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**SIVAS CUMHURİYET UNIVERSITY
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES**

**IMPROVING METHANE YIELD AND NUTRIENT RECOVERY OF WASTE
BIOLOGICAL SLUDGE WITH MICROWAVE DISINTEGRATION**

PhD THESIS

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I hope that this research, based on experimental facts, will contribute to all those interested in working in this field, and I dedicate it to all environmental engineers and those interested in protecting the environment.

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ÖZET

MİKRODALGA DEZENTEGRASYONU İLE ATIK BİYOLOJİK ÇAMURUN BİYOGAZ VERİMİNİN VE NUTRİENT GERİ KAZANIMININ İYİLEŞTİRİLMESİ

Ali ALHRAISHAWI

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Kentsel yerleşim alanlarındaki nüfus artışı, belediye atıksu arıtma tesislerinde (AAT) atık biyolojik çamur (ABÇ) üretiminin yükselmesine neden olmaktadır. AAT'de, ABÇ yönetimindeki en önemli sorun, yüksek bertaraf maliyeti ve yasal kısıtlamalardır. ABÇ, içerdiği organik madde, azot ve fosfor ile sürdürülebilir enerji kaynağı ve gübre olarak değerlendirilebilecek önemli bir kaynaktır. Son yıllarda, anaerobik çürütme (AÇ) ünitesinde üretilen biyogaz verimini arttırmak ve ABÇ hacmini azaltmak amacıyla daha çevre dostu ve ekonomik yöntemler geliştirmek için deneysel çalışmalar yürütülmektedir.

AÇ sürecinin etkinliği, ABÇ'nin parçalanması (ön arıtma) ile geliştirilebilir. Parçalama işleminde, ABÇ'nin yavaş ve kısmen parçalanabilir organik bileşenleri, AÇ sürecinde biyolojik olarak kolay kullanılabilir bileşiklere dönüştürülür. ABÇ'nin parçalanması, organik ve inorganik maddelerin çözeltiye salınmasını sağlarken, AÇ reaktörünün girişindeki organik madde derişiminin yükselmesi, çürütme verimini artırır. Biyolojik çamurun karmaşık yapısı, kimyasal, termal, biyolojik veya bu yöntemlerin birlikte uygulanması ile parçalanabilir.

Çevre mühendisliği çalışmalarında mikrodalga (MD) ısınlama, kirlenmiş toprak ıslahı, atık bertarafı, mineral işleme ve aktif karbon rejenerasyonu ve ağır metal içeren biyolojik çamur stabilizasyonunda uygulanan termal bir yöntemdir.

Tez çalışmasında, biyokimyasal metan potansiyeli (BMP) testinde CH_4 üretimini iyileştirmek için ABC parçalanmasında MD çalışma koşulları optimize edilmiştir. Ham ve santrifüjlenmiş ABC için MD ışınlamanın enerji tüketimi ve BMP testi ile enerji geri kazanımı değerlendirilmiştir. BMP testinde üretilen $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$ 'un geri kazanılması için strüvit çökeltme işlemi gerçekleştirilmiştir.

MD'nin sıcaklık artış hızı, gücü ve bekletme süresi, 90°C ve 110°C hedef sıcaklıkları için en uygun çalışma koşullarını belirlemek amacıyla test edilmiştir. Enerji tüketimi ve parçalanma derecesi (DD) dikkate alındığında, optimum işletme koşulu, 900 W güç, $2^\circ\text{C}/\text{dak}$ sıcaklık yükselme hızı, 90°C hedef sıcaklık ve hedef sıcaklıkta 5 dak tutma süresi olarak belirlenmiştir.

MD deneyleri, ABC'nin MD ışınlamasıyla başarılı bir şekilde parçalandığını ve sıvıdaki organik bileşiklerin derişiminin önemli ölçüde arttığını göstermiştir. MD'nin optimum koşullar altında çalıştırılmasıyla sıvı fazdaki çözünmüş kimyasal oksijen ihtiyacı (çKOI), karbonhidrat ve protein salınımının sırasıyla yaklaşık 36, 17 ve 3,6 kat arttığı belirlenmiştir. ABC'nin spesifik yüzey alanı (SYA) $70,9 \text{ m}^2/\text{kg}$ iken MD işlemi ile parçalanmış biyolojik çamur için $217,8 \text{ m}^2/\text{kg}$ 'a kayda değer bir artış gözlenmiştir. Bununla birlikte, susuzlaştırma karakteristiği önemli ölçüde kötüleşmiş ve ABC için 1.02×10^3 olan susuzlaştırma direnci, dezentegrasyon sonrası 2.04×10^4 'e yükselmiştir.

BMP testleri, MD'nin optimum işletim koşulları altında yaklaşık %1,27 toplam katı madde (TKM) içeren biyolojik çamur kullanılarak gerçekleştirilmiştir. Sonuçlar, kontrole kıyasla, 1/1 ve 2/1 substrat/aşı oranı için dezentegre biyoçamurla beslenen ünitelerde CH_4 üretiminin sırasıyla %12 ve %45 oranında arttığını göstermiştir.

Ayrıca, % 3,4 TKM içeren santrifüjlenmiş biyolojik çamur ile deneyler gerçekleştirilmiş ve dezentegre biyoçamura kıyasla CH_4 üretiminde iyileşmeler gözlenmiştir. Enerji geri kazanımı MD enerji ihtiyacını karşılamak için yeterli olmasa da, santrifüjlenmiş biyoçamur için MD'nin enerji tüketimi, dezentegre biyoçamura göre yaklaşık 3 kat azalmıştır.

Parçalanmış ve ham biyoçamurdan üretilen CH_4 'ın değerlendirilmesinde Gompertz Modifiye, Birinci dereceden kinetik, Lojistik ve Transfer fonksiyonu olmak üzere dört

kinetik model kullanılmıştır. İşletme koşulları altında, modeller 0,953 ile 0,998 arasında oldukça yüksek bir korelasyon katsayısı (R^2) göstermiştir. Birinci dereceden, Gompertz Modifiye ve Lojistik modellerle karşılaştırıldığında, Transfer fonksiyonu modeli, CH_4 üretim verilerine genel olarak en iyi uyumu sağladığı belirlenmiştir.

BMP testinde üretilen atıksudaki NH_4-N and PO_4-P 'nin geri kazanılması amacıyla çeşitli $Mg:N:P$ molar oranları için strüvit çöktürme deneyleri gerçekleştirilmiştir. 1,25:1:1 ve 1,50:1:1, $Mg:N:P$ molar oranlarında struvit çökeltmesi ile BMP testinden sonra atıksudaki NH_4-N 'un %82–90'ı ve PO_4-P 'unun %90–96'sı geri kazanılmıştır.

Anahtar Kelimeler: Biyokimyasal metan potansiyeli, biyoçamur dezentegrasyonu, enerji değerlendirmesi, mikrodalga, struvite çökeltimi

ABSTRACT

IMPROVING METHANE YIELD AND NUTRIENT RECOVERY OF WASTE BIOLOGICAL SLUDGE WITH MICROWAVE DISINTEGRATION

Ali ALHRAISHAWI

PhD Thesis

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The growth of population in urban areas leads to an increase in waste biological sludge (WBS) production in the municipal wastewater treatment plants (WWTP). The most important problem on the WBS management in WWTP are the high disposal cost and legal constraint. The WBS is an important resource that can be considered as a sustainable energy source and fertilizer with its organics, nitrogen and phosphorus content. In recent years, experimental studies have been carried out to develop more environmental friendly and economical methods in order to reduce the volume of WBS and increase in biogas yield produced in an anaerobic digestion (AD) unit.

The effectiveness of AD process can be improved by the disintegration (pretreatment) of WBS. In the disintegration process, slow and partial degradable organic fractions of WBS are converted into the readily biologically available compounds in the AD process. While the disintegration of WBS provides the release of organic and inorganic substances into solution, increase of organic substances concentration at the inlet of AD reactor improves the digestion efficiency. The intricate biosludge structure can be broken down by pretreatment procedures like chemical, thermal, biological, or a combination of these methods.

In the environmental engineering studies, the microwave (MW) irradiation is thermal method applied in contaminated soil reclamation, waste disposal, mineral processing and activated carbon regeneration and stabilization of heavy metal-containing biosludge.

In this thesis, the operational conditions of MW irradiation on the WBS disintegration was optimized in order to improve CH₄ production in the biochemical methane potential (BMP) test. For the raw and centrifuged WBS, energy consumption and recovery in the MW irradiation and BMP test, respectively, were evaluated. In order to recover the NH₄-N and PO₄-P produced in BMP test, the struvite precipitation was carried out.

The temperature ramping rate, power, and holding time of MW were tested in order to determine the optimal operational conditions for target temperature of 90°C and 110°C. Considering the energy consumption and disintegration degree (DD), the optimal condition was determined at the power of 900 W, ramping rate of 2 °C/min, target temperature of 90 °C, and the holding time of 5 min at the target temperature.

MW experiments indicated that the WBS was successfully disintegrated by MW irradiation and the concentration of organic constituents in liquor increased significantly. Operation of MW under the optimal conditions, it was determined that the release of soluble chemical oxygen demand (sCOD), carbohydrate, and protein in the liquid phase increased about 36, 17, and 3.6 times, respectively. The specific surface area (SSA) of WBS was 70.9 m²/kg and a notable increase was observed to 217.8 m²/kg for disintegrated biosludge by the MW treatment. However, dewatering characteristic deteriorated significantly and dewatering resistance increasing from 1.02x10³ for WBS to 2.04x10⁴ for disintegrated biosludge.

The BMP tests were carried out by using biosludge contained about 1.27% total solid (TS) under the optimal operational conditions of MW. Results indicated that compared to control, CH₄ production increased by 12% and 45% in units fed with disintegrated biosludge for the substrate/inoculum ratio of 1/1 and 2/1, respectively.

Additionally, experiments were carried out with the centrifuged biosludge contains the TS of 3.4% and improvements in CH₄ production was observed compared to the disintegrated biosludge. Although the energy recovery was not sufficient to cope with the MW energy

need, the energy consumption of the MW for centrifuged biosludge was reduced by about 3 times compared to the disintegrated biosludge.

Four kinetic models, which were Gompertz Modified, First-order kinetic, Logistic, and Transference function, were used in an analysis of CH₄ produced from disintegrated and raw WBS. Under the operational conditions, the models demonstrated a notably high correlation coefficient (R^2) between 0.953 and 0.998. Compared to the First order, Gompertz Modified, and Logistic models, it was determined that the Transference Function model fitted the CH₄ production data the best overall.

In order to recover NH₄-N and PO₄-P in the wastewater produced in BMP test, the struvite precipitation experiments for various molar ratios of Mg:N:P were carried out. By the struvite precipitation at Mg:N:P molar ratios of 1.25:1:1 and 1.50:1:1, 82–90 % of NH₄-N and 90–96 % PO₄-P in wastewater were recovered after the BMP test.

Keywords: Biochemical methane potential, biosludge disintegration, energy assessment, microwave irradiation, struvite precipitation

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ABBREVIATIONS

AD:	Anaerobic digestion
BMP:	Biochemical methane potential
DD:	Disintegration degree
EPS:	Extracellular polymeric substances
HPH:	High pressure homogenous
HRT:	Hydraulic retention time
MAP:	Magnesium ammonium phosphate
MW:	Microwave
PSD:	Particle size distribution
sCOD:	Soluble chemical oxygen demand
SS:	Suspended solid
SFR:	Sludge filter resistance
SRT:	Sludge retention time
tBMP	Theoretical biochemical methane potential
tCOD:	Total chemical oxygen demand
TS:	Total solids
VS:	Volatile solid
VSS:	Volatile suspended solid
WWTP:	Wastewater treatment plant
WBS:	Waste biological sludge

1. INTRODUCTION

1.1. Wastewater problems on ecosystem

The concept of circular economy has gained traction as a promising approach to address the challenges posed by unsustainable consumption and waste generation. By emphasizing the principles of reducing, reusing, recycling, and recovering energy from waste materials and wastewaters, sustainable waste management systems offer multifaceted benefits. One of the significant advantages lies in reducing pollution, both in terms of air and water quality. Proper management of waste and wastewaters helps mitigate the release of harmful substances into the environment, thereby safeguarding ecosystems and human health (Gómez–Sanabria et al., 2018). Moreover, these systems contribute to the decarbonization of the energy sector by tapping into the energy potential inherent in waste materials and wastewaters.

Technologies like anaerobic digestion (AD) or waste–to–energy processes enable to obtain energy from organic waste, providing an alternative and renewable energy source while reducing the needs of deposits volume in landfills. Furthermore, recycling and reusing materials from wastes contribute to resource conservation, reducing the reliance on raw materials and the energy–intensive processes involved in their extraction and production. It promotes a closed–loop system, where materials retain their value and utility through multiple lifecycles. The integration of various disciplines and approaches into sustainable waste and wastewater management systems are crucial for achieving a more balanced and resilient relationship between human activities and the environment. It requires collaborative efforts from policymakers, businesses, communities, and individuals to implement innovative solutions that prioritize sustainability, reduce the strain on natural resources and ecosystems (Gómez–Sanabria et al., 2018).

A sewage sludge management is indeed a multifaceted challenge that requires careful attention to technical, economic, and environmental considerations. The regulations and standards often aim to strike a balance between effective treatment, cost–efficiency, and minimizing the environmental impact of waste disposal. The potential for sewage biosludge as a biomass energy source is intriguing. The organic contents of biosludge

holds promise for renewable energy production through processes like AD or pyrolysis, which can generate biogas or biofuels while mitigating the volume of waste sent to landfills. This approach aligns with the principles of sustainability by both reducing waste and producing cleaner energy. Advancements in technology and ongoing research are crucial for improving the efficiency and sustainability of sewage biosludge management. Finding of innovative ways to convert waste materials into usable energy and valuable by-products, it can not only address waste management concerns but also contribute to the renewable energy sector. Moreover, as these practices evolve, it's essential to ensure that they are accessible and feasible in worldwide. Implementing cost-effective and environmentally friendly approaches is key to widespread adoption and achieving long-term sustainability goals (Jeong et al., 2019; Kumar, 2013).

Increase of population cause the significantly increase of municipal and industrial wastewaters production. The average amount of wastewater produced in developing countries is between 30 and 70 m³/year.person. The wastewater produced in a city of one million people would be enough to irrigate roughly 1,500–3,500 ha. Due to the numerous urgent problems affecting our waste management process, the wastewater problem needs to be addressed ecologically (Kumar, 2013). The collection and treatment of wastewater in small settlements population equivalents (PE) (PE < 2,000) is not precisely controlled under the existing EU regulation. There are many small settlements in Central and Eastern Europe and improper wastewater treatment from these settlements contaminated groundwater and the surface waters. The wastewater management in rural areas must be integrated with the wastewater treatment products (such as water, nutrients, and biomass) and agriculture and/or energy production (Istenič et al., 2023). The ecosystem and human health are suffered when these pollutants enter natural water systems without being handled. The wastewaters, which contains a variety of organisms including *Escherichia coli*, is harmful for the environmental health and also causes algal blooms and eutrophication, which deplete oxygen and destroying recreation area results in the economic life (Ishii and Sadowsky, 2008).

The treatment of wastewater is important for the environment and sustainable development. In the biological processes, which pollutant converted to the microorganisms and final products such as CO₂, N₂, H₂O under an aerobic condition, is

one of the most applied method in the wastewater treatment (Wei et al., 2003). The biosludges, which consist of mainly water and variety of organisms, is settled in a tank and some of them is returned to the biological reactor in the suspended growth process, while remaining is transferred to the sludge management processes such as dewatering, AD, landfill area etc.

High water and organic content of biosludge, along with the presence of pathogens, heavy metals, and persistent organic pollutants, make its treatment and disposal difficult. While the global sludge production is expanding at an unstoppable rate, sludge management environmental quality standards are getting more demanding and economically pressing, necessitating low-cost solutions to lessen the mounting costs brought on by the rapid sludge generation (Liu et al., 2022). Theoretically, following the biological wastewater treatment, up to 85–95% of the heavy metals, phosphorus, harmful bacteria, 40–50% of the organic components, and 20–30% of the total nitrogen in the influent of wastewater treatment plants (WWTP) might finally take part in the waste biosludge (WBS) (Wei et al., 2020).

1.2. Biosludge production

The costs associated with biosludge treatment in WWTP indeed constitute a substantial portion of operational expenses, typically ranging from 50% to 60%. Additionally, the expenses related to electrical energy, accounting for approximately 25% to 40%, contribute significantly to the overall operational costs (Alhraishawi and Aslan, 2022). The disposal of WBS produced in the WTPs is increasingly regarded as a major environmental concern due to stricter legislative constraints and regulations. This concern is primarily due to the potential environmental impacts of improper disposal methods, as well as the need to adhere to increasingly stringent environmental standards. Given the high operational costs related to biosludge treatment and the substantial energy consumption, exploring more efficient and sustainable methods becomes imperative. This is not only to reduce operational expenses but also to address environmental concerns associated with waste disposal. Strategies such as optimizing treatment processes, exploring alternative energy sources, implementing advanced technologies for the sludge

treatment, and focusing on recovery from waste materials can play pivotal roles in mitigating these challenges (Alhraishawi and Aslan, 2022).

Worldwide, municipal WWTPs produce 45 million tons dry of sewage biosludge per year. In the United States, China, and the European Union, the average annual production of sewage biosludge ranges from 18 to 33 million tons in dry weight (Capodaglio, 2023; Ferrentino et al., 2016). Data indicated that in 13 largest producing countries in Europe, the average secondary biosludge production between 2010 and 2017 ranged between 181 and 1,850 gigagrams (Gg) of total solids (TS) per year. This results in an average specific production of 21 ± 4 kg of TS/person.year. Costs for processing, transportation, and disposal rise with the sewage biosludge volume increases. As a result, the management of sewage biosludge has grown into a significant economic and environmental problem (Di Capua et al., 2020). More than 660,000 tons/year of dry stabilized biosolids were produced in Canada and it was reported that the annual cost of managing biosolids was almost equal to half of overall operational cost of wastewater treatment (Spinosa, 2011). According to Nabaterega et al., (2021) urban WWTPs in high–and middle–income nations produce high amount of biosludge. Urban wastewater treatment facilities in the USA and China create about 7.2 and 6.2 million dry metric tons/year biosludges, respectively. However, Canada and the majority of Europe produce between 0.66 and 0.2 million dry metric tons of biosludge annual (Nabaterega et al., 2021). Various estimates of the amount of biosludge produced in Mexico per year range from about 640,000 tons to as much as 10,000 tons (Spinosa, 2011). Australia produces 3 million tons of wet biosludge annually, while Europe, the United States, and China collectively produce 240 million tons (Wang et al., 2017). In Japan, sewage biosludge was produced in excess of 2.2 million tons on a dry basis in 2013, and this amount is steadily rising (Khandaker et al., 2020). In 2015, more than 2 million tons of dry sewage biosludge was produced annually in Morocco. In 2018, South Korea produced 11,219 tons of sewage biosludge per day, with an estimated energy production of about 2,493 tons of solid fuel, or the equivalent of 31,313 gigajoules per day (Kim et al., 2021). In Türkiye, 79% of the population resides in municipalities that receive WWTP service. In Türkiye's current WWTPs, 1,169,612,481 m³/year of wastewater was treated biologically, producing about 318,503 tons of biosludge as dry solid matter (TUIK, 2018). Istanbul's wastewater treatment facilities were expected to

create more over 160 thousand tons of biosludge in 2020. In contrast, more than 200 tons of wet sewage biosludge were produced every day in Ankara, Eskişehir, Bursa, Adana, Gaziantep, and Antalya (Abusoglu et al., 2019). In 2018, 644 municipalities were served by a total of 991 WWTPs, with the following split of treatment types: physical (55), biological (527), advanced (203), and natural (206). Türkiye handled 45.3% of its wastewater using advanced treatment, 25.4% using biological treatment, 25.4% using physical treatment, and 0.41% using natural treatment (Abusoglu et al., 2021).

1.3. Reuse of waste organic matters

The shift toward renewable energy sources and the utilization of biomass presents a promising way for the sustainable development and circular economy. Biomass, including agricultural waste and municipal solid waste, holds immense potential for conversion into valuable chemical compounds, energy, and fuels. Through innovative conversion technologies, such as pyrolysis, fermentation, and gasification, biomass can be transformed into biofuels like bioethanol and biodiesel, providing alternatives to fossil fuels. Additionally, biochemical processes can yield valuable chemical compounds used in various industries, reducing dependency on non-renewable resources (Li et al., 2019; Náthia-Neves et al., 2018). The allure of biomass lies not only in its vast availability but also in its role in waste management. By repurposing agricultural and municipal waste, it is not only reducing environmental burdens such as landfill usage and greenhouse gas emissions but also create economic opportunities. This approach promotes a more sustainable and efficient use of resources while reducing our reliance on finite fossil fuels. Investment in research and development further enhances biomass conversion technologies, making these processes more economically viable and environmentally friendly. As continue to advance these technologies, the bioeconomy seen as a beacon for a more sustainable and circular approach to resource utilization, reducing waste and enhancing the practicality of renewable energy sources (Li et al., 2019; Náthia-Neves et al., 2018).

Given the abundance of organic waste feedstock accessible globally, AD-recovered biogas has the potential to meet 6% of primary energy demand and a fifth of the world's natural gas needs. Although AD has the potential to make a major contribution to energy

needs, biogas is still an underutilized resource with just 47–95 billion kWh of electricity produced from it in 2012, making up 0.2–0.4% of our total power production. The average heating value of dried WBS (12,000–20,000 kJ/kg) is lower than that of conventional coal and petroleum (30,000–40,000 kJ/kg) but nearly equal to that of lignite coal (11,700–15,800 kJ/kg).

1.4. Biosludge constituents

The features of biosludge vary greatly since they depend on the type of industrial effluents discharged into sewage systems as well as influent wastewaters. The sewage sludge can be divided into three basic categories: primary sludges, biosludges and chemical sludges (Menezes et al., 2022). In order to decrease the loading rates of pollutants into the biological reactor, typically pretreatment units, such as screening, grit chambers, and flotation used to separate large objects, sand, and oily substances in the influent wastewaters. The primary sludge is rich in easily biodegradable organic matter, has a high potential for biogas production in AD process, and typically has good dewaterability (Sakaveli et al., 2021). Because of the WBS, which is drawn from the settling tank located after biological reactor, has a more complex composition and less readily biodegradable compounds than primary sludge. Compared to primary sludge, WBS contains less fat, fiber, more protein and phosphorus. Whereas WBS typically has an earthy smell and a brown, crystalline appearance, the primary sludge is typically gray, sticky, and smells very bad. The typical properties of primary and WBS are presented in Table 1.1 (Kor–Bicakci et al., 2019).

Table 1.1 Characteristics of primary and activated sludge in wastewater treatment plants (Kor–Bicakci et al., 2019)

Parameter	Properties	
	Primary sludge	WBS
Total Solids (TS, %)	1–6	0.4–1.2
Volatile Solids (VS, %)	60–85	60–85
Fat and grease (% of TS)	8–18	8–12
Protein (% of TS)	20–30	32–41
Fibers (% of TS)	16	17
N (% of TS)	1.5–4	2.4–5
Phosphorous (% of TS)	0.8–2.8	2.8–11
pH	5–8	6.5–8
C (% of Volatile Matter)	51	52
H (% of Volatile Matter)	7	6.7
N (% of Volatile Matter)	4.5	7.5
O ₂ (% of Volatile Matter)	33.5	33
Alkalinity (mg CaCO ₃ /L)	500–1,500	580–1,100
Organic acids (mg/L)	200–2,000	1,100–1,700
Energy content (kJ/kg Volatile Suspended Solids, VSS)	23,000–29,000	19,000–23,000

Organic biomolecules, such as proteins, sugars, humic compounds, and microbial organisms make up the WBS. The WBS is denoted by the chemical formula $C_7H_{11}O_3N$ and primary sludge by the chemical formula $C_{23}H_{35}O_8N$ (C:H:O:N = 61:8:28:3) (Barber, 2020). There are three structural levels in the sludge structure: primary particles, which have a diameter of 2.5 μm ; secondary particles, which have a diameter of 13 μm and are connected by exopolymers; and developed tertiary structures, which have an average diameter of 125 μm . It was also reported that extracellular polymeric substances (EPS) in the WBS was a significant component and that the biosludge clumps' inside was a multi-scale structure with huge pores that could spread across the clumps (Xu et al., 2020). Prokaryotic and eukaryotic organism both produce EPS, which is a characteristic of microorganisms in natural environments. The EPS is an intricate mixture of polymers with a high molecular weight that includes sugars, proteins, humic and uronic acids, nucleic acids, lipids, and more. Numerous mechanisms, including as secretion, cell lysis, and absorption, contribute to EPS buildup. The microorganisms used in biological wastewater treatment take the form of microbial aggregates like biofilms, sludge flocs, and granules.

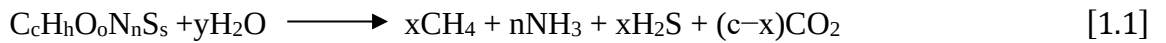
The EPS make up a significant amount of about 50% to 80% (w/w) of the total weight in the biofilm (Shi et al., 2017).

In order to disintegrate the microbial cell walls, which are made of peptidoglycan, protein, and lipid bilayers, anaerobic bacteria must release exogenous enzymes. Because decomposition of these components is challenging, in the AD process has trouble breaking down more than 35% of the organic matter in the secondary biosludge. A biological hydrolysis of cell is therefore regarded as a rate-limiting phase in the majority of WBS (Kim et al., 2019).

1.5. Anaerobic digestion process

The historical evidence indicated that the use of biogas to heat bathing water as early as the 10th century BC in Assyria and Persia. In the Middle Ages, combustible gas was produced from the decomposition of organic matter in lakes. In 1808, the CH₄ was produced in the anaerobic condition by using the cattle manure (Meegoda et al., 2018).

The most widely used biosludge stabilization technology available today is AD process, which converts organic constituents of biosolids to biogas, a mixture of CH₄, CO₂, and trace amounts of other gases as shown in Eq 1.1 in the absence of molecular oxygen. The four stages of AD process are hydrolysis, acidogenesis, acetogenesis, and methanogenesis; different types of microorganisms carry out each stage, and the AD process depends on interactions between these microorganisms. The waste contains different types of organics constituents are taken into single-stage reactor; all four processes are carried out concurrently. The remaining part of the waste in the reactor is subsequently drawn at the end of a predetermined retention period or when biogas generation stops (Anukam et al., 2019). The four digestive phases are shown in a simplified flow in Figure 1.1 as discussed below.



$$x = \frac{1}{8} \times (4c + h - 2o - 3n - 2s)$$

$$y = \frac{1}{4} \times (4c + h - 2o - 3n - 3s)$$

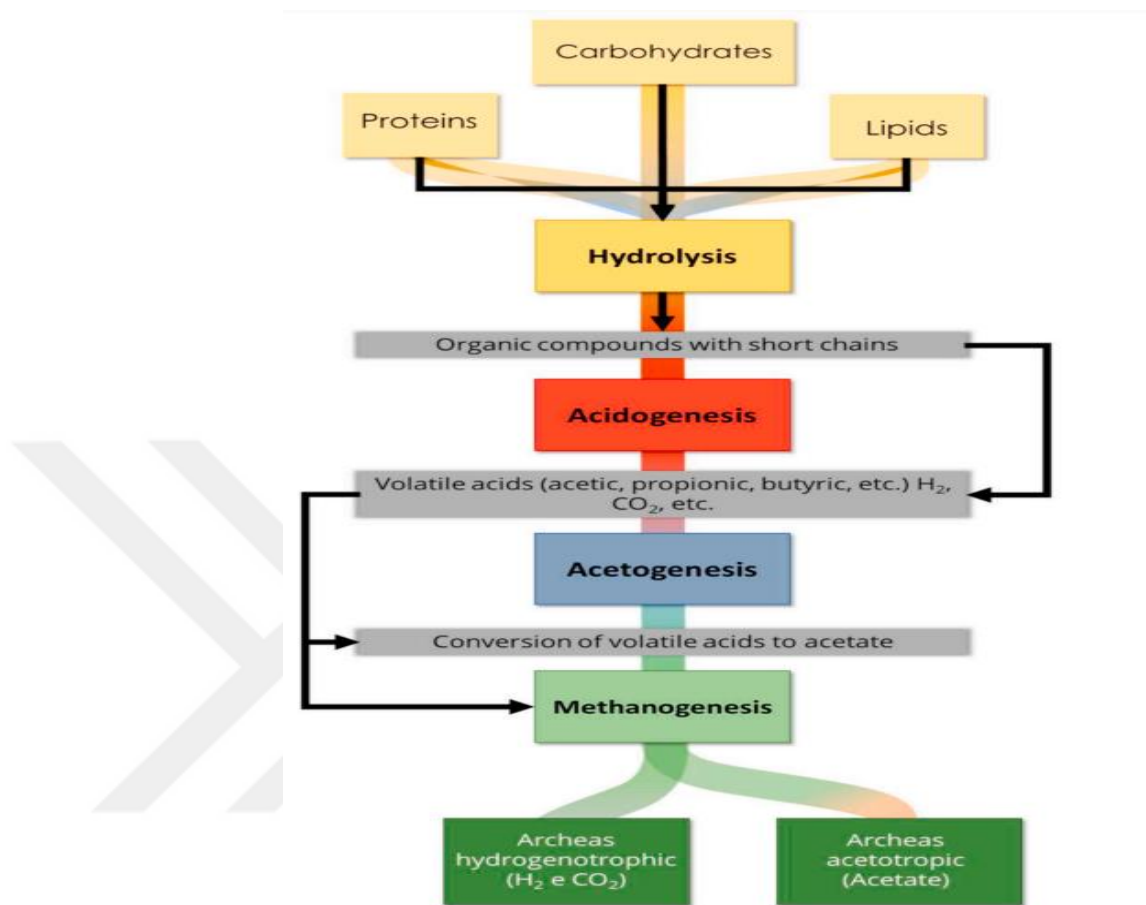


Figure 1.1 A representative phases diagram of AD process (Cremonez et al., 2021)

An extracellular hydrolytic enzyme of acidogens take part in the initial step of process to break down complex organic compounds that bacteria cannot directly consume into soluble monomers (Li et al., 2019). In this stage, the proteins, lipids, and carbohydrates, which are complex high-molecular-weight organics are hydrolyzed into soluble molecules like amino acids, fatty acids, and short-chain sugars. It is the crucial phase of AD process since the rate at which the complex substrates are broken down by enzymes determines how quickly bacteria can absorb these substances (Zhang et al., 2014). The hydrolyzed organics are taken up by bacteria to use in their metabolic cycles, which results in the production of volatile organic acids (including acetic, propionic, lactic, and formic acids) (VOCs) as well as some alcohols and gases like CO₂ and H₂ (Zhang et al., 2015). Organic acids produced during the acidogenesis phase are converted to acetic acid by a

few number of homoacetogenic bacteria during the acetogenesis process (Li et al., 2019). The core elements of the typical AD process are the acetoclastic and hydrogenotrophic CH_4 pathways. There is a longer period of time needed for digestion since acetoclast methanogens grow more slowly than hydrolytic methanogens (doubling time of bacteria varying from 5 to 7 days versus 4 to 8 hours). Acetate, an organic acid that is produced during the biodegradation of complex organic materials, can build up during digestion and lead to process instability because of slowed acetoclast methanogenesis kinetics (Khan et al., 2019). The key chemical routes carried out synergistically by the methanogenic Archaeas were described in Equations (1.2)–(1.6) (Cremonez et al., 2021; Li et al., 2019).



For efficient AD, maintaining specific micro–and macronutrients levels and environmental conditions like alkalinity, pH, and temperature play pivotal roles in sustaining the activity of microbial community (Coelho et al., 2011).

1.5.1. pH and alkalinity

A stable pH ranges typically between 6.5 and 7.5 is essential for the microbial consortia involved in AD. Alkalinity acts as a buffer, helping to maintain a consistent pH level despite fluctuations caused by the breakdown of organic matters. Adequate alkalinity ensures that the microbial community can function optimally (Zhai et al., 2015).

1.5.2. Nutrients

Microorganisms involved in the AD require various nutrients, including both micronutrients (such as iron, nickel, cobalt, and molybdenum) and macronutrients (such as carbon, nitrogen, phosphorus, and sulfur), for their growth and metabolism. These elements are crucial components of enzymes and co–factors involved in biochemical reactions during the digestion process. As presented in Table 1.2, these components are typically consisting in the biosludge (Coelho, 2011).

Table 1.2 Ranges of elements suitable for AD (Coelho, 2011)

Element	dry weight (g/g)
C	0.37–0.44
H	0.055–0.065
N	0.095–0.128
P	0.005–0.028
S	0.0056–0.012
Na	0.003–0.04
K	0.0013–0.05
Ca	0.001–0.0045
Mg	0.0009–0.00053
Fe	0.0007–0.0028
Ni	0.0000065–0.00018
Co	0.00001–0.00012
Zn	0.00005–0.00063

1.5.3. Temperature

The temperature of AD reactor influences the activity, diversity of microorganisms and rate of biogas production. The temperatures around 35–40 °C and 50–60 °C are the most applied ranges for the mesophilic and thermophilic conditions in AD process, respectively (Coelho, 2011).

1.6. Energy and recovery of resources

Fossil fuels, which is one of the most important energy sources, account for about 80% of all energy consumption globally. This is obviously in opposition to the requirement to reduce the use of fossil fuels because of their significant negative effects on the environment, particularly the release of pollutants and greenhouse gases. The exploitation of so-called non-conventional fossil resources has become economically feasible due to the limited supply of readily available fossil fuels and the concurrent rise in demand (Hijazi et al., 2016). A sustainable energy system based on fossil fuels appears unattainable. Energy obtained by the usage of biomass currently makes up two thirds of renewable energy in Europe, and it will be crucial to meet the Renewable Energy Directive's goal of 20% renewable energy by 2050 for final energy consumption. The capacity of bioenergy worldwide was about 83 GW by the end of 2012. First place went

to the United States with 62 TWh annually, then Germany with 37 TWh, Brazil with 36 TWh, and China with 27 TWh (Hijazi et al., 2016).

The primary energy source for the municipal WWTP comes from CH₄ produced in the anaerobic digesters. The recovered CH₄ is typically used to run gas engines, which generates thermal and electrical energy that is used in the plant. CH₄ recovery can offset roughly half of the WWTP's electricity costs, which account for around 80% of total operating expenses (Shen et al., 2015). One of the main greenhouse gases is CH₄, which is released into the atmosphere naturally when the sewage biosludge is deposited in the landfills. The AD is an environmental friendly process, which lowers the CO₂ generation when electricity is produced using CH₄ rather than fossil fuels. Tyagi et al., (2013) reported that by using a primary settling and activated sludge as substrates in the AD process could produce 362–612 and 275–380 mL of biogas/gVS, respectively. Nwokolo et al., (2020) found that the CH₄ production from goat (402–500 mL/g) and pig manures (204.0–438.4 mL/gVS) replaces the other manures by obtaining the volume of CH₄ about 0.7, 223.5, and 251.4 mL/gVS from the lignin, hemicellulose, cellulose components of manures. The range of CH₄ production from industrial wastewaters between 25–429 mL/g VS were observed. The lowest CH₄ yield, 25 mL/g VS was produced by barley waste used to make instant coffee substitute, whereas 429 mL/gVS was produced by using paper mill wastewater (Nwokolo et al., 2020).

Determining the characteristics of biosludges, which are C/N ratio, moisture, and pH, are important for improving the yields of CH₄ production in AD process. As well as the concentrations of potentially toxic materials in biosludges should be lower than the inhibition level and considering the usage possibility of residues produced in the AD process such as an agricultural purpose are important. The production CH₄ from different substrates are illustrated in Table 1.3.

Table 1.3 CH₄ production from various substrates
(Kasinath et al., 2021; Nwokolo et al., 2020).

