INVESTIGATION OF METHANE PRODUCTION POTENTIAL OF INDUSTRIAL SLUDGES MIXED WITH DOMESTIC SLUDGE DURING ANAEROBIC DIGESTION

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ABSTRACT

INVESTIGATION OF METHANE PRODUCTION POTENTIAL OF INDUSTRIAL SLUDGES MIXED WITH DOMESTIC SLUDGE DURING ANAEROBIC DIGESTION

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Anaerobic digestion has been established as a sludge stabilization and biogas production method for domestic sludge. However, anaerobic digestion has limited success in industrial sludge applications. In this thesis sludge from two different Organized Industrial Districts (OIDs) and textile industry are mixed with urban wastewater sludge with and without ultrasound pretreatment to investigate their energy production potential by using BMP tests. Sludges were digested alone (A for industrial, D for domestic sludge) or in mixtures (B: 2:1 industrial: municipal; C: 1:2 industrial: municipal; E: 0.5:2.5 industrial: municipal). During the operation biogas amount and methane percentage were measured.

At the end of reactor operation, removals of total solids (TS), total suspended solids (TSS), volatile solids (VS) and volatile suspended solids (VSS) as well as pH were measured. TS removal for OID I, OID II and textile sludges were found as 11%, 11%, 8%, respectively for industrial sludge samples only (reactor A). On the other hand, VS removal were found as 20%, 20%, 11%, respectively for the same reactors. COD removal for OID I, OID II and textile sludges alone were found as 17%, 15%, 6.5%, respectively. When the municipal sludge was digested its average TS, VS and COD removals were 23%, 46% and 36%, respectively. The co-digestion reactors performed in accordance with the proportion of sludge that they contained. The methane amount produced per g of COD destroyed for only the industrial sludges were 0.11 L/g, 0.13 L/g and 0.12 L/g, respectively. The industrial sludges co-digested with the domestic sludge have biogas production potentials. Even though adding industrial sludge reduced the observed biogas amount to lower than that expected, results show that it is possible to co-digest industrial sludge with municipal sludge together.

Keywords: Anaerobic digestion, Co-digestion, Industrial wastewater sludge, Ultrasound pretreatment

ÖZ

ENDÜSTRİYEL ARITMA ÇAMURLARININ EVSEL ÇAMUR İLE KARIŞTIRILARAK ANAEROBİK ÇÜRÜTÜCÜ İLE METAN ÜRETİM POTANSİYELİNİN BELİRLENMESİ

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Evsel çamurun stabilizasyonun ve biyogaz üretiminin sağlanması için anaerobik çürütücüler kurulmuştur. Fakat endüstriyel çamurlar için anaerobik çürütücülerin uygulanmasında sınırlı sayıda uygulama bulunmaktadır. Bu çalışma kapsamında, iki farklı organize sanayi bölgesinde (OSB) ve tekstil endüstrisinde üretilen çamurlar, kentsel çamur ile karıştırılarak ultrasonla ön arıtım uygulanarak ve uygulanmayarak enerji üretim potansiyeli biyokimyasal metan üretim testi ile belirlenmiştir. Çalışmada kullanılan çamurlar oranları ile birlikte sadece endüstriyel çamur (A), sadece evsel çamur (D) veya karışımlar (B: 2:1 endüstriyel: evsel; C: 1:2 endüstriyel: evsel; E: 0,5:2,5 endüstriyel: evsel) olarak belirlenmiştir. Çalışma boyunca biyogaz miktarı ve metan yüzdeleri ölçülmüştür.

Reaktör işletimlerinin sonunda, toplam katı madde, toplam askıda katı madde, uçucu katı madde ve uçucu askıda katı madde giderimleri ve pH ölçülmüştür. Sadece endüstriyel çamur içeren örneklerde (reaktör A), Toplam katı madde giderimi OSB I, OSB II ve tekstil endüstrisi için sırasıyla %11, %11 ve %8 olarak belirlenmiştir. Öte yandan, uçucu katı madde giderimleri, aynı reaktörler için; %20, %20 ve %11 olarak tespit edilmiştir. KOİ giderimleri ise OSB I çamuru için %17, OSB II çamuru için

%15 ve tekstil endüstrisi çamuru için %6,5 olarak belirlenmiştir. Sadece evsel çamurun anaerobik çürütücüdeki ortalama giderimleri ise %23 toplam katı madde, %46 uçucu katı madde ve %36 KOİ'dir. Birlikte çürütme reaktörleri, reaktörlerin içerdikleri çamur oranlarına göre gerçekleştirilmiştir. Birim KOİ gideriminin metan üretim miktarına oranı, reaktör A bazında bakıldığında, OSB I için 0,11 L/g, OSB II için 0,13 L/g ve tekstil endüstrisi için 0,12 L/g'dır. Endüstriyel çamurlar evsel çamur ile birlikte çürütüldüğünde biyogaz üretim potansiyeline sahiptirler. Endüstriyel çamur eklendikçe üretilen biyogaz miktarında azalma beklenenden çok olmasına rağmen sonuçlara göre, endüstriyel çamur ile evsel çamurun birlikte çürütülmesi mümkün gözükmektedir.

Anahtar Kelimeler: Anaerobik çürütücü, Birlikte çürütme, Endüstriyel atıksu çamuru, Ultrasonla parçalama

To my family and Hakan Kort…

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LIST OF ABBREVIATIONS

BMP: Biochemical Methane Production

OID: Organized Industrial District

COD: Chemical Oxygen Demand

TS: Total Solid

TSS: Total Suspended Solid

Us: Ultrasonicated Sample

VS: Volatile Solid

VSS: Volatile Suspended Solid

WWTP: Wastewater Treatment Plant

CHAPTER 1

INTRODUCTION

Sludge, defined as by-product of wastewater treatment processes, is generated both from the settlement of the solids already present in wastewater and by the formation of biomass produced during dissolved organics removal in wastewater treatment plant (Vesilind et al., 1985). Inorganic and organic content of sludge, as well as the large quantities cause environmental concerns. Due to potential environmental problems and public health concerns, together with economic and institutional factors, sludge management has critical importance (EPA,1978). Even though sludge represents only 1% to 2% of treated wastewater volumetrically, management of it is complex (Andreoli and Sperling, 2007). Complicated treatment methods, limited disposal options and high disposal costs make sludge a challenging material to manage. Sludge management has also high cost ranged between 20% and 60% of total operation cost of wastewater treatment plant. After stabilization and dewatering processes, sludge is either sent to landfill, applied to land or incinerated. Two options involving landfill and incineration are more common ways of sludge management in European countries (Gude, 2015; Kelessidis and Stasinakis, 2012).

Anaerobic processes are used to convert organic compounds to biogas (having high methane content) with microbial activity under anaerobic and dark conditions at specific temperatures. Important parameters of anaerobic degradation process involve temperature, pH and alkalinity, nutrient requirements, head space, trace materials and toxicity (Speece, 1996). These parameters affect the performance of anaerobic digestion and determine the biogas production. Conducting biochemical methane potential (BMP) tests analyzes anaerobic biodegradation and biogas production potential of organic substrates under laboratory conditions.

Recently, energy generation from sludge has been more popular than other use/disposal alternatives of sludge. Anaerobic digestion helps with the sludge disposal problem by generating energy from it as methane and decreasing the sludge quantities significantly (Lier, 2008). Anaerobic digestion has been well-established and internationally accepted stabilization and biogas production method for domestic sludge. It can create a sustainable solution for sludge management challenge, since it reduces the sludge quantities as well. In Europe, biogas production with anaerobic digestion has gained popularity and highly in use (Lora Grando et al., 2017), whereas it is much less common in Turkey.

Characteristics of municipal and industrial sludge differ dramatically. The treatment of industrial sludge may be more challenging since it includes hazardous and/or toxic materials such as heavy metals and toxic organic chemicals in its composition. Therefore, anaerobic digestion has limited success in industrial sludge applications. There is a trend Worldwide of co-digesting different types of wastes together, to optimize the processes and maximize the benefits obtained. Co-digestion of sludge and organic fraction of municipal solid wastes (Sosnowski et al., 2003; Mattioli et al., 2017), sludge and agricultural wastes (Merlin and Boileau, 2013; Ward et al., 2008), manure and other types of organic wastes (Iacovidou et al., 2012; Esposito et al., 2012; Dai et al., 2016) are examples for this. With this perspective, it is plausible to investigate co-digestion of different types of sludges such as industrial and municipal to produce biogas. Unfortunately, there are limited number of such studies in literature. Most organized industrial districts host companies from different industrial sectors, so they generate mixed industrial wastewater. As a result, sludge with a mixture of different contaminants at a variety of concentrations may be formed. Since microbial species responsible for anaerobic digestion and methane production are very sensitive to inhibitors and toxic chemicals, presence of contaminants in sludge affect digestion negatively. When these sludges are mixed with municipal sludge, toxic properties of industrial sludge can decrease (at least simply by dilution), and their biogas production potential may increase. With this approach, organized industrial district sludges that are difficult to manage by themselves, may become an alternative energy source before final disposal. Using methods like ultrasound pretreatment, sludge biodegradability can be improved, and biogas production can be increased (Zhang, 2010; Show et al., 2007). When anaerobically digesting industrial sludges a pretreatment method such as ultrasonication may also help with the biodegradability.

In Turkey single industrial establishments gather under Organized Industrial Districts (OIDs) by which they have enhanced financial and environmental management. This approach results in higher amount of wastewater and sludge production with varying characteristics (Şenlier and Albayrak, 2011). On the other hand, textile industry in Turkey is accepted as one of the leading sectors in the economy. Turkish textile and its exports have gained more and more importance over years (Duran and Temiz Dinç, 2016). For this reason, textile sector has been producing higher amount of wastes and wastewaters over the years.

The purpose of this study is to test the anaerobic digestion performance of sludge samples from two organized industrial district (OIDs) as well as a textile industry WWTP when they are alone and when they are co-digested with municipal sludge. To investigate this, sludge samples taken from Ankara Central Wastewater Treatment Plant, OID Wastewater Treatment Plants and Textile Industry Wastewater Treatment Plant are used. Different proportions of these sludges are mixed and used in anaerobic reactor set-up. BMP tests are used for the evaluation of biodegradability and the biogas production potential of these mixed sludges. To test the effect, ultrasonication pretreatment is also applied to selected BMP sets. Biogas production potential and the removal of volatile solids and chemical oxygen demand are determined for BMP tests operated for different sludge mixtures with and without ultrasound pretreatment process.

CHAPTER 2

LITERATURE REVIEW

Sludge is defined as the solid by-products produced as a result of wastewater treatment processes. It contains substantial amount of organic matter from different sources, pathogenic microorganisms, metals and toxic compounds (Andreoli and Sperling, 2007). Due to its composition, it should be disposed by using safe methods to protect environment and people. Sludge generation as a result of wastewater treatment operations depends on wastewater amount and composition. Larger quantities of sludge are formed when wastewater treatment includes advanced processes. Moreover, sludge composition depends on treatment types, e.g., physical, chemical and biological treatment. For these reasons, wastewater treatment process sequence completely determines sludge quantity and quality (Sanin et al., 2011; Metcalf and Eddy, 2003). The characteristics of wastewater and the units of wastewater treatment plant affect the composition of sludge (Amanatidou, 2015).

Typical physical, chemical and biological characteristics of sludge is given in Table 2.1 (Sanin et al., 2011). All these parameters play significant role during sludge management. Sludge show differences according to wastewater treatment plant types and processes used in its source. Basically, sludge in wastewater treatment plant is produced as a result of screening, grit removal, pre-aeration, primary sedimentation, biological treatment and secondary sedimentation processes (Metcalf and Eddy, 2013). In general, sludges produced from screening and grit removal processes consists of inorganic or non-biodegradable components. They are not considered for further processing and disposed to landfills. Raw wastewater obtained from primary sedimentation tank, defined as primary sludge, has high COD value. General COD value of raw sewage ranges from 200 to 700 mg/L (Choksi et al., 2015). Biological sludge or secondary sludge is the result of biological treatment step and collected from the secondary settling tank bottom (Demirbaş et al., 2017). Primary, activated or mixed sludge are retained in thickening unit for further concentration of the solids. Furthermore, biological sludge is stabilized in aerobic and anaerobic digestions (Metcalf and Eddy, 2013). Primary, secondary, thickening and digestion sludges are the main sludge sources used for energy production.

In European Union, daily amount of sludge produced reaches more than 8.3 million ton of dry solids according to Urban Waste Water Treatment Directive (Karagiannidis et al., 2011). Nearly 76.3 million ton dry sludge is directly sent to landfill areas (Zhang et al., 2007).

Table 2.1: *Typical wastewater sludge characteristics*

Physical Characteristics	• Specific gravity • Solids concentration • Floc/particle size and shape • Distribution water • Filterability and dewatering • Rheology • Floc structure and porosity • Thermal conductivity
Chemical Characteristics	• Surface charge and hydrophobicity • Nutrients and fertilizer value • Heavy metal and toxic organics
Biological Characteristics	• Microbial community • Surface polymers

Because of its large volume and undesirable nature, management of sludge is one of the major challenges for wastewater treatment plants (Andreoli and Sperling, 2007; Jimenez, et al., 2004).

Parallel to the increase in industrial activities, industrial wastewater amount and the amount of industrial wastewater sludge are also increasing, globally. Industrial sludge has more problematic properties, compared to domestic sludge since it generally includes more heavy metals, toxic substance and, by-products and pesticides. Industrial sludge recovery is difficult due to its aforementioned content, and requires more sophisticated approaches (Cunningham, 2013; Cieślik, et al., 2015).

2.1. Sludge Treatment Methods

Sludge treatment include six stages, thickening, stabilization, conditioning, dewatering, disinfection and final disposal/beneficial use in general (Sanin et al., 2011). Thickening removes water and so reduce the sludge volume physically. Gravity thickening, flotation, centrifuge and belt filter press are thickening methods. At stabilization step, the amounts of biodegradable organic matter and volatile solids are removed. Therefore, stabilization provides about 38% reduction in volatile solids (Sanin et al., 2011). Stabilization includes anaerobic and aerobic digestion, thermal treatment and chemical stabilization. Conditioning stage is a sludge dewatering preparation process by adding chemical products. This addition increases the dewatering capability of sludge and improves the capture of solids in sludge. Chemical and thermal are mentioned as the type of conditioning. Dewatering also reduces volume of sludge since water is removed from sludge. This stage has an important role on sludge transportation and disposal cost. Drying beds, sludge lagoons, filter press, centrifuge, belt filter press, vacuum filter and thermal drying are used for dewatering process. Pathogenic microorganisms are removed with disinfection processes. Disinfection affects final disposal options because it is not crucial if sludge is incinerated or disposed in landfill. Lime addition, thermal treatment, composting and wet air oxidation provide the disinfection on sludge. The aim of final disposal/beneficial use is to provide final destination of the by-products. Final disposal stage involves agricultural recycling, recovery of degraded areas, land farming, non-agricultural use, incineration, wet air oxidation and sanitary landfill options (Sperling, 2007; Sanin et al., 2011; Spellman, 2008; Turovskiy and Mathai, 2006).

2.2.1 Sludge Stabilization and Methods

The high amounts of pathogenic microorganisms, easily putrefiable matter and unpleasant odor are part of raw sludge. The aim of stabilization processes is stabilizing the biodegradable fraction of organic matters in sludge. As a result of sludge stabilization, harmful properties of raw sludge are eliminated. Odor, volatile solids and pathogens reduction, alteration in oxygen uptake rate for aerobic activity indication and in gas production for anaerobic activity indication, nitrification, total organic carbon, biochemical oxygen demand, chemical oxygen demand and adenosine triphosphate are mentioned as stability parameters (Sanin et al., 2011; Kazimierczak, 2012). The stabilization process is divided into three groups; biological, chemical and thermal stabilization. Biological stabilization promotes the stabilization of the biodegradable fraction of organic matter by using specific bacteria. Chemical stabilization depends on chemical oxidation of organic matters. Thermal stabilization is attained from the heat action on the volatile fraction (Sperling, 2007).

Physical stabilization involves heat stabilization and irradiation. Lime stabilization and chemical fixation are common types of chemical stabilization. Aerobic digestion, anaerobic digestion, composting and vermistabilization are known as biological stabilization types that is commonly used sludge stabilization methods (Sanin et al., 2011; Peirce, 1998).

2.1.1.1. Anaerobic Digestion of Sludge

Anaerobic digestion can help to decrease pollution with removal of organic waste effectively as well production of renewable energy (Elmashad and Zhang, 2010; Kim et al., 2003). In fact, anaerobic digestion of organic waste is widely used during waste stabilization since this waste should be treated before disposed in environment (Tufaner and Avşar, 2016). Anaerobic digestion, a multi-stage biochemical process, provides organic matter stabilization of sludge with degradation by bacterial activity in oxygen-free environment (Andreoli and Sperling, 2007). During this process, different types of complex organic compounds in sludge are converted to methane (CH_4) and carbon dioxide (CO_2) gases, which the reaction is shown: (Sanin et al., 2011)

$$\textit{Organic matter} + H_2O \rightarrow CH_4 + CO_2 + \textit{new bacterial cells}$$

The process consists of three steps shown below in Figure 2.1. First stage is named as hydrolysis where complex organic matters such as carbohydrates and cellulose are broken down simple organic compounds (sugars and amino acids). After obtained soluble compounds, acidogenesis takes place as second stage of anaerobic treatment. In this stage, microorganisms convert from these simple compounds to long chain fatty acids. At the last stage, volatile acids are turned into acetate and H_2 gases converted to CH_4 by acetogens and methanogens, respectively (Speece, 1996). Approximately 70% methane gas is produced from acetate as main precursor (Henze, 2008).

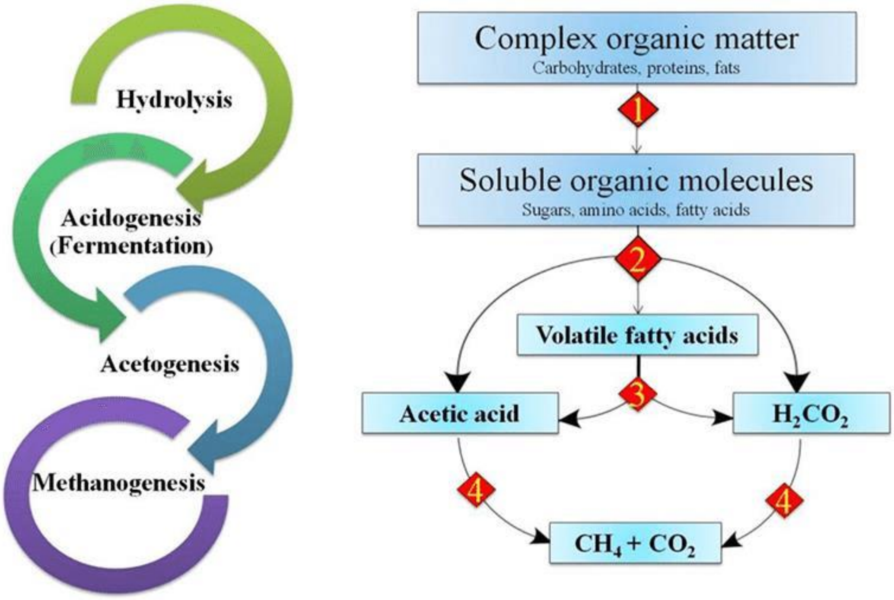


Figure 2.1: Anaerobic digestion process stages (Dussadee, et al., 2016)

To provide optimal anaerobic digestion process, the effects of some parameters named as temperature, pH and alkalinity, macro and micro nutrients requirements, inhibitory materials and toxicity have significant influences. Electron donor and acceptor, adequate metabolism time and carbon source for synthesis are other parameters to influence anaerobic digestion (Speece, 1996). Anaerobic digestion depends on optimum operating conditions and inhibition effects since the degradability of organic components are one of the determinant factors on biological stabilization (Li et al., 2017).

Temperature is one of the most crucial parameters that affects the reaction rates of anaerobic process since microbial growth rate depends on it. Temperature determines whether mesophilic or thermophilic processes become dominant in anaerobic digestion. On mesophilic operation, it changes from 10 to 35^{o}C. Whilst, the ranges of optimum temperature are accepted between 55 and 65 ^{o}C for thermophilic condition

(McCarty and Rittmann, 2018). Furthermore, temperature control is less difficult in mesophilic digester compared to thermophilic ones (Gerardi, 2003).

pH and alkalinity are accepted as other most important parameters to provide performance and stability to the anaerobic process. The conversion organic matter during anaerobic metabolic stages leads to alteration of pH values; however, enzymatic activity of microorganisms influenced by pH variation. Therefore, pH range that is 6.5 to 7.5 for methane forming bacteria should be regulated (Nayono, 2010). Moreover, alkalinity also affects carbonic-acid system which dominates the buffering on anaerobic process (McCarty and Rittmann, 2018).

