ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE ENGINEERING AND TECHNOLOGY

EFFECT OF ULTRASONIC AND MICROWAVE DISINTEGRATION ON PHYSICO-CHEMICAL AND BIODEGRADATION CHARACTERISTICS OF WASTE ACTIVATED SLUDGE

M.Sc. THESIS

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To my family,

FOREWORD

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ABBREVIATIONS

COD : Chemical Oxygen Demand
BOD : Biological Oxygen Demand
TS : Total Solid
TCOD : Total Chemical Oxygen Demand
PSD : Particle Size Distribution
DD : Disintegration Degree
DDSCOD : Disintegration Degree based on Soluble Chemical Oxygen Demand
SCOD : Soluble Chemical Oxygen Demand
WAS : Waste Activated Sludge
OUR : Oxygen Uptake Rate
MW : Microwave Irradiation
US : Ultrasonication
TKN : Total Kjedahl Nitrogen

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EFFECT OF DISINTEGRATION ON THE PHYSICOCHEMICAL PROPERTIES AND BIODEGRADABILITY OF WASTE ACTIVATED SLUDGE

SUMMARY

Increasing with sludge production , sludge treatment and disposal methods became more popular because of local and global legislations. Legislations bring alot of necessities for treatment or disposing of sludge. Especialy the last decades, sludge treatment and disposal methods is being important. The costs of sludge treatment and sludge removal also increase in parallel to the increase in sludge amount and it becomes a primary component for total wastewater treatment costs. Excess sludge treatment or disposal processes involve many important issues in terms of finance, technology and environment. So, another methods become prior such as disintegration methods.

In this study, two disintegration methods were examined in 2012 and 2013. These are ultrasonication and microwave irradiation. These methods are based on breaking cells or flocks and to observe more available organic substances. It provides more biodegradability.

To understand the effect of mechanical disintegration method ultrasonication was applied to untreated sludge. During the ultrasonication studies, different specific energy were used because specific energy is important parameter for efficiency of ultrasonication. Aslo, effects of specific energies on the solubilisation of organic matters were observed. The results of sonication experiments pointed out that the increase in SCOD release (i.e. sludge disintegration degree) exposed an increasing trend with prolonging the specific energy input and ultrasonic density at all TS levels tested. The disintegration of WAS by ultrasonic pretreatment involved two stages where the initial rapid phase at relatively low specific energy input values was followed by a subsequent slower one for energy dosages higher than 30000 kJ/kg TS. A value of 1.5 W/mL was determined as the optimum ultrasonic density since the incremental disintegration rates were negligible. Sonication exhibited similar disintegration efficiencies for the studied WAS samples, regardless of different sampling periods.

Raising up to the temperature higher than the boiling point enhanced the disintegration degree of microwave pretreatment throughout the investigated TS range; whereas at a constant temperature, microwave heating of WAS at three different TS concentrations yielded almost similar disintegration performances. The improvement in the microwave irradiation efficiency declined by elevating the treatment temperature from 175 to 190^{o}C. For all TS contents applied, no significant difference in solubilization degree was obtained at the exposure times above 10

minutes. The disintegration rates of the examined WAS samples remained consistent despite different sampling dates.

Both ultrasonication and microwave irradiation achieved SS and VSS removal efficiencies in the range of 22–37% coupled with lower TS and VS reductions of only up to 5%, generating totally different profiles in terms of solid particles as compared with raw WAS samples. The initial COD levels did not appreciably change during the applied pretreatment processes. Sonicated WAS at the specific energy input of 30000 kJ/kg TS provided a COD solubilization rate (25–26%) very similar to that of the irradiated counterpart at the microwave temperature and contact time of 175ºC and 10 minutes, respectively. Variations in DOC release under selected operating conditions revealed similar patterns as those of SCOD. Disintegration by ultrasonication and microwave irradiation increased the concentrations of nitrogen and phosphorus species in the liquid phase.

This research would be an interesting issue for further research to evealuate impact of ultrasonication and microwave irridation processes on the PSD of other significant parameters reflecting the extracellular and intracellular constituents of disintegrated WAS portions; namely, proteins, carbohydrates and lipids.

Performing a comprehensive study at pilot scale and conducting a techno-economic feasibility analysis may provide a deeper insight both in the interpretation and scaling up of the results.

DEZENTEGRASYONUN ATIK AKTİF ÇAMURUN FİZİKOKİMYASAL ÖZELLİKLERİ VE BİYOLOJİK AYRIŞABİLİRLİĞİ ÜZERİNDEKİ ETKİSİNİN İNCELENMESİ

ÖZET

Çamur üretimindeki artışla birlikte; lokal yada global regulasyonlar sebebiyle, çamur arıtım yada bertaraf yöntemleri giderek önem kazanmıştır. Regulasyonlar çamur arıtımı yada bertarafı için bir çok gereklilik içermektedir. Regulasyonlar çamurun arıtılma veya bertaraf gerekliliklerini,limit değerleri, arıtım yada bertaraf sırasında dikkat edilmesi gerekenleri, emisyon kaynakları gibi çevresel faktörleri incelemekte ve bunlarla ilgili gereklilikleri ve kısıtlamaları içermektedir.

Çamur üretiminin artması ile birlikte çamur arıtım yada çamur bertaraf yöntemleri gereksinimide artacaktır. Nekadar fazla çamur oluşmaya başlarsa arıtım yada bertaraf gereksinimi o yönde paralel olarak artacaktır. Bu artış maliyetteki artışıda beraberinde getirecektir. Çamur arıtım yada bertaraf yöntemleri finansal,teknolojik ve çevre açısından birçok önemli noktayı içermektedir. Çamur arıtım yada bertaraf yöntemlerinin maliyeti yüksektir. Arıtım ve bertaraf yöntemleri maliyetleri yüksek olmasının yanı sıra başka edişeleri de beraberinde doğrurur.Örneğin, çamuru yakma veya toprağa gömme yöntemleri çevresel etkileri yüksek olan yöntemlerdir. Bu sebeplerden dolayı dezentegrasyon yöntemleri gibi daha az maliyetli yöntemler giderek öncelik kazanmaktadır.

Bu çalışmada 2012 ve 2013 yıllarında atıksu artıma tesisi havalandırma havuzundan alınan numuneler üzerinde iki dezentegrasyon methodu çalışılmıştır. Deneysel çalışmalar iki yıl üst üste olarak ilerletilmiştir. Bu yöntemler ultrasonikasyon ve mikrodalga irradiasyonudur. Her iki yöntemde hücrelerin veya flokların kırılması ile organik maddenin daha uygun hale gelebilmesini esas alır. Hücrelerin veya flokların kırılması daha fazla biyodegradibilite kazandırmaktadır.

Mekanik dezentegrasyon yöntemlerinin etkisini anlayabilmek için arıtılmamış çamura ultrasonikasyon uygulanmıştır. Ultrasonikasyon çalışmaları süresince, spesifik enerjinin ultrasonikasyon verimliliği açısından önemli olması sebebiyle, farklı spesifik enerjiler uygulanmıştır. Böylece, spesifik enerjinin organik madde çözünürlüğünde üzerindeki etkisi de gözlenmiştir. 2012 yılında ilk çalışmalar yapılırken 2013 yılında yapılan çalışmalara nazaran daha farklı spesifik enerjiler kullanılarak organik madde çözünürlüğü üzerindeki etkileri incelenmiş ve optimum spesifik enerjiler seçilmiştir. 2013 yılındaki çalışmalarda ise optimum olarak seçilen spesifik enerjiler kullanılarak deneyler yürütülmüştür. 2012 ve 2013 yılındaki çalışmaların birbirleri ile olan tutarlılığı göz önüne alınarak sonuçlar yorumlanmıştır.

Sonikasyon deneylerinin sonuçları göstermiştir ki, SCOD salınımı (yani, atık çamur dezentegrasyon derecesi), test edilen tüm TS seviyelerinde uzayan spesifik enerji girdisi ve ultrasonik yoğunluk ile yükselen bir trend açığa çıkarmıştır. Ultrasonik ön işlem ile WAS dezentegrasyonu, iki aşama içermektedir. nispeten düşük spesifik enerji girdisi değerlerindeki ilk hızlı aşamayı, 30000 kJ/kg TS'den daha fazla enerji dozajları için daha yavaş bir aşama takip etmiştir. Artan dezentegrasyon oranları göz

ardı edilebilir olduğundan, 1.5 W/mL değeri optimum ultrasonik yoğunluk olarak belirlenmiştir. Farklı örnek alma periyotlarına bakılmaksızın, sonikasyon çalışılan WAS örnekleri için benzer dezentegrasyon verimlilikleri sergilemiştir.

Fiziksel dezentegrasyon yöntemlerinin çamur üzerindeki etkisini incelemek amacıyla Mikrodalga irradiasyonu kullanılmıştır. Mikrodalga irradiasyonunun organik madde çözünürlüğü üzerindeki etkisini inceleyebilmek açısından uygulanan iki önemli parametre mevcuttur. Bunlar uygulanan sıcaklık ve uygulama süresidir. 2012 yılında sürdürülen çalışmalarda farklı sıcaklıklar ve zamanlar kullanılmıştır. 2013 yılında ise 2012 yılındaki sonuçlara istinaden optimum sıcaklık ve zaman olarak belirlenen 175 ^{0}C, 10 dakika kullanılarak mikrodalga dezentegrasyon metodu incelenmiştir. Sıcaklığın kaynama noktasından daha yüksek bir sıcaklığa yükseltilmesi, araştırılan TS aralığında mikrodalga ön işlem dezentegrasyon derecesini arttırmıştır; sabit bir sıcaklıkta ise, üç farklı TS konsantrasyonunda WAS'ın mikrodalga ile ısıtılması neredeyse aynı dezentegrasyon performanslarını sağlamıştır. İşlem sıcaklığının 175^{o}C'den 190^{o}C'ye çıkarılmasıyla, mikrodalga irradyasyon verimliliğindeki artış azalmıştır. Uygulanan tüm TS içerikleri için 10 dakikadan fazla maruziyet sürelerinde, çözünürleşme derecesi bakımından anlamlı bir farklılık elde edilmemiştir. İncelenen WAS örneklerinin dezentegrasyon oranları, farklı örnek alma tarihlerine rağmen tutarlı kalmıştır.

2012 ve 2013 yılında elde edilen sonuçlar, dezentegrasyon yöntemleri olan ultrasonikasyon ve mikrodalga irradiasyonunun, çamurun TKOİ,TKM azalma sağladığını göstermektedir.Toplam KOİ'nin azalması ve çözünmüş KOİ'nin artması çamur arıtımı açısındançok önemli bir parametredir. Çalışmada yürütülen sonuçlar, bu iki dezentegrasyon metodunun olumlu sonuçlarına işaret etmektedir

Sonikasyon deneylerinin sonuçları SCOD salınımı (yani çamur dezentegrasyon derecesi) test edilen bütün TS seviyelerinde spesifik enerji girişi ve ultrasonik yoğunluğun artışına bağlı olarak paralalel artış göstermektedir. Aktif çamurun ultrasonik dezentegrasyonu iki aşamadan oluşmaktadır ki başlangıçtaki hızlı faz düşük spesifik enerji giriş değerleri ardından yavaş fazda 30000 kJ / kg TKM 'den daha yüksek enerji girişleri ile peşpeşe gerçekleşmektedir.Sonikasyon deneyleri ,farklı zamanlarda alınan aktif çamur numunelerinde benzer dezentegrasyon verimliliği göstermiştir.

Kaynama noktasından daha yüksek bir sıcaklığa erişildiğinde mikrodalga irradiasyon yönteminin dezentegrasyon değeri çalışılan TKM değerinde artmaktadır.Sabit sıcaklıkta ise üç farklı TKM değerinde benzer dezentegrasyon performansı göstermiştir. Mikrodalga irradiasyon verimli,liğindeki artış sıcaklığın 175 'ten 190 ^{0}C'ye çıkarılması ile azalış göstermiştir. Bütün TKM konsantrasyonlarındaki çalışmalarda, 10 dakika uygulama süresinin üstünde solubilizasyon derecesinde önemli bir artış gözlenmemiştir. Mikrodalga irradiasyon deneyleri ,farklı zamanlarda alınan aktif çamur numunelerinde benzer dezentegrasyon verimliliği göstermiştir.

Hem ultrasonikasyon hemde mikrodalga irradiasyon, AKM ve UAKM gideriminde 22–37% aralığında verimlilik göstermiştir. TKM ve UKM gideriminde ise sadece 5%'lik bir giderim sağlanmıştır.İlk KOİ değerlerinde önemli bir değişiklik pretreatment uygulaması süresince olmamıştır. 30000 kJ/kg TKM spesifik enerji uygulamasında sonikasyon 25-26% aralığında KOİ solubilizasyonu sağlamıştır ki bu 175^{0}C 10 dakika mikrodalga uygulaması ile benzer sonuçları içermektedir. Ultrasonikasyon ve mikrodalga ile yapılan dezentegrasyon sıvı fazdaki azot ve fosfor konsantrasyonlarında artış sağlamıştır.

Mikrodalga ve ultrasonikasyon proseslerinin etkisini yorumlamak için sekuensel filtrasyon/ultrafiltrasyon ile PBD tabanlı KOİ fraksinasyonu uygulamak yararlı yöntemlerden biridir.Ultrasonikasyon yönteminin en göze çarpan etkisi >1600 nm partikül aralığındaki partikül dağılımıdır.Yüksek spesifik enerji değerlerinde sonikasyon <2 nm çözünmüş boyut aralığında kademeli artış göstermektedir.

Dezentegre edilmiş WAS miktarlarının hücre dışı ve hücre içi bileşenlerini, yani proteinleri, karbonhidratları ve lipitleri, yansıtan diğer önemli parametrelerin PSD'si bakımından ultrasonikasyon ve mikrodalga irradyasyon proseslerinin etkisinin değerlendirilmesi gelecekteki araştırmalar için ilginç bir konu olacaktır. Pilot ölçekte kapsamlı bir çalışma gerçekleştirmek ve tekno-ekonomik fizibilite analizi yürütmek, sonuçların hem yorumlanması hem de sayılarının arttırılması açısından daha derin bir içgörü sağlayabilir.

1. INTRODUCTION

In response to the enforcement of the legislations regarding the wastewater treatments, the research of more efficient treatments for wastewater is being increased. The legislations sets limits for some of the established sanitary determinants e.g. biological oxygen demand (BOD), chemical oxygen demand (COD), suspended solids and the nutrients, nitrogen and phosphorus. This leads to an increase in sewage sludge production and causes a large problem to community and wastewater treatment plants operators. They need to eliminate more sludge, whereas disposal routes (incineration, land disposal and land application) are subject to more social constraints. Sludge stabilization, composting, anaerobic digestion, thickening, dewatering and drying are the common treatment methods. Disposal, landfilling and incineration are the common disposal methods. Among the widely used treatment and disposal methods, there are composting, stabilization, landfilling and incineration. The cost of these treatment methods is highly dependent on the volume and water content of the produced sludge. In order to reduce sludge volume and improve sludge dewatering characteristics, various physical and chemical methods have been examined and used, such as thermal hydrolysis (Wilson and Novak, 2009), mechanical disintegration (Kampasa et al., 2007), ultrasonic treatment (Feng et al., 2009), hydrolysis and acidification (Liu et al., 2008), microwave irradiation (Park et al., 2009; Eskicioglu et al., 2007), ozonation (Yan et al., 2009), and alkaline addition (Neyens et al., 2003).Ultrasonic process causes to cavitation bubble formation in the liquid phase These bubbles grow and then violently collapse when they reach a critical size. Cavitational collapse generates intense local heating and high pressure on liquid–gas interface, turbulence and high shearing phenomena in the liquid phase. Mechanisms of the ultrasonic process are influenced by three factors: supplied energy, ultrasonic frequency and nature of the influent. Cell disintegration is proportional to supplied energy.(Bougrier et al,2004)

This study experimentally investigated the individual effects of ultrasonication and microwave irradiation processes on the disintegration of municipal WAS.

Purpose of thesis

The aim of this research is to investigate the effect of ultrasonication and microwave irraditon on the sludge solubilization. Result of this research helps to evaluate the effects of disintegration methods on the sludge treatment.This work is to provide better insights into the disintegration of WAS by ultrasonication and microwave irradiation processes. Accrding to this, the work included four main research contents: (i) the raw (untreated), sonicated and irradiated WAS samples were analyzed for the calculation of sludge disintegration degree based on soluble chemical oxygen demand parameter (DDSCOD) to select optimum conditions of ultrasonic and microwave pretreatment, (ii) WAS samples before and after pretreatment were characterized for physico-chemical parameters to focus on the changes of sludge characteristics during disintegration, (iii) particle size distribution (PSD) analysis by sequential filtration / ultrafiltration was used as a supportive tool to interpret the effect of the applied pretreatment processes on the COD of disintegrated WAS samples and (iv) the impact of disintegration techniques on the biodegradability of WAS samples was investigated by evaluating the oxygen uptake rate (OUR) profiles obtained from respirometric measurements.

2. LITERATURE REVIEW

2.1 Explaining of Activated Sludge Process

An activated sludge process is able to just remove part of the contaminants. In this process the contaminants absorb to sludge, degrade biologically, evaporate or stay in the treated water. Sewage overflows and sewer leakages lead the entry of some wastewater into the environment already before wastewater has been led to the treatment plant. About 5- 20% of wastewater leaks into the environment because of the overflows or sewer leakages. This is means that some harmful chemicals are able to also enter into the environment with overflows and sewer leakages, to prevent that style of emissions; wastewater should be treated before it is discharged into the sewer (Joss et al. 2008).Figure 2.1 explains conventional wastewater treatment plant.

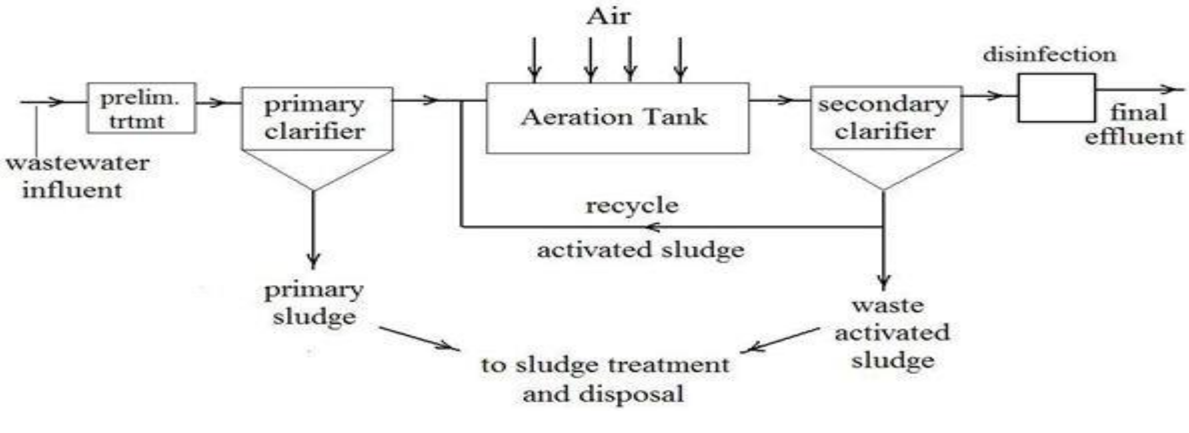


Figure 2.1 : Activated Sludge Wastewater Treatment Flow Diagram (Metcalf and Eddy, 2003).

Because of the enlargement of wastewater treatment, the generation of WAS has increased (Reynolds and Richards, 1996). The anaerobic digestion of WAS is desirable due to its reduced environmental impact, particularly reduced greenhouse gas emissions and through the generation of biogas as an alternative for fossil fuels (Gunaseelan, 1997; Chynoweth et al., 2001; Charters, 2001). The anaerobic digestion of WAS has several advantages: digested sludge is relatively stable and harmless to be disposed of, a low level of energy is required for digestion and the generated methane can be utilized as fuel. Consequently, there is a significant decrease in the energy requirements for digestion as compared to aerobic digestion. In addition, pathogenic microorganisms in WAS are reduced. However, long digestion times, requiring a large digester volumes are a significant disadvantage of the anaerobic digestion of WAS. The low rate of hydrolysis processes and the slow growth of methanogenic microorganisms which are responsible for the methanogenesis process limit the rate of anaerobic digestion (Wang et al., 1999).

