al., 2006). (Müller, 2001).

2.4.1.2 Acidogenesis Phase

In anaerobic digestion process, acidogenesis or acidification phase is the second part of conversion. At this stage the hydrolysed matters are transformed into simpler molecules like volatile fatty acids (e.g. acetic-, butyric acid and propionic-), aldehydes, alcohols and gases such as CO_2, NH_3 and H_2 (van Haandel et al., 2007).

2.4.1.3 Acetogenesis Phase

The end products of the acid production are acetic acid, hydrogen and carbon dioxide. Methanogenic bacteria can directly convert these materials into methane so acetogenic stage is only present where alcohols and organic acids are transformed into acetic acid by acetogenic bacteria (Gray, 2005). After all of this phase, hydrogen is produced and can be used for determination of the system efficiency because of its adjusting effect in acid production.

2.4.1.4 Methanogenesis Phase

Anaerobic degradation of sludge is completed with methane production phase. Two different groups of methane bacteria take role in methane production stage. One of these groups produces methane from moleculer hydrogen and the other group produces methane and bicarbonate by acetate and dicarbocylation. Methanogenesis phase prevents accumulation of acids and alcohol. By this way, reduction of system efficiency is also prevented (Metcalf & Eddy, 2003; Speece, 1996).

2.4.2 Advantages and Disadvantages of Anaerobic Digestion

Anaerobic digestion of sludges has many advantages and disadvantages. They are summarized as follows;

Advantages:

- Stabilizatin of sludge is qualified.
- Methane gas is produced as an end product.
- Produces more energy amount than the required energy.
- The end product, methane, can be used to heat and mix the reactor. Methane can also be used for other applications.
- Reactors don’t yield any odour or aerosols.
- Amount of total solids is reduced for disposal.
- Because of lower growth rate of anaerobes, nutrient requirement is low.
- 30% - 40% total solids (TS), 40% - 60% volatile solids (VS) may be destroyed.
- Pathogens are destroyed.
- Reactors can be operated seasonally.
- Rapid start-up of reactors possible after acclimation.
- Many of organic substances in municipal sludge are easily digestible except tannins, lignins, rubber and plastics.

Disadvantages:

- Reactors generally require heating.
- Hydrogen sulphide is also produced during the process.
- Additional alkaline material may be required.
- Pathogen destruction is less effective than aerobic stabilization.
- Low retention times are required (<24h).
- Heating and mixing equipments are required for operating reactor.
- Initial start-up period takes long time if growth rate of anarobs are slow.
- Digestion process is very sensitive to ambient conditions. So, the overall system is easily broken down and it is very hard to recover.
- Large reactor volume is needed.
- The supernatant is a critic and strong waste that should be sent to inlet line of the wastewater treatment plant.
- Cleaning operations are difficult.
- Possibility of explosion (Gray, 2005; Lee et al., 2005).

2.4.3 The Effect of Environmental Factors for Anaerobic Digestion Process

In all biological treatment processes, the metabolic activity of the microorganisms does not only affect the treatment of pollutants and contaminants. Also the existence of suitable environmental conditions affects and supports these activities, too. In anaerobic digestion processes, because of the critical nature of the process, environmental conditions require strict tracing and control preventing system failure (Anderson et al., 2003).

The important environmental factors for anaerobic digestion process are;

1. solids retention time,
2. hydroulic retention time,
3. temperature,
4. alkalinity,

5. pH,
6. the presence of inhibitory substances, i.e., toxic materials,
7. the bioavailability of nutrients and trace metals.

The first three factors are major in process selection while alkalinity is a function of feed solids and is significant in controlling the digestion process whether pH falls (Metcalf & Eddy, 2003).

2.4.3.1 Solids and Hydraulic Retention Times

Achieving destruction of volatile suspended solids (VSS) at anaerobic digester is depent on adequate residence time in well-mixed reactors. Sizing criteria are given as follows:

1. solids retention time (SRT), the medium time is needed for holding the solids in the digestion process,
2. the hydraulic retention time θ, the medium time is needed for holding the liquid in the digestion process.

For digestion systems without recycle in completely mixed conditions, hydraulic retention time equals to the solids retention time (θ=SRT). Hydrolysis, fermentation, acetogenesis and methanogenesis reactions are directly related to SRT. The success rate of each reaction increases if SRT results increase. Similary, decreasing SRT results decrease the success rate of the reaction. There is a minimum SRT for each reaction. Bacteria cannot grow rapidly and digestion process will fail if the SRT of the reactor cannot exceed the minimum SRT (Metcalf & Eddy, 2003).

2.4.3.2 Temperature

Different species of bacteria can live at different temperature ranges. Mesophilic bacteria are lived at temperatures between 35-40°C. Some species of bacteria are able to survive at the hotter temperatures. The bacteria that are lived at temperatures between 55-60°C are called as thermophilic bacteria. Methanogens are the member of the primitive group of archaea. This family are able to grow in the hostile conditions of hydrothermal vents. This kind of bacteria are resistant to heat (Davies, 2007).

Temperature doesn't only affect the population. It also affects the rate of gas transfers and the settling properties of biological solids.. In anaerobic digestion process, temperature is also significant in defining the rate of digestion, especially the rates of hydrolysis and methane formation. Most anaerobic processes are designed for operating in the mesophilic conditions between 30 and 38 ^{0}C. Other systems are designed to operate in thermophilic temperature range of 45 to 57 ^{0}C. All biological treatment processes' efficiency is influenced from temperature (Banik et al., 2007) and also low temperatures in anaerobic digestion cause low reactor performance (Kato et al., 1997). Figure 2.4 shows the effect of temperature on biogas production (Gray, 2005).

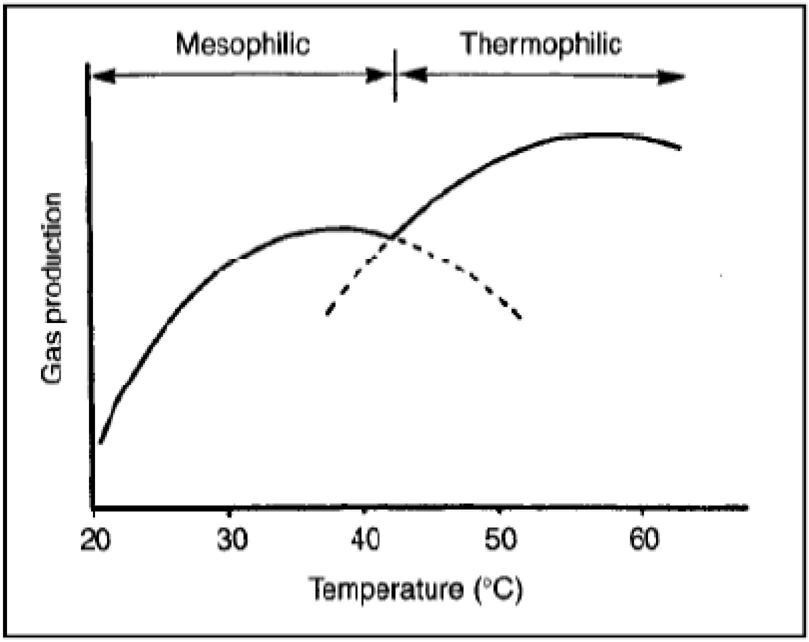


Figure 2.4 Effect of temperature on biogas production (Gray, 2005)

2.4.3.3 Alkalinity

Calcium, magnesium, and ammonium bicarbonates can be found as buffering substances in the anaerobic digester. Ammonium bicarbonate is produced from breakdown of protein in the raw sludge feed during anaerobic degredation: the other elements are found in the feed sludge. The alkalinity concentration in a digester is proportional to the solids feed concentration. A well–operated digester has a total alkalinity of 2000 to 5000 mg/L (Metcalf & Eddy, 2003). Optimum environmental conditions are summarized for anaerobic microorganisms in Table 2.1 (Speece, 1996).

Table 2.1 Optimum environmental conditions for anaerobic microorganisms (Speece, 1996).

Parameter	**Optimum Environmental Conditions**
Composition of Sludge	C,N,P and trace elements must contain, Toxic inhibitors and oxidizing elements must not be.
Temparature (^{0}C)	25-38 (mesophilic);50-60 (thermophilic)
COD/N/P	3000/10/1
pH	6.5-7.6
Alkalinity(mg $CaCO_3$/L)	1000-4000(2000)
Total Volatile Acids (VFA,mg/L)	< 1000-1500
Total Volatile Acid/ Alkalinity	< 0.1
Toxic Substances	---------

Main alkalinity consumer of a digester is carbon dioxide and not volatile fatty acids as is mostly relied (Speece, 1996). Carbon dioxide is generated in the fermentation and methanogenesis steps of the digestion process. Partial pressure of gas in a digester provides soluabilizing the carbon dioxide, then provides forming carbonic acid.Therefore the carbon dioxide concentration of the biogas is reflective of the alkalinity necessity. Additional alkalinity can be supplied by the supplement of sodium bicarbonate, lime, or sodium carbonate (Speece, 1996).

2.4.3.4 pH

Methane bacteria are very sensible to the environmental conditions. Presence of heavy metals or other toxicants like petrochemicals and oxygen negatively affect the methanogenic environment. The optimum pH range is 6.4 – 7.5 for anaerobic treatment (Vesilind, 1979).

2.5 Disintegration of Sludge Before Anaerobic Digestion

Disintegration or pretreatment of sludge means that applying external forces to sludge in order to disrupt sludge floc structure (Müller et al., 2004). Figure 2.5 shows the effect of disintegration mechanism on sludge flocs. Disintegration has been developed to fulfill the requirement for following sludge treatment and final disposal (Müller, 2001). The disintegration efficieny is proportional to the supplied energy (Khanal et al., 2007; Lehne et al., 2001).

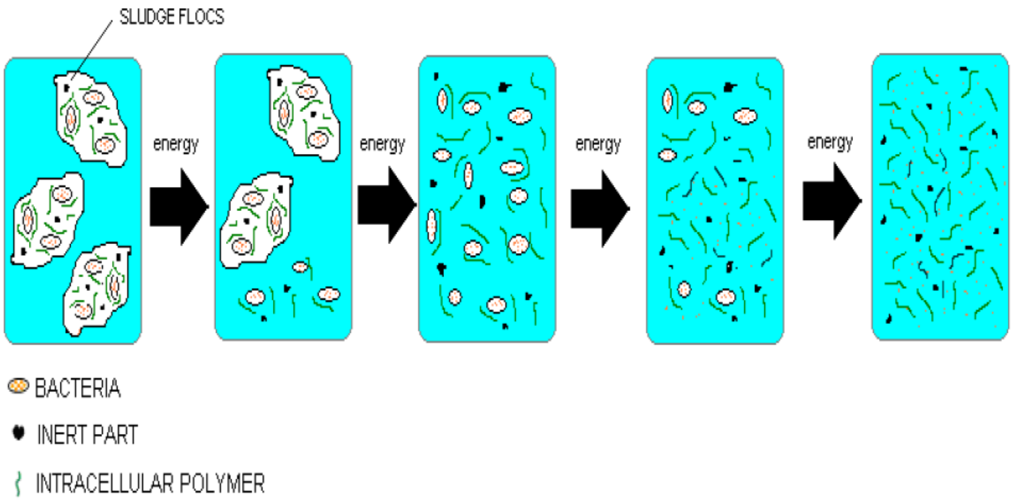


Figure 2.5 Effect of disintegration on sludge floc structure (Luning et al., 2007).

Sludge disintegration principally targets to overcome the rate-limiting step hydrolysis by converting the cell structure into bioavailable substrate. Therefore, bioavailability of microorganisms can be achieved by solubilizing the substrate.

2.5.1 The Advantages of Disintegration before Anaerobic Digestion Process

Applying disintegration process before anaerobic digestion has some effects on sludge reduction and sludge characteristics. The major effects are described as follows:

1) Stability: When intracellular organics in floc structure are solubilized, degradation of organics is improved and accelerated in anaerobic digestion (Müller, 2004). Volatile Solid (VS) reduction can be improved from about 45% to 60% or more by disintegration of waste activated sludge (WAS) with mixing of primary and secondary WAS in anaerobic digestion (Panter, 2002).

2) Sludge amount and disposal: While organic content degradation of sludge is enhanced by disintegration, the sludge amount that should be disposed of after stabilization is also decreased (Müller, 2001).

3) Bulking and Foaming: Application of a pre-treatment method can decrease bulking and foaming. During pretreatment flocs are also distructed and so smaller size flocs are able to compress and can settle better (Müller, 2001).

4) Biogas Production Efficiency: Higher degrees of organics using is supplied by pre-treatment and because of that biogas production efficiency in anaerobic digestion is increased (Rong et al., 2006).

5) Settling and Dewatering Quality: Dewaterability of sludge can be improved by applying a pretreatment process. Sludge flocs have the bound water captured by the cells. Application of a pretreatment method destroys the cell structure and releases the bound water. However, pretreatment processes may not affect the dewaterability of sludge on good way. As an example, thermal pretreatment is a well-known conditioning method between the pretreatment methods (Panter, 2002). If less intense disintegration distrupts a partial of floc structures, the effects in settling of sediment sludge are bad. But the settling of bulking sludge can be developed by the disruption of floc structures (Müller, 2003).

6) Reduction of Pathogens: Partial or complete reduction of pathogenic microorganisms can be obtained by disintegration. A well-known pretreatment method for sludge disinfection is thermal disintegration (Müller, 2001).

2.5.2 Disintegration Techniques

Disintegration can be put into practice with various instruments and methods. These can be categorised as following topics:

- **Physical disintegration**:
    - Cavitation: (High Pressure homogenizers, Ultrasonic homogenizers)
    - Thermal : (Thermal hydrolysis by microwave, Freezing and thawing)
    - Mechanical : (Impact grinding, Stirred ball mills, High performance pulse technique, The Lysat-centrifugal technique)
    - Radiation: (Gamma-irradiation)
- **Chemical disintegration: (**Acid or alkaline hydrolysis or using other chemicals like Fenton, Ozone etc.).
- **Biological disintegration:** (Enzymatic lysis, Temperature phased anaerobic digestion (TPAD)).
- **Combined disintegration:** (Combination of thermal and mechanical methods, Chemically enhanced thermal hydrolysis) (Perez-Elvira et al., 2006).

In this thesis, alkaline disintegration as chemical pretreatment, microwave pretreatment as a thermal method and the combined effect of these methods are investigated on anaerobic biodegradability of sludge. Therefore, these methods are given in more details towards the end of this section.

2.5.3 Chemical Disintegration

2.5.3.1 Acidic Disintegration

Acidic disintegration breaks down the cell wall. While the pH value was between 2.6 – 3.6, the negative charge on the surface was neutral. Therefore, the impulsive force between particles reduced to minimum and physical stability of sludge like dewatering and flocculation could be monitored. Research indicates that at pH 3 sludge volumes could be reduced up to 75% by dewatering. Also soluble solids could be enhanced by solubilization of intracellular structure. Finally pH 3 was the most proper pH for acidic pretreatment (Neyens et al. 2003).

2.5.3.2 Fenton Disintegration

Erden et al. (2010) were investigated the effects of Fenton process on anaerobic sludge bioprocessing. Before anaerobic sludge digestion, biological sludge samples were applied a ratio of 0.067 g Fe (II) per gram H_2O_2, and at 60 g H_2O_2/kg TS and 4 g Fe (II)/kg TS. Single stage anaerobic digester was used as control reactor and it was operated under thermophilic conditions. Control reactor was compared with two-stage anaerobic digester which includes mesophiclic digestion prior to thermophilic digestion. Results showed that Fenton process enhances the methane production and Fenton pre-treatment applied reactors were produced 1.3 times higher than the overall methange production when compared to control reactor.

2.5.3.3 Ozone Disintegration

The ozonation of sludge means that the reactions of floc disintegration, solubilization, and the following oxidation of discharged organics to carbon dioxide. Chu et al. (2009) were investigated the effect of ozonation and were confirmed the improvements in the biodegradability. Research proves that ozonation into the activated sludge didn’t make a significant improvement on effluent quality. But, ozonization process improved the settling properties of the sludge. They also propose recommended ozone dose ranges for wastewater treatment plants from 0.03 to 0.05 O_3/g TSS for achieving a balance between sludge reduction efficiency and total operation cost.

Zhang et al. (2009) investigated the sludge disruption and supernatant changes by using ozonation. According to their study, ozone was effectively lysed the sludge. Optimal ozone dose for sludge lysis was found 50 mgO_3/g DS. Only 10.4% sludge lysis was obtained at 25 mgO_3/g DS after 90 min and sludge decomposition could not be further improved at 80 mgO_3/g SS. After 105 minutes, the disintegration degree of sludge was calculated as 46.7% while the ozone dose was 50 mgO_3/g DS. The decrease rate for the content of sludge solid and volatile solid decreased by 49.1% and 45.7%, respectively. Results were also showed that the soluble chemical oxygen demand (SCOD) of sludge were improved by 699%; while total nitrogen, total phosphorus, protein, polysaccharide, and deoxyribonucleic acid improved by 169%, 2379%, 602%, 528%, and 556%, respectively. Heavy metals in sludge and supernatant were decreased, but the sludge size distribution could not be altered.

2.5.3.4 Alkaline Disintegration

Alkaline sludge disintegration is based on disruption of floc structure and cell wall by hydroxy radical (Li et al., 2008). At high pH values of center, the cell loses its viability. Alkaline saponifies the lipids in the cell walls that provide solubilization of membrane (Neyens et al., 2003). Also, natural shape losing of proteins and hydrolysis of RNA come true. In other words, chemical degradation and ionization of the hydroxyl groups ($–OH^{-} \rightarrow –O^{-}$) affect gels in sludge on large expansion and subsequent solubilization. The cell walls cannot resist the appropriate turgor pressure. For this reason, the disruption of cells and release of intracellular substances occur (Li et al., 2008).

Jin et al. (2009) were compared treatment methods and were stated that alkaline treatment has many advantages like simplicity of operating device, easy management of operation and high treatment efficiency. Lin et al. (1997) were examined the performance of anaerobic digestion by fedding waste activated sludge (WAS) which is disintegrated with NaOH. Four 1-L semi-continuous anaerobic reactors were used for this study. Reator A was used as control reactor and was fed with untreated WAS at 1% total solids (TS). Reactors B and C were also fed with untreated WAS at 1% TS which were disintegrated with NaOH at amount of 20 meq/L and 40 meq/L respectively. Reactor D was fed with untreated WAS at 2% TS which was disintegrated with 20 meq/L NaOH. Reactors were operated at 10 days. After 10 days, COD removals of reactors were found as 38, 46, 51 and 52% for reactors A, B, C and D respectively. When compared with the control reactor A, gas productions were increased by 33, 30 and 163% for reactors B, C and D respectively. The results were also showed that the dewaterability of digested sluge was advanced for reactor B, C and D. Capillary suction times were reduced from the range of 309-735 s to 148-389 s.

Saby et al. (2001) were studied on decreasing total amount of sludge by investigating the effect of chlorination. The appropriate dosage for chlorination was defined to be as 0.066 g Cl_2/g MLSS. According to this study, 65% of sludge production was reduced by returning this chlorinated sludge to the activated sludge system.

Chen et al. (2007) were examined on the influence of different pHs on hydrolysis and acidification of waste activated sludge (WAS). It was determined that each acidic or alkaline pH enhanced the SCOD concentration. But, the soluble chemical oxygen demand (SCOD) under alkaline conditions was seriously higher than other pHs. It was observed that the most significant components of soluble chemical oxygen demand (SCOD) were the soluble proteins and carbohydrates. In addition to this, their concentrations were higher at alkaline pH levels. The study showed that the total volatile fatty acids (VFAs) concentration could be improved by the increase of pH between 8.0–11.0. Methane production increased with acidic pH, with pH values from 4.0 to 6.0, but decreased with alkaline pH between 6.0 and 10.0. Alkaline fermentation of waste activated sludge (WAS) was favorable. WAS fermentation under alkaline conditions had also benefits for the recovery or removal of phosphorus and ammonia that could be applied by the methods of phosphorus precipitation, ammonia stripping or struvite formation.

In another laboratory-scale experiments of Yunqin et al. (2009) were investigated alkali disintegration effect on biogas production. Pulp and paper sludge was used as material in their study. Four completely mixed reactors that have 1 L capacity were used for theirs study. Anaerobic digestion was applied under mesophilic conditions at the retention time of 42 days. Different concentration of sodium hydroxide solution was applied for pretreatment to three reactors and the forth one was selected as the control reactor. Optimal dosage of NaOH for disintegration was 8 g NaOH/100 g TS_{sludge}. On the other hand, the microorganisms could be affected by sodium toxicity at the amount of 16 g NaOH/100 g. At the optimal dosage, flocs structure was disrupted well and particule size of sludge was reduced. Also, SCOD enhanced up to 83% while the peak value of VFA concentration reached 1040 mg acetic acid/L in anaerobic digester. The highest methane efficiency was $0.32m^3$ CH_4/kg $VS_{removal}$, with rate of 183.5% compared to the control reactor. The study showed that alkali/NaOH disintegration could be an efficient method for improving methane efficiency of pulp and paper sludge.

According to the study of Li et al. (2008) results indicated that sodium hydroxide (NaOH) was more appropriate than calcium hydroxide ($Ca(OH)_2$) for sludge disintegration. The most effective dose was about 0.05 mol/L (0.16 g/g dry solid) for NaOH treatment, and 60 – 71% solubilization of organic matters was attained in first 30 min. Low dose of NaOH (<0.2 mol/L) disrupted sludge dewatering ability obviously. For $Ca(OH)_2$ treatment, the disintegrated floc components and soluble organic polymers can be re-flocculated with the help of calcium cations. As a result, sludge disintegration effect was withstood and dewatering ability improved.

Torres et al. (2008) showed that sodium hydroxide (NaOH) was preffered due to provide greater solubilization efficiency than calcium hydroxide ($Ca(OH)_2$). Also, NaOH improves anaerobic digestion performance. Also, according to Kim et al. (2003) dibasic alkaline agents were found less soluble than mono basic agents. It was explained by the partial solubilization of the dibasic alkaline agents. Because of these reasons, in this thesis NaOH was preffered as the alkaline disintegration agent before anaerobic digestion.