Nutrient requirements influence the increase of biogas and methane production in anaerobic digestion process, and process stability (Clark and Deswarte, 2014; Amon et al., 2007). Macronutrients such as carbon, nitrogen, hydrogen, oxygen and sulfur that are main structure of microorganisms are used in microbial metabolic activity of anaerobic digestion (Mao et al., 2016; Lindorfer et al., n.d.; Banks and Heaven, 2013). The growth and activity of microorganism contingent upon micronutrients, one of the essential factors, in anaerobic digestion (Wilkie et al., 1986). On one hand, micronutrients (trace elements) such as zinc, iron and cobalt have significant influence on microorganisms' growth and anaerobic process performance whereas these nutrients lead to methane inhibition due to overdose (Sibiya et al., 2015; Khanal, 2011). In addition to these, when organics is difficult to hydrolyze, less biogas production is observed despite presence of more anaerobic microorganisms in sludge (Wang et al., 2003).

Presence of some substances in influent wastewater and/or through byproducts of metabolic activities of the microorganisms conduce toward toxicity. Ammonia, heavy metals, sulfide, halogenated compounds, phenol and long-chain fatty acids are commonly known example of toxic compounds for anaerobic process (Khanal, 2008). In addition, alcohols, alkaline cations, nitrate, sulfate, benzene ring compounds, chlorinated hydrocarbons, detergents and disinfectants, food preservatives, formaldehyde, hydrogen sulfide, organic-nitrogen compounds, oxygen, pharmaceuticals, solvents and volatile acids are accepted as inorganic and organic toxic chemicals for anaerobic digestion. Microorganisms producing methane gas can tolerate these toxic conditions if microorganisms have an ability of adaptation to constant toxic compound concentration, other toxic matters are absence or presence in the environment and operational conditions of anaerobic process changes (Gerardi, 2003).

Methanogenic organisms have high sensitivity to pH, temperature changes, acidogenic and acetogenic organisms demonstrates low and moderate sensitivity under various pH, temperature and toxic conditions (Andreoli and Sperling, 2007).

Compared to other stabilization processes, anaerobic digestion has benefits and drawbacks. During anaerobic process, the reduction of sludge volume and odor, pathogens elimination, the increment of sludge dewaterability performance and useful gas generation are achieved (J. Paul Guyer, 2011). In addition to these advantages, anaerobic process helps to reduce nitrogen and phosphorus supplementation and waste biomass disposal cost, installation space and operational attention requirements and chlorinated organic toxicity levels and also to eliminate off-gas air pollution, to avoid foaming with surfactant wastewaters and to biodegrade aerobic non-biodegradables (Speece, 1996). However, the effect of location and season, change in C/N ratio and so affecting biogas production. Long startup requirement to improve biomass inventory, less biodegradable matter content in sludge and insufficient condition for nitrification are mentioned as the disadvantages of anaerobic process (Speece, 1996;

Rajaram et al., 2016). Additional drawbacks for anaerobic digeston include the operational difficulty and cost in wastewater engineering operations. %35 of capital cost and %55 of annual operation and maintenance costs of a wastewater treatment plant is spent for anaerobic digestion (Knezevic, 1995).

To specify anaerobic biodegradation potential of a substance, the biochemical methane production (BMP) assay representing experimental value of the maximum quantity of methane generated per gram of VS can be used (Esposito, 2012). In other words, the BMP test gives information about biogas/biomethane available quantity from the degradation of a biomass and also denoted as Nm^3 biogas or methane/kg VS (Soldano et al., 2012). Furthermore, BMP is used as common and reliable method to evaluate the possibility of different substrate to co-substrate (Benito-Mora et al., 2018).

BMP performance is related to inoculum-nutrients ratio, medium, mixing, liquid and headspace volume (Angelidaki et al., 2009). TS, VS, nitrogen, phosphorus and especially COD in the substrate are crucial parameters to determine biogas production and organic matter removal (Buffiere et al., 2006; Raposo et al., 2008). Inoculum taken from active anaerobic digester is suitable to generate biogas (Angelidaki et al., 2009). The composition of the medium enables anaerobic microorganisms to use necessary nutrients and vitamins to reach optimal metabolism for digestion (Lindorfer et al., 2007). The transport restrictions between microorganisms and nutrients are eliminated by mixing, accumulation of sludge at the bottom of the tank is precluded (Vavilin et al., 2008) and a homogeneity is obtained.

BMP test is accepted as easy, repeatable and low-cost laboratory method for anaerobic digestion potential to evaluate biodegradability and methanogenic potential of certain waste sludge, compared to other anaerobic digestibility approaches. Furthermore, it is flexible enough to determine biogas production potential for different substrates (Moody et al., 2009; Benito-Mora et al., 2018). Other advantages of BMP assay are the identification of aerobic non-biodegradable components that depend on anaerobic process and the quantification of residual organic pollution realistically (Speece, 1996).

In laboratory studies experiments show that headspace volume impact on biogas accumulation because BMP test performance can decline if proper pressure in anaerobic reactor is not supplied (Valero et al., 2016).

2.2. Sludge Pretreatment Options

Biogas and methane gas amounts produced under anaerobic condition are enhanced with the use of pretreatment processes in sludge (Liu et al., 2018) since these methods provide sludge cell lysis and improve the hydrolysis of sludge. As a result of these methods, particulate matter solubilization and biological decomposition of organic polymers are also achieved (Zhang, 2010). These pretreatment options involve mechanical, chemical, thermal and biological treatment depicted in Figure 2.2 (Müller, 2001).

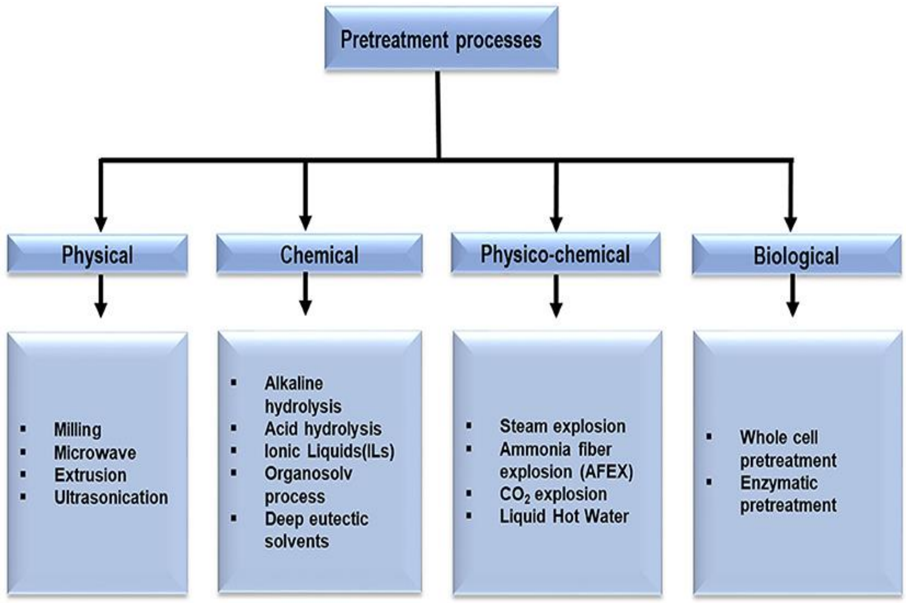


Figure 2.2: Pretreatment processes methods (Baruah, et al., 2018)

Whilst, thermal hydrolysis, ultrasound irradiation, microwave irradiation, fenton oxidation, catalytic wet oxidation and photocatalytic pretreatment are defined and used as single pretreatment approaches, combined use of these processes are also common pretreatment approaches (Anjum et al., 2016). Alkaline, conventional mechanical disintegration, ozone oxidation, are also known as common pretreatment methods (Wun, 2014).

Mechanical pretreatment helps disintegration of solid sludge floc particles in the substrate, to release cell compounds and expand specific surface area that enhance anaerobic bacteria to contact with substrate. These pretreatment applications have an importance on enhancing anaerobic digestion (Ariunbaatar et al., 2014). Ultrasonication mentioned below in Section 2.3.1, high pressure homogenization and grinding are the most preferred methods of mechanical pretreatment (Zhang, 2010).

Alkaline and acid hydrolysis, ozonation and other oxidation processes are recognized as chemical pretreatment methods (Neumann et al., 2016). During chemical pretreatment, cell wall and membrane in sludge are hydrolyzed with chemical reagents; heat, solubility of organic matter in microbial cells is enhanced. By using strong minerals acids, alkali and oxidation process, complex organic compounds are disintegrated (Tyagi and Lo, 2011). Applied pretreatment method and the substrate characteristics determine the efficiency (Ariunbaatar et al., 2014).

Thermal pretreatment is another effective sludge treatment process which enhances biological process such as biogas production potential, pathogen removal and dewatering. In thermal hydrolysis, low hydraulic retention time is achieved under high temperature conditions (Tyagi and Lo, 2012; Souza et al., 2013). The operation temperature of thermal pretreatment involving conventional heating or microwave irradiation methods varies between 60 and 270 ºC (Zhang, 2010; Tyagi and Lo, 2011).

Biological pretreatment involves enzymatic, aerobic and anaerobic methods (Müller, 2001; Brémond et al., 2018), as well. This additional stage enhances sludge solubility before the main digestion process (Carrère et al., 2010). Adding external enzymes provide better biogas and methane yield from complex organic substrates, by improving hydrolysis step in anaerobic process (Brémond et al., 2018). Hydrolysis enzymes improve hydrolysis of complex organic matters prior to anaerobic digestion (Lim and Wang, 2013). Enhanced hydrolytic stage contribute to enrichment of certain biomass (Brémond et al., 2018).

2.2.1. Ultrasonic Pretreatment of Sludge

A cyclic pressure wave, above the frequency for human hearing limit, defined as ultrasonication, widely used as a sludge pretreatment method. It is preferred and defined as environmental-friendly process because of its high disintegration performance, better technical and operational stability, (Tyagi et al., 2014). Ultrasonic pretreatment is an effective way to change physical (particle size distribution and settleability), morphological (with optical and electron microscopy), physico-chemical (soluble chemical oxygen demand and organic carbon), energy recovery (biogas and methane production) and engineering (dewaterability) (Li et al., 2015), parameters of sludge.

Cavitation is defined as the formation, growth and then collapse of micro-bubbles in a short span of time. High temperature and pressure change occur in liquid phase, due to rapid collapse and expansion of microbubbles. Therefore, cell membrane disrupts, and intercellular matter is released from cell into bulk liquor (Gogate, 2002). Temperature, ultrasound frequency and density have an impact on cavitation (Erden and Filibeli, 2010; Pilli et al., 2011). Cavitation at certain frequencies and temperature also produce OH•, HO_2•, H• radicals during ultrasonic pre-treatment. As a result, cell structure and floc matrix are damaged by mechanical and chemical process (Carrère et al., 2010).

Ultrasonication applied to sludge (i) reduce floc size; decreasing the size of microbial flocs and large sludge particles, (ii) brake cell; releasing intracellular organic compounds from cell because of the cell wall destruction and (iii) degrade macromolecules to short chain organic matter shown in Figure 2.3 (Zhang, 2010; Khanal et al., 2007). Ultrasonication enhanced hydrolysis reaction mentioned above is the rate limiting step during anaerobic digestion (Zhang, 2010). Moreover, methane production and sludge volume reduction are improved in acidogenesis, acetogenesis and methanogenesis processes since sludge particles are disrupted as a result of ultrasound pretreatment (Show et al., 2007).

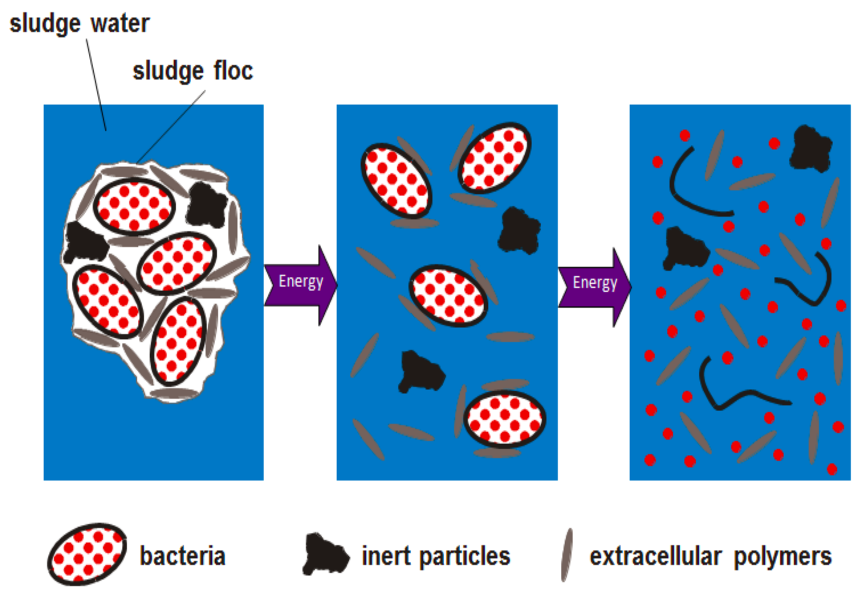


Figure 2.3: Sludge disintegration with ultrasonic pretreatment (Gallego-Juárez and Graff, 2014)

Generally, ultrasound pretreatment is applied at low frequency with specific energy between 1,250 and 40,000 kJ/kg TS (Neumann et al., 2016). The most useful ultrasonic frequency range changes from 20 to 200 kHz (Hua and Thompson, 2000). For sludge treatment, ultrasonic pretreatment with the highest efficiency at low frequencies (20 – 40 kHz) help dissociation of sludge flocs and the lyses of microorganisms depending on sonication time and power (Chu, 2002; Li et al., 2015). Furthermore, higher sludge concentrations provide higher pretreatment efficiency because it enhances the contacting possibility of particles in sludge (Carrère et al., 2010). Sludge solubilization results from higher specific energy input due to the balance between sludge solubilization and supplied energy (Tyagi and Lo, 2011). During ultrasonic pretreatment, the physical, chemical and biological properties of sludge change (Neumann et al., 2016).

Ultrasonic pretreatment can be implemented to both industrial and domestic activated sludge (Carrère et al., 2010; Cano et al., 2015). Ultrasonic pretreatment used for anaerobic digestion reduces energy consumption and enhance performance of anaerobic digestion (Carrère et al., 2010; Salsabil et al., 2009). As a result of sludge ultrasonication pretreatment, the efficiency of biogas production in batch system increases between 24% and 140% (Carrère et al., 2010). Solid reduction is enhanced and SRT is declined when ultrasonic pretreatment is applied (Tyagi and Lo, 2011). COD removal of unsonicated WAS was 11 to 39% less compared to sonicated one during anaerobic process, in terms of soluble COD (Khanal et al., 2007). In addition, ultrasonic pretreatment minimizes the probability of sludge bulking problem and pathogens based on ultrasonic intensity and time (Wünsch et al., 2002; Neis et al., 2008; Jean et al., 2000). Other advantages of ultrasonication are; better dewaterability for final sludge, no odor, by-products and clogging problems, and filamentous bulking and foaming control; although high capital and operational cost, and long-term performance for full scale system are known as drawbacks (Tyagi and Lo, 2011; Mahvi, 2009).

2.3. Beneficial Use of Sludge

Sludge disposal is a costly operation and has a burden on wastewater treatment plant. Landfilling, incineration and land application are typical sludge disposal/beneficial use methods all around the world. Recently, new environmental protection policies, brought critical changes for sludge common disposal methods (European Environment Agency, 1998; EPA, 2018). Landfill Directive in EU brought reduction requirement for the biodegradable wastes to be disposed into the landfills. This brings important limitation for sludge disposal into landfills. Land application of sludge is not in widespread use because of legislation restrictions and concerns over pathogens and toxic substances in sludge. Incineration is considered as the ultimate sludge use/disposal method and preferred some countries. This method makes sludge as an alternative/additional fuel in thermal process (Sanin et al., 2011; Peirce, 1998; Forster, 2003).

2.4. Co-Digestion of Wastes

During co-digestion, mixing sludges as substrates have environmental, technological and economic advantages, comparing a single sludge processing (Brown and Li, 2013). Sufficient waste reduction and biogas production might not be provided with monotype waste in the anaerobic digestion process. Because of this reason, mixing waste by anaerobic co-digestion process has synergetic effects to obtain proper biogas yield and volume reduction (Tufaner and Avşar, 2016). The dilution of potential toxic compounds, improved nutrient balance, support microbial community, synergistic effects on microorganisms and increase of biodegradability of organic compounds, biogas yield and digestion rate are provided by co-digestion (Sosnowski et al., 2003; Supaphol et al., 2011). In order to enhance substrate condition, co-digestion of carbon rich solid wastes is accepted as attractive approach (Wang et al., 2012). Co-digestion of industrial and municipal sludge might have a positive effect on COD reduction and organic compound degradation. In addition to this, low concentrations of heavy metals (Cr, Zn, Pb, Fe and Mn) can help anaerobic bacteria growth and not inhibit conversion from organic matters to methane gas. For these reasons, co-digestion of industrial and municipal sludges might be used as effective alternative sludge management method (Ağdağ and Sponza, 2005).

Although industrial wastewater includes readily degradable organic compounds to produce methane gas, heavy metals, organic toxicants and high salinity in industrial wastewater content prevent anaerobic microbial activity. Anaerobic process can be applied on different industrial wastewater sludge. Large amount wastewater including chromium, potassium, magnesium, sodium, iron and calcium from fishery industry affects anaerobic microbial activity in a negative way because of decrease methane production acceleration. High sodium and phosphate concentrations from food industry wastewater have no adverse effect on methane generation. In addition, BMP test which is conducted by using brewery and dairy wastewater involving calcium, cadmium, copper, potassium, magnesium, iron, lead, nickel, zinc and sodium does not influence inhibition significantly. Low heavy metal concentrations industrial wastewaters did not affect methane production. (Ko et al., 2012). High sodium concentrations cause toxic effect on anaerobic digestion (Feijoo et al., 1995).

Because of sludge composition, wastewater may have less methane production potential than co-digestion with macroalgae. In addition to this, pretreatment process (microwave, ultrasound and thermal) influence biogas and methane production in negative sense (Civelek et al., 2017).

Mixing, wastes and/or wastewaters to improve methane production is commonly used in treatment industry. Fishery wastes have low moisture content since it consists of high concentration of fat and oil. On the other hand, seagrass and macroalgae have higher moisture content (Rubia et al., 2006; Davis et al., 2000). Again, fishery wastes have high volatile solids because of fat and oil content, compared to seagrass/macroalgae. Co-digestion with fish waste including dead fish, skins, fish intestines and other unused matters (Sakar et al., 2009), seagrass and macroalgae provides high biogas yield (Nazurally, 2018).

The process of personal care product generates high carbon wastes; however, these wastes contain oxidants, dyes, ammonia, inhibitory and toxic compounds (Marsh et al., 2009). Inhibitory compounds in this industrial wastewater affect negatively biogas and methane production due to reducing methanogenic microorganisms' activity.

Similar wastewater content in textile and pulp and paper manufacturing inhibit these microorganisms; so, these industrial wastewaters has low anaerobic digestion performance (Ahammad et al., 2014). Secondary sludge from pulp industry contain residual cellulose, lignin and chemical matters due to pulping process (Kyllönen et al., 1988).

Pretreatment process such as thermal and caustic pretreatment help to improve the biogas production potential of pulp mill secondary sludge or personal care sludge (Wood et al., 2009).

2.5. Review of Industrial Sludges Used in This Research

Industrial organized district and textile sludge are one of the most difficult sludge types to treat. Besides that, adding industrial sludges decrease methane production during anaerobic process (Ağdağ and Sponza, 2005). By applying ultrasonic pretreatment, the negative effects on sludge composition can be decreased.

2.5.1. Industrial Organized District Sludge

Metal and similar industries such as machine manufacturing industries are accepted polluting processes of the environment (Alkaya and Demirer, 2013). Metal rich wastewaters are generally treated with conventional alkaline neutralization precipitation process. Limited settleability and dewaterability are one of the most important disadvantages of this process (Peters and Ku, 1987; Luo et al., 1992). Metal industries use significant amount of heavy metals and toxic/hazardous compounds involving volatile organics, acid/alkali fumes, hexavalent chrome, nickel and cyanides during their production process (Mohsen and Jaber,2002; Magalhães et al., 2005; Sthiannopkao and Sreesai, 2009; Telukdarie et al., 2006). Chromium, nickel and iron are known primary produced toxic substances in metal industries (Mohsen and Jaber, 2002). Besides that, these industries generate wastewater with high oil and biochemical oxygen demand, and hazardous sludge produced in wastewater treatment plant (Clarens et al., 2008; Ucaroglu and Talinli, 2012). The content of wastewater and sludge from machine manufacturing industries are also hazardous and difficult to manage. This sludge includes toxic and scrap metals, solvents and painting wastes, oils and suspended solids (Wang et al., 2004).