Substrate	CH₄ yield (mL/gVS)	CH₄ content (%)
Pig manure	250–150	70–80
Cow manure	200–250	55–75
Chicken manure	300–350	60–80
Sewage sludge	300–400	65–70
Straw, grass	200–250	54
Maize	250–450	52
Sugar beet	250–380	53
Microcrystalline cellulose	211.8	–
Hemicellulose	133.9	–
Food Waste	460	–
Vegetable food waste	425	–
Potato skin	276	–
Banana skin	277	–
Carrot petioles	309	–
Orange peel	230–333	–
Strawberry Extrudate	285–339	–
Textile wastewater	200–400	–
Paper mill effluent	220–340	–
Cheese whey and diary	280–350	–
Barley waste	25	–
Biodiesel wastewater	161	–
Sunflower oil cake	195	–
Pulp and paper mill sludge	429	–
Jatropha carcass oil cake	250	–
Sugarcane vinasse	350	–

The hydrolysis, which is the initial step of AD, is considered the rate limiting stage in the process due to the complex nature of biomass. Biomass consist of cellulose, hemicellulose, lignin, proteins, sugars, and lipids, which are not easily biodegradable. The transformation of WBS into alternative fuels, such as biofuels or biogas, not only represents a sustainable approach but reducing dependency on traditional fossil fuels. Optimizing and improving the AD with pretreatment techniques, particularly in biosludge

digestion, is crucial for maximizing biogas production and will be useful method for the potential of organic waste as a valuable renewable energy source.

In general, biosludge pretreatment helps to improve the efficiency of AD process by increasing organic matter bioavailability, enhancing CH_4 production rates, and reducing the retention time required for the digestion process as shown in Figure 1.2. This is useful for WWTP that aim to maximize energy recovery from biosludge while minimizing operating costs and environmental impacts.

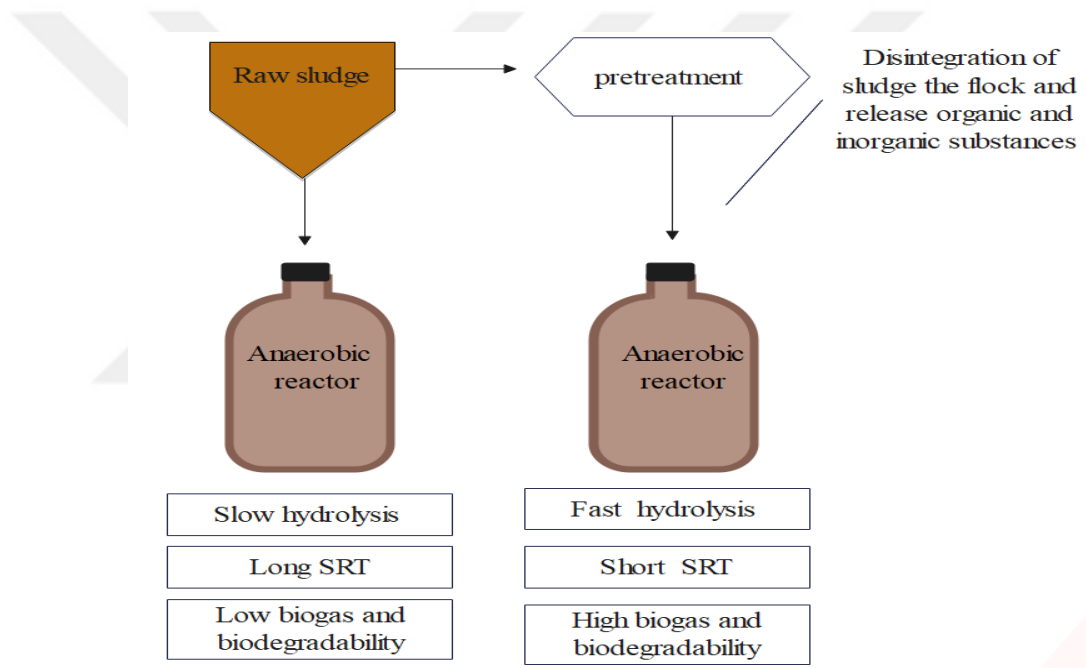


Figure 1.2 Schematic diagram of the disintegration of WBS (Zhen et al., 2017)

The WBS contains significant amounts of valuable nutrients found in protein-based compounds, such as nitrogen and phosphorus with a range from 2.4% to 5.0% and from 0.5% to 0.7% of the TS, respectively. With the decomposition and dissolution of WBS results in the release of $\text{NH}_4\text{-N}$, $\text{PO}_4\text{-P}$, and other elements into the liquid medium (wastewater). $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$ in the wastewater can be repurposed to form the slow soluble fertilizer, namely magnesium ammonium phosphate (MAP) (struvite), which can be directly applied to soil for agricultural use. Due to the cost of nitrogen (1.3 \$/Kg) and

phosphorus (2.6 \$/Kg) as the commercial fertilizer are significant, the nutrient contents of wastewater produced in the AD process represents a substantial economic value (Yadav et al., 2023).

It was determined that the dry WBS have an approximate value of 2.1 \$/person.year, equating to roughly 0.5 kg of P/person.year and 0.6 kilograms of N/person.year (Tyagi et al., 2013). It is considered that the significant potential of biosludge as a valuable resource not only for waste management but also for the recovery and reuse of essential nutrients in the form of fertilizers. The utilization of sewage biosludge as a source of nutrients for fertilizers represents an economically viable and environmentally sustainable approach. By repurposing these nutrients from sludge into fertilizers for agricultural use, it not only mitigates waste but also reduces the dependency on traditional commercial fertilizers, contributing to a circular economy and sustainable agricultural practices.

1.7. Mechanisms of biosludge disintegration

The high resistance of biosludge for dewatering and biodegradation can be reduced by pretreatment (disintegration) (Zhen et al., 2017). Because the cellular materials are released into the aqueous phase by the biosludge pretreatment–induced disruption of the floc structure and some bacterial cell walls, and result in the digestion rate is improved, retention time is shortened, and increase the biogas production yield in the AD reactor, due do the organisms have access to more nutrients (Banu et al., 2017).

The external forces, which can be categorized into three main groups, namely chemical, biological, or physical processes are breakdown the biosludge (Anjum et al., 2016; Mitraka et al., 2022).

- **Disruption of Cells and Floc Structures:** The biosludge often contains microbial cells and floc structures formed by aggregation. Disintegration can cause the disruption or breakdown of the cells, altering the overall composition and stability of the biosludge.
- **Release of Soluble Materials and Fine Particles:** The breakdown of biosludge components into smaller particles or dissolved materials like organic or inorganic compounds.

- **Chemical Reactions:** External forces can induce chemical reactions, which might result in the formation of new compounds or the breakdown of existing ones, within the biosludge, leading to changes in its chemical composition. The released constituents of biosludge can dissolve or are already in a dissolved state. Because of the small particle size and difference of the low density between the particles and its surrounding water, the particles or colloidal components that are unable to be separated from the liquid phase may stay in the solution.

On the other hand, the organic components have a large surface area in comparison to their size or are already liquefy, result in the easy the hydrolysis process and they are readily biodegradable.

1.7.1. Biosludge disintegration methods

Through four successive stages (i.e., hydrolysis, acidogenesis, acetone generation, and methanogenesis), a microbial consortium biologically stabilizes a mixture of primary and secondary sludge in the AD process without the presence of molecular oxygen. In order to reduce reliance on fossil fuel energy and greenhouse gas emissions, the AD process is an affordable and environmentally friendly method of producing CH₄-enriched biogas, which can be burned to generate electricity and/or waste heat, or converted into renewable gas and transportation fuel (Kor-Bicakci et al., 2019). Aside from its many benefits, the AD has certain drawbacks, such as a lower biodegradation efficiency (only 30–50%) and a longer hydraulic retention time (HRT) (up to 30 days), both of which increase the capital costs of treatment plant (Gahlot et al., 2022).

The AD theoretically converts lipids, proteins, and carbohydrates to CH₄ at varying rates: 1,014 NL CH₄/kg VS, 740 NL CH₄/kg VS, and 370 NL CH₄/kg VS, respectively. However, challenges persist within the AD systems, encompassing limited CH₄ yield, extended HRT, and incomplete substrate digestion (Atelge et al., 2020). The intricate biosludge matrix is behave the physical and chemical barriers, impeding enzymatic breakdown, hindering hydrolysis rates, reducing biogas output and sludge dewaterability, and generating pathogen-rich Class B biosolids. The biosludge pretreatment with various methods has been under investigated to speed up the traditional AD processes and to cope with the operational limitations (Gahlot et al., 2022). The intricate sludge structure is

broken down by pretreatment procedures like chemical, thermal, biological, or a combination of these methods as shown in Figure 1.3. These pretreatment techniques have been shown to reduce solid mass, rupture EPS complexes, and enhance CH₄ production during AD in a pilot laboratory experiment. The pretreatment is necessary to manage the usage of substrates in order to maximize the AD efficiency. It also enhances the amount of soluble substrate and the microbial decomposition, reduces the viscosity of SS and also the overall cost of sludge management.

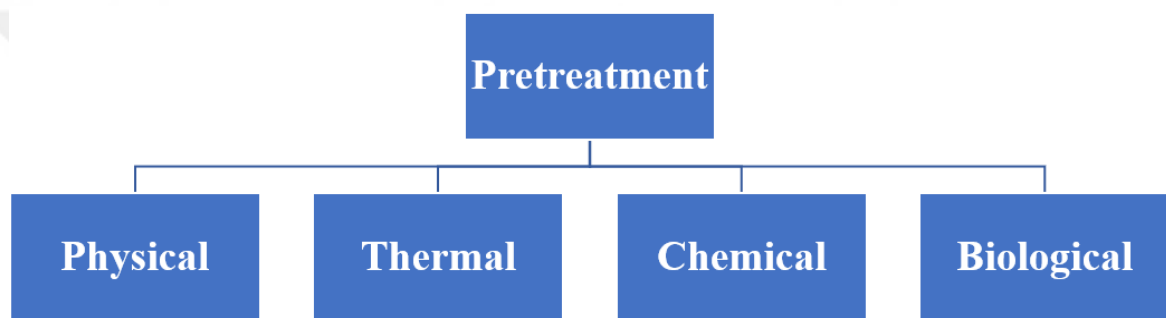


Figure 1.3 Biosludge pretreatment methods to improve AD process (Zhen et al., 2017).

1.7.2. Pretreatment methods

Various pretreatment methods such as ultrasonication (Braguglia et al., 2011), high pressure homogenous (HPH) (Nabi et al., 2019), chemical (Devlin et al., 2011), electro kinetics (Salerno et al., 2009), biological (Anjum et al., 2016), microwave (MW) irradiation (Ebenezer et al., 2015) have been applied for the WBS disintegration in order to improve the CH₄ yield in the AD process and the minimize the biosludge volume. Since the MW irradiation were applied in this PhD thesis, detailed information about MW was presented below and information on the other methods were given briefly.

A. Ultrasonication

The bacterial cell wall of biosludge can be successfully destroyed by ultrasonic pretreatment. Occurrence of high cell pressure in the organisms by the application of ultrasonication, which produce the free radicals like the hydroxyl radical ($\bullet\text{OH}$), hydrogen radical ($\bullet\text{H}$), nitrogen radical ($\bullet\text{N}$), oxygen radical ($\bullet\text{O}$), and also mechanical water shear,

which forces brought on by low-frequency ultrasonic cavitation, contributes to ultrasonication's effectiveness. The biosludge hydrolysis may be efficiently accelerated by ultrasound, also increase the reduction rate of VSs, and totally disintegrate biomass in 5–10 minutes. As a result, ultrasonic pretreatment can boost biogas output by 50% for according to the SSs (Nguyen et al., 2017; Tyagi et al., 2013). It was reported that the ultrasonication pretreatment enhanced the biogas generation by 40–58 %, solubilizes organic molecules, stimulated biological activity, and release of enzymes in the organisms were observed (Rincón et al., 2014). With the combined thermal and ultrasonic pretreatment, more efficient breakdown of soluble proteins, sugars, and other organics in the sludge was reported. Results indicated that the biogas production increase of about 19% and the rate of VSs removal increased to more than 50% with the hybrid thermal and ultrasonic pretreatment (Liu et al., 2021). The ideal ultrasonic intensity was found to be 1.5 W/mL and it was observed that the release of soluble chemical oxygen demand (sCOD) increased linearly when the energy doses was lower than 30,000 kJ/kg TS (Doğruel et al., 2017).

B. High pressure homogenous (HPH)

An application of rapid pressure gradient of up to 900 bar with a high-pressure homogenization (HPH) processing cause a cavitation, powerful shear forces, significant turbulence, and a subsequent pressure drop, resulting in the release of high sCOD concentrations from the organic wastes and hydrolysis of macromolecules (Nabi et al., 2019). A successful organic release from solids to liquid phase of biosludge after the HPH pretreatment was indicated by the degree of disintegration (DD) and the sCOD concentrations increase with the elevation the homogenous pressure and circulation. Additionally, $\text{NH}_4\text{-N}$ was also released along with VOCs. The average sludge volume decreases noticeably from 48.26 μm to the range of 9.375–15.54 μm as a result of the severe disruption of sludge flocs cause by the HPH pretreatment (Fang et al., 2015). However, the greatest degree of sludge disintegration of about 44% as the sCOD was reported at 80 MPa with four homogenization cycles for the biosludge containing 9.58 g TS/L (Zhang et al., 2012).

C. Chemical pretreatment

A chemical pretreatment with reagents like acids, alkalis, and oxidants stands out as a promising method for breaking down complex organic wastes, enhancing biogas production in the AD process by hydrolyzing (Nguyen et al., 2021). Alkaline compounds played a significant role in wastewater and biosludge treatment, enhancing the AD process with the disintegration and dissolution processes. The alkaline pretreatment caused an organic matter to bigger, increasing enzymatic accessibility and sludge biodegradability. Addition of NaOH between the concentrations of 5–21 g/L could increase the sCOD solubility of approximately 40% COD in biosludge (Jákóti et al., 2021).

Hydrogen peroxide (H_2O_2), an affordable and potent oxidizer and could be used combined (hybride) with Fenton/Fenton-like reactions or physical pretreatments such as MW irradiation for wastewater and sewage sludge removal (Jákóti et al., 2021).

D. Electro kinetics disintegration

The electrochemical pretreatment of biosludge, where cytoplasm breakdown, is classified based on the input voltage into micro-, low-, and high-voltage (kV), each leading to distinct electrochemical mechanisms (Zeng et al., 2022). Various oxidants like hypochlorous acid, hypochlorite (HOCl and OCl^-), hydroxyl radicals ($\bullet\text{OH}$), and H_2O_2 are generated in the process (Rahman et al., 2014). After the electro-pulse processing of WBS, it was observed that the exocellular polymers (ECP) and sCOD/total chemical oxygen demand (tCOD) ratio increased significantly by approximately 4.5 and 6.5 times, respectively. It was reported that the bioludge pretreated with pulse power produced 2.5 times more biogas in the batch AD process compared to untreated sludge (Choi et al., 2006).

E. Biological pretreatment

Absolutely, there are some effective biological pretreatment methods for organic compounds degradation and waste management. Enzymatic hydrolysis, aerobic and anaerobic digestion, fungal treatments, and bio-surfactants are indeed crucial techniques in breaking down complex organic compounds into simpler forms, aiding in subsequent processes or waste treatment (Nguyen et al., 2021). Enzymatic hydrolysis involves using

enzymes to breakdown complex molecules, like cell walls, into smaller units, thus accelerating the degradation of VSS and increasing the sCOD concentration (Anjum et al., 2015). Temperature phased anaerobic digestion (TPAD) is a notable approach that combines thermophilic and mesophilic anaerobic conditions to maximize the efficiency of organic matter breakdown. Starting with a thermophilic pretreatment unit before moving to mesophilic AD enhances the degradation of organic material (Zhen et al., 2017).

F. Thermal pretreatment

In the thermal pretreatment method, to provide hydrolysis of organics in order to improve their digestibility, the biosludge or other organic wastes are heated at high temperatures (Nguyen et al., 2021). Thermal pre-treatment causes the deterioration of the sludge gel structure and the release of organic matter into the sludge flocs. This method can be applied at both low ($<100^{\circ}\text{C}$) and high ($>100^{\circ}\text{C}$) temperatures (Sahinkaya and Sevimli, 2013). When the wastes have high concentration of proteins, carbohydrates, and lipids, the thermal pretreatment is most effective since it increases the rate of organic matter breakdown and biodegradation. TPAD, which involves acidogenesis at $40\text{--}75^{\circ}\text{C}$ and methanogenesis at $35\text{--}37^{\circ}\text{C}$, is a component of thermal pretreatment. Thermal pretreatment may range from $35\text{--}100^{\circ}\text{C}$ to $100\text{--}275^{\circ}\text{C}$ (Pilli et al., 2014). The type of substrate, temperature range, and reaction time affect the thermal pretreatment effectiveness. Lower treatment temperatures and longer reaction times could increase COD solubilization (Gahlot et al., 2022). Generally, it was observed that the longer treatment times at higher temperatures was better for the release of compounds (Appels et al., 2010). Compared to the pretreated sludge at 70°C , at which biogas production increased about 50% (Climent et al., 2007), a factor of 11 increase was determined in biogas output of pretreatment at 90°C for 60 min (Appels et al., 2010). Bougrier et al., (2008) reported that the solubility of COD increased for the all various sludge samples at the temperatures below 200°C , linearly with treatment temperature. Carbohydrate solubility was more important than protein solubility at temperatures below 150°C . It was also reported that heating the anaerobic sludge digestion process to 190°C increased biogas generation (Bougrier et al., 2008). On the other hand, Elliott and Mohammed, (2012) found that extreme temperatures ($>150^{\circ}\text{C}$) and longer duration time might cause

the formation of refractory compounds. The thermal pretreatment at low-temperature was a low-cost method for the biosludge hydrolysis, with mid thermal pretreatment (60–75 °C) for 3–15 h being the most advantageous. Low-temperature pretreatment (60–70 °C) might boost hydrolysis rates while decreasing dewaterability (Gahlot et al., 2022). Temperatures exceeding 100°C, on the other hand, would cause increased the cell disintegration and release of EPS content, affecting organic matter breakdown, biodegradation, and biogas production. However, CH₄ production might decrease due to unstable microbial populations, which result in large quantities of organic and acidic intermediates (Gahlot et al., 2022).

1.7.3. Microwave disintegration

MW irradiation is operating between 1 mm and 1 m, with corresponding frequencies of 300 MHz and 300 GHz (Aguilar-Reynosa et al., 2017). When high-frequency electromagnetic radiation interacts with dipole molecules, it either initiates rapid heating in the molecules or activates the dipoles in dispersion phase, which results in rapid heating and the destruction of the cell structure as well as the release of bound water (Rao et al., 2019). As can be seen from the Figure 1.4, the dipole tends to orient in the direction of external electric field E when a medium with permanent dipole such as water. Similar to how the ions experience fast translational motions, the dipoles can rotate with the alternating electric field E, such as MW irradiation. These translational or rotational motions within the polar medium result in "internal friction," which heats the medium (Palma et al., 2020). Although the energy consumption for sludge heating is generally very high, MW heating is more efficient than the conventional heating. Conventional heating involves both conductive and convective heat transfer phases, which leads to a slower heating rate (relative to MW) and uneven heating over the reactor wall surface, which may cause local overheating and collapse from unstable molecules as shown in Figure 1.5 (Hasham et al., 2021). During conventional heating due to the materials are heated from the outside to in, the heat loss cannot be avoided. In contrast, MW irradiation heat materials directly internally, minimizing heat loss through convection and conduction (Ahn et al., 2009). MW irradiation have energy-efficient internal heating that is quickly induced by dipole rotation and ionic conduction by directly delivering MW energy to the

molecules in the reaction mixture (Sweygers et al., 2022). Zaker et al., (2019) reported the distinction between irradiation and conventional heating in Table 1.4.

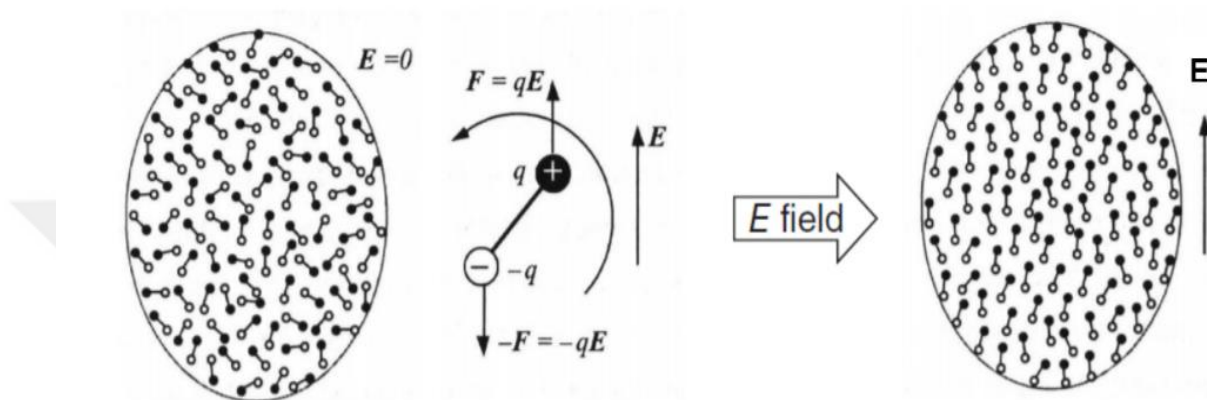


Figure 1.4 MW heating with translational or rotational motions (Palma et al., 2020).

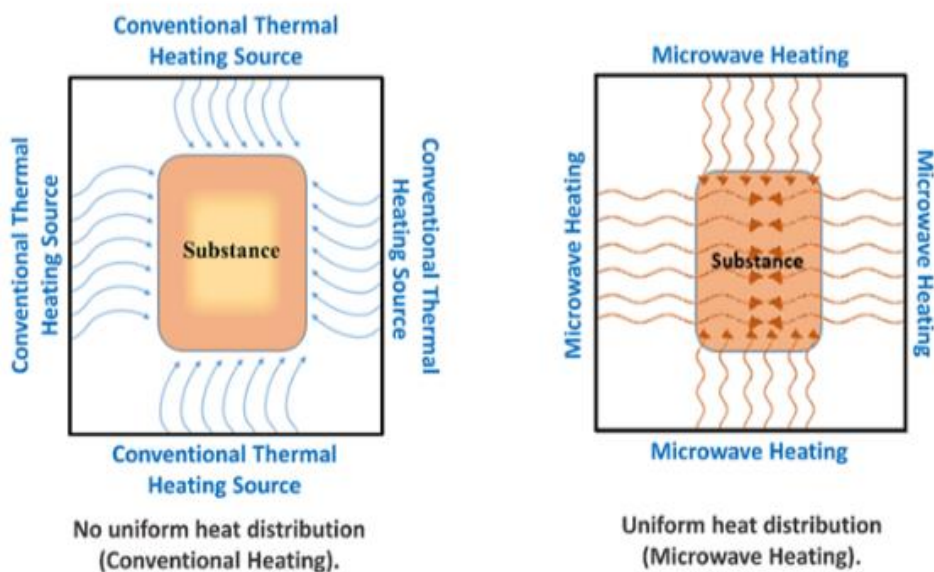


Figure 1.5 The MW and conventional furnace heating (Hasham et al., 2021)

Table 1.4 The heating condition difference between the MW and conventional in the disintegration of organic materials (Zaker et al., 2019).

Feature	MW heating	Conventional heating
Heating speed	Quick and consistent heating	Slow and irregular
Energy	Conversion of energy	Transfer of energy
Heating type	uniform heating at the molecular level with in-core volumetric heating	Surface heating via radiation, convection, and conduction
Hot spot	Hot spot: a result of a material's dielectric characteristics or the inhomogeneity of the microwave field	No hotspot
Heating time	< 1 second	Due to the material's thermal conductivity, it is slow and inefficient.
Electricity conversion	Higher electricity conversion	Low electricity conversion efficiency
Selective	swift and powerful heating for polar materials	Nonselective
Controlled heating	When the power is turned on or off, the power input starts and stops immediately	Less controllable
Contaminants	Low	High

The flocculent matrix of sludge is disintegrated by the MW through its unique thermal and athermal effects, which is thought to be an efficient way to increase sludge dewaterability (Zhang and Yao, 2022). With increasing the MW power and contact duration, the sludge disintegration efficiency measured in terms of disintegration degree (DD) become more efficient. The MW irradiation of biosludge increase in sCOD and VSS solubilization (Faruqi et al., 2021). The MW pretreatment enhances the AD process by breaking down the organic matters, result in the increase of cumulative volume of CH₄ at a high rate (Liu et al., 2020). Because the HRT can be shortened from 20 days to 10 or even 5 days in the AD process, where applied after the MW disintegration, the AD stabilization rate can be improved (Ahn et al., 2009). In the co-digestion of wastes, it was determined that the cumulative CH₄ production was higher than about 20% than the control (Liu et al., 2020). Table 1.5 shows some pretreatment technologies and their

impact on sludge decomposition and biogas production (Elalami et al., 2019; Zhen et al., 2017).

Table 1.5 Variations of CH₄ production of AD processes fed with biosludge disintegrated with different pretreatment methods and operational conditions (Elalami et al., 2019; Zhen et al., 2017).

Pretreatment and operational conditions	Type of sludge	Performance
Ultrasonic: 3,380 kJ/kg	Activated sludge	42% CH ₄ production
Ultrasonic: 20 kHz, 750 W, 5,742 kJ/kg TS	Secondary sludge	16.9% VS removal
Ultrasonic: 24 kHz, 300 W, ~5,000 kJ/kg	Activated sludge	+35% CH ₄ yield
Ultrasonic: 15 min in an ice bath, 20 kHz, 50 W (353 J/ gTS)	Sewage sludge	+34% of CH ₄ produced
MW: 2,450 MHz, 900W, 12 min, 1,814 kJ/L	Dairy activated	+57% biogas production, +64% VS removal
MW: 2.45 GHz, 800 W, 1 min, 96 kJ/kg TS	Thickened sludge	+ 20%biogas production
MW: 800 W, 3.5 min, 336 kJ/kg TS	Activated sludge	+50% biogas production, +66.6% dry solid removal
MW: 1,250 W, 2,450 MHz, 100% intensity	Thickened sludge	+106% biogas production
MW: 20,000 J/g TS for 63s	Sewage sludge	+20% CH ₄ production
MW:2.45 GHz, 120 °C for 2 h	Thickened activated sludge	+14% of biogas produced
Electrokinetic disintegration: 10 kWh/m ³	Activated sludge	+100% CH ₄ production
Electrokinetic disintegration :19 kV, 110 Hz, 1.5 s	Activated sludge	+2.5 times higher biogas production
Electrokinetic disintegration : ~34 kWh/m ³	Activated sludge	+33% CH ₄ production, +18% tCOD removal
Chemical: 8.75 mL HCl/kg wet sludge, pH: 2	Activated sludge	+14.3% CH ₄ yield
Chemical : 170 °C, pH 5–6 (H ₂ SO ₄), 1 h	Anaerobically digested sludge	+2–2.5 times VSS removal +14–21% CH ₄ production
Chemical: 0.1 mol NaOH/L	Sewage sludge	+1.5% biogas yield
Chemical: 8 g NaOH/m ³ wet sludge (pH: 8)	Activated sludge	+9.7% TS removal +11.5% VS removal
Chemical: 0.1 g O ₃ /g	Sewage sludge	84.22–78.24 mL/d for biogas COD Oxidization of organics: 38%
Chemical: 50 mg H ₂ O ₂ /g TS, 7 mg Fe/g TS in sludge, pH 2.0	Secondary sludge	+1.8 times CH ₄ yield +10% CH ₄ production +13% CH ₄ potential
Biological : Anaerobic treatment at 55 °C for 12–24 h	Secondary sludge	CH ₄ productivity was improved by 23%

2. PRETREATMENT OF WBS WITH MW

Water evaporation during dehydration by MW significantly impacts properties of WBS such as compaction/deposition ratio, resistivity, and capillary suction time may irreversibly deteriorate after a specific turning point, where depends on the irradiation intensity and duration (Vialkova et al., 2021). The MW pretreatment has shown promise in enhancing CH₄ production in the AD process and eliminating coliforms in municipal sludge.

In addition to disrupt the flocs and release bound organic matter into solution, MW pretreatment can also break down EPS-shielded microfloc assemblies' cell walls, releasing intracellular organic matter via two different pathways thermal and athermal. The impacts of heat include breakdown of organic matter, including the denaturation of membrane proteins, the release of intracellular organelles, and exceeding the boiling point of intracellular fluid (potentially leading to cell wall breakdown). Athermal effects are created by polar and polarizable molecules or polarized side chains of macromolecules quickly oscillating and striving to adapt to the incoming electromagnetic waves, also known as the non-thermal MW effect or particular effects of electromagnetic radiation (Bozkurt and Apul, 2020). Thermal effects are produced by dipole rotation (at higher frequencies) and ionic conduction (at lower frequencies). The former is the result of electrophoretic (conductive) migration of dissolved ions in the electromagnetic field, while the latter is produced by the rotation of dipole molecules (such as water) as a result of the field's polarity changing repeatedly (Jákói et al., 2021). The characteristics of MW irradiation significantly affect dielectric properties, leading to effective cell disintegration in waste treatment processes. Key parameters include target temperature (°C), irradiation period (min), and input power or specific energy (Watt or kJ/kg TS) effect the biosludge disintegration (Kavitha et al., 2016).

The target temperature of MW is very important on the conversion of organic compounds. Chan et al. (2007) reported that within the temperature range of 80–120°C, the organics became soluble, while the concentrations of dissolved organic decreased when the temperatures exceeding 120°C, due to the conversion of some organic matter to CO₂. However, at very high temperatures, the efficiency of MW might decrease, due to water

evaporation in the biosludge, resulting in increased material viscosity (Chan et al., 2007). For effective breakdown of the biosludge economically, balancing energy between the input–output and reaction temperature was crucial (Vialkova et al., 2021). In optimizing the dissolution rate of biosludge, it is possible to regulate the temperature ramping rate (increase the heating time by decreasing the heating rate) to reach the target temperature. Compared to rates of 6°C/min and 11°C/min, it was observed that at the ramp heating rate not exceeding 3°C/min, the soluble of sCOD, sugar, and protein were 17%, 9%, and 26% higher, respectively (Koupaie and Eskicioğlu, 2016)

Also, Kor–Bicakci et al., (2019) emphasizes the positive effect on the sludge dissolution, biogas production, and organic matter biodegradation rates, all related to longer heating time at the ramping rate not exceeding 2.5°C/min (Kor–Bicakci et al., 2019). Toreci et al., (2010) and Park et al., (2009) supported also Koupaie and Eskicioğlu's (2016) findings, indicating the biosludge dissolution and increased sCOD, sugars, and proteins released at ramping rates ranging from 2.9°C/min to 3.7°C/min. Appels et al. (2010) found that the concentrations 400 mg sCOD/L, 136 mg sugar /L, and 125 mg protein/L for raw sludge at the conditions of 90°C and 15 min of MW irradiation, while increase to 1,600 mg sCOD/L, 165 mg sugar/L, and 748 mg protein/L for pretreated sludge.

The energy input of MW significantly affect the release of organic molecules and breakdown of sludge. Serrano et al., (2016) found that for the difference in sCOD concentrations before and after pretreatment, 700 W of input power was more effective than 400 W. While, compared to the MW power of 400 W, there was a substantial increase of 215% at 700 W, it was observed the variations of sCOD was relatively low about 25–30% for a power input of 20,000 J/g TS and 30,000 J/g TS, respectively. Kuglarz et al., (2013) observed a noticeable enhancement in sCOD and protein release at 900 W compared to 700 W of power input. Yang et al., (2013) reported protein concentration increased from about 1,255 to 2,015 mg/L by the increase in specific energy from 9,600 to 38,400 kJ/kg TS. Similarly, carbohydrate content increased from about 294 to 635 mg/L.

2.1. MW energy consumption

Absolutely, energy input and output are critical considerations when it comes to energy generation from CH₄ or any other source. The efficiency of energy conversion processes

are influenced by various factors, such as the type of equipment used, composition of the being processed materials (like sludge composition in the case of CH₄ generation), operating conditions, and environmental factors all impact the overall efficiency of energy production (Carrère et al., 2010).

Efforts to maximize the energy output in relation to the input are fundamental not only for the economic viability of energy generation but also for minimizing the environmental impact. Improving technology, optimizing operating conditions, and using equipment that is more efficient are ways to enhance energy output relative to input, which contributes to a more sustainable and economically feasible energy generation process (Carrère et al., 2010). There are two ways to express the results: either as the ratio of energy between output energy (E_o) and energy input (E_i), (E_o/E_i) or as the energy balance between E_o and E_i ($E_o - E_i$). Thus, net energy production is indicated by a positive energy balance or an energy ratio higher than 1.0 (Passos et al., 2014). When considering furnace power, disintegration volume, disintegration time, moisture content, and the power consumption parameter can be used to compare MW results simultaneously under various operating conditions. Passos et al., (2014) reported the energy output from the production of biogas was about 7.8 times higher than the energy input for the MW pretreatment of centrifuged biosludge, while the E_o/E_i ratio was lower than 1.0 for the MW pretreated biosludge contained 200 mg VS/L.

The charged materials are affected by the magnetic field, whereas the polar materials by electric field. The medium's particles can interact with the MW electromagnetic field to directly transform electromagnetic energy into the thermal energy. The MW heating is the result of insulating medium exposed to an electromagnetic field absorbing MW energy. The average rate at which the temperature rises as a result of MW energy absorption is found using Equation (1.7) (Lee et al., 2020).

MW pretreatment indeed relies on the interaction between high-frequency electromagnetic radiation and the dipole molecules of organic materials. This interaction causes molecular rotation and generates heat within the material, resulting in rapid heating. As the temperature increases, so does the energy consumption by the MW. This relationship between temperature and energy consumption is depicted in Figure 2.1 (Al

Ramahi, 2020). The ability of material to absorb MW energy and transform it into the thermal energy is known as dielectric loss. As a result, the temperature rises more quickly in the early stages because the sludge absorbs more MW energy. On the other hand, the effects on dielectric loss also increase with the sludge temperature. After being exposed to MW heating continuously, high temperature causes the expand of biosludge volume and its density to decrease, which further reduces the material's heat capacity. Therefore, the bulk density of sludge (ρ_0) and the material's heat capacity (C_p) vary according to the MW energy and irradiation time (Lee et al., 2020).

$$P_{abs} = \frac{\Delta T \rho C_p}{\Delta t} = 2\pi\beta\epsilon_0\epsilon''e_{\beta\beta}E^2 \quad [1.7]$$

where P_{abs} is the conversion of power in volume unit (W/m^3), β is the frequency of the irradiation (Hz), free space permittivity is represented by ϵ_0 (8.854×10^{-12} F/m), the complex part of dielectric's relative permittivity is represented by $\epsilon''e_{\beta\beta}$, whereas ρ is the material's density (kg/m^3), C_p is the material's specific heat ($J/kg.^{\circ}C$), E stands for electric field in (V/M), Δt for time interval (seconds), and ΔT for material temperature rise ($^{\circ}C$).

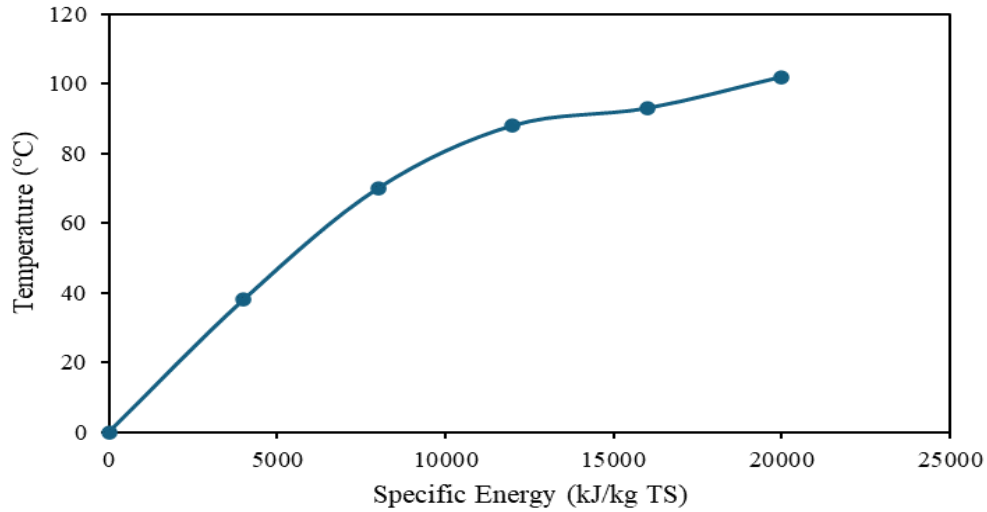


Figure 2.1 Correlation between higher temperatures and specific energy (Al Ramahi et al., 2020).