2.5.4 Thermal Disintegration

Table 2.2 Overview of some thermal pre-treatment studies.

Study	**Treatment Conditions**	**Results**
Kim et al., 2003	121 ^{0}C – 30 min	VS reduction increased by 30%
Valo et al., 2004	170 ^{0}C – 15 min	TS reduction is increased by 59% Gas production is increased by %92
Ferrer et al., 2006	170 ^{0}C – 15 min	Thermophilic digestion has positive effect on gas production Higher temperature (110-134 ^{0}C) did not have any effect
Climent et al., 2007	70 ^{0}C – 134 ^{0}C 90 min – 9 h	Biogas production is increased 50% at 70^{0}C-9h High temperature did not have any effect.
Bougrier er al. 2007	135 ^{0}C – 190^{0}C	Methane production is increased by 25% at 190^{0}C
Jeong et al., 2007	120 ^{0}C – 30 min	Methane production is increased by 25%
Phothilangka et al., 2008	Thermo-pressure-hydrolysis process	Biogas production is increased by 80%
Perez-Elvira et al., 2008	170 ^{0}C – 30 min 3 bar	Methane production is increased by 50%
Nges et al., 2009	25, 50, 70 ^{0}C 48 h	Methane production is increased by 11% at 50 ^{0}C

Thermal disintegration disrupts cell walls in sludge by applying high temperature. Thermal treatment is integrated in the sludge treatment units with the aim to decrease sludge production, improve biogas production in anaerobic digesters, obtain pathogen inactivation and improve sludge dewaterability.Various temperatures, ranging from 60 to 270 ^{0}C have been investigated in literature. It was shown that, temperatures above 100 ^{0}C, treatment temperature is more important than treatment time. On the other hand, temperatures above 180 ^{0}C cause the production of persistent soluble organics or toxic/inhibitory intermediates; therefore it leads to reduce the biodegradability. Low temperature thermal treatment (below 100 ^{0}C) has been indicated as an effective treatment for improving biogas production for both primary and secondary sludge. Treatment time takes more dominant role than treatment temperature at low temperatures (Appels et al., 2010). The results of some recently published studies are shown in Table 2.2. Microwave disintegration, which is one of thermal disintegration methods, is used on this thesis. So, microwave disintegration is covered with more detail instead of describing all thermal disintegration methods.

2.5.4.1 Microwave Disintegration

Any electromagnetic radiation in the microwave frequency range from 300 MHz to 300 GHz is called as microwave radiation. For example, microwave ovens that are used in domestic and industrial applications generally operate at a frequency of 2.45 GHz. However, microwave can not heat all materials directly. According to microwave permeability, materials can be classified into three groups; conductors, insulators and absorbers. This classification is also illustrated in Figure 2.6. Materials that absorb microwave radiation are called dielectrics (Jones et al., 2002). Dielectrics have two important properties and these are;

- Very few charge carriers exist in dielectrics. Little charge carried through the material when an external electric field is applied.
- The molecules or atoms of the dielectric exhibit a dipole movement.

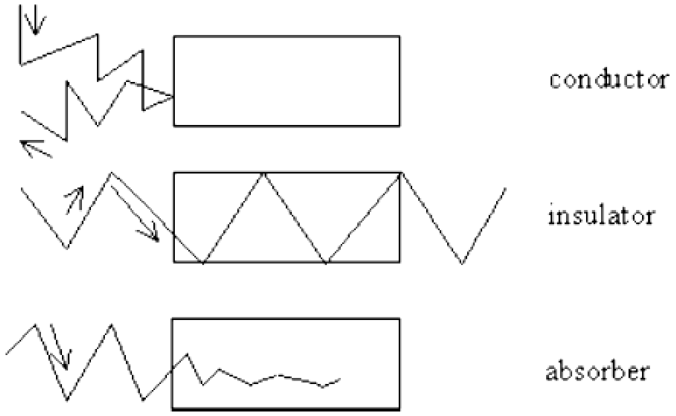


Figure 2.6. Microwave absorption characteristics for conductor, insulator and absorber.

The importance of dipole movement of dielectrics can be better described with defining dipole term. A dipole is two charges which have equal magnitude and opposite signs, separated by a finite distance. When an external electric field is applied to a dielectric material, distortion of the electron cloud around molecules or atoms induce a temporary dipole movement. This dipole movement generates friction inside the dielectric. Afterwards, the energy is dissipated as heat form. Because of dielectric properties of a material are changed with temperature, density, moisture content and material geometry, some regions of material are produced higher energy when standing waves are passed through the material (Jones et al., 2002). Sewage sludge, which has dielectric properties and high water content, is an absorber that microwave irradiation can be applied on (Wojciechowska, 2005).

The advantages of microwave radiation are rapid heating, ease of control, pathogen destruction and low cost. Destruction of pathogens is occurred due to thermal effects of microwaves. Because of these advantages, microwaves are used in many applications such as decomposition of organic materials, sterilization of medical waste and inactivation of microorganisms (Ahna et al., 2009).

There are many applications of microwave irridiation in environmental engineering. Usually preferred areas can be explained as contaminated soil remediation, waste processing, minerals processing, activated carbon regeneration, contaminated soil vitrification, treatment and recovery of volatile organic compounds (VOC), waste sludge processing (Jones et al., 2002).

Various studies are given in the literature based on the effects of MW technique in sludge-handling processes (Beszedes et al., 2011). Eskicioglu et al. (2009) studied the effect of inoculum acclimation on methane production. In their study, mesophilic conditions was applied to microwave disintegrated of thickened waste activated sludge (TWAS). Microwave pretreatment was used between 50 and 175^0C. According to results methane production was improved and soluble to total chemical oxygen demand (SCOD/TCOD) ratios increased from 9±1 (control) to 24 ± 3, 28 ± 1 and 35 ± 1% at 120, 150 and 175^0C, respectively. Biological Methane Potential (BMP) tests showed that at 175 ^{0}C, biogas efficiency was 31± 6% higher than control after 18 d of digestion inspite of acute inhibition in the first 9 days. It's also mentioned that acclimization of inoculum did not only speed up biogas production and also biodegradation of disintegrated sludge was increased.

Toreci et al. (2009) investigated the effect of microwave pretreatment at high temperature (175 ^{0}C) and microwave intensity to waste activated sludge. In their study, single and dual stage semi continuous mesophilic anaerobic digesters were used at different sludge retention times (SRTs) (5, 10 and 20 days). At low SRTs (5 and 10 days), MW pretreatment had same effect like the other sludge stabilization techniques. It was mentioned that MW pretreatment had a negative effect on digestion at low SRTs and this had been proved by lowering MW intensity. It was also stated that single stage digesters with MW pretreatment had better performance than dual-stage digesters.

Qiang et al. (2009) studied the effect of MW irradiation on sludge dewaterability. To evaluate sludge dewaterability, capillary suction time (CST) and specific resistance of filtration (SRF) were used. To explain the changes in sludge dewaterability soluable chemical oxygen demand (SCOD), extracellular polymeric substance content (EPS) and sludge particle size were determined. Results showed that at short time period, microwave application slightly improved the sludge dewaterability. But, when microwave was applied at long time period, sludge dewaterability was significantly worsen. Experiments showed that maximum sludge dewaterability was achieved at 900 W and 60 s by generating sludge with optimal disintegration (1.5–2%), EPS concentration (1500–2000 mg/L) and particle size distribution (120–140 µm).

Qiang et al. (2010) investigated the physical and chemical properties of the waste activated sludge after microwave pretreatment at optimal result of microwave irradiation with 900 W and 60 s. Their results showed that, the energy and contact time of microwave irradiation had significant effect on physical and chemical properties of sludge. Supernatant turbidity, soluabilization of volatile suspended solids, EPS and SCOD were increased with contact time and this was proportional to microwave application. It was mentioned that microwave disintegration did not only change the physical and chemical properties of sludge, it had also improved sludge stabilization.

2.5.5 Thermochemical Disintegration

Penaud et al. (1999) examined different NaOH doses of alkaline pretreatment. This study showed that COD solubilization achieved 63% when 4.6 g NaOH/L was implemented. When doses exceed 4.6 g NaOH/L, COD solubilization increased slowly. Biodegradability rates increased from 22 to 58%, while the highest biodegradability rates were obtained with the alkaline doses of 4-5 g NaOH/L. However, when the applied dose was 26.1 g NaOH/L, biodegradability rate was under 5%. It was the the inhibition of the system because of the large amounts of chemicals. Also, alkaline pretreatment were combined with thermal pretreatment at 140°C for 30 minutes. While alkaline dose was under 5 g NaOH/L, biodegradability rates were higher for the heated samples.

Neyens et al. (2003) studied on alkaline thermal hydrolysis to a lesser extent. According to this research by comparing the effect of monovalent/divalent cations of K^+/Na^+ and Ca^{2+}/Mg^{2+} on the sludge dewaterability, only using Ca^{2+} gived the best results. So, to improve dewaterability while reducing the sludge amount $Ca(OH)_2$ was used. Results showed that at 100 °C; at pH ≈ 10 and 60 min. reaction time, nearly all of the pathogens are removed. At these conditions, capillary suction time (CST) was decreased from 34 to 22 s and the amount of DS was reduced to 60% of the initial amount.

Vlyssides et al. (2004) investigated the solubilization of waste activated sludge under a medium range temperature (50-90°C) and pH in the alkaline region (8-11) for a pretreatment stage of anaerobic digestion. This study was derived a linear polynomial hydrolysis model between the hydrolysis rate coefficient, pH and temperature by comparing the experimental findings. The results showed that at temperature 90°C and a pH 11, the concentration of the VSS was 6.82% and the VSS reduction was 45% after ten hours. During this period, soluable COD was 70000 mg/l and the total efficiency for methane production is 0.28 L/g of VSS loading.

Liu et al. (2008) investigated various treatment methods for determining solubilization and acidification of waste activated sludge such as thermo-acid, thermo-alkaline, ultrasonic-alkaline, ultrasonic-acid. Their results show that thermo-alkaline significantly improved the solubilization of WAS at high concentration 7.4%. Thermo-alkaline pretreatment also improved the efficiency of WAS acidification. The ratio of VS to total volatile fatty acids (TVFAs) was 0.230. The experimental results also showed that thermo-alkaline and ultrasonic-alkaline had similar results for solubilization and acidification of WAS.

Dogan et al. (2009) studied on combined alkaline and microwave pretreatment of waste activated sludge. In their research, MW irradiation was used at 160°C and NaOH was used as an alkaline material. The results showed that soluable COD to total COD ratio (SCOD/TCOD) of WAS increased from 0.005 (control) to 0.18, 0.27, 0.34 and 0.37 for combined methods of MW and pH 10, 11, 12 and 12.5 respectively. This study was also showed that dewaterability was also increased by combining microwave irradiation and alkaline pretreatment.

Wang et al. (2009) investigated the effect of H_2O_2 dosing on sludge pretreatment by advanced oxidation process (AOP) of microwave by using the break down mechanism of H_2O_2 into water and molecular oxygen by catalase in waste activated sludge via batch experiments. Results showed that at temperature 80°C higher H_20_2 dosing ratio increased the SCOD and total organic carbon (TOC) releasing into supernatant. According to H_2O_2/TCOD ratios of 0.1, 0.5, 1, 2, 4, the percentages of consumed H_2O_2 in the AOP of microwave and H_2O_2 treating WAS were 25.38%, 22.53%, 14.82% and 13.61% respectively.

Yu et al 2010, studied the microwave enhanced oxidation process (MW/H_2O_2-AOP) for treating municipal sewage sludge for determining solids disintegration, pathogen destruction, nutrient solubilization and regrowth. After sludge was treated at 70 °C with more than 0.04% H_2O_2 pathogen destruction was found (1000 CFU/L) in terms of fecal coliform concentrations. After 72 hours of treatment, significant regrowth of fecal coliforms was observed. But, at the same temperature if H_2O_2 rate was reached 0.08% of higer, no growth was observed. This investigation was also showed that soluable chemical oxygen demand increased with an increase of hydrogen peroxide dosage at 70 °C.

CHAPTER THREE
MATERIALS & METHODS

3.1 Sludge Properties

During this research waste activated sludge (WAS) was periodically taken from the return line of secondary sedimentation tank of Güneybatı Wastewater Treatment Plant located in Izmir City, Turkey, which is advanced biological treatment plant with a flow capacity of 21.600 m^3/day.

Inoculum sludge used in BMP Assay, batch reactors and the start-up of the semi-continuous reactors, was taken from the yeast industry, Pakmaya WWTP Inc., Izmir. The properties of inoculum sludge and activated sludge are given in Table 3.1.

Table 3.1 The properties of inoculum sludge and activated sludge.

Parameters	Activated Sludge	Inoculum Sludge
pH	7.05 ± 0.1	7.93 ± 0.12
EC (mS / cm)	8.87 ± 0.12	25.3 ±0. 2
ORP (mV)	35 ± 2	-451 ± 3
TS (%)	0.78 ± 0.01	12.08 ± 0.11
VS (%)	49.87 ± 0.35	34.25 ± 0.25
SS (mg/L)	5333 ± 47	9680
VSS (mg/L)	3753 ± 127	11533,3
SCOD (mg/L)	320	5400
TN (%)	3.26	5.38
TP (mg/kg)	1198	3470
CST (s)	25.7 ± 2.3	535.8± 2.1

3.2 Central Composite Design

In this thesis, in order to obtain the optimized conditions (time and temperature parameters) central composite design was used for microwave pretreatment. Central composite design is an experimental method that is useful in response surface methodology, for building a quadratic model for the response variable. Design Expert 8 from Stat-Ease Inc. was used to realize this design. Response function coefficients were calculated for each independent variable from experimental data by iteration. The response function of the system was;

$$E = k_0 + k_1A + k_2B + k_{12}AB + k_{11}A^2 + k_{22}B^2 \qquad \text{(Eq. 1)}$$

Where;

E is the predicted response function,
A and B are independent variables,
k_0 is the constant,
k_1 and k_2 are the linear coefficients,
k_{12} is the cross product coefficient,
k_{11} and k_{22} are the quadratic coefficients.

3.3 Sludge Disintegration Methods

3.3.1 Microwave Pretreatment

Microwave irradiation was achieved with Berghof, MWS-4 Microwave System. MWS-4 has a maximum power of 2300 W. Microwave power output is 1450 W with the frequency of 2450 MHz. Operating temperature range is 80 – 300 °C. Pressure measurement range is 0 – 150 bar. 12 teflon vessels with a capacity of 60 mL was used for the operation. Temperature in the vessels was recorded by the infrared radiation of the samples and it was displayed on the digital screen of MWS-4 in every 15 seconds. Figure 3.1 shows microwave system and teflon vessels.

Figure 3.1 (a) MWS-4 (b) Teflon vessels.

According to the central composite design results, different temperature and time parameters were applied to microwave system. Microwave irridation was performed alone 35 mL waste activated sludge (WAS) in each vessel with a total 420 mL of sludge for disintegration. At the end of operation according to the disintegration degree (%DD) result, time and temperature results were applied to BMP assays, batch and semi-continuous reactors as optimum parameters.

3.3.2 Alkaline Pretreatment

The purpose was to examine alkaline pretreatment of waste activated sludge (WAS) at pH 8, 9, 10, 11, 12 and 12.5 to determine the optimum pH value. 420 mL waste activated sludge (WAS) was filled in a glass beaker and 1 N NaOH was added into beaker until pH 8 was obtained. Then sample was mixed with a magnetic stirrer for half an hour at 100 rpm for homogenous distribution of alkaline agent. This operation was repeated separately for each pH values that are mentioned above to obtain the optimum pH for disintegration. Figure 3.2 illustrates the mechanism that used for alkaline disintegration.

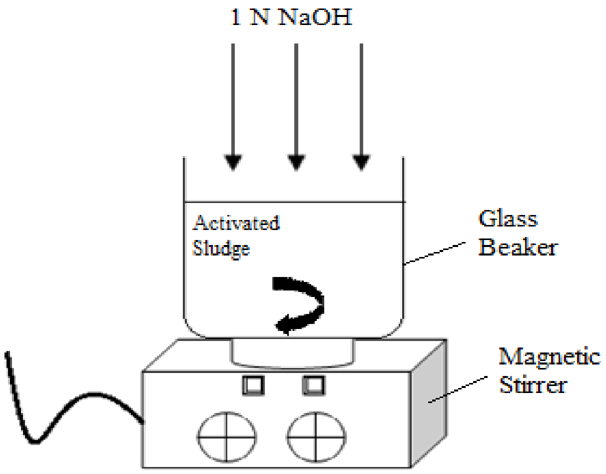


Figure 3.2 Illustration of alkaline pretreatment equipment.

3.3.3 Thermochemical Pretreatment

For the combined system of microwave and alkali treatment; chosen optimum pH value was applied to 420 mL sludge filled in a glass beaker and stirred for half an hour. Then this sample was put into vessels and microwave irridation was applied at optimum time and temperature values. After co-treatment application BMP tests were done in triplicate.

3.4 Anaerobic Batch Studies

3.4.1 Biochemical Methane Potential (BMP) Assay

In order to see the effect of microwave, alkaline and thermochemical pretreatment methods on anaerobic biodegradability, biochemical methane production (BMP) assay was applied (Owen et al., 1979). To make a comparison, BMP test was applied to both raw and disintegrated sludge samples. For this test, 1/1 ratio (as volume) of samples and inoculum was added to a 250 mL bottle. To provide an optimum anaerobic microbial growth, basal medium (Speece, 1996), which contained all the necessary micro and macronutrients, was added to bottle with the ratio of 20% of working volume (120 mL). Table 3.2 shows basal medium components used in this study.

Table 3.2 Basal medium components.

0.3 g/L Na_2S	0.05 g/L $CaCl_2$
0.4 g/L $MgSO_4$	0.4 g/L KCl
0.08 g/L $(NH_4)_2HPO_4$	0.4 g/L NH_4Cl
0.04 g/L $FeCl_2$	0.01 g/L $CoCl_2$
0.01 g/L KI	0.01 g/L $Na(PO_3)_6$
0.5 mg/L $MnCl_2$	0.5 mg/L $AlCl_3$
0.5 mg/L $ZnCl_2$	0.5 mg/L NH_4VO_3
0.5 mg/L $CuCl_2$	0.5 mg/L H_3BO_3
0.5 mg/L $NaWO_4$	0.5 mg/L $NiCl_2$
0.5 mg/L Na_2SeO	0.5 mg/L $NaMoO_4$
0.01 g/L sistein	

All bottles were cleaned with a gas mixture of 75% N_2 and 25% CO_2 for 5 minutes to supply anaerobic conditions before BMP test. After contaminants are added, bottles are also capped with silicone stopper and siliconized with silicone gun to protect anaerobic medium. Then, the serum bottles were heated constantly at 37±1 ◦C in an incubator. Methane gas productions were measured daily by using liquid displacement method that contains 3% NaOH (w/v) distilled water (Razo Flores et al., 1997). BMP assays were run for 35 days. The experiments were done in triplicate. Figure 3.3 shows incubator and bottles that used for BMP assays in the incubated medium.

Figure 3.3 BMP Assays in the incubated medium and a view of incubator

3.4.2 Anaerobic Batch Reactors

For this study, reactors were specially made of pyrex-glass with a total volume of 3 L. Sample volume was set to 2.3 L and volumes of sludge samples are determined according to this volume. By using BMP results, batch reactors were operated with 50% and 75% microwave pretreated sludge in comparison with control reactors. For each ratio of microwave pretreated sludge, batch reactors were operated during 30 days. Similar to BMP assay, 1/1 ratio (as volume) of samples and inoculums were used with basal medium components which was 20% of the working volume (2.3 L). Before operating reactors, gas mixture of 75% N_2 and 25% CO_2 were applied during 5 minutes for removing oxygen from the reactors. As shown in Figure 3.4, reactors were capped with silicon stopper and siliconized to supply anaerobic conditions. During the operation, reactors were shaked regularly and heated constantly at 37±1 ◦C and methane gas productions were measured daily. Liquid displacement method by using 3% NaOH (w/v) containing distilled water was used for gas measurement

(Razo-Flores et al., 1997). Analyzes were done by taking sample from reactor for every 5 day of the operation period. View of pyrex glass reactors is shown in Figure 3.4.

Figure 3.4 View of pyrex-glass reactors.

3.5 Anaerobic Semi-continuous Reactors

Two pilot scale anaerobic reactors with 8.5 L each volume were used for anaerobic semi-continuous studies. The reactors were made from stainless-steel and controlled by PLC. Major control parameters of PLC were temperature and mixer motors. Mechanical mixers were used for stirring the reactors and heating of reactors was obtained by thermostats. The reactors were operated at 37 ± 2 °C under mesophilic conditions and temperature was provided constantly by heat transfer oil jacket. Figure 3.5 shows the reactors that were used in the semi-continous anaerobic digestion experiment.

At start-up phase inoculum sludge, which was provided from yeast industry of Pakmaya WWTP Inc. Izmir, was fed to the anaerobic reactors. Two anaerobic reactors were fed with 7 L of inoculums sludge and sludge was withdrawn each day till ½ volume of the reactor and the same amount of waste activated sludge was fed to the reactors step by step. During the operation, sludge retention times were selected as 15 days. According to selected sludge retention time, daily withdrawn and feed amount of sludge was calculated and applied as 0.47 L.

Figure 3.5 Illustration of anaerobic semi-continuous reactors

Control reactor was operated with raw sludge in parallel for the comparison of the reactor that was fed with disintegrated sludge at optimum conditions in order to observe the effect of pretreatment on anaerobic sludge digestion. Optimum disintegration conditions were determined before anaerobic semi-continuous digestion study.

3.6 Analytical Methods

After pretreatment application, for the specification of disintegration performance of sludge, total solids (TS), volatile solids (VS), suspended solids (SS), volatile suspended solids (VSS), chemical oxygen demand (COD), total nitrogen (TN), total phosphorus (TP), particle size distribution were analyzed. To see the effect of disintegration processes on supernatant characteristics of sludge, soluble chemical oxygen demand (SCOD) was analyzed for the calculation of “disintegration degree, DD” parameter.