While large quantities water is not used by the furniture manufacturing process, a considerable amount of wastewater is produced from finishing stage during painting process (Scheneider et al., 2003). The main pollution sources are specific preservatives, coating materials for wood surfaces and wood painting (Kaczala et al., 2009; Santos Lage et al., 2010). Volatile organic compounds are used in dye solvents and wood preservatives. The wastewater of wood furniture industries includes high organic matter, low macronutrients and highly contaminated soluble organics (Nasr et al., 2012).

Basic and commodity chemicals are used in the production process of polymers, pharmaceutical products, bulk petrochemicals and intermediates, other derivatives and basic industrials, fertilizers and organic/inorganic chemicals (Awaleh and Soubaneh, 2014). Chemical industrial wastewater consists of highly concentrated organic and inorganic pollutants which are toxic and resistant to apply biological treatment for some conditions. In addition to this, it includes acids, bases, color, low in suspended solids, toxic materials (EPA, 1998). These pollutants in wastewater generated from chemical industries dramatically decrease the applicability of biological processes (Guomin et al., 2009; Fayza et al., 2007). Some chemicals and processes such as phenol and rubber synthesis inhibit microorganisms' activity; therefore, wastewater discharge standards cannot be fulfilled (Ding, 2006). Many compounds in chemical industries are accepted as toxic, mutagenic, carcinogenic and simply non-biodegradable (Fayza et al., 2007). Because of these reasons, wastes of chemical industries are different from domestic sewage; so, pretreatment is essential to manage these sludges (Meric et al., 1999).

Tanks and pipes cleaning, cooling, floor scouring, bottle washing and juice production generate process wastewater in most beverage industries (Matošić et al., 2009; Ait Hsine and Benhammou, 2002). When produced beverages, some raw materials such as orange, grape, sugar and phosphates) increase organic load of wastewater (Al-Mutairi et al., 2004). Beverage industrial wastewater includes phosphorus, orthophosphate, nitrate and iron (Amuda and Amoo, 2007). For soft drink industries, sugar and other easily biodegradable substances found in high concentration in process water (Chen et al., 2006). Wastewater from these industries involves suspended solid, organic substances, nitrates, phosphates, sodium and potassium (Nweke et al., 2015).

Food waste is highly variable since its source and composition significantly differ from one process to another (Zhang et al., 2007). Food industrial wastewater contains organic substances (in dissolved or colloidal state), oil/greases, phosphorus, carbohydrates such as sugar, pectins, flavouring and coloring additives and high nitrogen compounds, mainly ammonium nitrogen form (Ait Hsine et al., 2004; Zhukova et al., 2011; Falletti et al., 2015; El-Gohary et al., 1999). Because of washing and disinfection processes of food industries, small amount chemicals can be found in this wastewater (Falletti et al., 2015). Moreover, food waste management might be difficult due to high moisture content (Davidsson et al., 2008).

2.5.2. Textile Industry Sludge

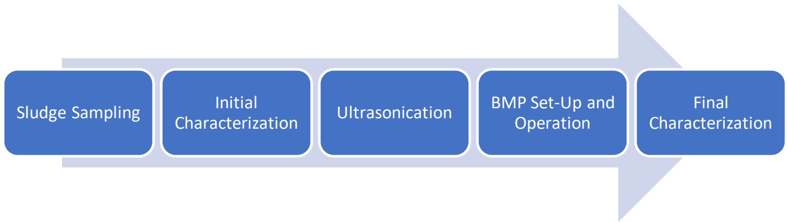
Textile dyeing sludge endangers the environment because of its large amount, complex composition and persistence in the environment (Meng et al., 2016). Textile dyeing sludge consists of high content of organic matter, nitrogen, phosphorus, potassium and micronutrients (Mohamed et al., 2018), heavy metals (cadmium, chromium, lead etc.) and persistent organic pollutants (polycyclic aromatic hydrocarbons and aromatic amines) in sludge (Guo et al., 2018; Ning et al., 2003) pose a danger for the environment. The textile industrial processes consisting of high COD, suspended solids, toxic materials, heavy metals, salt, dyes and chemicals are known as one of the largest toxic wastewater sources since these processes such as dyeing, and finishing consume high amount of water (Gebrati, et al., 2018; Yurtsever et al., 2015; Nigam et al., 1996). Reactive dye compounds pass through conventional activated sludge system without degradation and accumulate in sludge; therefore, they have a toxic effect on biological system (Willmot, et al., 2008). Wastewater coming from dying process is the most significant pollutant of textile industry processes because it increases biochemical oxygen demand concentration and declines dissolved oxygen concentration in water environment (Chaeibakhsh et al., 2004). Because of the characteristics of textile wastewater, its sludge involves high amount of volatile organic compounds and heavy metals so landfilling and composting are less desirable disposal options for this sludge (Alleman, 1987). Sludge pretreatment methods are not very effective to minimize the hazardous effects of textile sludge. Physico-chemical properties and biodegradability of them do not change much during ultrasonic pretreatment (Zou et al., 2019).

CHAPTER 3

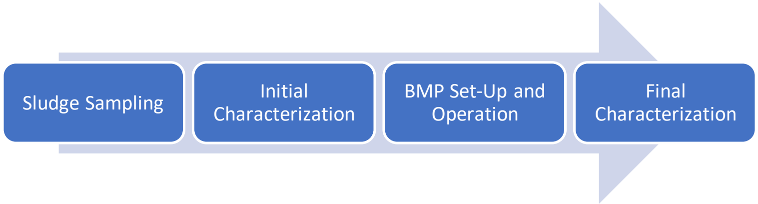
MATERIALS AND METHODS

Within the scope of this study, several experiments were planed and implemented to investigate the energy production and toxicity control in industrial sludges during anaerobic digestion. BMP experiments were the first step of the evaluation of energy production potential on industrial sludges. Three different BMP test sets were conducted, to determine the performance of industrial sludges on anaerobic digestion efficiency. Ultrasonic homogenization is included in the experimental design as a physicochemical sludge pretreatment process, to evaluate the effect of sludge disintegration on the whole process. In the first two experimental sets, sludge samples from two Organized Industrial Districts (OID) were tested for BMP with and without the ultrasonic pretreatment. In the third experimental set BMP of sludge sample from textile industry is determined with ultrasonic pretreatment. A brief summary of the experimental steps is given in Figure 3.1.

First Set of BMP (OID I)



Second Set of BMP (OID II)



Third Set of BMP (Textile Industry)

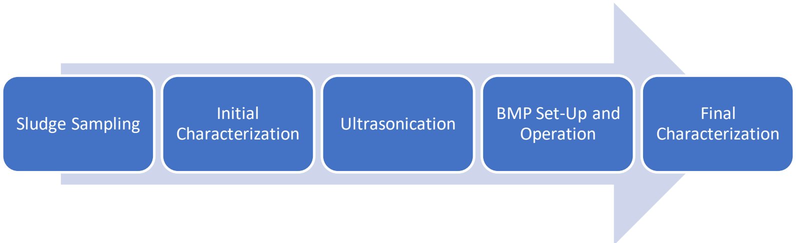


Figure 3.1: Summary of experimental steps

3.1. Sludge Samples Used

Two different sludge types were used one for seed and one for waste: which were anaerobically digested sludge (ADS) and waste activated sludge (WAS), respectively. Anaerobic seed sludge was taken from the anaerobic digesters in Ankara Central Wastewater Treatment Plant for all the experiments conducted. The WAS samples which acted as "waste" to be treated were collected from the return line of biological treatment units in Ankara Central Wastewater Treatment Plant as well as OID I, OID II and Textile Industry Wastewater Treatment Plants.

The first sludge sample from the Central Wastewater Treatment Plant of Ankara, that treats municipal wastewater is used as a reference sample. The average daily flow rate of this treatment plant is stated as 765,000 m^3 and it serves a 5,445,500 population. Municipal wastewater is treated with a conventional activated sludge system, preceded by preliminary treatment and primary treatment. Hydraulic retention time is reported to be 4 hours in aeration basin. The amount of sludge treated in this municipal wastewater treatment plant is reported as 250 ton KM/day. The sludge from primary and secondary sedimentation units are collected and transmitted to a gravity thickener. Then the sludge is treated in eight mesophilic anaerobic digesters each has a 11,250 m^3 volume. Generated gas from these digesters contains 65 - 70% methane in its composition. In addition to biogas production, 6% total solid reduction is taking place in these anaerobic digestors. The digestate is sent to landfill after dewatering in decantor centrifuge.

The first organized industrial district sludge on which anaerobic treatment was applied was taken from OID I. According to the order of size, OID I has industrial sectors from metal, machine manufacturing, food, beverage and chemical products industries. When wastewater composition is considered, it has rather high COD of 2,559 mg/L and 1,300 mg/L of suspended solids. This plant capacity is 24,000 m^3/day, but the current wastewater flow is 18,000 m^3/day. In chemical treatment unit, alum is used for precipitation if required. Conventional aeration activated sludge is used as biological treatment unit in wastewater treatment plant. A sludge dewatering process, decantor, with polymer conditioning is applied. The process flow diagram of OID I is given below (Figure 3.2).

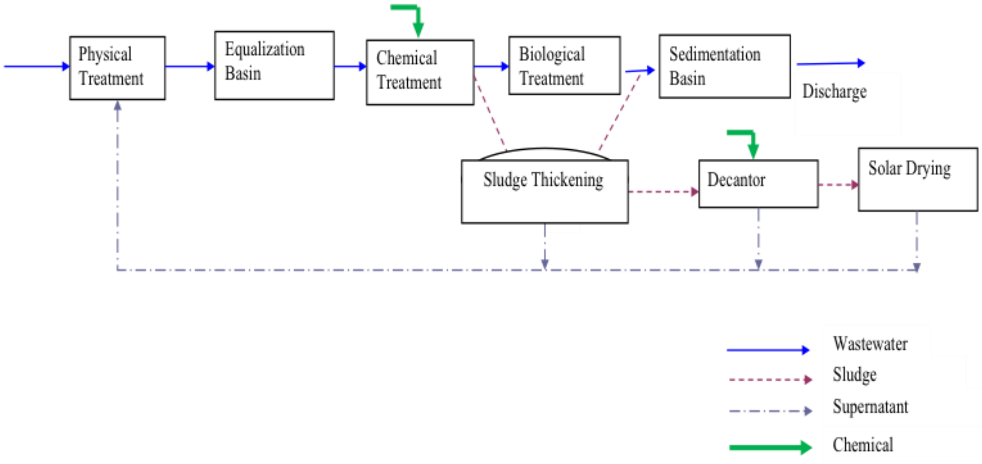


Figure 3.2: OID I wastewater treatment plant flowchart

OID II involves a number of industrial sectors including machine manufacturing, metal, food, chemical product and wood processing and furniture production given in the order of number of operating facilities. Especially, metal industry remains in the forefront of wastewater contribution. Furthermore, most of industries in OID II have pre-treatment processes; therefore, the characteristics of this wastewater might not pose a complication to treat it. Treatment plant's capacity is 7,000 m^3/day while its average flow is 6,500 m^3/day. The average influent COD value is 2,500 mg/L while the average suspended solid concentration is 900 mg/L. Physical, chemical and biological treatment (flowchart is given Figure 3.3) are used in this plant. Alum and polyelectrolyte are used in chemical treatment. Biological treatment includes anaerobic phosphorus removal system and conventional activated sludge system. If required, lime is added to help with sludge stabilization.

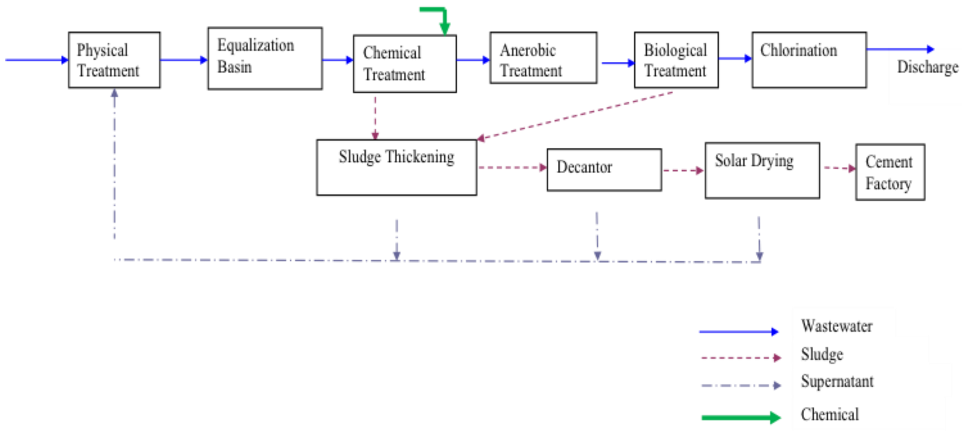


Figure 3.3: OID II wastewater treatment plant flowchart

Textile industry involves knitting, dyeing and chemical finish operations so as to obtain fabric. Raw fabric is produced in knitting process. After this step, dyeing is conducted in two separate processes, including plain or pad - batch dyeing. During plain dyeing process, fabric is dyed with hot water, dye and chemicals. In pad - batch dyeing, fabric is placed in canister by adding dye and chemicals and then it is wrapped around cylinder. Dye fabric is washed with water and acid to remove excess dye and chemicals following weaving and neutralization. When the sludge sample was collected for the experiments, dyeing and washing processes intentionally were selected to be in operation in this textile factory. Wastewater treatment plant capacity is 3,000 m^3/day and its average flow is 1,400 m^3/day. The average COD and suspended solid concentrations are 999 and 177 mg/L, respectively. The flow diagram of the plant is given in Figure 3.4. Biological treatment of wastewater is achieved using extended aeration activated sludge system, after which decolorant chemical is added in chemical treatment process. Sludge from primary and secondary clarifiers is taken to filter press for sludge dewatering.

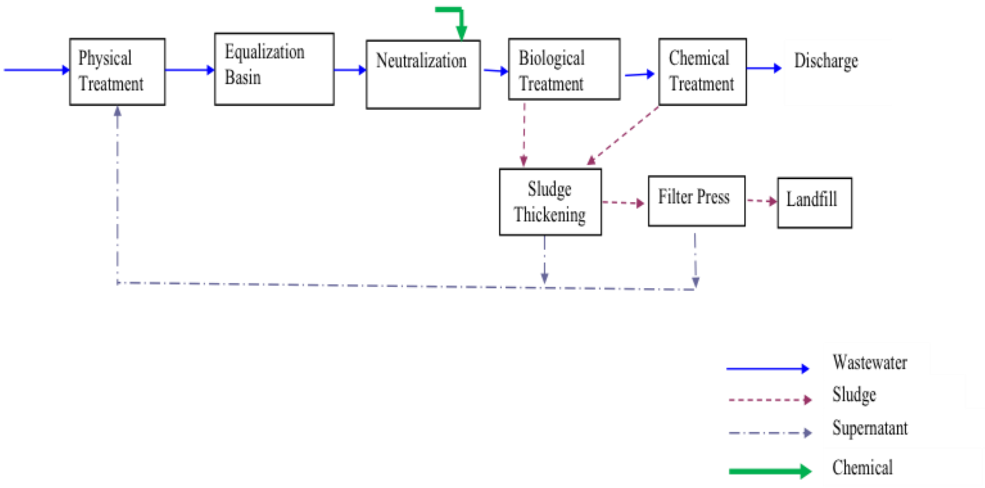


Figure 3.4: Textile industry wastewater treatment plant flowchart

3.2. Reactor Set-up and Operation

In these experiments, after anaerobic seed sludge and WAS were taken from the selected wastewater treatment plants, they were left to settle throughout four or five hours. TS, TSS, VS and VSS concentrations, COD and pH values of each sludge were measured. These measurements were used to adjust F/M ratio for all the reactors. F/M ratios were adjusted to 1 (g VS/g VSS) in the reactors.

As mentioned above, initial measurements were used to adjust sludge volume in accordance with F/M ratio of 1 before BMP reactors with different mass ratios were set. For all mass ratios, each BMP reactor had 250 mL in total volume with 200 mL of bottles were used as effective volume. To conduct the analyses mentioned above for each reactor in the initial conditions, more sludge samples were prepared in the same mass ratios. After sludge samples were put inside the reactors, each reactor was purged with 99% purity nitrogen gas for 10 minutes to eliminate oxygen. Following purging process, bottles were capped tightly and incubated at 35°C. Figure 3.5 shows

BMP bottles in the incubator. All reactors were setup in triplicates. The BMP tests lasted approximately 30 days.

Figure 3.5: The setup of BMP bottles

From the three sets of reactors operated, OID I and Textile Wastewater sludges were also subjected to ultrasound pretreatment to see if sonication helped to overcome the negative effect of industrial sludges in terms of biodegradability. The process is described in Section 3.2.1.

Biogas measurement and determination of methane percentage were conducted daily for the first fifteen days. In the last fourteen days, these parameters were measured once in two days. After biogas production was diminished at day 29, all reactors belonging to three different BMP tests were terminated. The measurement frequency of some parameters monitored in all sets of BMP experiment are shown in Table 3.1.

Table 3.1: *Parameters and their measurement frequency during all BMP experiments*

Parameter	**Measurement Frequency**
TS (mg/L), TSS (mg/L), VS (mg/L), VSS (mg/L), COD (mg/L), pH	Before reactors setup (day 0) and after reactor termination (day 29)
Biogas Volume (mL) and Biogas Composition (%CH_4, %CO_2, %N_2)	Days 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 17, 19, 21, 23, 25, 27, 29

3.3. Ultrasound Pretreatment

Sartorius Labsonic P (Sartorius AG, Germany) used in sonication has a 22 mm probe. Sonication procedure specifications are given in Table 3.2.

Table 3.2: *Specifications of sonication process*

Sonication frequency	24 kHz
Probe Size	22 mm
Sonication Power	255 W
Sample Volume	250 mL
Sonication Density	0.73 W/mL
Sonication Time (min)	15

Before setting these reactors, waste activated sludge from OID I and textile industry were sonicated in 250 mL portions. During sonication, samples were placed on ice to prevent heating impact due to sonication process. Sonication time was selected as 15 min which was previously found to be an effective duration (Apul and Sanin, 2010). Ultrasonication device is shown below in Figure 3.6. Both ultrasound pretreatment effect and differences between sonicated sludge and not sonicated sludge are given in Results section in Chapter 4.

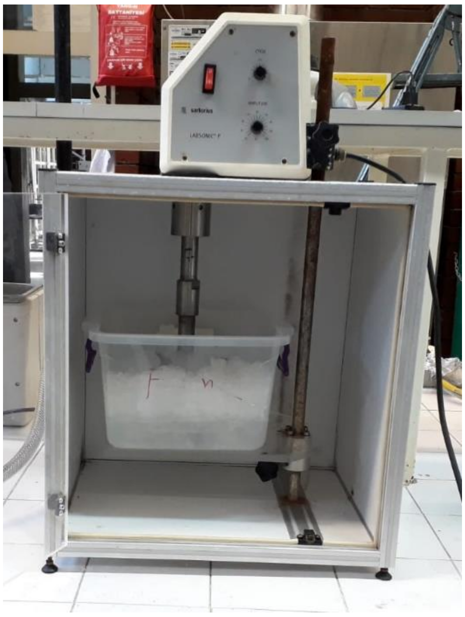


Figure 3.6: Ultrasonication system

3.4. . Reactor Set-up for Different Sludge Samples

<u>OID I SLUDGE</u>

For the first group of OID I, industrial sludge with and without ultrasonic pretreatment was mixed with municipal sludge at different mass ratios. Ten sets of triplicate BMP reactors were operated. Different sets shown in Table 3.3 were as follows: OID I sludge only (A_1), sonicated OID I sludge only (UsA_1), 2:1 (w/w) OID I sludge to municipal sludge (B_1), 2:1 (w/w) sonicated OID I sludge to municipal sludge (UsB_1), 1:2 (w/w) OID I sludge to municipal sludge (C_1), 1:2 (w/w) sonicated OID I sludge to municipal sludge (UsC_1), municipal sludge only (D_1), 0.5:2.5 (w/w) OID I sludge to municipal sludge (E_1), 0.5:2.5 (w/w) sonicated OID I sludge to municipal sludge (UsE_1) and seed only (S_1) were prepared. The reactor E is only set-up in this group to see if it can cause any significant difference. Since E is close to sample D because of low industrial sludge mass ratio, reactor E was not constructed on other BMP sets. Table 3.4 and Table 3.5 give information about the solid concentrations before reactor setup and mixture composition of sludges using OID I BMP assay, respectively.