According to the previous investigations , the WAS reduction studies were mainly classified into two categories (Mahmood and Elliott, 2006): (1) sludge reduction trough post treatment; and (2) in-situ activated sludge reduction in the process of sewage treatment. Post treatments are related to the sludge reduction methods. To reduce excess sludge that has already been produced during sewage treatment process. There are a lot of methods to reduce WAS. For example ; single or a combination of physical, chemical and biological methods have been applied to reduce WAS (Lou et al., 2011, Saby et al., 2002, Wang et al., 2011 and Zhang et al., 2007). On the other hand, the high operational complexity and expenses, together with a large amount of energy consumption are considerable problems. Comparing with the post treatment, in-situ excess sludge reduction process is of prominent advantages. The important property of in-situ excess sludge reduction is to minimize the sludge yield from the source of sewage treatment process itself. There are some successful investigations related to in-situ excess sludge reduction process (Guo et al., 2007, Wei et al., 2009, Xing et al., 2008 and Yu et al., 2006). Sustainable sludge handling may be defined as a method that meets requirements of efficient recycling of resources, without supply of harmful substances to humans or the environment (Commission of European Communities, 1998).

Sludge reduction can be achieved by lysis-cryptic growth of microorganisms. The biomass grows on the lysates that dissolved from its own. When microbial cells are disintegrated, the microorganism cell contents would be released into the liquid, and these organic autochthonous substrates are reused by itself for metabolism (Chu et al., 2009).

Sludge lysis-cryptic growth technologies would result in an increase in the organic matters, including SCOD and phosphorus concentration in the effluent. These increased organic matters might exasperate the effluent quality in the BSTSs during long-term operation.

2.2 Problems Related to Sludge

Treatment sludge refers to the liquid or semi-solid and odorous waste items including certain amounts of solids inside depending on its treatment method and obtained from the primary and secondary clarifiers as a result of wastewater treatment process.

The sludge production causes activated sludge process treatments of domestic and industrial wastewaters.

It is important to increase widespread application area of activated sludge processes and wastewate treatment.The costs of sludge treatment and sludge removal also increase in parallel to the increase in sludge amount caused by activated sludge processes and it becomes a primary component for total wastewater treatment costs. The increase in sludge amounts constitutes a serious problem (Chu et al., 2009). Excess sludge treatment or disposal actions involve 40 or 60% of total cost nearly (Wei et al., 2003; Demir et al., 2011). Excess sludge treatment or disposal processes involve lots of significant issues in terms of finance, technology and environment.Landfilling or incineration methods among traditional methods have put forward serious legal limitations and restrictions in some countries (Moussavi et al., 2008). Landfilling requires a certain area and incineration creates a serious problem in terms of air emission. Besides, excess sludge is created as a result of biological treatment and taken as secondary solid waste (Moussavi et al., 2008). This increase observed either in waste sludge production or in waste sludge treatment and removal costs have made it necessary to manage and control the wastewater sludge occurred due to activated sludge systems (Dogruel et al., 2006). Possible applications of disintegration methods such as ozonation, ultrasonication, microwave irridation, alkaline pretreatments are cost effective. They obtain sludge reduction and cost saving. Capital cost may be not less than the other treatment, but operatonal cost is less than other methods.

The amount of sludge produced in a wastewater treatment plant is dependent on its operational parameters. Some of the characteristics of the sludge are also dependent on not only the type of wastewater being treated but also on the operational parameters applied in the process. In any case, sludge production is almost always significant, and a substantial portion of operating costs goes to process and dispose excess sludge, often as much as 50-60% of the total operational costs (Barret, 1996; Weemaes and Verstraete, 1998). Table 2.1 shows data for sludge production in several states in Europe and the US.

Table 2.1: Sludge Production and disposal methods in Europe and North America. (Source:UN 2002)

	Annual Production (10 küp dry tons)	**Agriculture**	**Disposal Method (Percentage of Total) Lanfill**	**Incineration**	**Other**
Austria	320	13	56	31	0
Belgium	75	31	56	9	4
Denmark	130	37	33	28	2
France	700	50	50	0	0
Germany	2500	25	63	12	0
Greece	15	3	97	0	0
Ireland	24	28	18	0	54
Italy	800	34	55	11	0
Luxemburg	15	81	18	0	1
Holland	282	44	53	3	0
Portugal	200	80	13	0	7
Spain	280	10	50	10	30

Switzarland	50	30	20	0	50
UK	1075	51	16	5	28
US	5357	36	38	16	10
Ontario	150	-	-	-	-

The volume of wastewater subjected to treatment has been increasing steadily in the last decade, due to both the growing population, and the increasing coverage of urban and rural areas with sewer drainage and treatment systems. In cities that show noticeable industrial growth, further increases of the volume of wastewater to be treated are measured.

Hence, wastewater treatment may convert a water pollution problem into a solid waste disposal problem. With the quantity of sludge to dispose increasing, and the options to dispose of it decreasing (with bans on ocean and landfill disposal as examples), management of this residue is a very important concern.

Landfilling is a high-cost method, which requires field and design process. Besides, the gases resulting from landfilling must be refined, which also causes an additional cost. Incineration is also a high-cost method in terms of its design and gas refinement.

The international contracts and increasing sensitivity especially in terms of environmental issues in recent years have required taking serious steps on wastewater treatment. Activated sludges have several sources and these sludges differ both in terms of quality and quantity. The amount of treatment sludge depends on the contamination level of wastewater, its characteristics and the physical, chemical, physicochemical, biological and similar methods applied in treatment facilities. The process of activated sludge is removal or disposal ,there is no specific regulation to apply.

Many provisions are included in several regulations and official statements in Turkey in relation to the treatment sludges. In this view, all environmental regulations are reviewed on sludge management and related documents are determined. Here follows the relevant regulations and official statements, given together with their names in this section. The following regulations and official statements are examined in detail under separate titles.

- Regulations on General Principles of Waste Management (Official Gazette dated 05.07.2008 and numbered 26927)
- Regulations on Using Domestic and Urban Treatment Sludges within Soil (Official Gazette dated 03.08.2010 and numbered 27661)
- Regulations on Controlling Water Pollution Soil (Official Gazette dated 31.12.2004 and numbered 25687) and Administrative Procedure Communiqué of Regulations on Controlling Water Pollution (Official Gazette dated 10.10.2009 and numbered 27372)
- Regulations on Controlling Solid Wastes (Official Gazette dated 14.03.1991 and numbered 20814)
- Regulations on Controlling Hazardous Wastes (Official Gazette dated 14.03.2005 and numbered 25755)
- Regulations on Waste Incineration (Official Gazette dated 06.10.2010 and numbered 27721)
- Regulations on Organized Storing of Wastes (Official Gazette dated 26.03.2010 and numbered 27533)
- Regulations on Urban Wastewater Treatment (Official Gazette dated 08.01.2006 and numbered 26047)
- Technical Procedures Communiqué of Wastewater Treatment Plants (Official Gazette dated 20.03.2010 and numbered 25527)
- Recovery Communiqué of Several Non-Hazardous Wastes (Official Gazette dated 17.06.2011 and numbered 27967)

Regulations on general principles of waste management (official gazette dated 05.07.2008 and numbered 26927)

This legislation aims to determine the general principles from waste production to their disposal by enabling an appropriate administration both for human health and environmental protection. In this view, waste classification is required to have a better control of waste management, therefore creating a detailed waste list under 20 main groups. Here, treatment sludges are included in Section 19 in the Waste List stated in the Regulation Attachment IV under Code 19.08 and the Category of Wastewater Treatment Plants Not Defined in Other Words that is defined as – Wastes resulting from water treatment plants obtained from waste management plants and other off-site waste water treatment plants and intended for human consumption and industrial use. The wastes listed under this category with Codes 19, 08 and 05 are accepted as non-hazardous, having no such marks (A) or (M) in addition to urban treatment sludges that are defined as sludges resulting from urban waste water treatment.

Regulations on using domestic and urban treatment sludges within soil (official gazette dated 03.08.2010 and numbered 27661)

The objective of this regulation is to take necessary precautions on soil use for treatment sludges and to determine sustainable development plans in accordance with them. The regulation includes technical and administrative principles on controlled use of treatment sludges obtained via refining domestic and urban wastewaters without harming soil, plants, animals and humans. This regulation is prepared basing on the relevant section on sludge use in agriculture defined previously in Regulations on Controlling Soil Pollution, which was in effect before the application date of this regulation. The regulation defines raw sludge as treatment sludges resulting from treatment plants of domestic or urban wastewater, which is similar to domestic and urban wastewater in terms of its composition or from other treatment plants or from sewage tanks and similar treatment plants. It also defines stabilized sludge as domestic and urban treatment sludges stored for a long term or processed under biological, chemical or thermal operations in order to reduce its hazards to human health caused by biological decomposition and use. In accordance with this regulation, it is strictly prohibited to use raw sludge in the soil and the ranges stated in Appendix I-B, Appendix I-C and Appendix I-D should never be exceeded for stabilized sludge use in the soil.

Regulations on controlling water pollution soil (official gazette dated 31.12.2004 and numbered 25687) and administrative procedure communiqué of regulations on controlling water pollution (official gazette dated 10.10.2009 and numbered 27372)

This regulation defines legal and technical principles required to realize a sustainable development plan in consistent with the protection of aboveground and underground waste resources of our country and with their best use via preventing water pollution. This regulation includes quality classifications of water environments and their purposes of use, planning principles and prohibitions on protecting water quality, discharge principles and discharge permit principles of wastewaters, principles on wastewater treatment plants and other procedures and principles to monitor and audit any action for preventing water pollution. In accordance with these principles, waste water discharge in waste water treatment plants are required to keep treatment sludges away, not to prevent their use and to cause any pollution in the surroundings. In addition to these principles stated in the regulations, it is strictly prohibited that any substance which negatively affects the purification efficiency of treatment plants, operation of sludge plants, sludge disposal or sludge evaluation be given to waste water underground plants. It is also stated in the regulation that discharging treatment sludges and sewage sludges into receiver water environments is strictly prohibited as in Regulations on Urban Wastewater Treatment. According to this regulation, storing tanks of treatment sludges must be leak-proof in order to protect the underground waters. In view of the sea pollution, it is prohibited to dispose treatment sludges into the sea and coastline. Regulations on Administrative Procedures Communiqué on Controlling Water Pollution involves the principles on getting a permit for discharging all types of domestic, urban and/or industrial wastewater directly into the receiver environments. In accordance with this communiqué, the applications to get a permit on discharging wastewater directly into the receiving environments should involve information on their treatment and disposal. The sludge amount, caused by a management, tons of solid/number of days must be stated in technical data sheet on wastewater discharge and sludge treatment methods must be described to take precautions or sludge analyses if it is to be used in agriculture.

Regulations on controlling solid wastes (official gazette dated 14.03.1991 and numbered 20814)

The objective of Regulations on Controlling Solid Wastes is to determine, apply and develop principles, policies and programs on directly or indirectly transferring all types of wastes and residuals into the nature without giving any harm to the environment, their storage, transport, disposal and prohibition of similar operations, to prevent any pollutant in the air, water or soil from harming flora and fauna, natural resources and ecological balance by determining a certain discipline on consumption materials, which may affect the environment negatively. This regulation involves principles on collecting, transporting, recovering, evaluating, disposing and making industrial treatment plant sludges harmless, which are not classified as hazardous wastes and treatment sludges caused from domestic wastewater treatment plants in industrial and commercial plants which domestic solid waste characteristics in addition to not being hazardous and large solid wastes scattered into green areas, parks and gardens in residential locations. The regulation defines the treatment sludge as the dewaterized and dehydrated sludges that occur as a result of physical, chemical and biological operations in domestic and domestic-type industrial wastewater. Besides, solid waste definition also involves treatment sludges. In the section, which describes on-site collection and transportation of solid wastes separately, it is strictly prohibited to pour solid wastes into the seas, lakes and similar receiver environments, streets, forests and environment to prevent any negative effect and it is obliged to transport all domestic and domestic-type industrial wastes collected in exclusively covered vehicles without polluting the environment in terms of appearance, odor, dust, permeability and similar factors under the statement – When collecting non-domestic solid wastes or storing them in a plant, containers and tanks at desired volumes and shapes can be used without giving any harm to human health and environment, destroying its landscape and disturbing the environment in terms of odor, dust, etc.

Regulations on organized storing of wastes (official gazette dated 26.03.2010 and numbered 27533)

The objective of this regulation is to determine general principles and other technical and administrative issues required to follow in terms of preventing environmental pollution by reducing the negative effects of leachate at a minimum level, which may occur during their disposal via organized storing of wastes and storage gases on soil, air, underground water and surface waters, and in terms of receiving wastes into organized storing plants, making technical designs of storage floors in accordance with waste types and building organized storing plants, their operation and closing down and their controlling and maintenance after the closure, recovery of available organized storing plants, their closure and maintenance after the closure.

This regulation involves general procedures and principles on organized storing of wastes and their receiving into the organized storing plants with technical principles on organized storing plants and precautions to be taken, audits to be made and responsibilities to be subjected. However, it is stated that raw sludge, stabilized treatment sludge and compost applications into the soil as fertilizer or soil amendment are out of this regulation.

Regulations on urban wastewater treatment (official gazette dated 08.01.2006 and numbered 26047)

The objective of this regulation is to protect the environment against the negative effects of collection of urban and certain types of industrial-based wastewaters, their treatment and discharge into sewage systems and it involves basic principles and procedures to monitor, report and audit this discharge in terms of this regulation. It also describes such terms as treatment sludges, less sensitive water areas, primary treatment, domestic wastewater, industrial wastewater, equivalent population, estuary, sensitive water areas, secondary treatment, sewage systems, urban wastewater, coastline water, eutrophication, wastewater collection zones and appropriate treatment. The definition of treatment sludge in the regulation refers to raw or stabilized sludges, which come out of urban wastewater treatment plants. This regulation strictly prohibits discharging treatment sludges and sewage sludges into the receiver water environments. This regulation bases on Regulations on Controlling Soil Pollution for using or disposing the treatment sludges coming out of urban wastewater treatment plants in soil and starting from 03.08.2010, Regulations on Controlling Soil Pollution have been abolished and new Regulations on Using Domestic and Urban Treatment Sludges in Soil is published for using treatment sludges in soil, therefore requiring to take this regulation - Regulations on Using Domestic and Urban Treatment Sludges in Soil as a base. This regulation also requires that status reports on the disposal of urban wastewater and treatment sludges will be prepared every two years by the concerning directorates and submitted to the Ministry via the highest rank officials in the province. If found necessary by the Ministry, the management is obliged to update this information every two years and submit them to the Ministry. The concerning regional directorates must prepare a program to apply this regulation with the highest rank official in the region and the administrative chief must submit information to the Ministry. Within the framework of principles on discharging industrial wastewaters into sewage systems, the industrial wastewaters discharged into the sewage system must never hinder refining the treatment sludges and the treatment sludges must environmentally be acceptable and safely disposed by having a pre-treatment.

Regulations on waste incineration (official gazette dated 06.10.2010 and numbered 27721)

The objective of this regulation is to reduce the negative effects of waste incineration on environment, especially on air, soil, surface waters and underground waters due to emissions and to prevent and limit the risks which may occur against human health and environmental population. This regulation involves the minimum conditions required for waste incineration and co-incineration plants. When the treatment sludges are used solely or as an additional fuel, Regulations on Incineration of Wastes will apply. The regulations also describe incineration plants and co-incineration plants and the main purpose of co-incineration plants are defined as the ones, which aim energy production or products, using wastes as alternatives or additional fuel or disposing wastes via thermal methods. If co-incineration process aims to dispose wastes via thermal methods and not to produce energy, then it is regarded as an incineration plant. If nominal thermal power value of fuel is 40% or more supplied from wastes, it is defined as co-incineration plant; and if nominal thermal power value of fuel is provided more than 40%, then it is defined as incineration plant in the regulation. The same emission limit values apply in terms of incineration or co-incineration of hazardous and non-hazardous wastes in the regulation. In addition to this, chimney gas limit values are also defined for incineration and co-incineration plants, incineration plants (Appendix-4) must provide emission limit values more strictly than co-incineration plants (Appendix-2). The regulation also defines the provisions on wastewater and residues caused by these incineration and co-incineration plants besides their permits, operation, audit and monitoring.

Environmental legislations of European Union (EU)

The first determinant document of European Union (EU) on wastewater management is Communal Strategies on Wastewater Management, published in Commission Communiqué. Waste management in EU is organized via such legislations on waste managements operations together with framework waste legislations, several others on certain types of wastes and some other directives and complementary items stated in reports and inventories. The framework directive on waste water management, waste treatment operations and all regulations, legislations and directives on waste flows are summarized in Figure 2.1. The basis of waste regulations in European Union involve Framework Waste Directives and this legislation also includes Directives on Incineration of Wastes (2000/76/EC), *which state other directives on waste management operations*, Council Decisions on Waste Receiving in Storing Areas (2003/33/EC), Directives on Organized Storing (99/31/EC), Directives on Preventing and Controlling Integrated Pollution (2008/1/EC), Directives on Urban Wastewater Treatment (91/271/EEC) and Directives on Packages and Package Wastes, stating the directives on exclusive waste management (94/62/EC), Directives on Treatment Sludges for protecting the nature and soil during their use in agriculture (86/278/EEC), Directives on Waste Oils (75/439/EC is abolished after transferred to New Framework Directives on Wastes in 12.12.2010 (2008/98/EC), Working Documents on Sludges – 3rd Draft (27.04.2000), Directives on Wastes of Extraction Industries (2006/21/EC), Directives on Wastes of Electrical and Electronical Equipments (2002/96/EC-2002/95/EC), Directives on Dead Batteries and Accumulators (91/157/EEC and 98/101/EC), Directives on Scrapped Vehicles (2000/53/EC), Directives on Polychlorinated Biphenyl (PCB) and Polychlorinated Terphenyls (PCT) (96/59/EC), Directives on Industrial Wastes with Titanium Dioxide (78/176/EEC, 82/883/EEC, 91/692/EEC), Directives on Using the Energy Obtained from Renewable Sources (2009/28/EC).

2.3 Sludge Treatment and Disposal

There are many different methods used in sludge treatment and disposal. The appropriateness of these methods into the environment and financial issues should be taken into consideration. In Table 2.2, sludge pre-treatment methods are indicated schematically. Sludge stabilization, composting, anaerobic digestion, thickening, dewatering and drying are the common treatment methods. Disposal, landfilling and incineration are the common disposal methods. Among the widely used treatment and disposal methods, there are composting, stabilization, landfilling and incineration. In relation to the disposal processes, the parameters on sludge characteristics of these processes are stated in Table 2.3. These parameters are about the sludge characteristics and important in terms of determining applicability of disposal methods and their efficiency.

Table 2.2 : Various Methods During Sludge Pre-Treatment (EPA, 1997).