For system assessments of anaerobic semi-continuous digester, pH, and temperature (T^0C) were monitored daily while alkalinity, VFA and redox potential (ORP) values were measured regularly during the operation. Also, for batch system these parameters were measured for every five day during the operation period of 30 days.

In order to control the performance of anaerobic batch and semi-continuous digesters, total solids (TS), volatile solids (VS), suspended solids (SS), volatile suspended solids (VSS), chemical oxygen demand (COD), soluble chemical oxygen demand (SCOD), particle size distribution, total nitrogen (TN), total phosphorus (TP) were analyzed. Daily total gas and methane gas were measured during the operation period.

Capillary suction time (CST) test was examined to observe dewatering characteristics of disintegrated sludge and anaerobically digested sludges.

Generally all of the measurements in this study were done in triplicate for calculating the standart deviation. All analyses were regularly done according to Standard Methods (APHA, 2005).

3.6.1 Disintegration Degree

After the application of disintegration process, for definition of disintegration efficiency “disintegration degree, DD” parameter which is developed by Muller (2000), can be thought as the main parameter. High disintegration degree is proportional to the high DD values. Disintegration degree is calculated using following equation.

$$DD = [(COD_1 - COD_2) / (COD_3 - COD_2)].\ 100 \qquad \text{(Eq. 2)}$$

Where;

COD_1 is COD sludge's supernatant concentration after disintegration application,

COD_2 is COD sludge's supernatant concentration before disintegration,

COD_3 is COD sludge's supernatant concentration after chemical disintegration

Chemical disintegration is processed the sludge at 90 °C for 10 minutes after the addition of NaOH. Sludge's supernatant was obtained with centrifugation and centrifugation is carried out at 10 000 rpm, and 4°C for 20 min.

3.6.2 Total Solid (TS), Volatile Solid (VS), Suspended Solid (SS) and Volatile Suspended Solid (VSS) Analysis

TS was done according to Method 2540B (APHA, 2005) and VS was done according to Method 2540E (APHA, 2005). For the measurement of total solids and suspended solids of sludge samples, an oven Nuve FN 400 model was used. For the volatile solids and volatile suspended solids measurements of sludges a muffleoven Nuve brand MF 120 model was used at 550 ^{o}C temperature. Glass-fiber filter was used for SS and VSS measurements according to Standart Methods. Nuve FN 400 model oven and Nuve MF 120 muffle oven are shown in Figure 3. 6.

(a) (b)

Figure 3.6 (a) Nuve FN 400 model oven (b) Nuve MF 120 muffle oven

3.6.3 TCOD and SCOD Analysis

TCOD and SCOD parameters were analyzed by using Open Reflux Method. For SCOD measurements, sludge samples were centrifuged for 20 minutes at 10000 rpm with 5804 R Eppendorf Centrifuge and supernatants were analyzed for SCOD. TCOD samples were diluted 1/40 with pure water and SCOD samples were diluted to 1/20 with pure water before analysis. Figure 3.7 shows the centrifuge and boiling stove.

Figure 3.7 Illustration of centrifuge and boiling stove

3.6.4 pH, ORP and EC Measurements

pH, oxidation reduction potential (ORP) and electrical conductivity (EC) values were measured by WTW model 340i multi analyzer. This analyzer is shown in Figure 3.8.

Figure 3.8 View of WTW model 340i multi analyzer

3.6.5 Particle Size Analysis

Particle size distributions were monitored using a Malvern Mastersizer 2000QM analyzer. Figure 3.9 illustrates the analyzer.

Figure 3.9 Particle size analyzer

3.6.6 Volatile Fatty Acid (VFA) and Alkalinity Analysis

For the assessment of batch and semi-continuous systems, VFA and Alkalinity were analyzed by using titrimetric methods regularly. According to Buchaer (1998) method, for the determination of VFA values, samples were filtered through a 0.45 µm membrane filter. Alkalinity values were calculated using following equation.

$$\text{Total Alkalinity (mg/L } CaCO_3\text{)} = (T*N*50000)/V \qquad \text{(Eq.3)}$$

Where;

T= consumption of H_2SO_4 until pH of sample is equal to 4.5, mL
N= normality of H_2SO_4
V= volume of sample, mL.

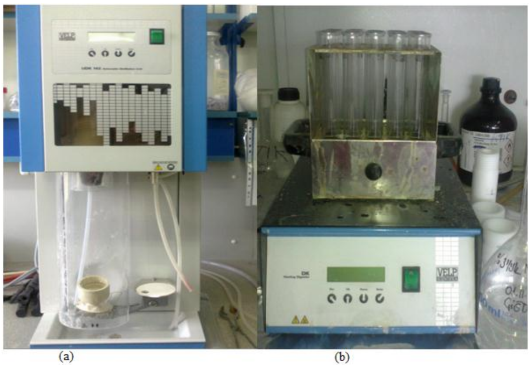
3.6.7 DOC Analysis

For DOC concentration measurements a Hach Lange, IL 550 TOC-TN analyzer was used that shown in Figure 3.10. For this measurement, sludge was centrifugated at 10000 rpm for 20 minutes to obtaine the dissolved part of sludge samples. Sludge samples were diluted to 1/40 with pure water before analysis.

Figure 3.10 View of Hach Lange IL 550 TOC-TN analyzer

3.6.8 Total Nitrogen (TN) and Total Phosphorus (PO4 – P) Analysis

In disintegration period, for determination of total nitrogen (TN) Micro-Kjheldal method was used.Velp DK heating digester was used for sludge sample’s digestion. For distillation part of the experiment Velp UDK 142 distillation unit was used. 0.02 N H_2SO_4 was used in the titration part. Figure 3.11 shows the digester and distillation units for determination of total nitrogen (TN).



(a) (b)

Figure 3.11 (a) distillation unit (b) heating digester.

Total phosphorus (PO4 – P) experiment was done according to Stannous Chloride Method 4500 P-D (APHA, 2005). Also Perkin ELMER LAMBDA 25 UV/VIS spectrophotometer was used at 690 nm.

Figure 3.12 View of spectrophotometer

In the digestion period, Total nitrogen (TN, #14537) and total phosphorus (PO4-P, #00616) were analyzed. NOVA 60 photometer was used for photometric measurements. By centrifuging of sludge samples at 10000 rpm during 20 minutes, sludge's supernatant was obtained for TN and TP analysis.

3.6.9 Measurement of Methane and Total Gas Produced

Total and methane gas productions of the anaerobic batch reactors were done by liquid displacement method that gas passes through distilled water containing 2%(v/v) H_2SO_4 and 10% (w/v) NaCl for total gas and 3%(w/v) NaOH for methane. This method was also applied for semi-continuous reactors’ gas measurements. Figures 3.13 and 3.14 show the gas measuring system used in the study.

Figure 3.13 Gas measuring system for semi-continuous reactors.

Figure 3.14 Gas measuring system for batch reactors.

3.6.10 Capillary Suction Time (CST)

For the determination of dewaterability properties of sludge samples capillary suction time (CST) test was applied. The purpose of CST test in the disintegration process was to examine breaking up the floc structure of sludge and observing the dewaterability properties of pretreated and non-pretreated sludges. CST tests were also examined after anaerobic batch and semi-continuous reactors.

During this study, CST values were measured using a Triton 304 M CST-meter that shown in Figure 3.15. Sludge sample was placed in a small cylinder that has 1.8 cm diameter of the instrument on a Whatman #17 filter paper sheet. A digital display that indicates the time for liquid displacement exists in CST- meter. When liquid travel time is shorter,it means that sludge dewaterability is better. For this experiment, all CST measurements were done in triplicates.

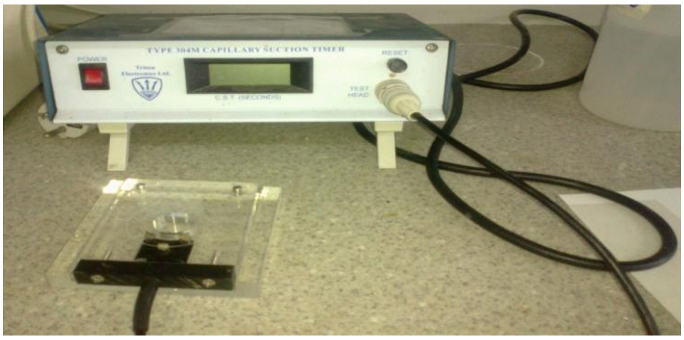


Figure 3.15 View of Triton 304 M CST-meter

CHAPTER FOUR
RESULTS & DISCUSSION

4.1 Optimization Studies

4.1.1 Optimization Study of Microwave Irradiation

For the optimization step of Microwave Irradiation, Central Composite Design method was applied to see the effect of microwave irradiation on sludge cell distruption. By using Central Composite Design method; minimum, maximum and central points of experimental parameters (Table 4.2) are arranged with the help of the coded form given in Table 4.1.

According to the Central Composite Design study, experimental data were achieved with studying at the 11 different experimental points that consist of four axial, factorial and three central points. When minimum (-1) and maximum (+1) points data were entered into the Design Expert8 programme, -α, + α and central (0) values were given by circumscribed type model of Central Composite Design. Alpha (α) value was chosen as orthogonal quadratic and this value, which was calculated by programme, was equal to 1.14744.

Table 4.1 coded forms of experimental points

Experimental no	**A**	**B**
1(axial)	-1	-1
2(axial)	-1	+1
3(axial)	+1	-1
4(axial)	+1	+1
5(factorial)	- α	0
6(factorial)	+ α	0
7(factorial)	0	- α
8(factorial)	0	+ α
9(central)	0	0
10(central)	0	0
11(central)	0	0

Temperature and time parameters were chosen like the important factors and appointed as A and B, respectively. Temperature (A) varied between 90 and 150 ^{0}C, and time (B) was ranged between 10 and 40 minutes. Minimum values were 85.58 ^{0}C and 7.79 minutes. Maximum values were 154.42 ^{0}C and 42.21 minutes. Central ones were given as 120 ^{0}C and 25 minutes. Results were similar with the study of Hu et al, (2009).

Table 4.2 Experimental data points regarding the temperature (A) and time (B).

Experimental no	**A (Temperature,^{O}C)**	**B (Time, minute)**
1(axial)	90	10
2(axial)	90	40
3(axial)	150	10
4(axial)	150	40
5(factorial)	85.58	25
6(factorial)	154.42	25
7(factorial)	120	7.79
8(factorial)	120	42.21
9(central)	120	25
10(central)	120	25
11(central)	120	25

Disintegration Degree (DD) parameter was chosen as response function for the optimization study to see the Mirowave Irradiation effect on sludge distruption.

Final equation of actual factors (temperature and time) was given as;

$$DD = +38.70214 -1.02231*Temp.+1.20522* Time+0.017094*Temp.* Time+6.11996E-003* Temp.^2-0.053419* Time^2 \quad \text{(Eq. 4)}$$

These mentioned eleven factors that mentioned in Table 4.2 were operated with microwave irradiation and as response DD (%) was calculated. Predicted disintegration degrees were obtained from response function according to the Eq.4. At this time,observed disintegration degrees were obtained from the experiment and calculated according to the Eq.2. For Microwave Irradiation, the correlation coefficient (R^2) between the observed and predicted values of DD was %94.89. Result showed that the observed and predicted values of disintegration degrees were very close. This comparision is shown in Table 4.3.

Table 4.3 Comparision of predicted and response DD (%)

Experimental no	**Predicted DD (%)**	**Response DD (%)**
1(axial)	15.38	18.36
2(axial)	26.92	20.54
3(axial)	53.84	55.40
4(axial)	96.15	88.35
5(factorial)	26.92	31.47
6(factorial)	84.61	83.90
7(factorial)	30.76	31.37
8(factorial)	34.61	38.16
9(central)	55.76	52.17
10(central)	51.92	52.17
11(central)	53.84	52.17

For the optimization of Microwave Irradiation, DD was calculated according to the Eq.4 for each point with increasing 10 ^{0}C in the range of between 90-150 ^{0}C. At the same time, that was applied for the time parameter in the range of 10-40 minutes with a 5 minutes increasing. Results are shown in Figure 4.1. According to the Figure 4.1 the optimum temperature and time were 150 ^{0}C at 35 minutes with the maximum DD of 89.54 %.

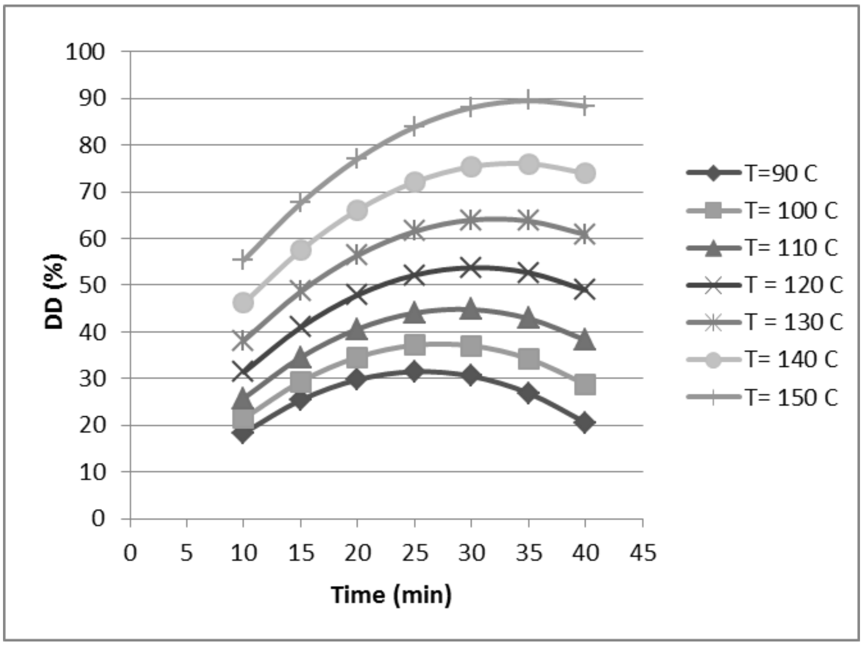


Figure 4.1. Variations of DD with different temperature parameters at different minutes.

In addition to calculation of disintegration degree, total solids (TS) and volatile solids (VS) was also evaluated to see the effect of microwave and thermochemical degradation on sludge cells. The amount of volatile solids in sludge is important for the anaerobic biodegradation. TS and VS values of sludge cake that pretreated at different temperature and time values were measured. Results are shown in Figure 4.2 and Figure 4.3.

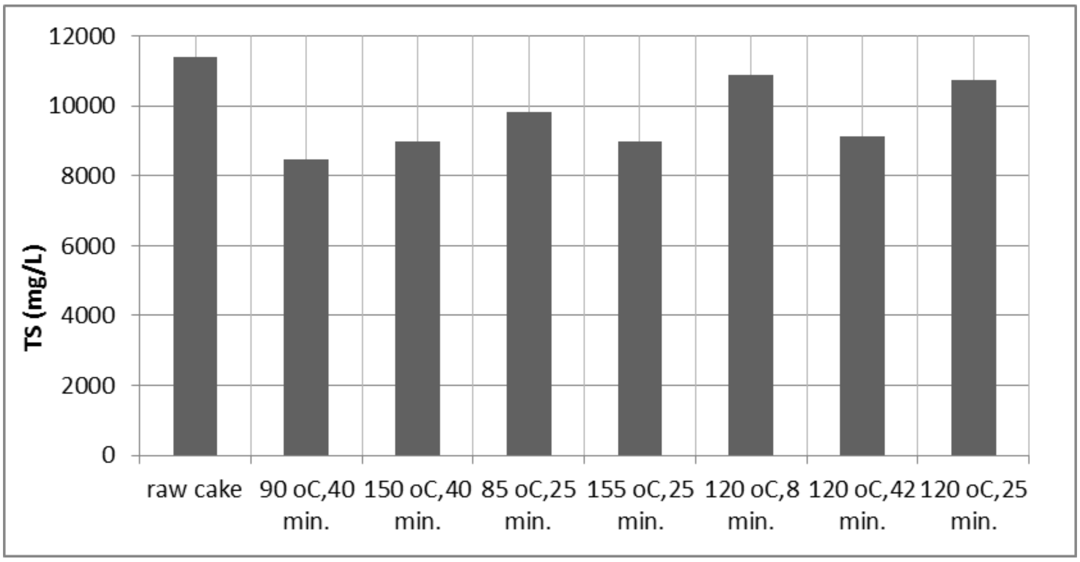


Figure 4.2. Variations of TS with different temperature and time parameters.

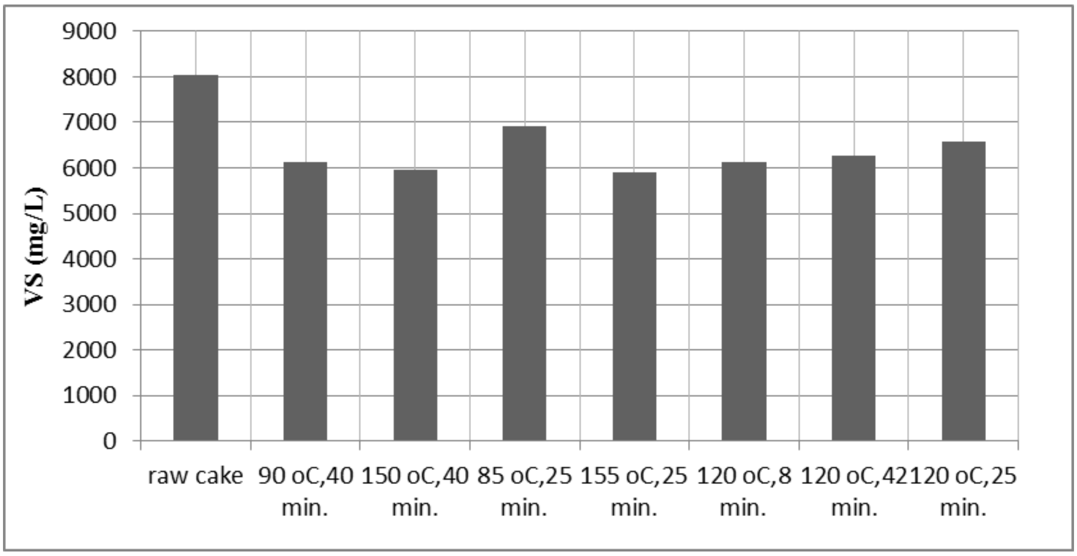


Figure 4.3. Variations of VS with different temperature and time parameters.

4.1.2 Optimization Study of Alkaline Pretreatment

pH values (8, 9, 10, 11, 12 and 12.5) were thougt as the variable parameter for alkaline disintegration and according to the Eq.2, disintegration degree (Muller, 2000) parameter were calculated based on the SCOD and thought as the main response. Figure 4.4 shows the variation of SCOD at different pHs. SCOD values were measured at given pH values.

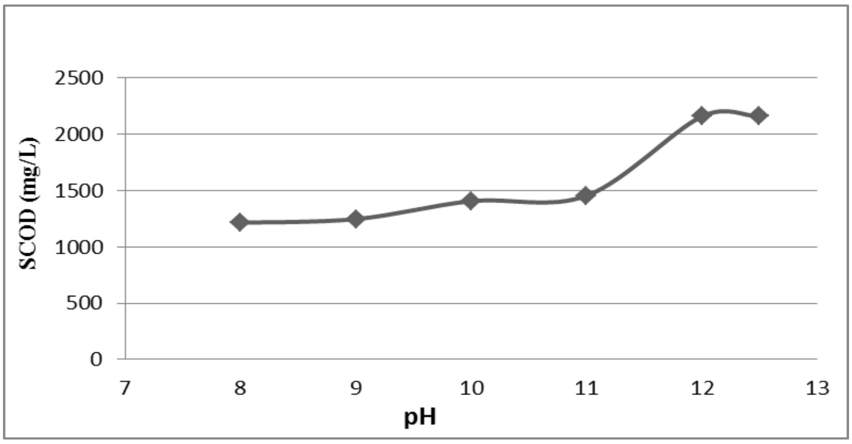


Figure 4.4. Variations of SCOD at different pH values

Figure 4.5 shows the variation of disintegration degree at different pH values. SCOD values showed the same trend with DD(%). The maximum disintegration degree of 157.81 % was obtained for pH 12. Similar results were achieved by Chen et al (2008). At pH value 12.5, DD value did not changed.

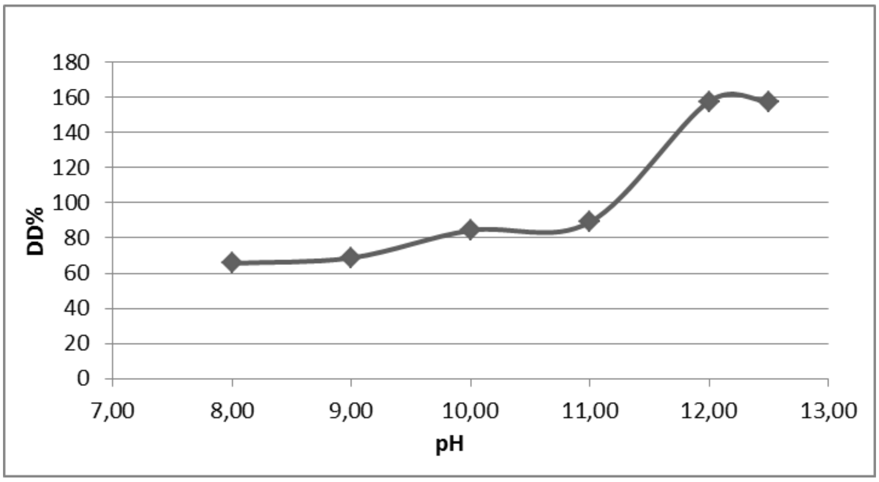


Figure 4.5 Variation of pH values with the disintegration degree.