Table 3.3**:** *Mass ratios of sludge in BMP bottles for OID I BMP assay*

Reactor Labels	Municipal Sludge Mass Portion	OID I Sludge Mass Portion	Sonication
A_1	0	3	
UsA_1	0	3	√
B_1	1	2	
UsB_1	1	2	√
C_1	2	1	
UsC_1	2	1	√
D_1	3	0	
E_1	2.5	0.5	
UsE_1	2.5	0.5	√
S_1	0	0	

Table 3.4: *Solid concentrations of sludge used in OID I BMP assay*

Sludge Type	TS (g/L)	TSS (g/L)	VS (g/L)	VSS (g/L)
Anaerobic Seed	23.48	19.99	12.60	11.27
Municipal WAS	9.32	8.68	7.73	6.18
OID I WAS	37.28	32.95	31.65	28.06

Table 3.5: *Volumes of different sludge types in OID I BMP bottles*

Mixture	**Label**	**Seed Volume (mL)**	**Municipal Sludge Volume (mL)**	**OID I Sludge Volume (mL)**	**Distilled Water (mL)**	**Total Volume (mL)**
Seed + only OID I sludge	A_1	97.00	0.00	138.20	4.80	240.00
Seed + only ultrasonic OID I sludge	UsA_1	97.00	0.00	138.20	4.80	240.00
Seed + 2:1 OID I sludge	B_1	97.00	47.10	92.10	3.80	240.00
Seed + 2:1 ultrasonic OID I sludge	UsB_1	97.00	47.10	92.10	3.80	240.00
Seed + 1:2 OID I sludge	C_1	97.00	94.30	46.00	2.70	240.00
Seed + 1:2 ultrasonic OID I sludge	UsC_1	97.00	94.30	46.00	2.70	240.00
Seed + only municipal sludge	D_1	97.00	141.40	0.00	1.60	240.00
Seed + 0.5:2.5 OID I sludge	E_1	97.00	117.80	23.00	2.20	240.00
Seed + 0.5:2.5 ultrasonic OID I sludge	UsE_1	97.00	117.80	23.00	2.20	240.00
Seed	S_1	97.00	0.00	0.00	143.00	240.00

OID II SLUDGE

In the second part, OID II sludge was mixed with municipal sludge using different mass ratios. Five sets of triplicates BMP bottles with F:M = 1.0 were set up. Set contained OID II sludge only (A_{II}), 2:1 (w/w) OID II sludge: municipal sludge (B_{II}), 1:2 (w/w) OID II sludge: municipal sludge (C_{II}), municipal sludge only (D_{II}) and seed only (S_{II}) reactors shown in Table 3.6. Table 3.7 depicts solid concentrations of anaerobic seed sludge, OID II and municipal waste activated sludge right before mixing for reactor setups. Whilst, Table 3.8 demonstrates using sludge volume required for this BMP assay.

Table 3.6: *Mass ratios of sludge in BMP bottles for OID II BMP assay*

Reactor Labels	**Municipal Sludge Mass Portion**	**OID I Sludge Mass Portion**
A_{II}	0	3
B_{II}	1	2
C_{II}	2	1
D_{II}	3	0
S_{II}	0	0

Table 3.7: *Solid concentrations of sludge used in OID II BMP assay*

Sludge Type	**TS (g/L)**	**TSS (g/L)**	**VS (g/L)**	**VSS (g/L)**
Anaerobic Seed	21.96	18.45	13.19	12.38
Municipal WAS	9.26	8.77	6.03	5.93
OID II WAS	14.10	12.44	6.74	6.56

Table 3.8: *Volumes of different sludge types in OID II BMP bottles*

Mixture	**Label**	**Seed Volume (mL)**	**Municipal Sludge Volume (mL)**	**OID II Sludge Volume (mL)**	**Distilled Water (mL)**	**Total Volume (mL)**
Seed + only OID II sludge	A_1	79.00	0.00	145.10	17.90	242.00
Seed + 2:1 OID II sludge	B_1	79.00	54.00	96.70	12.30	242.00
Seed + 1:2 OID II sludge	C_1	79.00	108.00	48.50	6.50	242.00
Seed + only municipal sludge	D_1	79.00	162.20	0.00	0.80	242.00
Seed	S_1	79.00	0.00	0.00	163.00	242.00

TEXTILE INDUSTRY SLUDGE

During BMP test with textile industrial sludge, nine triplicate sets were set up by mixing with two different sludge that are textile industry and municipal waste activated sludge in the ratio of different mass. These reactors shown in Table 3.9 were named as textile sludge only (A_t), ultrasonic textile sludge only (UsA_t), 2:1 (w/w) textile sludge (B_t), 2:1 (w/w) ultrasonic textile sludge (UsB_t), 1:2 (w/w) textile sludge: municipal sludge (C_t), 1:2 (w/w) ultrasonic textile sludge: municipal sludge (UsC_t), municipal sludge only (D_t), 0.5:2.5 (w/w) ultrasonic textile sludge: municipal sludge (UsE_t) and seed only (S_t). Table 3.10 and Table 3.11 indicate solid concentrations about textile and municipal sludge before mixing sludge to set up reactors and sludge volume put in BMP bottles, respectively.

Table 3.9: *Mass ratios of sludge in BMP bottles for textile industry BMP assay*

Reactor Labels	**Municipal Sludge Mass Portion**	**OID I Sludge Mass Portion**	**Sonication**
A_t	0	3	
UsA_t	0	3	√
B_t	1	2	
UsB_t	1	2	√
C_t	2	1	
UsC_t	2	1	√
D_t	3	0	
UsE_t	2.5	0.5	√
S_t	0	0	

Table 3.10: *Solid concentrations of sludge used in textile industry BMP assay*

Sludge Type	**TS (g/L)**	**TSS (g/L)**	**VS (g/L)**	**VSS (g/L)**
Anaerobic Seed	24.94	18.74	14.51	12.16
Municipal WAS	10.47	8.53	6.05	5.18
Textile Industry WAS	21.97	19.25	4.35	2.64

Table 3.11: *Volumes of different sludge types in textile industry BMP bottles*

Mixture	**Label**	**Seed Volume (mL)**	**Municipal Sludge Volume (mL)**	**Textile Industry Sludge Volume (mL)**	**Total Volume (mL)**
Seed + only textile sludge	A_t	63.50	0.00	177.50	242.00
Seed + only ultrasonic textile sludge	UsA_t	63.50	0.00	177.50	242.00
Seed + 2:1 textile sludge	B_t	68.50	46.00	127.50	242.00
Seed + 2:1 ultrasonic textile sludge	UsB_t	68.50	46.00	127.50	242.00
Seed + 1:2 textile sludge	C_t	74.00	99.00	69.00	242.00
Seed + 1:2 ultrasonic textile sludge	UsC_t	74.00	99.00	69.00	242.00
Seed + only municipal sludge	D_t	80.50	161.50	0.00	242.00
Seed + 0.5:2.5 ultrasonic textile sludge	UsE_t	77.00	129.00	36.00	242.00
Seed	S_t	242.00	0.00	0.00	242.00

3.5. Analytical Methods and Biogas Measurement

Parameters including TS, VS, TSS, VSS, and COD and pH were measured for each sludge sample both before reactor set-up, at the beginning and end of reactor operation. In addition to these parameters, volume and composition of produced biogas were monitored.

3.5.1. Solids Concentration Analyses

The triplicate analyses of TS, VS, TSS and VSS parameters were conducted in aforementioned times in Table 3.1. Standard Methods 2540B and 2540E were used to determine TS and VS values of sludge, whereas Standard Methods 2540D and 2540E were used as guideline for TSS and VSS analyses, respectively (APHA, AWWA, and WEF, 2005).

3.5.2. Chemical Oxygen Demand

By using HACH LCK-514 kits range of which was between 100 and 2,000 mg/L and HACH DR 3900 spectrophotometer (Hach Company, Colorado, USA), COD was measured for each sludge. All sludge samples were diluted in the ratio of 1/50 when COD measurements belonging to them were conducted in duplicates.

3.5.3. pH Measurement

Before doing the analyses, pH calibration was done by using standard pH solutions (pH values of 4, 7 and 10). According to Standard Method 4500H (APHA, AWWA, WEF, 2005), pH measurements for each sludge were measured by CyberScan PC 510 pH-meter and EC-PH510/21S probe (Eutech Instruments Pte Ltd., Spain).

3.5.4. Gas Volume and Composition

To measure produced biogas volume from BMP assays of each sludge samples, a water displacement unit shown below Figure 3.5 was used. During experiments, biogas is formed inside of the serum bottles where its pressure increases since the volumes of these bottles were constant. A needle connected to the water displacement unit is used to release the pressure of the bottles and at the same time measure the volume of gas produced. Then, it comes to equilibrium with atmospheric pressure and the volume change in the water displacement unit is measured. The displaced water volume shows produced biogas amount in the reactors.

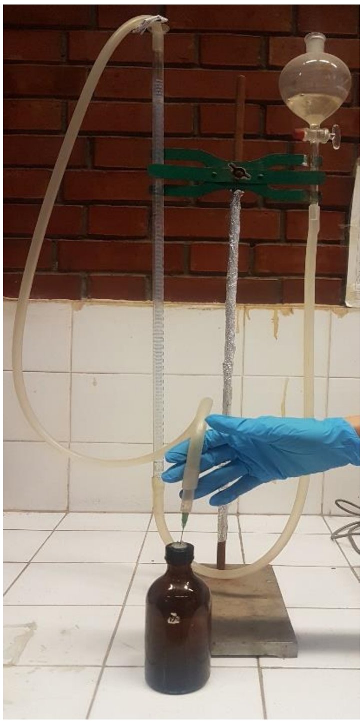


Figure 3.7: Water displacement unit

The biogas composition produced in each experimental setup was determined with Agilent Technologies 6890N Gas Chromatograph (GC) (Agilent Technologies, California, USA) by using thermal conductivity detector (TCD). It was fitted a HP-Plot Q capillary column with dimensions of 30.0 m x 530 μm x 40.0 μm. The flow rate of helium which is the carrier gas is 29 cm/s. So as to start the gas measurement, the GC's program was set at 45°C temperature for the first minute. In the later step, this temperature was risen to 65°C at a rate of 10°C/min. Before gas composition of experimental setups was measured, two different calibration standards including different gas compositions which are 65% methane, 25% carbon dioxide, 10% nitrogen and 25% methane, 55% carbon dioxide, 20% nitrogen were used for device calibration. Following this calibration, produced gas compositions were measured daily in triplicates using a Hamilton Samplelock syringe (Hamilton Company, Nevada, USA) of 500 μL volume.

3.5.5. Computation of Calculated Methane Yield

Calculated methane yield of all reactors with different mixing ratios, provides the evaluation of how different observed results are from the one obtained by simple addition. To compute the calculated yield values of mixed sludge samples, methane yield per unit amount of COD destroyed for all BMP sets are added in accordance with their mixing ratios as given in Table *3.12*.

Table 3.12. *Calculated yield values for mixing samples*

Reactor Label	**Theoretical Yield**
B	$((A_{yield}/3)*2) + ((D_{yield}/3)*1)$
UsB	$((UsA_{yield}/3)*2) + ((D_{yield}/3)*1)$
C	$((A_{yield}/3)*1) + ((D_{yield}/3)*2)$
UsC	$((UsA_{yield}/3)*1) + ((D_{yield}/3)*2)$
E	$((A_{yield}/3)*0.5) + ((D_{yield}/3)*2.5)$
UsE	$((UsA_{yield}/3)*0.5) + ((D_{yield}/3)*2.5)$

CHAPTER 4

RESULTS AND DISCUSSION

Each wastewater sludge has different biogas production potential. The efficiency of biogas production from wastewater sludges through two complimenting ideas is investigated in this thesis. It is investigated if the co-digestion of industrial sludge with low biogas production potential can be carried out with domestic sludge. Besides, the impact of industrial sludge on biogas production potential of domestic sludge is quantified.

4.1. BMP Results of Organized Industrial District I

Sludge received from OID I is tested for its biogas production potential with or without added domestic sludge. The BMP test of OID I was conducted for 29 days. Once the biogas production has stopped at about day 29, the reactors were dismantled. Both at the beginning and end of the experiments, the sludge samples from the reactors were tested for TS, VS, biogas volume and composition, COD and pH.

4.1.1. Biogas and Methane Productions

As mentioned, the whole BMP test took 29 days for OID I. During the first 15 days, biogas amount and methane content of the reactors were measured on a daily basis. After 15 days since the gas production slowed down, the gas measurements were carried out every two days until reactors were terminated. Cumulative and daily gas production of the reactors are given in Figure 4.1 and Figure 4.2, respectively. These values are the averages of three replicate reactors where error bars demonstrate standard deviations of the three replicates. The results show that biogas and methane generation from samples have an inverse relationship with the amount of OID I sludge in the reactors.

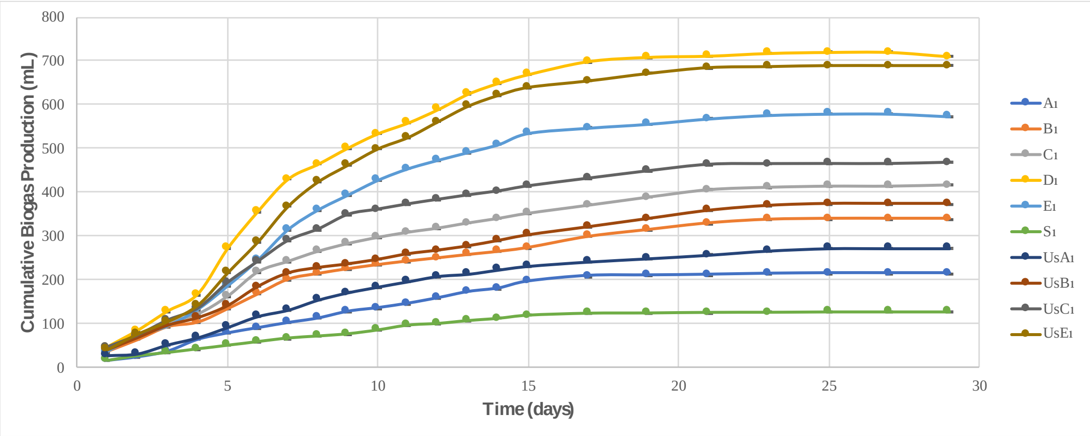


Figure 4.1: Cumulative biogas production of different sludge mixtures of OID I

Highest biogas volume is observed as 720 mL in reactors which has only municipal wastewater sludge, (D_1) (Figure 4.1). Reactor S_1 (only the seed sample) has the lowest amount of produced total biogas volume (127 mL), compared to other reactors. The amount of biogas produced in sludge reactors A_1, B_1, C_1, E_1, UsA_1, UsB_1, UsC_1 and UsE_1, with and without ultrasonication, decreased with the increasing industrial sludge content in the mixture. Sonication pretreated sludge samples have produced much higher amount of biogas than their untreated counterparts. In mixtures, UsE_1 sample generated much higher biogas (689 mL) than all other reactors with mixed sludges. This reactor contained the least amount of industrial sludge in its feed composition. Sludge mixtures in E_1, UsC_1, C_1, UsB_1 and B_1 reactors produced 573, 468, 416, 374 and 340 mL biogas, respectively. On the other hand, UsA_1 sample (273 mL) produced more biogas than A_1 sample (215 mL). It is seen that the differences of biogas production between mixed sludge samples E_1, UsE_1 and other samples are high. When these results are evaluated, it can be concluded that OID I sludge inhibit lowers production and this effect increases with the increasing OID I sludge in the mixture.

Content of industrial sludge may include toxic and inhibitory substances effective on biogas production in these sludge samples.

The highest biogas volume is observed on day 7 for almost all samples. After 7th day, daily biogas generation for all sludge samples decreased, the decrease continued until day 15 (Figure 4.2). Possible reason of the peak observed on day 7 is the biogas produced from hydrolyzing organic substances.

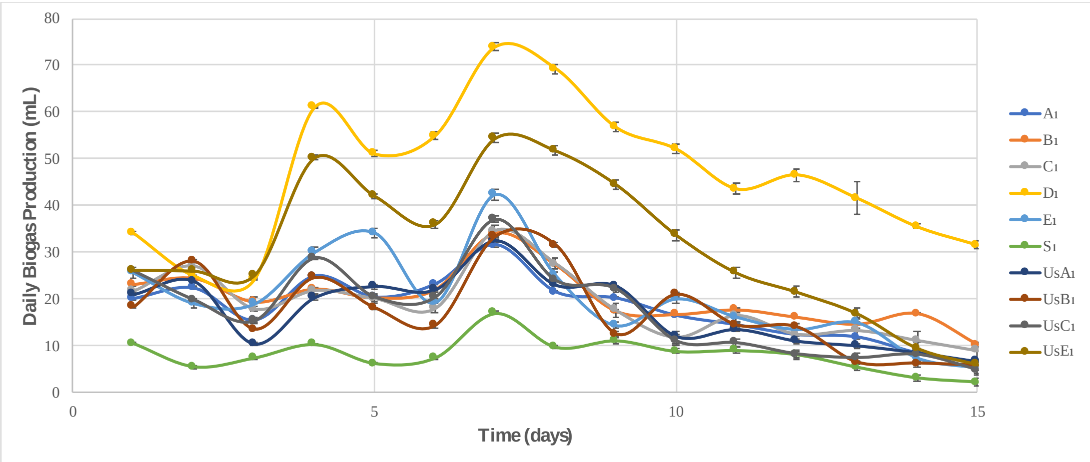


Figure 4.2: Daily biogas production of different sludge mixtures of OID I

Figure 4.3 and Figure 4.4 demonstrate cumulative and daily methane production for the first 15 days, respectively. Methane generation values and their standard deviations are calculated with three replicates of samples. 59% of the biogas from reactor D_1 is methane. Among sonication pretreated sludge samples, biogas produced in UsE_1 reactors contained 55% methane, in sample UsC_1 methane content was 54%, in sample UsB_1 methane content was 47% and finally in sample UsA_1 methane content was 31%. Without ultrasound pretreatment, in sample E_1 methane content was 53%, in sample C_1 methane content was 52%, in sample B_1 methane content was 42% and finally in sample A_1 methane content was 33%. Results show that sonication has a slight positive effect on the methane percentage in the total gas.

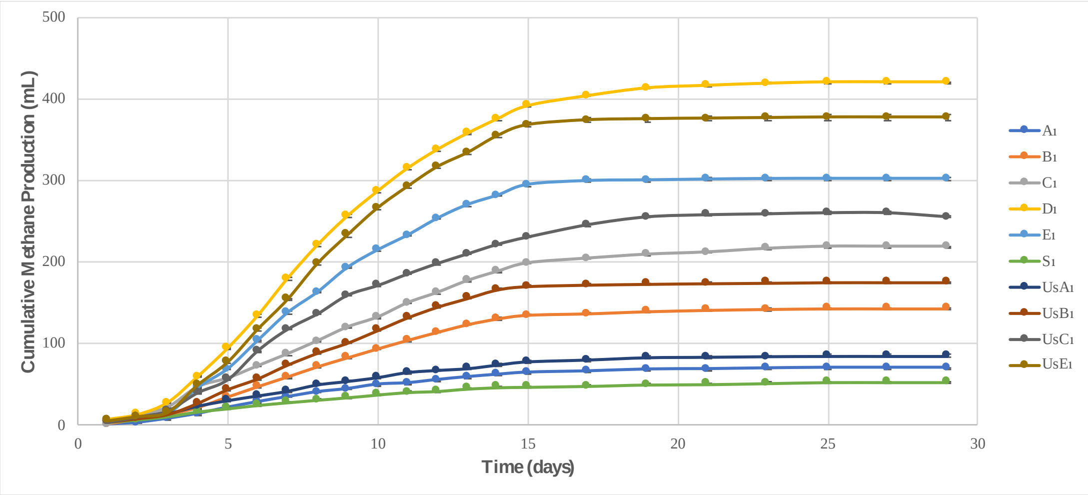


Figure 4.3: Cumulative methane production of different sludge mixtures from OID I

Likewise biogas production, sample D_1 has the highest methane generation (420 mL) while sample S_1 produced the lowest methane (53 mL), in terms of volume. Samples of UsE_1, E_1, UsC_1, C_1, UsB_1, B_1, UsA_1 and A_1 generated 377, 302, 255, 218, 175, 143, 84 and 70 mL methane gas, respectively. Methane production is affected negatively possibly due to the composition of industrial sludge. OID I industrial sludge can include organic and long-chain fatty acids and high concentration of ammonia which are determined as inhibitors for methane bacteria. In addition to them, some unknown inhibitors and toxic substances in industrial sludge may have an impact on the activity of methane bacteria negatively (Chen et al., 2008).