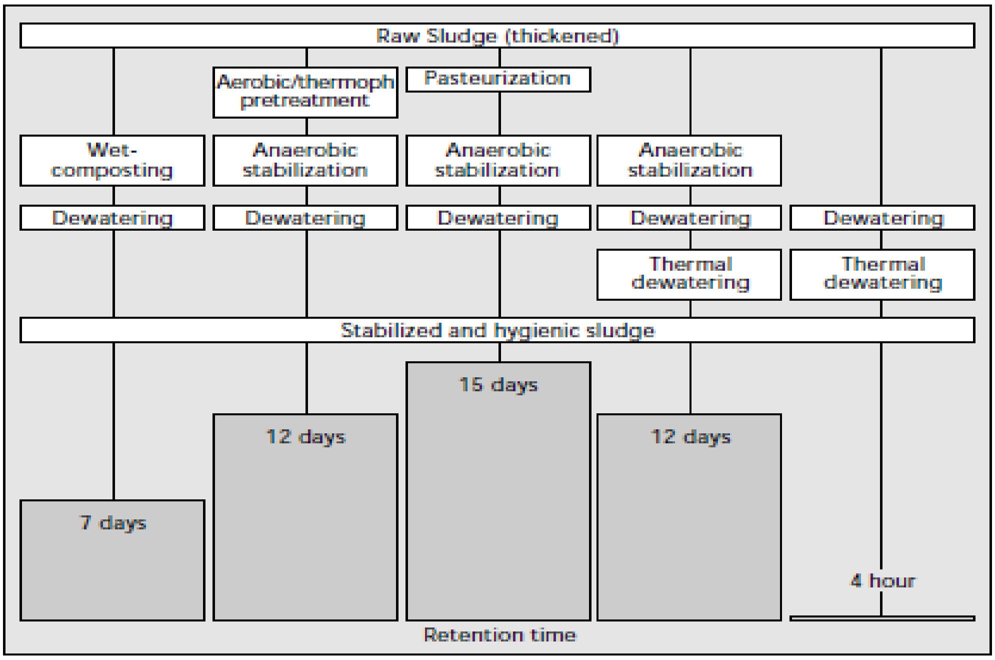


Table 2.3 : Disposal and Use Operations Apparatus (C.N.R,1980)**.**

Method of Treatment and Disposal													
		Stabilisation											
Parameter	Sedimentation	aerobic	anaerobic	chemical	thermal	Thickening	Dewatering	Drying	Transportation	Landfilling	Composting	Agriculture	Incineration
Temperature		x	x				x	x			x		x
Density						x		x	x				
Rheological prop.							x	x	x	x		x	x
Settleability	x					x	x						
Solids concentr.	x	x	x	x	x	x	x	x	x	x	x	x	x
Volatile solids		x	x	x	x				x	x	x	x	x
Digestability			x										
pH		x	x	x			x				x	x	
Volatile acids			x										
Fats and oils		x	x									x	
Heavy metals			x							x	x	x	x
Nutrients		x	x								x	x	
Particle size	x					x	x						
CST						x	x						
Spec. resistance						x	x						
Compressibility							x						
Centrifugability							x						
Calorific value													x
Leachability										x			
Microbiol. prop.		x	x								x	x	

This table includes the relation between parameters as well as methods. The table also displays that parameter is significant for which method and their effects. Therefore it definateley shows which parameter will change and which method will be effective for which parameter when any of these methods is applied.

2.3.1 Stabilization

Raw sludge is biologically active because it contains biodegradable compounds. Stabilisation is of importance in regard to hygienisation because the odours are reduced (Naturvårdsverket, 2003). Stabilization is the term used to denote the process of BOD reduction. The stabilisation process can be carried out under aerobic or anaerobic conditions. After stabilisation, the volume has decreased, hygienisation has occurred and the sludge is no longer regarded as active.

Biological stabilization processes, such as anaerobic and aerobic digestion, are widely adopted in order to reduce the total mass of sludge to be disposed of and to produce well stabilized bio-solids and to generate bio-energy such as methane gas (Khanal et al.,2007).

Besides, Sludge stabilization is one of the most favored and ordinarily used techniques for the sludge disposal. Stabilization process turns raw sludge into a less offensive form and leads to an efficient pathogen reduction, removal of organic matter as well as odor potential (Kim and Hao, 1990). The pretreatment action will have been based upon the needs of this process that may also have been chosen for the manufacture of a product appropriate for a specific ultimate disposal routes, such as application on agricultural lands, incineration or other burning processes. These techniques are microbiological (aerobic or anaerobic) or chemical. When the action has not ended in a notable loss of water (e.g., through evaporation in composting) the ultimate product will be dewatered again in advance of final disposal. Contaminants inside raw sludge may be defiant and endure linked to solids. If so, then as the entire size of sludge is lessened during treatment, concentrations within the ultimate product will be more than in the raw material (Birkett and Lester, 2003).

2.3.2 Aerobic digestion

Aerobic digestion is a process where the sludge is placed in an aerated vessel. The decomposition is performed by aerobic micro organisms and this generates heat. If the process is working adequately, more than 70°C can be reached. Usually the sludge is subjected to 50 to 65°C for 5 to 6 days and most of the harmful organisms are destroyed. One drawback is that the energy costs are 5 to 10 times higher than for anaerobic digestion. (European Commission, 2001)

The aerobic digestion process consists of two steps (1) the direct oxidation of biodegradable matter and (2) endogenous respiration where cellular material is oxidized. The operating temperature and Solids Retention Time SRT condition which is important factor in the effective operation of aerobic digesters are the main parameters affecting performance of the aerobic digestion process. The aerobic sludge digester (ASD) operated at high temperature (thermophilic condition usually maintained within 50–70ºC) offers several advantages like, high sterilization ability, decreasing the odour of sludge and high sludge reduction (Mason et.,al 1992Banat et al., 2000).

If we mentioned about aerobic digestion process,Aerobic digestion has a great resemblance to the activated sludge process. With the contribution of substrate interrupted, the microorganisms are imposed to devour their own energy reserves to survive. This is called endogenous phase, where in nonexistence of food supply, the biodegredable cell mass is aerobically oxidized to carbon dioxide, ammonia and water. Ammonia is oxidized to nitrate during the reaction in line with the equation 3.1 (Andreoli et al., 2007). $C5H7NO2 + 7O2 \rightarrow 5CO2 + NO3 - + 3H2O + H+$ (3.1) It has been known for so long that once a microbial population has deployed occuring exogenous substrate to the level that there is deficient substrate to conserve the population, endogenous respiration begins. The population then lessens in mass and numbers. Aerobic digestion is projected to focus on waste cells and to lessen their numbers and mass via endogenous respiration (Erbes et al., 1980).

2.3.3 Anaerobic digestion

Anaerobic digestion is a bacterial decomposition process and stabilizes organic waste items, creating methane and carbon dioxide. It enables a 35% decrease in the amount of sludge (European Commission, 2001).The decomposition process in a digester has several stages. Carbohydrates, fats and proteins are broken down in different steps and finally converted into methane gas and carbon dioxide. (Nilsson, 2002) The produced biogas may be utilized as electricity on the plant or used elsewhere. The temperature is normally kept around 35°C and the retention time should be more than 20 days in order to receive a good stabilization and hygienization but other retention times and temperatures also exists. Pathogens are reduced during digestion and to which extent depends on the temperature and retention times used. (European Commission, 2001)

Anaerobic digestion is the most popular method used in sludge treatment (Bougrier et at., 2007). The biological hydrolysis, which is the first step of this method, is rate limiting step for sludge digestion (Shimizu, 1993). Figure 2.2 indicates biological hydrolysis steps.

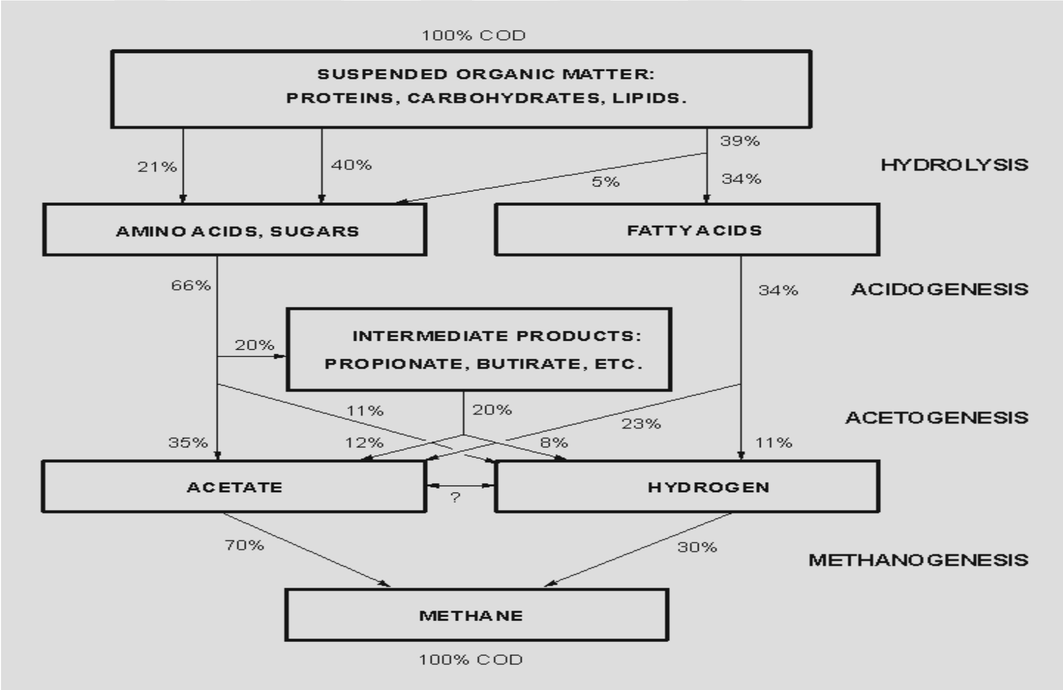


Figure 2.2 : Anaerobic Digestion Steps (Adrianus van Haandel et al., ; Jeroen van der Lubbe et al.,2012).

Hydrolysis

In general, hydrolysis is a chemical reaction in which the breakdown of water occurs to form H+ cations and OH- anions. Hydrolysis is often used to break down larger polymers, often in the presence of an acidic catalyst. In anaerobic digestion, hydrolysis is the essential first step, as Biomass is normally comprised of very large organic polymers, which are otherwise unusable. Through hydrolysis, these large polymers, namely proteins, fats and carbohydrates, are broken down into smaller molecules such as amino acids, fatty acids, and simple sugars. While some of the products of hydrolysis, including hydrogen and acetate, may be used by methanogens later in the anaerobic digestion process, the majority of the molecules, which are still relatively large, must be further broken down in the process of acidogenesis so that they may be used to create methane. Hydrolysis is the very slow process.

Acidogenesis

Acidogenesis is the next step of anaerobic digestion in which acidogenic microorganisms further break down the Biomass products after hydrolysis. These fermentative bacteria produce an acidic environment in the digestive tank while creating ammonia, H_2, CO_2, H_2S, shorter volatile fatty acids, carbonic acids, alcohols, as well as trace amounts of other byproducts. While acidogenic bacteria further breaks down the organic matter, it is still too large and unusable for the ultimate goal of methane production, so the biomass must next undergo the process of acetogenesis.

Acetogenesis

In general, acetogenesis is the creation of acetate, a derivative of acetic acid, from carbon and energy sources by acetogens. These microorganisms catabolize many of the products created in acidogenesis into acetic acid, CO_2 and H_2. Acetogens break down the Biomass to a point to which Methanogens can utilize much of the remaining material to create Methane as a Biofuel.

Methanogenesis

Methanogenesis constitutes the final stage of anaerobic digestion in which methanogens create methane from the final products of acetogenesis as well as from some of the intermediate products from hydrolysis and acidogenesis. There are two general pathways involving the use of acetic acid and carbon dioxide, the two main products of the first three steps of anaerobic digestion, to create methane in methanogenesis:

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

$CH_3COOH \rightarrow CH_4 + CO_2$

While CO_2 can be converted into methane and water through the reaction, the main mechanism to create methane in methanogenesis is the path involving acetic acid. This path creates methane and CO_2, the two main products of anaerobic digestion. (http://www.e-inst.com/biomass-to-biogas/)

2.3.4 Composting

Composting is an aerobic process and involves mixing carbon source substances with wastewater items. Sludge composting aims biological sludge stabilization, therefore developing their agricultural use and use for other purposes. Composting is consisted of decreasing water content in sludge as possible within aerobic degradation of organic items.

Composted sludge is used for agricultural purposes. If sludge incineration method is preferred, composting is used as pre-treatment in order to decrease the water content. However, composting the sludge first and incinerating it later cost too much. Besides composting some organic items may decrease the calorific value of sludge (EPA, 1997). Table 2.4 indicates the advantages and disadvantages of composting method.

Table 2.4: Advantages and Disadvantages of Composting Process.

Advantages	Disadvantages
• Used for agricultural purposes and sludge obtained with decreases in volume • Increasing water content	• High costs of treatment • Energy consumption for aeration

2.3.5 Sludge thickening

The sludge produced at the wastewater treatment plant contains a lot of water and it has to be thickened in order to reduce the volume and cost for the following treatments. The thickening methods purpose is to remove some of its free water. Flotation may be a suitable method for chemical and biological sludge while primary sludge is best thickened by various sedimentation processes. Centrifugation can be used either for thickening or dewatering purposes. (European Commission, 2001)

2.3.6 Dewatering

Dewatering means that the volume of the sludge is greatly reduced by separating water. Raw sludge contains high amounts of water, usually more than 95% by weight (Casey, 1997). It is only possible to remove a certain proportion of free and capillary water (Lindquist, 2003). Different dewatering processes are drying beds, centrifuging, filter belt and filter press. All processes except drying beds requires the addition of a chemical conditioning agent.

2.4 Sludge Disposal Methods

There are two alternatives for disposal of sludge: mono-deposits where only sludge is disposed of, and mixed deposits where the sludge from the municipal waste water treatment plant is disposed of together with the municipal solid waste. In the latter case, it is customary to utilize the gases from the deposit (methane and CO2).

Conditions for sludge disposal (sanitary landfill) are regulated by the ‘Technical Directives’ in each country. Considering the present strict regulations and the limited number of the potentially suitable disposal sites only regional sludge deposits can be considered. It is also desired/required that below the deposit a water tight (e.g. clay) layer should be established to prevent infiltration into the ground water. Selection of the feasible site has to fulfill other criteria as well. Among these the most important ones are the safety distance from various establishments such as residential areas, public roads, river dikes, etc. It is of paramount importance that the selected site should not be covered even temporarily by inland waters, or be located on the area of water bases (aquifers). Another point is that the land should not be of high value from an agricultural point of view and the future development plan is not to be intercepted by the establishment of the sludge deposit.(Bresters, Coulomb, Deak, Matter, Saabye, Spinosa, Utvik,1997)

2.4.1 Incineration

Incineration of sludge either as a single or together with other waste items is a widely used method. The sludge to be incinerated should be 40% of self-soluble solid content without an additional source of incineration. The solid content of a normally dissolved sludge dewatered (Dissolved Solid) is 25% (Lindquist, 2003). Its calorific value is 10-20 MJ/kg DS (Lindquist, 2003). In incineration method, it is possible to use the energy inside the sludge.

The agricultural use of sludge and applications of landfilling require many strict legal restrictions and limitations. Especially the regulations on air emission should absolutely be followed. In this view, although the incineration method has high cost of investment, it is expected that legal restrictions on incineration and collection of gas occurred and its treatment be increased in following periods, shows in Table 2.5 (EPA, 1997).

Table 2.5 : Advantages and Disadvantages of Incineration Process (EPA, 1997).

Advantages	**Disadvantages**
• Serious decrease in volume after incineration • Energetic valorization of sludge • Low sensitivity to sludge composition • Odor minimization	• High cost of investment • Generally used for high volumes • Creates a transfer cost for sludge incineration area • Requires an increase in the amount of gas occurred and emission control • High operational costs

2.4.2 Landfilling

This process collects the sludge under a surface.In many countries, there are many legal restrictions on its design, operation and leakage increase. Leakages are generally dangerous and may contain heavy metal and other contaminants inside. Landfill gases are normally observed to spread methane and carbon dioxide. Some landfills are used as heating and energy sources for other purposes by collecting the gases.

In following years, it is predicted that landfilling will be used as a final solution for surface pollution and area requirements (EPA, 1997).

2.4.3 Sludge disintegration

Biological treatment technology for the purification of both domestic as well as industrial wastewater streams used the activated sludge process ,by generating waste activated sludge (WAS) as the main by product (Lee, Chung, Yu, Rhee, 2009;100:4597–4603, Tang , Yu , Huang , Luo, Zhuo, 2010;101:5092–5097 and Yan , Feng , Zhang , Zhu , Zhou, 2010;9:1776–1782) The great amount of WAS generated has been numerously by growing as a result of the quantitative and qualitative expansion of wastewater treatment as well as progressively more stringent environmental regulations (Kim, Bae, Oh , Lee, Choi, 2002;82:157–164, Xiao , Yang, Liu, 2013;254–255:57–63.) The Costs associated with processing as well as disposing WAS is able to account for up to 50% of the operating costs of a wastewater treatment plant (Li , Li , Liu , Zou, 2012;123:189–194) the minimization of WAS production has become one of the most challenging problems in the field of biological wastewater treatment. As a conclusion reliable sludge treatment processes are necessitated for the efficient as well as economical management of WAS so as to decrease the volume and organic and inorganic complement of biosolids, as well as to destruct pathogens, whereas maintaining features for soil amendment and land reclamation goals (Dacera, Babel , Parkpian, 2009;167:866–872) Anaerobic digestion process is the most general applied sludge treatment method because it decreases the sludge volume, generates energy-rich gas in the form of methane and yields a nutrient-containing final product (Kim, Jeong , Oh , Shin, . 2010;44:3093–3100) but , owing to the slow degradation rate of WAS, its application has always been restricted by long retention times of 20–30 days to attain even moderate efficiencies of 30–50 percent (Baier,Schmidheiny, 1997;36:137–143, Weemaes, Grootaerd , Simoens , Verstraete, 2000;34:2330–2336.) Another traditionall treatment used for the stabilization of WAS is the aerobic digestion process.However; long retention time as a conclusion the complicated and non-homogeneous nature of sludge, high energy consumption and wide construction cost are the main drawbacks of the aerobic digestion technology (Barbusinski, Koscielniak, 1997;36:107–114, Moussavi, Asilian, Jamal, 2008;4:122–127.) In order to accelerate the degradation of the organic compounds in WAS and therefore; to maximize the reduction efficiency in digesters, the rate limiting step of hydrolysis such as solubilization has to be developed by pretreating it before digestion.