2.2. Effect of MW pretreatment on biogas production in the AD process

In the AD process, the application of MW technology has shown notable improvements in AD performance and CH_4 production compared to the untreated samples. Alagöz et

al., (2018) demonstrated that biogas and CH₄ yields were 20–30% higher than controls in the both batch and continuous flow AD process fed with the MW pretreated biosludges at boiling temperatures. Hong (2002) found that high pretreatment temperatures, specifically at 100°C, increased CH₄ production by 23% for the primary sludge (PS) and 15% for activated sludge. Eskicioglu et al., (2007a and b), investigated the impacts of MW density, temperature, and biosludge concentration on the WBS dissolution. Concluded that the pretreatment temperature and biosludge concentration significantly affected WBS dissolution and subsequent biogas production, while the MW density did not play a significant role in influencing the digestion process. Toreci et al. (2009) found that the biogas yield in AD process fed with the biosludge pretreated at the MW temperature of 96°C was higher than the biosludge exposed to lower temperatures of 75°C and 50°C. However, the percentage increase over milder thermal pretreatment was not substantial, while the CH₄ production increased notably within the range of 120°C to 180°C was observed. This led to a hypothesis that most easily biodegradable solids had already been broken down, or certain compounds might have formed during higher temperature pretreatment, inhibiting digestion processes. In the study noted a significant drop in CH₄ production when the temperature was higher than 180°C. The decline of biogas yield was attributed to a Maillard reaction occurring between aminoacids and low molecular weight sugars in the biosludge at higher temperatures, defined as the formation of end products that were difficult to degrade and hinder AD process (Toreci et al., 2009).

The MW pretreatment process provides better stability with shorter hydraulic retention time (HRT) in the AD reactor. When the biosludge was pretreated with MW at 91.2°C target temperature and 7 min of irradiation time, considering the VS reduction efficiency, the time to achieve steady state and the rate of gas production at steady state with the pretreated sludge were roughly twice faster and 20% greater than in the control reactor (Park et al., 2004). It was observed that the biogas production improved by 79% in the AD reactor treating MW–pretreated biosludge, compared to the control, while the sCOD and VS decreased by 64% and 27%, respectively (Park et al., 2004). Furthermore, when comparing MW–digested biosludge to control and conventionally heated digested sludge, the biogas production in the AD unit was 68% higher at 5 days of sludge retention time (SRT) (Koupaie and Eskicioglu , 2015).

Koupaie and Eskicioglu, (2015) determined as the optimal conditions at the pretreatment temperature of 80°C and a heating rate of 3°C/min and the highest biogas yield of 24.7% improvement over the control in both biogas and CH₄ yields. Conversely, the lowest biogas production was determined at an extreme pretreatment conditions of 160°C with heating rate of 11°C/min. These findings showed that operation of MW at above a certain temperature threshold, the organic components in the medium change, leading to the limitation of use of anaerobic organisms even in the case of acclimated in AD reactor (Koupaie and Eskicioglu , 2015).

In conclusion, employing MW irradiation for the biosludge disintegration prior to the AD process offers several advantages, such as improved dewaterability of the digestate, reduced SRT, increased biogas production, and enhanced solids destruction. However, before considering AD testing, MW operational conditions must be optimized considering power input and output. It is essential to understand the diversity and composition of the resident bacterial communities involved in the AD process. This knowledge helps provide biokinetic parameters for the design and optimization of digestive units (Zhen et al., 2017).

2.3. Nutrient release after pretreatment

After the AD process significant concentrations of macro and microelements release was observed because of the biosolids degradation. The process regarding the treatment of AD supernatant highlights the challenges and opportunities in wastewater treatment. After the AD of WBS, produced supernatant contains high concentrations of NH₄-N and PO₄-P, which pose both environmental and operational concerns. The return of supernatant to the beginning of WWTP necessitates additional treatment steps to manage the increased ammonia content. Returning the supernatant increase the pollutant loads on treatment plant and subsequently also the operational costs.

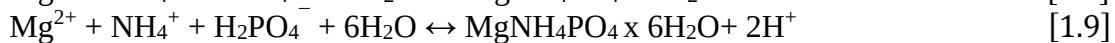
Nutrients can be recovered by applying chemical precipitation and adsorption, and more advanced methods such as bioelectrochemical systems, osmotic membrane bioreactors etc. (Ye et al., 2020). The recovery of NH₄-N and PO₄-P as a struvite crystallization precipitation/magnesium ammonium phosphate hexahydrate (MAP) offers a solution to cope with the wastewater treatment challenges. Anaerobic digestate produces struvite, a slow-release fertilizer rich in magnesium, phosphorus, and nitrogen, which is a successful

method for recycling nutrients back into nature (Palominos et al., 2021). Efforts to develop and optimize these treatment processes, like struvite crystallization, are crucial for sustainable wastewater management, minimizing environmental impacts, and potentially reducing operational costs in the long run.

2.3.1. Struvite precipitation

Monovalent or divalent ions such as lead (Pb^{2+}), manganese (Mn^{2+}), magnesium (Mg^{2+}), ammonia (NH_4^+), potassium (K^+), sodium (Na^+), copper (Cu^+), and nickel (Ni^+) are found in struvite type crystals. The most prevalent and stable form of magnesium ammonium phosphate, or $MgNH_4PO_4 \cdot 6H_2O$, is known by its white orthorhombic crystalline prismatic structure (Siciliano et al., 2020). Phosphorus content of 13% in struvite makes it a valuable phosphorus fertilizer and its 6% N and 10% Mg contents also contribute to its effectiveness by supporting plant growth. Struvite is slightly soluble in neutral and alkaline environments, but it is easily soluble in acidic medium (Rahman et al., 2014). Since it doesn't easily soluble with rain, it can be effectively applied as fertilizer in flooded areas. Except from large single crystals, very small crystals, curds, and gelatinous masses, pure struvite is a white crystalline powder (Siciliano et al., 2020; Rahman et al., 2014).

The constituents of wastewater as well as the process parameters affect the production of struvite. Furthermore, the pH of wastewater should be adjust to about 9–10 for improving the precipitate quality (Gherghel et al., 2019). Because of the formation of NH_3 and $Mg(OH)_2$, the deterioration of struvite formation was observed when the pH was higher than 11.0 (Gherghel et al., 2019; Rahman et al., 2014). The struvite precipitation decrease the pH of solution, because of the soluble PO_4 -P crystallizes, which indicates that HPO_4^{2-} or $H_2PO_4^-$ rather than PO_4^{3-} is the dominant form of P in the struvite formation reaction as shown in Equations 1.8 and 1.9 (Darwish et al., 2016).



When the amounts of Mg^{2+} , NH_4^+ , and PO_4^{3-} in the liquid surpass the dissolution concentrations, the struvite is formed. A wide pH range between 7.0–11.5 could result in the precipitation of struvite, but it was reported that 7.5–9.5 was the ideal range (Rahman et al., 2014). The struvite formation is depend on several factors, including pH, aeration

rate, temperature, the presence of Ca^{2+} in the reacting medium, and the concentration and molar ratios of Mg^{2+} , NH_4^+ , and PO_4^{3-} (Siciliano et al., 2020).

For the struvite formation, applying of a molar ratio of N:P:Mg as 1:1:1 was widely determined in the literature by adjusting the concentrations of NH_4^+ , PO_4^{3-} , and Mg^{2+} ions (Rahman et al., 2014; Tansel et al., 2018; Wu et al., 2022). Overdosing of reagents might be necessary due to competitive ions, which can react with PO_4^{3-} , and Mg^{2+} ions, present in the wastewaters (Biswal et al., 2020). Depends on the operational conditions and wastewater characteristics, different molar ratios were determined for the effective recover of $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$ by struvite precipitation. In wastewaters where sufficient molar ratio cannot be provided, the precipitation can be increased by adding externally P and Mg sources into the solution. In this way, more than 90% of $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$ recovery from wastewater is possible by encouraging the formation of insoluble MAP compounds or hydroxides (Ander, 2010; Lavanya et al., 2021; Muhmood et al., 2018; Öztürk and Bali, 2023; Tonetti et al., 2016).

3. OBJECTIVE AND SCOPE

Processing of WBS accounts for approximately 60% of the total cost of WWTP. Additionally, as a result of stringent legal regulations regarding its disposal, the WBS is considered as a very important environmental problem.

The AD is a biological process that converts organic wastes (biosludge, animal manure, organic-containing domestic garbage) into CH_4 -rich biogas, a renewable energy source for heating and electricity. The AD process ensures the reduction of pathogens and odor in organic waste and also reduces the negative impact on climate change through a decrease in greenhouse gas emissions resulting from anthropogenic waste.

Considering its stabilization and energy recovery potential, the AD is considered a suitable option for sustainable WBS management. The effectiveness of AD process can be improved by limiting the hydrolysis step as a result of breaking the chemical bonds of hydrolyzable compounds with the pretreatment before the AD process.

Phosphorus is a basic component for agricultural fertilizers and recovering from the wastes is important, due to it is a non-renewable resource. Significant amount of $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$ released by the breakdown and dissolution of WBS in the AD reactor can be obtained as potentially usable compounds in direct soil application or in the production of plant fertilizers such as struvite.

This study aimed to determine the optimal MW operational conditions, such as target temperature, ramping rate, holding time, and power, in order to achieve the breakdown of biosludge, considering the release of sCOD, $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$ from the WBS. The optimal MW operational conditions under the experiments were determined not only considering the released compounds from the biosludge but also MW energy. Considering previous studies, the target temperatures of 90°C and 110°C was defined and the MW was operated at the power of 900 W and 1,800W.

After determining the optimal MW operational conditions, the BMP tests were performed to determine the difference between the volumes of CH_4 produced by AD of raw WBS and disintegrated biosludge. Additionally, in order to evaluate the effect of VS concentrations on the MW energy input and CH_4 production in the AD process, BMP tests

were carried out with biosludge with VS concentration increased by centrifugation of WBS.

Chemical composition of wastewaters and WBS structures after MW disintegration and AD process were tested for evaluating the reusability and disposing methods. The struvite precipitation experiments were conducted to the wastewaters contains high concentrations of $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$ obtained from the BMP test to recovery of nutrients.

By optimizing MW operating conditions for treating and disposing of WBS, this study was not only goal to the environmental concerns related to effective waste management but also sustainable development. This study is consistent to evaluate the potential of waste materials rich in organic matter and nutrients and also the broader goal of sustainable resource management and circular economy principles. The schematic diagram of experimental studies is presented Figure 3.1.

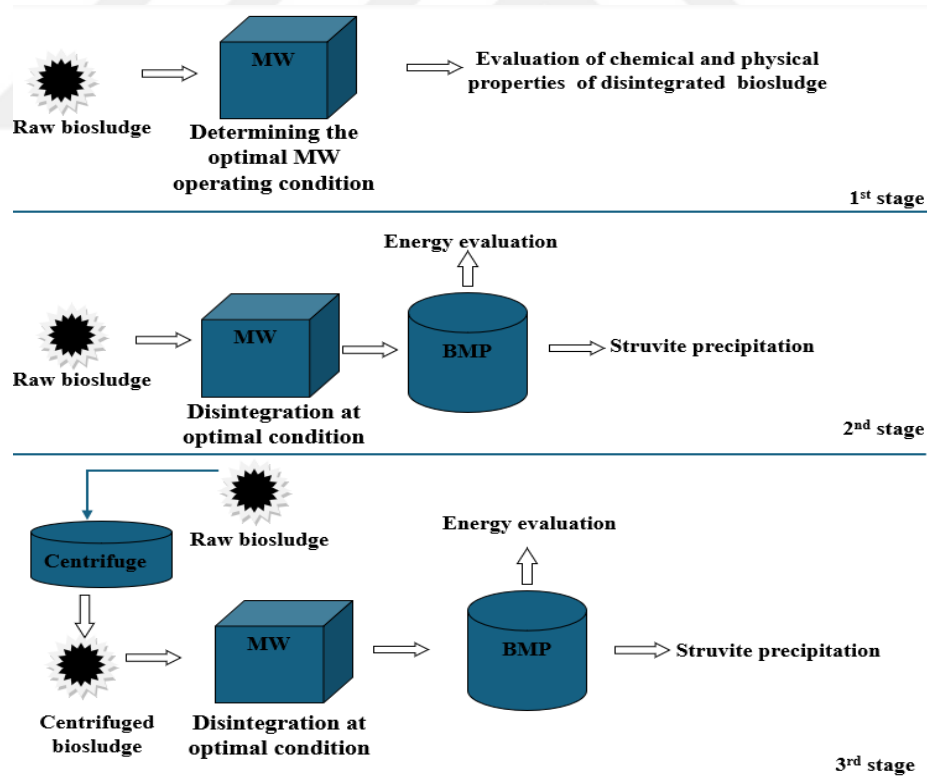


Figure 3.1 Experimental steps carried out within the scope of study

4. MATERIALS AND METHODS

Experimental study was carried out in three phases.

1st Step: To determine the optimal MW operational conditions (power, target temperature, ramping rate, holding time) for the WBS disintegration by considering the sCOD and the DD. The target temperatures were selected 90°C and 110°C. The appropriate target temperature was determined based on the highest sCOD release and DD, and the lowest energy consumed.

2nd Step: Experiments were carried out at the temperature of 90°C, determined as an optimal condition in the first step, followed by the CH₄ production, energy analysis, and struvite precipitation.

3rd Step: To determine the effect of WBS contained high amount of TS on energy consumption and CH₄ production at the temperature of 90°C.

4.1. WBS samples

The WBS used in the study were taken from the recycling line of the WWTP in Sivas/Türkiye. The WWTP is an extended aeration activated sludge system designed for carbon, nitrogen and phosphorus removal with a population of 345,000 equivalent and a capacity of 78,516 m³/day. The WBS were immediately transferred to the laboratory (Environmental Engineering Laboratory/Sivas Cumhuriyet University) and experimental studies were carried out in the MW in the same day to avoid fermentation or other microbial activities (Yu et al., 2010). Throughout the experimental study, after disintegration in the MW, the samples, which centrifuged or filtered, were stored in a refrigerator at +4°C.

4.2. Operational conditions of MW

Irradiation was carried out by using a MW device (MA179-001; MAXI-44; Milestone) with a maximum temperature of 200°C, power of 1,800 W, pressure of 35 bar and frequency of 2450 MHz (Figure 4.1). MW device has 44 Teflon vessels with a capacity of 100 mL. The temperature in vessels was recorded by infrared imaging of the samples on a digital display every 15 s.

MW pretreatment consists of three stages as follows: (1) ramp heating rate ($^{\circ}\text{C}/\text{min}$) from room temperature ($25 \pm 5^{\circ}\text{C}$) until the target temperature is reached, (2) holding time at the target temperature (3), and (4) cooling time in order to allow vessels to be opened safely.

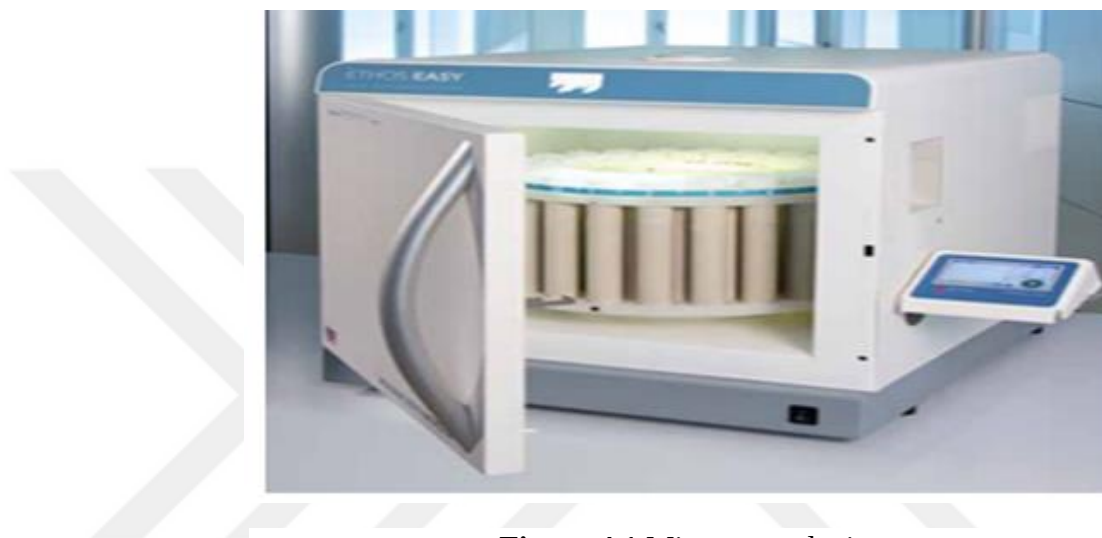


Figure 4.1 Microwave device

4.3. Preparation and enrichment of inoculum

In order to enrich the anaerobic organisms for the Biochemical Methane Potential (BMP) tests, bacteria was growth in a 5L batch reactor in a suspended growth condition at $35 \pm 2^{\circ}\text{C}$, with a magnetic stirrer and with a pH of 7.5 ± 0.5 . In order to provide anaerobic conditions, possible O_2 in the reactor mixed liquor, was washed with N_2 gas for 5 min (Azbar et al., 2009) or Na_2SO_3 was added until the dissolved O_2 concentration was lower than 0.5 mg/L (Huynh et al., 2019). The batch reactor was operated for 6 months with daily WBS additions in order to fed bacteria at the SRT of 40 days by drawing appropriate volume mixed liquor. The sample was drawn from the batch reactor for the soluble sCOD, $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$ analysis in daily in order to follow the bioreaction and also the pH and O_2 concentration in the unit were measured.

4.4. Biochemical methane potential (BMP) tests

The BMP tests were carried out by the use of MW disintegrated and raw WBS (control), which were mixed with the inoculum. The ratio of WBS/inoculum were applied to each reactor in specific proportions, as shown in Table 4.1. 500 mL bottles of serum were used as the anaerobic reactors. To create anaerobic conditions, the reactors were closed with silicone caps and N₂ gas was passed through the units for 3 min. The BMP units were kept in a shaker water bath (Julabo SW23) at a mesophilic temperature of 37°C and mixed continuously at 160 rpm to ensure proper distribution of substrates and organisms. The BMP tests were performed until the cumulative curve almost reached a plateau, i.e., the time at which daily CH₄ production was about zero.

Table 4.1 Mixing ratios of BMP tests.

2nd step	
WBS/inoculum ratio (1/1)	
Substrate (mL)	Inoculum (mL)
150	150
3rd step	
WBS/inoculum ratio (1/1)	
Substrate (mL)	Inoculum (mL)
100	100

CH₄ measurements were carried out daily according to the liquid displacement method by passing the biogas (CO₂ + CH₄) coming out of the unit through a solution containing 3% NaOH. The solution of NaOH is absorbed CO₂ in the biogas and converted to carbonate and CH₄ is passed from the NaOH solution (Figure 4.2) (Esposito, 2012).

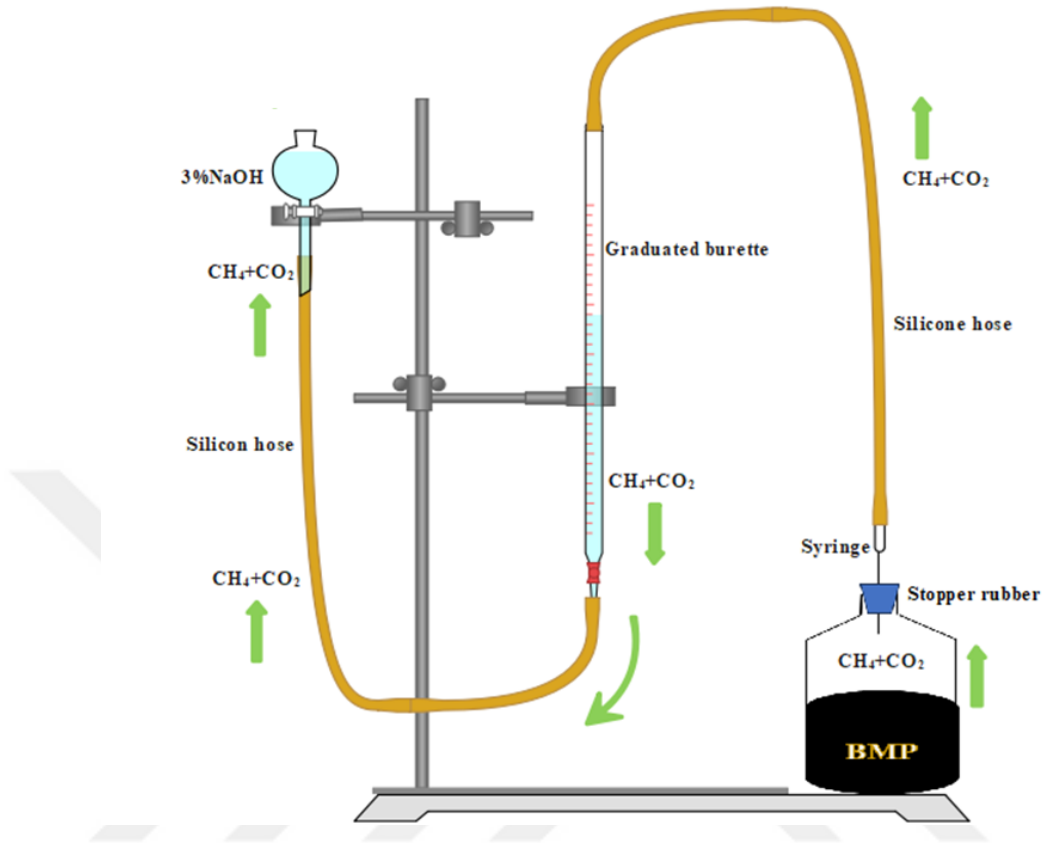
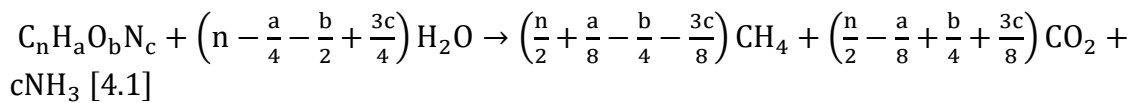


Figure 4.2 Schematic diagram for the BMP tests

4.4.1. Calculation of theoretical biochemical methane potential and biodegradation

In defining the theoretical biochemical methane potential (tBMP), the atomic structure of the biomass (O, H, N, C, S), which was based on the stoichiometric equation, was determined and calculated according to Equations (4.1 and 4.2)



$$tBMP \left(mL \frac{CH_4}{gvs} \right) = \frac{22,4(n/2 + a/8 - b/4 - 3c/8) \times 10^3}{12n + a + 16b + 14c} \quad [4.2]$$

Biodegradation was calculated using the Buswell Equation (4.3) according to (Steffen et al., 2017)

$$\text{Biodegradability (\%)} = \frac{\text{cumulative CH}_4 \text{ (mL/gvs)}}{\text{Theoretical CH}_4 \text{ (mL/gvs)}} \times 100 \quad [4.3]$$

4.5. Energy assessment

In order to evaluate energy efficiency of the MW disintegration on total energy, which was calculated considering the input energy in the MW operation and CH₄ production in the AD process, the change in CH₄ production by disintegrated and raw WBS in the BMP tests were calculated. The energy input for MW pretreatment was calculated in accordance with irradiation duration, power, and TS or VS, as indicated in Equation (4.4) (Passos et al., 2014) and (4.5) (Gómez–Sanabria et al., 2018; Kavitha et al., 2016) .

$$E_i = \frac{P \times t}{S \times V} \quad [4.4]$$

$$E_o = \Delta \text{CH}_4 \times \xi \times \eta \quad [4.5]$$

E_i : energy input (kJ/g_{vss}); P : power (kW); t : heating time (hours); V : sample volume (L); S : TS/VS concentration of raw WBS (g/L); E_o : energy output (kJ/g_{vss}); ΔYCH_4 : difference between disintegrated and raw WBS CH₄ yield (m³ CH₄/g_{vss}); ξ : the CH₄ sub–heating value (35,800 kJ/m³ CH₄) and the energy conversion efficiency is taken as 90% (η).

Equation (4.6) was also used to compute the energy produced by AD's major product, CH₄ (Pasarari et al., 2021).

$$E_m = \frac{C\text{CH}_4 \times \xi \times \eta}{\text{VS}_{\text{rem}}} \quad [4.6]$$

Where, E_m is energy of CH₄ output (kJ/g VS removed), $C\text{CH}_4$ refers to cumulative CH₄ production in incubation period (mL), and VS_{rem} is g VS removed in incubation of digestion.

4.6. Struvite precipitation

For the struvite precipitation, the sludge/liquid samples from BMP unit was centrifuged and the supernatant was collected in tubes by solid–liquid phase separation. Measurements of pH, electrical conductivity (EC), NH₄–N, PO₄–P, and Mg²⁺ in the supernatant were performed. According to the characteristics of decant, the elements not sufficient for the struvite precipitation were identified and if necessary, according to the

missing element, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ was added as a source of Mg^{2+} and $\text{PO}_4\text{-P}$, respectively. The struvite precipitation experiments were carried out for different molar ratios of Mg:N:P by adding Mg^{2+} and $\text{PO}_4\text{-P}$ at a room temperature (between 20 and 25 °C) and a pH range of 9.5 to 10.0 with a 25 mL sample.

1M of NaOH was used to adjust the pH. After mixing for 1 h at 120 rpm with a magnetic stirrer, the mixture was centrifuged for 10 min at 4100 rpm to draw the settled part at the bottom. The remaining concentrations of $\text{PO}_4\text{-P}$, and $\text{NH}_4\text{-N}$ in the upper liquid were measured to evaluate the precipitation efficiency.

4.7. Kinetic and statistics studies

4.7.1. Kinetic studies

Four kinetic models, which were Gompertz Modified, First-order kinetic, Logistic, and Transference Function, were used in an in-depth analysis of CH_4 produced from WBS disintegrated at various temperatures and raw WBS. The equations of kinetics are presented in Table 4.2 (Li et al., 2012; Yuan et al., 2016). Through these above models, the cumulative CH_4 production at time (A , mL CH_4/gVSS), CH_4 potential yield (A_0 , mL CH_4/gVSS), the maximum CH_4 production rate (μ_m , mL $\text{CH}_4/\text{g VSS.day}$), the duration of the late stage (λ , day) and the hydraulysis rate (k , day^{-1}) were determined. Nonlinear analysis of these models was performed using SPSS version 26.

Table 4.2 Kinetic model equations

Models	formula	
First order kinetic	$A = A_0 \times (1 - \exp(-kt))$	[4.7]
Gompertz modified	$A = A_0 \times \exp \left\{ -\exp \left[\frac{\mu_m \times e}{A_0} \times (\lambda - t) + 1 \right] \right\}$	[4.8]
Logistic	$A = \frac{A_0}{1 + \exp \left\{ 4 \times \mu_m \times \frac{\lambda - t}{A_0} + 2 \right\}}$	[4.9]
Transference Function	$A = A_0 \times \{1 - \exp[-\mu_m \times (t - \lambda)/A_0]\}$	[4.10]

4.7.2. Statistics studies

In order to determine optimal conditions, the Response Surface Methodology (RSM) was used to investigate the impact of temperature and heating rate on the release of sCOD, DD, and specific energy consumption.

4.8. Analytical method

All the measurements were carried out in the clear samples which were centrifuged and then the supernatant was filtered through 110 mm rapid filter paper. For the analysis of sugars and proteins, the sample supernatant was filtered through 0.45µm filter paper. The sCOD was analyzed with the dichromate closed reflux titrimetric method and alkalinity, Ca^{2+} , Mg^{2+} , total solid (TS), suspended solid (SS), volatile solid (VS), volatile suspended solid (VSS) and etc. were carried out according to APHA (1998). $\text{NH}_4\text{-N}$ (Merck, 14752), $\text{PO}_4\text{-P}$ (Merck, 114848), Protein test (Merck, 1103070500) and sugar measured with the MERCK PHARO 100 instrument. The pHs and EC of samples were measured with Hanna pH and EC meter.

Fourier Transform Infrared (FTIR), scanning electron microscopy (SEM), energy-dispersive X-ray analysis (EDX), particle size distribution (PSD), specific surface area (SSA), and heavy metals analyses were performed at the Advanced Technology Research and Applications Center at Sivas Cumhuriyet University, and XRD analyzes were performed at the Technology Research and Applications Center at Recep Tayyip Erdoğan University, and the elemental analysis (O, H, N, C, S) of the WBS was carried out in the Scientific and Technological Research Center of Inonu University.

Experimental studies that MW disintegration and BMP performed at various operational conditions and sample analyses were carried out at least three times and average values were presented in figures and tables.

4.8.1. Procedure of protein and sugar tests

The protein concentration was measured by the Bromet method in which bovine serum albumin (BSA) was used to prepare the standard solutions for drawing the calibration curve.

Protein analyzes were performed with a spectrophotometer at a wavelength of 546 nm. Sugar was analyzed using the anthrone method (Ludwig and Goldberg, 1956). In this method, sugars are dehydrated by H₂SO₄ to form furfural. The active form of the reagent is anthranol, an enol tautomer of anthrone, which reacts by condensation with the carbohydrate derivative furfural to give a dilute green–blue color in concentrated solutions, which is determined by the colorimetric method. In the analysis of sugar, 1 mL of the sample is placed in each tube, 5 mL of anthrone reagent is added to it, mixed well by vortex, cooled to room temperature, and the optical density is measured at 620 nm with a spectrophotometer. The unknown sample concentration is found by using the previously prepared glucose curve.

4.8.2. Disintegration degree

The effectiveness of disintegration can be defined with the “degree of disintegration, (DD) as the main parameter. High DD values mean a high degree of disintegration and is calculated according to Equation 4.11 (Jin et al., 2016).

$$DD = \frac{SCOD_{mw} - SCOD_{raw}}{SCOD_{NaOH} - SCOD_{raw}} \times 100 \quad [4.11]$$

Where; sCOD_{MW} is sCOD concentration of WBS’s supernatant after MW disintegration; sCOD_{raw} is sCOD concentration of WBS’s supernatant before disintegration (raw WBS); sCOD_{NaOH} is sCOD concentration of WBS’s supernatant after NaOH disintegration.

4.8.3. Specific filter resistance

To ascertain the biosludge performance in mechanical dewatering procedures, the specific filter resistance (SFR) parameter was computed. An experimental setup with a Buchner funnel was used to determine the SFR test. 100 mL of the biosludge sample are transferred into the Buchner funnel in the SFR experiment after the filter paper has been moistened with clean water. Gravity drainage takes two min, at which point the two–bar vacuum pump is activated. Up until no more water can be extracted, the filtrate volume is measured and recorded. Following this time frame, the biosludge cake is taken out of the filter and put inside a weighing plate. The cake's wet weight is measured, and once it is dried in the oven, the total suspended particles in mg/L on the filter are also calculated. Equation (4.12) was used to compute the particular SFR (Zhang et al., 2022).

$$\text{SFR} = \frac{2 \times P \times A^2 \times b}{\mu \times W} \quad [4.12]$$

SFR = Specific filter resistance, m/kg

P = Pressure (N/m²)

A = Area (m²)

b = V, slope of V/t graph (sec/m⁶)

μ = Viscosity = 11 × 10⁻⁴ (N.sec/m²)

w = Weight of cake to filtrate volume, (Kg/m³)

The 'b' value in the formula is the coefficient of x in the equation appearing on the graph created by writing T/V values on the y-axis and V values on the x-axis.

5. RESULTS AND DISCUSSION

5.1. MW pretreatment application

5.1.1. Optimization studies

Due to tendency of the WBS to decompose within three days' post-collection, the WBS samples were drawn from the Sivas WWTP at each stage of the experiments and analyses were promptly conducted upon sample collection to ensure data accuracy and reliability.

In order to determine the most appropriate MW power according to sCOD and DD% of the disintegrated biosludge properties, the MW was operated under the conditions presented in Table 5.1.

Table 5.1 Operational conditions of MW

Temperature (°C)	Power (W)	Heating rate (°C/min)
75–90–110	900–1,800	2–4–6

Since it was determined in the preliminary experimental studies that the sCOD value changed as a result of the disintegration of biosludge samples even though they were stored in the refrigerator, the WBS sample was brought from the Sivas WWTP for each experiments in the MW disintegration and experiments were completed within two days.

The average initial properties of raw WBS was; sCOD: 64 ± 10 mg/L, pH: 7.56 ± 0.22 , $\text{NH}_4\text{-N}$: 0.45 ± 0.2 mg/L, $\text{PO}_4\text{-P}$: 7.7 ± 1 mg/L, TS: $12,000 \pm 500$ mg/L, and SS: $10,900 \pm 500$ mg/L.

5.1.1.1. Biosludge disintegration at the MW power of 1,800 W

The results indicated that as the temperature or specific energy applied to the biosludge for disintegration increase, the concentrations of sCOD and DD elevated (Table 5.2). The sCOD concentration was 1,650 mg/L at the target temperature of 75°C with the heating rate of 6 °C/min, while the sCOD concentration increased after the decreasing to 2°C/min. Increase of the target temperature to 90°C, increase of the sCOD concentration was observed and the sCOD concentration was determined to be approximately 2,174 mg/L at 2°C/min. The sCOD concentration of 1,872 mg/L at the target temperature of 110°C and

heating rate of 6°C/min indicated that the biosludge dissociation by MW was lower compared to the operating conditions of 90°C and 2°C/min. The highest concentration of sCOD was determined to be 2,400 mg/L at the MW operational condition of 110°C and 2°C/min.

At the temperatures of 110°C and 90°C with the lowest heating rate of 2°C/min resulting in the highest DD level of 67.8% and 61.4%, respectively. It was concluded that higher temperatures and slower heating rates were more effective for dissociating the biosludge compounds at MW pretreatment.

In the studied experimental conditions of MW, at which reached the longest time to the target temperature, better sCOD solubility and DD level were determined. High sCOD concentrations shows the solubilization of organic constituents, the rise in sCOD is cited as the primary success parameter for pretreatment in literature (Bozkurt et al., 2020; Hong, 2002; Jackowiak et al., 2011; Kor–Bicakci et al., 2019).

Table 5.2 Variations of sCOD and DD at the MW power of 1,800 W

Target Temperature (°C)	Heating rate (°C/min)	sCOD (mg/L)	DD (%)	Specific Energy (kJ/kg TS)
Raw WBS	–	64	–	–
75	2	1,880	52	125,600
75	4	1,728	48.2	90,000
75	6	1,650	46	77,400
90	2	2,174	61.4	147,600
90	4	1,886	53	111,240
90	6	1,731	48.7	106,560
110	2	2,400	67.8	207,360
110	4	2,032	57.0	153,720
110	6	1,872	52.0	143,280

The specific energy of MW increases with longer exposure times, leading to the significant disintegration of biosludge and the release of organic matters (Doğruel et al., 2017). For the heating rate of 2°C/min, the sCOD concentration and DD were determined higher at the temperature of 110°C compared to the values obtained at 90°C. However, it

was calculated that the energy consumption was approximately 40% more to reach to the temperature of 110°C.