4.1.3 Thermochemical Pretreatment Study

To see the effect of combined microwave and alkaline pretreatment study, each optimum values were applied together. Firstly pH of sludge was obtained at 12 and then optimum value of microwave irradiation (150 ^{0}C for 35 minutes) was applied to alkaline pretreated sludge.

Total nitrogen and total phosphorus were measured for raw, microwave and microwave + alkaline (thermochemical) pretreated sludge to see the effects of these methods on disintegration of biological sludge. Figure 4.6 and Figure 4.7 show the variation of total nitrogen and total phosphorus.

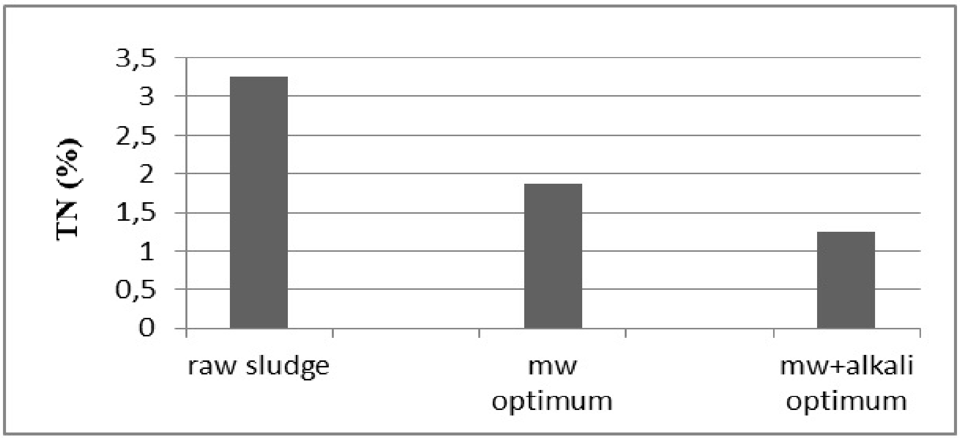


Figure 4.6 Variation of TN (%) values with disintegration methods.

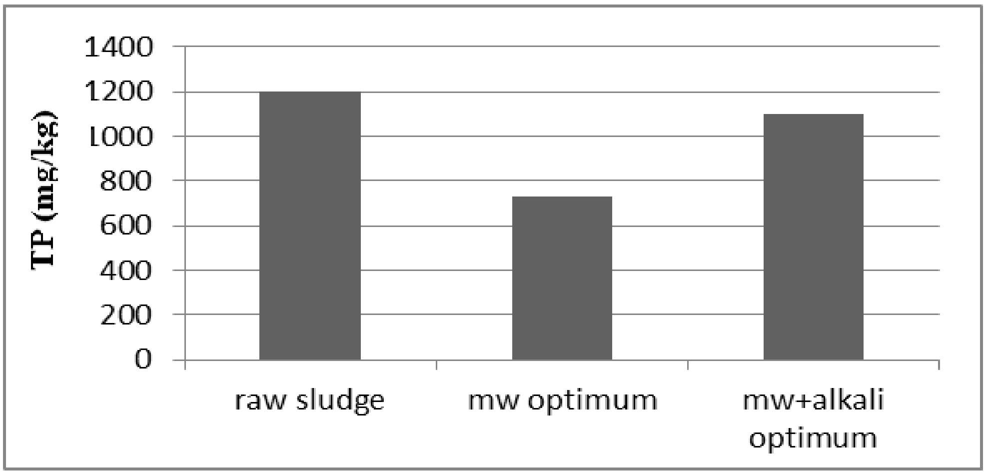


Figure 4.7 Variation of TP (%) values with disintegration methods.

A particle size distribution in sludge after microwave and microwave + alkaline (thermochemical) pre-treatment at optimum points was used as another response to see the floc disintegration effect of these methods on sludge. In addition, the effect of microwave and thermochemical disintegration on solubilization sludge' solids was evaluated with suspended solids (SS) and volatile suspended solids (VSS) measurements. For the determination of sludge filterability characteristics of disintegrated sludge samples, CST parameter was also measured.

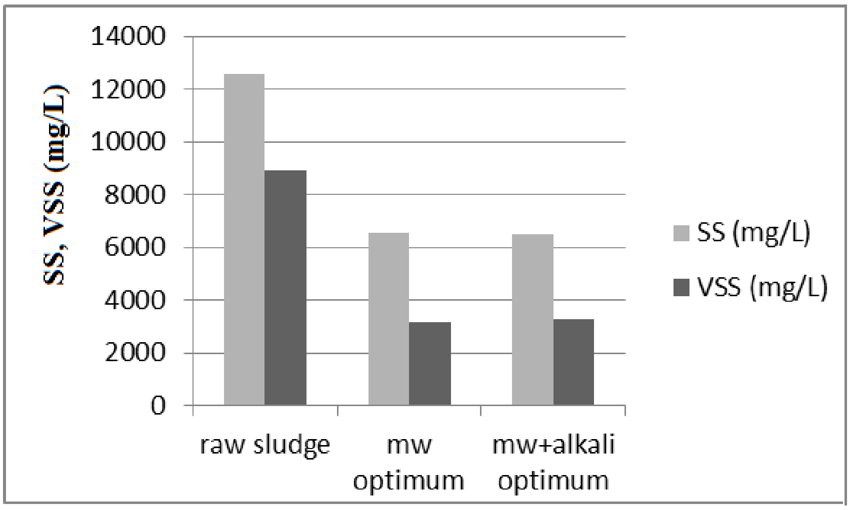


Figure 4.8 Variation of SS and VSS (mg/L) values with disintegration methods.

Figure 4.8 shows the variation between SS and VSS under each different disintegration optimum points. SS and VSS content of sludge was decreased by the disruption of the sludge flocs. SS and VSS results showed that both microwave and microwave+alkali combined pre-treatment played an important role in sludges' floc destruction.

Table 4.4 and Figure 4.9 summarize the particle size results under microwave and thermochemical disintegration experiments. Reductions in particle size were obtained in thermochemically disintegrated sludge comparing in raw sludge. Particle size reductions can be seen in Table 4.4. For thermochemical disintegration, surface weighted mean was decreased from 23.55 μm for raw sludge to 16.651 μm and this can be explained as a decrease of 29.3%. Chen et al. (2008) was reported a similar observation before. They reported decrease of 10%, 50% and 90% of the particles were below 5, 17 and 156 µm, respectively for thermochemical pre-treatment.

Table 4.4 Particle size changes with thermal and thermochemical disintegration methods.

	Particle size (µm)				
	Surface weighted mean D[3,2]	Volume weighted mean D[4,3]	d (0.1)	d (0.5)	d (0.9)
Raw sludge	23.55	59.935	14.275	49.449	121.229
Mw disintegrated sludge	33.617	117.178	21.624	73.174	286.410
Mw+Alkali disintegrated sludge	16.651	61.271	9.233	35.393	120.149

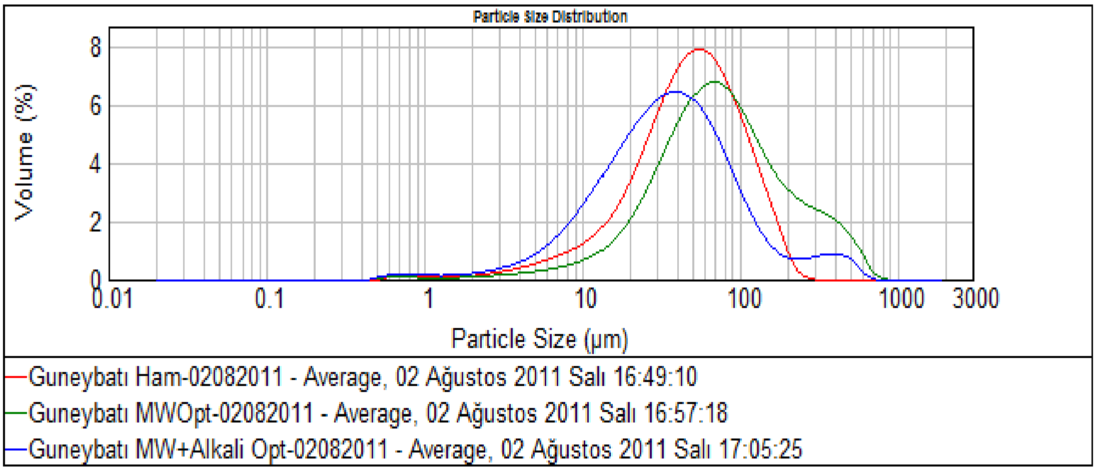


Figure 4.9 Variation of particle size values with disintegration methods.

For the determination of the filterability characteristics of sludge after pre-treatment studies, CST test was applied for each experiment. CST variations with pre-treatment studies are given in Figure 4.10. CST increased highly with the disintegration methods of microwave and combination of microwave and alkali pre-treatment. The maximum CST value was seen at disintegrated sludge with microwave irradiation at 100.13 seconds. It was seen that microwave pre-treatment deteriorates the filterability of sludge.

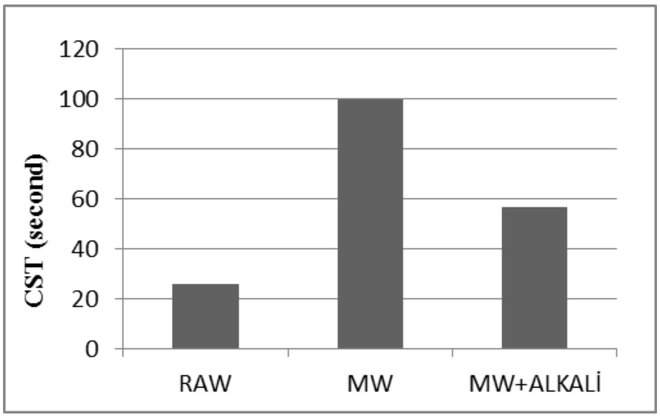


Figure 4.10 Values of CST with different disintegration methods.

4.2 Biochemical Methane Potential (BMP) Assay

In order to see the effect of microwave, and thermochemical pretreatment methods on anaerobic biodegradability, biochemical methane production (BMP) assay was applied. To make a comparison, BMP test was applied to both raw and disintegrated sludge samples at the 35 days of operation period until gas production ceased.

Figure 4.11 shows the results of cumulative methane production of pretreated sludges in comparision with control reactor. Results showed that maximum cumulative methane production was achieved for microwave pretreated sludge and microwave pre-treatment of sludge can be an alternative for improving the anaerobic digestion. Cumulative methane production of raw sludge was found as 102.30 mL, while methane production was found as 160.1 mL for microwave application. On the other hand, methane production of thermochemically pretreated sludge was lower than raw sludge and this was described as the inhibition of the system because of the large amounts of alkaline agents and was comparable to the results of Penaud et al. (1999).

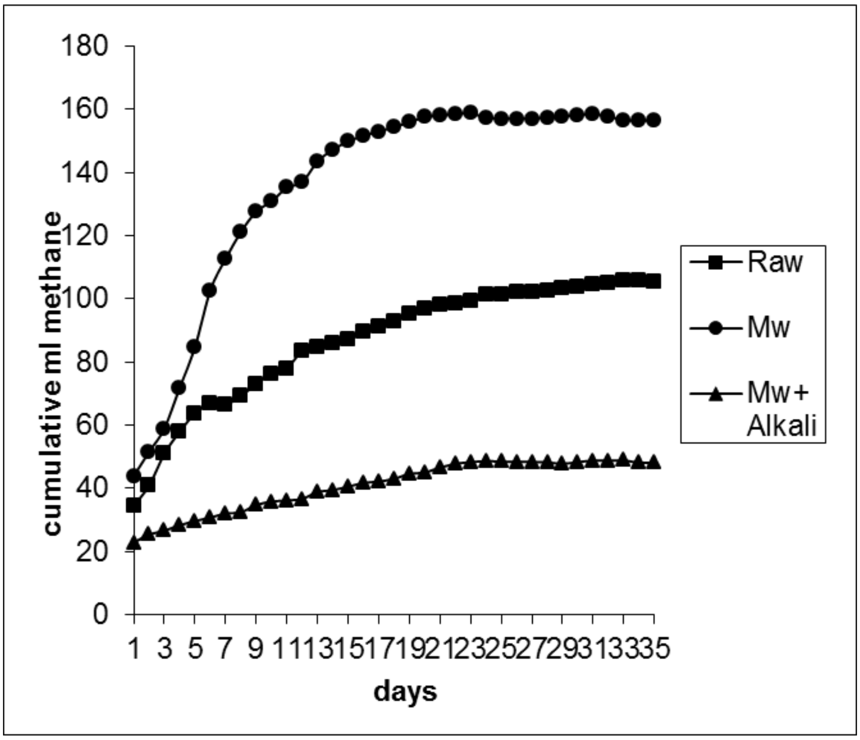


Figure 4.11 Results of BMP tests of disintegrated sludge samples.

4.3 Anaerobic Batch Reactors with Microwave Irradiation

After optimization studies, anaerobic batch digestion study were carried out according to BMP results. Because of the inhibition effect of alkaline agents, only microwave pretreatment method was selected as disintegration method. According to this decision, because of the large volume of semi-continuous rectors, SRT was obtained as 15 day of operation time and Θ was calculated as 467 ml. But, this disintegrated sludge amount was not supplied by microwace irradiation at ones and ratios for reactor feeding were approved. Because of these reasons, batch reactors were operated with 50% (coded MW (1/2)) and 75% (coded MW (3/4)) microwave pretreated sludge in comparison with control reactors. For each ratio of microwave pretreated sludge at 150 ^{0}C for 35 minutes, batch reactors were operated during 30 days with working volume (2.3 L). During the operation, reactors were heated constantly at 37±1 ^{0}C in mesophilic conditions without mixing in the incubator.

4.3.1 Batch Reactors with 50% Microwave Pre-treated Sludge

4.3.1.1 Batch Reactors' Stability

In digestion study with 50% Microwave Pretreatment, pH, temperature, alkalinity, volatile fatty acids (VFA), redox potential (ORP) and electrical conductivity (EC) values were measured regularly during the operation period for control of anaerobic digester stability.

For digester stability control, pH is an important parameter. For anaerobic biological treatment systems, optimum pH range is between 6 to 9 (Filibeli et al., 2000). pH varied from 7.05 to 7.34 in reactor contents as seen in Figure 4.12

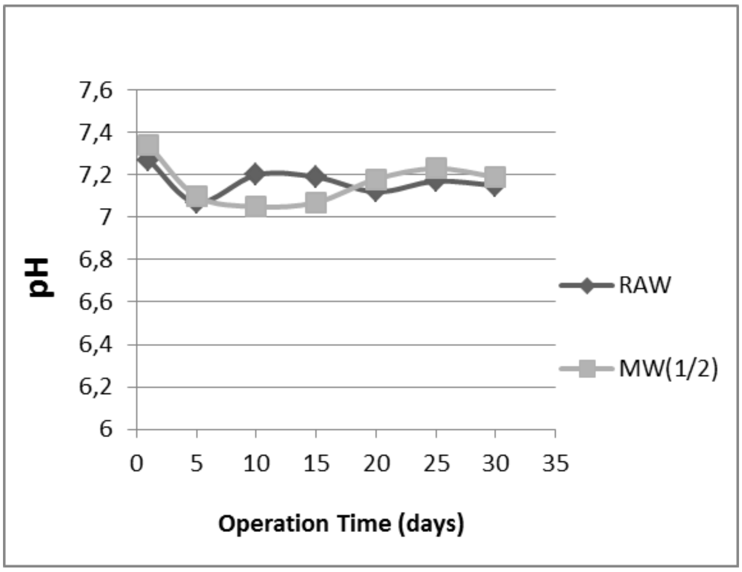


Figure 4.12 pH changes in reactors.

Oxidation Reduction Potential (ORP) in reactor was in the very negative range of –390 mV and – 470 mV and was observed as seen in Figure 4.13.

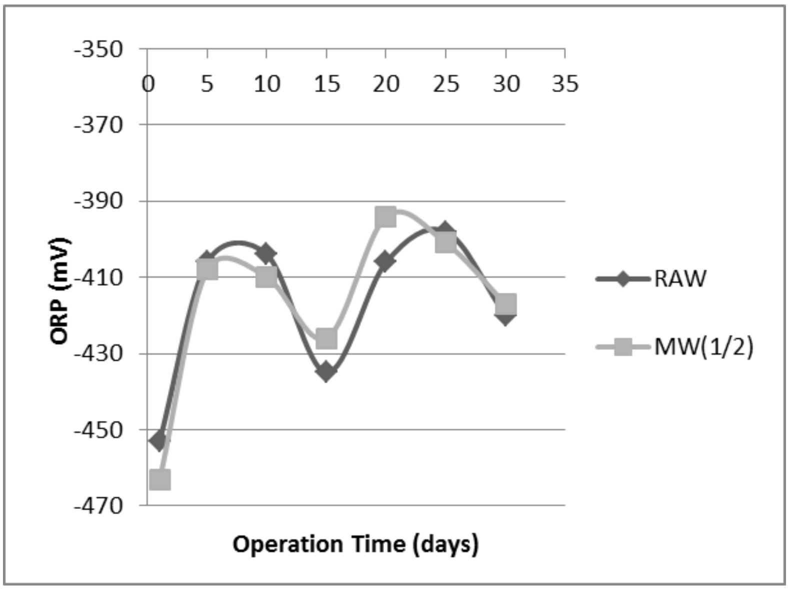


Figure 4.13 Variation of ORP values in reactors.

EC values were in the range of 17.96-19.77 mS/cm shown in Figure 4.14

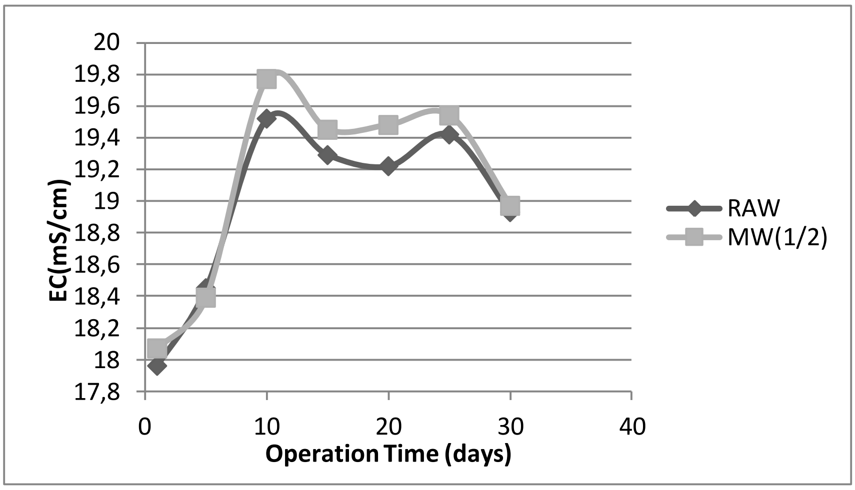


Figure 4.14 Variation of EC values in reactors.

Alkalinity is an important measurement for anaerobic digestion because it controls the pH. In anaerobic systems operate; bicarbonate alkalinity is the major interest (Speece, 1996). Total alkalinity values were measured regularly. Results of alkalinity measurements are shown in Figure 4.15. Alkalinity measurements were in the range of 2320 – 3800 mg CaCO3/L during the operation period.

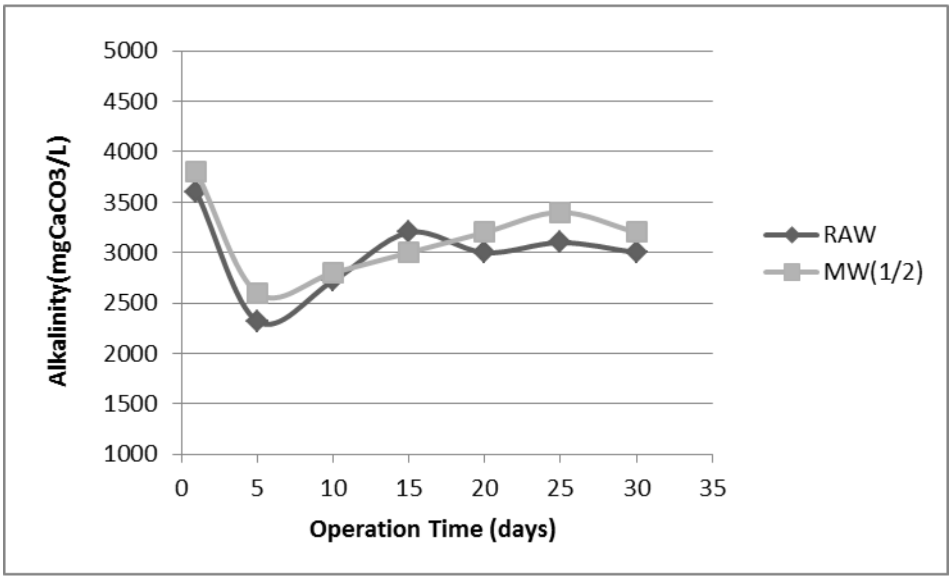


Figure 4.15 Variation of EC values in reactors.

VFA results are showed in Table 4.16. VFA values were under 1000- 1500 mg/L that is not proposed for anaerobic methanogens (Malina and Pohland, 1992).

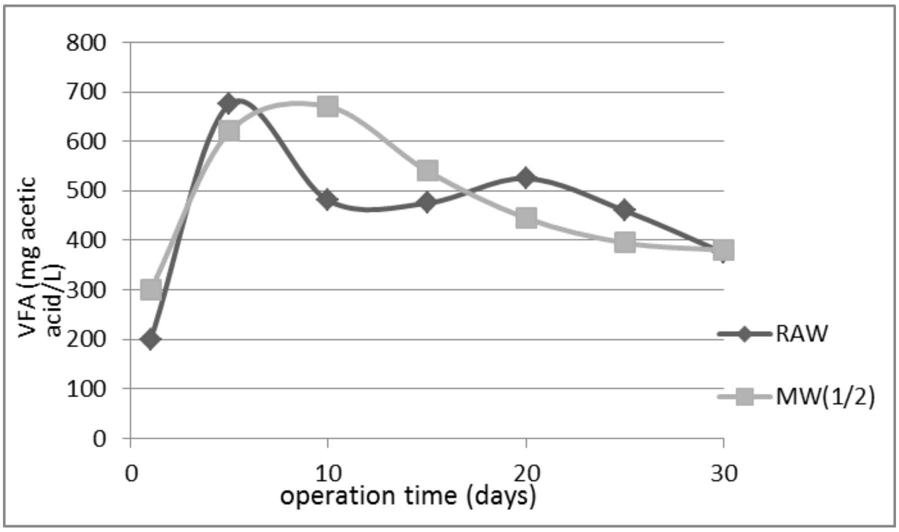


Figure 4.16 Variation of VFA values in reactors.