Considerable pretreatment processes that is sludge disintegration techniques have therefore been introduced to disrupt the WAS floc structure leading to the release of extracellular and intracellular materials into the aqueous phase and conversion of slowly biodegradable particulate organics into more biocompatible low-molecular-weight compounds (Dogan, Sanin, 2009;43:2139–2148, Park, Ahn, Hwang,Lee, . 2010;101:S13–S16) In this context, different physical as well as chemical methods have been examined and used, such as ultrasonication (Feng X, Lei, Deng , Yu , Li, 2009;48:187–194, Pham, Brar, Tyagi , Surampalli, 2009;163:891–898) microwave irradiation (Park, Ahn , Hwang , Lee, 2010;101:S13–S16, Eskicioglu , Terzian, Kennedy , Droste , Hamoda, 2007;41:2457–2466.) mechanical disintegration Lehne, Müller,Schwedes, 2001;43:19–26 , Kampas , Parsons, Pearce, Ledoux, Vale, Churchley, Cartmell 2007;41:1734–1742], ozonation (Dytczak , Londry , Siegrist , Oleszkiewicz 2007;41:543–550,Yan , Chu , Xing , Yu , Sun , Jurcik, 2009;43:195–203.], Fenton oxidation acidification (Woodard , Wukasch 1994;30:29–38, Liu , Liu , Chen , Du , Chen.2008;28:2614–2622.) alkaline addition (Neyens, Baeyens, Creemers. 2003;97:295–314.Lin , Chang , Chang 2007;62:85–90) thermal energy (Bougrier , Albasi, Delgenès , Carrère 2006;45:711–718. Sahinkaya, Sevimli, Aygun,2012;65:1809–1816) and biological hydrolysis with enzymes(Ayol, Filibeli, Sir, Kuzyaka2008;43:1528–1535).The ultrasonic pretreatment of sludge is an effective method for breaking-up microbial cells to extract intracellular material (Tiehm , Nickel , Zellhorn , Ne ,2001;35:2003–2009) Ultrasonic process triggers off acoustic cavitation in the liquid phase where microbubbles are produced, grow, become unstable and then undergo violent collapse at high velocity, by resulting in intense temperature rise of the bulk solution and generation of extremely high pressure at the liquid-gas interface (Chu , Chang , Liao , Jean , Lee. 2001;35:1038–1046 ,Gogate , Kabadi 2009;44:60–72.) Ultrasonic wave induces some physico-chemical impacts such as formation of hydromechanical shear forces, thermal decomposition of volatile hydrophobic substances in the sludge and production of OH•, HO2•, O•, N• and H• radicals acting as oxidizing agents Bougrier, Carrère, Delgenès 2005;106:163–169. Wang , Wang , Ji,2005;123:145–150) Among these mechanisms, hydromechanical shear forces produced by cavitation are predominantly responsible for the ultrasonic WAS disintegration(Huan, Yiying , Mahar , Zhiyu, Yongfeng,2009;161:1421–1426).and are most effective at low ultrasonic frequencies below 100 kHz (Pilli , Bhunia , Yan , LeBlanc , Tyagi , Surampalli,2011;18:1–18) while the contribution of the oxidizing effect of free radicals becomes greater as ultrasonic intensity is grew(Wang , Wang , Ji,2005;123:145–150)The sludge disintegration efficiency depends both on sonication parameters such as power input, time, intensity, density and sludge characteristics which are type, volume and total solids concentration (Bougrier, Carrère, Delgenès 2005;106:163–169, Pilli , Bhunia , Yan , LeBlanc , Tyagi , Surampalli ,2011;18:1–18.) Ultrasonication facilitates numerous advantages like efficient sludge disintegration, enhanced biodegradability, deveoloped biosolids quality, increased biogas production, no chemical addition, less retention time and sludge reduction [Pilli , Bhunia , Yan , LeBlanc , Tyagi , Surampalli ,2011;18:1–18.). Ultrasonic treatment of WAS is an energy-intensive process; thus, operating conditions of sonication should be optimized to eliminate concerns on its practical application(Zhang, Zhang, Yang , Liu 2008;99:9029–9031.Sahinkaya, Sevimli 2013;27:238–246)Microwave irradiation addresses a wide range of application areas in environmental engineering, including remediation of various wastes (contaminated soils, sludge or wastewater), inactivation of microorganisms and regeneration of activated carbon Jones , Lelyveld, Mavrofidis , Kingman , Miles 2002;34:75–90, Nüchter , Ondruschka , Bonrath , Gum. 2004;6:128–141]. The mechanism of microwave irradiation encompasses “thermal” and so-called “non-thermal” effects. It is generally thought that the destruction of microorganisms principally takes place due to the thermal effect which refers to the process that generates heat as a result of the absorption of the microwave energy by water or organic complexes marked by either constant or induced polarization (Yu , Chan, Liao, Lo 2010;181:1143–1147) Conversely, non-thermal effect is not associated with the temperature increase (Hong, Park , Lee 2004;38:1615–1625) and caused by the polarised parts of macromolecules aligning with the poles of the electromagnetic field, leading to the possible breakage of hydrogen bonds and alteration of the hydration zone (Tyagi, Lo.2013;18:288–305.) The major factors of microwave pretreatment that affect dielectric materials include temperature, radiation time and penetration depth (Hong, Park , Lee 2004;38:1615–1625). Microwave heating provides many advantages over the conventional thermal processes such as rapid heating, high reaction rate, ease control, compactness, space saving and energy efficiency (Jones , Lelyveld , Mavrofidis, Kingman, Miles. 2002;34:75–90, Tyagi , Lo2013;18:288–305). Microwave irradiation has proved to be an efficient tool for cell destruction and release of extracellular polymeric substances and intracellular materials into the soluble phase (Eskicioglu, Kennedy, Droste2006;40:3725–3736, Ahn, Shin ,Hwang 2009;153:145–150) enhancement of volatile solid destruction and biogas production (Eskicioglu,Terzian, Kennedy , Droste , Hamoda 2007;41:2457–2466, Tyagi, Lo 2013;18:288–305, Hong , Park , Teeradej, Lee , Cho , Park 2006;78:76–83) and improvement in sludge dewaterability (Park , Ahn , Kim , Hwang 2004;50:17–23, Toreci, Kennedy , Droste 2009;43:1273–1284) Total solids concentration, treatment temperature, power intensity, reaction time and sludge type (primary, secondary, mixed) are the main factors affecting the degree of sludge disintegration by microwave pretreatment (Park, Ahn , Hwang , Lee 2010;101:S13–S16, Tyagi , Lo 2013;18:288–305) Although microwave application is an energy intensive process, the microwave irradiation energy required per unit mass of sludge is lower than the energy required for sonication to attain the same degree of solubilisation, indicating that microwave disintegration may be a rapid and cost-effective technique for sludge pretreatment (Ahn, Shin ,Hwang 2009;153:145–150, Park , Ahn , Kim , Hwang ,2004;50:17–23).

The results show that there is a close link between the size of the particles and the increase in biodegradability of the sludge. In general, the higher the disintegration, the higher the production of methane and reduction of VS. The same trend can be observed in the energy consumption, since for high disintegration results, it is necessary to apply a high amount of energy. In some cases, the material resulting from the disintegration is not as biodegradable, so the type of substrate produced by the pretreatments is also an important factor.

Disintegration process is the outward release of cell fluid in decomposed form by breaking down the microbiological cell wall. When the cell wall is broken down, then the dissolved substrate releases take place, which are biologically soluble very easily (Bougrier et at., 2007).

There are some different disintegration methods used as pre-treatment forms in order to improve hydrolysis and to reduce the amount of excess sludge in activated sludge process. These methods are classified as mechanical, physical and biological ones (Delgenes et al., 2003). The purpose of these pre-treatments is to make organic compounds more soluble and/or to minimize their dimensions. In this way, it is possible to observe a decrease in residual sludge amount and digestion times and an increase in the amount of biogas (Bougrier, 2006).

The key point of sludge disintegration is to rupture the cell wall and to facilitate the release of extracellular and intracellular matter. This will accelerate the subsequent aerobic/anaerobic sludge digestion processes and reduce the retention time needed during digestion (Kepp et al., 2000; Nah et al., 2000; Pavlostathis and Gosset, 1986; Tiehm et al., 2001; Zhang et al., 2010). The lysis of microorganisms by high shear processes releases the intracellular constituents, including cytoplasm and nucleic acids, many of which are readily biodegradable. The role of cellular lysis and the subsequent degradation and mineralization of intracellular material is considered as a potentially important component in solids reduction (Tiehm et al., 2001; Wang et al., 2005; Yu et al., 2008). Sludge decomposition/digestion can be improved by many pre-treatment methods, includes thermal hydrolysis, ozonation, acidification or alkaline hydrolysis, enzymatic lysis,high pressure homogenizers, mechanical disintegration, and ultrasound (Khanal et al., 2007; Neyens and Baeyens, 2003; Tiehm et al., 2001; Zhang et al., 2010).

2.5 Sludge Disintegration Techniques

2.5.1 Mechanical Methods

Mechanical sludge disintegration methods are generally based on the disruption of microbial cell walls by shear stresses. In mechanical disintegration, the breakup of cells and floc structure occurs in minutes instead of days, and the intracellular components are released and readily available for biological degradation. Several techniques have been reported to apply mechanical shear to sludge.

Mechanical methods require some level of energy for creating a break down in cell walls. This energy is obtained via moving pieces, pressure or similar methods. Here are some mechanical methods:
Another type of mechanical pretreatment was reported by Dohanyos *et al*. (1997). This method uses a centrifuge equipped with a special impact gear, which uses the energy generated by the centrifuge to partially destroy sludge cells without any additional energy demand. The results showed an increase of 13.6% in methane yield

from combined sludge (primary plus WAS) and an average 31.8% increase when digesting WAS only.

- Stirred ball mill: Disintegration by crushing of particles
- High pressure homogenizer: Disintegration by cavitation effects due to sudden pressure release
- Ultrasonic homogenizer: Acoustic generation of cavitation, which leads to sludge disintegration
- Mechanical jet technique: It shows similarities with dissolved air flotation. Sludge stream is pressurized to 5 - 50 bar, the pressure is subsequently released across a nozzle and the sludge stream impinges on a splash plate
- Ball mill shakers were reported to efficiently disintegrate activated sludge bacteria, having a disintegration yield of 90%, but with high energy consumption (approximately 60 MJ/kg TDS) (Weemaes and Verstraete 1998). Baier and Schmidheiny (1997) increased the VS removal by 38 – 57% and the methane production by 10% after the application of sludge disintegration by ball milling. Another method developed was high pressure homogenization. In a high pressure homogenizer, the sludge is compressed to 60 MPa. The suspension then leaves the compressor through a valve at a high speed, smashing on an impaction ring. The cells are hereby subjected to turbulence, cavitation and shear stresses, resulting in cell disintegration. Cell disintegrations up to 85% were achieved at relatively low energy levels (30 – 50 MJ/m3) (Harrison, 1991). found an enhancement in biodegradability of sewage sludge to 80 – 83% by a sonication treatment of 4 – 8 min duration at 55ºC.

Although disintegration yields may be very satisfactory, the energy demand for these processes can be high. Farkade *et al.* (2006) reported that hydrodynamic cavitation was the most energy efficient process among different mechanical disintegration techniques. (Miguel 2012,) Also based on cavitation processes, ultrasound can be used to disrupt cell walls. Ultrasound uses sound waves that generates cavitation (implosion) processes in liquids giving rise to local high-temperature hotspots over 1000ºC and pressure increases up to 500 bar. Rivard and Nagle (1996) (Miguel 2012,)

2.5.1.1 Ultrasonication

Ultrasonic pretreatment of WAS is the process of supplying pressure wave which leads to formation of cavitation bubbles in the liquid phase. When these bubbles of cavitation reach a critical dimension, they collapse dramatically. This cavitational bubble creates an extreme heating and high pressure in liquid-gas interface. It creates turbulence and high shearing phenomena in liquid phase. Thus, sonication is a combination of different phenomena: chemical reactions using radicals, pyrolysis, combustion and shearing (Bougrier et al.,2005). However, it was found that hydro-mechanical shear forces are predominantly responsible for ultrasonic activated sludge disintegration (Wang et al., 2005). Ultrasonic pretreatment give a great effect on the physical, chemical and biological characteristic of WAS (Chu et al., 2001). The efficiency of sonication depends on many factors during the process such as sonication duration, temperature increment, ultrasonic frequency, energy supplied, total solids (TS) content of WAS. Ultrasound is a cyclic sound pressure with a frequency greater than the upper limit of human hearing, this limit being approximately 20 kilohertz (20,000 hertz). Figure 2.3 shows the range of frequency range from infrasound to ultrasound.

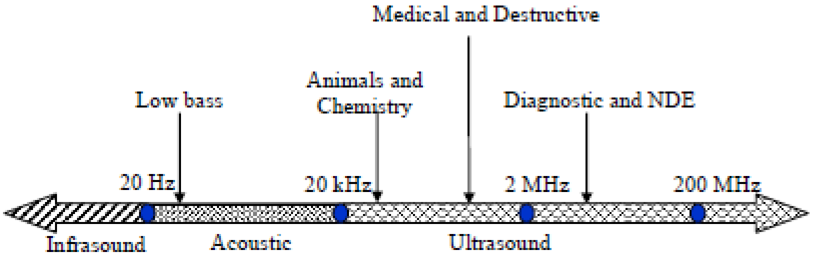


Figure 2.3 : Ultrasound Range Diagram.

Energy (J or kJ) or power (W or kW) input supplied by ultrasound plays a very important consideration with respect to economic aspect. Normally, ultrasound gives a good effect to sludge disintegration at high energy input which leads to increase the operation cost of the treatment. Thus, quantification of energy/power input has to be properly supplied to get the effective sludge disintegration. According to Bougrier et al (2005), specific supplied energy lower than 1000 kJ/kg TS is used to reduce flocs size and supplementary energy will be used to break down flocs or cells. It is not necessary to supply energy higher than 7000 kJ/kg TS as it does not give significant increase in biogas production. The degree of disintegration does not depend on only power input but also the treatment time (Tiehm et al., 2001). Total energy requirement depends on the operation duration. Thus, optimum energy supplied and operation duration needs to be investigated for higher degree of disintegration. Hence, the operating cost will be reduced. The power or energy supplied for sludge disintegration can be expressed in a number of ways as elucidated below.

The important parameters affecting the ultrasonic disintegration are power input, TS content, sonication time and volume of sludge to be sonicated These parameters can be lumped together into a single parameter, commonly known as specific energy input (Es).

Khanal et al. (2006c) investigated the effect of TS content and energy input on SCOD release. The results are presented in Figure 2.10. SCOD release showed an increasing trend with increase in both TS and energy input.

However, the release in SCOD slowed sown at an energy input of over 35 kWs/g TS for all TS contents. Based on linear regression analysis, SCOD releases were 1.6, 2.2, 2.5 and 3.2 mg/kWs at TS content of 1.5, 2.0, 2.5 and 3.0%, respectively. This corresponds to 38, 59 and 98 % increase in SCOD release at TS contents of 2.0, 2.5 and 3.0%, respectively as compared to 1.5%. Wang et al. (2005) also observed the sludge disintegration at ultrasonic density of 1.44 W/mL for different TS contents and sonication durations. SCOD can reach 2785 and 2261 mg/L for the TS content of 1% and 0.5%, respectively for 10 min sonication duration. When the disintegration time is 30 min, the SOCD can reach 9019 and 3966 mg/L for the solid content of 1% and 0.5%, respectively.

There are many advantages and disadvantages of ultra sonication method. These are shown in Table 2.6.

Table 2.6 : Advantages and Disadvantages of Ultrasonication.

Advantages	Disadvantages	References
• It is a low-cost and efficient operation when compared to other methods. • Production of an in-situ carbon source for denitrification plants. • It enables control against filamentous bulking and foaming. • Better digester stability • It develops the volatile organic destruction. • It creates an increase in biogas production. • Better sludge dewaterability	• Capital and operating costs due to immaturity of technology. • Long-term performance data of ultrasound system in full-scale are still limited.	Harrison and Pandit,1994; Tiehm et al., 2001; Hogan et al., 2004; Yin et al., 2004; Sandino et al., 2005 and Khanal et al., 2006a

Evaluation of ultrasonic disintegration

Ultrasound pretreatment is believed to change the physical, chemical and biological properties of WAS, and improved and stabilized the AD which lead to increase the biogas production. A high pressure wave of ultrasound will produce a high sharing force which breaks down bacterial cell wall and releases the intracellular into aqueous phase. In addition, ultrasound also helps to deagglomerate the biological flocs and disrupts large organic particles into smaller size particles.

Thus, the degree of sludge disintegration has to be evaluated base on physical chemical which increase in SCOD and protein concentration, and release of NH3 and biological (heterotrophic count and specific oxygen uptake rate) properties. Detailed discussion of each property is presented in the following section.

a. Physical evaluation

Particle size analysis, microscopic image, turbidity, and sludge dewaterability are some of the techniques used to judge the degree of ultrasonic disintegration. Physical evaluation, particularly particle size distribution and microscopic image analysis have been widely employed for simplicity as qualitative measures of sludge disintegration.

Particle size analysis

Particle size distribution is one of the factors affecting the AD. The smaller particle size gives a large surface area which leads to increase the AD efficiency. Therefore, ultrasound was found to be very effective to break down particles size in WAS. Particle size distribution during sonication operation depends upon on power input, sonication frequency, sonication duration and sludge characteristic. Bougrier et al. (2005) performed an ultrasonic treatment of WAS using 20 kHz frequency and different specific energy inputs. The study was investigated the particle size distribution within the ranged from 0.4 to 1000 μm. The volume occupied by small particles increased with the increasing of specific energy supplied: for Es = 14, 550 kJ/kg TS particles of 1μm occupied 1.5% of the whole volume, whereas they occupied 0.1% in the untreated sample.

Similarly, Chu et al. (2001) found that the floc size of WAS reduced accordingly to the sonication density and duration times. At the sonication density of 0.11 W/mL, there is almost no effect on the floc size. Only when the sonication density has exceeded 0.22 W/mL would the particle size apparently decrease. The higher sonication densities of 0.33 and 0.44 W/mL reduce particle size from 98.9 μm (mean diameter) to 22 and 3 μm after 20 min sonication duration, respectively. The decrease trend of particle size after sonication seems less effective even higher sonication density is supplied.

Bougrier et al. (2006) compared the particle size reduction amongst sonication, ozonation and thermal treatment. Ultrasound was operated at 20 kHz frequency and about 225 W supplied power. It was found that the flocs size is reduced from 36 μm to 10.7 and 9.6 μm with Es of 6250 and 9350 kJ/kg TS, respectively. Tiehm et al. (2001) was concluded that the lower ultrasonic frequency (20 KHz) gives higher sludge disintegration efficiency which leads to reduce median sludge particle size as well as to increase in turbidity of the sludge sample.

Yan et al. (2010) examined at 15000 kj/kg DS. It was found the mean particle size was 13.1 μm which was only one half of taht original WAS. Increasing of specific energy gave positive effect on the mean particle size reduction of WAS.

Microscopic image evaluation

The sludge disintegration has widely examined based on visual observation using light and electron microscopes. Basically, the architecture of floc after sonication within 40 min at 0.11 W/mL is the same as the original sludge even the floc structure becomes somewhat looser and some filamentous bacteria have been exposed outside. However, the structure integrity of floc has almost completely broken down after 40 min sonication at 0.33 W/mL (Chu et al., 2001). Khanal et al. (2006b) was investigated on structural changes of WAS at a constant power input of 1.5 kW and a frequency of 20 kHz with respect to different sonication times. During 2 min of sonication, the srructural integrity of flocs as well as filaments was significantly disrupted without appreciable destruction of bacterial cells. Up to 10 min sonication, nearly complete disintegration of flocs and filament-like structures with a few scattered bacterial cells was observed. When the sludge was sonicated for 30 min, more or less complete break-up of cell walls was observed with several punctured cells.

b. Evaluation of chemical

Chemical evaluation of ultrasonic pretreatment basicly concentrates in sludge disintegration effectiveness.SCOD has played a significant role for sludge disintegration evaluation.Besides after appling pretreatment protein and Ammonia (NH3) are the significant parameters investigated.

SCOD assessment

After ultrasonic pretreatment, microbial cells are broken down and the organic matters are released to the aqueous phase which leads to increase the soluble organic substances measured in term of SCOD. Ultrasonic also disintegrates extracellular matter including organic debris and extracellular polymeric substances (EPS), which become part of SCOD. Therefore, SCOD is the main parameter of the evaluation.

Ultrasonic pretreatment efficiency depends on several factors such as sonication frequency, TS content, influent sludge characteristics, sonication duration, temperature, and power supply. Thus, to find out the unity of sludge disintegration evaluation, SCOD released with respect to specific energy input is commonly applied. Khanal et al. (2006a) investigated the sludge disintegration efficiency with several specific energy inputs. Specific energy of 35 kJ/g TS was found to be the optimum power input for the highest SCOD released. Moreover, Wang et al. (2006) investigated the SCOD release at ultrasonic density of 0.768 W/mL with different sonication times.The increment speed of SCOD was slow down after 20 min disintegration time. In order to evaluate the sludge disintegration efficiency regarding the COD data, one parameter known as "degree of disintegration (DD)" was commonly used for many researchers. Tiehm et al. (2001), Rai et al. (2004), Bougrier et al. (2005) and Nickel and Neis. (2007) used degree of disintegration (DD_{COD}) modified by Müller and Pelletier (Modified version from Kunz and Wagner). DD_{COD} is the comparison between SCOD release by ultrasonic disintegration and a maximum SCOD release obtained by alkaline addition (chemical disintegration).DD_{COD} can be calculated as bellow equation:

DD_{COD}= [($SCOD-SCOD_0$)/($SCOD_{NaOH}-SCOD_0$)] x 100 (Eq.1)

Where,

SCOD : Soluble COD of sonicated sample (mg/L)

SCODo : Soluble COD of untreated sample (mg/L)

SCODNaOH : Soluble COD of reference sample alkaline disintegration (mg/L)

SCODNaOH is believed to be the maximum COD release of the complete disintegration of sludge and use as a reference COD. It normally carries out by treating the sludge sample with 1 M NaOH in the ratio of 1:2 for 10 min at 90 ^{o}C.

NH3 assessment

Ammonia nitrogen (NH3-N) is also one of the parameters investigated during sludge disintegration. Khanal et al. (2006b) studied the NH_3-N released of WAS after sonication with several TS contents and specific energy inputs. The author found that NH_3-N concentration reached a fairly constant level at lower specific energy input compared to SCOD released, for example, 20 kWs/g for 2.0, 2.5, and 3% TS, and 10 kWs/g for 1.5% TS.

Bougrier et al. (2005) investigated nitrogen solubilization of WAS after ultrasonic treatment which performed at different specific energy inputs. The total Kjeldahl nitrogen (TKN) was found to be constant whatever the specific energy. It can be concluded that ultrasound did not contribute to nitrogen mineralization or vitalization. On the other hand, the organic nitrogen and ammonia concentration in the aqueous phase was increased while organic nitrogen in particle was decreased. The maximum nitrogen solubilization was obtained for a supplied energy of 10,000 kJ/kg TS.