5.1.1.2. Biosludge disintegration at the MW power of 900 W

As observed previous experiment, the sCOD concentration in biosludge liquid and also DD level increased with biosludge disintegration at low heating rates and high target temperatures (Table 5.3). At the target temperature of 75 °C, no significant difference was observed in sCOD concentration (1,620–1,770 mg/L) for the studied heating rates. The observed increase in sCOD concentration and the DD to 2,080 mg/L and 61%, respectively, occurred at the temperature of 110°C and heating rate of 2°C/min. On other hand, at the target temperature of 90°C and the same heating rate, these values reached 1,934 mg/L and 56.8%.

Table 5.3 Variations of sCOD and DD at the MW power of 900 W

Target Temperature (°C)	Heating Rate (°C/min)	sCOD (mg/L)	DD (%)	Specific Energy (kJ/kg TS)
Raw WBS	-	92.3	-	-
75	2	1,792	52.2	122,400
75	4	1,678	48.6	79,920
75	6	1,624	47	75,600
90	2	1,944	56.8	145,080
90	4	1,788	52	107,640
90	6	1,726	50	76,680
110	2	2,080	61	197,280
110	4	1,970	57.6	145,440
110	6	1,841	53.7	112,320

The consistency of these results with the obtained previous experiment with the MW power of 1,800 W approach suggests that as the duration of exposure to irradiation prolongs, improved the effectiveness the disintegration of biosludge, leading to a greater release of organic materials into the medium. Eskicioglu et al. (2009) also observed that the melting of sludge increased as the temperature rose from 50°C to 120°C, particularly at a low heating rate. A linear relationship between the release of organic materials and longer exposure to irradiation was reported (Ahn et al., 2009; Eskicioglu et al., 2009; Kor-Bicakci et al., 2019; Lo et al., 2018; Saha et al., 2011).

The key findings suggest that MW irradiation, within specific heating rates (ranging from 1.2 to 4°C/min) and temperature ranges (50–175°C) can lead to the dissolution of sludge and the liberation of organic compounds. Toreci et al., (2010) also reported that pretreatment of biosludge using MW irradiation process at temperatures higher than the boiling point could enhance the solubilization, but excessively high temperatures should be avoided. When the biosludge is subjected to high temperatures, it can lead to the formation of melanoidins and humic acids, which can hinder the AD process (Shahriari et al., 2012). In addition to temperature, the heating profile (slow heating versus rapid heating) plays an important role in enhancing the release of organic compounds and accelerating the elimination of pathogens and other contaminants, thus enhancing the efficiency of subsequent treatment processes such as the CH₄ production in the AD process or facilitating disposal (Saha et al., 2011).

Considering the energy consumption, despite the slightly higher concentration of sCOD was observed at 110°C compared to the MW target temperature of 90°C, the sCOD increase was negligible level due to the approximately 36% more energy needs.

The results of RSM statistical study regarding the release of sCOD from the biosludge indicated that reducing the heating ramp rate enhances the release of sCOD, by increasing the heating time (Figure 5.1–5.3). The relationship between heating ramp rate and the sCOD release can be explained by factors such as the time required for the biosludge to undergo relevant chemical transformations or the effectiveness of heat transfer throughout the biosludge mass. The low heating rates had a positive effect on the release of sCOD, as illustrated in Figure 5.1. The same applies to temperatures, meaning that the higher the target temperature, the greater the release of sCOD, especially in the dark area between 90°C and 110°C (Figure 5.2). Koupaie et al., (2016) also observed similar relationship between the target temperature and heating rate on the organic compounds release from the biosludges. In summary, the data and analysis suggested that lowering the heating ramp rate and increasing the temperature and heating time were effective strategies for enhancing the release of sCOD from biosludge.

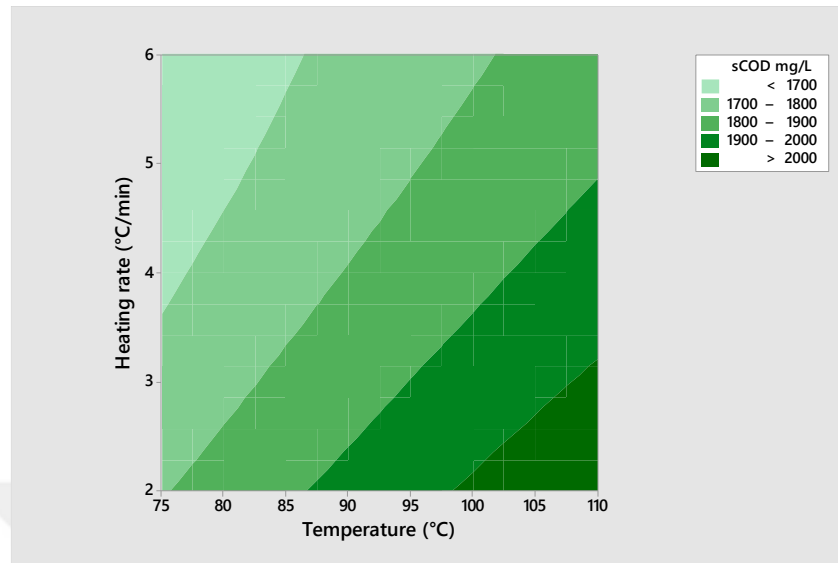


Figure 5.1 The RSM for sCOD

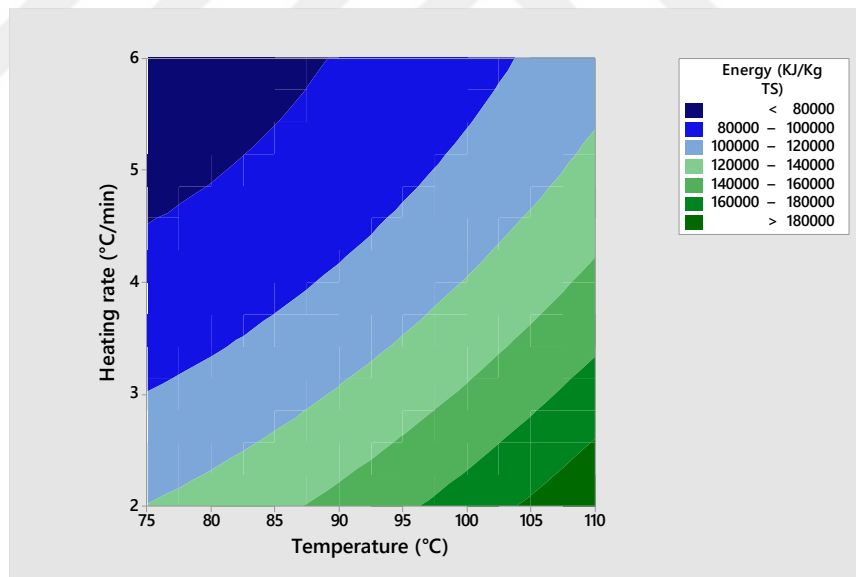


Figure 5.2 The RSM for energy consumption

This phenomenon could be due to various factors such as increased kinetic energy of molecules at higher temperatures, which enhances the dissolution of solids, or it might involve chemical reactions that facilitated the breakdown of biosludge particles into more soluble forms (Dudley et al., 2015). The analysis of variance proved the statistically significant effect of heating ramp rate on the sCOD releasing ($p\text{-value} = 0.033 < 0.05$).

Contour lines show the extent to which the increase in temperature corresponds to the release of sCOD. The darker the area, the greater the release of sCOD (Figure 5.2). The increase in temperature corresponded to the release of sCOD in statistically by the p value= 0.001<0.05. This indicated that there was a direct relationship between the temperature rise and the specific energy consumption during the breakdown process. Therefore, it is important to consider the combined effects of temperature, heating rate, and duration of irradiation exposure on the energy requirement for the breakdown of compounds.

Eswari et al. (2016) observed a notable trend characterized by the rapid release of soluble organic compounds, including sCOD, protein, and carbohydrate, particularly in the context of MW technology application. In addition, noted that MW has the capacity to disrupt the complex block structure of WBS. This disruption leads to the breakdown of cell walls, causing both extracellular and intracellular cytoplasmic substances to enter the soluble phase as the specific energy input increases. However, the pretreatment process caused the increase in cost of treatment (Eswari et al., 2016). Based on the RSM analysis for the optimal conditions, as shown in Figure 5.3, the minimum energy consumed was 141,300 kJ/kg TS (as Y), the maximum sCOD concentration was 1,940 mg/L, and the maximum DD was 56.7%, which was similar to the conditions of 90°C and 2°C/min as shown in Table 5.3.

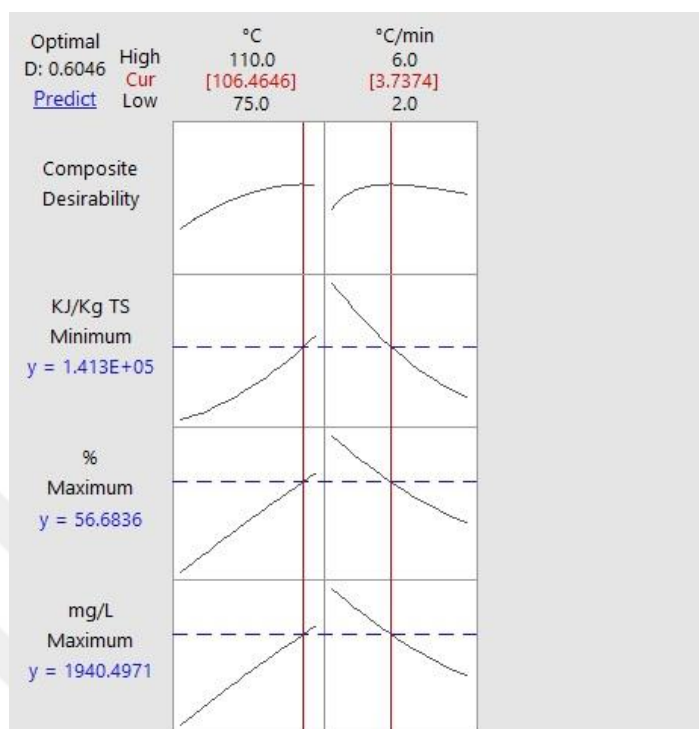


Figure 5.3 The optimal MW operational conditions for biosludge.
 (%: represents the DD; mg/L: represents sCOD concentration;
 kJ/kg TS: represents the specific consumed energy)

5.1.1.3. Comparison of biosludge disintegration at different MW power operation

Biosludge decomposition carried out at different MW powers were compared taking into account sCOD and specific energy consumption. Under the operational conditions of MW at both powers, the highest sCOD concentration was determined at the lowest heating rate and the highest operating target temperature of 2°C/min and 110°C, respectively. In the study, observed that the difference in sCOD and DD between the MW powers of 1,800 W and 900 W were not significant under the operating conditions. Bohdziewicz et al., (2011) reported a similar observation where the difference in sCOD and DD was not significant when comparing two MW powers of 700 W and 1,000 W. Elagroudy et al., (2013) suggested that the dissolution of biosludge aggregates during pretreatment might be the primary factor contributing to the sCOD increase, particularly at longer contact times and higher temperatures using lower MW density. However, Park et al., (2010) and Kor-Bicakci et al., (2019) found that the sCOD concentration increased when the MW

power was reduced to achieve the same target temperature. On the other hand, Climent et al., (2007) reported that no significant differences in sCOD solubility were detected at different energy levels. The difference between the results was estimated probably due to the change in energy absorption in the experimental environment (Sólyom et al., 2011).

Lower power consumption is often desirable for various reasons, including cost-effectiveness and environmental sustainability. Based on the results obtained from both power levels, under the operational conditions for the later studies, the MW power of 900 W was determined more appropriate, which the energy consumption was lower than the 1,800 W.

5.1.1.4. Determining the optimal operational conditions of MW

A holding time of 5 min was applied to the MW operational conditions that was previously determined. The highest sCOD release and DD level, and lowest energy consumption was considered in order to evaluate the holding time effect on the biosludge disintegration. In the study, the MW was operated at the ramping rate of 2°C/min to reach to the target temperatures of 75°C, 90°C, and 110°C and irradiation was continued for 5 min at the target temperatures to further breakdown the biosludge and release nutrients into the medium. Applying the retention time of 5 min resulted in the elevation of disintegration of biosludge and increased of DD level and sCOD concentrations compared to conditions without retention time Table 5.4.

Table 5.4 The variations of sCOD concentrations and DD at the operation of MW with 5 min holding time for optimum conditions (900 W, 2°C/min)

Target temperature (°C)	Holding time (min)	sCOD (mg/L)	DD (%)	Specific Energy (kJ/kg TS)
75	0	1,792	52.2	122,400
90	0	1,944	56.8	145,080
110	0	2,080	61	197,280
75	5	2,346	64.3	348,480
90	5	2,832	78.2	457,200
110	5	3,148	88.5	646,200

Ara et al., (2014) reported that the solubility of the sludge gradually increased as the holding time was increased from 1 to 10 min. However, it was found that the holding time of more than 10 min did not produce significant improvements in solubility compared to

the additional energy expended. Coelho et al., (2011) underscored the importance of carefully managing pretreatment conditions, cautioning that excessive exposure to high temperatures, particularly with prolonged holding times, could yield unfavorable outcomes such as might lead to enzyme inactivation, reduced biodegradability of nitrogenous organic materials, and the potential for NH_3 concentrations to reach inhibitory levels.

The energy consumption of MW under the operational conditions exhibited a positive correlation with rising temperatures in this study and resulted in a notable dissolution of the biosludge and subsequent release of organic materials into the medium.

In the first run (without holding time), the highest sCOD and DD values were determined at the temperature of 110°C, followed by 90°C, but the difference was not high. In addition, it was determined that the energy expenditure at a temperature of 90°C less than 110°C. The MW target temperature of 90°C was considered appropriate for disintegration from an economic standpoint.

In the second run (with holding time of 5 min), the rate of DD% and sCOD concentration increased with the temperature and applied energy, and this increase was higher than the results of the first run. The increase of DD% in the second run compared to the first run was 23%, 37.6% and 45% for the target temperatures of 75°C, 90°C and 110°C respectively. However, as expected the energy requirements in the second run were much higher than in the first run due to the 5 min holding time. Additionally, the biosludge volume disintegrated in the MW in the second cycle 160 mL was lower than the first run 480 mL. The calculation of energy expenditures is inversely proportional to the applied volume. Therefore, it was considered that the second run was the most appropriate in terms of sCOD and DD. The higher DD or/sCOD values indicates the effectiveness of disintegration and result in improved the anaerobic digestion process.

The RSM results, as shown in Figure 5.4, showed that the lowest energy consumption with the highest value of sCOD and DD% was for the conditions (90°C and 5 min), where the optimum RSM results were; input energy= 448,400 kJ/kg TS, sCOD= 2,767.7, and DD=77.5, which is line with to the experiment (true experiment) disintegration output input energy= 457,200 kJ/kg TS, sCOD= 2,832 mg/L, DD=78.2% (Table 5.4)

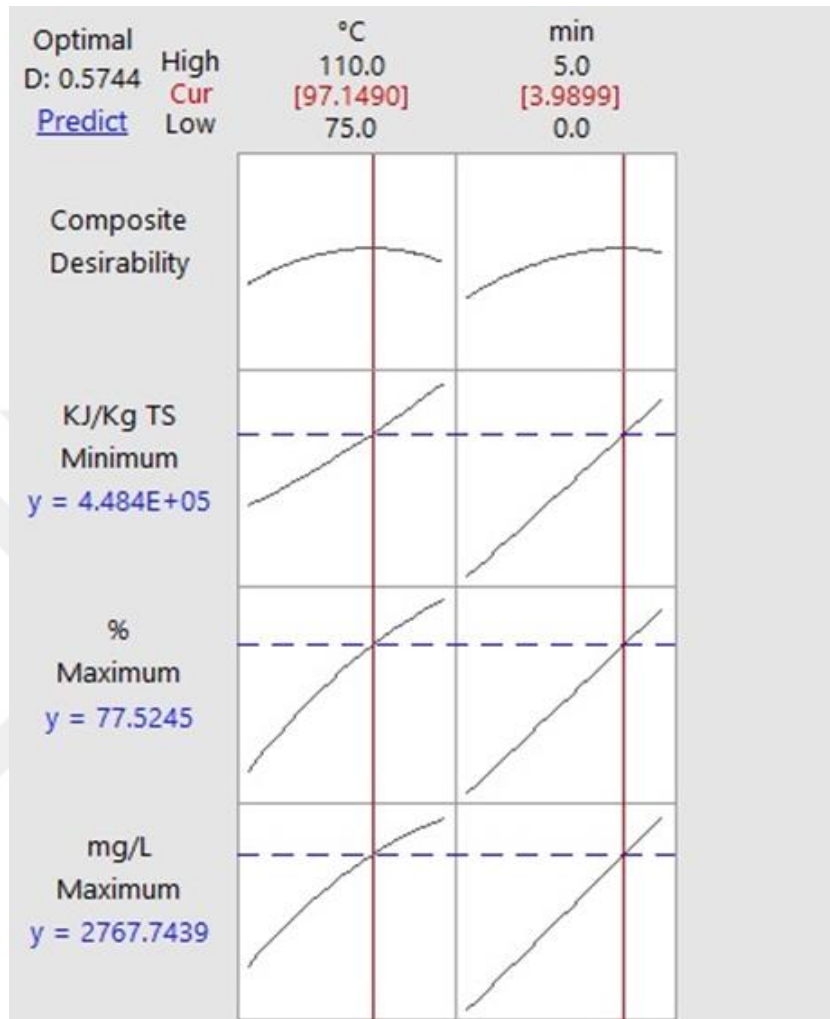


Figure 5.4 The definition of optimal MW operational conditions

In the 2nd run, compared to the target temperature of 110°C, the difference of rate of DD (13%) and the sCOD (11%) concentration obtained at 90°C was negligible considering the input MW energy need about 29% was lower. Optimal MW operating conditions were determined as the target temperature, ramp rate, retention time and power, 90°C, 2°C/min, 5 min, and 900 W, respectively.

5.2. Composition of disintegrated biosludge at optimal MW conditions

Compositions of disintegrated biosludge by the MW irradiation under optimal conditions and raw WBS are given in Table 5.5.

Table 5.5 Characteristics of raw and disintegrated WBS

Parameter	Unit	Raw WBS	Disintegrated biosludge
pH		7.33	7.91
EC	ms/cm	1.2	1.58
TS	mg/L	11,840	12,422
sCOD	mg/L	87.9±1.4	3,136±26
DD	%	–	71.5±1.04
Protein	g/L	0.44±0.035	1.55±0.085
Sugar	mg/L	5.44±0.6	92.16±1.8
NH ₄ ⁺ –N	mg/L	10±1.16	10.5±0.61
PO ₄ –P	mg/L	11±0.31	20.66±0.23
Alkalinity	mgCaCO ₃ /L	440±22.8	350±45.75
SFR	m/kg	1.02x10 ¹³	4.02x10 ¹⁴
Energy consumption	kJ/kgTS	–	441,000
Particle size distribution	d10 µm	37.7	14.2
	d50 µm	260	14.3
	d90 µm	410	67
SSA	m ² /kg	70.9	217.8
Mg	mg/L	24.7	14.9
Na	mg/L	128.7	69
Ca	mg/L	22.3	52.2
Al	mg/L	0.09	0.04
Zn	mg/L	0.04	0.3
K	mg/L	23.5	61.2

5.2.1. Effect MW on sCOD releasing

Exposure of biosolids to MW irradiation could potentially disturb the intricate structure and result in the release of various components, including EPS and intracellular biopolymers like proteins and sugars, from the biosolids structure into the soluble phase. As can be seen from the Table 5.5, while the raw WBS was about 88 mg/L, significant increase of sCOD concentration to about 3,136 mg/L (increase of approximately 3,504 %) after MW disintegration was observed.

Eskicioglu et al., (2006) revealed a substantial rise in sCOD content from 3,621 to 8,669 mg/L, when the biosludge was pretreated with the MW at the temperature of 96°C, reflecting 139% increase rate. Akgul et al., (2017) also observed 73% increase in the rate of sCOD release under MW irradiation conditions, with a target temperature of 80°C, a

heating rate of 7°C/min, and a holding time of 1 min. The rate of increase in sCOD reached 388 % with the MW irradiation under the conditions of 100°C temperature, rise rate of 27 °C/min, and retention time of 5 min (Eskicioglu et al., 2008). The percentage of sCOD after pretreatment of biosludge increased to 214% under MW irradiation conditions of 80 °C and a heating rate of 16°C/min (equivalent to irradiation time of 3.5 min) and without holding time (Appels et al., 2013). Koupaie et al., (2015) observed higher improvement in solubilization when using low heating rate of 2.9°C/min compared to the higher heating rate of 7.5°C/min. Although, compared to the temperature of 90°C, the increase in sCOD was limited at the MW target temperature of 70°C, the release of sCOD was determined more pronounced after a pretreatment time of 15 min at 90 °C (Appels et al., 2010). Appels et al., (2010) reported that after 30 min of pretreatment at 90°C, the sCOD was already 18 times higher than that of the untreated sludge and increase to a net increase of 2,500%.

The release of organics is attributed to the disruption of chemical bonds in cell walls and membranes, which leads to the release of intracellular organic material, caused by the thermal treatment. Additionally, EPS, which include polysaccharides, proteins, nucleic acids, and humic acids, are degraded and released from the cell walls under these conditions (Appels et al., 2010).

Although the previous studies also applied a target temperature similar to this study, the rate of increase in sCOD was much lower was determined than our study. The reason of higher increase rate of sCOD than previous studies was thought that the MW irradiation was longer exposure time that reached about 40 min with the low heating rate and holding time. This demonstrates the importance of exposure time in irradiation pretreatments for biosludge. Borges (2009) found that as the temperature and heating time increased the dissolve more of organic matter from the biosludge and caused to access the material easier and more available for potential biological degradation in the following processes.

5.2.2. Effect MW on sugar and protein release

As in sCOD, there was a significant increase in sugar and protein concentrations compared to the untreated raw sludge. The concentrations of sugar and proteins in raw biosludge were 5.44 mg/L and 0.44 g/L, respectively, and after subjecting the biosludge to MW disintegration, increase in the concentrations of sugar and protein, reaching 92 mg/L and

1.55 g/L, respectively. At a temperature of $96 \pm 2^{\circ}\text{C}$ and with a MW power of 1,000W, it was observed 1.9 fold increase in the concentration of soluble protein compared to untreated sample (Elagroudy et al., 2013). At a temperature of 80°C and power of 800 W, the concentrations of protein and sugars were 77 mg/L and 390 mg/L for the raw sludge and increased to 285 mg/L and 1.31 g/L for the disintegrated sludge, respectively (Appels et al., 2013). The concentrations of proteins and sugars were as observed as 1.17 g/L and 0.69 g/L in the raw biosludge, when the MW target temperature was 100°C , in the decomposed biosludge increased to about 11.5 g/L (increase of 882 %) and 3.3 g/L (increase of 378 %), respectively (-Liu et al., 2016). Toreci et al., (2010) reported that the concentrations of sugars and proteins increased from 168 and 202 mg/L for raw sludge to 304 and 260 mg/L, respectively, for disintegrated sludge at a target temperature of 100°C and a heating rate of $7^{\circ}\text{C}/\text{min}$, while as the heating rate was decreased to $3^{\circ}\text{C}/\text{min}$, the concentration of sugars and proteins increased to 408 and 402 mg/L, respectively. Ahn et al., (2009) applied the MW irradiation at 700 W and 91°C to disintegrate the WBS and observed significant increases from 0.15 to 0.9 g/L for proteins and 0.07 to 0.7 g/L for carbohydrates. At a temperature of 96°C and heating rate of $15^{\circ}\text{C}/\text{min}$, by the increase rate of 150% for proteins and 13.7% for sugars, elevation of the concentration of protein and sugar from 0.088 g/L to 0.22 g/L and 80 mg/L to 91 mg/L, respectively was determined (Eskicioglu et al., 2006).

Conversely, higher sugar and protein release by the MW irradiation was determined in this study than the previous studies due to the biosludge was exposed to irradiation for a longer period by the application lower ramping rate of $2^{\circ}\text{C}/\text{min}$. On the other hand, at temperatures higher than 80°C , reduction in the concentrations of sugars and proteins in pretreated biosludges could be occurred due to the reducing sugars could polymerize in the soluble phase and transform again into the particulate phase (Eskicioglu et al., 2007c). However, it was not observed the decline of proteins and sugars concentrations in this study. The MW irradiation at temperatures exceeding the boiling point, compared to a higher heating rate of $7.75^{\circ}\text{C}/\text{min}$, while a low heating rate of $2.25^{\circ}\text{C}/\text{min}$, significantly enhances the disintegration of biopolymers and the release of proteins. The slower heating process was reported as more effective in breaking down the biosludge and releasing biopolymers and proteins (Kor-Bicakci et al., 2019). Application of MW irradiation at

high levels and for extended contact times, the biosludge flocs could be effectively disintegrated, destroy cellular structures, and release intracellular. The MW irradiation generates heat within the biosludge, leading to the rupture of cell walls and membranes which allows the soluble proteins, which are normally contained within the cellular structures, to be released into the liquid. As a result, the concentration of soluble proteins in the aqueous phase increases (Xiao et al., 2020). The increased concentration of soluble protein after MW irradiation could be attributed to the disruption of the cell wall and/or cell membrane by the irradiation process.

5.2.3. Release of $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$

As can be seen from the Table 5.5, the MW pretreatment led to an increase in $\text{PO}_4\text{-P}$ concentration from 11.0 mg/L to 20.7 mg/L in the biosludge. However, change of $\text{NH}_4^+\text{-N}$ concentration, which was about 0.5 mg/L, was negligible after the pretreatment, indicating that the MW irradiation did not have a significant effect on breakdown of compounds contain nitrogen in biosludge under the operational condition.

Because the $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$ release after MW disintegration is not high, recovery of nutrients by struvite precipitation was infeasible. On the other hand, after MW irradiation, reduction of $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$ concentrations were observed in the previous studies (Biswal et al., 2020; Ruffino et al., 2015). Kumar et al. (2020) reported the reduction of about 30% NH_4^+ and 12% $\text{PO}_4\text{-P}$ contents in the biosludge, which was disintegrated at the temperatures between 80–120°C. The NH_4^+ reduction has been linked to NH_3 volatilization, which can occur at high pH and high temperatures. Additionally, Ruffino et al. (2015) attributed the reduction of NH_4^+ to caramelization or Maillard reactions at temperatures above 80°C. The decrease in $\text{PO}_4\text{-P}$ release at high temperatures, as reported by Biswal et al. (2020), is due to the physical adhesion of phosphate to sludge particles or chemical changes, such as precipitation or complexation, leading to a more stable state.

5.2.4. Particles size distribution (PSD)

Pretreatment of solids effectively reduces particle size, while enhances their homogeneity in the WBS (Yenenneh et al., 2015). The particle size distribution is typically characterized

by measures such as dp10, d50, and d90, representing the diameters at which 10%, 50%, and 90% of the particles (by volume) fall, respectively (Yildiz and Cömert, 2020).

After disintegration, decrease of the particle sizes (ratio were 80–84%), which caused the increase of SSA illustrated as dp10, d50, and d90 in Table 5.5, caused the favorable impact by enhancing homogeneity of biosludge. By an increment ratio of about 207%, the SSA of raw WBS increased from 70.9 m²/kg to approximately 217.8 m²/kg after MW pretreatment at 90°C. This enhancement in SSA, which could improve the efficiency of various treatment processes, such as biodegradation, adsorption of contaminants, indicated that the MW pretreatment effectively breakdown the biosludge.

Due to the MW irradiation, which interacts with materials at the molecular level, energy indeed causes constant movement and rubbing between particles, leading to their breakdown into smaller pieces (Chang et al., 2011). Zhang et al., (2021) also determined that the MW irradiation with the power of 700 W led to increase in the particle size because of the presence of hydrophilic groups with numerous negative charges on the surface of the sludge. Normally, the biosludge maintains their stability due to electrostatic repulsion. With the MW irradiation, a rapid rotation of polar particles within the biosludge is occurred, disrupting its bulk structure and destabilizing the “steady state,” resulting in increased particle size (Zhang et al., 2021). Chang et al., (2011)'s highlighted a significant reduction in biosludge particle size after prolonged exposure to MW irradiation due to the constant friction between molecules within the sludge, which resulted in the destruction of the zeta potential and the surface electrical double layer structure.

5.2.5. Effect of MW on SFR process

The SFR of raw biosludge was approximately 1.0×10^{13} while it increased to 4.0×10^{14} at the target temperature of 90°C (Table 5.5). The MW pretreatment lead to changes in the biosludge, potentially affecting its filtration resistance, possibly due to changes in the structure or composition, such as the degradation of hydrophilic EPS. Initially, this process could be effective in altering biosludge properties and aiding dewatering. However, prolonged exposure of MW irradiation could lead to deterioration in dewaterability due to excessive destruction of the biosludge's bulk structure by the release

of intracellular material into liquid and increasing its viscosity (Chang et al., 2011; Faruqi et al., 2021; She et al., 2021; Vialkova et al., 2021; Yeneh et al., 2015; Zhang et al., 2021).

5.2.6. Heavy metals release

During the wastewater treatment, heavy metals accumulate in WBS through physicochemical and biological interactions. Organic–metallic complexes are the primary forms through which this accumulation occurs. Approximately 50% to 80% of heavy metals present in wastewater are accumulating in WBS during the treatment process. The total heavy metal content in WBS accounts for 0.5% to 2.0% of the TS present in the biosludge, which indicates a significant concentration (Li et al., 2021). Sumida and Sumida, (2013) reported that the biosludge comprises primarily of three nutrients: N, P, and K. Normally, Na and Ca were plentiful, but Mg and S were present as a concentration of mg/L, and the remaining components were usually present at a concentration of µg/L or less. Heavy metals in biosludge could exist in various chemical forms, including exchangeable (easily released), bound to carbonates, bound to iron and manganese oxides, bound to organic matter, and residual forms (tightly bound). Different forms have varying degrees of stability and susceptibility to release under the thermal treatment conditions (Appels et al., 2010).

The concentrations of Na, Mg, and Al in raw WBS were about 129 mg/L, 25 mg/L, and 0.09 mg/L, respectively. Following MW pretreatment, a decrease in the amounts of minerals in the biosludge was observed. However, Al Ramahi, (2020) reported an increase in Mg, Ca, Cu, and K concentrations in the aqueous phase after MW disintegration. The lowest Na concentration of about 69 mg/L was determined in the biosludge at 90°C. It appears that the relationship between the decrease in Na⁺ concentration and the increase in MW temperature above 75°C, which might lead to the precipitation of carbonate or phosphate forms, as discussed by (Wang et al., 2016).

Mg concentration was highest at 24.7 mg/L in the raw WBS and concentration decreased to 14.8 mg/L after MW disintegration. While the soluble organic matter liberated during the heat pretreatment could act as an effective flocculant, increased the reflocculation phenomena might also be related to the lower amounts of Ca and Mg at higher disintegration temperatures (Tonanzi et al., 2021). Wang et al (2016) also reported Mg

concentration decrease by the MW pretreatment at the temperature of 100 °C compared to the raw WBS

Moreover, the hybrid MW pretreatment facilitated the simultaneous release of Mg^{2+} , NH_4^+ , and PO_4^{3-} from the biosludge. Simultaneous release could reduce the overall cost of chemical required for Mg^{2+} specifically for struvite precipitation (Jiang et al., 2018; Wang et al., 2016).

The concentration of Zn in raw WBS was about 0.04 mg/L and an increase of 605% ratio increased to 0.3 mg/L after MW pretreatment. Appels et al., (2010) noted that the temperature and duration of the irradiation had a major effect on the release of minerals into medium. It was reported that the disintegrated biosludge had 406% Zn higher compared to the raw WBS (Appels et al., 2010).

In the raw WBS, K and Ca concentrations were 23.5 and 22.3 mg/L, respectively. When the MW pretreatment was applied at 90°C, their concentrations rose sharply to approximately 61 and 52 mg/L. When the cells are breakdown, certain divalent cations, which combined ionically with negatively charged phospholipids to help maintain the membrane, such Ca^{2+} were released (Ahn et al., 2009). An increase in concentration of Ca^{2+} in the supernatant was observed also by Bohdziewicz et al., (2011). This increase aligns with the hypothesis that MW cause the disintegration of bacterial cell membranes. However, Bohdziewicz et al. (2011) did not find a significant impact of MW power on the release of Mg^{2+} and reported that while MW might affect certain aspects of bacterial cell integrity, it might not necessarily disrupt all cellular components or processes to the same extent.

Jiang et al. (2018) was no observe variation of Mg^{2+} content between the raw and disintegrated WBS when subjected to MW treatment at 240 W, while the Ca^{2+} level significantly decreased. In contrast, it was reported the concentrations of Ca, Mg, and K increased after MW disintegration at various temperatures. Specifically, a slightly higher concentration of metals was found at 120°C Jiang et al., (2018). However, a clear trend regarding the variation of metal concentrations could not be determined (Wong et al., 2006). Improved release of Zn and K was determined after the biosludge disintegration at the temperatures of 75°C and 90°C (Appels et al., 2010; Lizama et al., 2017). Bohdziewicz

et al. (2011) found that under full power MW irradiation at 900 W, a small amount of Ca^{2+} was released whilst did not affect the release of Mg^{2+} ions. Similar observation for Ca^{2+} and Mg^{2+} was reported by Wang et al. (2016) at the MW temperature of 100°C. Results indicated that the effect of MW on the release of elements might vary depending on the specific ion and process conditions (Wang et al., 2016). Improved diffusion of the release of Zn and K, thus enhancing the release of these nutrients after applying furnace sludge disintegration at temperatures of 75°C and 90°C (Appels et al., 2010; Lizama et al., 2017).

5.2.7. SEM

The SEM analysis aim to scrutinize the surface morphology, crystallography, and surface composition of samples. Initially, particles of raw WBS exhibited a tightly bound configuration within a large bulk structure and inherent cohesion Figure 5.5 (a). However, following the MW pretreatment, the biosludge's block structure appeared notably loose and dispersed, evident from the presence of block fragments dispersed Figure 5.5 (b). Notably, with disintegration by MW, the dispersion of the biosludge intensified, indicating a correlation between temperature and disintegration efficiency. Zhou et al., (2010) observed that the raw WBS exhibited significant porosity and harbored filamentous bacteria. However, following 7 min irradiation period, the structural integrity of the blocks had been compromised. It was observed the surface of pretreated biosludge featured small, dispersed, loose particles and exhibited notably reduced porosity compared to the raw sludge, which comprised larger, more porous pieces.

Because the MW was able to break up the biosludge particles into tiny bits that resembled powder, the biosludge became more pliable and looser than it had been in the raw, as shown in Figure 5.5 (a), and consequently, when the MW disintegration applied, the biosludge's dewatering process worsened. The SEM pictures showed that MW pretreatment might impair the tightness and the surface structure of biosludge.

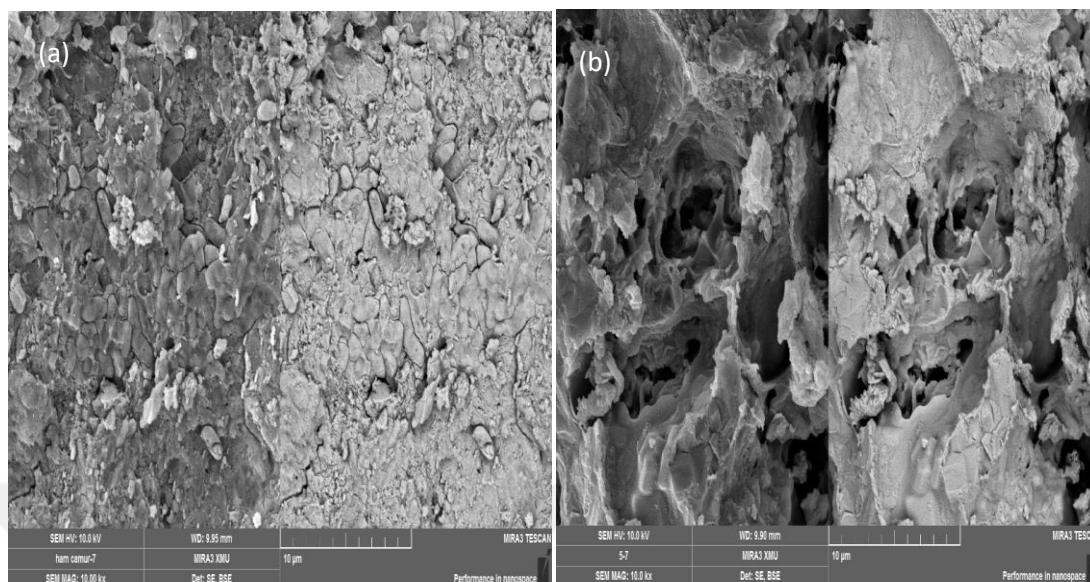


Figure 5.5 SEM images of raw (a) and MW pretreated biosludge (b)

5.2.8. FTIR

FTIR is indeed a crucial analytical technique used in chemistry for distinguishing between organic and inorganic chemical substances. It operates on the principle of functional group characterization, which is fundamental to organic chemistry (Invernizzi et al., 2018). In FTIR spectroscopy, a sample is exposed to infrared radiation, which causes the molecules within the sample to vibrate in characteristic ways. Different functional groups within molecules absorb infrared radiation at specific frequencies, resulting in unique patterns or spectra and the functional groups present in a sample and infer the chemical composition and structure of the substance can be identified (Invernizzi et al., 2018).