4.3.1.2 Anaerobic Digestion Performance of Sludge

For anaerobic digesters' performance, total solids (TS), volatile solids (VS), suspended solids (SS), volatile suspended solids (VSS), dissolved organic carbon(DOC), total oxygen demand (TCOD), soluble chemical oxygen demand (SCOD),particle size distribution, and methane gas were analyzed during the operation period.

Total solids changes in reactor contents are given in Figure 4.17. In control reactor total solids varied between 3.97% and 3.75%. In the MW (1/2) coded reactor, TS varied between 3.95% to 3.74 and the minimum value was 3.74 % at 20th day for MW (1/2) coded reactor.

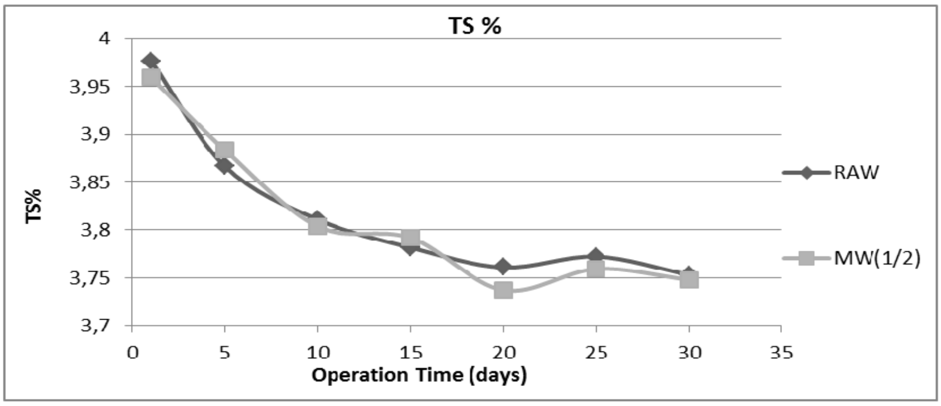


Figure 4.17 Total solid (TS %) changes in reactors.

Volatile solids changes in reactor contents are given in Figure 4.18. VS concentrations in MW (1/2) reactor were lower than control reactor. At the end of the operation, decrease in VS was recorded as 15 % according to the first operation day in control reactor. This ratio was determined as 19.7 % for MW (1/2) reactor.

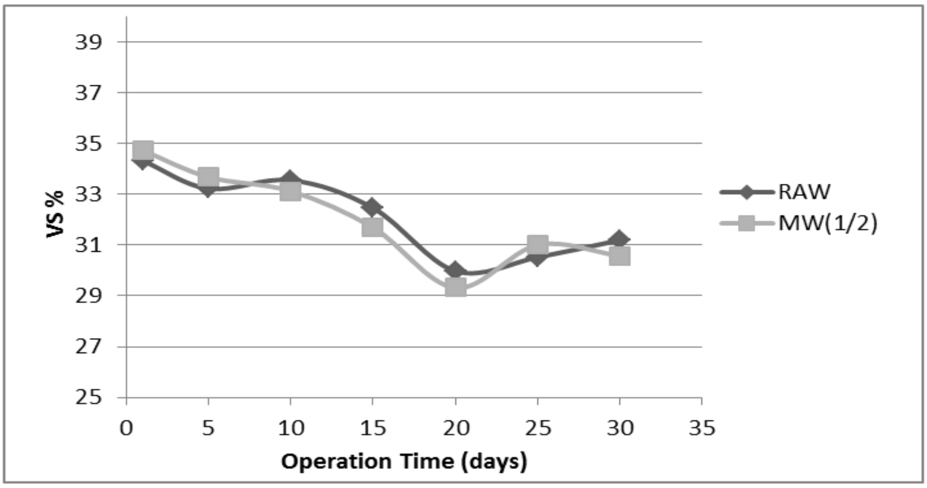


Figure 4.18 Volatile solid (VS %) changes in reactors.

The disruption of the cell walls of sludge was also effected in decreasing SS contents of the sludge in digestion. SS contents of reactors fed with microwave pretreated sludge were lower than control reactors but the difference between them was not higher. At the end of the operation time, according to the first operation day results decreases in SS (Figure 4.19) were observed as 37 % and 39 % for control reactor and MW (1/2) reactor, respectively.

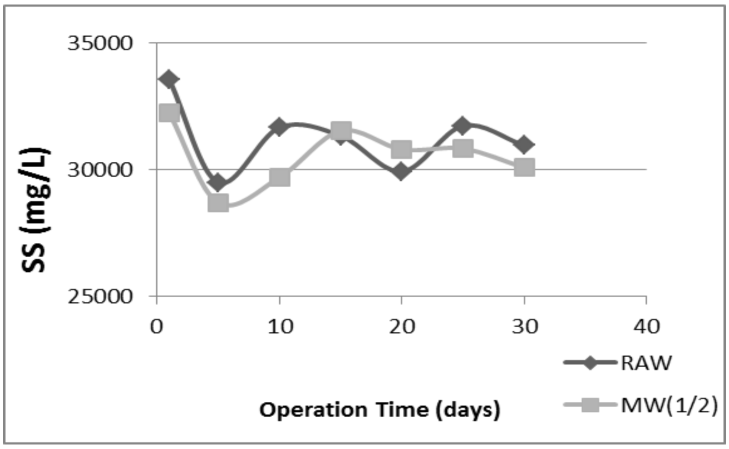


Figure 4.19 Suspended solid (SS %) changes in reactors.

VSS results were shown in Figure 4.20. Minimum VSS value of 9327 mg/L was obtained at the end of 30th day of operation and the value was 12883 mg/L at the end of first operation day. At the end of the operation, decreases in VSS were observed as 20 % and 28 % for control and MW (1/2) reactor, respectively

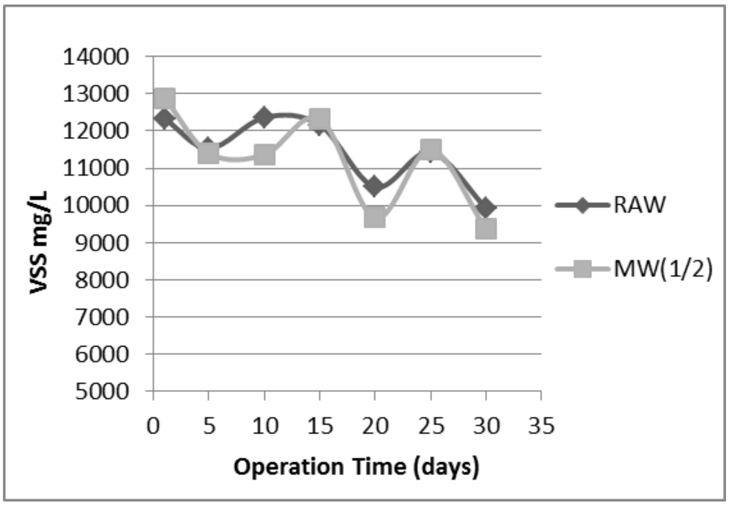


Figure 4.20 Volatile suspended solid (VSS %) changes in reactors.

Figure 4.21 shows the results of cumulative methane production of 50% microwave pretreated sludge in comparision with control reactor. Results showed that cumulative methane production of control reactor was found as 693.5 mL, while methane production was found as 765 mL for microwave application. Gas value of reactor with pretreated sludge was higher than control reactor.

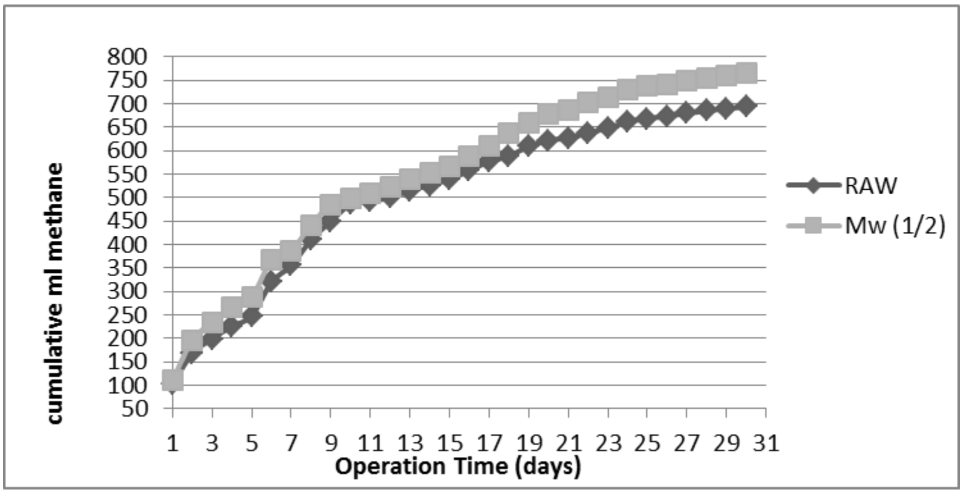


Figure 4.21 Results of cumulative methane gas of reactors.

Increase in DOC with microwave irradiation shows that microwaved sludge stabilizes higher degree in biological digestion processes than non-microwaved sludge. Minimum DOC value of 0.73 g/L was obtained at the end of 30th day of operation and the value was 1.23 g/L at the end of first operation day. Results are shown in Figure 4.22.

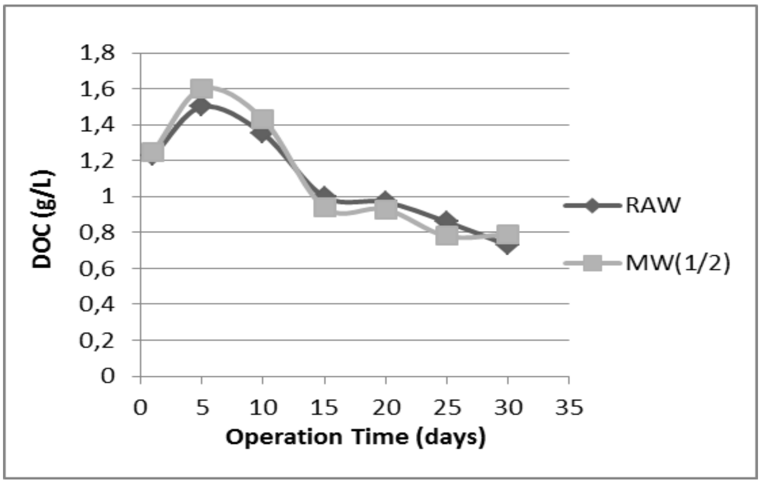


Figure 4.22 shows the variation of DOC (mg/L) in reactors.

SCOD results are given in Figure 4.23. The variation of SCOD showed close trend with the variation of DOC. The maximum value of 9600 mg/L SCOD was obtained at 5th days of operation period for MW (1/2) reactor.

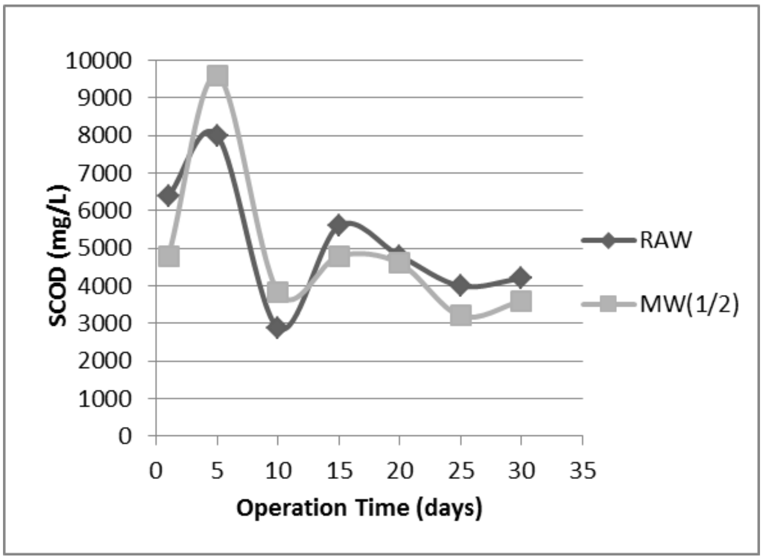


Figure 4.23 shows the variation of SCOD (mg/L) in reactors

COD results are shown in Figure 4.24. At the end of the operation time, according to the first operation day results decreases in COD were observed as 31 % and 40 % for control reactor and MW (1/2) reactor, respectively.

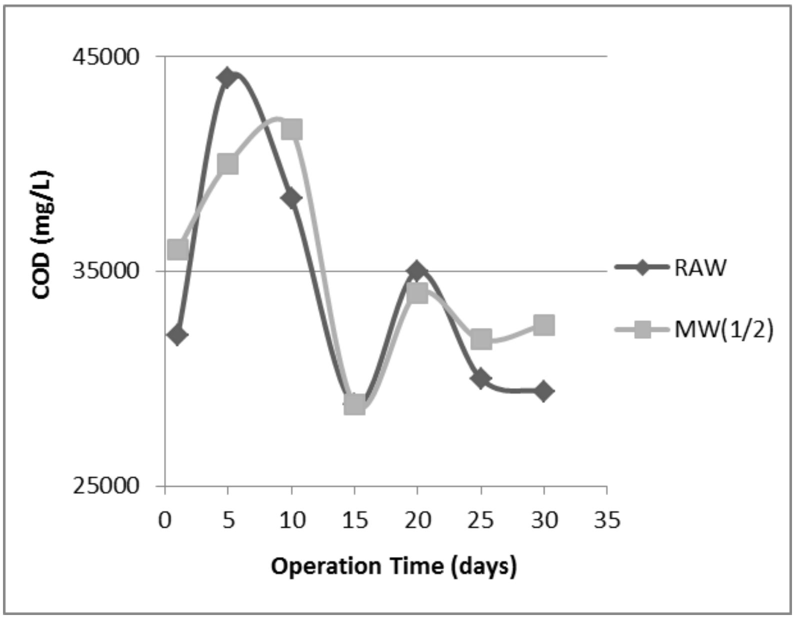


Figure 4.24 shows the variation of SCOD (mg/L) in reactors

The reduction in particle size generally means an easier hydrolysis of solids in anaerobic digestion. That means an accelerated and enhanced degradation of the organic fraction of the solids (Xie et al., 2009). Table 4.5 summarizes the particle size variation for control reactor. For control reactor, surface weighted mean was decreased from 11.835 μm to 9.581 μm and this can be explained as a decrease of 20 %. Also, volume weighted mean was decreased from 64.495 μm to 39.495 μm and 38.8 % decrease is seen.

Table 4.5 summarizes the particle size variation for control reactor.

	Particle size (μm)				
Operation days	Surface weighted mean D[3,2]	Volume weighted mean D[4,3]	d (0.1)	d (0.5)	d (0.9)
1	11.835	64.495	7.276	28.353	154.364
5	13.351	75.297	8.305	31.212	211.493
10	12.855	62.384	7.911	28.894	151.235
15	13.231	141.822	8.023	33.815	471.865
20	10.869	55.730	6.680	27.525	126.334
25	9.969	59.514	5.996	27.635	149.668
30	9.581	39.831	5.798	24.243	96.495

Table 4.6 summarizes the particle size variation for the MW (1/2) reactor. Decrease ratio of surface weighted mean and volume weighted mean were 46.7 % and 47.11 %, respectively. And results were approximately 1.75 times higher than results of control reactor.

Table 4.6 summarizes the particle size variation for MW (1/2) reactor.

	Particle size (μm)				
Operation days	Surface weighted mean D[3,2]	Volume weighted mean D[4,3]	d (0.1)	d (0.5)	d (0.9)
1	18.079	60.211	10.808	29.719	150.364
5	13.402	53.019	8.355	28.189	115.764
10	10.658	49.250	6.487	27.389	122.331
15	11.419	51.822	7.123	26.185	121.685
20	10.684	61.625	6.417	26.724	115.143
25	10.007	54.374	6.061	25.572	131.180
30	9.678	31.847	6.011	22.024	74.181

4.3.1.3 Dewatering Performance of Sludge after Digestion

Vaxelaire and Cezac (2004) mentioned about the common use of CST to characterize the sludge dewaterability. Dewaterability of sludge of exposure to microwave radiation, was 766.6 s while in the case of control reactors' sludge, it was 640.2 s. at the end of the operation period. Increasing of the contact time does not only consume more energy, it also worsens the conditioning effects. And variation of CST values is given in Figure 4.25.

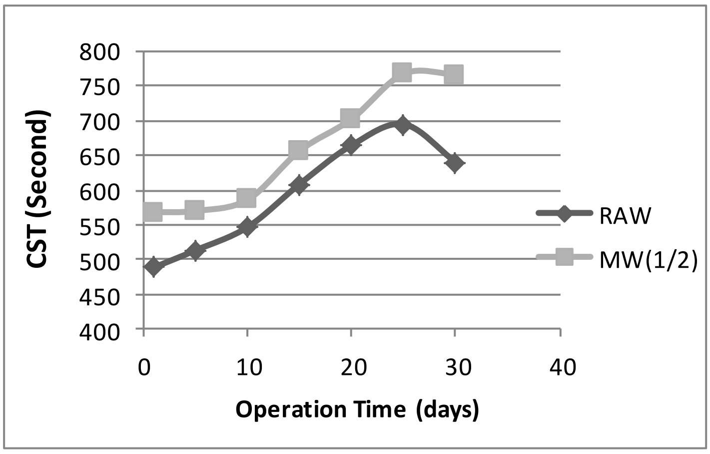


Figure 4.25 shows the CST variation in reactors.

4.3.2 Batch Reactors with 75% Microwave Pre-treated Sludge

4.3.2.1 Reactors' Stability Control

For stability of control and MW (3/4) digesters; pH, temperature, alkalinity, volatile fatty acids (VFA), oxidation reduction potential (ORP) values were measured regularly during the operation period. Temperature was kept costant at 37 ^{0}C by using an incubator for heating.

During operation time, pH varied from 7.38 to 7.31 in control reactor and in MW (3/4) digester content as variation was from 7.5 to 7.4 as seen in Figure 4.26. Results showed that conditions were appropriate for anaerobic digestion and no high range differences between pH values was obtained.

ORP means the capacity of a solution to oxidate or degrade. Oxidation Reduction Potential (ORP) in reactors was in the very negative range of –407 mV and – 438 mV and was observed as seen in Figure 4.27.

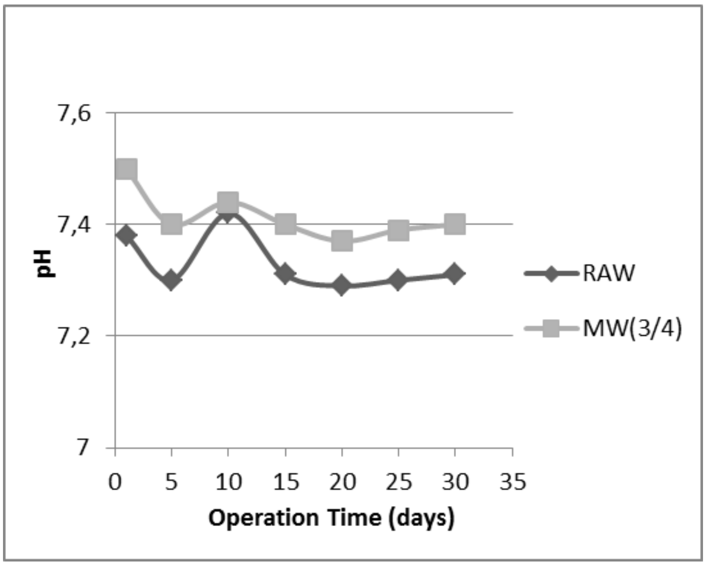


Figure 4.26 shows the pH variation in reactors.

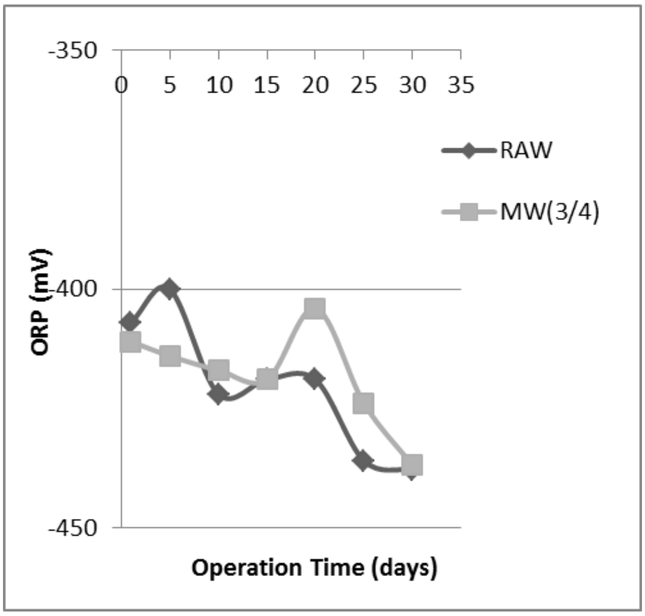


Figure 4.27 shows the ORP variation during anaerobic digestion.

EC values were in the range of 15.05-17.56 mS/cm shown in Figure 4.28.