Feng ; investigated ammonium nitrogen and nitrogen solubilization of WAS after ultrasonic treatment which performed at different specific energy inputs. When SE> 5000 kj/kgTS, nitrate nitrogen concentration was increased.

2.5.2 Physical methods

Thermal methods are widely used as physical methods. Thermal methods require more energy than mechanical methods do. Although mechanical methods are proved to be efficient, they are complex and expensive.

Thermal pretreatment includes heating of sludge to temperatures in the range of between 150 ºC and 200 ºC.The pressures measure in the range of 600 and 2500kPa(Barlindhaug, and Ødegaard, 1996).The Cambi corporations which included thermal hydrolysis in Norway improved a sludge treatment process. The company includes heating sludge to 180 ºC during 30 minutes, as a result of solubilization of nearly 30% of the sludge.An increase biogas production of 150% was recounted as well as a decrease of 50% in the solids volume was detected by experts. (Weemaes and Verstraete, 1998).(Miguel 2012)

2.5.2.1 Microwave pre-treatment

Microwave (MW irradiation has necessitated much more attention in particularly domestic environment, industrial and medical applications.Microwave has been utilized in different environmental implications which include decomposition of organic materials,medical waste ,
microorganisms ,pyrolysis phase separation and extraction processes ,soil remediation remediation of hazardous and radioactive wastes coal desulphurization sewage sludge treatment ,chemical catalysis and organic/inorganic syntheses .The implication of MW for environmental engineering projects is based on the property of the MW, such as rapid as well as selective heating(Neelancherry Remya, Jih-Gaw Lin∗,2010)

In today’s world ,owing to the MW is quick and selective heating,energy effevtiveness,capacity to advance and quality of product and decreased hazardous production formation and emmissions ,Microwave has known widespread popularity as an impactive thermal method for sludge treatment. (Jones et al., 2002)

Microwaves are used in many and varied applications including organic decomposition, the sterilization of medical waste and inactivation of microorganisms in foods ,animal manure,soil (Hong et al.,2004)

Microwave (MW) pre-treatment is an alternative method to conventional thermal pre-treatment and its potential has been well recognized in sludge treatment (Mudhoo and Sharma, 2011). The mechanism of the microwave treatment consists of a thermal and an athermal (non-thermal) effect. The thermal effect is caused by the interaction of the oscillating electrical field with dipolar molecules like water, proteins, fats and other organic complexes. The resulting molecular rotation of the permanently and induced dipoles leads to friction which ultimately will result in heating the sludge (Dogan and Sanin, 2009, Eskicioglu et al., 2007a, Yu et al., 2010 and Park et al., 2004).Microwave method provides disrupting the sludge floc and cell and releasing the organic matter into soluble phase.

Microwave pre-treatment applications aim to increase the sludge solubility (Eksicioglu et al., 2009; Park and Ahn, 2011) and to increase the biogas production besides developing sanitization (Eksicioglu et al., 2009; Park and Ahn, 2011). Thermal disintegration is generally realized by thermal hydrolysis where sludge is heated to 130 - 200°C for about several minutes at high pressures. Microwave method is an advantageous method to apply, because it enables quick heating and pathogen destruction,producing environmentally safe sludge and it is easy to control besides having low overall cost (Hang et al., 2004)

When the microwave pretreatment is applied; organic matter (BOD, COD), nutrients (Nitrogen, Phosphorous) concentrations increasing are observed. (Wojciechowska, 2005).

Some previous studies are related to, the effects of microwave energy on contact time, sludge COD, BOD, nitrogen,phosphorous, spesific resistance to filtration and capillary suction time (Danesh et al., 2008; Eskicioglu et al., 2007; Pino-Jelcic et al., 2006)

If we mentionet about “athermal effect”,”it is used for microwave.It is related in effect which is never associated with increased temperature.(Hong et al.2004)The microwave energy marked by both constant and induced polarization.The microwave is converted into heat derived from the internal resistance of rotation (Zieli_nski et al., 2007). (Park et al. 2009).Expert found out that the temperature,power,total solid conentration importantly impacted the solubilization degree of sludge. According to Wojciechowska (2005) he reported the increase of organic matter which is biochemical oxygen demand,COD and nutrients that is Nitrogenous,Phosphorus focus in the sludge liquor under microwave situations.Former studies have concentrated in how microwave energy and communicate time iöpacted the sludge’s COD, biochemical oxygen willings nitrogenous, phosphorus, specific resistance to filtration, and capillary suction time (Danesh et al., 2008; Eskicioglu et al., 2007; Pino-Jelcic et al., 2006; Wojciechowska, 2005). A very few reports have focused how microwave irradiation impacted different physical as well as chemical characteristics of WAS.

If we explain the advantages of microwaves, applications involve quick heating, pathogen destruction,ease of control, compactness and then low cost. Despite being investigated by lots of researchers who examined whether like irradition has a non-thermal impact, destruction of microorganisms is considered to emerge because of thermal impact of microwave exposure (Johng-Hwa Ahn, Seung Gu Shin, Seokhwan Hwang, 2009).

The use of microwave energy for processing materials has the potential to offer similar advantages in processing times and energy savings. In conventional thermal processing, energy is transferred to the material through convection, conduction, and radiation of heat from the surfaces of the material. In contrast, microwave energy is delivered directly to materials through molecular interaction with the electromagnetic field. In heat transfer, energy is transferred due to thermal gradients, but microwave heating is the transfer of electromagnetic energy to thermal energy and is energy conversion, rather than heat transfer. In traditional heating, the cycle time is often dominated by slow heating rates that are chosen to minimize steep thermal gradients that result in process-induced stresses. For polymers and ceramics, which are materials with low thermal conductivities, this can result in significantly reduced processing times. Thus, there often is a balance between processing time and product quality in conventional processing. As microwaves can transfer energy throughout the volume of the material, the potential exists to reduce processing time and enhance overall quality (E.T. Thostenson, T.-W. Chou, 1999).

Thermal treatment at 190 ˚C was more impactive than treatment at 135 ˚C in terms of total COD, lipids, carbohydrates as well as protein removals and methane production. However, treatment at 190 ˚C produced refractory soluble COD. In all cases, with or without pre-treatments, lipids degradation yield (67% without pre-treatment and 84% with 190 ◦C treatment) was higher than carbohydrates (56% without pre-treatment and 82% with 190 ◦C treatment) and proteins (35% without pre-treatment and 46% with 190 ˚C treatment) degradation yields. Methane production increased by 25% after the 190 ˚C treatment C. (Bougrier, J.P. Delgen`es, H. Carr`ere, 2006)

Parketal. observed 19% and 22% increases in SCOD concentration after MW pretreatment of WAS(TS-3%) at91.2 1C and boiling temperature, respectively. Hong etal. applied a treatment temperature of 72.5 1C and observed a notable increase from 8% (control) to 18% in COD solubilisation for MW pretreated WAS (TS-4.1%). Eskiciogluetal. observed that COD solubilisation increased from 9% (control) to 24% after MW pretreatment of sludge (TS-5.4%) at 96 1C.
However, in their subsequentstudy, Eskiciogluetal. applied a higher MW temperature (175 1C) toWAS (TS-3%)and observed a significant increase from 9% (control) to 35% in COD solubilisation.

Eskicioglu et al. (2007b) examined at the range of 50 - 96 ^{0}C, SCOD / TCOD ratios were 12 - 12 %. Eskicioglu et al. (2007) examined at 50, 75, 96, 120, 150, 175 ^{0}C microwave pretreatment temperatures and the SCOD to TCOD ratios were 9 %, 12 %, 21 %, 24 %, 28 %, 35 %. Hang et al., 2006; examined at 72.5 ^{0}C and SCOD / TCOD ratio increased from 8 % to 18 %.

Previous studies show that ammonium nitrogen and nitrate nitrogen with microwave temperature (Eskicioglu et a., 2007; Feng et al., 2009). Also, SCOD / TCOD ratio increased after the microwave.

2.6 Chemical Methods

In chemical pretreatments, an acid or basic reagent is added to the sludge to solubilize the sludge floc and microbial cells. Other chemical compounds such as powerful oxidants can also be used in chemical pretreatments, with the conversion of some organic matter to carbon dioxide along with the break-up of cell walls and sludge flocs. The addition of acid improves sludge solubilization at ambient and elevated temperatures, while for alkaline pretreatment, variable results have been found. Some researchers report very good results while others report no effect on the solubilization, and subsequent digestion of the sludges. Alkaline pretreatments have the advantage of being compatible with the subsequent biological treatment, usually not requiring neutralization prior to the anaerobic digestor. Alkaline hydrolysis has been reported to significantly increase organic yield from acidogenesis (Hashimoto et al., 1991).

Alkaline nature plays a significant effect to the sludge disintegration efficiency due to its fast solubilization into aqueous solution. The alkaline agents which can be used are NaOH, KOH, $Ca(OH)_2$, $Ma(OH)_2$, etc. Almost every published paper had reported that monobasic agents are the most preference because it solutes very fast into the sludge. As a result, sludge was significantly disintegrated. Alkaline treatment of WAS using NaOH were thoroughly investigated by many researchers: Kim et al. (2002), Lin et al. (1997), Lin et al. (1999) and Chiu et al. (1997). However, few studies were investigated the effect of different alkaline agents in WAS disintegration (Kim et al., 2003 and Li et al., 2007).
Moreover, lime agent was also studied by Vlyssides and Karlis, (2004), and Torres and Lloréns. (2007) due to its cheap cost compared to NaOH.

Kim et al. (2003) investigated the efficiency of alkaline pretreatment on WAS solubilization with various alkaline agents: NaOH, KOH, $Mg(OH)_2$ and $Ca(OH)_2$. The experiment was performed at a constant pH of 12. The authors found that monobasic agents, particularly NaOH, resulted in higher solubilization percentages than dibasic agents either at ambient or thermal temperature (Figure 2.12). For example, SCOD release from adding NaOH was 39.8% and 51.8% while 15.3% and 17.1% of that from adding Ca(OH)2 at ambient and at 121 ^{o}Ctemperature, respectively.

Li et al. (2007) observed the behavior of WAS solubilization using NaOH and Ca(OH)2 with various alkaline doses. The authors concluded that NaOH was more effective than Ca(OH)2 for sludge solubilization due to the reason that bivalent cation (Ca2+) is the key matter connecting cell with EPS. Hence, calcium cation helps the dissolved organic polymers to re-flocculate the fragments produced by alkaline treatment.(Buntrith,2008)

Tanaka *et al*. (1997) tested the addition of NaOH to WAS, and found a solubilization percentage of VSS of 15% for an alkaline dose of approximately 0.6 g NaOH/g VSS. The methane production was 50% higher compared to the control for a dose of 1 g NaOH/gVSS.

Lin *et al*. (1997) tested the addition of two different concentrations of NaOH (20 and 40 meq/L) to sludges with two different solids concentrations (1 and 2%). The methane production was between 19 and 286% higher in the sludge pretreated compared to the control sludge. The amount of soluble COD increased from a total COD/soluble COD ratio of 2 to 38% in the test with 1% TS sludge pretreated with 40 meq/L NaOH.(Miguel,2012)

Among chemical processes, the treatment using ozone is of special interest, because no chemicals are needed and no increase in salt concentration occurs. The aim of ozone pre-treatment is a partial oxidation and a hydrolysis of the organic matter. A complete oxidation is avoided and instead larger molecules are cracked into smaller ones and hardly degradable compounds are transferred into more easily degradable ones.

When ozone oxidization is compared to other disintegration methods, it generally enables a higher level of decomposition of organic substances. As a result of ozone process, which aims to decrease the biomass multiplication speed and to create a sludge mineralization, the cell walls of microorganisms are destructed, releasing cytoplasm into the body sludge water and water-insoluble macromolecules are divided into smaller pieces and become water-soluble. During sludge ozonization process, decomposition of organic substances takes place in two steps. The first one of this is the solubilization, observed during the disintegration of suspended solid items and the second is the mineralization, observed during the oxidization of organic items in dissolved form. The effects of sludge ozonization may refer to mineralization and solubilization concepts, the changes observed in solid substance characteristics, re-flocculation of suspended small particles and balancing of particle size distribution, improvement of sludge sedimentation characteristics and changes in microorganism populations as a result of removing filament bacteria in an apparent form (Zhang etal., 2008; Bougrier et al.; 2007;Chu et al.,2009)

In the case of the methods of the chemical disintegration of the solid organic fraction, the energy of the chemical reactions is used. It is often associated with the appropriate environment conditions in which the reaction is supposed to occur, for instance: the appropriate temperature and pressure. The selection of the reagent and its doses as well as the selection of the appropriate time and temperature of the running of the process are a subject of studies conducted by various authors, but they are not that numerous for thermal disintegration. Most of the publications are based on studies with the use of alkaline reagents. The authors suggest that from the point of view of substrate solubilisation, alkaline disintegration is more effective than acid treatment; it is also possible to avoid corrosion of the plant (Rocher et al., 1999). On top of this, a similar effect of the solubilisation of organic coal compounds is obtained with a lower consumption of alkali reagents than acid ones, which translates into the costs of the given technology (Cassini et al., 2006). Cassini et al. (2006) compared the effectiveness of acid hydrolysis (H_2SO_4) and alkali hydrolysis (NaOH) at a time of 8 h and at room temperature (Cassini et al., 2006). With the same dose of the reagent (20 mmol/dm3), the solubilisation of organic compounds (COD) in sewage sludge amounted to 11% for acid treatment and 60% for alkaline treatment. However, attention must be paid to the fact that the high concentrations of Na+ and K+ ions have an inhibitory effect on the methane fermentation process (Mouneimne et al., 2003). A comparison of the effectiveness of the use of various acid reagents proves lower cell lysis with the use of HCl than H_2SO_4. Acid disintegration (H_2SO_4) is recommended as the sludge conditioning method before its dewatering (Neyens and Baeyens, 2003). Most of the publications refer to the individual conditions of conducting studies, mostly for sludge with a dry solid concentration below 2% (Valo et al., 2004; Lin et al.; 1997; Chiu et al., 1997).

The range of ozone doses reported in the literature is 0.02–0.5 gO3/g TSS. The most important parameter in evaluating the performance of sludge ozonation is the efficiency of the sludge solubilization. Generally, the reported efficiency of sludge solubilization has been 30–60% using ozone oxidation. As seen in tables below, when the ozone dose increases, SCOD concentration also increase.Meanwhile, DD ratio is directly proportional with SCOD concentration as shown in Figure 2.4 and 2.5.

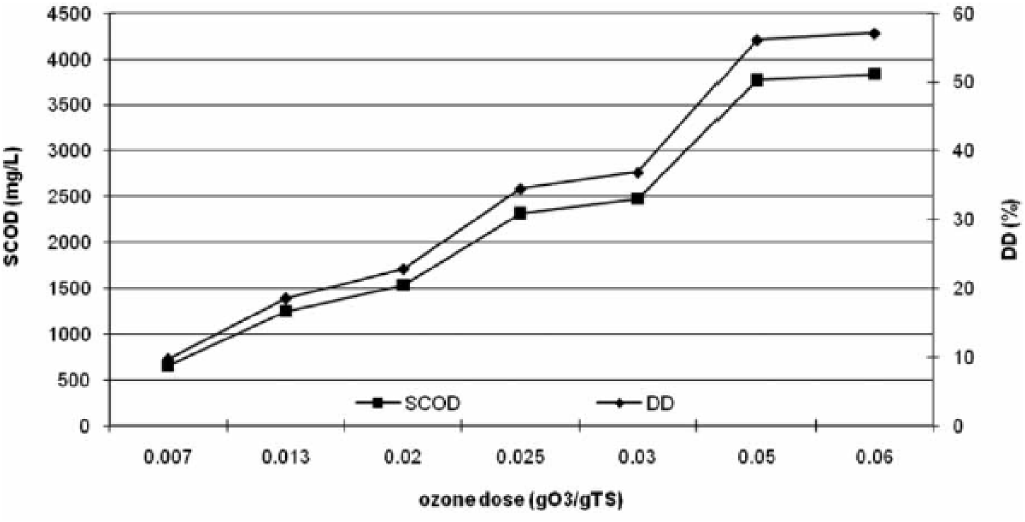
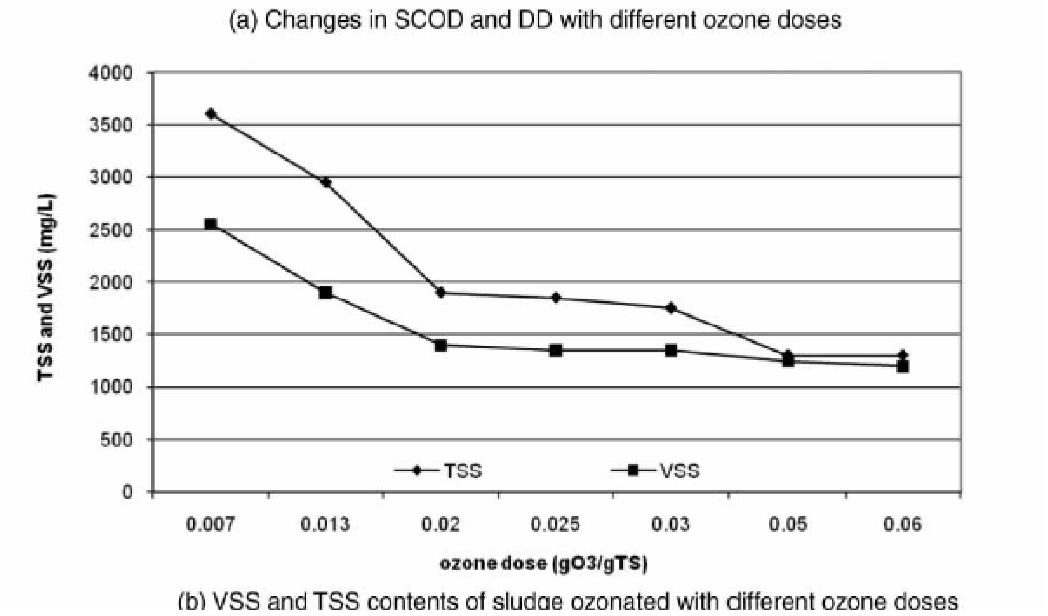


Figure 2.4 : SCOD concentration rate according to Ozone Dose.


(a) Changes in SCOD and DD with different ozone doses

(b) VSS and TSS contents of sludge ozonated with different ozone doses

Figure 2.5 : Fate of return activated sludge after ozonation: an optimization study for sludge disintegration.

2.7 Biological Methods

The enzymatic lysis cracks the compounds of the cell wall by an enzyme-catalyzed reaction. However, the costs for enzymes are high. Enzymatic lysis is also of interest in combination with mechanical disintegration, because the intracellular liquid contains lysis enzymes. They can cause a further disintegration of the cells after mechanical treatment (http://www.stowa-selectedtechnologies.nl.html,2006).

Enzymes catalyze the degradation of organic substances in sludge as a function of the substrate which is explained enzyme-substrate models like the key and lock model or space filling model.The up shotof the enzyme additions during biological sludge stabilization process is the enhanced degradation of EPS -proteins and polysaccharides- and the other biological slimes and gels and improved there leasing capacityof water (e.g.Barjenbruch and Kopplow, 2003, Ayol 2005, Deyet al. 2006, Roman et al. 2006) The enzymatic sludge treatment is proposed modifications of a bioprocessed sludge structure during anaerobic digestion that transform into the physical-chemical responses in sludge conditioning and in turn during dewatering process.The conditioning and dewaterability responses of enzymatically treated sludges can be evaluated using simple filterability tests like capillary suction time(CST) and specific resistance to filtration (SRF). As explained by Ayol and Dentel (2005), although the methods give a general idea on dewaterability behaviors of the conditioned biosolids, they cannot be asserted to simulate the full-scale dewaterability performance ofmechanical dewatering units due to the lack of any response of the samples to pressure or shear.(Ayol et al., 2007)

3. MATERIALS AND METHODS

3.1 Sources of WAS Samples

Experimental studies were conducted by experts on two different WAS samples taken from the return activated sludge line of a full-scale municipal wastewater treatment plant in Istanbul, Turkey. The plant was designed for a treatment capacity of 500000 tons daily and directed in biological nutrient removal mode with an average sludge retention time of 20 days. The first sample was used to discover the impacts of experimental conditions on physico-chemical characteristics of WAS and to develop the sludge disintegration efficiency by optimizing the sludge pretreatment which is ultrasonication and microwave irradiation processes. Prior to pretreatment having experiments, the original total solids concentration of the first sample was adjusted to the appropriate value by diluting with ultrapure water or removing supernatant after settling gravitationally in order to evaluate the impact of the solid content on the sludge disintegration performance. The other second sample was subjected to disintegration at optimum conditions of ultrasonic and microwave pretreatment to check the consistency of the data derived from experiments performed on the first sample. The activated sludge seed used for the respirometric measurements were sourced from the aeration tank of the wastewater treatment facility.Sludge samples were stored in plastic containers at 4^{o}C prior to use to avoid feasible biodegradation. The characteristics of the investigated WAS samples are summarized in Table 3.1. As is evident from this table, the organic content of the sludge samples could be characterized by a total COD level of around 8175±115 mg/L, with a 99% contribution (8100±110 mg/L) from the particulate fraction (i.e. retentate on 450 nm pore size membrane filter). The relatively low soluble COD / total COD (SCOD / TCOD) ratio reflected the potential for sludge disintegration through transformation of particular compounds into more soluble species.