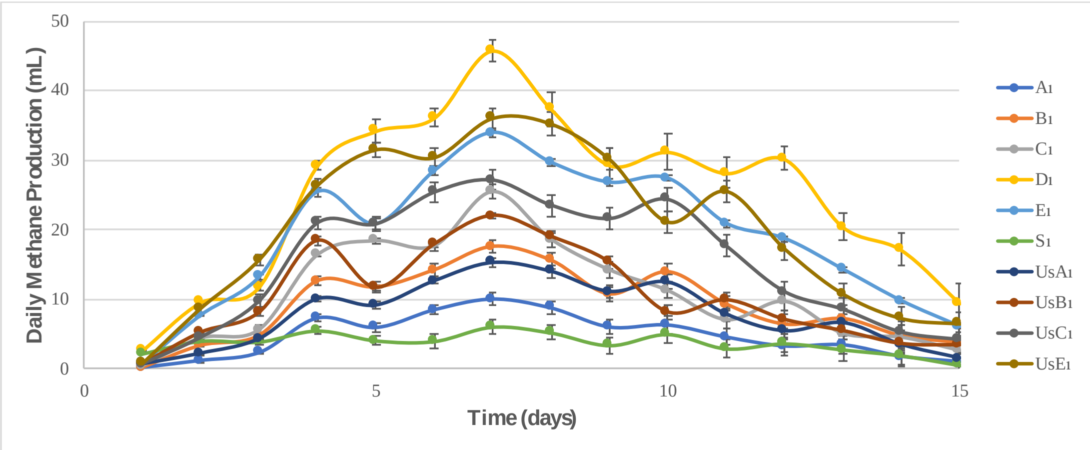


Figure 4.4: Daily methane production of different sludge mixtures from OID I

The rapid increase of methane production between days 3 and 4 in Figure 4.4, shows hydrolyzed organic compounds' conversion. Up to the 3rd day, methane generation can be attributed to the initial soluble organic substances. Similar to daily biogas production, the main peak point of daily methane production is determined on day 7. After this day, the amount of methane production starts to decrease. It is seen in Figure 4.4 that the industrial sludge inhibits the hydrolysis step of anaerobic digestion. Industrial sludge has lower degradation and particulate organic conversion. This trend is similar to expected daily methane production in literature (Feng et al., 2013; Elbeshbishy et al., 2012).

4.1.2. BMP Performance Indicators

During biogas production solid concentrations and COD values decrease in the reactors. These changes are determined during reactor set-up and take-down.

4.1.2.1. Changes in Solids Concentrations and pH

The average values of initial and final TS and VS concentrations, and their removal rates during anaerobic condition are shown in Table 4.1. The TS and VS values are measured in triplicates; so, the data in Table 4.1 show the standard deviations calculated as well. Although sample S_1 has much lower TS value, other samples are similar in initial and final TS magnitudes. TS removal during anaerobic digestion changes between 20 and 25 percent in literature (Köksoy and Sanin, 2010; Bougrier et al., 2006). In reactor D_1, the highest TS removal (25.35%) was observed. The TS removal percent of the reactor A_1 and UsA_1 (10.97 and 11.39%, respectively) was less than half of the removal rate in sample D_1. The TS removal rates of reactors UsE_1, E_1, UsC_1, C_1, UsB_1 and B_1 were 20.40, 19.71, 18.58, 18.09, 14.90 and 12.34%, respectively. As expected, TS removal rates decreased as industrial sludge amount increased in samples. Sample D_1 has highest VS destruction percentage as 47.84% which is similar to literature value (De la Rubia et al., 2002). Sample A_1 and UsA_1 involving only industrial sludge had 19.81 and 23.21% VS removal, respectively, which was less than half of the one observed in sample D_1. Sample D_1 was followed by sample UsE_1 (41.22% VS removal), E_1 (39.25% VS removal), UsC_1 (33.69% VS removal), C_1 (33.17% VS removal), then UsB_1 (31.22% VS removal) and finally B_1 (29.43% VS removal). Similar to TS, VS removal rates also decreased as industrial sludge amount increased in samples.

Table 4.1: *Initial and final TS and VS concentrations and their removal rates during anaerobic digestion for OID I*

Reactor Code	**TS_i (g/L)**	**TS_f (g/L)**	**TS Removal (%)**	**VS_i (g/L)**	**VS_f (g/L)**	**VS Removal (%)**
A_1	16.73±0.01	14.89±0.02	10.97	10.02±0.05	8.03±0.09	19.81
B_1	17.36±0.08	15.22±0.02	12.34	10.51±0.02	7.42±0.08	29.43
C_1	17.85±0.07	14.62±0.01	18.09	10.82±0.01	7.23±0.1	33.17
D_1	16.04±0.06	11.97±0.05	25.35	9.78±0.01	5.10±0.04	47.84
E_1	18.28±0.02	14.68±0.09	19.71	11.54±0.02	7.01±0.04	39.25
S_1	10.82±0.01	8.66±0.03	19.94	7.00±0.04	4.99±0.04	28.58
UsA_1	16.91±0.05	14.98±0.04	11.39	10.33±0.06	7.93±0.01	23.21
UsB_1	17.24±0.08	14.67±0.05	14.90	10.81±0.02	7.43±0.01	31.22
UsC_1	17.94±0.04	14.60±0.1	18.58	11.36±0.08	7.53±0.05	33.69
UsE_1	18.42±0.02	14.66±0.06	20.40	11.77±0.06	6.92±0.02	41.22

In addition to TS and VS, TSS, VSS and pH are also measured in the reactors (Table 4.2). The TSS, VSS and pH values are measured in duplicate. The data in Table 4.2 show the standard deviations calculated as well.

Table 4.2: *Initial and final TSS and VSS concentrations and pH values during anaerobic digestion for OID I*

Reactor Code	**TSS_i (g/L)**	**TSS_f (g/L)**	**TSS Removal (%)**	**VSS_i (g/L)**	**VSS_f (g/L)**	**VSS Removal (%)**	**pH_i**	**pH_f**
A_1	11.76± 0.02	10.92± 0.04	7.14	7.69± 0.01	6.07± 0.04	21.07	6.2	6.9
B_1	11.82± 0.03	10.57± 0.01	10.58	7.83± 0.03	5.84± 0.03	25.42	6.9	7.0
C_1	11.95± 0.01	10.27± 0.07	14.06	7.95± 0.06	5.65± 0.04	28.93	6.9	7.0
D_1	13.88± 0.07	10.62± 0.03	23.49	9.23± 0.03	5.01± 0.08	45.72	7.0	7.1
E_1	13.16± 0.03	11.79± 0.05	18.01	8.01± 0.02	5.46± 0.02	31.84	7.2	7.3
S_1	8.03± 0.06	7.53± 0.02	6.23	5.72± 0.03	4.33± 0.01	24.30	7.3	7.5
UsA_1	13.67± 0.01	12.44± 0.08	8.99	7.74± 0.08	6.02± 0.01	22.22	6.8	6.9
UsB_1	13.80± 0.09	11.92± 0.03	13.62	7.88± 0.04	5.77± 0.06	26.78	7.0	7.2
UsC_1	13.89± 0.03	11.45± 0.04	17.57	7.99± 0.02	5.59± 0.08	30.04	7.1	7.2
UsE_1	13.94± 0.02	11.05± 0.02	20.73	8.03± 0.09	5.14± 0.02	35.99	7.1	7.3

Although sample S has much lower TSS and VSS value, other samples are similar in initial and final TSS and VSS magnitudes. Reactor D_1 and mixed UsE_1 sample have higher initial TSS values when compared others. In reactor D_1, the highest TSS and VSS removal (23.49% and 45.72%, respectively) was observed. The TSS and VSS removal percent of the reactor A_1 (7.14% for TSS and 21.07% for VSS, respectively) was less than half of the removal rate in reactor D_1. The TSS removal rates of reactors UsE_1, E_1, UsC_1, C_1, UsB_1, B_1 and UsA_1 were 20.73, 18.01, 17.57, 14.06, 13.62, 10.56 and 8.99%, respectively. TSS removal rates decreased as industrial sludge amount increased in samples. Sample A_1 and UsA_1 involving only industrial sludge had 21.07 and 22.22% VSS removal, respectively, which was less than half of the one observed in sample D_1. Sample D_1 was followed by sample UsE_1 (35.99% VSS removal), E_1 (31.84% VSS removal), UsC_1 (30.04% VSS removal), C_1 (28.93% VSS removal), then UsB_1 (26.78% VSS removal) and finally B_1 (25.42% VSS removal). Similar to TSS, VSS removal rates also decreased as industrial sludge amount increased in samples. Last parameter (pH) has pretty much similar values for each reactor, both at the reactor start-up and reactor take-down. The reactor A_1 which contains only the industrial sludge has slightly lower pH value.

Biogas yield w.r.t volatile solid destroyed for all samples is investigated. Figure 4.5 shows these results. The highest biogas produced in liters per gram VS destroyed is 0.77 L/g in sample D_1. The typical biogas yield value is 0.81 L/g in the literature (WEF and ASCE/EWRI, 2009). Biogas produced per unit amount of VS destroyed is found for reactor UsE_1 as 0.711 L/g, reactor E_1 as 0.630 L/g, reactor UsC_1 as 0.608 L/g, reactor C_1 as 0.579 L/g, reactor UsB_1 as 0.574 L/g, reactor B_1 as 0.570 L/g, reactor UsA_1 as 0.568 L/g and reactor A_1 as 0.538 L/g. The ratio of biogas produced per g of VS destroyed decrease as the portion of industrial sludge increase; however, the differences between reactors (especially A_1, B_1 and C_1) are not high.

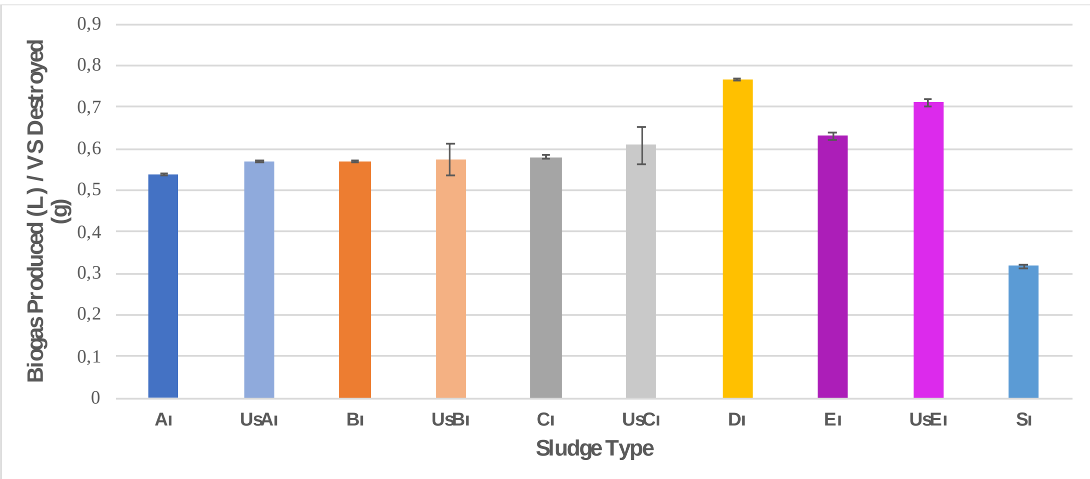


Figure 4.5: Biogas yield in liters per gram VS destroyed from OID I BMP Set

4.1.2.2. Change of Chemical Oxygen Demand during BMP Test

Initial and final COD concentrations of samples for OID I BMP assay and their removal percentages are given in Table 4.3. Reactor D_1 had the highest COD removal percentage (36.50%), this result is comparable to previous studies (Apul and Sanin, 2010). Like VS removal, COD removal rates increase with increasing municipal wastewater sludge. Pretreated sludge samples (UsE_1, UsC_1, UsB_1 and UsA_1) had 31.44, 27.92, 23.46 and 18.73% COD removal, respectively. The COD removal values of sample C_1, B_1 and A_1 involving untreated OID I sludge were 25.78, 21.76 and 16.92%, respectively.

Table 4.3: *Initial and final COD concentrations and removal ratios during anaerobic digestion for OID I BMP Set*

Reactor Code	COD_i (g/L)	COD_f (g/L)	COD Removal (%)
A_1	18.87±0.08	15.68±0.04	16.92
B_1	19.60±0.07	15.34±0.01	21.76
C_1	20.54±0.07	15.23±0.09	25.78
D_1	17.50±0.01	11.11±0.07	36.50
E_1	21.74±0.09	15.33±0.07	29.74
S_1	12.52±0.03	10.57±0.03	15.55
UsA_1	19.08±0.05	15.51±0.07	18.73
UsB_1	20.02±0.04	15.32±0.02	23.46
UsC_1	21.18±0.02	15.26±0.05	27.92
UsE_1	22.30±0.05	15.29±0.01	31.44

Figure 4.6 demonstrates methane yield per unit amount of COD destroyed for different mixture ratios of sludge. Reactors A_1 and D_1 includes industrial and municipal sludge only, respectively. Sample B_1, C_1 and E_1 are mixed industrial and domestic sludges at 2:1, 1:2 and 0.5:2.5 ratios, respectively. Sample UsB_1, UsC_1 and UsE_1 involve ultrasound industrial and domestic sludge at the same ratios. The theoretical maximum

yield of convertion from COD to methane for organics is specified as 0.395 L methane/g COD destroyed (Speece, 1996). Only reactor D_1, with the highest methane yield of 0.33 L/g, is close to this maximum value. Reactor D_1 is followed by reactor UsE_1 (0.27 L/g), reactor E_1 (0.24 L/g), reactor UsC_1 (0.22 L/g), reactor C_1 (0.21 L/g), reactor UsB_1 (0.19 L/g), reactor B_1 (0.17 L/g) and then reactor UsA_1 (0.12 L/g) and finally reactor A_1 (0.11 L/g).

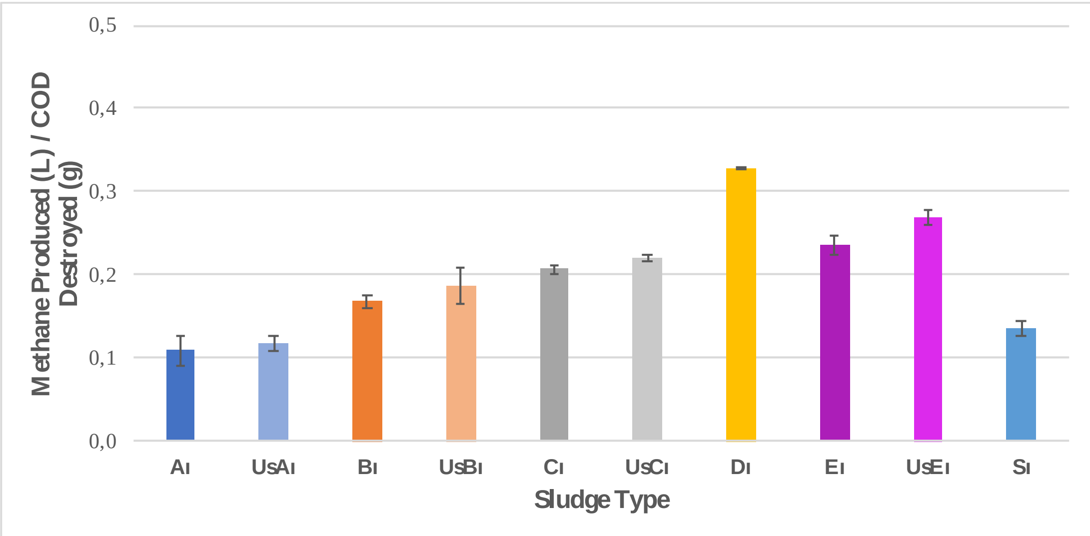


Figure 4.6: Methane yield in liters per gram of COD destroyed from OID I

To evaluate the effect of mixing industrial sludge from OID I with domestic sludge at 2:1, 1:2 and 0.5:2.5 portions with and without ultrasound pretreated industrial sludge, expected/calculated methane productions are compared with observed ones. In Figure 4.7, the green bars are calculated by simple summations of expected productions from the data obtained for sample D_1 (0.11 L/g), A_1 (0.036 L/g) and UsA_1 (0.039 L/g) in accordance with their mixing ratios. For pretreated samples, reactor UsE_1 (0.29 L/g) has better calculated methane yield than observed one (0.27 L/g). The reactor UsC_1 (0.22 L/g) underperformed when comparing calculated value (0.26 L/g). Reactor UsB_1 observed yield (0.190 L/g) had performed slightly better than calculated one (0.187).

On the other hand, reactors E_1, C_1 and B_1 are mixed industrial sludge without ultrasound pretreatment. Their observed methane yield is 0.24, 0.21 and 0.17 L/g, respectively. However, calculated methane yields of these samples are determined as 0.29, 0.26 and 0.18 L/g, respectively. Expected values for untreated samples are higher than observed ones. The results of reactor B_1 and UsB_1 (observed vs calculated) are very close to each other that the effect can be neglected. However, this cannot be seen in other reactors. According to these results, mixing OID I sludge with municipal sludge reactors were not able to perform to the expected level in terms of methane yield. However, results indicate that sludge in mixture from this OID can be co-digested with municipal sludge without experiencing much problems.

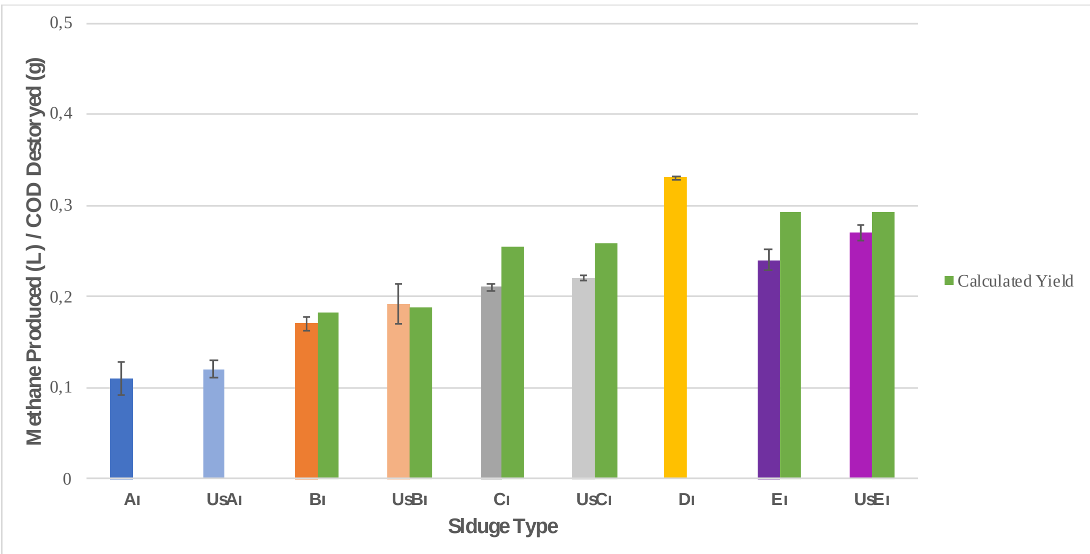


Figure 4.7: Methane yield in liters per gram COD destroyed compared with calculated this value from OID I

4.2. Results of OID II BMP Set

Biogas production potential of the second OID (OID II) is investigated using similar mixing ratios, as well. These samples could not be sonicated in this set since the sonicator was broken. The BMP assay of OID II was again conducted for 29 days.

The reactors were terminated when biogas productions approached or dropped down to zero. During reactor operation and after reactor termination parameters including TS, VS, biogas volume and composition, COD and pH were measured. Results of BMP test for OID II are given in the following sections.

4.2.1. Biogas and Methane Productions

Biogas amount and its composition (methane percentage in produced biogas) were measured daily during the first 15 days. Thereafter, these measurements were conducted every two days until reactors were terminated. Figure 4.8 and Figure 4.9 demonstrate how cumulative biogas production and daily biogas production of samples for first 15 days change, respectively. These values represent average values of three replicates for all sludge mixtures. Error bars showing standard deviations of three replicates shown on Figure 4.8 are less than 5% for this BMP set. According to the experimental results, biogas and methane production from BMP reactors followed a trend that is in inverse relationship with the amount of added OID sludge.