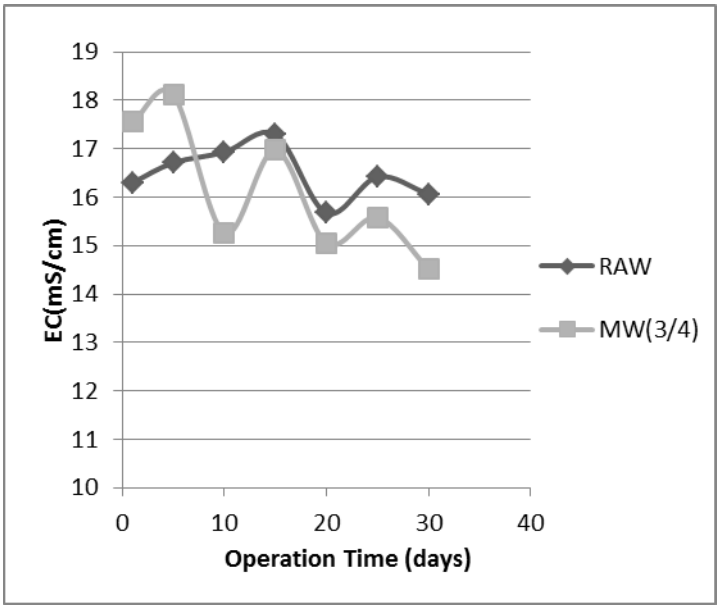


Figure 4.28 shows the EC variation during anaerobic digestion.

A well–established digester has a total alkalinity of 2000 to 5000 mg/L (Metcalf & Eddy, 2003). Total alkalinity measurements in the reactors were shown in Figure 4.29. The range of alkalinity was measured 2935 – 4875 mg $CaCO_3$/L.

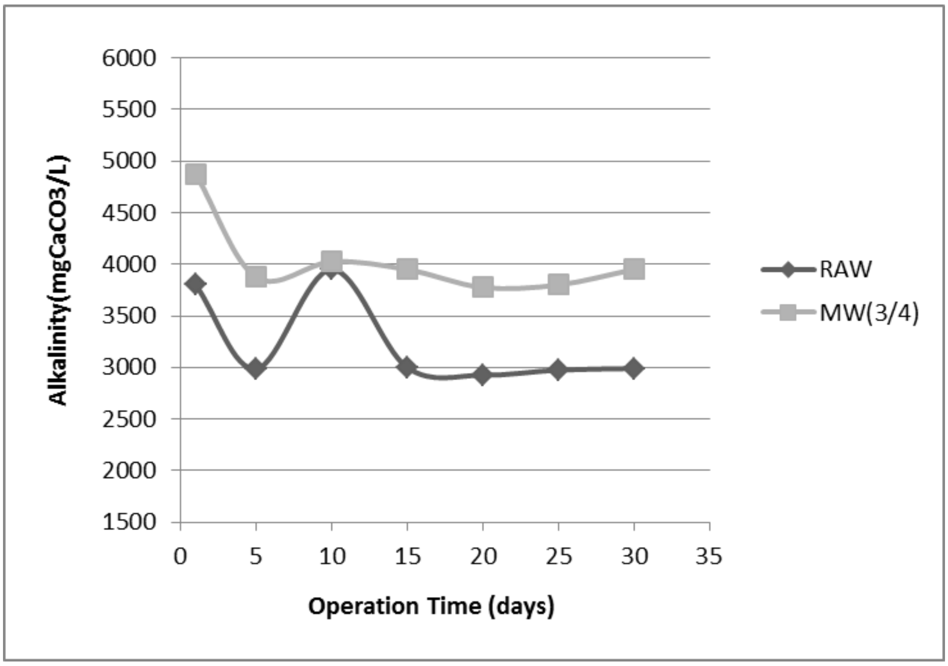


Figure 4.29 shows the alkalinity variation during anaerobic digestion for each reactor.

Volatile fatty acids (VFA) changes in reactor contents are given in Figure 4.30. During the operation, maximum value for VFA was recorded as 615 mg acetic acid/L at 5th day in MW (3/4) reactor and minimum value was 150 mg acetic acid/L at the 1th day.

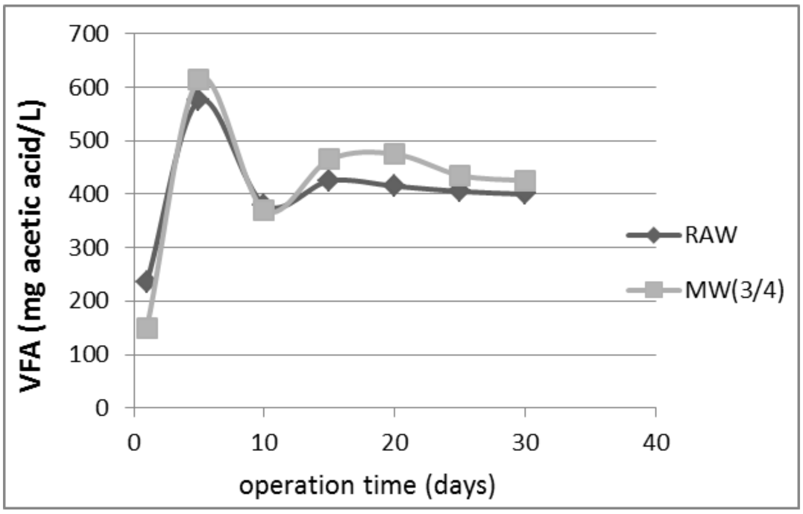


Figure 4.30 shows the VFA results during anaerobic digestion for each reactor.

4.3.2.2 Anaerobic Digestion Performance of Sludge

For performance evaluation ofanaerobic digesters, total solids (TS), volatile solids (VS), suspended solids (SS), volatile suspended solids (VSS), dissolved organic carbon (DOC), total oxygen demand (TCOD), soluble chemical oxygen demand (SCOD),particle size distribution, and methane gas were analyzed during the operation period.

Total solids changes in reactor contents are given in Figure 4.31. In control reactor total solids varied between 4.1% and 3.91%. In the MW (3/4) coded reactor, TS varied between 4.34% to 3.95 and the minimum value was 3.69 % at 20th day for MW (3/4) reactor.

Volatile solids mean the organic matter for microorganisms that capable of anaerobically stabilizing sludge. Volatile solids changes in reactor contents are given in Figure 4.32. VS concentrations in MW (3/4) reactor were lower than control reactor. The minimum value was 33.2 % at 25th day for MW (3/4) reactor.

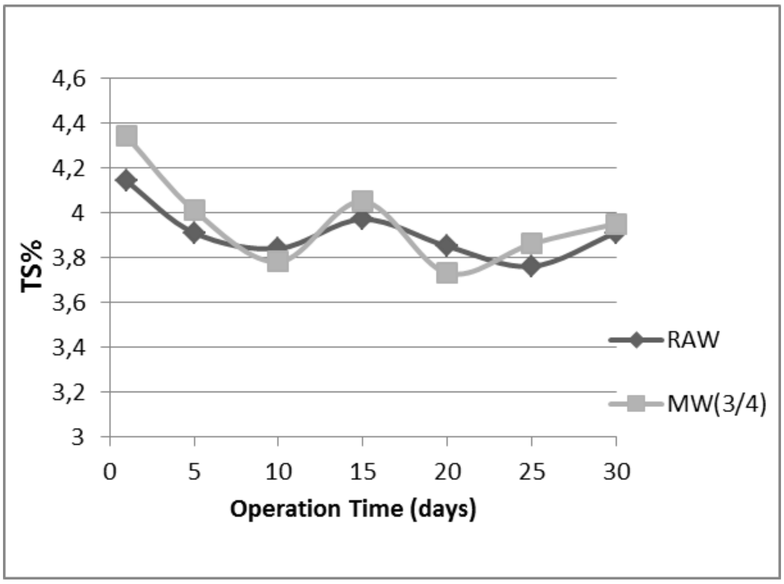


Figure 4.31 TS variation during anaerobic digestion for each reactor.

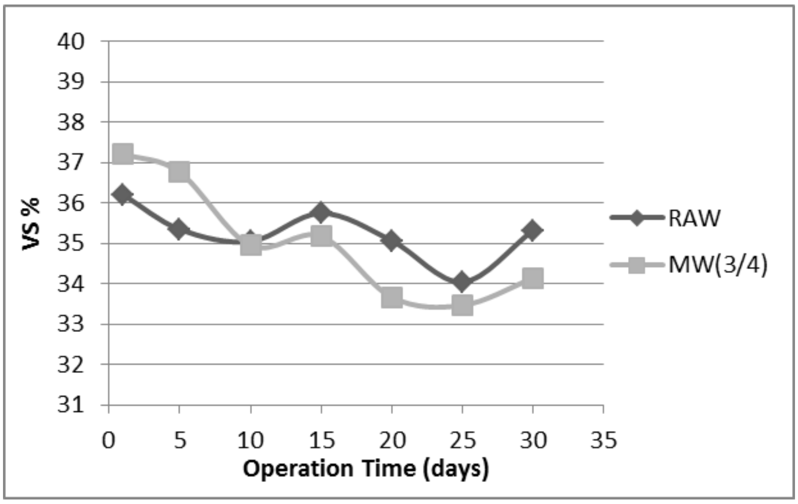


Figure 4.32 VS variation during anaerobic digestion for each reactor.

SS contents of reactors fed with microwave pretreated sludge were higher than control reactors but 5th and 15th days' values were lower. At the end of the operation time, according to the first operation day results decreases in SS (Figure 4.33) were observed as 22 % and 24 % for control reactor and MW (3/4) reactor, respectively.

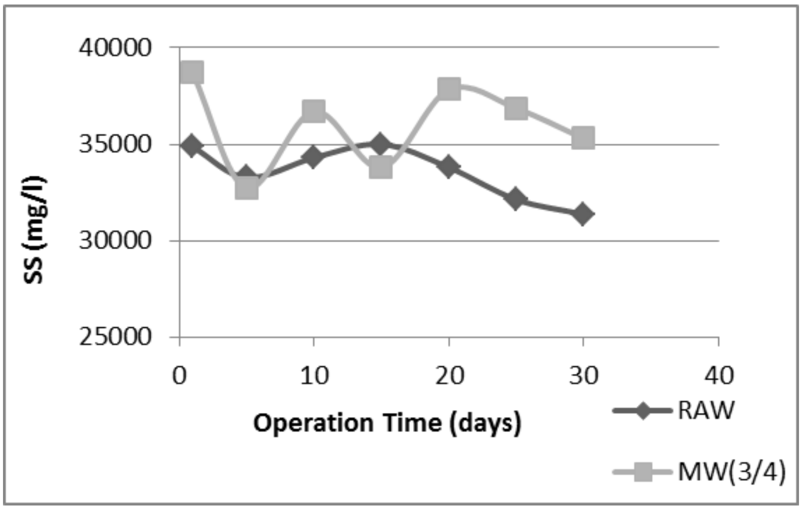


Figure 4.33 SS variation during anaerobic digestion for each reactor.

In Figure 4.34 minimum VSS value of 13267 mg/L was obtained at the end of 30th day of operation and the value was 16067 mg/L at the end of first operation day. At the end of the operation, decreases in VSS were observed as 21,1 % and 24,7 % for control and MW (3/4) reactor, respectively. The minimum value achieved at the 25th day at 11100 mg/L for control reactor.

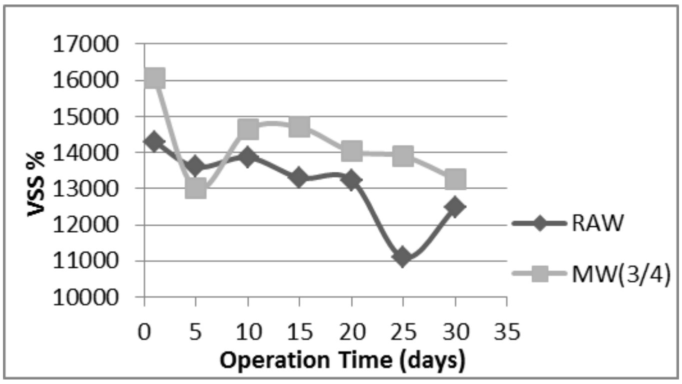


Figure 4.34 VSS variation during anaerobic digestion for each reactor.

COD results are shown in Figure 4.35. At the end of the operation time, according to the first operation day results decreases in COD were observed as 24.7 % and 26.3 % for control reactor and MW (3/4) reactor, respectively.

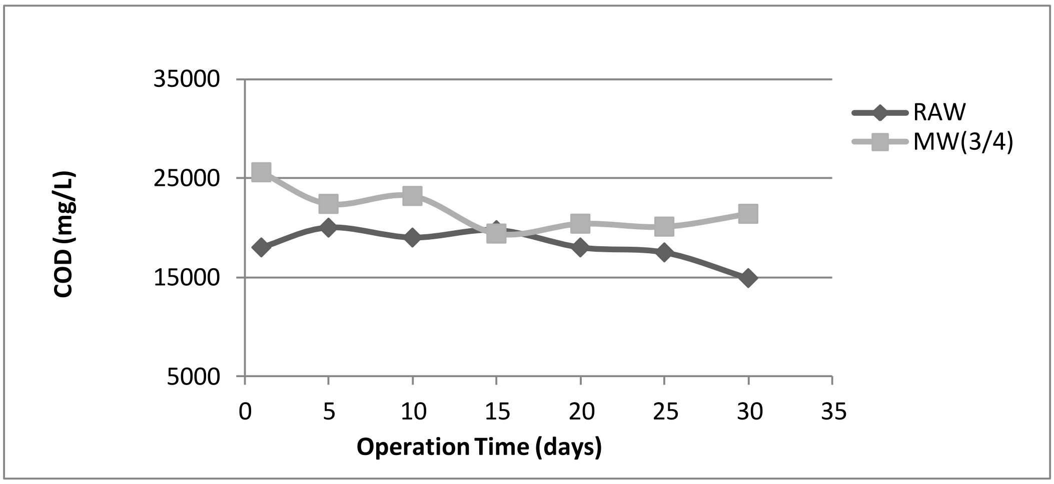


Figure 4.35 COD variation during anaerobic digestion for each reactor.

The variation of SCOD is shown in Figure 4.36. The maximum value of 7200 mg/L SCOD was obtained at 5th days of operation period for MW (3/4) reactor and this value was 1.8 time higher than control reactor.

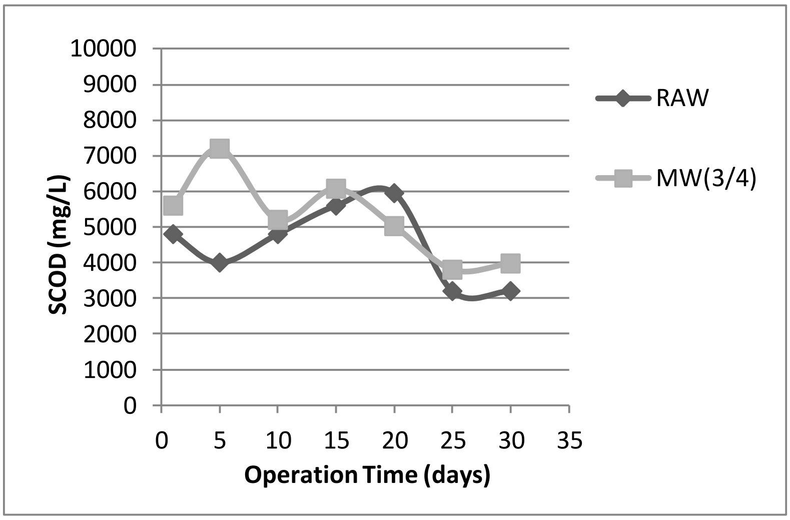


Figure 4.36 SCOD variation during anaerobic digestion for each reactor.

Increase in DOC with microwave irradiation at 5th day shows that microwaved sludge stabilizes higher degree in biological digestion processes than non-microwaved sludge. Minimum DOC value of 0.73 g/L was obtained at the end of 30th day of operation and the value was 0.9 g/L at the end of the first operation day. Results are shown in Figure 4.37.

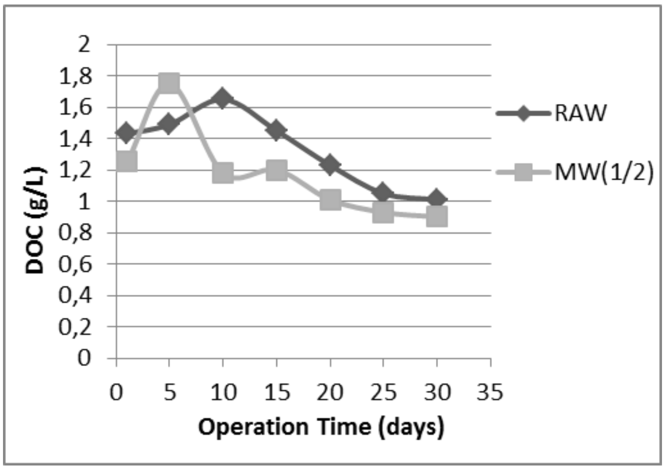


Figure 4.37 DOC variation during anaerobic digestion for each reactor.

Figure 4.38 shows the results of cumulative methane production of MW (3/4) in comparision with control reactor. Results showed that cumulative methane production of control reactor was found as 651.2 mL, while methane production was found as 804.3 mL for microwave application. Gas value of reactor with pretreated sludge was 1.24 times higher than control reactor.

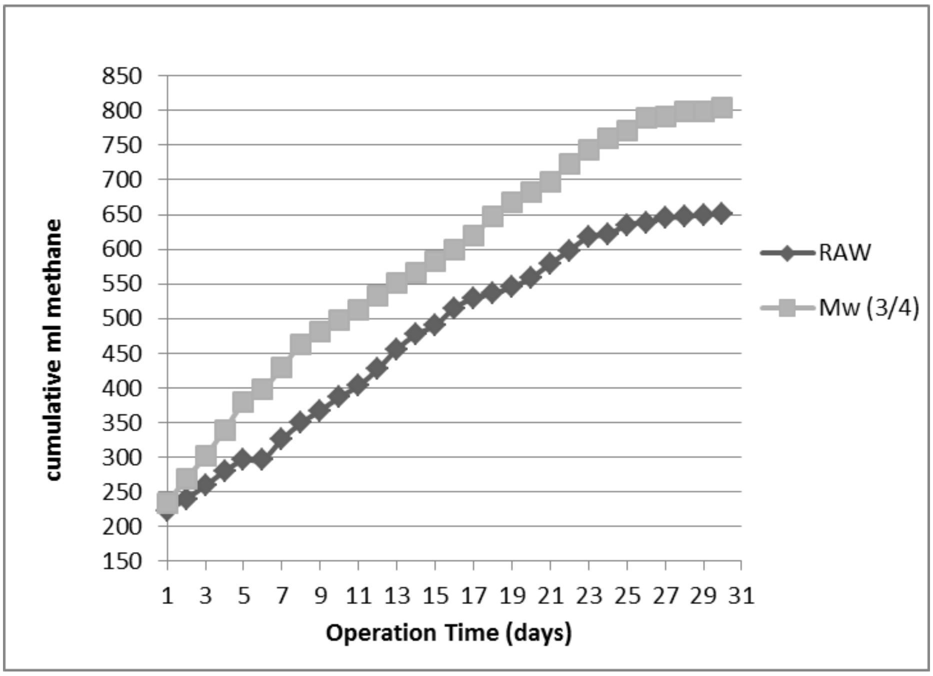


Figure 4.38 cumulative methane gas production during anaerobic digestion for each reactor.

Table 4.7 summarizes the particle size variation for control reactor. In control reactor, surface weighted mean was decreased from 12.894 µm to 10.006 µm. Also, volume weighted mean was decreased from 68.240 µm to 60.959 µm.

Table 4.7 summarizes the particle size variation for control reactor in 30th days.

Operation days	**Particle size (µm)** Surface weighted mean D[3,2]	Volume weighted mean D[4,3]	d (0.1)	d (0.5)	d (0.9)
1	12.894	68.240	7.978	33.310	163.937
5	11.676	51.480	7.124	30.649	126.003
10	11.795	54.437	7.232	31.583	136.125
15	11.100	61.322	6.971	32.191	156.554
20	10.244	39.031	6.363	27.879	90.602
25	11.623	68.674	7.341	32.512	163.877
30	10.006	60.959	7.170	32.148	140.368

Table 4.8 shows the particle size variation for the MW (3/4) reactor. In control reactor, surface weighted mean was decreased from 11.366 µm to 9.760 µm. Also, volume weighted mean was decreased from 71.139 µm to 64.174 µm.

Table 4.8 summarizes the particle size variation for 75 % microwaved reactor in 30th days.

Operation days	**Particle size (µm)** Surface weighted mean D[3,2]	Volume weighted mean D[4,3]	d (0.1)	d (0.5)	d (0.9)
1	11.366	71.139	7.107	30.735	189.768
5	12.577	213.475	7.304	34.972	886.865
10	10.483	56.673	6.309	28.116	147.497
15	10.886	59.551	6.802	26.857	142.480
20	8.936	37.063	5.282	24.332	91.002
25	7.725	34.304	5.061	24.282	87.168
30	9.760	64.174	5.826	27.808	160.916

4.3.2.3 Dewatering Performance of Sludge after Digestion

Dewaterability of sludge of exposure to microwave radiation, was 1500.1 s while in the case of control reactors' sludge, it was 998.7 s. at the end of the operation period. Increasing of the contact time can be explained as worsened conditioning of sludge. Variation of CST values is shown in Figure 4.39.

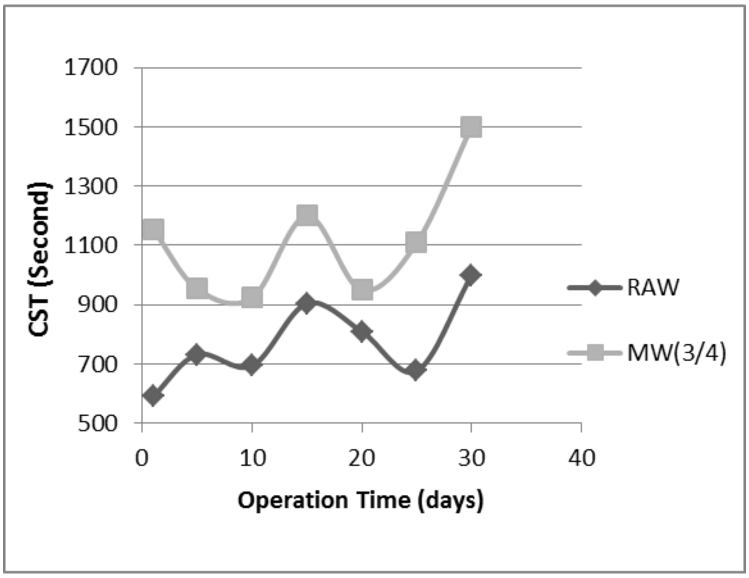


Figure 4.39 VS variation during anaerobic digestion for each reactor.