Table 3.1. Characteristics of WAS samples.

Parameter	Unit	Sample 1	Sample 2
pH	---	7.18	7.09
Total solids (TS)	mg/L	11305	10555
Volatile solids (VS)	mg/L	6310	5980
Suspended solids (SS)	mg/L	10490	9960
Volatile suspended solids (VSS)	mg/L	6005	5770
Total chemical oxygen demand (TCOD)	mg/L	8290	8060
Soluble chemical oxygen demand (SCOD)	mg/L	80	75
Dissolved organic carbon (DOC)	mg/L	20	20

3.2 Disintegration Methods

3.2.1 Ultrasonication

Ultrasonic pretreatment The ultrasonic disintegration experiments were performed using an ultrasonic homogenizer (BandelinSonopuls HD 2200, Berlin, Germany) equipped with a VS 70T probe having a diameter of 13 mm and a length of 130 mm as shown in Figure 3.1. The ultrasonication equipment was directed at a constant frequency of 20 kHz under a power supply of 200 W to be success an impactive sludge disruption. During sonication tests, the amplitude value was set as 100% and various ultrasonic density (UD) levels ranging from 0.5 to 2.0 W/mL were applied. For each set of experiments, the corresponding volume of WAS sample was placed into a glass beaker and subjected to sludge disintegration at various sonication durations in the range of 1–40 min. The ultrasonic probe was dipped 2 cm below the sludge surface at the middle of the beaker. The temperature control of sonicated samples was accomplished through ice pellets around the beaker. The specific energy input (ES) was considered as the major variable parameter for the evaluation of sludge disintegration performance and defined as the product of the ultrasonic power and time divided by the sample volume and the initial total solids concentration. In the course of experimental studies, each set of ultrasonication conditions was performed in triplicate so as to minimize random error. The sonicated WAS samples were used to record the amount of SCOD release to determine the optimum conditions with respect to specific energy input and ultrasonic density and further subjected to sequential filtration / ultrafiltration experiments and respirometric measurements.

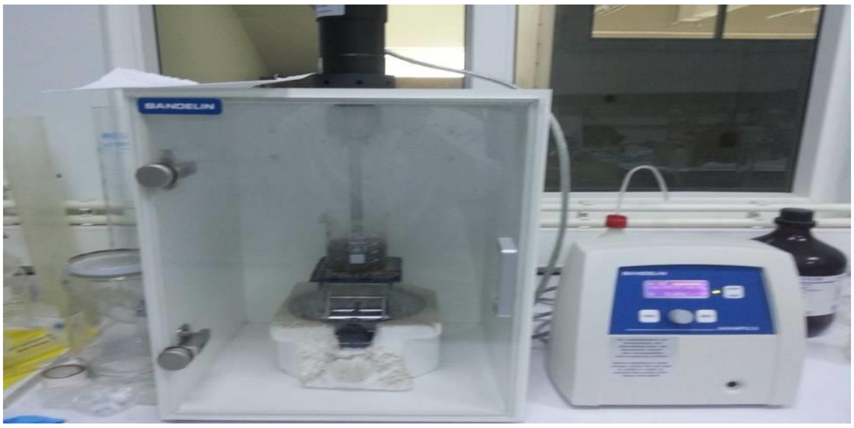


Figure 3.1 : Ultrasonic Homogenizer.

During the ultrasonic disintegration, 7 different specific energies were applied to determine the optimum value. Specific energies were chosen according to previous studies (Bougrier et al., 2005; Yagci, 2011; Yan, 2010; Khanal 2007; Zhang 2007). These are; 5000, 10000, 30000, 20000, 25000, 50000, 100000 kj/kg TS. Also, to understand the effect of specific energy on the disintegration efficiency 4 ultrasonic densities were accomplished (Bougrier et al., 2005; Yagci, 2011; Yan, 2010; Khanal 2007; Zhang 2007). These are 0.5, 1.0, 1.5, 2.0 W/ml. Ultrasonic density equation were given in Equation (3.1) . Reactor volumes were found by using Equation (3.1). These are 100, 133, 200, 400 ml. It means that there were 4 set to complete the experiment. Sonication times were found by using specific energy equation as shown below in Equation (3.2). For all specific energies, 200 W power was applied. In addition to these; after the ultrasonication step, to designate the efficiency of disintegration, soluble COD experiments were done. For these experiments, after every ultrasonication set, 50 ml sample was separated and the other parts were centrifuged (Hettich Universal 320) during 10 minutes at 9000 rpm. Subsequently, The supernatant was filtered from 0,45µm filter. All these steps were done for every concentrate samples. The important point is to determine the optimum specific energy, volume and concentration.

$$Ultrasonic\ density(W/ml) = [Power(W)/Reactor\ Volume(ml)] \quad (3.1)$$

$$Specific\ Energy\ (Es)\left(\frac{kj}{kgTS}\right) = \frac{[Power(W)x\ Sonication\ Time(t)]}{\left[Reactor\ Volume\ (L)xTS\ Conc.\left(\frac{kg}{L}\right)\right]} \quad (3.2)$$

3.2.2 Microwave pre-treatment

The other method is microwave pretreatment; for this process microwave oven (Milestone ETHOS One SK -10) was used as shown in Figure 3.2.

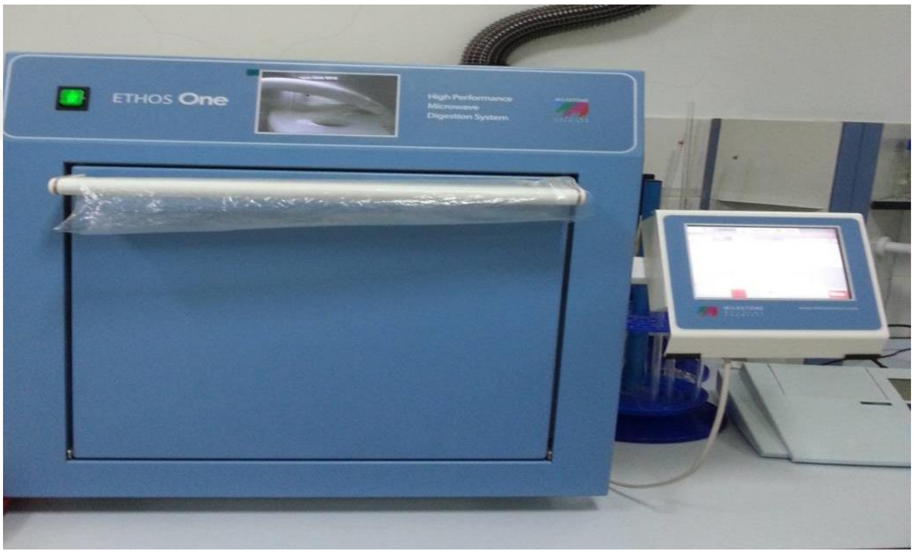


Figure 3.2: Microwave Oven**.**

Microwave irradiation WAS samples were digested through a closed-vessel as shown in Figure 3.3 and Figure 3.4, microwave system having a maximum temperature of 300°C, power output of 1500 W, pressure of 100 bars and frequency of 2450 MHz. In each experimental run, the volume of the sludge transferred into the microwave vessels was fixed at 25 mL. Ten vessels were placed on the rotation turntable inside the microwave unit and processed simultaneously. WAS samples were irradiated for three different periods of 10, 20 and 30 minutes at a wide variety of microwave temperatures ranging from 100 to 190°C. Process parameters (exposure time and temperature) were controlled by using the EasyControl software package. The test procedure was repeated three times for each experimental condition in order to decrease random error. The microwaved sludge samples were cooled to room temperature in the sealed vessels to avoid evaporation of organics, analyzed for the determination of the SCOD concentration to evaluate the microwave irradiation efficiency and further used for sequential filtration / ultrafiltration tests and respirometric analyses.

The microwave device protective cover can be opened when the temperature arrives approximately 80^{o}C. After that, solution in the vessels transfers the marked flasks. For these experiments, after every microwave is set, 50 ml sample was separated and the other parts were centrifuged (Hettich Universal 320) during 10 minutes at 9000 rpm. Subsequently, The supernatant was filtered from 0,45µm filter. All these steps were done for every concentrate sample. The important point is to determine the optimum temperature and time.

Taking the increase in SCOD concentration into consideration, optimum concentrations and times are determined. In the studies conducted in July 2012, it is observed that SCOD increase in x concentration at 175^{0}C is relatively more than the ones at 100^{0}C and 150 ^{0}C when the temperatures and time ranges applied are compared. No significant increase is observed when the results of SCOD concentrations at 10-minute and 20-minute applications at 175^{0}C are compared. Therefore, 10-minute is taken as optimum DT.

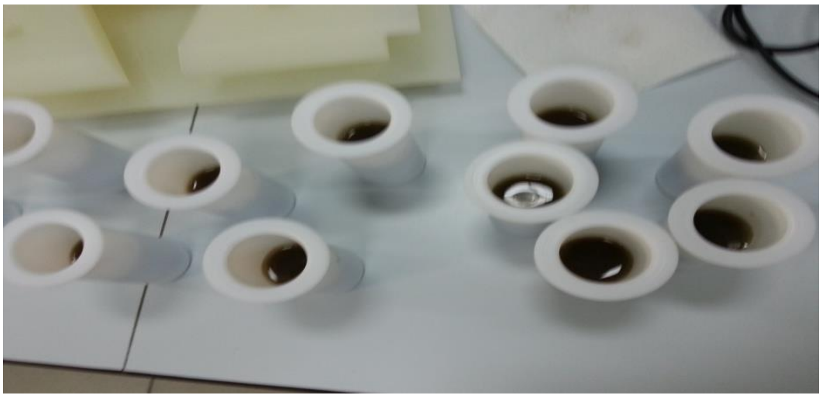


Figure 3.3 : Samples in the vessels.

Figure 3.4 : Vessel into segments.

3.2.3 Physico-chemical characterization

Physico-chemical characterization WAS samples before and after disintegration were analyzed for pH, total solids (TS), volatile solids (VS), suspended solids (SS), volatile suspended solids (VSS), total and soluble chemical oxygen demand (TCOD and SCOD), dissolved organic carbon (DOC), soluble total Kjeldahl nitrogen (STKN), ammonium nitrogen ($NH4^+$ -N), nitrite and nitrate nitrogen ($NO2^-$ - N and $NO3^-$ - N) and phosphate phosphorus ($PO4_3^-$ -P) parameters. The supernatants obtained after centrifuging (Hettich Universal 320, Tuttlingen, Germany) the raw and pretreated WAS samples at 9000 rpm for 15 min were filtered through 0.45 μm pore size membrane filters to provide soluble portions. All analytical procedures used for physico-chemical characterization were performed in accordance with the procedures outlined in Standard Methods (APHA, AWWA, WPCP.); whereas the COD parameter was determined by the closed reflux titrimetric method as described in International Standard ISO 6060 (International Standards Organization. Water Quality 1986)DOC measurements were carried out on a Shimadzu TOC-5000A analyzer (Shimadzu Corporation, Kyoto, Japan) equipped with an autosampler. $NO2^-$ -N, $NO3^-$ -N and $PO_4\ {}_3^-$ -P concentrations were determined by ion chromatography (Dionex ICS-1500 unit, Sunnyvale, CA, USA) coupled with a conductivity detector and an analytical column AS14A (Dionex IonPac). The pH measurements were conducted using an Orion model 920A pH-meter. All sample analyses were performed at room temperature. Each assay was run in a minimum of three replicates and each data point was calculated as the average of the triplicate. The sludge disintegration performance of ultrasonication and microwave irradiation was represented by the disintegration degree (DDSCOD). It was calculated as the ratio of SCOD increase by the disintegration process to the maximum possible SCOD increase, as given in the following equation (Müller JA.; 2000;41:123–130.) :

DDSCOD = [(SCODd – SCODr) / (SCODNaOH – SCODr)] x 100 where SCODd is the soluble COD concentration of the pretreated sludge (mg/L), SCODr is the soluble COD concentration of the raw (untreated) sludge (mg/L) and SCODNaOH is the soluble COD concentration after alkaline disintegration (mg/L). The alkaline Table 1 disintegration was applied by mixing the raw sludge sample with 1 M NaOH solution at a temperature of 90°C for 10 min

3.2.4 PSD analyses

PSD analyses Sequential filtration / ultrafiltration tests were carried out using a continuously stirred cell (Amicon 8400, Millipore, USA) with a volumetric capacity of 400 mL and a regulated nitrogen gas supply to create a positive pressure of 0.6–1.2 atm in the filtration device. Size fractionation experiments were accomplished in accordance with the procedures reported by Dülekgürgen et al. (Dülekgürgen , Doğruel , Karahan , Orhon. 2006;40:273–282)The pretreated sludge samples were filtered consecutively through conventional disposable filters with pore sizes of 1600 nm (Millipore AP40, glass fiber), 450 nm (Durapores HV, polyvinylidene fluoride (PVDF)) and 220 nm (Durapores GV, PVDF) (Millipore Corp., Bedford, MA 01730, USA). The permeates obtained from the final filtration step were successively passed through a series of chemically compatible ultrafiltration membrane discs with nominal molecular weight cut-off values of 100, 30, 10, 3 and 1 kDa (PL series, Millipore). The particulate fraction was defined as the remaining part above AP40 glass fiber filter (>1600 nm), presumably containing the settleable (>105 nm) and most of the supracolloidal (103–105 nm) substances; the soluble portion, reflecting the bulk of the dissolved constituents (1600 nm), colloidal (2–1600 nm) and soluble (< 2 nm) components.

3.2.5 OUR measurements

The impact of disintegration on the biodegradability of WAS samples were evaluated through respirometric tests which were performed with an Applitek Ra-Combo continuous respirometer (Nazareth, Belgium). Following disintegration by ultrasonication and microwave irradiation, total (unfiltered) disintegrated WAS samples along with disintegrated WAS filtrates obtained from AP40 glass fiber filter

(1600 nm) and 1 kDa ultrafiltration membrane disc (2 nm) were exposed to a series of respirometric analyses. OUR measurements were carried out first with acclimated biomass seed alone to observe the initial endogenous respiration level. In each run, a nitrification inhibitor (Formula 2533™, Hach Company, USA) was used to suppress the oxygen utilization due to nitrification. Pretreated WAS samples reflecting (i) the entire size spectrum, (ii) the sum of colloidal and soluble ranges and (iii) solely the soluble portion were added to the respirometer to yield a food-to-microorganisms ratio (S0/X0) of 0.20 mg COD / mg VSS. The profiles derived from OUR measurements were used to determine the biodegradability related COD fractionation at three operational size categories; namely particulate (>1600 nm), colloidal (2–1600 nm) and soluble (< 2 nm) components. The total biodegradable COD (CS) and its fractions (i.e. the readily biodegradable COD (SS), the rapidly hydrolysable COD (SH) and the slowly hydrolysable COD (XS)) were calculated using the oxygen consumption during the respirometric tests; whereas the total inert COD and its fractions (i.e. the soluble inert COD (SI) and the particulate inert COD (XI)) were obtained from the differences between the measured COD contents of the pretreated sludge samples and the amounts of oxygen utilized. The assessment of the COD fractions was previously described in more detail by Doğruel et al. (Doğruel S, Genceli EA, Babuna FG, Orhon D.; 2006;81:1877–1885.).

3.3. Analyses

3.3.1 Sludge characterisation

To measure effect of disintegration on the solubilization, the first step is raw sludge characterization and then pretreatment methods application, as a final step; ultrasonicated sludge and microwaved sludge characterization were done by using analytical methods.

Analytical methods involve some parameters measurement. In this study, these parameters are; pH measurement, Total Solid (TS), Total Suspended Solid (TSS), Suspended Solid (SS), Volatile Suspended Solid (VSS), Total Volatile Suspended Solid (TVSS), Total Dissolved Solid (TDS), Total Organic Carbon (TOC), Dissolved Organic Carbon (DOC), Total Kjeldahl Nitrogen (TKN), Dissolved Kjeldahl

Nitrogen (DTKN), Ammonium Nitrogen (NH4-N), Total phosphorous (TP), Dissolved Phosphorus (DP), Alkalinity measurement.

For pH measurement, pH/milivolt meter (ThermoOrion) was used.Total and dissolved organic carbon analyses were measured in accordance with High Temperature Combustion Method (APHA,2005) that number is 5310 B in Standard Methods. Shimadzu TOCV-CPN model automatic sample receiver Total Organic Carbon measurement device was used. TKN, ammonium nitrogen and phosphorous measurements were done by using TKN set (Gerhardt, Germany) in accordance with Standard Methods. Furhermore, SS and VSS measurements were done according to Standard Methods (APHA,2005). Measurements of COD were accomplished according to ISO 6060 Standard Method (International Organization for Standardization, 1986).

3.3.2 Sequential filtration/ultrafiltration

To observe PSD based COD fractionation, sequential filtration/ultrafiltration method was used. For this experiment; a continuously stirred cell with a volumetric capacity of 400mL (Amicon, Model 8400) was used as the filtration / ultrafiltration unit, and was operated under positive pressure (0.6–1.2 atm; N2 as the inert gas). Operational parameters, such as temperature and working pressure, applied during the sequential filtration/ultrafiltration experiments were within the ranges recommended by the manufacturers. Conventional disposable filters with pore sizes of 1200–1600nm (Millipore AP40, glass fiber), 450nm (Durapores HV, polyvinylidene fluoride (PVDF)), and 220nm (Durapores GV, PVDF) (Millipore Corp., Bedford, MA 01730) were used for sequential filtration. Permeate from the final filtration step was successively passed through ultrafiltration membrane discs with nominal molecular weight cut-off (MWCO) values of 100, 30, 10, 3, and 1 kDa (PL series, Millipore, MA). In order to provide consistency among the different size units of ultrafiltration and filtration, the nominal MWCO values given in kDa units were approximated to the corresponding particle size values defined in nm, by using the approach described by Cheryan (1986) and McGregor (1986).