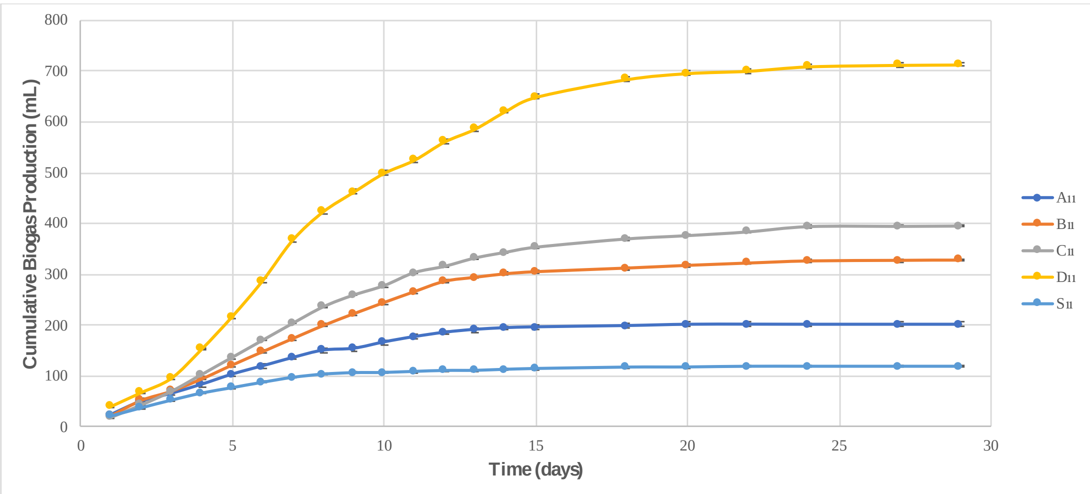


Figure 4.8: Cumulative biogas production of different sludge mixtures of OID II

From Figure 4.8, it can be seen that reactor D_{II} which includes only municipal wastewater sludge has the highest produced biogas amount (714 mL) when compared to the total gas production of other samples. On the other hand, the lowest amount of gas production is observed in S_{II} which includes only the seed sample. The mixed samples of B_{II} and C_{II} are observed to have their gas production rates in parallel with the sludge mixing ratios. As expected, in reactor C_{II} produced much higher biogas (395 mL) than in reactors A_{II} and B_{II} (201 mL and 328 mL, respectively) due to lower industrial sludge ratios. When the gas productions of reactors C_{II} and D_{II} are compared, it is seen that the difference between them is high. This result shows OID II sludge may have in its composition substances that might inhibit biogas generation. The comparison of total gas production in these mixed samples indicate that biogas production decreased with added industrial sludge quantity because of possible toxic or inhibitory contents of industrial sludge. In other words, samples had more biogas production when the amount of municipal sludge in mixtures increased.

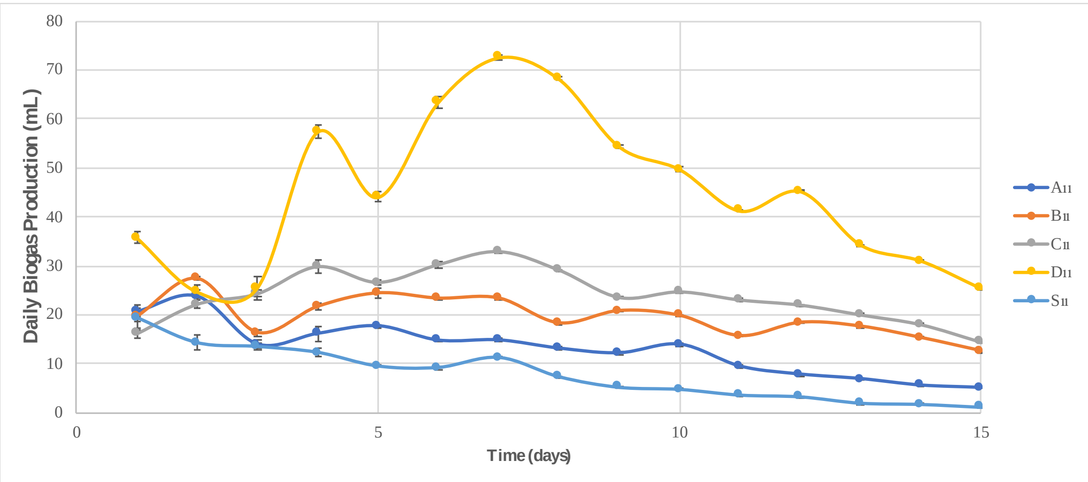


Figure 4.9: Daily biogas production of different sludge mixtures of OID II

Figure 4.9 shows that the maximum amount of biogas production is seen on day 7 for reactors D_{II} and C_{II}, while it is on day 2 for samples A_{II} and B_{II}. Following these days daily biogas production for all samples decreased until day 15. The seed sample (S_{II}) had its maximum daily biogas production on day 1. The humps on the graphs for most of the samples indicate that up to the 3rd day, soluble organics have been converted to biogas. Then, the biogas production from hydrolyzed organics possibly caused the peak on day 7.

Cumulative methane production is depicted in Figure 4.10 while Figure 4.11 shows daily methane production for the first 15 days. Methane production values given in Figure 4.10 and Figure 4.11 are average of three replicate samples likewise biogas production graphs. Standard deviations (shown as error bars in Figure 4.10) are determined to be less than 5% of the three replicate averages. Examining methane values, it is seen that nearly 53% of the produced biogas is methane from reactor D_{II}, although these values for other reactors are lower than the percentage of D_{II}. In reactor C_{II} methane was 46.31%, in reactor B_{II} methane was 41.38% and finally in reactor A_{II} methane was 32.73% of the total gas.

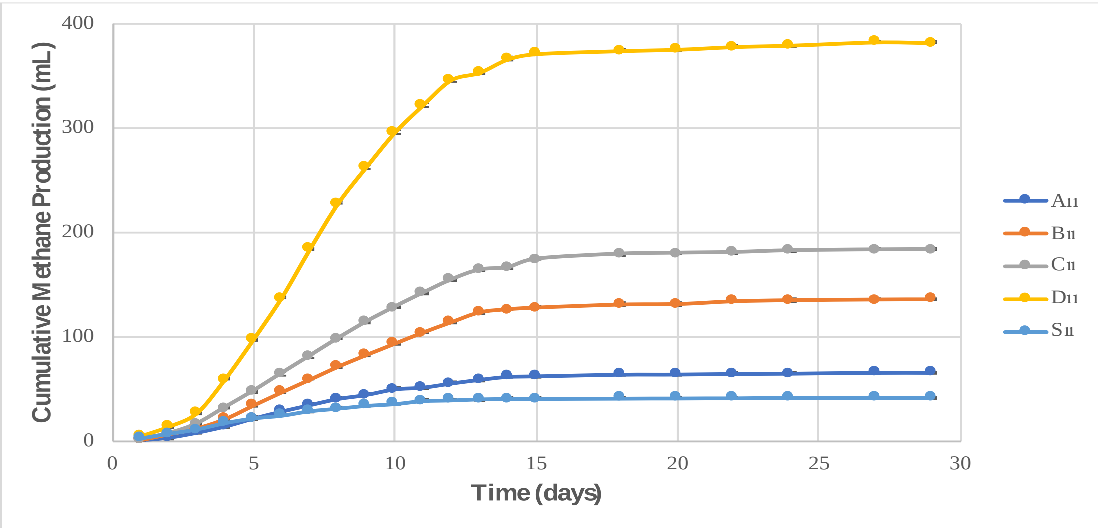


Figure 4.10: Cumulative methane production of different sludge mixtures from OID II

Similar to biogas production, the highest methane generation (382 mL) is from reactor D_{II}, whereas the lowest generation is determined from S_{II} (seed) sample (42 mL). This is as expected, since seed is already digested sludge. Reactors of C_{II}, B_{II} and A_{II} produced 183, 136 and 66 mL methane, respectively. This trend of decreasing methane with the increasing portion of industrial sludge in sample is similar to the one for total gas production. This can be explained by the inhibitory effect of industrial sludge influencing methane production rates in negative sense.

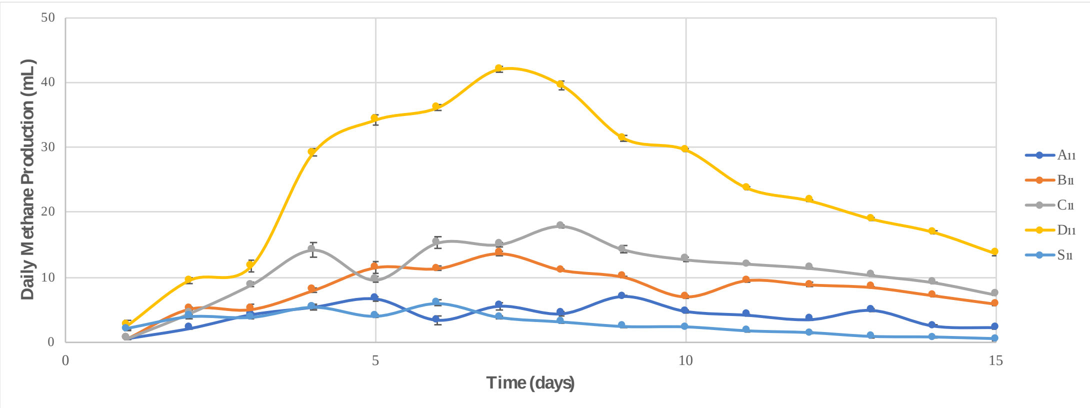


Figure 4.11: Daily methane production of different sludge mixtures from OID II

The steep slope in methane production between days 3 and 4 in Figure 4.11 for sole domestic sludge reactor indicate the conversion of hydrolyzed organics; methane production before this point can be attributed to the initial soluble organics. The main peak point of daily methane production observed on day 7, is similar to the one observed for daily biogas production. The amount of methane production starts to decrease from after day 7. From the graph, it looks as if the industrial sludge is inhibiting the hydrolysis step of anaerobic digestion, since the reactors with industrial sludge all stay at the low end of the graph. Although, in the first few days methane production from soluble organics seems equal for all sludge types, the particulate organic conversion and further degradation are slower for industrial sludges.

4.2.2. BMP Performance Indicators

Changes in the reactors which contained OID II sludge during biogas production is an indicator of the performance. Changes in solid concentrations and VS and COD removal rates between the reactor set-up and take-down are determined and evaluated separately.

4.2.2.1. Changes in Solids Concentrations and pH

Table 4.4 summarizes the average values of initial and final TS and VS concentrations, and their removal rates during anaerobic digestion process. The TS and VS values are measured in triplicates; so, the data in Table 4.4 show the standard deviations calculated as well. Table shows that the initial TS values are similar in magnitude (except for S_{II}, which is relatively much lower). Similarly, final TS values are also within the same small range with each other (except for S_{II}). In reactor D_{II}, 21.15% TS removal was observed, which was consistent with values reported in literature (Köksoy and Sanin, 2010; Apul and Sanin, 2010; Bougrier et al., 2006). The removal rates of TS in reactors decreased as the portion of industrial sludge increased in reactors. The TS removal percent of reactor A_{II} (10.65%) was less than half of the removal rate in reactor D_{II}. Mix B_{II} and C_{II} TS removal rates were 14.78% and 16.57%, respectively. Similar to TS removal rates, VS removal rates seem to show parallel trend with a decline as the amount of industrial sludge increase in the mix. Reactor D_{II} yielding highest biogas and methane production values shows the highest VS destruction percentage as 45.17%. This removal ratio was parallel to VS removal value in literature (De la Rubia et al., 2002). Reactor D_{II} was followed by reactor C_{II}, then B_{II} and finally A_{II}. Reactor A_{II} which contained only industrial sludge had about 20% VS removal, which was less than half of the one observed in reactor D_{II}. Although industrial sludge type is different from the one in this study, olive mill industrial sludge involving hazardous pollutants was found to have a low VS reduction (Benito-Mora et al., 2018). Similar results possibly due to inhibitory effects of industrial sludge is observed in this BMP set. Other reactors including different amount of industrial sludge underperform VS reduction. Reactor B_{II} had 26.35% and reactor C_{II} had 29.39% removals for VS, following the opposite trend of the amount of industrial sludge in the mixtures.

Table 4.4: *Initial and final TS and VS concentrations and their removal rates during anaerobic digestion for OID II*

Reactor Code	**TS_i (g/L)**	**TS_f (g/L)**	**TS Removal (%)**	**VS_i (g/L)**	**VS_f (g/L)**	**VS Removal (%)**
A_{II}	16.67±0.01	14.90±0.08	10.65	9.84±0.1	7.91±0.06	19.66
B_{II}	16.72±0.02	14.24±0.1	14.78	10.36±0.03	7.63±0.06	26.35
C_{II}	17.83±0.01	14.87±0.06	16.57	10.48±0.03	7.40±0.01	29.39
D_{II}	15.31±0.03	12.07±0.01	21.15	9.38±0.02	5.14±0.03	45.17
S_{II}	10.43±0.01	8.69±0.01	16.68	6.27±0.06	4.68±0.08	25.27

In addition to TS and VS, TSS, VSS and pH are also measured in the reactors (Table 4.5). The TSS, VSS and pH values are measured in duplicate. The data in Table 4.5show the standard deviations calculated as well.

Table 4.5: *Initial and final TSS and VSS concentrations and pH values during anaerobic digestion for OID II*

Reactor Code	TSS_i (g/L)	TSS_f (g/L)	TSS Removal (%)	VSS_i (g/L)	VSS_f (g/L)	VSS Removal (%)	pH_i	pH_f
A_{II}	15.35± 0.01	14.57± 0.04	5.08	9.52± 0.01	7.78± 0.03	18.28	7.2	7.3
B_{II}	15.43± 0.06	13.85± 0.01	10.24	9.89± 0.03	7.45± 0.01	24.67	7.1	7.2
C_{II}	16.73± 0.08	13.98± 0.02	16.44	10.14± 0.03	7.23± 0.05	28.70	7.1	7.0
D_{II}	13.45± 0.02	10.62± 0.01	21.04	9.05± 0.02	5.01± 0.07	44.64	7.0	7.5
S_{II}	8.76± 0.02	8.29± 0.05	5.37	5.88± 0.06	4.48± 0.01	23.81	7.4	7.5

Although sample S has much lower TSS and VSS value, other samples are similar in initial and final TSS and VSS magnitudes. In reactor D_{II}, the highest TSS and VSS removal (21.04% and 44.64%, respectively) was observed. The TSS and VSS removal percent of the reactor A_{II} (5.08% for TSS and 18.28% for VSS, respectively) was less than half of the removal rate in sample D_{II}. The TSS removal rates of reactors C_{II} and B_{II} were 16.44 and 10.24%, respectively. TSS removal rates decreased as industrial sludge amount increased in samples. Sample A_{II} involving only industrial sludge had 18.28% VSS removal which was less than half of the one observed in sample D_{II}. Sample D_{II} was followed by sample C_{II} (28.70% VSS removal) and B_{II} (24.67% VSS removal). Similar to TSS, VSS removal rates also decreased as industrial sludge amount increased in samples. Last parameter (pH) has similar values for each reactor, both at the reactor start-up and reactor take-down.

Produced biogas per gram of volatile solids destroyed for all samples is demonstrated in Figure 4.12. The biogas produced per unit amount of VS destroyed is an indicator of healthy digester and is highest (0.85 L/g) in reactor D_{II}. Biogas production per g of VS destroyed of the industrial sludge in mixtures with municipal sludge (mix B_{II} with 0.60 L/g and mix C_{II} with 0.64 L/g) are much lower than that of only municipal sludge. On the other hand, sludge A_{II} had 0.52 L/g, with the lowest biogas production per unit amount of VS destroyed. For this reason, the ratio of biogas produced per g of VS destroyed decrease as the possible inhibitory effects of industrial sludge increase. The typical biogas yield value is 0.81 L/g in literature (WEF and ASCE/EWRI, 2009).

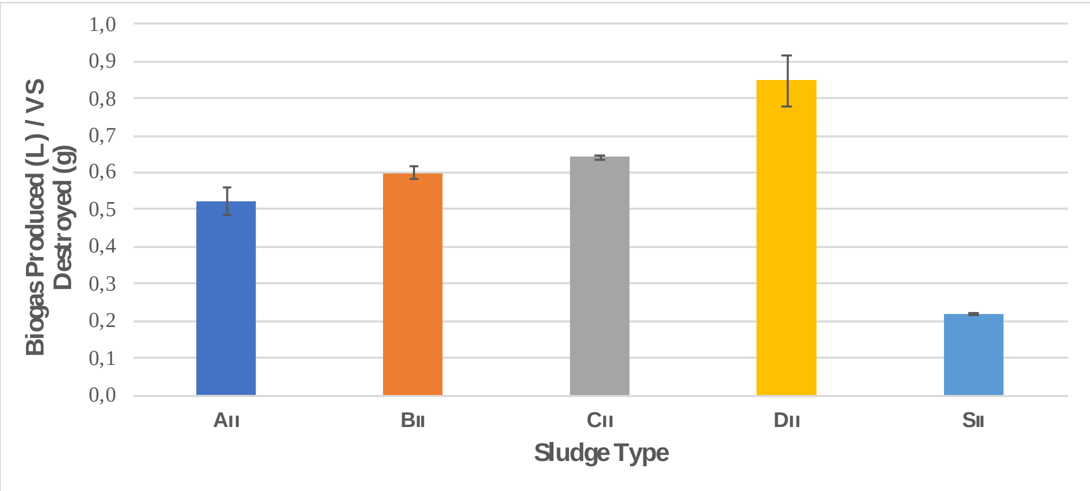


Figure 4.12: Biogas yield in liters per gram VS destroyed from OID II BMP Set

4.2.2.2. Change of Chemical Oxygen Demand during BMP Test

Shown in Table 4.6 are initial and final COD concentrations of OID II and their removal percentages. As expected, the highest COD removal percent (35.5%) belong to sample D_{II} with a value similar to previous studies (Apul and Sanin, 2010; Köksoy and Sanin, 2010; Bougrier et al., 2006). Similar to the earlier discussed data, addition of industrial sludge decreases COD removal; such that reactor C_{II} sample had 21.6 % and reactor B_{II} sample followed that with 19.7 %. Reactor A_{II} had the lowest value at 15.3 %.

Table 4.6: *Initial and final COD concentrations and removal ratios during anaerobic digestion for OID II BMP Set*

Reactor Code	**COD_i (g/L)**	**COD_f (g/L)**	**COD Removal (%)**
A_{II}	17.17±0.06	14.54±0.01	15.29
B_{II}	17.22±0.03	13.82±0.02	19.73
C_{II}	17.71±0.07	13.88±0.06	21.59
D_{II}	16.72±0.01	10.77±0.02	35.54
S_{II}	11.96±0.03	10.19±0.09	14.78

Figure 4.13 shows methane productions normalized with the amount of COD destroyed with respect to different sludge types and mixtures of sludges. The theoretical maximum yield converted from COD to methane for organics is specified as 0.395 L methane/g COD destroyed (Speece, 1996). For all samples, methane produced per g of COD destroyed are less than this maximum yield. Figure 4.13 shows that reactor D_{II} has the maximum amount of methane produced per unit amount of COD destroyed. The methane yield of reactor D_{II} is 0.32 L/g. Reactor D is followed by reactor C_{II} (0.24 L/g) and then reactor B_{II} (0.20 L/g) and finally reactor A_{II} (0.13 L/g).

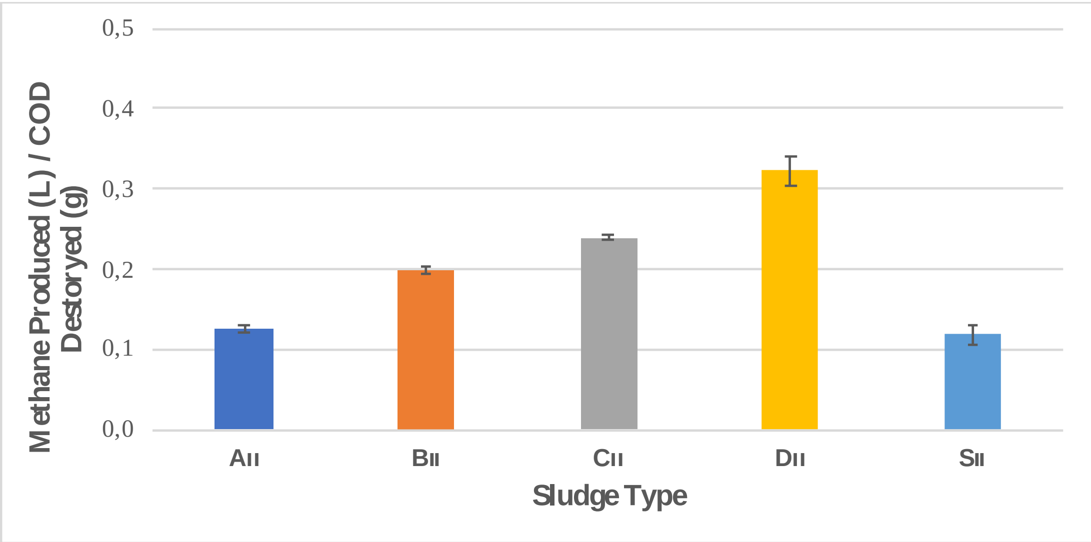


Figure 4.13: Methane yield in liters per gram of COD destroyed from OID II

When the effect of mixing industrial sludge from OID II with municipal sludge at 2:1 and 1:2 ratios is further evaluated by comparing expected (calculated) methane productions with the observed ones, one can make further comments. The green bars in Figure 4.14 for mixtures B_{II} and C_{II} are calculated by simple additions of expected productions from the data obtained for reactor D_{II} (0.11 L/g) and A_{II} (0.04 L/g) in accordance with their mixing proportions. It is seen from Figure 4.14 that reactor C_{II} (0.24 L/g) slightly underperformed compared to the calculated result (0.26 L/g). On the other hand, reactor B_{II} (0.20 L/g) has performed slightly better compared to the calculated result (0.19 L/g). However, the results (observed vs calculated) are very close to each other that the effect can be neglected. With this approach, one can state that mixing OID II sludge with municipal sludge had neither negative not positive effect on methane yield. This clearly indicates that sludge in mixture from this OID can be co-digested with municipal sludge without experiencing any problems.