The functional groups in the raw and MW disintegrated biosludge were identified by FTIR, with a scan range selection of $500\text{--}3,500\text{ cm}^{-1}$ (Figure 5.6 a, b). The functional group is composed of four areas: regions I (single bond), II (triple bond), III (double bond), and IV (fingerprint), which fall between the wavenumber ranges of $2,000\text{--}2,500$, $1,500\text{--}2,500$, and less than $1,500\text{ cm}^{-1}$, respectively (Nandiyanto et al., 2019).

According infrared spectroscopy analysis of various functional groups in biosludge samples, the spectral range between $3,000$ and $3,700\text{ cm}^{-1}$, several functional groups can

be identified, including OH groups from carboxylic acids, alcohols, phenols, and water, as well as NH or NH₂ groups. It appears that the presence of OH and NH/NH₂ functional groups was consistent across different types of biosludge samples, whether raw or pretreated. Additionally, that the intensity of peaks corresponding to these functional groups were slightly higher in the treated samples compared to raw biosludge as shown in Figure 5.6 (b).

Bohdziewicz et al., (2014) confirmed that the most significant impact on the release of O–H and N–H bonds, particularly at wavelengths ranging from 3,000 to 3,350 cm⁻¹, resulted from pretreatment using MW energy at 1200 W. Results suggests that the application of MW energy at a specific power level had a notable effect on the behavior of these chemical bonds, likely influencing the release or activation of O–H and N–H groups within the studied materials or compounds. The absorption peaks; oxygen, such as 2,921 cm⁻¹ and 2,853 cm⁻¹ for =CH₂ and 1,630 cm⁻¹ for CO–NH extension, indicate the presence of these functional groups in the molecule being analyzed (Qiu et al., 2021). The numbers provided (2,921 cm⁻¹, 2,853 cm⁻¹, and 1,630 cm⁻¹) represent the wavenumbers at which these absorption peaks occur. These wavenumbers are characteristic of specific chemical bonds and can be used to identify the functional groups present in a molecule. The absorption peaks observed for both treated and untreated samples ranged from 1,520–1,530 cm⁻¹ (representing C–O), 1,411–1,414 cm⁻¹ (representing CH₂), and 1,026–1,031 cm⁻¹ (representing –OH). The compounds at wavelengths 1,520–1,530 cm⁻¹ and 1,411–1,414 cm⁻¹ were comparable for both raw and pretreated samples.

The appearance of high peaks at 1,026–1,031 cm⁻¹, especially in the disintegrated biosludge compared to the raw material, suggests changes in the chemical composition of the material. These peaks are indicative of the presence of carbon or oxygen chains containing functional groups such as esters or organic acids. The similarity to the study conducted by (Yue et al., 2021), which identified peaks associated with C–O, CH₂, and –OH functional groups at 1,555 cm⁻¹, 1,410 cm⁻¹, and 1,038 cm⁻¹, respectively. In the wavelength region between 1,000 cm⁻¹ and 1,100 cm⁻¹, compounds containing N–C and C=C bonds were detected. This observation is consistent with the findings reported in a study by Tian et al., (2021).

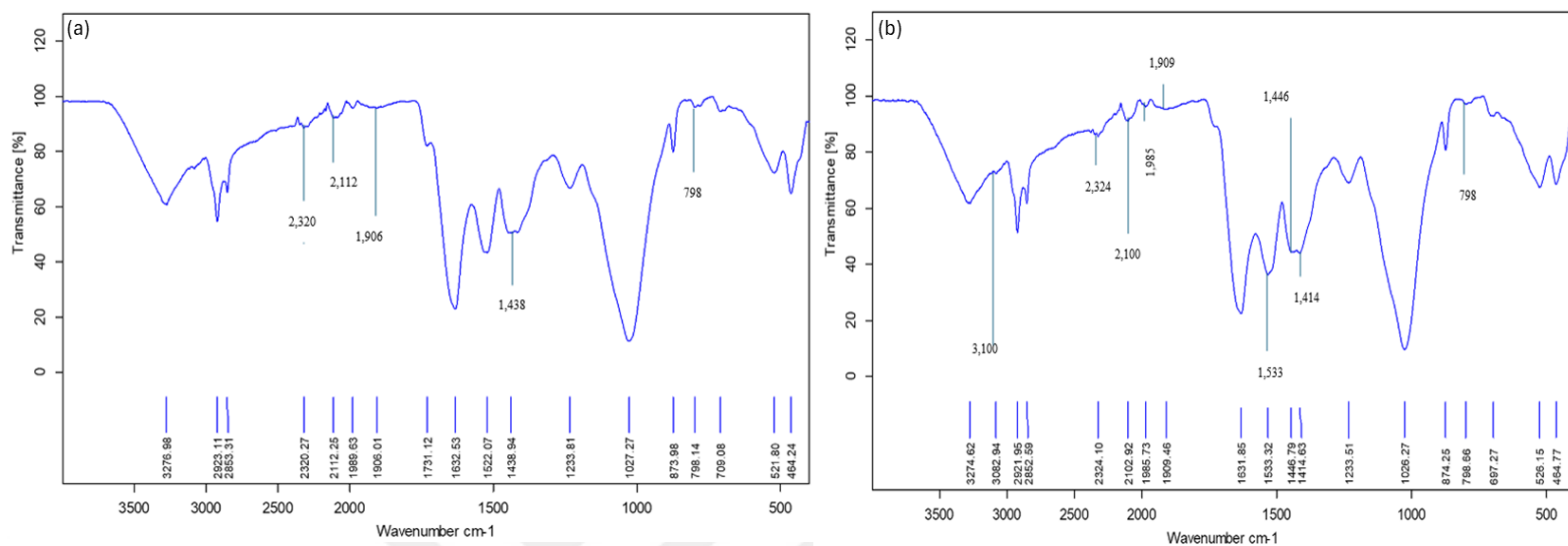


Figure 5.6 Functional group analysis based on FTIR for raw WBS (a) and disintegrated biosludge (b).

5.3. BMP Studies

5.3.1. Disintegration of WBS and BMP preparation

As a result of biological sludge disintegration optimization study using the RSM design, the MW operational conditions at the power of 900 W, the target temperature, heating rate and holding time of 90°C, 2°C/min, and 5 min, respectively, were chosen as the ideal conditions for biological sludge disintegration. After disintegration of biosludge under the MW optimum conditions, the BMP tests were carried out to determine the pretreatment effect on CH₄ production by comparing with raw biosludge.

The substrate/inoculum ratio (S/I), which effect the balance of microorganisms and efficiency of process, is a critical parameter in AD process ratio (Demichelis et al., 2022). Too high S/I ratio could lead to inhibition of microbial activity due to the acidification within the system by the destruction of balance and synergy between different microbial species (Li et al., 2022). On the other hand, at a low S/I ratio, maximum CH₄ production might not be achieved because lack of enough substrate to stimulate the enzymes required

for AD process (Ziaee et al., 2021). Considering the previous studies the ideal S:I ratios of 1:1 and 2:1 (Demichelis et al., 2022; Li et al., 2014, 2022; Ziaee et al., 2021) were selected in the BMP tests.

The BMP units fed with raw and the disintegrated biosludges were presented as C1, C2 and MW1, MW2 for the S/I ratios of 1:1 and 2:1, respectively. BMP tests lasted 54 days and before and after the tests analysis were carried out to evaluate the performance of AD and quality of wastewater. The raw and disintegrated biosludges composition were presented in Table 5.6.

The pH was between 6.65 and 7.81, which indicated that the S/I ratios were suitable. Previous studies suggest that the appropriate pH value for fermenting and methanogens microorganisms ranges 5.0 to 8.5 and 6.5 to 7.8, respectively (Fang et al., 2014; Houtmeyers et al., 2014; Yang et al., 2015).

Table 5.6 Characteristics of raw and pretreated WBS

Parameter	Units	Raw WBS	MW pretreated WBS
pH	–	7.58±0.11	6.84±0.08
EC	ms/cm	1.048±0.021	1.178±0.013
sCOD	mg/L	95±20	2,452±25
DD	%	–	70.87±3.6
Protein	g/L	0.653±0.0006	1.031±0.005
Sugar	mg/L	10.5±3	110±6
TS	mg/L	11,315±120	11,040±90
VS	mg/L	8,475±62	–
SS	mg/L	9,840±130	9,110±115
VSS	mg/L	8,780±69.5	–
NH ₄ -N	mg/L	10.3±0.31	22±0.73
PO ₄ -P	mg/L	17.6±0.42	33.6±1.32
Energy Consumption	kJ/gVSS	–	130.77
C	%	34.84	–
N	%	5.805	–
O	%	29.72	–
H	%	4.60	–
S	%	1.036	–

5.3.1.1. sCOD variation

As depicted in Figure 5.7, with the removal percentages of 71% and 73%, reduction in sCOD concentrations were observed for the C1 and C2 from 261.5 and 340 mg/L to 75.6 and 90 mg/L, respectively. In the MW1 and MW2 units, the sCOD concentrations dropped from 1,569 mg/L and 1,761 mg/L to 129 mg/L and 219 mg/L, respectively. The removal efficiency reached to about 92% and 88% for the MW1 and MW2, which were higher than the C1 and C2 units, respectively. The results indicated that the pretreatment of biosludges with MW irradiation provided more biodegradable compounds for the organisms compared to the control reactors results in the potential benefits in the AD process. Park et al. (2011) obtained about 51% COD removal efficiency when the biosludge was disintegrated at the target temperature of 80°C and MW power of 1,000 W with the irradiation time 5 min, while the efficiency was 38.1% for the control. After a reaction time of 25 days in the BMP with biosludge disintegrated in the MW (10 min. irradiation and power of 1,500 W) achieved a removal efficiency of 57%, whereas the control reactor only achieved 28% (Tas et al., 2018). It was reported that the sCOD removal efficiency significantly improved from 14% in the control reactor to 74% in the MW pretreated biosludge after a 15 min irradiation time and biogas was produced immediately after starting the reaction (Özön et al., 2019). In comparison to biosludges exposed to short period of irradiation and control BMP units, sCOD reduction was greater in the BMP units fed with MW pretreated biosludges at high energy and extended irradiation period (Christopher, 2019; Park and Ahn, 2011; Savoo and Mudhoo, 2018). The difference of sCOD reduction between the raw and pretreated biosludge caused from the inherent organic properties of raw biosludge, which restricted the efficiency of organic matter decomposition (Park et al., 2011).

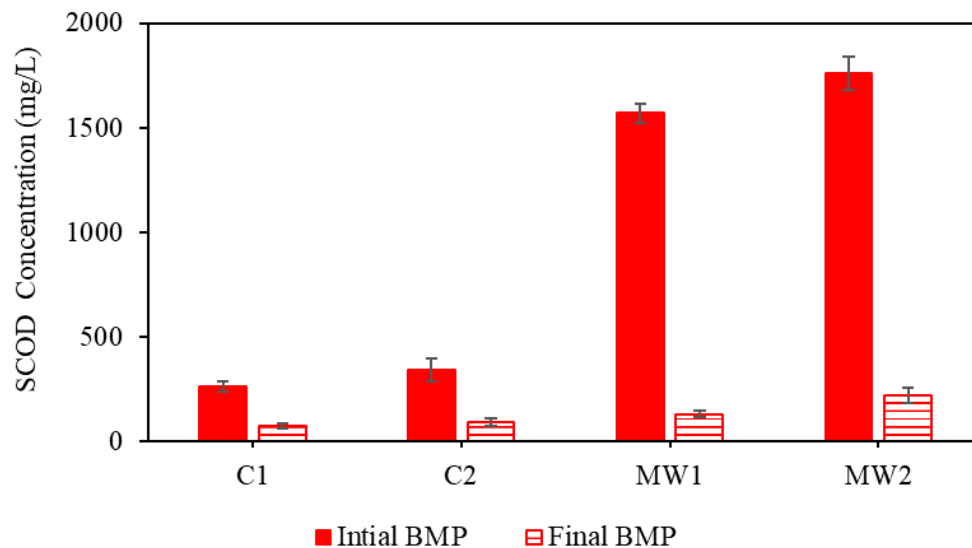


Figure 5.7 Variation of sCOD before and after BMP test

5.3.1.2. Protein variation

The protein concentrations obtained in BMP study are depicted in Figure 5.8. Protein concentrations decreased from 0.87 and 0.83 g/L to 0.72 and 0.56 g/L for C1 and C2, respectively, while in the MW1 and MW2, it decreased from 1.21 and 1.14 g/L to 0.60 and 0.65 g/L, respectively. Compared to controls, protein consumptions in the BMP units fed with MW treated biosludge were higher.

Three types of organic matters namely protein, carbohydrate, and lipid in the VS are consumed by the organisms in AD process and ultimately transformed into biogas (Wu et al., 2021). MW disintegration enhanced the degradation of extracellular polymeric substances. The reduction of protein found in the internal structure (exopolymers) of microorganisms rather than their external structure is attributed to its conversion to amino acids or completely $\text{NH}_4\text{-N}$ (Bougrier et al., 2007; Raszka et al., 2006; Yu et al., 2017).

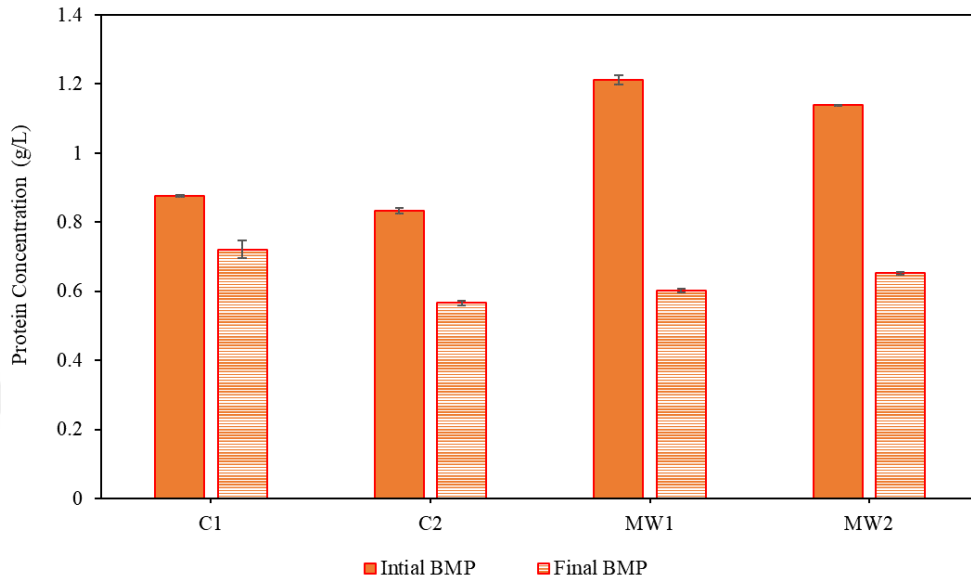


Figure 5.8 Variation of protein concentration before and after BMP test

Results of the previous studies also indicated significantly higher protein consumption in the AD process using pretreated biosludge than the control (Akbay et al., 2021; Appels et al., 2013; Houtmeyers et al., 2014). However, in the study conducted by Wett et al., (2010), they observed inhibition in the AD process with the thermal pretreatment of biosludge, particularly at temperatures between 160–180°C. It was noted that while protein hydrolysis increased with temperature, there was a significant increase in NH_3 concentration by 64% in the bioreactor, which negatively affected the gas production and protein reduction.

5.3.1.3. $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$ variation

Compared to the initial $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$ concentrations, the concentration significantly increased after AD of biosludges due to the destruction of organisms. $\text{NH}_4\text{-N}$ concentration was about 99 mg/L in the C1 and C2 and rose to about 310 mg/L with the AD process (Figure 5.9). Initial $\text{NH}_4\text{-N}$ concentration was about 90 mg/L in the control, at the end of BMP tests, increased to 367 mg/L and 425 mg/L in the MW1 and MW2, respectively. After the AD process, increase of $\text{NH}_4\text{-N}$ was approximately 3 and 4 times in the control and disintegrated biosludge fed units, respectively. $\text{NH}_4\text{-N}$

concentrations in the BMP units were lower than the inhibition level, which was reported as a typically concentration of 2,000 mg/L in the AD process (Wu et al., 2021). As could be seen from the results that release of $\text{NH}_4\text{-N}$ into medium was higher in the MW pretreated biosludge used AD process, compared to the controls.

Zhou et al., (2023) reported that the amount of soluble nitrogen increased when the protein hydrolyzed and medium was became more acidic. During the AD process, soluble nitrogen content in the liquid is gradually increase because the organic constituents such as proteins etc. are used as substrates by the anaerobic bacteria (Zhou et al., 2023). It was reported that the thermally pretreatment of biosludge was enhance the degradation of proteins and release of $\text{NH}_4\text{-N}$ during the AD process (Gahlot et al., 2022; Liu et al., 2018; Wu et al., 2020).

$\text{PO}_4\text{-P}$ concentration remained relatively stable before and after the BMP tests, except for reactor MW2, which increased notably about 24.3% (Figure 5.10). Bi et al. (2012) also observed about 25% $\text{PO}_4\text{-P}$ increase after the AD.

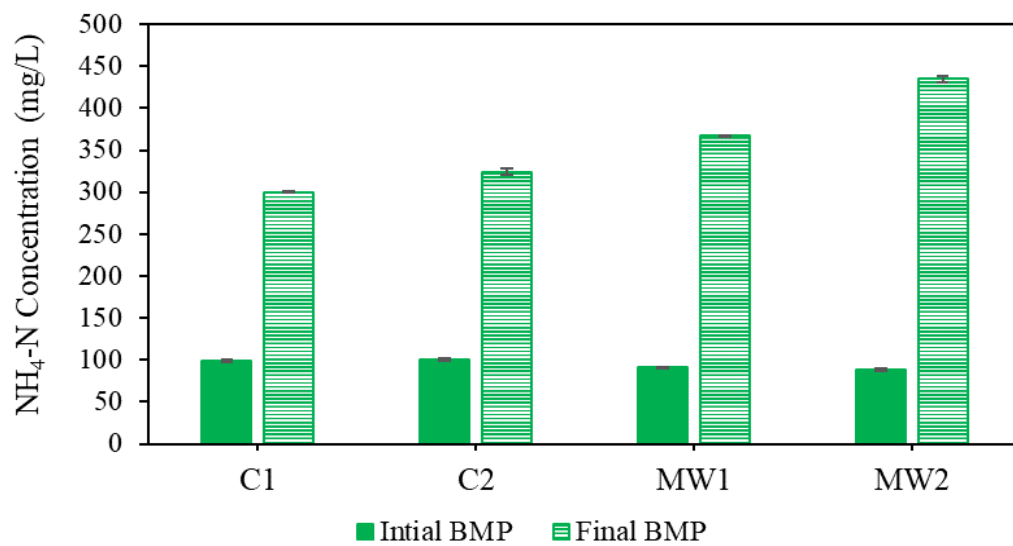


Figure 5.9 Variation of $\text{NH}_4\text{-N}$ concentrations before and after BMP

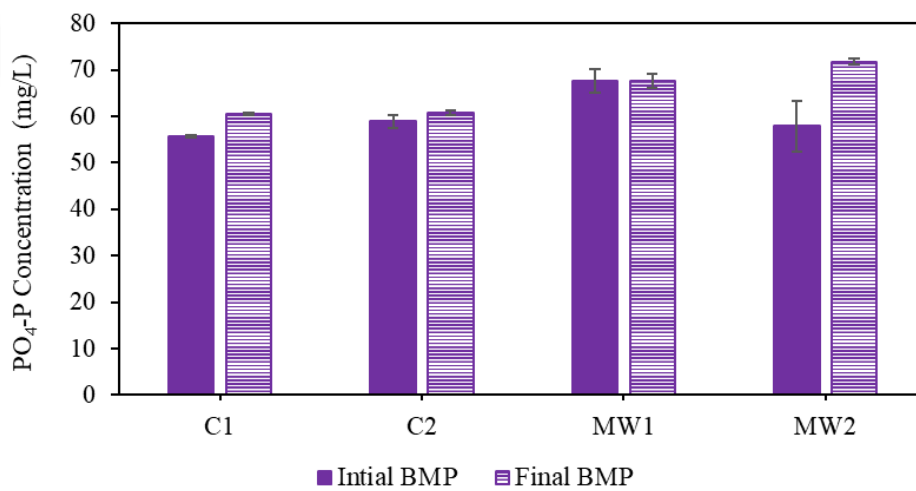


Figure 5.10 Variation of $\text{PO}_4\text{-P}$ concentrations before and after BMP

5.3.1.4. TS, SS and VSS variation

The solid and volatile compounds are the important parameter to evaluate the efficiency of anaerobic digesters. The TS, SS and VSS were measured in both control and MW disintegrated biosludge. Significant difference was not observed in the TS reduction about (28%–32%) between the control and MW pretreated biosludge (Figure 5.11).

Pilli et al., (2015) observed that despite about 2% increase of TS reduction in reactors with thermally disintegrated biosludge, there was no significant difference in the degradation of TS between the thermally treated and raw sludge at the end of AD process. Aboulfotoh et al., (2022) also reported the equal TS removal of about 15.9% for the MW pretreated and control reactors. These findings align with our study, indicating that the TS reduction was between the control and MW treated biosludge, which were already close together in terms of performance. Results indicated that there might be improvements with certain pretreatments like thermal disintegration, while the overall difference might not be substantial.

Figure 5.12 shows that there was a slight increase in the removal efficiency of SS in the MW pretreated reactors compared to controls. For the C1 and C2, the reduction were about 23.8% and 22.7%, respectively, while in the MW1 and MW2, the reduction were 25.3% and 29.7%, respectively. Compared to the control, about 7% SS removal efficiency in the AD process by the MW pretreatment of biosludge at the temperature of 120°C for 30 min was determined (Naran et al., 2016).

The VSS concentration in the C1 and C2 decreased from 7,080 and 7,390 mg/L to 5,330 and 5,130 mg/L, respectively, while it decreased from 6,537 and 6,747 mg/L to 4,100 and 4,040 mg/L in the MW1 and MW2, respectively (Figure 5.13).

Results indicated that in the pretreated reactors, the removal efficiency of both VSS and SS were higher compared to the control reactors. Specifically, VSS removal ranged from 37.3% to 44.2% in the pretreated reactors, while in the control reactors they ranged from 24.7% to 30.5%.

Organic matter reduction is a key indicator of efficiency, effectiveness, and environmental benefits of the AD processes (Lizama et al., 2018). The removal efficiency of VS was

more effective than that of SS in predisintegrated biosludge reactors because the VS was utilized by anaerobic bacteria in the AD process (Yao et al., 2016). The biosolids reductions, measured in VS and VSS, were approximately 60% (w/w) after 18 days digestion period for the thermally pretreated sludge (Ding et al., 2017). This reduction percentage was comparable to that achieved by untreated biosludge after a longer 30 days in AD process. The trends in biosolids reduction also indicated an accelerated CH_4 production during BMP tests for the thermally pretreated biosludge compared to secondary raw biosludge (Ding et al., 2017). A detailed investigation revealed that the pretreated biosludge with a temperature of 70 °C in the AD reactors obtained the most VSS elimination compared to control reactors (Yi et al., 2013).

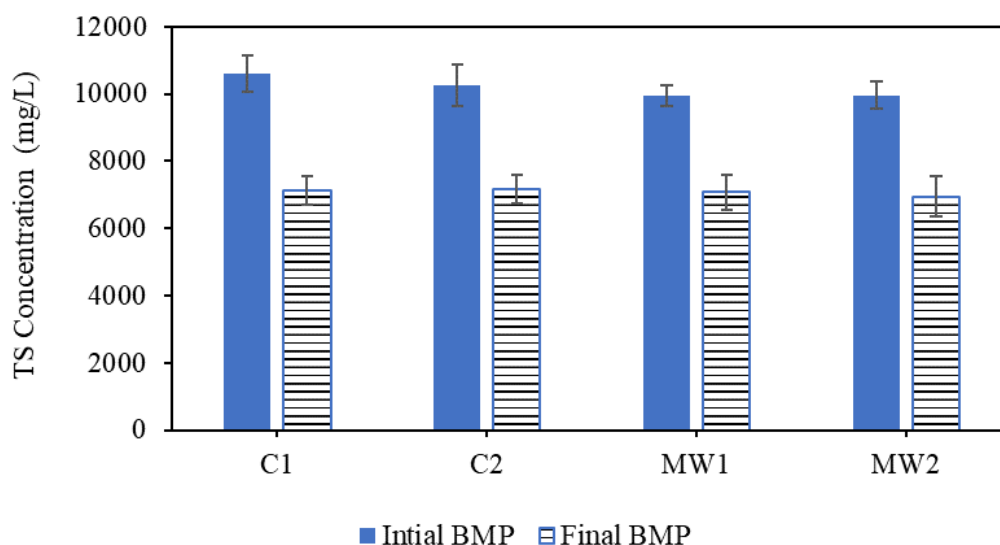


Figure 5.11 Variation of TS concentrations before and after BMP

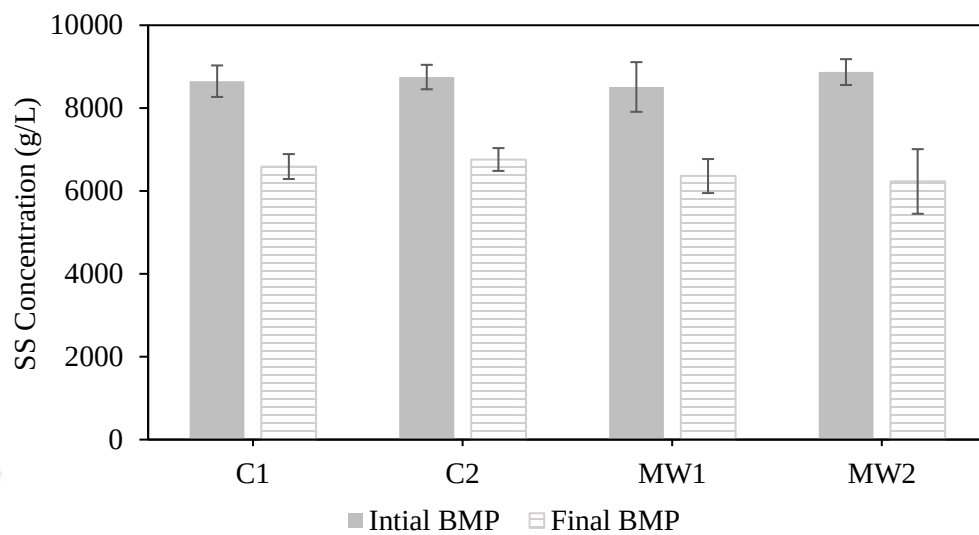


Figure 5.12 Variation of SS concentrations before and after BMP

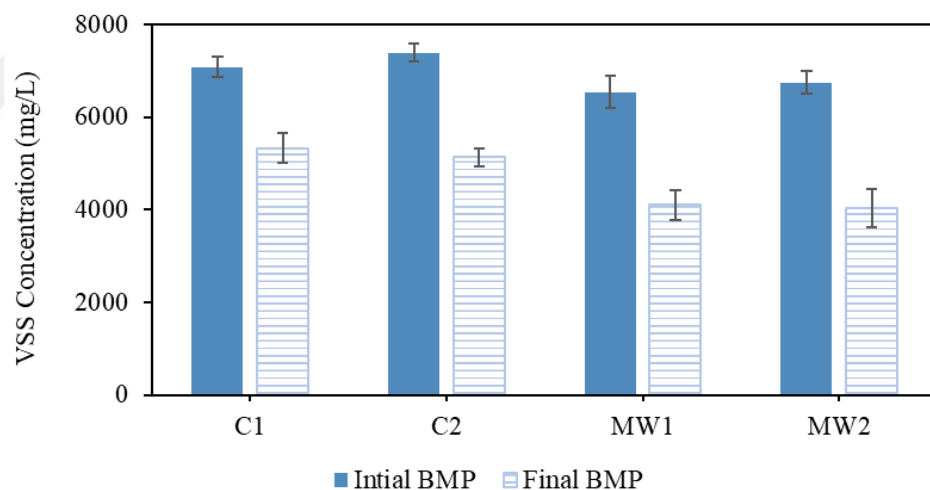


Figure 5.13 Variation of VSS concentrations before and after BMP

5.3.1.5. SFR variation

The filtration characteristics of biosludges, both control and MW pretreated, were tested. The SFR was used as a parameter to evaluate the dewaterability of biosludge. As can be seen from the Figure 5.14 that the SFR values increased significantly after the AD in all tests.

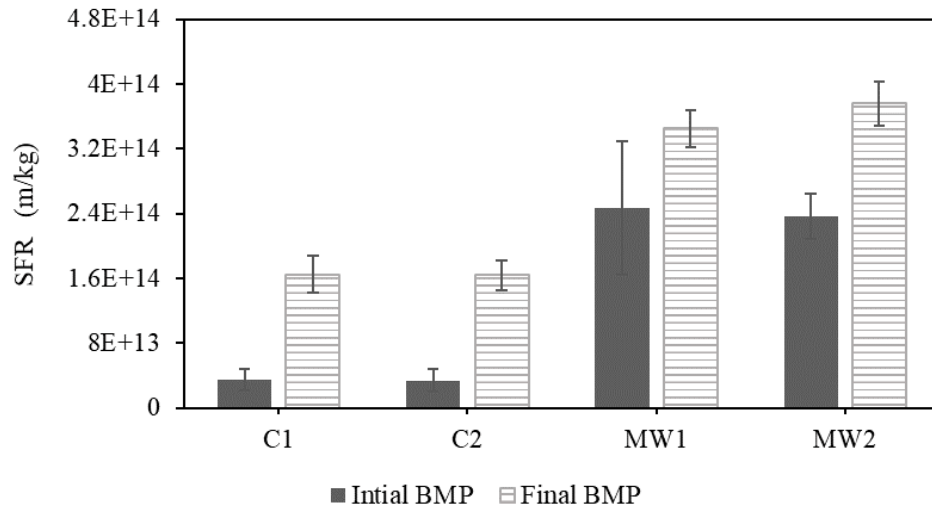


Figure 5.14 Variation of SFR before and after BMP test

In the C1 and C2, the SFR increased from 4.44×10^{13} m/kg and 3.38×10^{13} m/kg to 1.65×10^{14} m/kg and 1.64×10^{14} m/kg, respectively. The SFR for MW1 and MW2 elevated from 2.47×10^{14} m/kg and 2.37×10^{14} m/kg to 3.45×10^{14} m/kg and 3.76×10^{14} m/kg, respectively.

The deterioration of SFR, which indicated the decrease in ability of digested biosludge dewaterability, was reported for the application of AD process (Jang and Ahn, 2013; Park and Ahn, 2011) and thermal pretreatment (Liu et al., 2012; Zhang et al., 2021).

5.3.2. CH₄ production

The effect of MW pretreatment on AD of WBS with different mixing ratios (S/I) was studied using mesophilic-operated BMP tests. The results are presented in terms of daily CH₄ production as mL CH₄/g VSS.day and cumulative CH₄ production as mL CH₄/g VSS (Figure 5.15 and 5.16). The highest daily CH₄ production was 25.1 and 23.2 mL/gVSS.day for C1 and C2, respectively, while the production was significantly higher than the controls for MW1 and MW2 about 33.2 and 27.1 mL/gVSS.day, respectively. The improvement in CH₄ production was notable at the first days of BMP test. CH₄ production indicated that it was able to effectively balance between CH₄ production and acidification stage with a sufficient pH buffering capacity in the BMP units with the selection of convenient S/I ratio (Ma et al., 2019), particularly at MW1. The pretreatment of biosolids not only increase the hydrolysis and biodegradation of the slowly degradable biosludge particles but also ensured that the fermentation process proceeded smoothly without inhibitory effects, ultimately leading to efficient CH₄ recovery (Alagöz et al., 2018; Azizi et al., 2019; Jiang et al., 2018; Kor–Bicakci et al., 2019).

In the experiment, long reaction time in BMP time was due to the presence of complex organic compounds in controls that require more time for microbial decomposition. On the other hand, the extended period in the MW reactors was observed due to the presence of higher amounts of easily degradable materials in the pretreated digesters that continued to be utilized by methane bacteria. Similar observation was reported by (Eskicioglu et al., (2007 a,b,c).

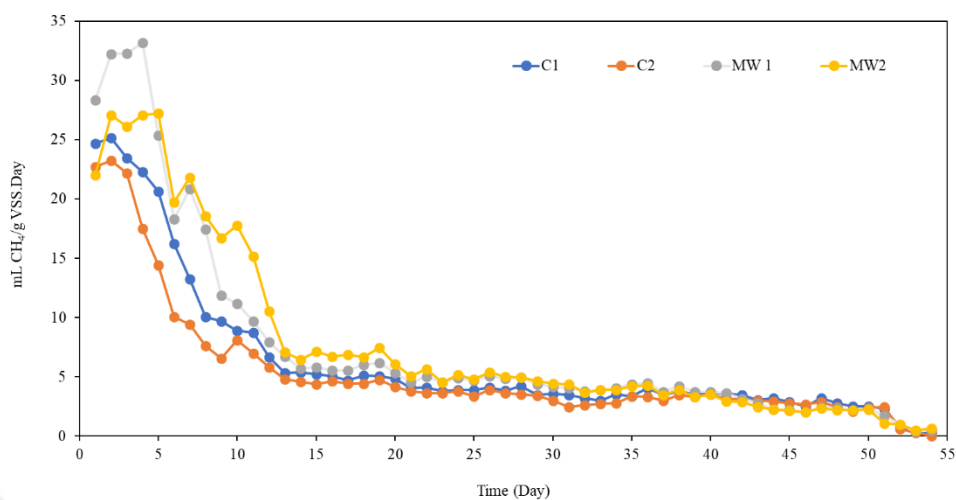


Figure 5.15 Daily CH₄ production

Cumulative CH₄ production in the C1 and C2 was about 366 and 288 CH₄ mL/gVSS, respectively. As expected, with the disintegration of WBS by the MW irradiation before the BMP test, significant improvement of CH₄ volume was determined and the cumulative CH₄ volume of 411 and 419 mL/gVSS was observed for the MW1 and MW2 reactor, respectively (Figure 5.16). The total CH₄ yield improvement by the biosludge disintegration was varied between about 12 % and 45%, compared to the control reactors.

Saha et al. (2011) reported that using MW pretreated WBS in batch digesters with a low heating rate of 1.35°C/min to 4.47°C/min resulted in a significant increase in CH₄ production (70%) compared to control samples. Following thermal pretreatment at the target temperature of 60°C, 80°C, and 100°C, it was observed the yield of CH₄ generation rose by 13.7%, 27.0%, and 29.0%, respectively (Biswal et al., 2020). Alqaralleh et al., (2019) observed an increase in the CH₄ yield from 303 mL/gVS to 429 mL/gVS by the application of pretreatment at a temperature of 95°C with a low ramping rate of 3.5°C/min. Similar CH₄ yield increase in the AD process by disintegration of WBS was reported in the literature under various operational conditions of MW (Ebenezer et al., 2015; Eskicioglu et al., 2008; Kennedy et al., 2007).