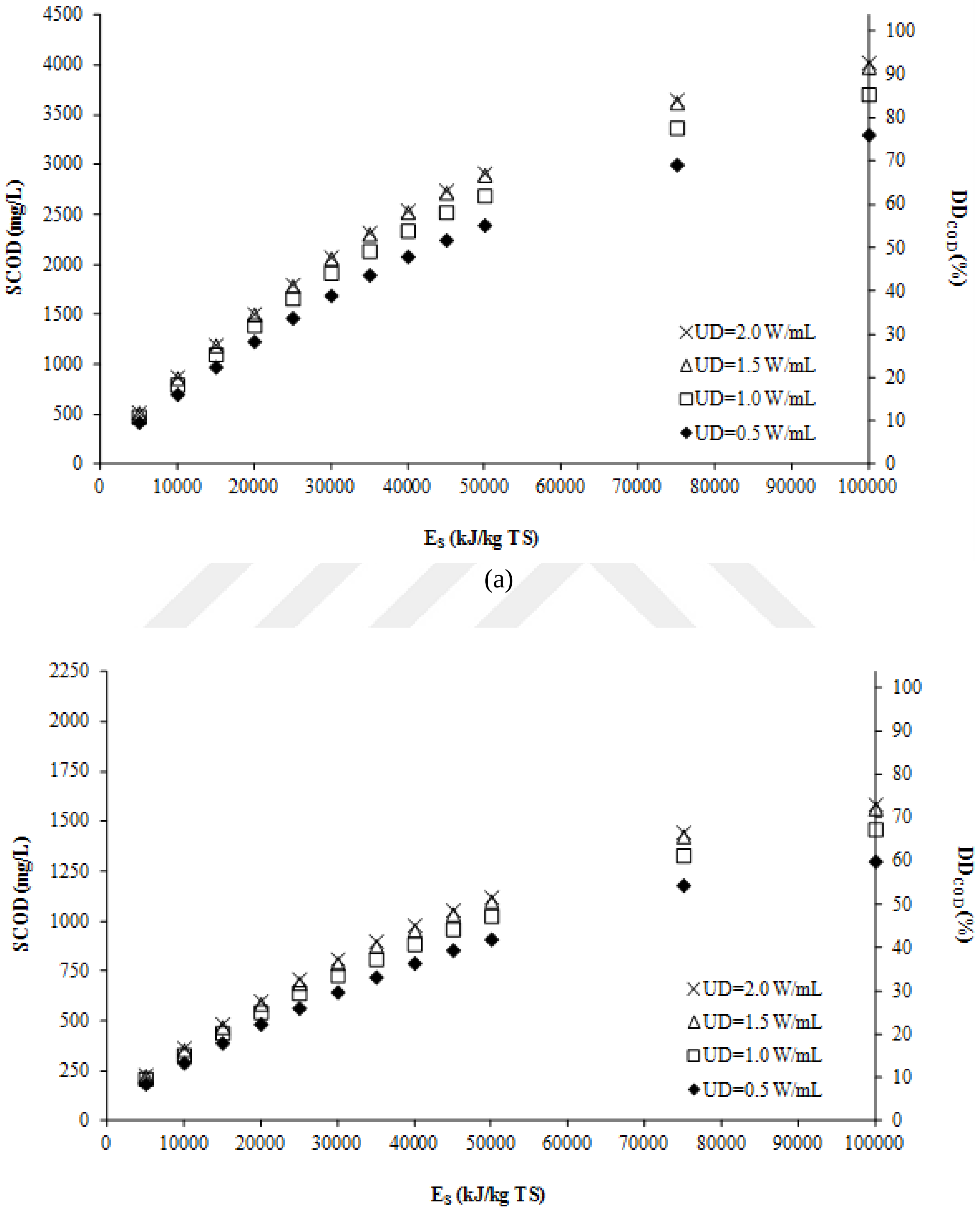
4. RESULTS

4.1 Ultrasonication

Ultrasonication refers to the distruption of large organic molecules and their transformation into small pieces. During this stage, the physical, chemical and biological characteristics of the sludge all change. An increase of 50% is observed in biogas production in full-scale applications of ultrasonification (Pilli et al., 2010).

Disintegration Degree can be evaluated about physical changes include PSD, turbidity, settleability, mass composition and microscopic examination. Chemical changes include SCOD increase, an increase in protein concentration, nitrate nitrogen and increased NH3 release. Biological changes include hetetrophic count and specific oxygen uptake rate (Pilli et al., 2010)

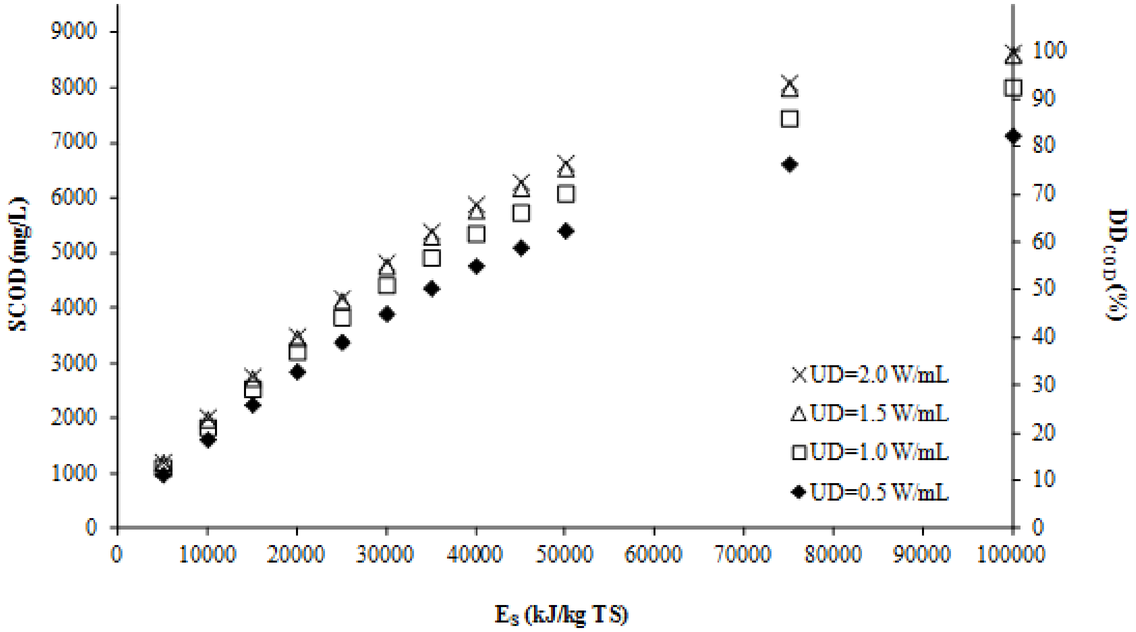
According to Ultrasonic pretreatment, The first part of the experimental study was designed to investigate the impact of specific energy input (ES) and ultrasonic density (UD) on the disintegration performance to determine optimum sonication conditions for sludge liquefaction. Prior to sonication tests, the initial TS concentration (1.13% w/v) of the first WAS sample was adapted to 0.57% by diluting with ultrapure water and 2.26% by avoiding supernatant after settling gravitationally in order to supply a better insight on the effect of solid content. In this context, a series of ultrasonic disintegration experiments were carried out on the first WAS sample containing 0.57%, 1.13% and 2.26% TS concentration at a constant frequency of 20 kHz and various ultrasonic density (UD) levels ranging from 0.5 to 2.0 W/mL. The first WAS sample was subjected to different sonication times in the range of 1–40 min so that the specific energy input provided varied from 5000 to 100000 kJ/kg TS. As a result of ultrasonic pretreatment, as displayed in Figure 4.1, indicated that SCOD release (i.e. sludge disintegration degree based on soluble COD parameter, DDSCOD) exhibited an ascending trend with increases in both specific energy input and ultrasonic density at all TS contents. Evaluation of the data also revealed a fairly linear increase in the DDSCOD at low specific energy input values (namely, until 30000 kJ/kg TS) since the most vigorous particle disruption was achieved in the initial period of sonication as a result of the rapid cavitation impact arising from powerful transient bubbles generated in fractions of microseconds (Show, Mao , Lee 2007;41:4741–4747.When the sonication density was fixed at 1.5 W/mL and the specific energy input was raised from 5000 to 30000 kJ/kg TS, the disintegration degree of sludge was improved from 10 to 46% and from 12 to 54% at the initial TS concentration of 1.13% and 2.26%, respectively. Under the same operating conditions, the rate of sludge disintegration declined for extended specific energy input values (> 30000 kJ/kg TS) and were determined in a range of 90–99% for prolonged ultrasonic pretreatment at 100000 kJ/kg TS. Hence, specific energy inputs of 5000 and 30000 kJ/kg TS were selected for further sonication tests, mainly based on results associated with the first activated sludge sample, but also in view of the fact that they corresponded to the initial period of ultrasonication where the particle disruption was most profound due to the explosive cavitational effect. Providing an upper threshold value, 100000 kJ/kg TS was also included as an additional specific enerpy input to evaluate its impact on the sequential filtration / ultrafiltration tests and respirometric measurements. The experimental findings displayed in the figure additionally showed that no significant change in the sludge disintegration degree was observed throughout the applied ultrasonic densities from 1.5 to 2.0 W/mL at all TS levels. Therefore, the optimum sonication density securing a satisfactory sludge disintegration was determined as 1.5 W/mL for subsequent experiments. Comparison with literature data is quite difficult as a variety of factors including sonication parameters (specific energy input, exposure time, sonication intensity, ultrasonic density) and sludge characteristics (type, TS content, volume) affect the sludge disintegration efficiency. Yet, the results obtained were in agreement with those of other studies where similar quantities of SCOD release and / or disintegration degrees had been reported for the investigated TS concentrations.



(a)

(b)

Figure 4.1: Effect of ultrasonic pretreatment on sludge solubilization – Sample 1: (a) 0.57%, (b) 1.13%



(c)

Figure 4.1 (contunity): Effect of ultrasonic pretreatment on sludge solubilization – Sample 1: (c) 2.26% TS concentration.

Considering the conclusion derived from preliminary experiments, the second WAS sample was subjected to ultrasonic pretreatment at the selected sonication density of 1.5 W/mL and specific energy inputs of 5000, 30000 and 100000 kJ/kg TS. SCOD contents determined experimentally for the second WAS sample together with corresponding disintegration degree levels are depicted in Table 4.1. It is parallel to the experimental studies conducted at optimum conditions, a linear interpolation was applied to experimental data of the first WAS sample to estimate its disintegration performance at the TS concentration of 10555 mg/L. In this way, the linear interpolation method provided a basis for comparative evaluation of the samples tested, on the basis of equal initial TS levels. Experimental findings, summarized in Table 4.1, demonstrated a constant sludge disintegration efficiency pattern for both WAS samples, regardless of different sampling periods.

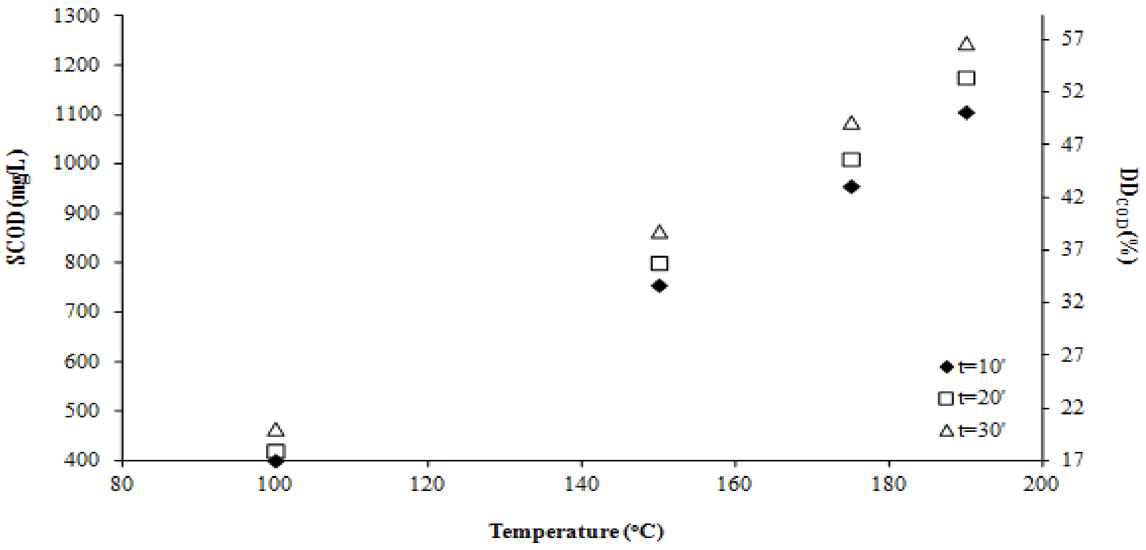
Table 4.1: Comparison of disintegration performance of WAS samples after ultrasonication at optimum experimental conditions.

UD (W/mL)	E_S (kJ/kg TS)	Sample	SCOD (mg/L)			DD_{SCOD} (%)		
			TS=5655 mg/L	TS=11305 mg/L	TS=10555 mg/L	TS=5655 mg/L	TS=11305 mg/L	TS=10555 mg/L
1.5	5000	1	225[a]	515[a]	475[b]	9[a]	10[a]	10[b]
		2	---	---	475[a]	---	---	10[a]
	30000	1	790[a]	2060[a]	1890[b]	35[a]	46[a]	45[b]
		2	---	---	1900[a]	---	---	44[a]
	100000	1	1565[a]	3980[a]	3660[b]	72[a]	92[a]	89[b]
		2	---	---	3670[a]	---	---	87[a]

a: experimentally measured
b: theoretically calculated

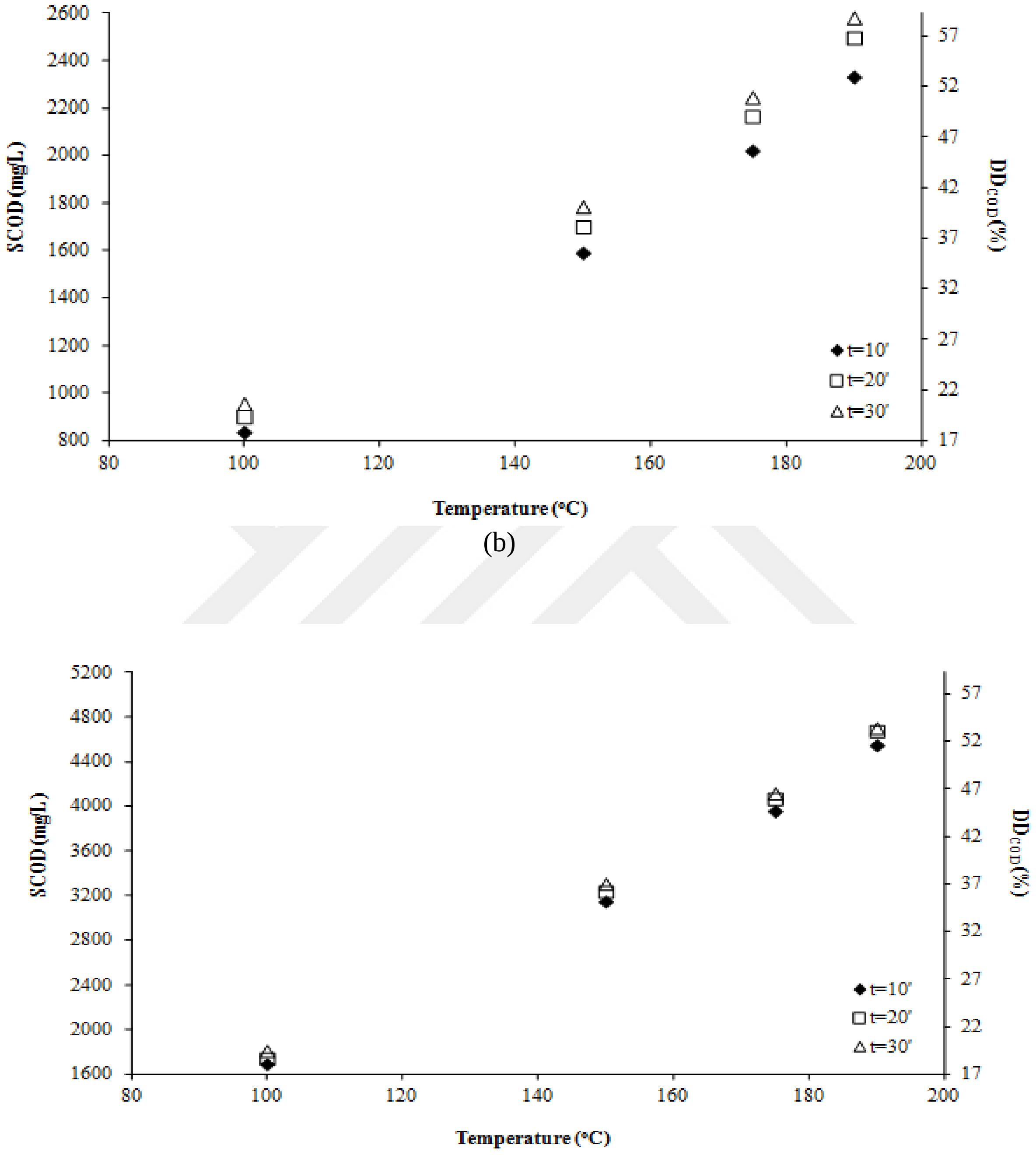
4.2 Microwave Pre-Treatment

Microwave irradiation The first part of the experimental survey was devoted to exploring the optimum exposure time and temperature for microwave pretreatment. Before microwave irradiation experiments, the original TS level (1.13% w/v) of the first activated sludge sample was adjusted to 0.57% through adding ultrapure water and 2.26% by decanting the supernatant liquid in order to examine the impact of solid content on disintegration performance. Hence, the first WAS sample at three different TS concentrations was exposed to microwave disintegration where the applied temperature and period varied from 100 to 190°C and 10 to 30 minutes, respectively. The experimental findings, as presented in Figure 4.2, revealed that the sludge disintegration performance of microwave pretreatment was improved with rising the temperature higher than the boiling point at each TS content. The increase in both SCOD amount and disintegration degree might be attributed to the disruption of complex WAS floc structure and release of extracellular and intracellular constituents, such as proteins, carbohydrates and lipids, into the bulk liquid phase Eskicioglu, Terzian , Kennedy, Droste , Hamoda. 2007;41:2457–2466, Eskicioglu , Kennedy, Droste. 2006;40:3725–3736) When the irradiation time was set as 10 minutes and the treatment temperature was elevated from 100 to 175°C, microwave pretreatment at 0.57% TS concentration resulted in an increase of SCOD level from 400 to 955 mg/L, corresponding to a sludge cell disintegration efficiency of 17 and 43%, respectively. mg SCOD per gram TS ratios stayed almost at the same level although the TS contents were raised from 0.57% to higher values, indicating that microwave process performed at a constant temperature induced almost similar sludge disintegration degrees, regardless of the TS concentration applied. An analogous phenomenon was also observed by Toreci (Toreci , Kennedy, Droste 2010;31:766–773)who investigated the effect of microwave treatment on sludge character at temperatures higher than 100°C, Figure 4.2 Table 4.4 using two different intensities and TS levels. On the other hand, the increment of the sludge disintegration rate became smaller with the increase of the treatment temperature from 175 to 190°C. As apparent from Figure 4.2, changing the contact time from 10 to 20 or 30 minutes resulted in no further considerable increase in solubilization efficiency at all TS concentrations. This observation was in agreement with earlier studies which reported that the exposure time had practically no additional impact on the improvement of disintegration degree above 20 minutes.(Valo , Carrère , Delgenès 2004;79:1197–1203, Prorot , Eskicioglu , Droste , Dagot , Leprat 2008;35:1261–1268.). Accordingly, a pretreatment temperature of 175°C and an irradiation time of 10 minutes were selected as the optimum operating conditions to be used in the following experimental studies.



(a)

Figure 4.2: Effect of microwave pretreatment on sludge solubilization – Sample 1:(a) 0.57%



(b)

(c)

Figure 4.2 (contunity): Effect of microwave pretreatment on sludge solubilization – Sample 1: (b) 1.13% and (c) 2.26% TS concentration.

The next step of experimental examination covered microwave pretreatment of the second WAS sample where the applied temperature was set at previously determined optimum value of 175°C and the contact times were adjusted to 10, 20 and 30 minutes. The results of microwave heating, illustrated in Table 4.2, indicated that the shortest exposure time yielded a sludge disintegration efficiency of 43%; whereas an increase to an irradiation time of 30 minutes only provided an additional DDSCOD of 7%. Concomitantly, the disintegration degree of the first activated sludge sample at the TS level of 10555 mg/L was calculated using a similar procedure as for the ultrasonication experiments formerly mentioned. Thus, the linear interpolation technique enabled a comparative evaluation of the investigated WAS samples in terms of their disintegration performances. The experimental data outlined in Table 4.2 revealed that the sludge disintegration rates remained consistent even though different sampling dates were tested.

Table 4.2. Comparison of disintegration performance of WAS samples after microwave irradiation at optimum experimental conditions.