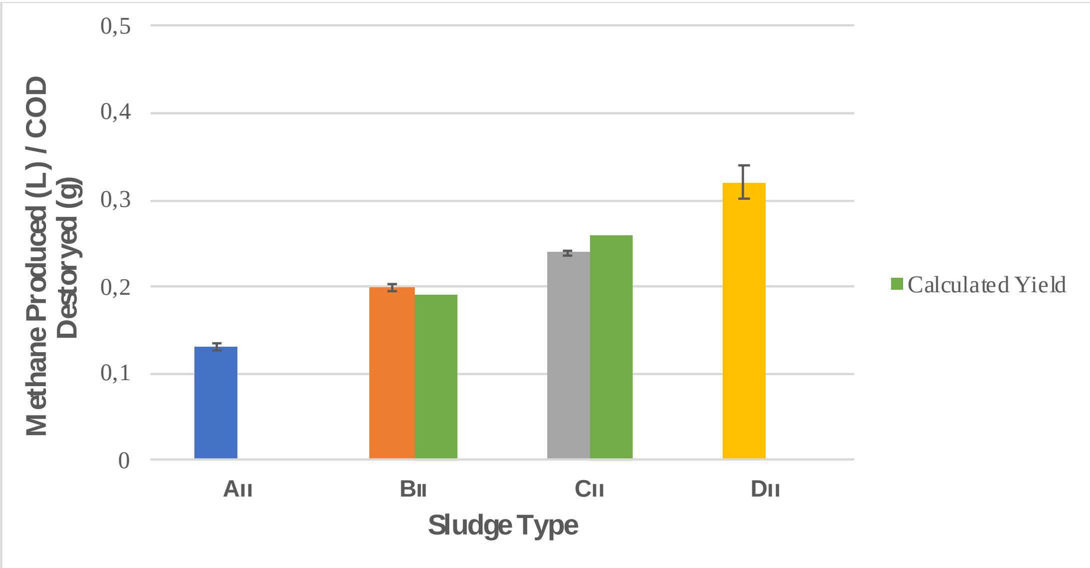


Figure 4.14: Methane yield in liters per gram COD destroyed compared with calculated this value from OID II

4.3. Results of Textile Industry BMP Set

The last group of reactors were operated with a textile industry sludge for 29 days. Similar to the earlier sets, parameters involving TS, VS, biogas volume and its composition, COD and pH were measured for this reactor operation and after reactor termination. After 29 days, reactors were terminated since measured biogas productions dropped down to zero. Results of textile industry BMP assay are given in the following sections.

4.3.1. Biogas and Methane Productions

Biogas amount and methane percentage in biogas were measured daily at the first 15 days. After 15 days, these measurements were continued every two days until the reactors were terminated. Figure 4.15 and Figure 4.16 show the change of biogas production and daily biogas production of reactors for the first 15 days, respectively. When these values were plotted, average values of three replicates for all sludge samples were used. Error bars representing standard deviations of three replicate samples are also shown on Figure 4.15 and Figure 4.16. The experimental results indicate that biogas and methane production from BMP reactors is again in inverse relationship with the addition of textile industry sludge.

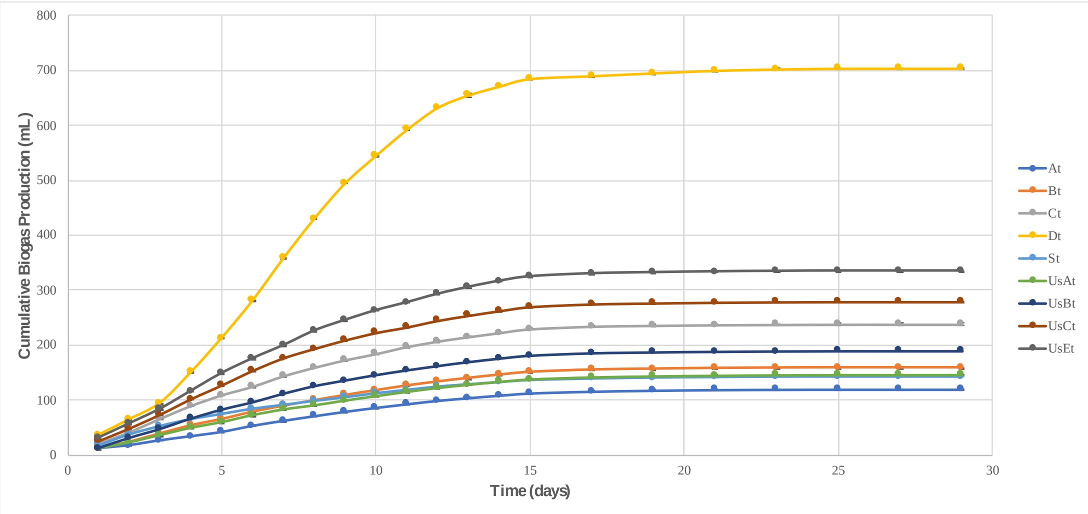


Figure 4.15: Cumulative biogas production of different sludge mixtures of textile industry

In Figure 4.15, reactor D_t (only municipal wastewater sludge) has the highest produced biogas amount (704.1 mL) when compared to the total gas productions of other reactors. On the other hand, the lowest amount of gas production is observed in reactor A_t involving only textile industry sludge. There is a remarkable difference between the performance of reactor D_t and the next follower reactor UsE_t; reactor D_t performed more than twice as high compared to UsE_t. The second lowest amount of biogas generation is 141.67 mL in seed sample (reactor S_t). The mixed samples of B_t and C_t, and their ultrasonicated counterparts of UsB_t and UsC_t, and UsE_t show resemblance for their gas production and sludge mixing ratios. Considering samples without ultrasound pretreatment, reactor C_t produced higher biogas (237.63 mL) than reactor A_t and B_t (127.1 and 168.77 mL, respectively). When other reactors with applied ultrasound pretreatment are observed, reactor UsE_t produced much higher biogas (334.7 mL) than reactors UsA_t, UsB_t and UsC_t (145.4, 188.6 and 278.93, respectively) because of lower industrial sludge amounts. Due to the sharp decrease in gas production with industrial sludge addition, textile industry sludge might have substances which may inhibit total biogas production in its composition. The comparison of total gas production in these mixed samples demonstrate that biogas production decreased with added textile industry sludge quantity because of possible toxic and inhibitory contents of this sludge. That is to say, samples had more biogas production when the amount of municipal sludge in mixtures increased.

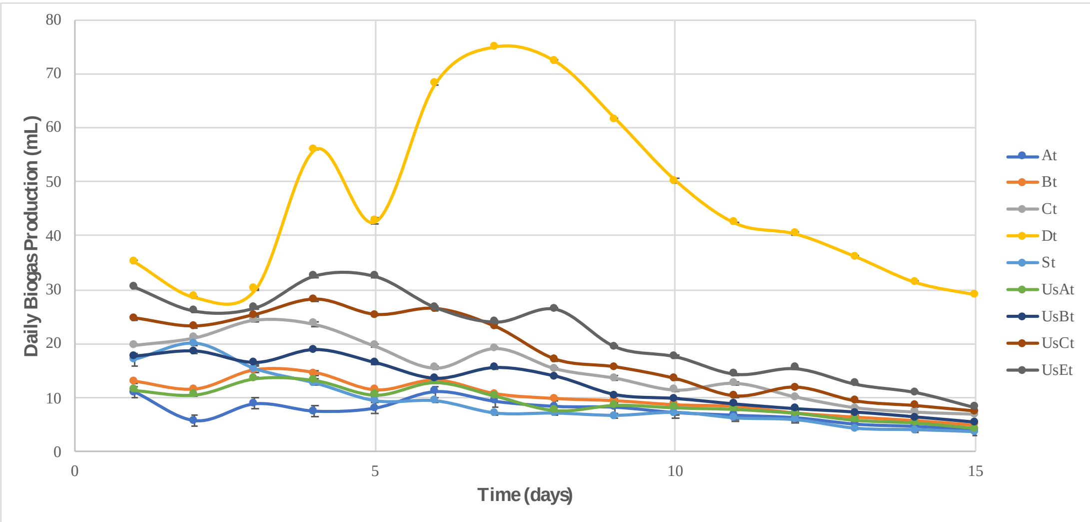


Figure 4.16: Daily biogas production of different sludge mixtures of textile industry

From Figure 4.16, the maximum amount of biogas production is observed on day 7 for reactor D_t while it is on day 4 for reactors Mix UsE_t and UsC_t. Following these days, daily biogas production for all samples diminished until day 15. The seed sample (S_t) and only textile sludge sample (A_t) had maximum daily biogas generation on day 1. The humps on the graphs for most of the samples show that up to the 3rd day, soluble organic compounds have been converted to biogas. Besides, the biogas from hydrolyzed organics possibly caused the peak on day 7.

Cumulative methane produced and the daily methane production for the first 15 days are represented in Figure 4.17 and Figure 4.18, respectively. The averages of three replicate samples are given in Figure 4.17 and 4.18. Standard deviations indicated as error bars in Figure 4.17 and Figure 4.18 are determined to be less than 5% of the three replicate averages similar to biogas production graphs. According to methane values, approximately 60% of produced biogas is methane from reactor D_t, while these values for other reactors are lower than this. In reactor UsE_t methane was 52.51%, in reactor UsC_t methane was 52.21%, in reactor UsB_t methane was 50.24%, in reactor UsA_t methane was 39.05%, in reactor C_t methane was 47.86%, in reactor B_t methane was 38.5% and finally in reactor A_t methane was 32% of the total biogas.

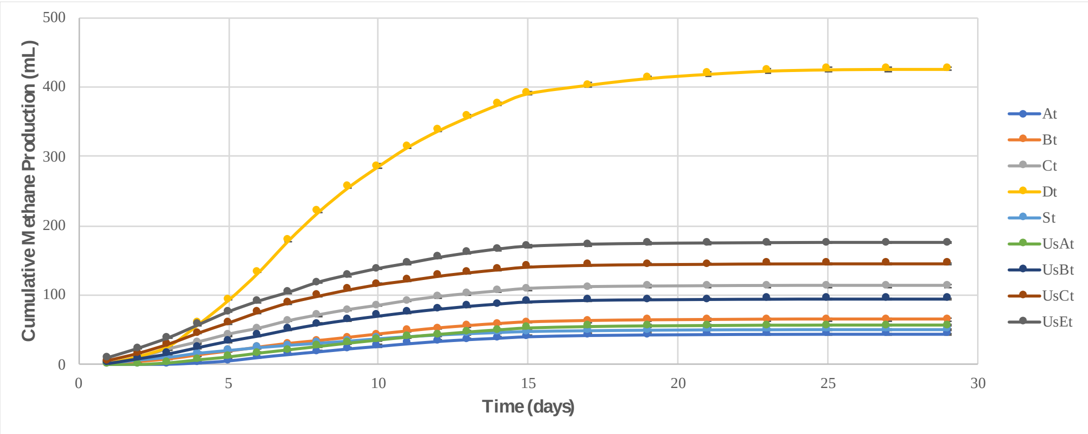


Figure 4.17: Cumulative methane production of different sludge mixtures from textile industry

Similar to biogas generation, the highest methane amount (425.9 mL) is from reactor D_t, while the lowest generation is determined from reactor A_t (41.4 mL). The second lowest methane production is determined from seed sample (S_t) (50.6 mL), as expected, because seed is already digested sludge. Reactors of UsE_t, UsC_t, UsB_t, UsA_t, C_t, B_t and A_t produced 175.8, 145.6, 94.7, 56.8, 113.7 and 64.9 mL methane, respectively. This trend of decreasing methane with the increasing ratio of textile sludge in reactor is similar to the one for total biogas generation. This result shows that the inhibitory effect of textile industry sludge influences methane production in negative way. For example, colorants and oxidants which may be used in textile industry involve NH_4 and hydrogen peroxide prevent methane production as inhibitor during anaerobic digestion (Ahammad et al., 2014).

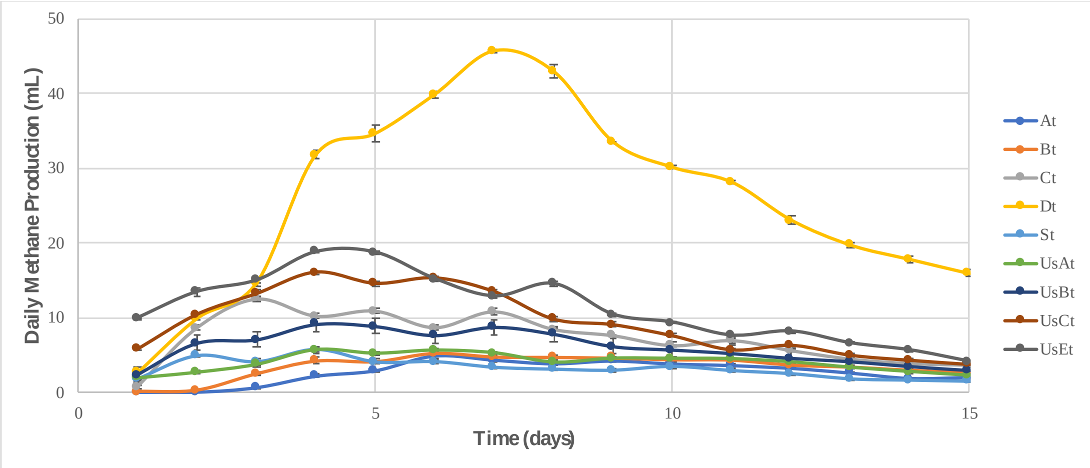


Figure 4.18: Daily methane production of different sludge mixtures from textile industry

The rapid increase of methane generation between days 3 and 4 show the conversion of hydrolyzed organic matters in Figure 4.18. Before this point, methane production can be attributed to the initial soluble organics. The main peak point of daily methane production indicated on day 7, is similar to the one observed for daily gas production. After day 7, methane amount starts to decrease. From the results, the reactors with textile sludge stay at the low end of the graph; so, this sludge may be inhibiting the hydrolysis step of anaerobic process. Although, in the first few days methane production from soluble organics seems equal for all sludge types, the particulate organic conversion and further degradation is slower for textile industry sludges.

4.3.2. BMP Performance Indicators

The changes in solid concentrations and COD removal ratios from the reactor set-up and take-down are represented in below parts.

4.3.2.1. Changes in Solids Concentrations and pH

Table 4.7 shows average values of three replicates of initial and final TS and VS concentrations, and their removal percentages during anaerobic digestion process. The TS and VS values are measured in triplicates; so, the data in Table 4.7 show the standard deviations calculated as well. The initial and final TS values are similar in magnitude (except for D_t and S_t, which is relatively lower). Reactor D_t had 22.08% TS removal, which was parallel with literature values (Bougrier et al., 2006). The removal percentages for TS in reactors decreased when the portion of textile sludge increased in samples. The TS removal of reactor A_t (8.09%) and UsA_t (8.56%) was less than half of the removal rate in reactor D_t. The TS removal percentages of reactors B_t, C_t, UsB_t, UsC_t and UsE_t were 11.11%, 13.58%, 11.74%, 15.32% and 16.14%, respectively. The highest VS destruction percentage is determined in reactor D_t (46.02%), which was consistent with values reported in literature (De la Rubia et al., 2002). Reactor D_t was followed by reactor UsE_t, UsC_t, S_t, C_t, UsB_t, B_t, UsA_t and finally A_t. Reactors A_t and UsA_t which contained only textile sludge without and with ultrasound pretreatment had about 16.56% and 17.18 VS removal, respectively, which was less than half of the one observed in reactor D_t. Similar results possibly because of inhibitory effects of textile sludge is observed in methane productions. Other reactors including different amount of industrial sludge underperform VS reduction. Reactors B_t, C_t, UsB_t, UsC_t and UsE_t had 22.87%, 25.10%, 23.48%, 26.74% and 28.86% removals for VS, respectively, following the opposite trend of the amount of industrial sludge in the mixtures. Textile industrial sludge has a toxic effect since reactive dye compounds accumulate in sludge without degradation in biological system (Willmot, et al., 2008). In addition, sludge pretreatment methods such as ultrasonication do not affect physico-chemical properties and biodegradability; so, these toxic effects in textile sludge cannot be minimized (Zou et al., 2019). The difference observed in the removal rates of samples in this study can be the result of aforementioned toxic effects.

Table 4.7: *Initial and final TS and VS concentrations and their removal rates during anaerobic digestion for textile industry*

Reactor Code	**TS_i (g/L)**	**TS_f (g/L)**	**TS Removal (%)**	**VS_i (g/L)**	**VS_f (g/L)**	**VS Removal (%)**
A_t	27.63±0.01	25.38±0.01	8.09	15.91±0.08	13.27±0.06	16.56
B_t	25.11±0.01	22.32±0.03	11.11	15.03±0.01	11.59±0.08	22.87
C_t	23.81±0.02	20.57±0.09	13.58	14.08±0.08	10.54±0.04	25.10
D_t	15.94±0.06	12.42±0.05	22.08	9.57±0.04	5.16±0.02	46.02
S_t	12.61±0.09	10.42±0.07	17.29	7.71±0.05	5.67±0.03	26.33
UsA_t	31.94±0.02	29.21±0.01	8.56	17.48±0.01	14.48±0.08	17.18
UsB_t	26.21±0.01	23.13±0.01	11.74	14.91±0.04	10.97±0.03	23.48
UsC_t	25.19±0.01	21.32±0.02	15.32	14.32±0.01	10.47±0.05	26.74
UsE_t	20.46±0.09	17.15±0.05	16.14	11.74±0.03	8.35±0.01	28.86

In addition to TS and VS, TSS, VSS and pH are also measured in the reactors (Table 4.8). The TSS, VSS and pH values are measured in duplicate. The data in Table 4.8show the standard deviations calculated as well.

Table 4.8: *Initial and final TSS and VSS concentrations and pH values during anaerobic digestion for textile industry*

Reactor Code	TSS_i (g/L)	TSS_f (g/L)	TSS Removal (%)	VSS_i (g/L)	VSS_f (g/L)	VSS Removal (%)	pH_i	pH_f
A_t	25.52± 0.09	23.83± 0.06	6.62	15.08± 0.09	12.88± 0.07	14.59	6.7	7.3
B_t	23.05± 0.01	21.34± 0.01	8.29	14.32± 0.01	11.47± 0.06	19.90	6.7	7.3
C_t	21.83± 0.08	19.36± 0.07	11.31	13.52± 0.06	10.32± 0.04	23.67	6.7	7.3
D_t	14.62± 0.01	11.53± 0.03	21.14	9.23± 0.05	5.03± 0.02	45.50	6.9	7.2
S_t	11.15± 0.06	10.38± 0.05	6.91	7.43± 0.04	5.64± 0.02	24.09	7.3	8.2
UsA_t	28.37± 0.02	26.32± 0.01	7.23	16.77± 0.01	14.23± 0.07	15.15	6.8	7.0
UsB_t	23.53± 0.01	21.04± 0.03	10.58	13.57± 0.02	10.68± 0.07	21.30	6.8	7.1
UsC_t	23.20± 0.04	20.21± 0.02	12.89	13.17± 0.08	9.74± 0.04	26.04	7.1	7.2
UsE_t	19.04± 0.08	16.10± 0.06	15.44	11.03± 0.04	7.91± 0.01	28.29	7.1	7.2

Although sample S has much lower TSS and VSS value, other samples are similar in initial and final TSS and VSS magnitudes. In reactor D_t, the highest TSS and VSS removal (21.14% and 45.50%, respectively) was observed. The TSS and VSS removal percent of the reactor A_t (6.62% for TSS and 14.59% for VSS, respectively) was less than half of the removal rate in sample D_t. The TSS removal rates of reactors UsE_t, UsC_t, C_t, UsB_t, B_t and UsA_t were 15.44, 12.89, 11.31, 10.58, 8.29 and 7.23%, respectively. TSS removal rates decreased as industrial sludge amount increased in samples. Sample A_t and UsA_t involving only industrial sludge had 14.59 and 15.15% VSS removal, respectively, which was less than half of the one observed in sample D_t. Sample D_t was followed by sample UsE_t (28.29% VSS removal), UsC_t (26.04% VSS removal), C_t (23.67% VSS removal), then UsB_t (21.30% VSS removal) and finally B_t (19.90% VSS removal). Similar to TSS, VSS removal rates also decreased as industrial sludge amount increased in samples. Last parameter (pH) has similar values for each reactor, both at the reactor start-up and reactor take-down.