A high-intensity pretreatment, which longer irradiation times, improve the biosludge disintegration and release of soluble organics and nutrients, thus enhancing clean energy

production. When the large floc particles in the WBS are broken down by heat treatment into smaller, the availability of bioreadily degraded materials in the AD and the production of renewable CH₄ energy are enhanced (Eskicioglu et al., 2009; Eskicioglu et al., 2007 a,b,c; Kennedy et al., 2007; Koupaie et al., 2015; Saha et al., 2011).

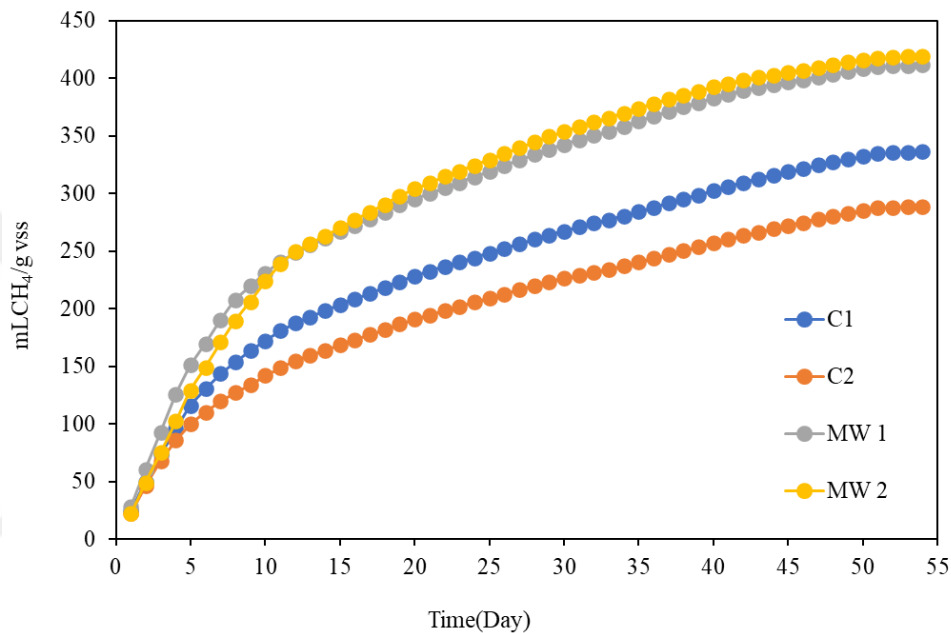


Figure 5.16 Cumulative CH₄ production

Despite the higher mixing ratio in the MW2, the deterioration of CH₄ production was not observed. The decrease in CH₄ production occurring in C2 might be due to the imbalance between acetogenic and methanogenic organisms activities because the accumulation of volatile acids (Haider et al., 2015) and need for more time to breakdown the complex organic compounds in the WBS (Chaher et al., 2023). By using the TS, VS, and elemental analyses of WBS, the basic chemical composition of biomass was determined as C_{7.1}H₁₁O_{4.5}N by using Buswell equation. Assuming that organic compounds were completely decomposed during the AD process and completely converted to CH₄ under ideal conditions, tBMP was calculated as approximately 424 mL CH₄/g VSS (Huynh et al., 2019; Yuan et al., 2019).

Considering the calculated tBMP, the highest biodegradation of approximately 98% was achieved in the MW2 with 419 mL CH₄/gVSS, followed by MW1 with 96% (Figure 5.17), whilst, the biodegradability was 79% and 68% for the C1 and C2, respectively. Results indicated that MW irradiation significantly enhanced the biodegradability and CH₄ production.

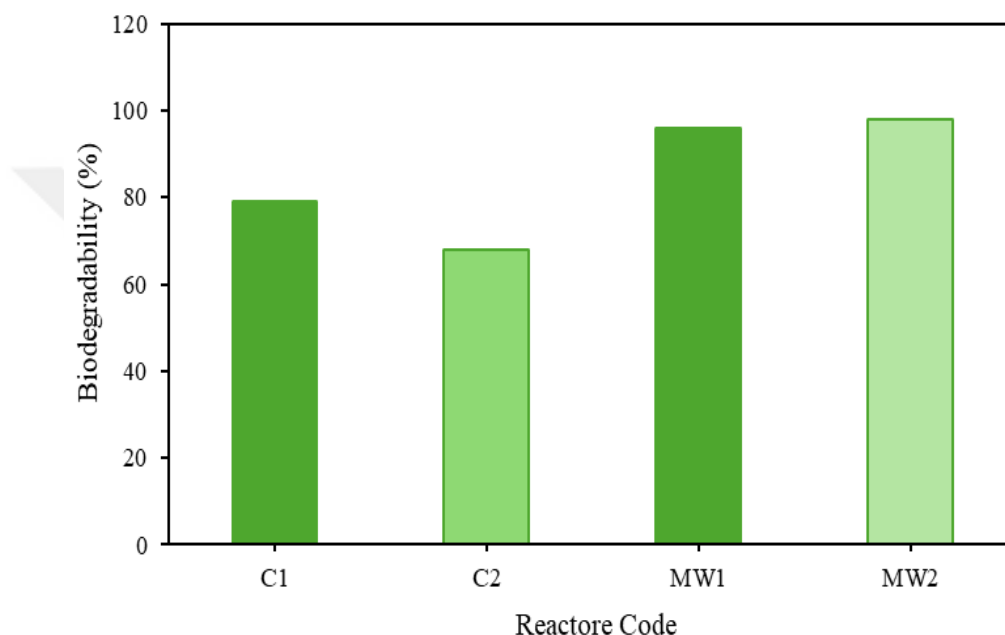


Figure 5.17 Biodegradability of raw and disintegrated biosludge

5.3.3. Kinetic studies

The kinetic models' predictions of CH₄ production during the mesophilic test are depicted in Figure 5.18–5.21. The kinetic parameters corresponding to these models are also presented in Table 5.7. All models demonstrated a notably high correlation coefficient (R^2) between 0.953 and 0.998. Compared to the First order, Gompertz modified, and Logistic models, the Transference Function model fitted the CH₄ production data the best overall. In the MW2 attained the highest R^2 value at 0.998 in Transference Function, followed closely by the First order model, which ranged from 0.967 to 0.992 in terms of R^2 value. When the performance models compared, especially two of the models;

Transference Function and First order had the highest R^2 of 0.99 and similar observation was reported in the previous studies (Kavan Kumar et al., 2023; Lihi et al., 2023).

The First order model rate constant (k) is a measure of rate at which a substance decomposes or reacts. In the context of biodegradation, k signifies the rate at which the biodegradable fractions are removed over time, leading to the production of biogas (Yusuf et al., 2011) and the rate of biogas generation increases with a positive and higher value of k (Budiyo and Sumardiono, 2014).

The k values recorded for C1, C2, MW1, and MW2 were 0.045, 0.057, 0.074, and 0.067 d^{-1} , respectively, as shown in Table 5.7. The reactors with pretreated biosludge exhibited higher k values indicated that the MW treatment was effective in releasing organics and accelerating bacterial access to these materials compared to the control, which prolonged cell breakdown occurred. Yangyang et al. (2016) noted that when organic waste was subjected to heat treatment at temperatures of 55°C and 70°C, there was a significant increase in k values compared to untreated substrates. The increase in k values by 15–47% and 4–47%, respectively, confirms the effectiveness of thermal treatment in enhancing the decomposition of organic matters, thus facilitating improved digestion performance (Li et al., 2016). Our results align with those of Rincón et al. (2016) who reported that the MW pretreatment had the highest k value of 1.95 d^{-1} at 4,377 kJ/kg TS of specific energy indicating a significant improvement over the control conditions.

In the lag phase (λ), bacterial cells adapt to new environmental conditions, synthesize enzymes and undergo various metabolic changes. Depends on the factors, such as the species of bacteria, composition of the growth medium, and environmental conditions, the actual growth rate during the lag phase slow or negligible (Li et al., 2016). Short λ level indicated the organisms adapted to conditions so fast, while the value of negative means that there was no significant lag time required for the organisms for utilizing the substrates (Abubakar et al., 2022). In such cases, λ is accepted zero that shows the biogas production begins almost immediately (Abubakar et al., 2022; Rajput et al., 2018).

In our study, the delay values ranged from 0.001 to 0.08 day with the lowest value determined for the Transference Function model 0.001 day. This suggests that no delay was recorded in all models, indicating that gas production commenced from the day of

incubation. Yuan et al., (2016) also reported that the Transference Function model had a shorter lag phase compared to other models.

Compared to the other models, the highest potential CH_4 production (A_0) and the maximum daily rate of CH_4 production (μ_m) was determined for the Transference Function. The A_0 and μ_m values for the pretreated biosludge reactors were higher than control group. For the models, A_0 values ranged between 286.8 mL/g VSS and 329.4 mL/g VSS and μ_m values ranged between 12.7 mL/g VSS.day and 16.3 mL/g VSS.day for the control. In the MW1 and MW2, A_0 values ranged between 418.8 mL/g VSS and 425.5 mL/g VSS, while μ_m values ranged between 16.4 mL/g VSS.day and 24.5 mL/g VSS.day. Results indicated that usage of disintegrated biosludge in AD process led to increase CH_4 production potential and maximum daily CH_4 production rates. The value of μ_m and A_0 were sequentially listed as follows; Transfer Function (23.97 mL/g VSS.day) > Gompertz modified equation (14.47 mL/g VSS.day) > logistic function (13.69 mL/g VSS.day) for μ_m and Transfer Function (211.4 mL/g VSS) > Gompertz modified equation (199.6 mL/g VSS) > Logistic (196.0 mL/g VSS) for A_0 (Li et al., 2012).

As can be seen from the Table 5.7 that the deviation for the models were lower than 5%. Rajput et al., (2018) reported that the prediction of CH_4 production from practical gas experiments was reliable if the deviation percentage was less than 10%. Considering this criterion, all models appeared to be valid because their deviations were within the acceptable range. However, the Transference Function model with the maximum deviation of 2% was accepted as the best among the applied models.

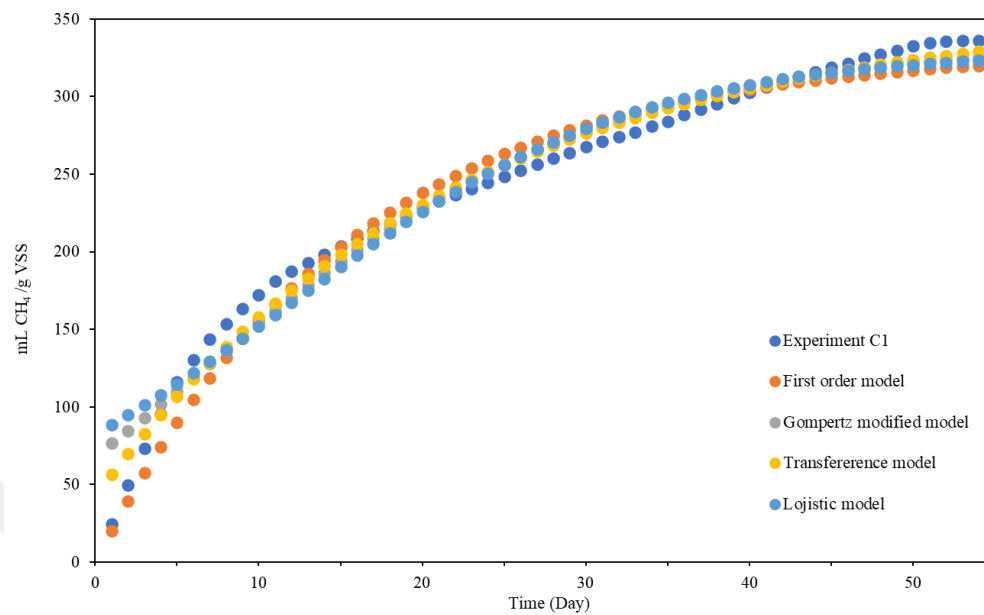


Figure 5.18 Cumulative production of CH₄-kinetic models for C1

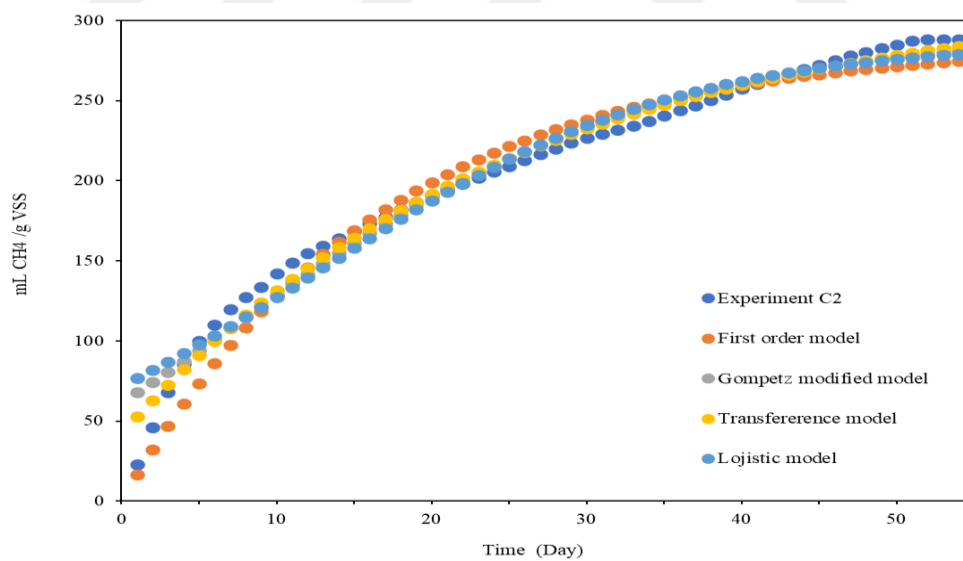


Figure 5.19 Cumulative production of CH₄-kinetic models for C2

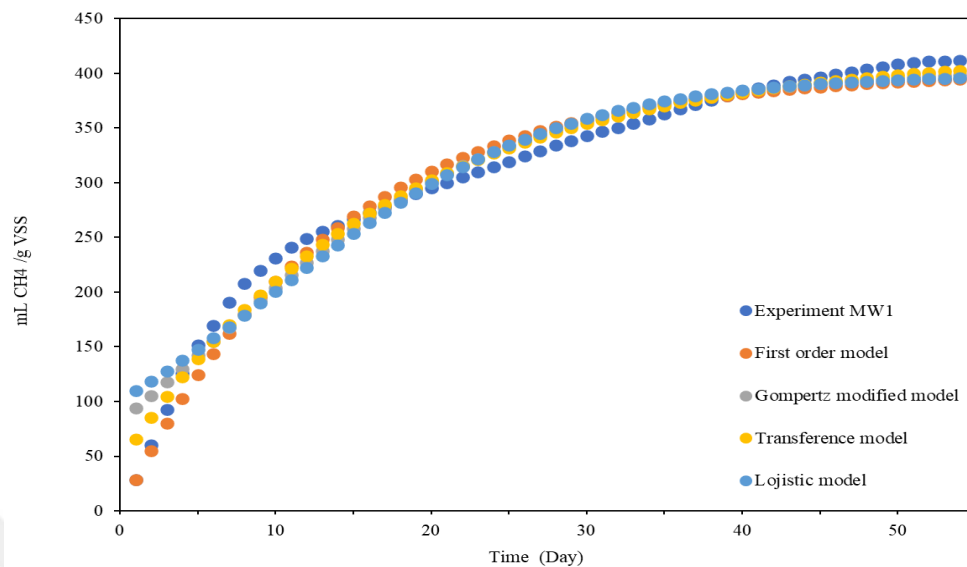


Figure 5.20 Cumulative production of CH_4 —kinetic models for MW1

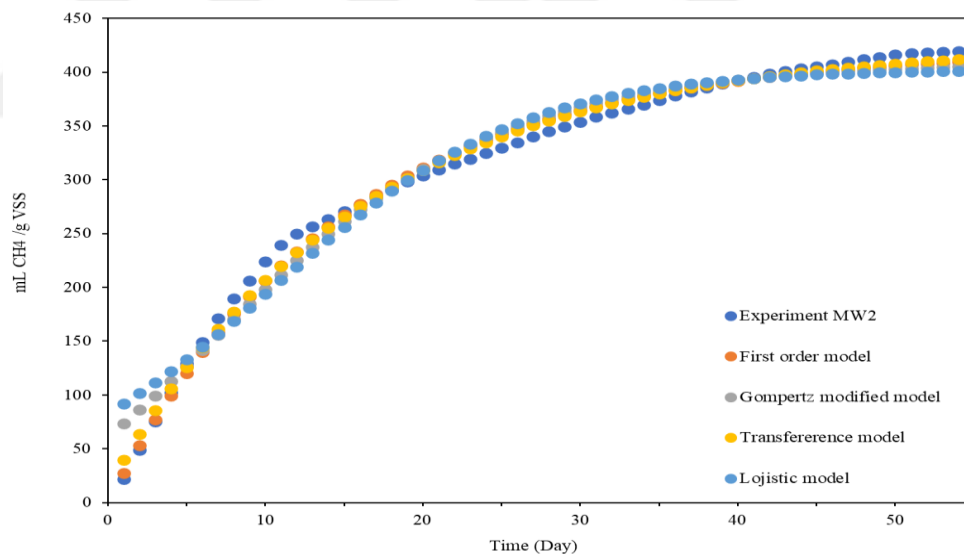


Figure 5.21 Cumulative production of CH_4 —kinetic models for MW2

Table 5.7 Kinetic parameters

Model	Reactor	R ²	Y (mL/gVS)	A ₀ (mL/gVS)	μ _m (L/gVS)	k (d ⁻¹)	λ (day)	Deviation (%)
First order	C1	0.971	320.12	330	–	0.045		4.8
	C2	0.967	274.66	286.196		0.059		4.9
	MW1	0.974	394.65	402.1		0.074		4.2
	MW2	0.992	409.39	420.4		0.067		2.4
Gompertz modified	C1	0.971	325.56	337.71	8.74		0.066	3.1
	C2	0.976	281.1	296.35	6.88		0.069	2.5
	MW1	0.967	398.4	405	12.55		0.070	3.2
	MW2	0.978	405.06	409.02	14.42		0.080	3.4
Logistic	C1	0.959	323.3	329.38	7.72		0.078	3.8
	C2	0.966	279.09	286.94	6.19	–	0.077	3.2
	MW1	0.953	395.72	399	10.83		0.079	3.9
	MW2	0.962	401.11	402.75	12.75		0.076	4.4
Transference Function	C1	0.985	329	355.04	12.75		0.001	2.1
	C2	0.987	283.97	316.69	16.33		0.0011	1.5
	MW1	0.983	402.68	418.8	16.47		0.001	2.2
	MW2	0.993	411.8	425.5	24.5		0.0012	1.9
Experiment	C1	0.909	336.28	–	25.2	0.0462	0	–
	C2	0.928	288.36		23.12	0.0521	0	
	MW1	0.857	411.91		35.29	0.0534	0	
	MW2	0.869	419.69		32.09	0.0563	0	

5.3.4. Struvite precipitation after BMP

After the BMP tests, the concentration of NH₄–N significantly increased, which was determined higher than 300 mg/L (Figure 5.9).

Before the struvite precipitation experiments with the supernatant of BMP tests, optimization experiments were carried out with synthetic wastewater in the laboratory to determine the molar ratio range considering previous studies (Ander, 2010; Lavanya et al., 2021; Öztürk and Bali, 2023; Tonetti et al., 2016; Kim et al., 2017; Muhmood et al., 2018; Zhang et al., 2009). In the struvite precipitation tests, Mg:N:P molar ratio of 1:1:1, 1.15:1:1, 1.25:1:1, 1.5:1:1 and 1.50:1.15 were selected considering previous experiments. Taking into account the initial Mg, NH₄–N and PO₄–P concentrations of the BMP test supernatant, the ions required for effective struvite precipitation were added to the liquid by calculating the missing amounts.

Increasing the molar ratio enhanced the removal efficiencies of both $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$ in the wastewater. As can be seen from the Figure 5.23 that the highest $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$ removal efficiency of about 90.06% and 90.41% was obtained at the mixing ratio of 1.50:1:1.15.

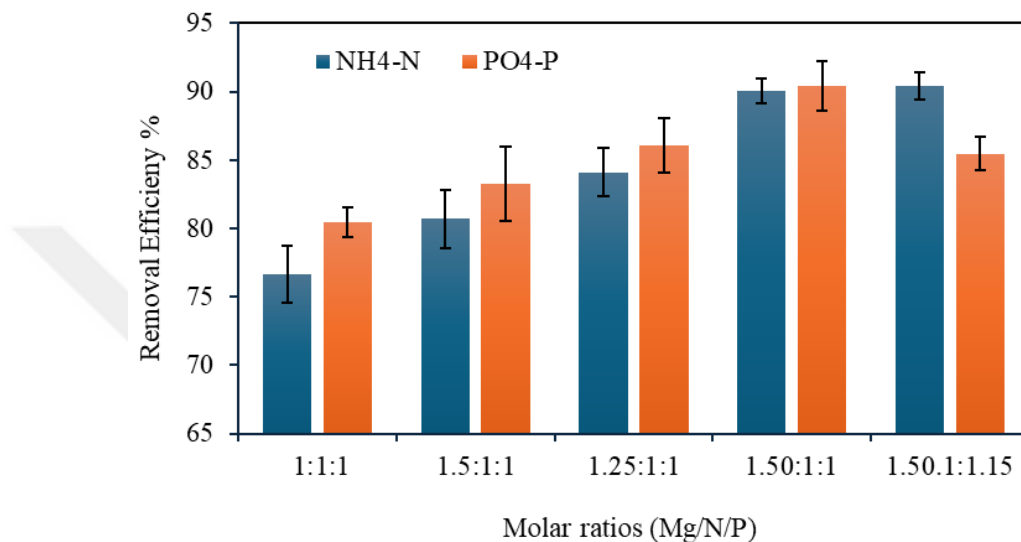


Figure 5.22 Removal efficiency of $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$ after struvite precipitation

The R^2 value represented the proportion of variance in the dependent variable (nutrient removal) that was predictable from the independent variable (the mole ratios of Mg:N:P). With R^2 ranging from 0.983 to 0.986, which indicated that the independent variable explained approximately 98% of the variability observed in the dependent variable. It means a strong and highly significant relationship between the increased mole ratios and nutrient removal.

From the SEM, EDX and XRD analysis, comprehensive insights into the physical, chemical, and structural properties of the precipitate can be obtained. From the SEM image it could be seen that a rod-shaped crystalline formations interconnected, resembling an X dendritic growth exhibiting the branches (Figure 5.23). Similar struvite crystal SEM image was reported by Meira et al., (2020).

The XRD profile peak shape of precipitate was detected as a crystal characteristic peak coinciding with the standard powder diffraction card peak of MAP, which demonstrated that the precipitate formed was struvite (Figure 5.24). The morphology and microstructure

of precipitates produced in the anaerobically digested supernatant at pH 9.5 were characterized. The locations and intensities of peaks in XRD pattern were determined to be like those in the reference struvite diffraction pattern ranged from 15° to 33° , which was the highest. The peak positions are consistent with the relevant literature (Kwon et al., 2021; Liu et al., 2020; Uysal et al., 2014; Uysal and Aydoğan, 2022). 2θ Characteristic diffraction peaks at 15.778° , 16.414° , 20.826° , 21.428° , 31.888° , and 33.225° indicated that the struvite target product was present in all sediments.

The EDX analysis also confirmed the presence of distinct absorption peaks for Mg, P, and N in the precipitate sample (Figure 5.25). As can be seen from the Figure that N and oxygen peaks appeared overlapping, but the oxygen peak was higher than the nitrogen peak. It was reported that an accurate identification of nitrogen became difficult because oxygen peaks were often stronger or more pronounced than nitrogen peaks. (Muhmood et al., 2018; Uysal et al., 2017).

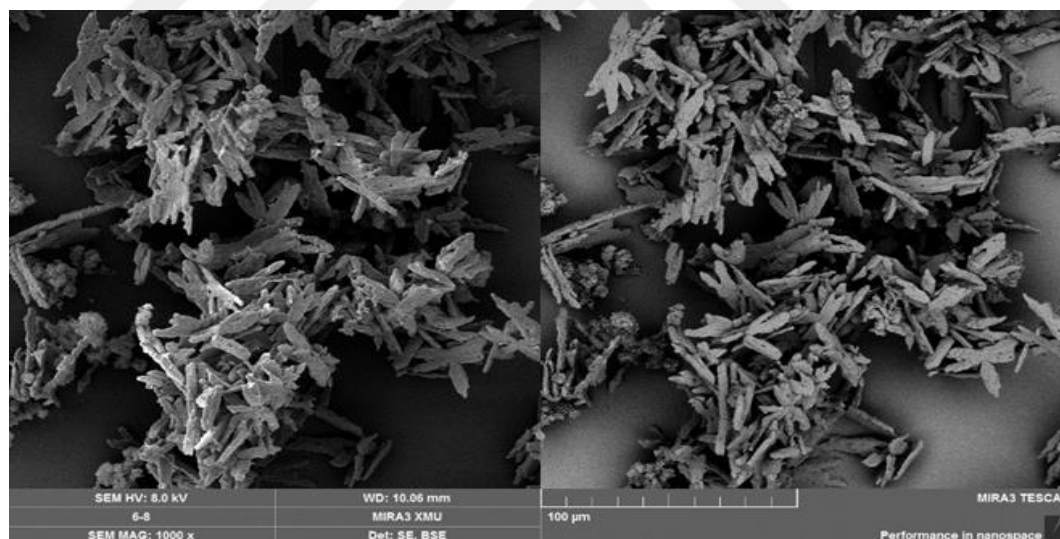


Figure 5.23 SEM image of precipitate under optimum conditions (pH = 9.5 and Mg:N:P =1.50:1:1)

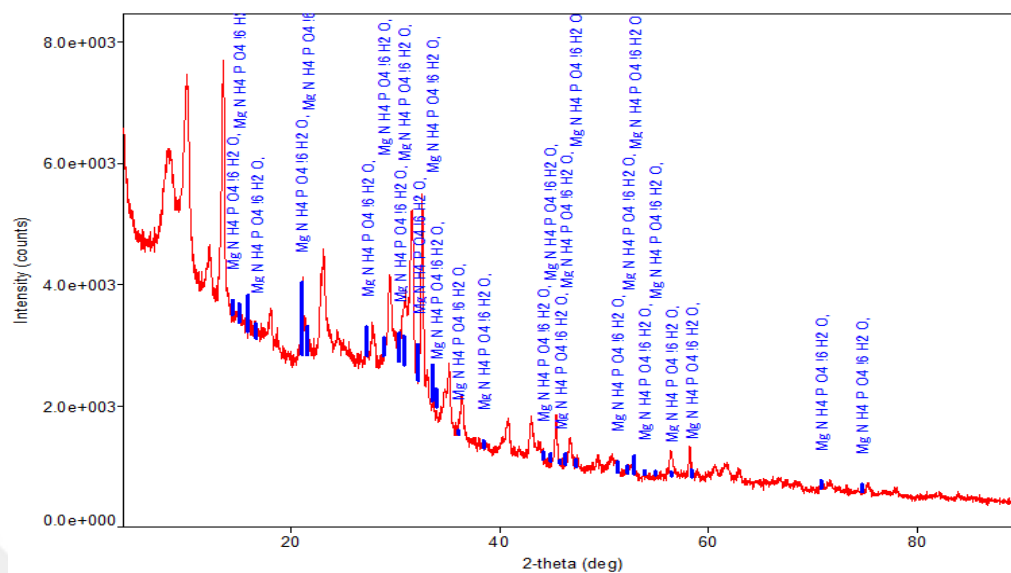


Figure 5.24 X-ray analysis for precipitate (pH = 9.5 and Mg:N:P =1.50:1:1)

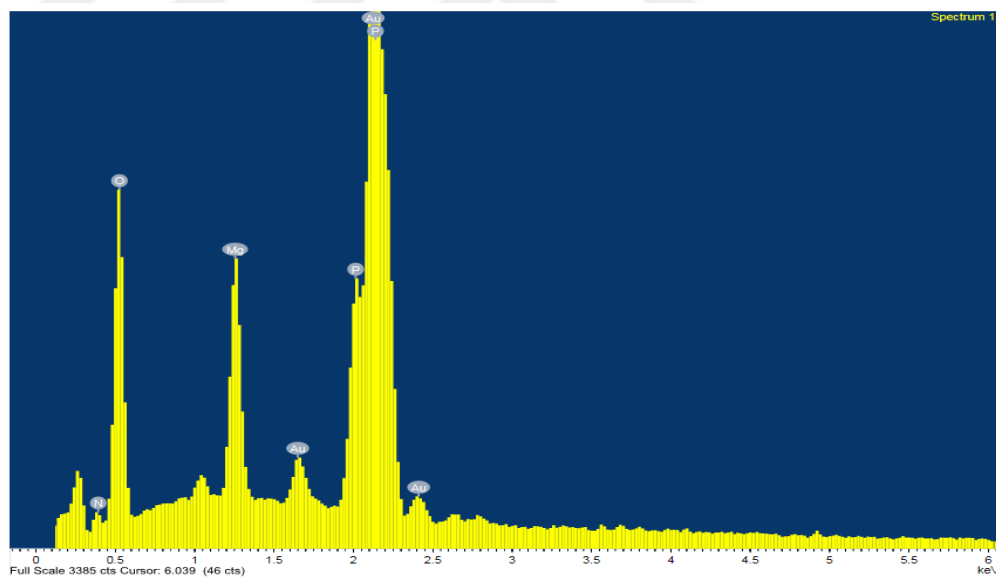


Figure 5.25 EDX data of dry precipitate (pH = 9.5 and Mg:N:P =1.50:1:1)

5.3.5. Energy assessment

Key factors in the design and operation of biosludge pretreatment plants are energy efficiency and energy recovery. The biosludge pretreatment systems may be made more economically viable and energy efficient by carefully assessing factors including target temperature, residence time, process design, and energy recovery possibilities (Kuglarz et al., 2013).

A crucial factor in determining the practicality of pretreatment methods on a broad scale is energy concerns. The extra CH₄ generated because of carrying out the pretreatment stage should, in theory, be sufficient to meet the energy requirements (Passos et al., 2013). The energy balance of MW pretreated WBS as shown in Table 5.8. The energy output to energy input ratio (E_o/E_i) was less than 1, ranging from 0.018 to 0.032, which indicated that the energy obtained from the AD process was significantly lower than the energy required for the MW operation. Even though the CH₄ produced in AD process after pretreatment was greater than that achieved in the control reactor, the improvement in CH₄ production was not sufficient to meet the energy requirement of MW disintegration.

The E_o/E_i ratio is greater than 1 indicates that the energy production exceeds the energy input, indicating positive energy generation (Passos et al., 2014). However, the E_o/E_i ratio is less than 1 indicates that the excess CH₄ energy output of the pretreated reactor is less than the energy input, resulting in a net negative energy production (Akgul et al., 2017; Hephzibah et al., 2015; Kavitha et al., 2018; Passos et al., 2013).

The slow heating rates increase the irradiation time in MW pretreatment result in more energy input (1.35–4.47°C/min, with heating periods ranging from 20 to 130 min) (Alqaralleh et al., 2019; Saha et al., 2011). Additionally, the VS concentration of WBS can also affect the MW energy consumption. The MW energy consumption is elevated at low VS contain WBS disintegration to achieve the desired level of pretreatment. Optimizing the VS concentration of WBS can improve the energy balance of MW pretreatment processes (Passos et al., 2013).

WBS thickening and dewatering may be necessary for more energy-intensive MW pretreatments (Córdova et al., 2018; Passos and Ferrer, 2015). Although techniques such as ultrasonication, MW, and steam explosion result in higher biomass solubility, they may

not always yield high biogas production due to the release of toxic or inhibitory compounds that may inhibit the AD process (Córdova et al., 2018). Kor–Bicakci et al., (2019) emphasized that while more intense pretreatment conditions led to higher solubilization and up to a 20% increase in biogas production, they also resulted in significantly higher specific MW energy input. Compared to the systems like UV and radio frequency (RF), the MW irradiation is still more costly for the biosludge pretreatment in large-scale applications (Kor–Bicakci et al., 2019). The net energy production following MW pretreatment in previous study is summarized in Table 5.9.

Table 5.8 Energy analysis of biosludge pretreatment

E_i (kJ/g VSS)	Ultimate CH₄ (mL/gVSS)	ΔCH₄ (m³/gVSS)		E_o (kJ/g VSS)	E_o/E_i
130.77	C1	336.30	MW1–C1	^a 2.43	0.018
	C2	288.36			
	MW1	411.91	MW2–C2	^a 4.23	0.032
	MW2	419.68			

a: represents the result of energy output after applying the CH₄ production difference (MW–C).

Table 5.9 The net energy produced in AD fed with the pretreated

E_i	Unite	E_o	*E_n	E_o/E_i	Reference
130.7	kJ/gVSS	2.43 4.23	–127	0.018–0. 032	Current study
28,580	kJ/tonne TS	1,847	–26,733	0.064	(Saha et al., 2011)
36,700	kJ kg VS	525.3	–36,174	0.014	(Passos et al., 2013)
269.4	kWh	43.6	–225.8	0.16	(Peng et al., 2018)
29,703	kWh/tonne VS	7,654	–22,049	0.2	(Alqaralleh et al., 2019)
612	kJ	1.74	–610	0.003	(Hephzibah et al., 2015)
70.3	kJ/g VS	3.22	–67	0.045	(Passos et al., 2014)
145.1	kJ/g **tVS	2.7	–142.4	0.018	(Jackowiak et al., 2011)

*E_n: net energy (E_o–E_i); **tVS: total volatile solid

5.4. BMP of centrifuged biosludge (CBs)

The temperature rises of biosludge during MW irradiation is directly related to its water content. Water, with its dipolar molecular structure, can absorb energy from MW irradiation and gradually become warmer. However, the temperature increase varies depending on the water content of the biosludge sample (Tang et al., 2010). Due to the high thermal capacity of water, which provides more energy absorption with only a slight increase in temperature, a relatively faster elevation of temperature in the biosludges with low water content was determined compared to those with high water content (Tang et al., 2010; Zaker et al., 2019). The biosludge concentration plays a crucial role in assessing the energy and economic feasibility of pretreatment processes. The energy requirements of biosludge often measured in kWh/m³, depends heavily on the characteristics of biosludges which its concentration, composition, and physical properties. If the TS concentrations of biosludge is high, generally require less energy for pretreatment compared to lower concentrations. It was reported that an additional 0.2 kWh of energy was consumed in the pretreatment process for every additional kilogram of TS in the biosludge (Cano et al., 2015).

The previous experimental studies indicated that the MW process was not economic due to its high energy input for the pretreatment of raw biosludge contains low amount of TS (Kor-Bicakci et al., 2019; Koupaie et al., 2018; Ruiz-Hernando et al., 2013; Ya-Wei et al., 2015).

5.4.1. CBs preparation

The biosludge was centrifuged and the supernatant was drawn, while a low liquid volume was intentionally kept at the upper of biosludge to avoid a high concentration that could negatively affect the heat transfer and absorption of MW energy in the reactor (Fang et al., 2017). After the biosludge centrifugation, the TS content increased from about 1.27% to 3.4%. Chemicals were not used in the biosludge thickening. The biosludge was transferred to a glass beaker and then the MW disintegration was performed at the target temperature of 90°C with the ramping rate of 2°C/min and 5 min holding time.

The BMP tests were carried out by using raw biosludge (Bs), pretreated biosludge (PBs), centrifuged biosludge (CBs), and pretreated centrifuged biosludge (PCBs). The BMP test

was performed with the biosludge with the TS ratio of 3.4% in order to evaluate the input energy requirement of MW disintegration and increase the E_o/E_i ratio.