4.4 Anaerobic Semi-continuous Reactors with Microwave Irradiation

Sludge digestion studies were carried out using two 8.5 L anaerobic reactors with 7L working volume. Reactors were operated at 37 ± 2 °C in mesophilic conditions for 30 days of operation period. Reactor operated as semi-batch system for the comparision of batch system. Sludge retention time as 15 days was applied during the operation. Sludge digestion procedure was given in detail in Chapter 3.5.

4.4.1 Semi-continuous Reactors' Stability Control

In anaerobic semi-continuous digestion study with microwave disintegration, pH, ORP and temperature parameters were monitored daily while alkalinity and volatile fatty acids (VFA) parameters were analyzed regularly to control anaerobic digester stability.

Temperature was kept at 37 ± 2 °C for two reactors and temperature changes in reactors were given in Figure 4.41. pH values given in Figure 4.40 varied from 7.05 to 7.52 in reactors.

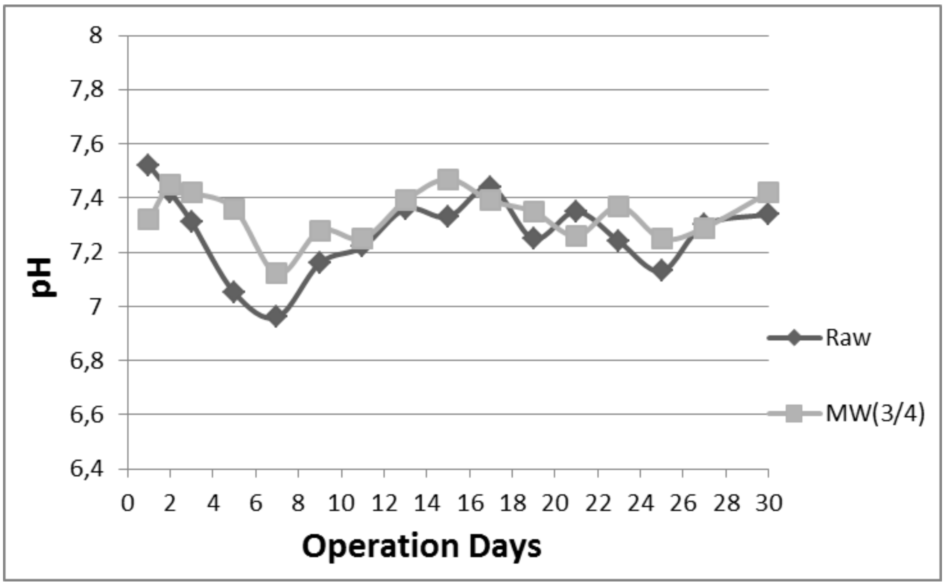


Figure 4.40 pH variation during anaerobic digestion for each reactor.

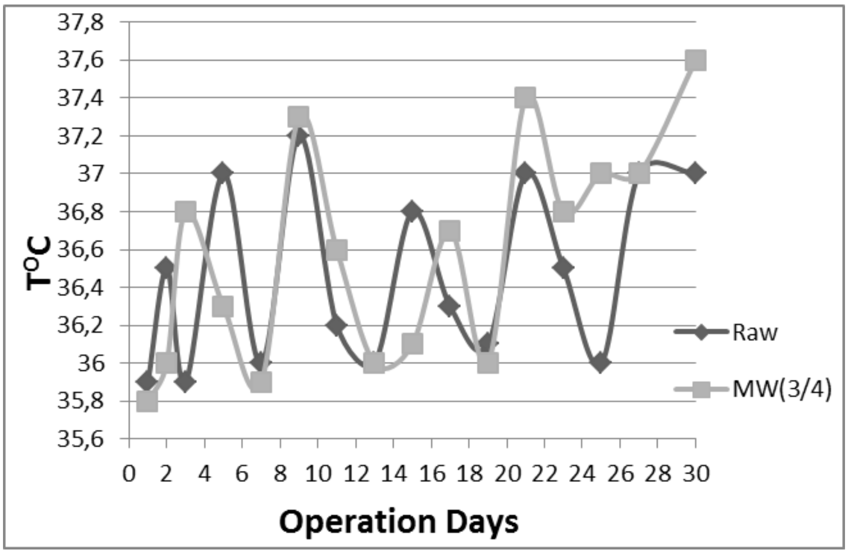


Figure 4.41 T^0C changes during anaerobic digestion for each reactor.

Oxidation Reduction Potential (ORP) in reactors were in the very negative range of –390 mV and – 450 mV and was observed as seen in Figure 4.42.

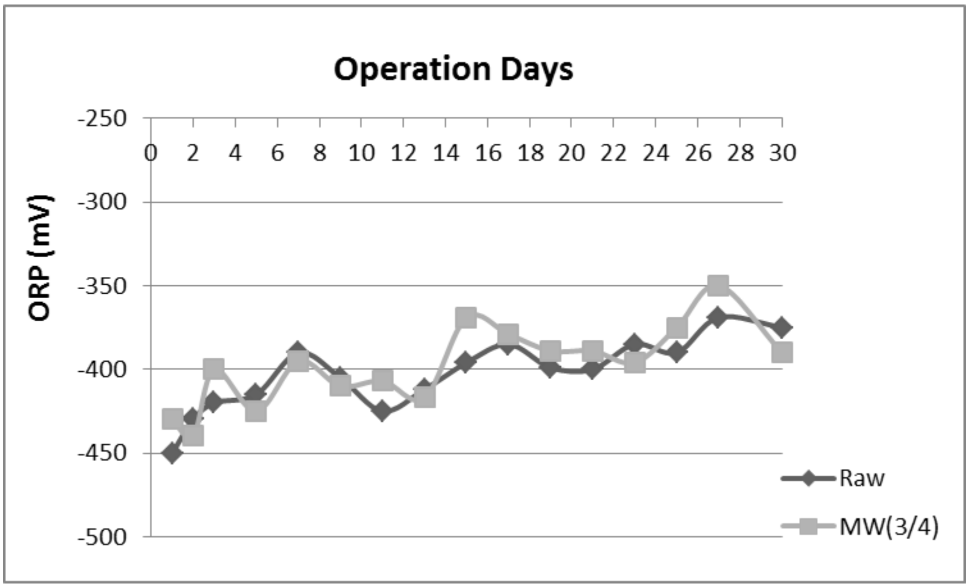


Figure 4.42 ORP variation during anaerobic digestion for each reactor.

In semi-continuous digestion study with microwave pre-treatment, total alkalinity values were measured regularly as a measure of the stability of the digestion. An alkalinity range of 3700 – 5024 mg $CaCO_3$/ L were measured during the operation period (Figure 4.43). Values did not exceed the recommended values as 2000 to 5000 mg/L (Metcalf & Eddy, 2003). Only high alkalinity value was recorded in the first operation day as 5024 mg$CaCO_3$/L and then values decreased highly till 11th days of operation, and then values were closer to the first day values. After 18th day values were similar with each other.

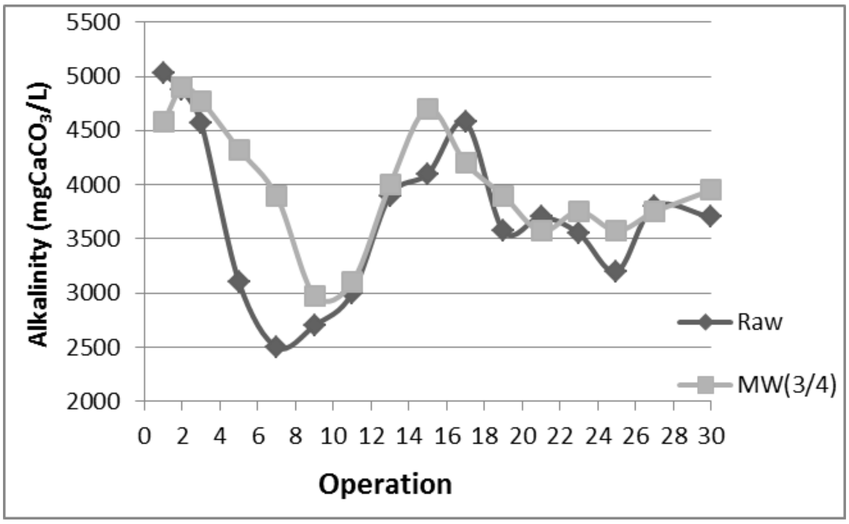


Figure 4.43 Alkalinity variation during anaerobic digestion for each reactor.

VFA content was also measured for reactor stability and results are shown in Table 4.44. VFA values above 1000- 1500 mg/L were not proposed for anaerobic methogens (Malina & Pohland, 1992). VFA values did not exceed proposed range even first operation days in semi-continuous system. In semi- continuous system, in control reactor, maximum VFA values were obtained at the 5th day as 675 mg/L during operation day, after that the values were decreased for each two reactor with increasing operation time.

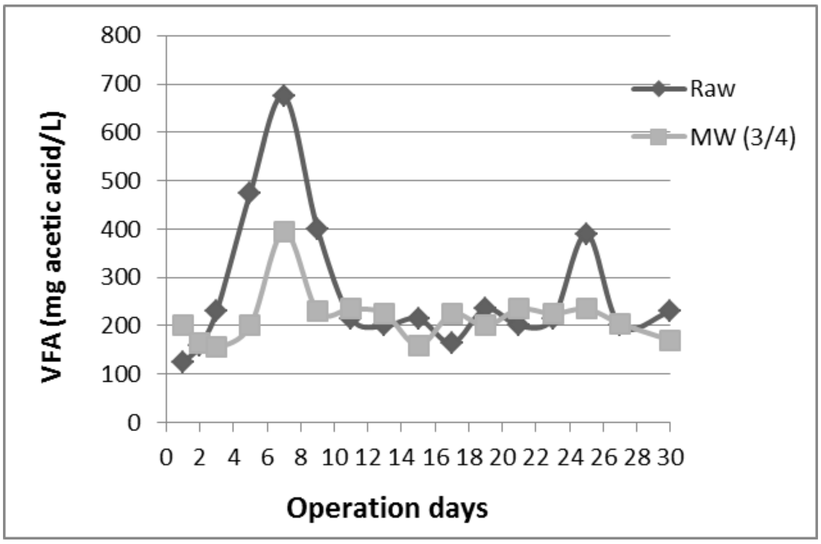


Figure 4.44 VFA variation during anaerobic digestion for each reactor.

4.4.2 Anaerobic Digestion Performance of Sludge

To compare of anaerobic digestion performance of sludge with microwave irradition, total solids (TS), volatile solids (VS), suspended solids (SS), volatile suspended solids (VSS), dissolved organic carbon(DOC), total oxygen demand (TCOD), soluble chemical oxygen demand (SCOD) particle size distribution, TN and PO_4-P, total and methane gas measurements were analyzed during the operation period.

In anaerobic digestion studies with microwave pre-treatment, total solids changes during the operation period are given in Figure 4. 45. According to this figure total solids concentrations in MW (3/4) reactor were lower than control reactor. At the end of the operation, decrease in TS was recorded as 45 % according to the first operation day in control reactor. This ratio was determined as 56.1 % for MW (3/4) reactor.

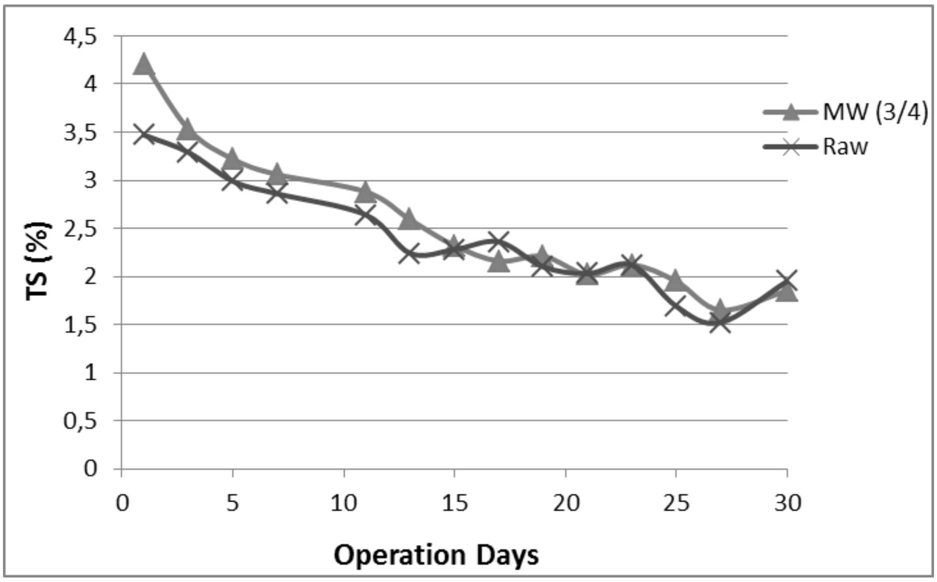


Figure 4.45 TS variation during anaerobic digestion for each reactor.

Volatile solids changes in reactor contents are given in Figure 4.46 In control reactor volatile solids varied between 66.2% and 51.13%. In the MW (3/4) coded reactor, TS varied between 72.6 % to 50.73 and the minimum value was 50.73 % at 30th day for MW (3/4) coded reactor.

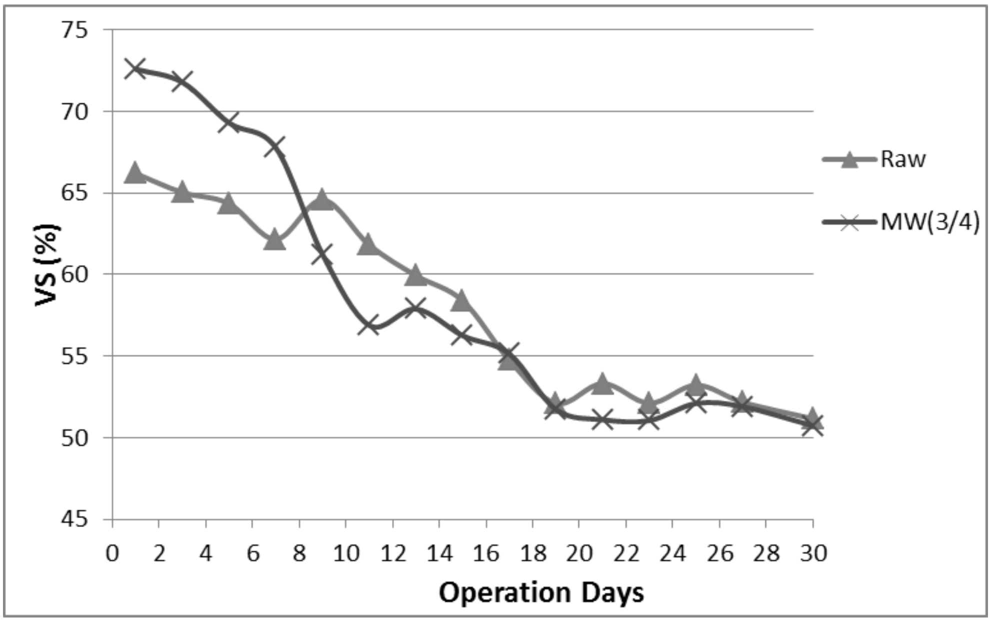


Figure 4.46 VS variation during anaerobic digestion for each reactor.

Figure 4.47 and Figure 4.48 gives the variation of SS and VSS as a function of operation time, respectively in anaerobic digestion studies with microwave pre-treatment.

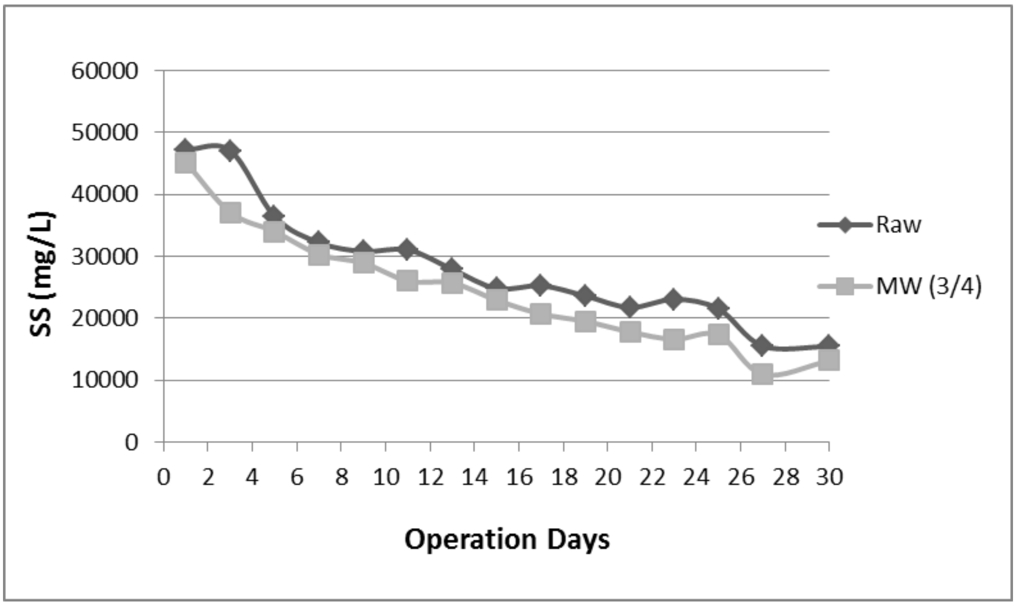


Figure 4.47 SS variation during anaerobic digestion for each reactor.

Decrease in SS and VSS occured in ten days of operation period in reactors operated as semi-continuous system. After ten days of operation SS and VSS had little change and approximately same values of SS and VSS were observed for 15 days of SRT. At the end of the first operation day, SS value for control, and MW (3/4) was determined as 47250 mg/L, 45150 mg/L, respectively. The value was 15450 mg/L, 13100 mg/L at the end of the operation period for control, and MW (3/4), respectively.

At the end of the operation period, VSS value for control, and MW (3/4) was determined as 9350 mg/L, 10500 mg/L, respectively. The value was 45150 mg/L, 37700 mg/L, at the end of the firs day of the operation period for control, and MW (3/4) reactors, respectively.

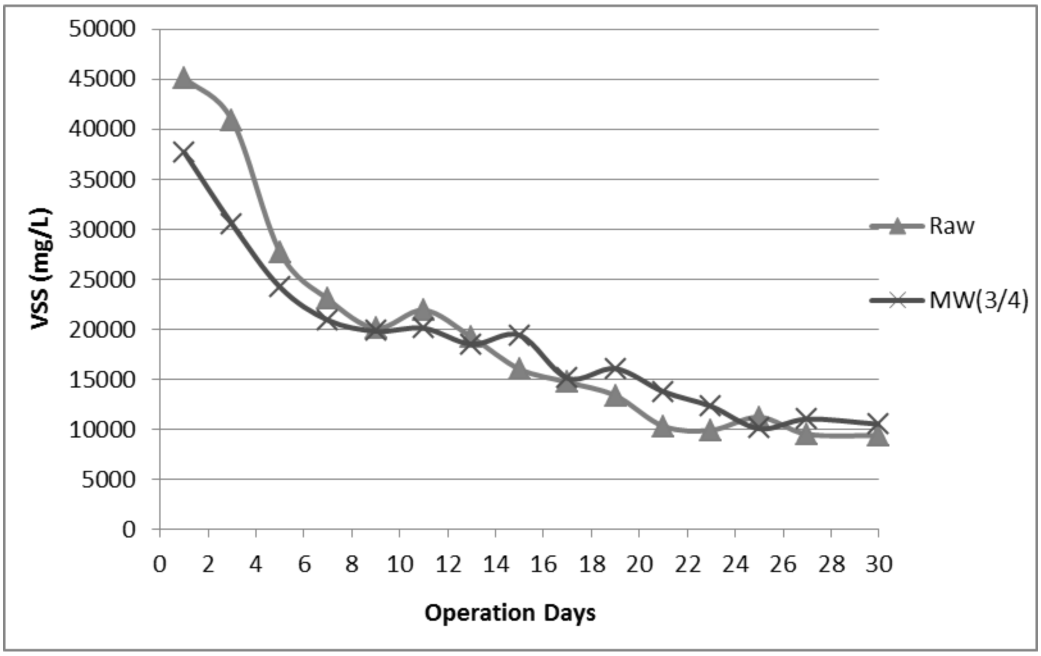


Figure 4.48 VSS variation during anaerobic digestion for each reactor.

Figure 4.49 and 4.50 show the results of total gas (L/d) and methane production (L/d) of reactors. Results showed that methane production of control reactor was found as 3.9 L/d, while methane production was found as 4.1 L/d for microwave applied reactor.