Produced biogas per gram of volatile solids removed for all reactors is shown Figure 4.19. The typical biogas yield value is 0.81 L/g in literature (WEF and ASCE/EWRI, 2009). The biogas produced per unit amount of VS destroyed is an indicator of healthy digester and is highest (0.80 L/g) in sample D_t. Biogas production per g of VS destroyed of the textile sludge in mixtures with municipal sludge (mix B_t with 0.247 L/g, mix C_t with 0.338 L/g, UsA_t with 0.243 L/g, mix UsB_t with 0.285 L/g, mix UsC_t with 0.371 L/g and mix UsE_t with 0.496 L/g) are much lower than that of only municipal sludge. The lowest biogas yield was 0.242 L/g in sample A_t. For this reason, the ratio of biogas produced per g of VS destroyed decrease as the possible inhibitory effects of industrial sludge increase.

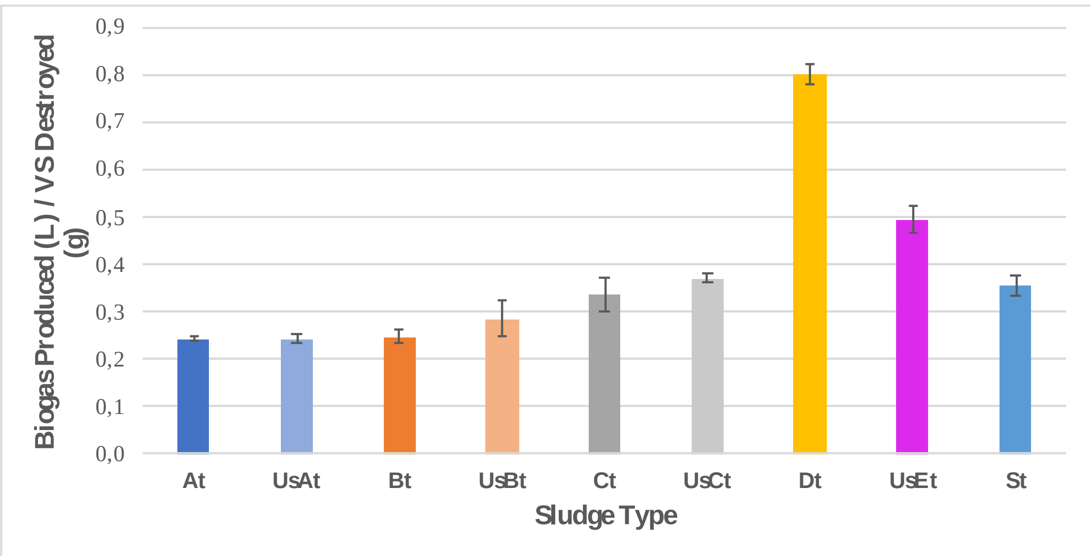


Figure 4.19: Biogas yield in liters per gram VS destroyed from textile industry BMP Set

4.3.2.2. Change of Chemical Oxygen Demand during BMP Test

Table 4.9 gives information about initial and final COD concentrations, and their removal rates for digestion of textile industry sludge. As expected, reactor D_t has the highest COD removal percentage (36.12%) which is a similar value to previous studies (Apul and Sanin, 2010). Likewise earlier discussed data, addition of industrial sludge decrease COD removal rates. Reactors UsE_t, UsC_t, UsB_t and UsA_t had 18.50%, 15.80%, 12.67% and 7.17% COD removals, respectively. Reactor C_t had 13.98% and reactor B_t followed that with 8.96%. Reactor A_t had the lowest value at 6.47%.

Table 4.9: *Initial and final COD concentrations and removal ratios during anaerobic digestion for textile industry BMP Set*

Reactor Code	**COD_i (g/L)**	**COD_f (g/L)**	**COD Removal (%)**
A_t	28.61±0.09	26.75±0.07	6.47
B_t	28.49±0.01	25.94±0.03	8.96
C_t	26.06±0.3	22.42±0.05	13.98
D_t	22.15±0.05	14.15±0.03	36.12
S_t	14.82±0.02	12.55±0.02	15.27
UsA_t	32.07±0.02	29.77±0.02	7.17
UsB_t	29.10±0.01	25.41±0.03	12.67
UsC_t	28.66±0.04	24.13±0.05	15.80
UsE_t	27.46±0.03	22.38±0.04	18.50

Methane yield normalized with the amount of COD destroyed is shown in Figure 4.20. Reactor A_t and D_t demonstrate only industrial and domestic sludge, respectively. On the other hand, reactors B_t and C_t consist of mixed sludge at 2:1 and 1:2 industrial and domestic sludge, respectively. Similarly, UsE_t is mixed sludge at 0.5:2.5 industrial and domestic sludge. For all reactors, methane produced per g of COD destroyed are less than theoretical maximum yield specified as 0.395 L methane/g COD destroyed (Speece, 1996). Reactor D_t has the maximum amount of methane produced per unit amount of COD destroyed. The methane yield of reactor D_t is 0.27 L/g. Reactor D_t is followed by reactor UsE_t (0.173 L/g), reactor UsC_t (0.161 L/g), reactor C_t (0.158 L/g), reactor UsB_t (0.130 L/g), reactor B_t (0.128 L/g), and then reactor UsA_t (0.125 L/g) and finally reactor A_t (0.113 L/g).

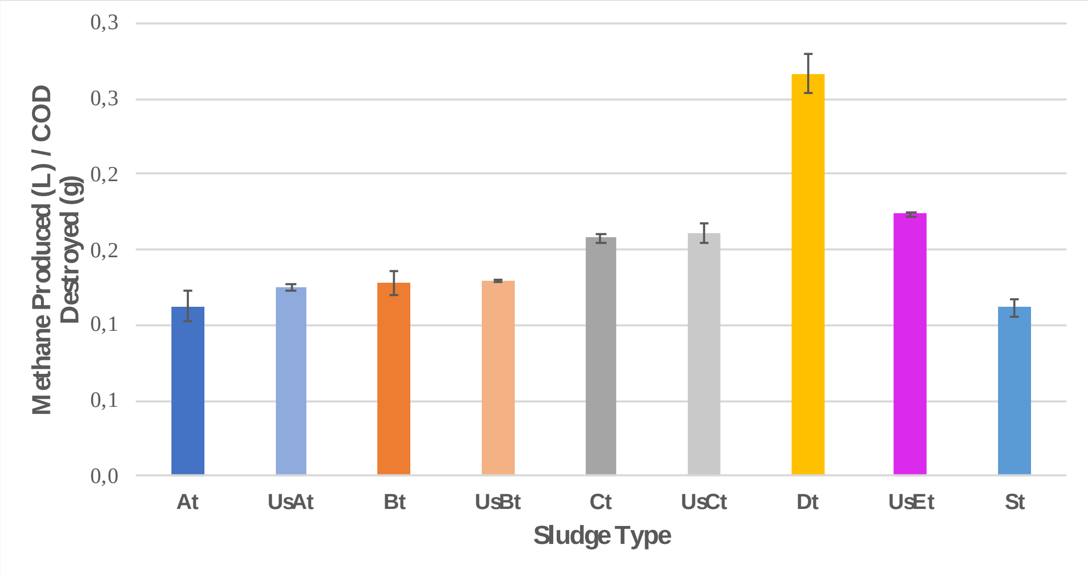


Figure 4.20: Methane yield in liters per gram of COD destroyed from textile industry

When the effect of mixing sludge from textile industry with municipal sludge at 2:1, 1:2 and 0.5:2.5 ratios is further evaluated by comparing expected (calculated) methane productions with the observed ones, one can make further comments. The green bars in Figure 4.21 for reactors B_t, C_t, UsA_t, UsB_t, UsC_t and UsE_t are calculated by simple summations of expected productions from the data obtained for reactor D_t (0.09 L/g), A_t (0.04 L/g) and UsA_t (0.042 L/g) in accordance with their mixing proportions. It is seen from Figure 4.21 that reactor C_t (0.16 L/g) slightly underperformed compared to the calculated result (0.22 L/g). On the other hand, reactor B_t (0.13 L/g) has performed slightly better compared to the calculated result (0.16 L/g). Likewise these values, observed values of reactors UsE_t (0.17 L/g), UsC_t (0.16 L/g) and UsB_t (0.13 L/g) substantially underperformed compared to the calculated values for them (0.24, 0.22

and 0.17 L/g, respectively). The effect of textile sludge seems to be pretty significant since the results (observed vs calculated) are seriously different with its increased addition to the domestic sludge. With this approach, one can state that mixing textile industry sludge with municipal sludge had negative effect on methane yield. This clearly indicates that sludge in mixture from this textile industry cannot be effectively co-digested with municipal sludge.

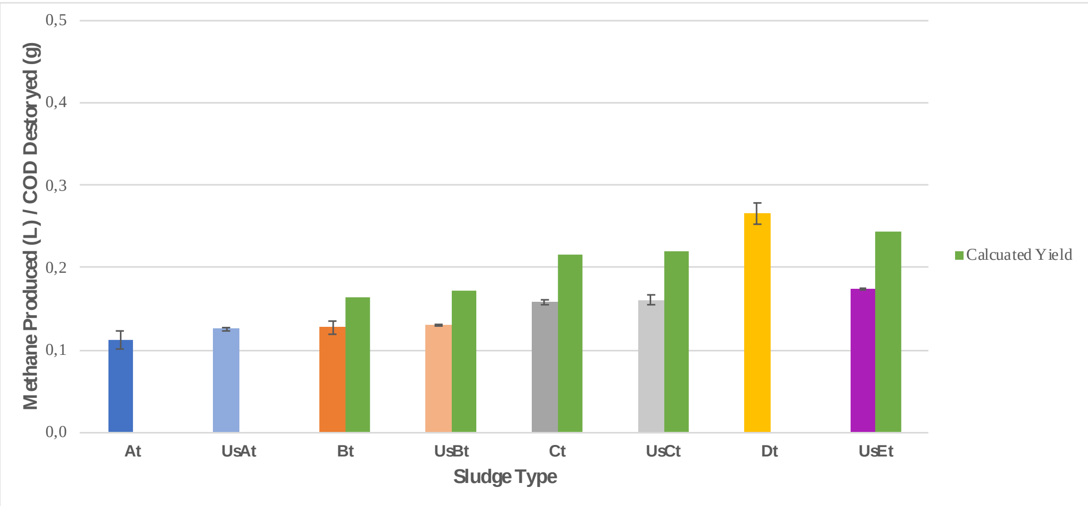


Figure 4.21: Methane yield in liters per gram COD destroyed compared with calculated this value from textile industry

4.4. Evaluation of Performance of Domestic Sludge Sampled at Different Times and Discussion of the Performance of Three Industrial Sludges

4.4.1. Evaluation of Domestic Sludge

Municipal waste activated sludge and anaerobic digested sludge from Ankara Central WWTP used in OID I, II and textile industry BMP sets were taken in different times of year. Biogas and methane production of all D samples taken at these different times from the same WWTP are evaluated. Comparing biogas and methane production of all D samples one can see that biogas and methane produced did not differ significantly and are consistent with each other (Figure 4.22 and Figure 4.23). The variability observed are within the expected experimental error.

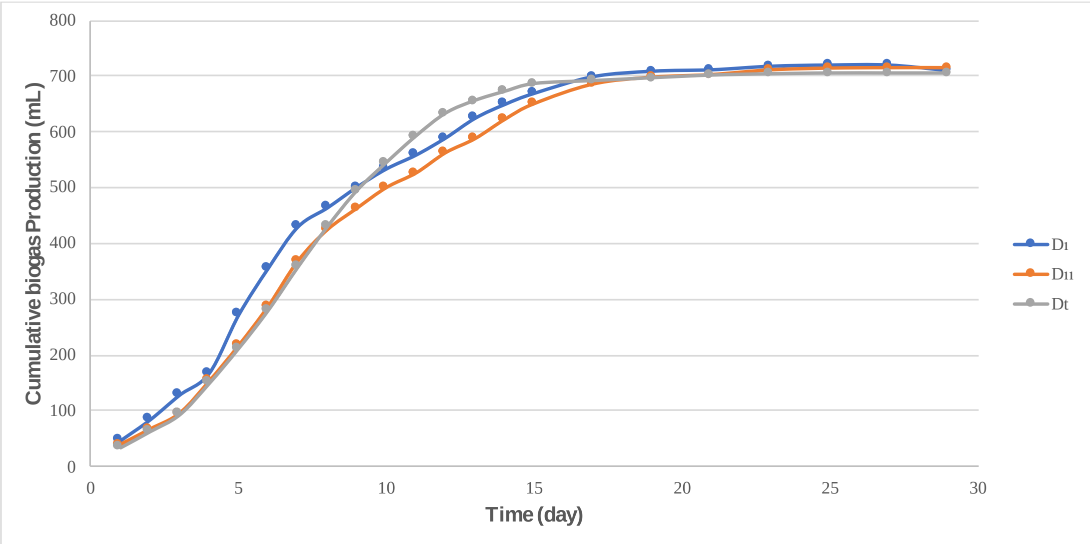


Figure 4.22: Cumulative biogas production of all D samples

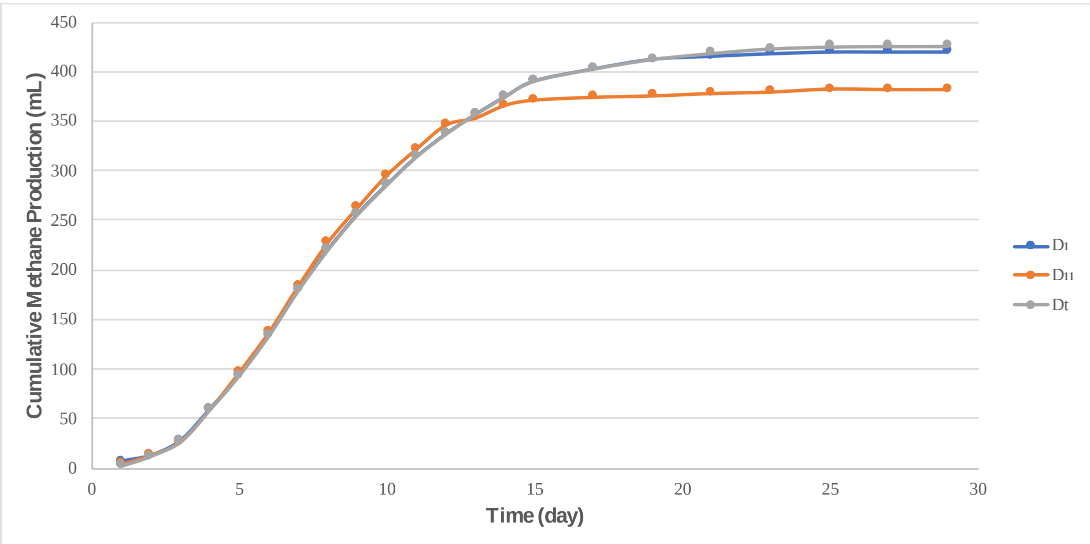


Figure 4.23: Cumulative methane production of all D samples

4.4.2. Performance of Three Industrial Sludges

Table 4.10 summarizes the information about TS, VS and COD removals, and methane percentage in biogas of three industrial sludge samples and their mixtures with the domestic sludge.

Table 4.10: *Performance summary of the three sets*

Parameters	Sample Code	OID I	OID II	Textile Industry
TS Removal (%)	A	10.97	10.65	8.09
	B	12.34	14.78	11.11
	C	18.09	16.57	13.58
	D	25.35	21.15	22.08
	E	19.71	-	-
	UsA	11.39	-	8.56
	UsB	14.90	-	11.74
	UsC	18.58	-	15.32
	UsE	20.40	-	16.14
VS Removal (%)	A	19.81	19.66	16.56
	B	29.43	26.35	22.87
	C	33.17	29.39	25.10
	D	47.84	45.17	46.02
	E	39.25	-	-
	UsA	23.21	-	17.18
	UsB	31.22	-	23.48
	UsC	33.69	-	26.74
	UsE	41.22	-	28.86
COD Removal (%)	A	16.92	15.29	6.47
	B	21.76	19.73	8.96
	C	25.78	21.59	13.98
	D	36.50	35.54	36.12
	E	29.74	-	-
	UsA	18.73	-	7.17
	UsB	23.46	-	12.67
	UsC	27.92	-	15.80
	UsE	31.44	-	18.50
Methane Percentage in Biogas	A	33	33	32
	B	42	41	39
	C	52	46	48
	D	59	53	61
	E	53	-	-
	UsA	31	-	39
	UsB	47	-	50
	UsC	54	-	52
	UsE	55	-	53

Comparing the performance of the sludge samples worked with, only textile sludge (sample A) has less TS, VS and COD removal rates compared to sludge samples taken from OIDs. The OID I and OID II samples and reactors A for both show almost identical performance for TS, VS and COD removal. Reactor A including textile sludge has less these removal rates and methane percent than other sludges. The removal performance of different parameters of reactors A belonging to all BMP assays, is less than half of the performances for reactor D values of all sets. The TS, VS and COD removal percent of all OIDs sludges are very close to half of that for municipal sludge sample values, while textile sludge sample has bigger difference. For this reason, textile sludge sample shows worse removal performance. Even though the initial COD of textile sludge was comparatively higher, this did not reflect on the removal percentages of VS and COD. The initial COD/VS ratios were also similar for all three sludges. When methane percentage in biogas of reactor D per reactor A are compared for OID I and II sludge samples, the ratios (sample D/ sample A for methane percentage in biogas) are determined similar (nearly 1.6). The reactor C of all three sludges has higher removal performances and methane percents than reactors B and A. Comparing all reactor Cs within themselves, OID I sludge has better performance for TS, VS and COD removals and produced methane percentage. With ultrasound pretreatment process, reactor UsE involving OID I has higher removal rates and methane percent in biogas than the one belonging to textile sludge. According to this comparison of these parameters for all sludge types, samples which include lower amount of industrial sludge has better performance than others.

When all the results are evaluated, it is seen that industrial sludges used in this work have biogas production potential but not up to the domestic sludge level. When domestic sludge and industrial sludges are mixed, intermediate results are obtained; and these are specific to the industrial sludge used. Comparing VS and COD removal rates of domestic sludge and mixed sludge samples, industrial sludge co-digested with domestic sludge leads to a decrease in removal percentages of domestic sludge. On the other hand, ultrasonication or other pretreatment alternatives or using acclimatized microorganisms may improve these results. Therefore, solutions can be case specific and the bigger picture, such as distance and costs, must be taken into account, while developing a management system for theses industrial sludges.

CHAPTER 5

CONCLUSION

The aim of this study is to determine the biogas production potential of industrial sludges using anaerobic biodegradation. Effect of pretreatment on performance is also evaluated. Two different OID and a textile industry sludge mixed with municipal sludge at different proportions is used to evaluate the possibility of co-digestion and its performance. The following conclusions are reached.

- Both the industrial sludges worked with and the domestic sludge have biogas production potentials. Industrial sludges alone have much lower biogas productions compared to domestic sludge.
- During the co-digestion, biogas production of domestic sludge is reduced as the amount of industrial sludge added is increased. In addition, methane content of biogas dropped as the amount of industrial sludge is increased. Where, textile industry sludge has the most significant negative impact on biogas production, OID I and OID II sludges have less negative impact with similar levels on biogas production.
- Even though for some reactors mixing reduced the observed biogas amount to lower than that expected from simple summation, results show that it is possible to co-digest industrial sludge with municipal sludge together.
- The TS and VS reductions as well as the COD removal rates which are among the performance indicators of anaerobic digestion are lower in industrial sludge compared to municipal sludge.

CHAPTER 6

RECOMMENDATIONS FOR FUTURE STUDIES

Regarding the results of this study, some different approaches can be recommended as future studies.

In this thesis ultrasonication was used as the pretreatment method for industrial sludge. Different pretreatment options such as ozonation, thermal and microwave can be tested to increase removal ratios and methane yield. An optimization study can be done for these kinds of sludges to see if there is any impact.

Solid concentrations, chemical oxygen demand and pH were measured in the scope of this study. There are other parameters like heavy metals or toxic substances that can be measured since the sludges are industrial origin.

Scope of this study was to evaluate the BMPs under different conditions. Seventy-two BMP bottles were set during this study. Larger scale batch or continuous reactors can be in operated to observe anaerobic treatment efficiency on industrial sludge in large scale.

Only three different industrial sludges were used in three BMP assays. Other sludge types need to be investigated.

Based on previous studies, F/M value was selected as one in this study. The performance of anaerobic treatment shows an alteration with F/M ratio. Parallel to this study, different F/M ratios may be applied provided the sludge types and mass ratios remain the same.

Acclimation was not applied on BMP sets in this study; however, acclimation with industrial sludge can be tried to enhance biogas and methane yields. Especially, for textile sludge, acclimation will help to improve methane yield and removal percentage.

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