5.4.2. Effect of MW irradiation on biosludge solubilization

5.4.2.1. sCOD solubilization

As in previous experiments, centrifuged biosludge degradation by MW irradiation was successfully achieved Table 5.10. Increasing the solid content of biosludge with centrifugation resulted in significant increase in the organic compounds, such as sCOD, protein and sugar release into the medium after MW irradiation.

Table 5.10 Characteristics of pretreated biosludge before and after centrifuge

Parameter	Unite	Raw Biosludge (Bs)	Pretreated Biosludge (PBs)	Centrifuged biosludge (CBs)	Pretreated Centrifuged Biosludge (PCBs)
pH	–	7.17 ±0.04	6.85±0.08	7.31±0.09	6.89±0.11
EC	ms/cm	1.37±0.05	1.54±0.03	1.33±0.04	1.27±0.01
TS	mg/L	12,650±92	10,605±250.5	34,066±933	27,915±1975
VS	mg/L	9,175±25	7,990±190	24,300 ±1633	21,190±1475
sCOD	mg/L	72.6 ±6	2,986± 126	81.4±11	6,400±320
Protein	g/L	0.385±0.025	1.08± 0.019	0.42±0.04	2.16±0.15
Sugar	mg/L	7.5±0.55	78±3	10.4±1.6	216.4±6.6
NH ₄ –N	mg/L	3.6±0.015	11.5±2	4.8±0.03	21.5±1.62
PO ₄ –P	mg/L	6.56±0.4	22.6±1.4	8.35±2.1	37.5±3.5
specific energy consumption	kJ/gVS	–	301	–	108.8

Initially, the sCOD concentrations in Bs and CBs were between about 72–81 mg/L. After applying MW irradiation, a significant increase in sCOD concentrations was detected and reaching up to 6,400 mg/L in PCBs, while it was approximately 3,000 mg/L for PBs. Increase of the TS concentrations in PCBs caused the release of sCOD about two times higher than the PBs by the application of MW irradiation. Specific energy consumption for the MW irradiation was determined about three times lower than the untreated biosludge.

Gil et al., (2019) reported that the sCOD release increased significantly in the centrifuged sludge pretreated at a specific energy of 18,000 kJ/kg TS. Tang et al. (2010) observed that

a high water content prevented the biosolids from dissolving at a given energy, but a low water level might promote the breakdown of organic matter with a lower energy input.

Park et al., (2010) demonstrated that the biosludge solubility (sCOD/tCOD) rose from 6% for the raw biosludge to 16–17% for centrifuged biosludge when subjected to the MW power of 400 W and temperatures ranging between 90–120°C. Similar results on the significant elevation of sCOD concentrations by the thermal pretreatment of biosludge contain high TS were reported (Dai and Zhou, 2010; Fang et al., 2017; Jeong et al., 2019; Jiang et al., 2021). However, in the biosludge containing too high TS, deterioration in the solubility and corresponding decrease in sCOD concentration occurred due to high viscosity that restricts heat transfer (Ahn et al., 2021). Jeong et al., (2019) reported that in order to achieve effective pretreatment when the thermal pretreatment was applied to the biosludge with high solids concentration more than 10 %, it was necessary to increase the thermal energy input or extend the residence time.

5.4.2.2. Protein and sugar releasing

Compared to the PBs, as expected that the MW pretreatment significantly increased the release of organic contents from the CBs. Protein concentration was 0.385 g/L and 1.08 g/L in the Bs and PBs, respectively. While the protein concentration of CBs was 0.42 g/L, after MW pretreatment increased to about 2.2 g/L. Significant improvement of protein concentration was determined for the PCBs which was about two times higher than the PBs.

As observed from the increase in sCOD and protein concentrations, the sugar content in the Bs about 10 mg/L improved about 10 and 22 times for the PBs and PCBs, respectively after the MW disintegration. Previous experimental studies were also indicated the release of sCOD, sugar, and protein from centrifuged biological sludge improved significantly after MW pretreatment at various operational MW conditions (Braguglia et al., 2015; Koupaie et al., 2017; Kor–Bicakci et al., 2019; Liu et al., 2016; Mehdizadeh et al., 2013; Yan et al., 2013).

5.4.2.3. $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$ releasing

As can be seen from the Table 5.10 that initial $\text{NH}_4\text{-N}$ concentrations were 3.6 mg/L and 4.8 mg/L for Bs and CBs, respectively, while by the pretreatment significantly increased to 11.5 mg/L and 21.5 mg/L, for PBs and CPBs respectively. Similar elevation of $\text{PO}_4\text{-P}$ concentration was also observed after MW irradiation. The highest $\text{PO}_4\text{-P}$ concentration of 37.5 mg/L was determined in the PCBs.

Depending on the TS concentrations in biosludge, release of $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$ by the pretreatment is varied (Fang et al., 2017; Jeong et al., 2019). Based on the results of one-way analysis of variance, a significant relationship between biosludge concentrations and the release of organic and inorganic nutrients after MW pretreatment was established. As the density of biosludge increases, there was a notable increase in the release of nutrients compared to raw biosludge (without centrifugation). The regression coefficients and corresponding p-values were as follows: sCOD ($R^2 = 0.995$, p-value = 0.03); Protein ($R^2 = 0.996$, p-value = 0.001); Sugar ($R^2 = 0.997$, p-value = 0.001); $\text{NH}_4\text{-N}$ ($R^2 = 0.921$, p-value = 0.040) and $\text{PO}_4\text{-P}$ ($R^2 = 0.955$, p-value = 0.022).

5.4.2.4. TS and VS reduction

The TS and VS contents of 12,650 mg/L and 9,175 mg/L in the Bs, and after centrifugation elevated to about 34 g/L and 24,3 g/L, respectively. With the MW disintegration of biosludge, about 16% and 13% reductions of the TS and VS were determined, while the reduction of centrifuged biosludge were about 18% and 10%, respectively. Following the biosludge's exposure to 30 min total irradiation time at the target temperature of 80°C, determined the reduction of TS and VS were 10% and 12.5%, respectively Fang et al., (2017). With the increasing MW intensity from 50% to 90% resulted in the significant reduction of 15.2% in TS over a 15 min irradiation period was reported by Uma Rani et al., (2013). Saha et al., (2001) reported similar observation with our results that indicating that MW pre-disintegrated biosludge at a low heating rate of 1.35–4.47°C/min enhanced the TS and VS reduction in comparison to the control group. Hephzibah et al., (2015) reported that the irradiation time of biosludge correlates with the decrease of VSs after

AD process and for the MW irradiation time of 5, 10, and 15 min, the VS reduction of about 27.2%, 28.8% and 30.6 % were obtained, respectively.

5.4.3. BMP studies

5.4.3.1. sCOD variation

Because of the effectiveness of MW disintegration of biosludge, the sCOD concentrations prior to the BMP test with PBs were typically greater than the control test fed with the Bs. In the control BMP, initial sCOD concentration was about 286 mg/L and decreased to 208 mg/L after the BMP test. In contrast to the decrease observed at the BMP test fed with raw Bs, sCOD concentration was increased from 295 mg/L to about 500 mg/L at the end of BMP test carried out using CBs.

CH₄ is produced as a result of consumption of organic substances released during AD process, which was carried out adding biomass as a substrate at the beginning of the BMP test. During the BMP test, primarily easily biodegradable organic compounds, which are released by the breakdown of biomass are consumed by anaerobic bacteria. The increase in sCOD concentration as a result of BMP test was due to organic compounds that could not be utilized by bacteria.

Throughout the AD process, upward trend of sCOD was observed when the biosludge contained solids of 9–10% was fed because of the accumulation of intermediates products such as VFA, which was depending on the sCOD concentrations (Takashima and Yaguchi, 2021). High accumulation of organic (VFA) or inorganic (NH₃) (Fang et al., 2017; Jeong et al., 2019; Gil et al., 2019; Ruffino et al., 2015; Yu et al., 2010) compounds in the reactor could create unfavorable conditions for methanogenic bacteria (Takashima et al., 2021).

When the anaerobic sludge digester contains high solids, the movement of soluble substrates within the medium is governed primarily by diffusional rather than convective transport (Liao et al., 2014). This means that the movement of sCOD and dissolved organic carbon (DOC) depends primarily on molecular diffusion rather than bulk fluid flow. The accumulation of soluble organic matter, especially sCOD can lead to formation of supernatant with high concentrations of these compounds. Since these substrates are

not efficiently converted into biogas due to insufficient mixing and microbial access, they contribute to the accumulation of sCOD in the supernatant (Liao et al., 2014).

The sCOD concentrations at the beginning and end of BMP tests, which was carried out in 71 days, for the Bs and CBs samples were presented in Figure 5.26. In the pretreated reactors designated as BMP units PBs and PCBs, the sCOD reduction was higher compared to the control. Initially, the sCOD concentration in reactors PBs and PCBs was 1,697 mg/L and 5,775 mg/L, respectively. After the BMP test, with a sCOD removal efficiency of about 73%, concentration decreased to 464 mg/L and 1,548 mg/L in reactors PBs and PCBs, respectively. Experimental results indicated that the MW pretreatment process was effective in producing the biodegradable organics in the AD process.

The decrease in TS, VS, and sCOD concentrations after the digestion process indicated that the organics were effectively consumed by bacteria and produced biogas as well as stabilizing the WBS (Aboufotouh et al., 2022).

Guo et al., (2016) also reported the sCOD reduction of about 27% in the reactor fed with pretreated biosludge contained high TS, while the reduction was not exceeding 6% in the reactor fed with the raw biosludge.

The concentration of sCOD after AD was high which was consistent with the study of Liu et al., (2017), who reported relatively high level of residual sCOD, like proteins and polysaccharides in the digested supernatant. It was observed that the non-biodegradable sCOD concentrations, which could not be utilized by bacteria in AD process, in the supernatant increased with the pretreatment (Liu et al., 2017).

It was concluded that the thermal pretreatment of biosludge at 90°C could enhance the reduction of sCOD, which might be attributed to the partial decomposition of biosolids or disruption of their structure caused by the pretreatment process. The pretreatment could make the sludge samples more accessible to hydrolytic enzymes, which could further facilitate the breakdown of organic matter in the sludge (Saha et al., 2011).

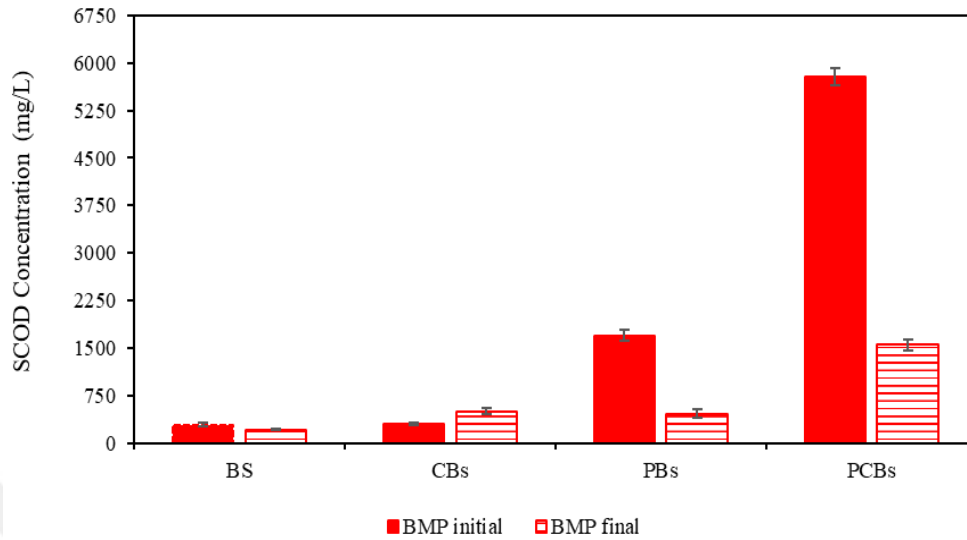


Figure 5.26 sCOD variations before and after BMP tests

5.4.3.2. Protein and sugar variation

The primary components of biosludge were proteins and carbohydrates, which were transformed into soluble forms during AD and pretreatment, which were efficient ways to dissolve biosludge (Guo et al., 2016). In the AD process, various groups of microorganisms play essential roles in the degradation of proteins. Each protein compound can only be broken down by specific types of proteases, which leads to differing degradation rates for different types of proteins. Additionally, the efficiency of protein degradation can be influenced by the surface-to-volume ratio of the particles involved in the digestion process (Yang et al., 2015).

After the BMP test, the protein concentrations decreased notably in all units (Figure 5.27). For the Bs and CBs fed reactors, the concentration decreased from 0.328 mg/L to 0.135 mg/L and from 0.307 mg/L to 0.088 mg/L, respectively. Decrease of protein concentrations in the BMP units fed with pretreated biosludges were significant. In the PBs and PCBs fed reactors, the concentration decreased from 0.56 mg/L to 0.166 mg/L and from 0.743 mg/L to 0.0813 mg/L, respectively.

In general, it appears that BMP units contained disintegrated biosludge had a higher reduction in protein concentrations compared to control. In the raw WBS fed BMP units,

the rate of protein decrease increased from about 59% for control to 71.4% for PBs. While the centrifuged biosludge fed BMP units, the protein decrease increased from 74.3% for the control to 89% for pretreated. After the AD of 67 days, the protein removal rate of 31% was observed within the furnace-degraded biosludge fed reactors, while it was determined about 11% in the control group (Houtmeyers et al., 2014).

As can be seen from the Figure 5.28 that the removal rate of sugars was greater in the pretreated reactors than in the control, as it was also the case with proteins. In the control reactors fed with Bs, the rate of sugar reduction was about 61 % while it rose to 86% in the PBs fed BMP unit. Similarly, sugar reduction ascended to 85.2% in PCBs contained BMP unit, while it was only 64% in control reactors with CBs.

Liu et al., (2016) reported that within the soluble EPS fraction, the higher amounts of proteins and polysaccharides in the pretreated reactors compared to the control reactor. It was reported that the pretreatment process might led to increase the release of proteins and polysaccharides into the soluble fraction of EPS (Liu et al., 2016).

Zou et al. (2020) found that after pretreatment of biosludge at 80°C, the concentration of soluble organic matter increased significantly and compared to the control unit, bacteria rapidly utilized organic matter, including proteins and sugars in the subsequent AD reaction. In the control group, the removal rate of proteins and carbohydrates ranged between 54–63%, while, in the disintegrated biosludge fed reactor, it was observed that the removal rate of proteins and carbohydrates significantly improved, ranging between 98–99% (Zou et al., 2020). Previous studies also demonstrated that the MW pretreatment accelerates the removal rate of protein and carbohydrates in the AD process compared to the control group (Eswari et al., 2016; Kavitha et al., 2016).

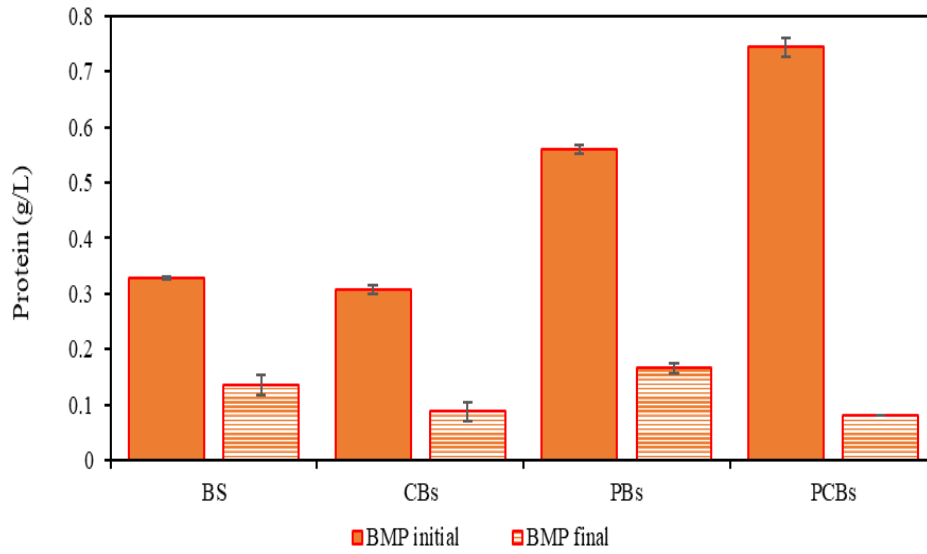


Figure 5.27 Variation of protein concentration before and after BMP

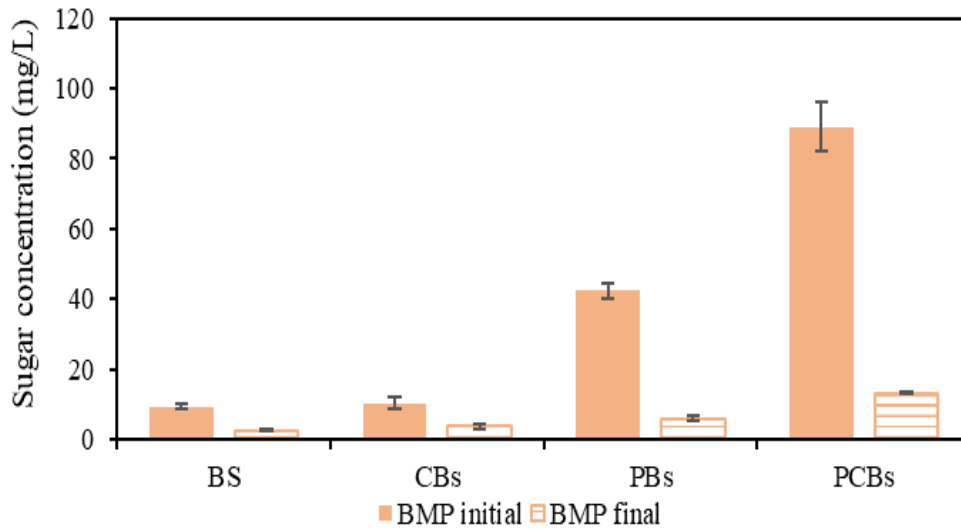


Figure 5.28 Variation of sugar concentration before and after

5.4.3.3. $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$ variation

Initially, the concentrations of $\text{NH}_4\text{-N}$ in Bs and PBs fed BMP units were about 85 mg/L and 87 mg/L, while increased significantly to about 284 mg/L and 340 mg/L after the BMP tests, respectively (Figure 5.29). In the AD process, the complex organic molecules, including proteins, was broken down into a simpler compound like ammonia and result in the increase in $\text{NH}_4\text{-N}$ concentration from 118 mg/L to 186 mg/L was observed (Zhang

et al., 2017). The results were consistent with the study conducted by Zou et al. (2020) reported significant increase in the concentration of $\text{NH}_4\text{-N}$ in the pretreatment group at the temperature of 80°C compared to the control group after 30 days of AD. In the control group, $\text{NH}_4\text{-N}$ concentration range was observed to be between 240 and 250 mg/L, while in the pretreated group ranged from 520 to 580 mg/L (Zou et al., 2020).

As observed in the release of $\text{NH}_4\text{-N}$ after the AD process, $\text{PO}_4\text{-P}$ concentration was increased also from average value of 63 mg/L in the controls to about 92 mg/L and 108 mg/L in the BMP units fed with Bs and PBs, respectively.

As can be seen from the Figure 5.30 that the initial concentrations of $\text{PO}_4\text{-P}$ lower than 80 mg/L before the BMP test, while significantly increased in the both PCBs and CBs fed BMP bottles to about 215 mg/L, compared to raw Bs fed BMP units.

Centrifugation of biosludge followed by the AD process, sharply elevation of both $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$ concentrations were determined compared to the WBS. While the initial $\text{NH}_4\text{-N}$ concentration was 84 mg/L in the CBs, increased to about 703 mg/L after BMP test. In the PCBs fed reactor contained about 92 mg $\text{NH}_4\text{-N}$ /L, it increased to 717 mg/L at the end of BMP test.

High concentration of Bs in the BMP bottles led to the release of large quantities of $\text{NH}_4\text{-N}$ during the AD process, especially in the PCBs fed units. However, despite the high release of NH_4^+ , did not observed inhibition effect on the AD process in both units. When the digested biosludge undergoes dewatering processes, such as centrifugation or filtration the concentration of nutrients such as nitrogen and phosphorus in the anaerobic digester supernatant increases dramatically (Hidaka et al., 2015; Liao et al., 2014).

Liu et al. (2018) observed that during the initial decomposition phase of biosludge pretreated with the $\text{MW-H}_2\text{O}_2$, a substantial amount of $\text{NH}_4\text{-N}$ was released due to the high solid content of sludge. Despite the increased release of $\text{NH}_4\text{-N}$, did not reported adversely impact the moderate stability of AD (Liu et al., 2018). Significant increase in $\text{NH}_4\text{-N}$ reached to 500 mg/L content of anaerobic reactor liquid after six days was attributed to protein degradation, while the effect of high concentration was very low on the AD (Wu and Song, 2020). Liao et al., (2016) reported that the total nitrogen (TN)

(NH_4+NH_3) release increased from 822 mg/L to 1,857 mg/L after AD of the dewatered biosludge fed control reactor. In contrast, in reactors containing disintegrated biosludge at a temperature of 80 °C and a heating time of 30 min, it was determined that the release of TN was elevated from 1,960 mg/L to 2,845 mg/L.

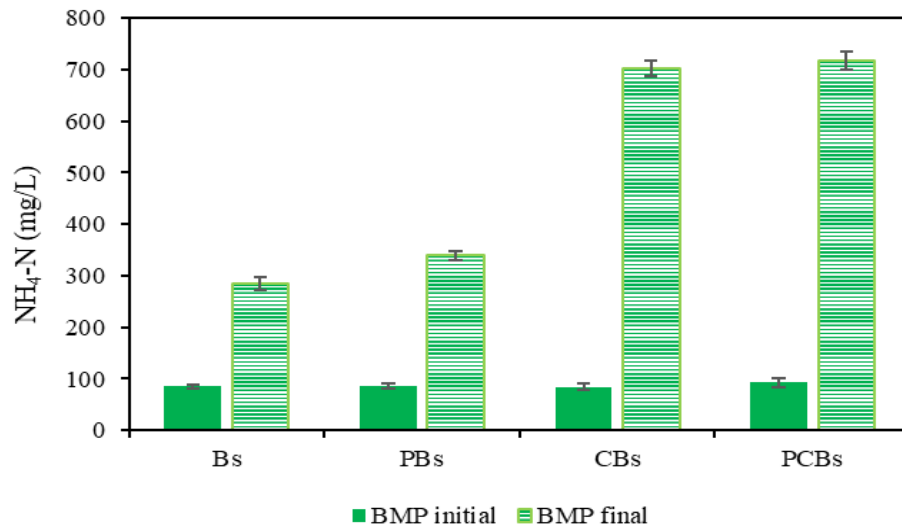


Figure 5.29 $\text{NH}_4\text{-N}$ concentrations in pretreated and centrifuged biosludge in the BMP tests.

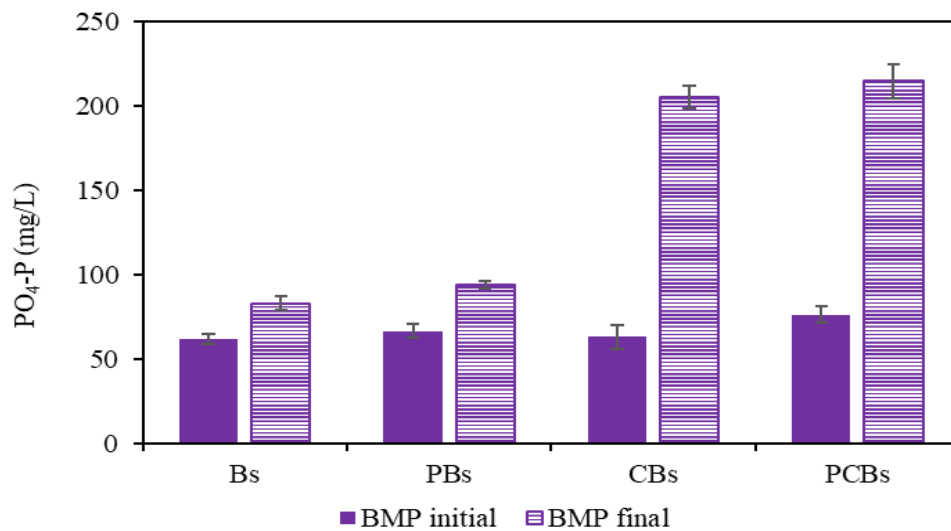


Figure 5.30 $\text{PO}_4\text{-P}$ concentrations in pretreated and centrifuged biosludge in BMP tests.

5.4.3.4. Total and volatile solids variation

Figures 5.31 and 5.32 show the reductions of TS and VS in the BMP bottles fed with different digestion biosludge. The results indicated that before and after the BMP tests, differences in the decline of TS and VS concentrations were negligible for the raw and centrifuged biosludges, while the bottles contained PBs showing reduction was slightly lower compared to PCBs. In the control, the TS level decreased from 11,085 mg/L to 9,248 mg/L with a decrease of 16.5%, on the other hand the VS declined from 7,725 mg/L to 5,730 mg/L with the decrease of 25.8%. Also, in the reactor containing PBs, the TS level decreased from 11,200 mg/L to 8,677.5 mg/L (reduction of 22.5 %) and the VS decreased from 7,675 mg/L to 5,197.5 mg/L (decrease of 32.3%). However, the rate of TS and VS reduction in the CBs was 21% and 30.7% and in the PCBs containing bottles was reached to 29% and 40 %, respectively. As expected, the decrease in TS and VS in bottles containing higher concentrations of biomass was higher than in those containing lower concentrations. Improvement in VS reduction in the AD process indicates more efficient breakdown of organic matters associated with increased CH₄ production (Akgul et al., 2017).

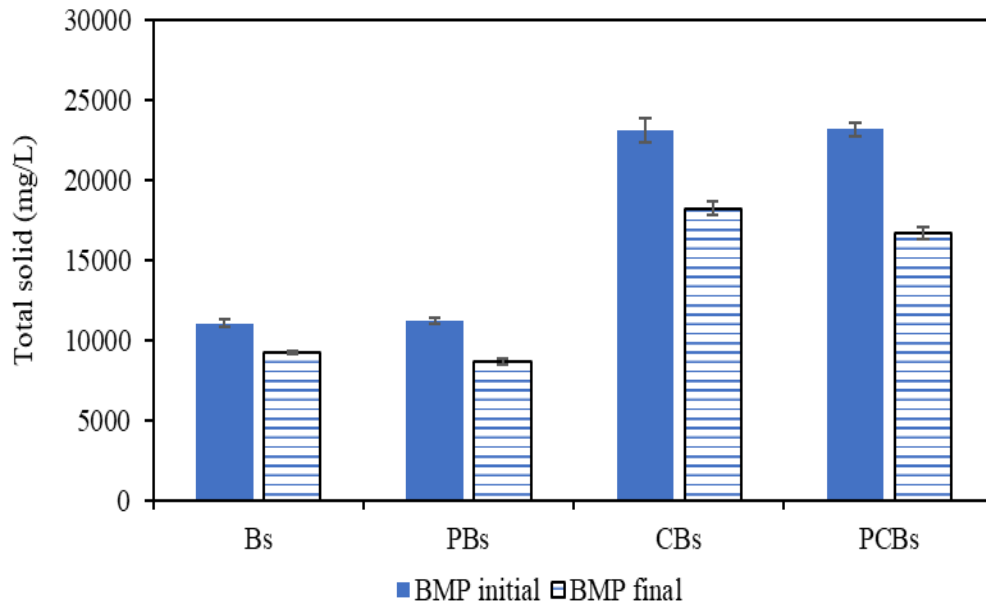


Figure 5.31 TS variation in before and after BMP test

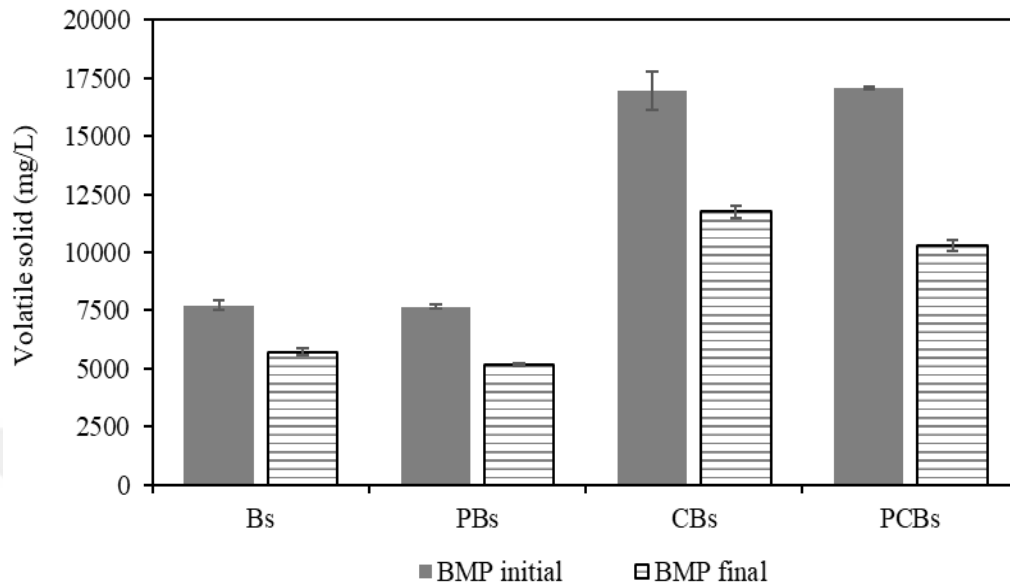


Figure 5.32 Volatile solid variation in before and after BMP test

Liao et al., (2014) found that at the initial TS content of 1.79%, the slow decomposition period was brief, with most degradable organic matter being removed during the fast decomposition period, while the slow decomposition period extended when the initial TS was increased to 4.47%, 10.28%, or 15.67%. Disintegration of biosludge contained high TS promotes hydrolysis rate, VS conversion efficiency and consequently biomethane production in the AD (Di Capua et al., 2020). Kor-Bicakci et al., (2019) observed that about 10% higher VS reduction in the centrifuged biosludge, which was exposed to MW irradiation of about 30 min compared to the control reactor. The study conducted by Liu et al. (2018) indicated that after 60 days digestion period, the reduction of VS from centrifuged biosludge was 35.3% for control, while was 46.8% in the MW pretreated biosludge.

5.4.3.5. CH₄ production

The generation of CH₄ in the AD process might be evaluated more effectively if data was expressed in mL of CH₄ fed or removed per gram of VS or/sCOD (Tas et al., 2018). The daily and cumulative CH₄ production in the BMP units fed with pretreated and raw biosludge are depicted in Figures 5.33 and 5.34, respectively. Compared to the controls

without pretreatment, higher CH₄ yields were determined in the BMP bottles fed with pretreated biosludge.

After the pretreatment, both the PBs and PCBs exhibited a significant enhancement in cumulative CH₄ production compared to the control. In the PBs reactor, the cumulative CH₄ production was about 386 mL, with the 21% improvement, it reached to 461 mL by feeding the bacteria with the PBs in the BMP test. In the BMP test with the CBs, the cumulative CH₄ production was about 903 mL, with the pretreatment of centrifuged biosludge, the highest CH₄ volume 1,126 mL was obtained with the improvement of about 25% compared to control. After the application of 5, 10, and 15 min MW irradiation time, Hephzibah et al. (2015) obtained that 274, 319, and 374 mL cumulative CH₄ volumes in the AD reactor fed with a biosolid content of 4%, respectively.

The highest daily CH₄ production rates were 12.5 mL/g VS.day with the Bs and 29.6 mL/g VS.day in unit fed with the PBs. With the use of the centrifuged biosludge, the highest daily CH₄ production rates of 16 mL/gVS.day and 19 mL/g VS.day were obtained in the BMP bottles fed with the CBs and PCBs, respectively.

At the end of the first week of operation, CH₄ gas production started to decrease across all BMP units due to the rapid consumption of easily utilized organic substrates. However, the decrease rate of CH₄ production in the PCBs was lower compared to the other reactors, because of the positive effect of pretreatment of biosludge, which released the organics more abundantly with high solid content. This has resulted in sustained or prolonged CH₄ production compared to the other reactors. Kavitha et al., (2018) also observed during the initial five days of CH₄ generation with a rapid increase in production.

Compared to the untreated WBS, the reason for improved biogas production yield of thickened WBS pretreated in MW was the elevation of biosludge solubility and digestibility. In addition, it could be achieved much volume of CH₄ production when the MW density increases with slower heating rate (Hephzibah et al., 2015). In recent days of experiments, minimal variance in CH₄ production between the BMP units, which could be attributed to providing the sufficient time in order to breakdown for the difficult organic materials, which might be formed by MW disintegration (Eskicioglu, et al., 2007b; Kor-Bicakci et al., 2019), and biosludge with high TS content (Liao et al., 2014). Azizi

et al., (2019) reported the formation of inhibitory compounds during the pyrolysis of municipal sludge cake at 160°C, which caused a lower CH₄ production in the first days of operation. The reason of CH₄ yield decrease was the Maillard reaction, which led to a decrease in sugar and protein levels (Azizi et al., 2019).

In the BMP tests, the cumulative biogas yield was about 300 mL/gVS and 330 mL/gVS determined for the PBs and PCBs, respectively, while it was about 246 mL/g VS and 271 mL/g VS for the Bs and CBs. The data indicated that the cumulative CH₄ production increased by approximately 22.3 % and 21.7 % for both the PBs and PCBs sludges fed reactors, compared to the control.

Effective CH₄ production was achieved in the AD process under the operational conditions of MW with the disintegration of biosludge. The pretreatment of biosludge at the moderate MW temperatures (<100 °C) and convenient irradiation time/heating rates could enhance CH₄ production without inhibiting the digestion process. Whilst, at high temperatures CH₄ production could be restricted (Azizi et al., 2019; Passos and Ferrer, 2015; Pilli et al., 2014).

As was assumed before the experiments, higher CH₄ production was determined by the usage of PBs and PCBs in BMP tests, respectively compared to the others. It was reported that a concentrated biosludge pretreated at 80°C for duration of 90 min resulted in the specific CH₄ production increased to 303 mL of CH₄/g VS, while the biodegradability elevated to 73% (Veluchamy and Kalamdhad, 2017).

Eskicioglu et al., (2007a) suggested that a higher solid concentration might lead to more efficient gas production. After the MW pretreatment of biosludge with a solid content of 5.4% at 96°C, 21% increase in CH₄ production was achieved compared to the control, while at a lower solid content of 1.3%, increase in gas production was about 15% (Eskicioglu et al., 2007a). Yan et al. (2013) observed that the dewatered and pretreated biomass at the temperatures ranging between 90–100°C for a duration pretreatment of 30 min provided in the biogas yields ranging from about 85 to 143 mL/g VS, compared to a control group 18.3 mL/g VS. With a high solid content (8–8.5%) of biosludge was disintegrated in the MW at 100°C and 600 W, 25% increase in CH₄ production was determined compared to the control group (Liu et al., 2018).

Feeding of high concentrations of biosludge into the AD reactor, the biodegradation rates could limit due to the restriction of microbial activity or the limitation of essential nutrients and enzymes transportation (Liao et al., 2016). It was concluded that the CH₄ yield in AD process could be significantly increased by the pretreated biosludge with MW and increasing the TS content. In order to ensure homogeneous biosludge mixing in the operation of AD reactor, the TS concentration should be optimized. MW operating conditions must be also optimized in order to achieve the highest CH₄ production possible, taking into account energy consumption in the MW operation.

Based on the stoichiometric composition of WBS, the empirical formula of biosludge was calculated as C_{8.14}H_{14.57}O_{3.52}N_{1.28}. From the elemental composition by using Eq. (4.2), the tBMP for biosludge was found as 524 mL of CH₄/g VS. The biodegradability calculated by Eq 4.3 for the untreated reactors Bs and CBs was 46% and 51%, respectively, but after MW pretreatment, it was 57.2% and 62.3% for PBs and PCBs, respectively (Figure 5.35). In this study, the biodegradability of biosludge contained high concentration of TS was higher than the raw biosludge, which is contradict with the results of study by Yuan et al., (2019). Yuan et al., (2019) explained this reason of results because of the dewatering of biosludge was carried out with the use of high molecular weight polyacrylamide-based flocculants as drying agent, high concentrations of biosludge about 20%, which negatively affect the biodegradation rates by hindering the microbial activity or transport of essential nutrients and enzymes (Liao et al., 2016).