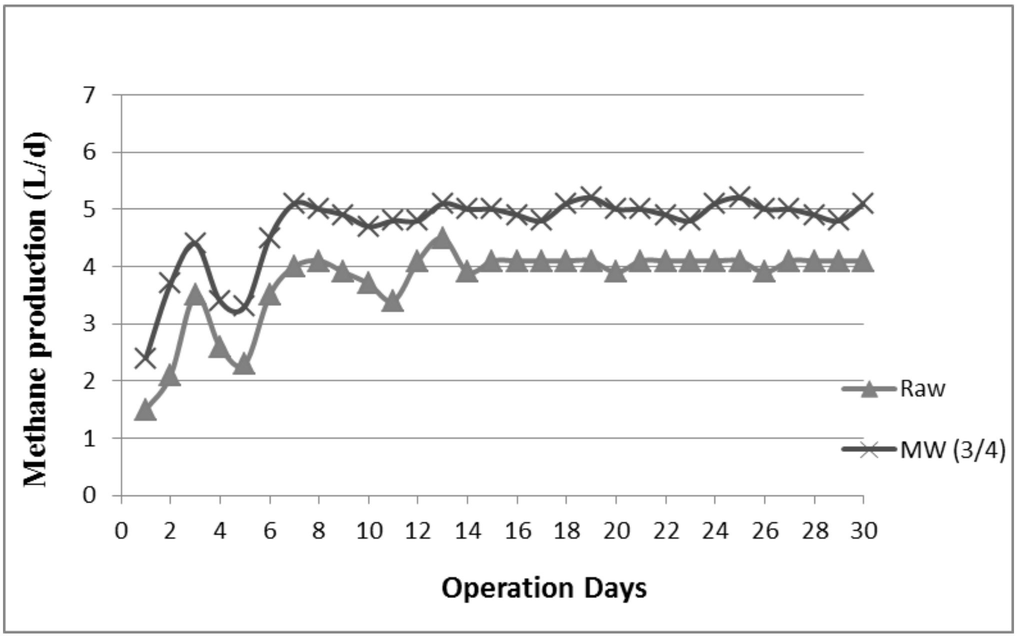


Figure 4.49 Methane gas productions during anaerobic digestion for each reactor.

Total gas production of control reactor was found as 8.2 L/d, while methane production was found as 10.1 L/d for microwave applied reactor.Gas value of reactor with pretreated sludge was higher than control reactor.

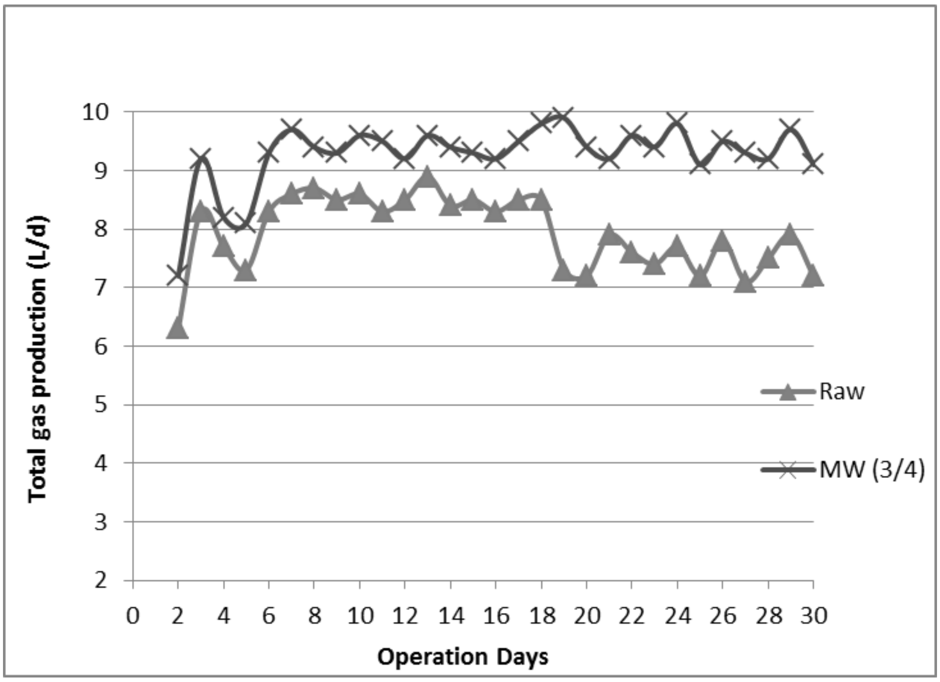


Figure 4.50 Total gas productions during anaerobic digestion for each reactor.

Increase in DOC with microwave irradiation shows that microwaved sludge DOC reduction was also higher in biological digestion process than non-microwaved sludge. Minimum DOC value of 0.52 g/L was obtained at the end of 30th day of operation and the value was 1.71 g/L at the end of the first operation day. Results are shown in Figure 4.51.

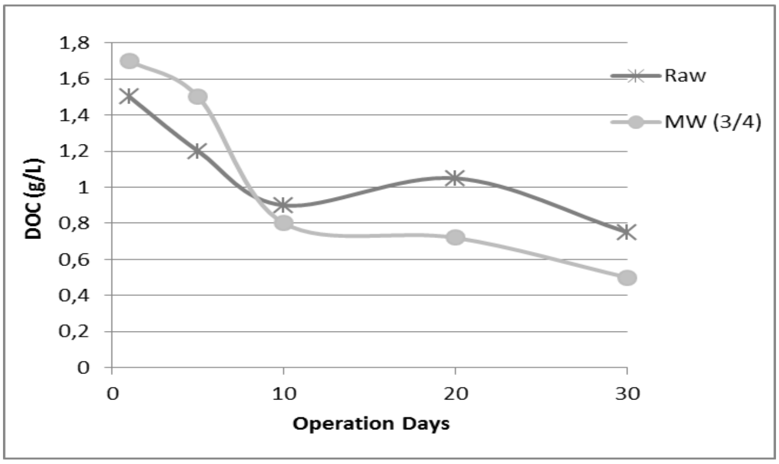


Figure 4.51 DOC variations during anaerobic digestion for each reactor.

COD and SCOD results are shown in Figure 4.52 and 4.53, respectively. At the end of the 30th days, according to the first operation day results decreases in COD were observed as 55 % and 58 % for control reactor and MW (3/4) reactor, respectively. On the other hand, the decrease in SCOD was 46.6 % and 49.1 % for control and MW (3/4) reactors, respectively.

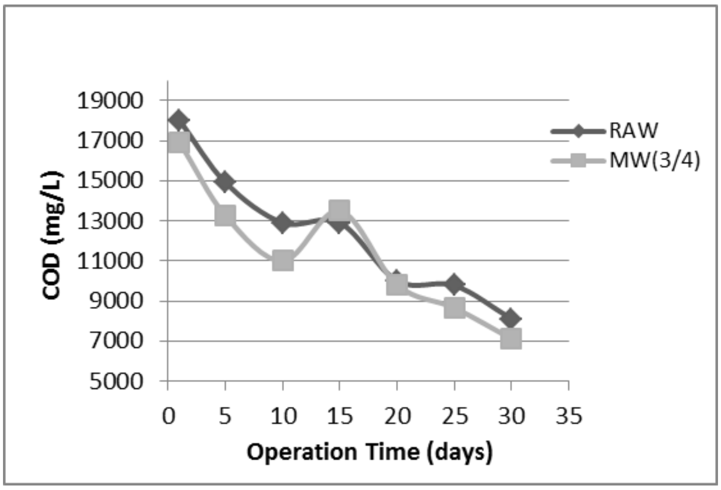


Figure 4.52 COD variations during anaerobic digestion for each reactor.

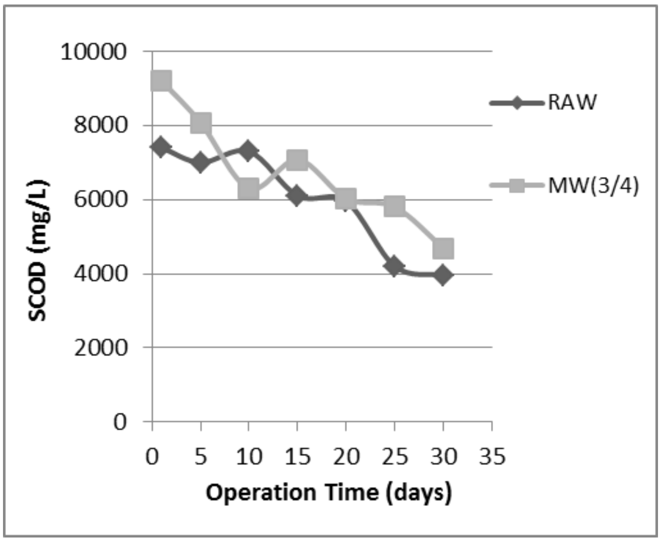


Figure 4.53 SCOD variations during anaerobic digestion for each reactor.

Total N and Total P results are summarized in Figure 4.54 and 4.55, respectively. Both two results show that total N and total P values decreased during anaerobic semi- continuous digestion. That decrease can be explained as the results of biological degredation for both two reactors. And higher decreases were obtained in pre-treated sludge with 75 % microwave irradiation in comparision to non-microwaved sludge.

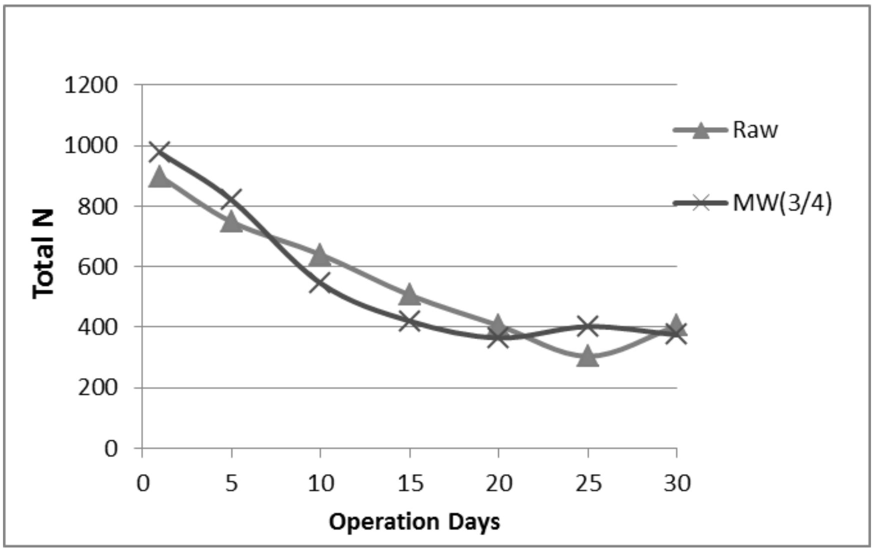


Figure 4.54 Total N variations during anaerobic digestion for each reactor.

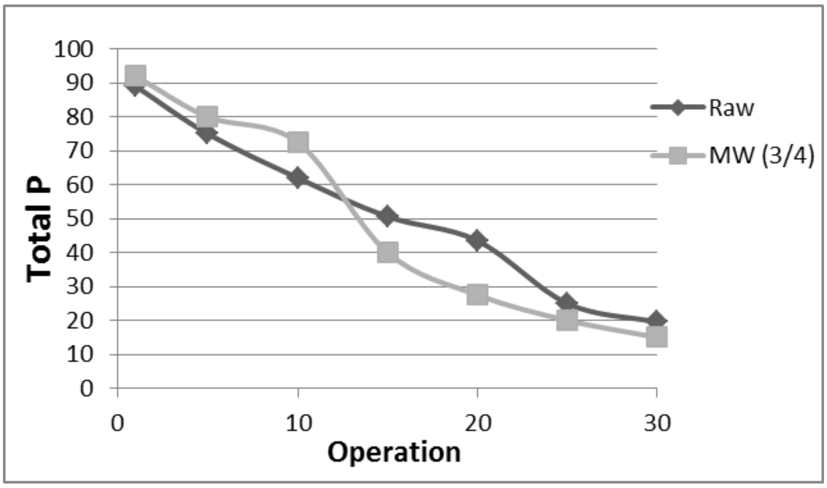


Figure 4.55 Total P variations during anaerobic digestion for each reactor.

For control reactor, surface weighted mean was decreased from 13.722 μm to 4.767 μm and this can be explained as a decrease of 65 %. Also, volume weighted mean was decreased from 76.613 μm to 32.947 μm and 57 % decrease is seen. Results are shown in Table 4.9.

Table 4.9 summarizes the particle size variation for semi-continuous control reactor in 30th days.

	Particle size (µm)				
Operation days	Surface weighted mean D[3,2]	Volume weighted mean D[4,3]	d (0.1)	d (0.5)	d (0.9)
1	13.722	76.613	7.521	20.890	270.246
5	11.045	65.051	7.304	32.206	149.819
10	7.272	57.444	3.445	27.808	160.916
15	4.622	33.051	2.970	25.859	77.223
20	4.527	32.837	1.810	23.771	75.483
30	4.767	32.947	1.530	19.034	72.066

Table 4.10 shows the particle size variations of MW (3/4) semi-continuous reactor. Surface weighted mean was decreased from 11.319 µm to 4.118 µm and this can be explained as a decrease of 63.6 %. Also, volume weighted mean was decreased from 86.195 µm to 24.903 µm and 71.1 % decrease is seen.

Table 4.10 summarizes the particle size variation for MW (3/4) semi-continuous reactor.

	Particle size (µm)				
Operation days	Surface weighted mean D[3,2]	Volume weighted mean D[4,3]	d (0.1)	d (0.5)	d (0.9)
1	11.319	86.195	7.796	34.642	265.026
5	7.966	51.863	4.656	28.320	130.905
10	5.339	30.202	2.069	21.837	71.575
15	3.856	23.541	1.902	15.657	52.470
20	2.771	15.652	0.887	10.055	39.618
30	4.118	24.903	1.357	15.146	66.015

4.4.3 Dewatering Performance of Sludge after Digestion

Dewaterability of microwave digested sludge was 606.3 s while in the case of control reactors' sludge was 312.5 s. at the end of the operation period. For both two reactors, contact time decreased in comparision to first days' results. But, MW (3/4) reactor's results were higher then control reactor. And this can be explained as worsened conditioning of sludge. Variation of CST values is shown in Figure 4.56.

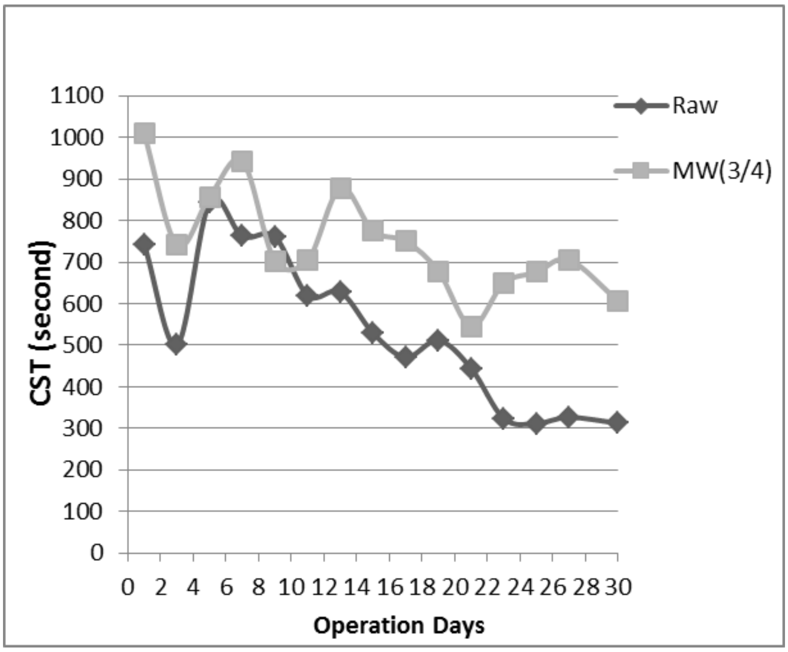


Figure 4.56 CST results during anaerobic digestion for each reactor.

CHAPTER FIVE
CONCLUSIONS & RECOMMENDATIONS

5.1 Conclusions

The effectiveness of microwave pre-treatment, alkaline pretreatment and the combination of these methods as thermochemical pre-treatment to anaerobic digestion were investigated with experimental studies in this thesis. According to the results, application of microwave irradiation as a pre-treatment method improved anaerobic digestion performance as more stabilization and biogas production.

In the disintegration studies, the effect of alkaline addition , microwave irradiation in a range of 90-150°C and the combination of alkaline and microwave pre-treatments in terms of SCOD, SS,VSS, TN, TP,CST and Particle Size were examined.

Firstly the effect of microwave irradiation was investigated with using the disintegration degree (DD) as a response. For this, Central Composite Design statistical programme was used and correlation coefficient (R^2) between the observed and predicted values of DD was %94.89. For microwave pre-treatment, maximum disintegration degree (DD %) was obtained as 89.54 % and the optimum temperature and time parameters were 150 ^{0}C, 35 minutes, respectively.

After microwave application alkaline pre-treatment was studied based on pH values as response and 1N NaOH was used for alkaline pre-treatments in order to obtain the optimum pH. At the end of the study, optimum pH value was obtained at pH 12 with the 157.81 % DD.

With obtained optimum points of microwave and alkaline combination, thermochemical pre-treatment was studied. Microwave and thermochemical pre-treatment effects were investigated in terms of CST, Particle Size, TN and TP. SS and VSS results were lower than raw sludge and microwave and microwave+alkali combined pre-treatment played an important role in sludges’ floc destruction. CST increased highly with the disintegration methods of microwave and combination of microwave and alkali pre-treatment. The maximum CST value was seen at disintegrated sludge with microwave irradiation at 100.13 seconds. It was seen that microwave pre-treatment deteriorates the filterability of sludge.

In order to see the effect of microwave, and thermochemical pretreatment methods on anaerobic biodegradability, biochemical methane production (BMP) assay was applied. Results showed that maximum cumulative methane production was achieved for microwave pretreated sludge and microwave pre-treatment of sludge can be an alternative for improving the anaerobic digestion. Cumulative methane production of raw sludge was found as 102.30 mL, while methane production was found as 160.1 mL for microwave application. On the other hand, methane production of thermochemically pretreated sludge was lower than raw sludge and this was described as the inhibition of the system because of the large amounts of alkaline agents.

In anaerobic batch studies, TS and VS concentrations in MW (1/2) and MW (3/4) reactors were lower than control reactors. Lower TS values for MW (3/4) reactor than MW (1/2) reactor were obtained. At the end of the operation, decrease in VS was recorded as 15% according to the first operation day in control reactor. This ratio was determined as 19.7 % for MW (1/2) reactor. VS decrease was 12, 1 % in control reactor and 20, 9 % was obtained for MW (3/4) reactor.

Microwave disintegration before anaerobic batch digestion led to higher reductions in SS and VSS content of sludge comparing the classical anaerobic digestion.

Batch reactors fed with microwaved sludge gave higher methane gas than control reactors. MW (3/4) reactor was more effective on methane production than MW (1/2) reactor. The highest methane gas production was obtained as 804.3 mL in MW (3/4) reactor while MW (1/2) was 765 mL at the end of the operation.

DOC concentrations of reactor contents decreased during operation time in all reactors and the higher reductions were observed from microwave pre-treated reactors in comparison control reactors.

For batch systems, high values of particle size were observed in the first day of operation period. Then values decreased for both MW (1/2) and MW (3/4) batch reactors.

Results of the CST tests as filterability characteristics of sludge in anaerobic batch systems, microwave radiation worsened the filterability characteristics of sludge because of the higher contact time.

In semi-batch reactors, total solids concentrations in MW (3/4) reactor were lower than control reactor. At the end of the operation, decrease in TS was recorded as 45% according to the first operation day in control reactor. This ratio was determined as 56.1% for MW (3/4) reactor.

Volatile solids changes in control reactor varied between 66.2% and 51.13%. In the MW (3/4) coded reactor, VS varied between 72.6% to 50.73% and the minimum value was 50.73% at 30th day for MW (3/4) coded reactor.

At the end of the first operation day, SS value for control, and MW (3/4) was determined as 47250 mg/L, 45150 mg/L, respectively. The value was 15450 mg/L, 13100 mg/L at the end of the operation period for control, and MW (3/4), respectively. At the end of the operation period, VSS values for control and MW (3/4) reactors were determined as 9350 mg/L, 10500 mg/L, respectively. The value was 45150 mg/L, 37700 mg/L, at the end of the firs day of the operation period for control, and MW (3/4) reactors, respectively.

Methane production of control reactor was found as 3.9 L/d, while methane production was found as 4.1 L/d for microwave applied reactor. Total gas production of control reactor was found as 8.2 L/d, while total gas production was found as 10.1

L/d for microwave applied reactor. Gas value of reactor with microwave pre-treated sludge was higher than control reactor.

Increase in DOC with microwave irradiation shows that microwaved sludge DOC reduction was also higher in biological digestion process than non-microwaved sludge.

At the end of the 30th days, according to the first operation day results decreases in COD were observed as 55 % and 58 % for control reactor and MW (3/4) reactor, respectively. On the other hand, the decrease in SCOD was 46.6 % and 49.1 % for control and MW (3/4) reactors, respectively.

Total N and total P values decreased during anaerobic semi- continuous digestion. That decrease can be explained as the results of biological degredation for both two reactors. And higher decreases were obtained in pre-treated sludge with 75 % microwave irradiation in comparision to non-microwaved sludge.

For control reactor in particle size reduction, surface weighted mean decrease ratio was 65 % and volume weighted mean was 57 %. For MW (3/4) reactor, this ratio was 63.6 % for surface weighted mean and 71.1 % decrease is seen for volume weighted mean.

Dewaterability of microwave digested sludge was 606.3 s while in the case of control reactors' sludge was 312.5 s at the end of the operation period. For both two reactors, contact time decreased in comparision to first days' results. But, MW (3/4) reactor's results were higher then control reactor. And this can be explained as microwave irradiation worsened the conditioning proporties of sludge.

5.2 Recommendations

In this study, the findings point the effectiveness of microwave irradiation and combined alkaline and microwave pre-treatment techniques on enhancement of biogas production. In further anaerobic digestion studies, the effect of combined alkaline and microwave pretreatment on biogas production can be investigated by the pH equalization to prevent the inhibition. In the microwave irradiation experiments for more conclusive results, full–scale studies should be done.

On the other hand, the cost of microwave irradiation can be comparatively high for treatment plants therefore; minimization of cost by additional modifications should be studied on. Not only different ratios for microwave pre-treatment but also combination of two different pretreatment methods can be done.

Thermophilic anaerobic digestion can be favored with microwave disintegration instead of mesophilic digestion.

In further studies, pathogenic activity of digested sludge can be investigated to determine the suitability for land application. So, it can eliminate the costs of transportation and disposal of digested sludge.

Conditioning methods can be applied after the digestion units to see the effect of microwave irradiation on final disposal.

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