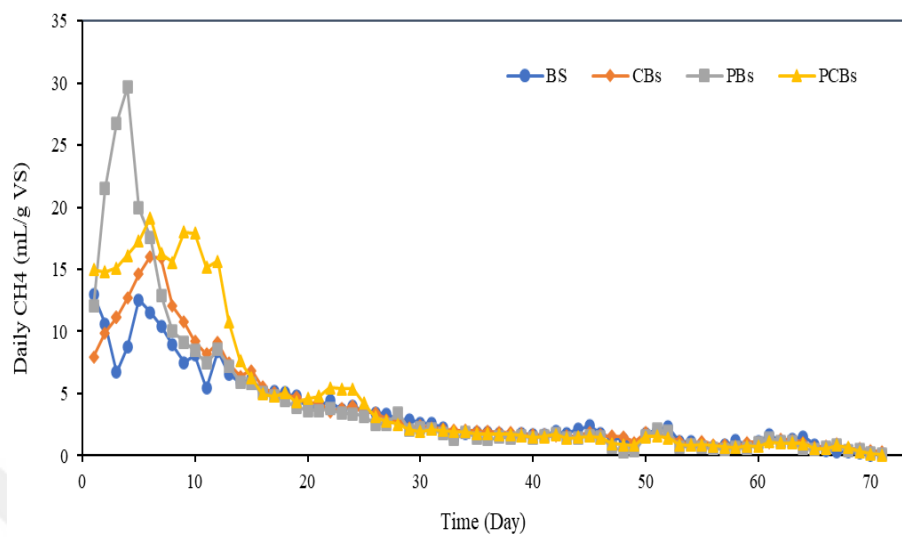


Figure 5.33 Daily CH₄ production in the BMP tests

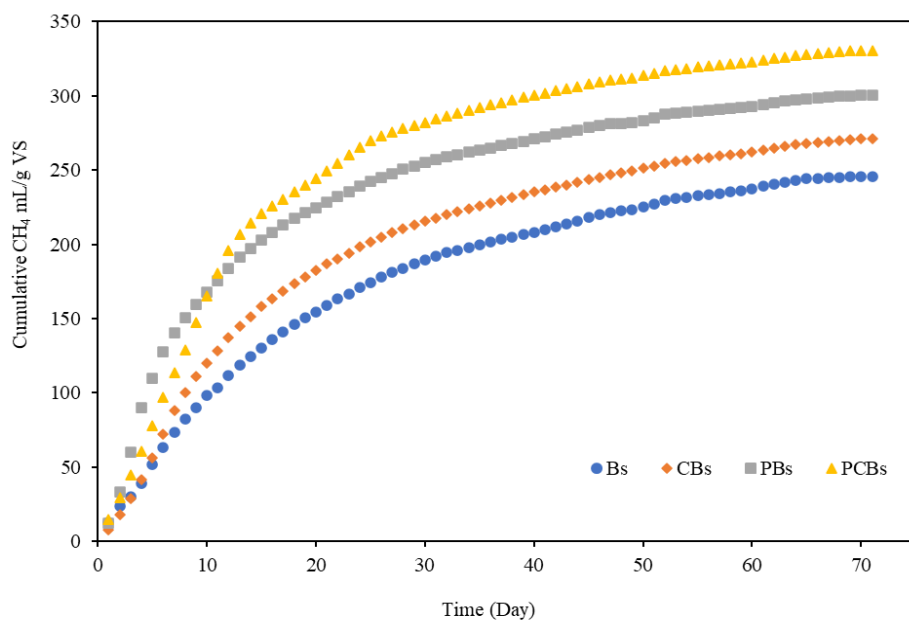


Figure 5.34 Cumulative CH₄ production in the BMP tests

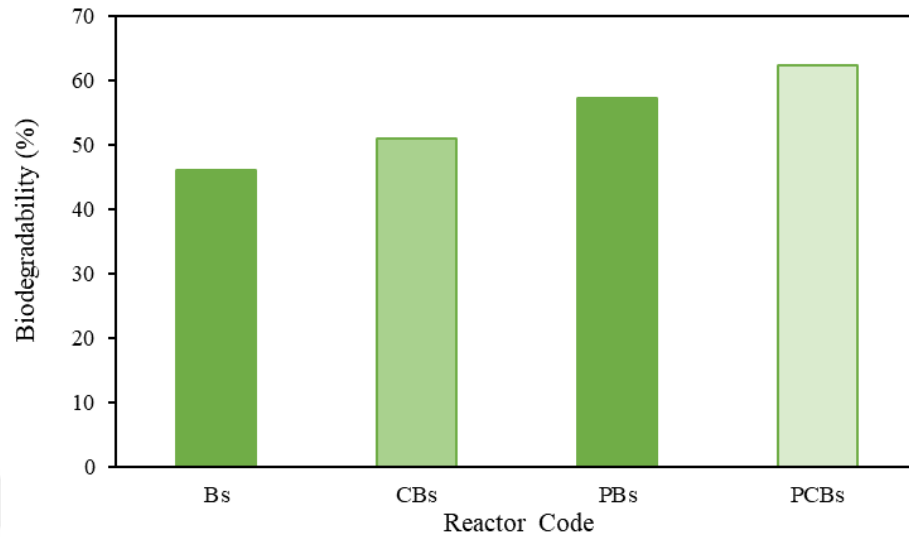


Figure 5.35 Biodegradability rate of BMP test

5.4.3.6. Energy assessment

Energy calculations are presented in Table 5.11 for both types of biosludges.

Table 5.11 Energy analysis of different biosludge

TS content %	E_i kJ/gVS	Reactor code	Ultimate CH_4 (mL/g VS)	$^a\Delta CH_4$ (m ³ /g VS)	E_o (kJ/gVS)	E_o/E_i
1.27	301	Bs	245.4	0.0000549	1.76	0.0058
		PBs	300.3			
3.4	108.4	CBs	271.4	0.000059	1.90	0.017
		PCBs	330.4			

a: represents the result of energy output after applying the CH_4 production difference (PBs – Bs) and (PCBs – CBs)

As can be seen from the Table that the produced energy in AD processes were lower than the requirement of MW irradiation for both centrifuged and raw biosludge under the operational conditions. Compared to the energy input of disintegration of raw biosludge, the E_i value was about 3 times lower due to the higher VS concentration in the centrifuged biosludge. The E_o/E_i ratio varied across different biosludge ranging from 0.0058–0.017. One important finding in this study was that the E_o/E_i ratio for the centrifuged biosludge

was also less than 1, indicating a low energy output compared to the input. However, because the reduced energy input of about 64%, significant increase of E_o/E_i ratio from 0.0058 to about 0.017 was determined by feeding the AD process with the centrifuged biosludge. Reduction in energy input might be considered a positive factor. The CH_4 production capacity of PBs and PCBs was 283 and 377 $\text{kJ/gVS}_{\text{removed}}$, respectively, while the Bs and CBs was 203 and 242 $\text{kJ/gVS}_{\text{removed}}$, which were calculated using the Equation (4.6).

Saha et al., (2011) found also that the energy consumption for the raw WBS was reported at about 412 kJ/g TS while decreased significantly to about 104 kJ/g TS for WBS with a solid content of 10%. This equated to a decrease rate of 7.74%, indicating a substantial improvement in energy efficiency as the sludge became more concentrated (Saha et al., 2011).

Application of the thermal methods such as MW irradiation for the disintegration of biosludge with the solid concentrations greater than 3% could enhance the yield of CH_4 production in the AD process and lead to self-sustainable energy production or even generate surplus energy (Liu et al., 2016).

Economically, pre-dewatering of biosludge has been offered the preferred scenario for large WWTPs. It was observed that raising the solids content in biosludge from about 1.2–4.1% to 10.7–18.3% through pre-dewatering reduced the energy consumption of pre-treatment (MW and UV) to a range of 54–94 % (Yuan et al., 2019; Kor-Bicakci et al., 2019).

Although an improvement of CH_4 yield in the AD process was obtained by using of disintegrated biosludge with high solid content, increase of the energy was not sufficient to compensate for the energy requirement of the MW pretreatment under the operational conditions.

5.4.3.7. Kinetic studies

The accumulated CH_4 production curve achieved for the control and disintegrated biosludge reactors was simulated using the four proposed kinetic models to examine the

specific CH₄. The experimental results in this study were used to fit the models, as shown in (Figures 5.36–5.39), and the kinetic parameters are presented in Tables 5.12.

Although the R² value for all applied models was high, the Transference Function model had the greatest R² value, ranging from 0.988 to 0.998, compared to the others. The First Order model had the second-highest R² value, with a correlation coefficient R² between 0.986 and 0.998. It is consistent with previous studies that found that the best fit was obtained using the Transference Function, which achieved the highest R² compared to other models and ranged between (0.983–0.997) (Li et al., 2012; Ugwu and Enweremadu, 2019).

The biogas production potential, maximum CH₄ production rate, hydrolysis rate, and lag phase duration was estimated by interpreting kinetic model parameters that best fit the experimental results.

Based on the First–Order model, it was observed that the parameter k increased with the application of MW disintegration compared to the control. The k value for Bs and CBs was 0.047 d⁻¹ and 0.055 d⁻¹, after the MW disintegration, increased to 0.079 d⁻¹ and 0.075 d⁻¹ for PBs and PCBs, respectively. It was reported that increase might be occurred due to the increased bioavailability by the pretreatment of biosludge and leads to rapid rate of AD process (Ugwu and Enweremadu, 2019). The λ value for the Bs and PBs was lower than zero indicates the AD process began immediately and the production of CH₄ (Khadka et al., 2022). Conversely, in the Transference Function model for the centrifuged biosludge reactors (CBs and PCBs) showed the highest λ values, which suggests that the bacteria require around half day to adjust to the high solids concentration. Results are consistent with a study by Akbay (2024). It was reported that the expected lag phase for all raw materials in the Transference Function model was less than one day, which implies that bacteria exhibit effective synergy in the medium, resulting in a shorter initiation time for biogas production, which continues over an extended period (Akbay, 2024).

In the Transference Function model, the A_0 values were the highest 252.7 and 269.6 mL/g VS for the Bs and CBs, while 294.9 and 328.8 mL/g VS for the PBs and PCBs, respectively. Moreover, the Transference Function model also exhibited the highest μ_m values, which were notably higher compared to other models. The μ_m values in the Bs and

CBs were 11.5 mL/gVS.day and 15.2 mL/gVS.day, respectively, while in the PBs and PCBs were 21.2 and 32.6 mL/gVS.day, respectively.

The results indicated significant enhancement in potential CH_4 production and maximum daily rate of CH_4 production by the usage of pretreated biosludge. The findings in consistent with previous study that indicated the Transference Function and First-Order models had the greatest A_0 (Ugwu and Enweremadu, 2019) and μ_m values compared to the Logistic and Gompertz modified models (Li et al., 2012). Theoretically, the μ_m value increases with the A_0 value, which implies that the CH_4 yield potential would form at a higher rate of CH_4 generation (Syaichurrozi et al., 2020). The difference between the cumulative gas data (Y) measured and predicted after 71 days in the first model was 1.2–3.5%, in the Gompertz modified model it was 2.8–4.3%, in the Logistic model it was 4.2–5.4%, and in the Transference Function model was 0.79–2.9%. Although the Transference Function model is the model with the least deviation, all models are considered valid because their deviation rate is less than 10% (Syaichurrozi et al., 2020; Ugwu and Enweremadu, 2019).

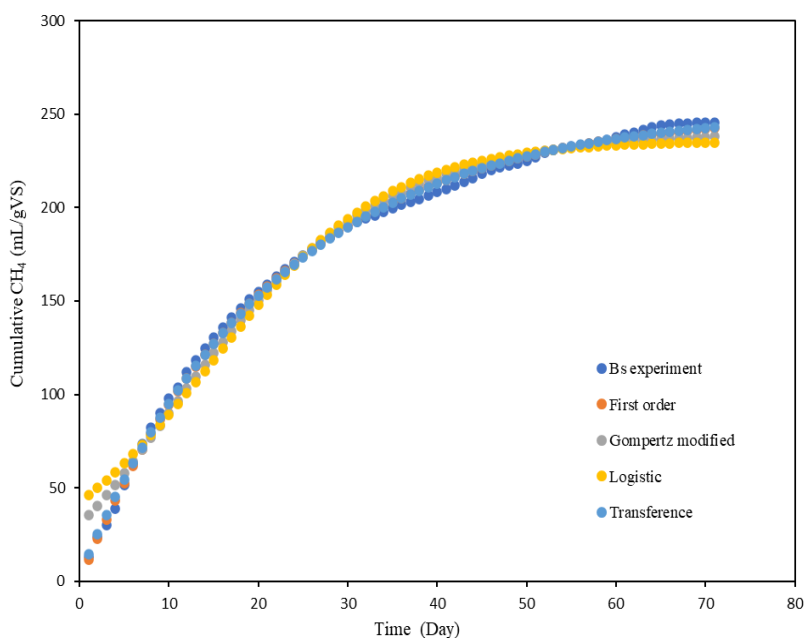


Figure 5.36 Models fitted with cumulative CH_4 production from BMP assay for Bs

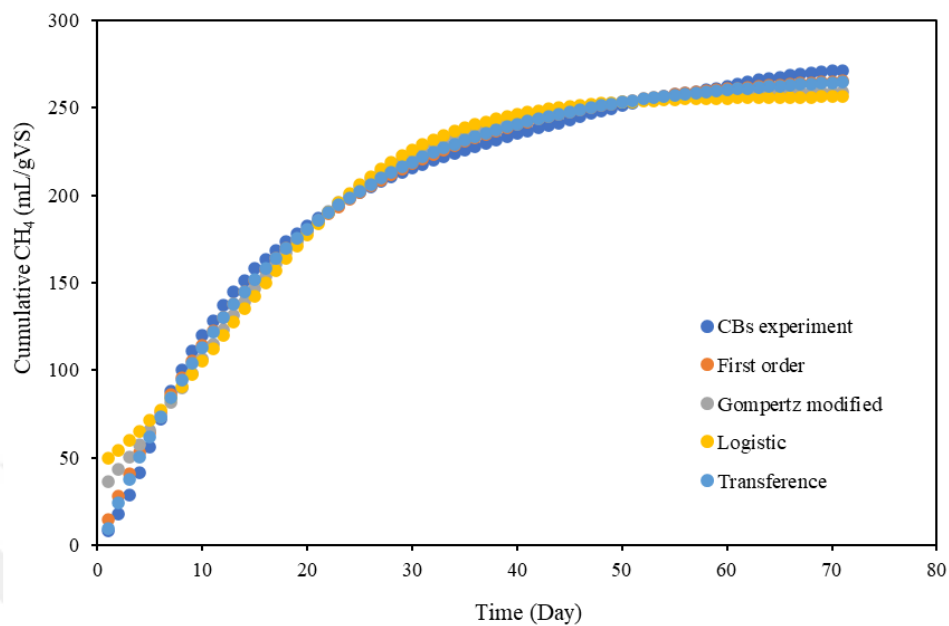


Figure 5.37 Models fitted with cumulative CH_4 production from BMP assay for CBs

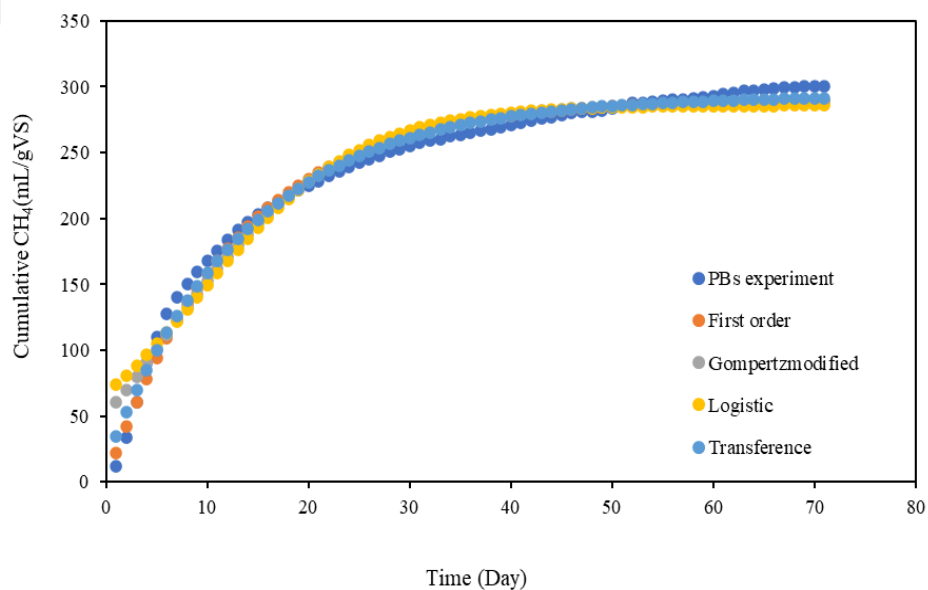


Figure 5.38 Models fitted with cumulative CH_4 production from BMP assay for PBs

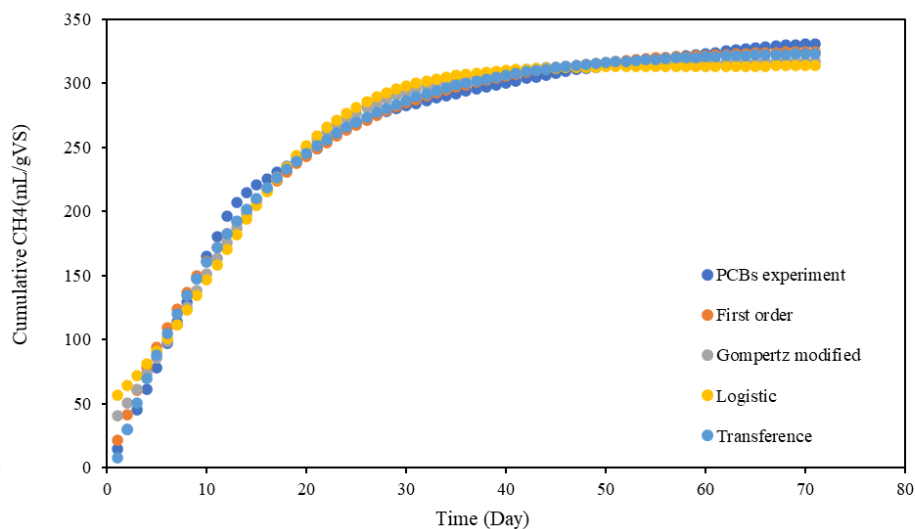


Figure 5.39 Models fitted with cumulative CH₄ production from BMP assay for PCBs

Table 5.12 Kinetic parameters

Model	Reactor	R ²	Y (mL/gVS)	A ₀ (mL/gVS)	μ _m (L/gVS)	k (d ⁻¹)	λ (day)	Deviation (%)
First Order	Bs	0.998	242.5	251.5		0.047	–	1.2
	CBs	0.995	265.4	271	–	0.055		2.1
	PBs	0.986	289.5	290.6		0.079		3.5
	PCBs	0.995	324.8	324.7		0.075		1.72
Gompertz Modified	Bs	0.988	238	240.5	6.6		–3.6	2.8
	CBs	0.981	259.3	260.4	8.4	–	–2.66	4.3
	PBs	0.967	287.87	288.3	10.6		–3.11	4.1
	PCBs	0.984	316.77	317	13.2		–1.4	4.1
Logistic	Bs	0.97	234.91	235.7	6		–4.7	4.2
	CBs	0.966	256.32	256	7.5		–3.44	5.4
	PBs	0.954	285.7	285.8	9.13		–6.3	4.8
	PCBs	0.97	313.6	313.6	12		–1.26	5.1
Transference Function	Bs	0.998	243	252.7	11.5		–0.293	0.97
	CBs	0.998	264.6	269.6	15.2		0.357	2.4
	PBs	0.988	295.3	294.9	21.2		–0.71	2.9
	PCBs	0.993	326.4	328.8	32.6		0.681	2.1
Experiment	Bs	0.976	245.4	–	12.9	0.048	0	–
	CBs	0.984	271.12		16	0.044	0	
	PBs	0.991	300.3		29.6	0.053	0	
	PCBs	0.972	330.5		19	0.055	0	

5.4.3.8. Struvite precipitation

The concentrations of NH₄–N (≥ 700 mg/L) and PO₄–P (≥ 200 mg/L mg/L) in the liquor after the BMP test fed with PCBs were very high, which was presented previous sections.

In the struvite precipitation experiments, two molar ratios of 1.25:1:1 and 1.15:1:1 for Mg, N, and P were tested to optimize the nutrient recovery. Because of the wastewaters drawn from the BMP bottles were not sufficient for the testing molar ratios, the molar ratios were determined with the precipitation tests, which were carried out with the synthetic wastewaters. Considering the initial $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$ concentrations in the supernatant of BMP effluents, higher than 90% of the removal efficiencies for both of the nutrients were determined with the defined molar ratios.

The pre disintegrated anaerobic supernatant exhibited the highest $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$ removal percentage of about 82% and 97%, respectively for the applied molar ratios (Figure 5.40). In contrast, in the supernatant of control reactors the removal rates was 81% and 88% for $\text{NH}_4\text{-N}$ and $\text{PO}_4\text{-P}$, respectively.

It was reported that higher concentrations of ammonium favor the formation of struvite crystals, making the precipitation an effective method for recovery of nutrients (Werkneh and Gebru, 2023). The chemical formula of struvite is $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ indicated that a mole of N is equal to a mole of struvite (Hao et al., 2008) and the logarithm of ionic NH_4^+ concentration in the crystal directly correlates with the saturation of struvite (Wu et al., 2022). When the wastewaters contain Ca^{2+} and the pH was high, P and Mg^{2+} tend to attach to some chemicals instead of struvite, a high N content might be end up being the sole benchmark used to determine the struvite content of precipitation.

From an environmental perspective, an overdose of PO_4^{3-} would lead to a greater concentration of PO_4^{3-} in the effluent (Zhang et al., 2009). The molar ratio of 1.15:1:1 ($\text{Mg}^{2+}:\text{NH}_4^+:\text{PO}_4^{3-}$) could be considered as convenient for the recovery of $\text{NH}_4\text{-N}$ from the anaerobic supernatant while preventing a significant concentration of PO_4^{3-} in the effluent. Figure 5.42 shows the diffraction pattern of four struvite powder samples with a reference struvite pattern. The XRD pattern of crystalline powder has significant peaks at values of 2-theta (2θ) ranging from $\sim 15^\circ$ to $\sim 38^\circ$, which indicated the presence of a crystalline phase in the samples. Furthermore, there were additional peaks beyond $\sim 38^\circ$, although they were less prominent compared to those in the $\sim 15^\circ$ to $\sim 38^\circ$ range. It is consistent with previous studies reported that the struvite crystalline formation occurs at

the main peaks that range between 12° and 40° (Rahman et al., 2011; Sreyvich et al., 2020; Zhang et al., 2009).

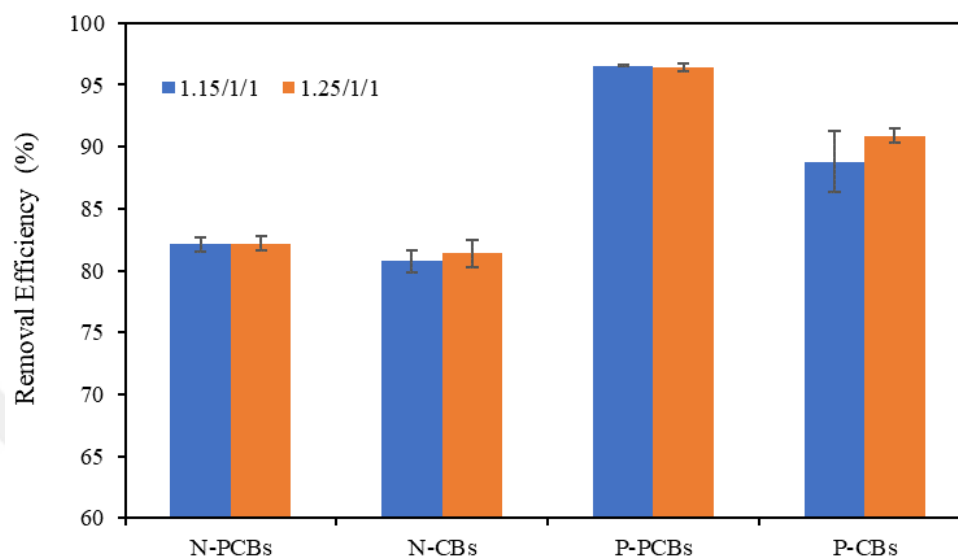


Figure 5.40 N and P removal efficiency at different molar ratio

The SEM–EDX analysis was performed to identify the surface characterization of the precipitates (Figures 5.41 and 5.43). The precipitate appears as regular-sized, smooth-surfaced, rhombic or pyramid-shaped crystals as seen in the SEM image, indicating that it is not fractured. While struvite crystals are often orthorhombic, they can sometimes take on spherical or dendritic shapes; cubic struvite crystals are also known to exist (Ali, 2005). Additionally, pyramid-shaped struvite crystals can form. These crystals eventually transform into arrowhead-shaped crystals with distinct faces that grow gradually in all directions (Sun, 2023). Regarding the EDX analysis, which reveals that the precipitation's surface composition includes high amounts of O, P, and Mg as well as the appearance of the element N, which suggests that the availability of the elements N is responsible for the formation of struvite-shaped crystals, Uysal et al., (2017) noted that in addition to the main elements the presence of significant P, Mg, N, O, and C in the dry precipitate for struvite suggests that struvite and some organic molecules from the hydrolyzed liquid co-precipitated.

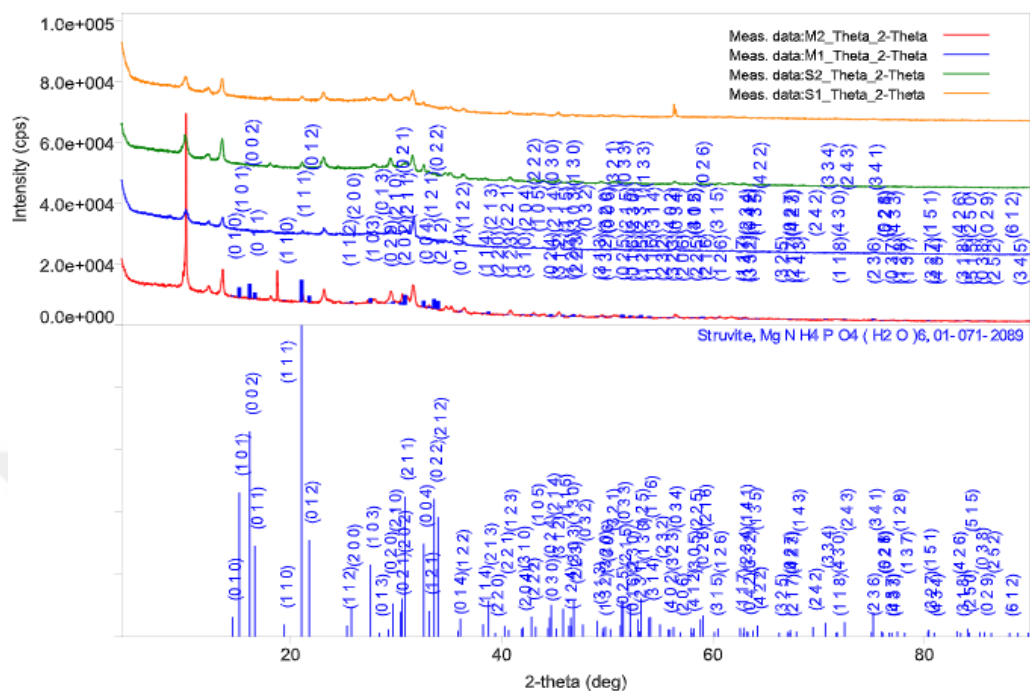


Figure 5.41 X-ray diffraction analysis of precipitate samples (pH = 9.5 and Mg:N:P=1.25:1:1)

S1(—): control samples with a molar ratio of (1.15:1:1), S2 (—): control samples with a molar ratio of (1.25:1:1); M1(—): pre-disintegrated biosludge samples with a molar ratio of (1.15:1:1); M2(—): pre-disintegrated biosludge samples with a molar ratio of (1.25:1:1).

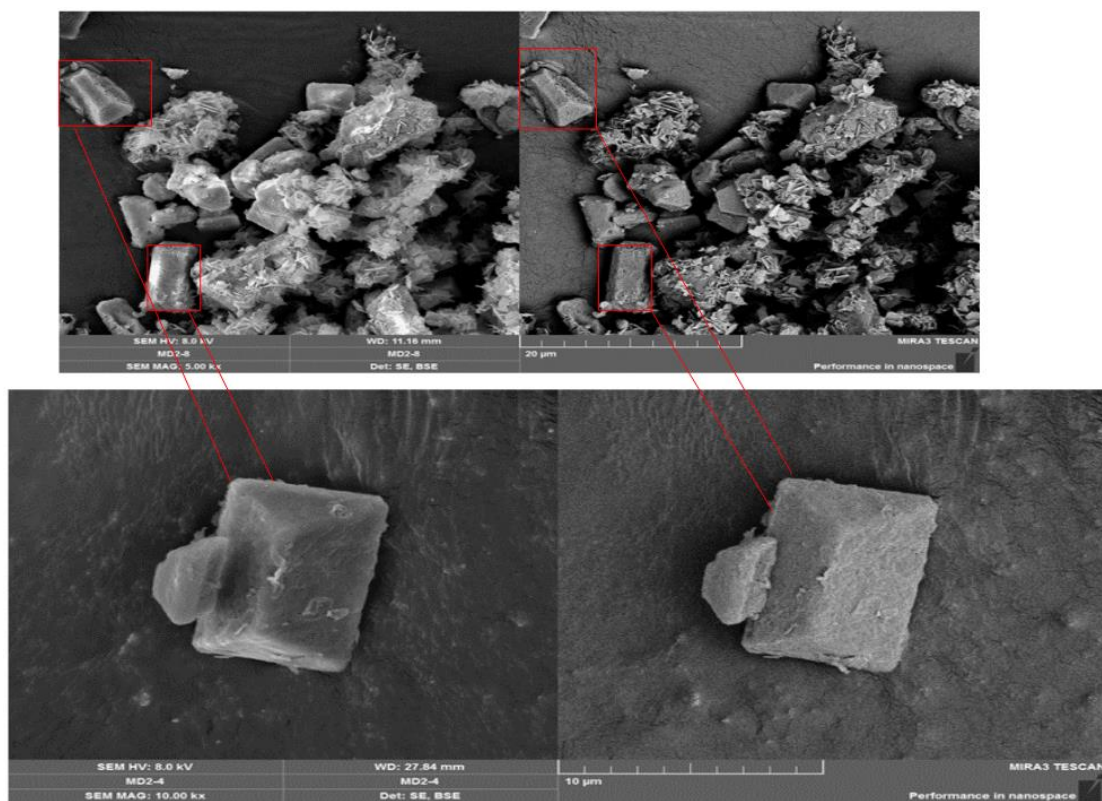


Figure 5.42 SEM image of crystal precipitate product (pH = 9.5 and Mg:N:P =1.25:1:1)

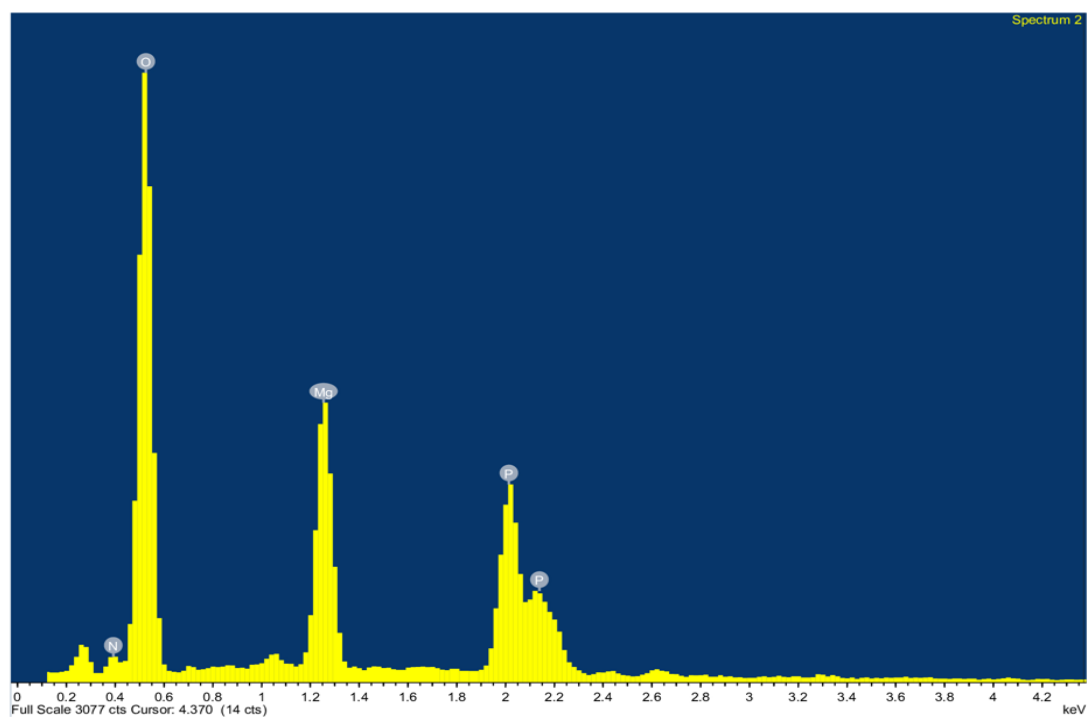


Figure 5.43 EDX analysis of dry precipitate (pH = 9.5 and Mg:N:P =1.25:1:1)

6. CONCLUSION

This study aimed to identify the optimal operational conditions of MW irradiation to improve the AD of WBS considering the energy. Experiments were conducted with raw WBS and centrifuged WBS, which contained about two times higher TS compared to the raw. The findings revealed that MW irradiation significantly enhanced the release of organic substances. Conversely, the process was not effective the release of $\text{NH}_4\text{-N}$ and adversely affected the dewatering properties of biosludge. However, high concentration of $\text{NH}_4\text{-N}$ in the wastewaters produced in the AD process was observed.

Considering the tBMP, the MW irradiation improved biodegradability and higher than 96% biodegradation was achieved for the disintegrated biosludge, while it was lower than 79% for the controls.

Increase of readily biological organic constituents in the MW disintegrated biosludge positively affect the AD process result in the elevation of CH_4 production yield was observed. It was determined that the increase in CH_4 production in pretreated units (PBs and PCBs) were about 45% and 21% higher than in control units (Bs and CBs).

Concerning the energy efficiency, results revealed that CH_4 produced in the AD process fed with the raw WBS did not meet the energy need of MW heating under the operational conditions. On the contrary, feeding of WBS included high TS% into the BMP unit, the energy consumption of MW heating decreased about three times compared to the raw biosludge and increase of CH_4 production was also observed in the AD process.

At the initial pH of about 9.5, approximately 82–90 % of $\text{NH}_4\text{-N}$ and 90–96% of $\text{PO}_4\text{-P}$ were recovered in the wastewater of BMP unit by struvite precipitation at Mg:N:P molar ratios of 1.25:1:1 and 1.50:1:1. The XRD, EDX, and SEM analyses were conducted to the precipitate and confirmed the form was struvite.

CH_4 was observed in the first day of BMP operation and it was determined that the lag phase (λ) values for models were negligible, an almost zero lag phase was determined with the Transference Function model. According to the calculated First-order model rate constant (k), compared to the control unit, which prolonged cell breakdown occurred, MW

disintegration of WBS was effective in releasing organics and accelerating bacterial access to these materials.



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