T (°C)	**t (min)**	**Sample**	**SCOD (mg/L)**			**DD$_{SCOD}$ (%)**		
			TS=5655 mg/L	**TS=11305 mg/L**	**TS=10555 mg/L**	**TS=5655 mg/L**	**TS=11305 mg/L**	**TS=10555 mg/L**
175	10	1	955[a]	2020[a]	1880[b]	43[a]	46[a]	45[b]
		2	---	---	1865[a]	---	---	43[a]
	20	1	1010[a]	2165[a]	2010[b]	46[a]	49[a]	48[b]
		2	---	---	2020[a]	---	---	47[a]
	30	1	1085[a]	2245[a]	2090[b]	49[a]	51[a]	51[b]
		2	---	---	2135[a]	---	---	50[a]

a: experimentally measured
b: theoretically calculated

4.3 Physico-chemical characterization

Physico-chemical characterization This part of the work was intended to experimentally study the impact of ultrasonication and microwave irradiation on the physical and chemical characteristics of WAS samples. Table 4 presents conventional characterization results of WAS samples after disintegration at the selected operating conditions. The experimental data indicated that both processes provided limited TS and

VS removal efficiencies of only up to 5%; whereas SS and VSS reductions were determined in a range of 22–37%, revealing that applied techniques changed the distribution of solid particles in the pretreated WAS samples. The VSS abatement rates obtained were found to be in agreement with the findings of Koroglu et al. (Koroglu , Zengin, Yagci, Artan 2012;33:1505–1510. who characterized sonicated WAS liquids as a possible carbon source for nitrogen removal. Comparative evaluation of the values outlined in Table 4.3 pointed out that the sludge disintegration by both processes had practically no effect on the TCOD of the investigated WAS samples since this parameter was virtually constant for all the conditions assayed, ranging between 7580 and 8290 mg/L. On the other hand, the degree of solubilization, expressed as the ratio between SCOD and TCOD concentrations, increased from its initial value of 1 to 6% at the specific energy input of 5000 kJ/kg TS. Sonication at the specific energy input of 30000 kJ/kg TS resulted in an COD solubilization rate of 25–26%, a level almost similar to that of the microwave irradiation performed at the optimum temperature and contact time of 175^{o}C and 10 minutes, respectively. When the latter was extended to 100000 kJ/kg TS, the solubilization ratio was significantly increased to a level of around 50%, thus reflecting the effectiveness of ultrasonic pretreatment on sludge disintegration. The percentage values of COD solubilization obtained in this study were fairly in consistent with previously reported literature data based on sludge reduction by microwave and ultrasonic (Feng , Lei , Deng , Yu , Li 2009;48:187–194, Yagci , Akpinar 2011;32:221–230) disintegration. Apart from SCOD, DOC contents in the supernatants of disintegrated WAS samples were also used as indices of carbon release where concentration variations of DOC under selected operating conditions were closely the same as those of SCOD. Similar observations were made for the low-frequency sonication of sewage sludge and microwave irradiation of meat processing wastewater sludge (Erden G.; 2013;34:711–718) The nutrient release patterns summarized in Table 4.3 demonstrated that both disintegration methods promoted the solubilization of nitrogen and phosphorus species. These results were in accordance with those of Yu et al.(Yu , Chan, Liao , Lo 2010;181:1143–1147.)and Wang et al. (Wang , Qiu , Lu , Ying 2010;176:35–40. who likewise concluded that the sludge disintegration by ultrasonication and microwave irradiation significantly increased the soluble N and P concentrations in the sludge supernatants.

Table 4.3: Changes in physico-chemical properties of WAS samples after disintegration at optimum experimental conditions.

Parameter	Unit	Raw WAS		Sonicated WAS (UD = 1.5 W/mL)						Microwave Irradiated WAS	
				5000 kJ/kg TS		30000 kJ/kg TS		100000 kJ/kg TS		T=175°C, t=10'	
		Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2
pH	---	7.18	7.09	7.29	7.18	7.45	7.33	7.49	7.37	7.43	7.31
TS	mg/L	11305	10555	10990	10245	10875	10130	10785	10040	10905	10160
VS	mg/L	6310	5980	6135	5810	6045	5720	5995	5675	6105	5780
VS/TS	---	0.56	0.57	0.56	0.57	0.56	0.56	0.56	0.57	0.56	0.57
SS	mg/L	10490	9960	8120	7575	7460	6910	6975	6420	7530	6980
VSS	mg/L	6005	5770	4660	4440	4220	4005	3865	3650	4405	4185
VSS/SS	---	0.57	0.58	0.57	0.59	0.57	0.58	0.55	0.57	0.58	0.60
TCOD	mg/L	8290	8060	7995	7755	7895	7655	7825	7580	7915	7675
SCOD	mg/L	80	75	515	475	2060	1900	3980	3670	2020	1865
SCOD/TCOD	---	0.01	0.01	0.06	0.06	0.26	0.25	0.51	0.48	0.26	0.24
DOC	mg/L	20	20	125	115	520	475	1030	940	500	455
STKN	mg/L	15	15	25	25	105	95	200	180	100	90
NH_4^+-N	mg/L	5	5	10	10	45	40	80	70	40	35
NO_2^--N	mg/L	0.08	0.07	0.20	0.18	0.87	0.79	1.50	1.36	0.82	0.74
NO_3^--N	mg/L	0.75	0.70	0.97	0.88	1.78	1.61	3.20	2.90	1.55	1.40
PO_4^{3-}-P	mg/L	2	2	3	3	13	12	25	24	12	11

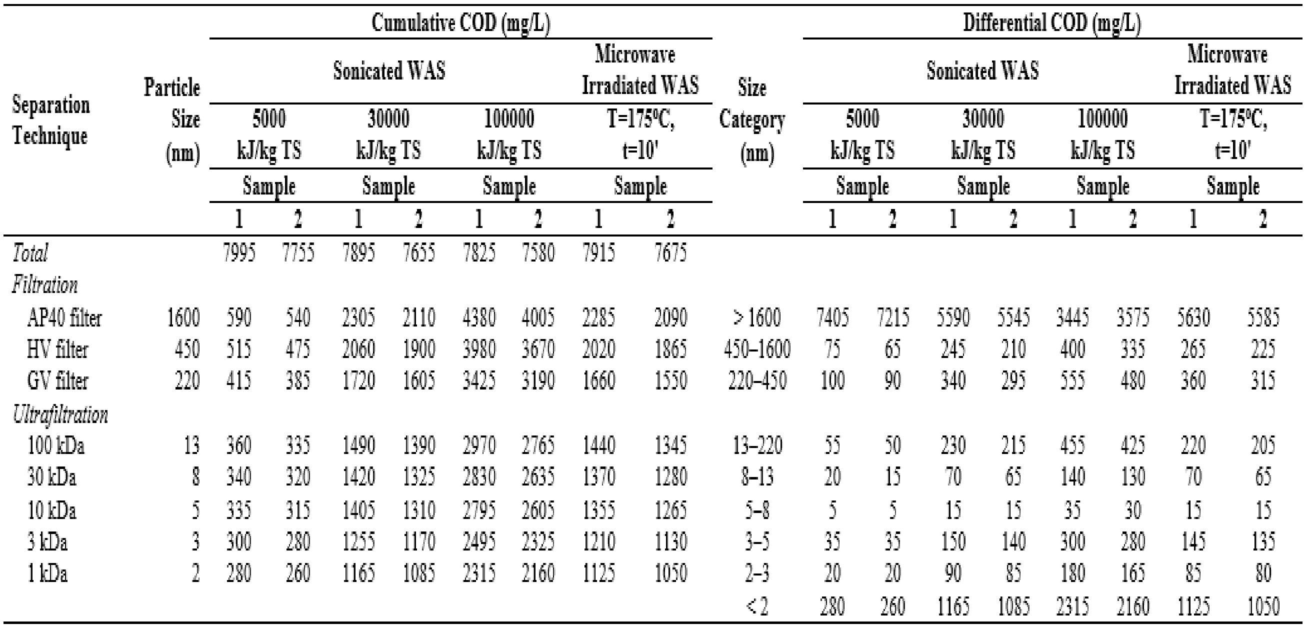
4.4 Particle Size Distribution Based COD Fractionation

PSD based COD fractionation analysis is made via using membranes with different pore sizes. COD is measured after using each membrane and the results are examined. Cumulative COD corresponds with the COD measurement at each filtration/ultrafiltration step. Differential COD is the difference between the measurements of two respective filtration steps. The following table and figures indicate the PSD analysis and differential COD values obtained, realized after applying such specific energies respectively as 5000 kJ/kg TS, 30000 kJ/kg TS and 100000 kJ/kg TS in July 2012. For pore sizes between 5-8 nm, the less the sizes get, the less differential COD values are obtained. However, there becomes an increase after 5-8 nm.

Figure 4.3 Table 4.4 PSD analyses A physical separation by means of sequential filtration / ultrafiltration tests was carried out to investigate the effect of ultrasonication and microwave irradiation on the PSD of organic carbon content present in disintegrated

WAS samples. The results obtained for the PSD-based COD fractionation are presented in Table 4.6, giving both the COD level of the permeate after each sequential filtration / ultrafiltration step as the cumulative value below the corresponding filter size and the differential value between the two consecutive filter sizes. The first values shown in the table were taken as the TCOD concentrations (sum of settleable, supracolloidal, colloidal and soluble portions) since no quiescent settling was applied prior to physical segregation experiments. The differential COD values at each size range were normalized against the corresponding TCOD contents and illustrated as percentage contributions in Figure 4.3 to better visualize the effect of the applied pretreatment processes. As apparent from the figure, in spite of different sampling times, physical categorization of the COD fractions into nine sequential size intervals ranging from 1600 down to 2 nm demonstrated similar trends for the two WAS samples studied. COD fingerprints after sonication at the specific energy input of 5000 kJ/kg TS indicated that the particulate size range (>1600 nm) was the predominant fraction with a 93% contribution; while the colloidal (2–1600 nm) and soluble (1600 nm to 46%; whereas colloidal and soluble size ranges corresponded to 25 and 29% of the TCOD content, respectively. The experimental results depicted in Figure 4. 3 revealed that the most apparent impact of ultrasonic disintegration on WAS samples was the shifting of the COD peak at the particulate fraction (>1600 nm) towards the lowest size range

Table 4.4 : Cumulative and differential COD values of WAS samples after disintegration at optimum experimental conditions.



Separation Technique	Particle Size (nm)	Cumulative COD (mg/L)								Size Category (nm)	Differential COD (mg/L)							
		Sonicated WAS						Microwave Irradiated WAS			Sonicated WAS						Microwave Irradiated WAS	
		5000 kJ/kg TS		30000 kJ/kg TS		100000 kJ/kg TS		T=175ºC, t=10'			5000 kJ/kg TS		30000 kJ/kg TS		100000 kJ/kg TS		T=175ºC, t=10'	
		Sample		Sample		Sample		Sample			Sample		Sample		Sample		Sample	
		1	2	1	2	1	2	1	2		1	2	1	2	1	2	1	2
Total		7995	7755	7895	7655	7825	7580	7915	7675									
Filtration																		
AP40 filter	1600	590	540	2305	2110	4380	4005	2285	2090	> 1600	7405	7215	5590	5545	3445	3575	5630	5585
HV filter	450	515	475	2060	1900	3980	3670	2020	1865	450–1600	75	65	245	210	400	335	265	225
GV filter	220	415	385	1720	1605	3425	3190	1660	1550	220–450	100	90	340	295	555	480	360	315
Ultrafiltration																		
100 kDa	13	360	335	1490	1390	2970	2765	1440	1345	13–220	55	50	230	215	455	425	220	205
30 kDa	8	340	320	1420	1325	2830	2635	1370	1280	8–13	20	15	70	65	140	130	70	65
10 kDa	5	335	315	1405	1310	2795	2605	1355	1265	5–8	5	5	15	15	35	30	15	15
3 kDa	3	300	280	1255	1170	2495	2325	1210	1130	3–5	35	35	150	140	300	280	145	135
1 kDa	2	280	260	1165	1085	2315	2160	1125	1050	2–3	20	20	90	85	180	165	85	80
										< 2	280	260	1165	1085	2315	2160	1125	1050

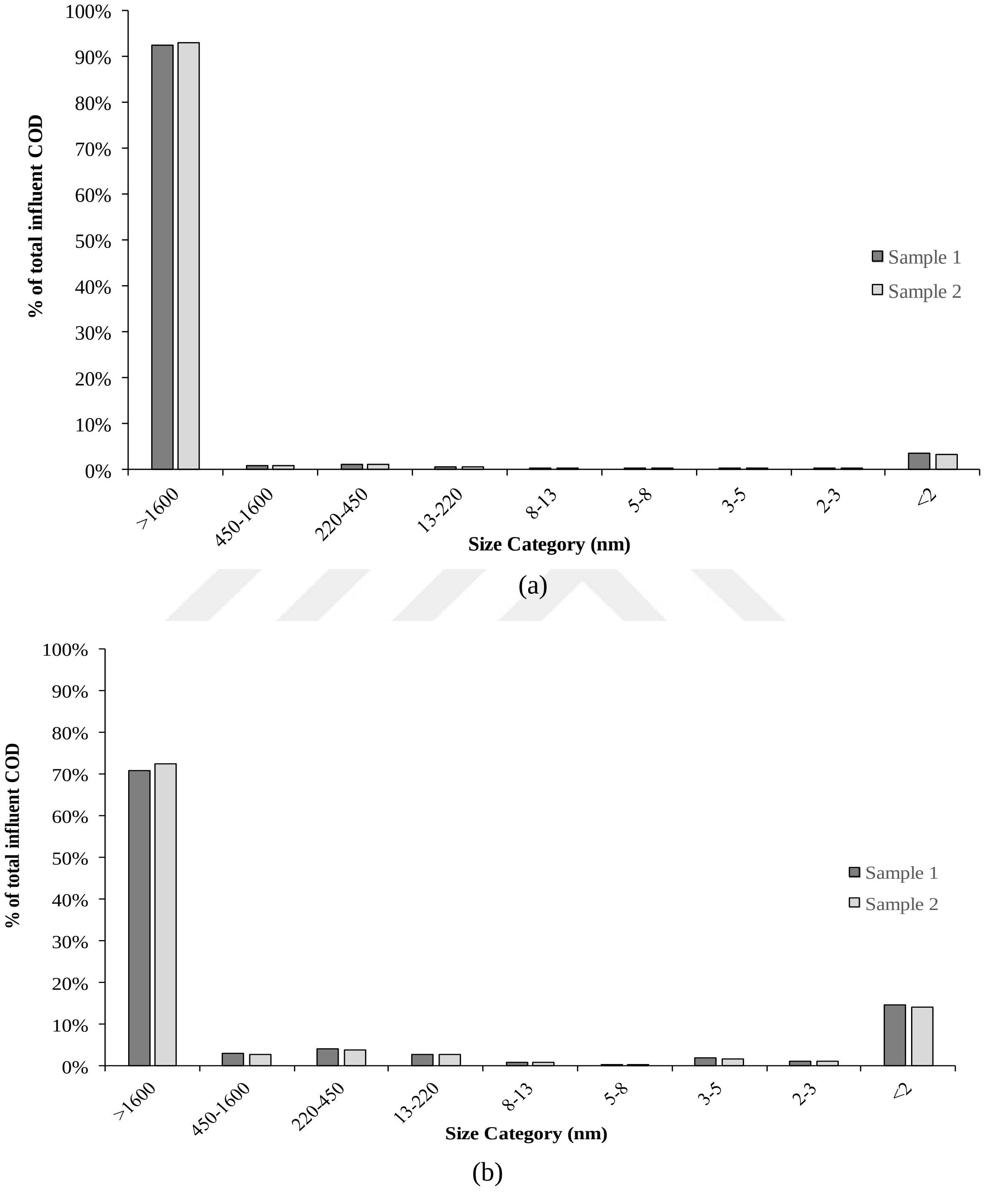
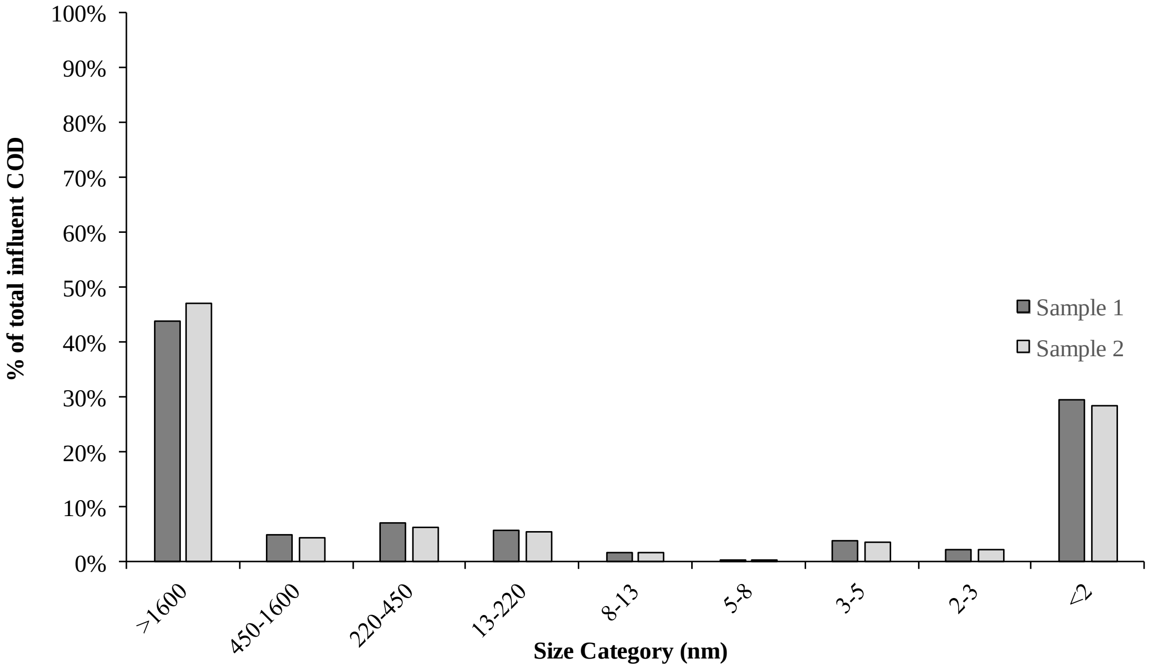
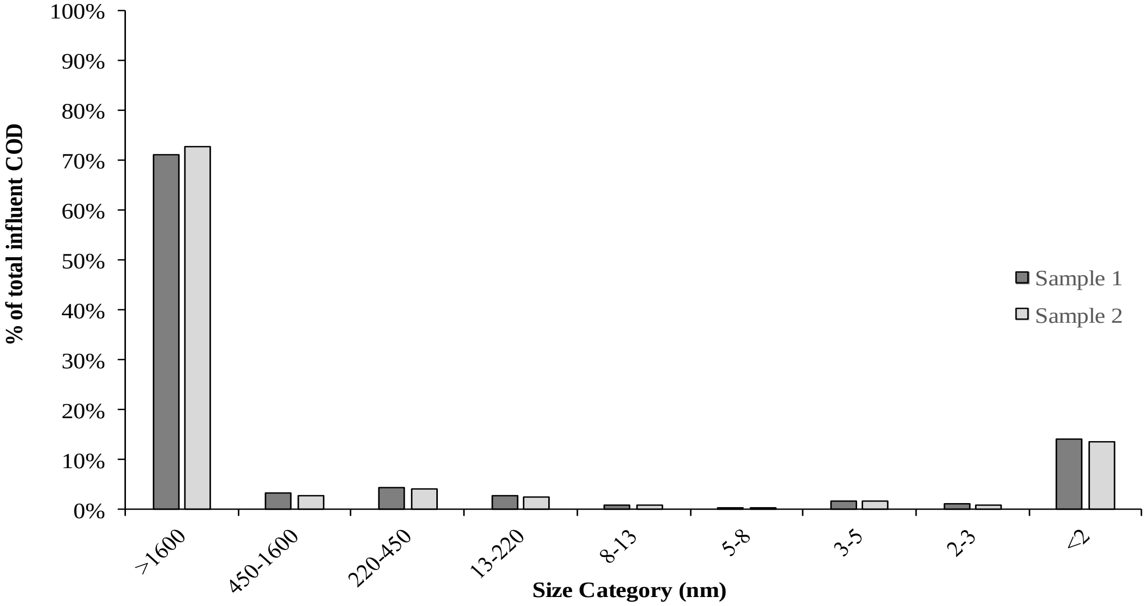


Figure 4.3: Impact of sludge disintegration on the PSD-based COD fractionation: (a) sonication E_S=5000 kJ/kg TS, (b) sonication E_S=30000 kJ/kg TS.



(c)



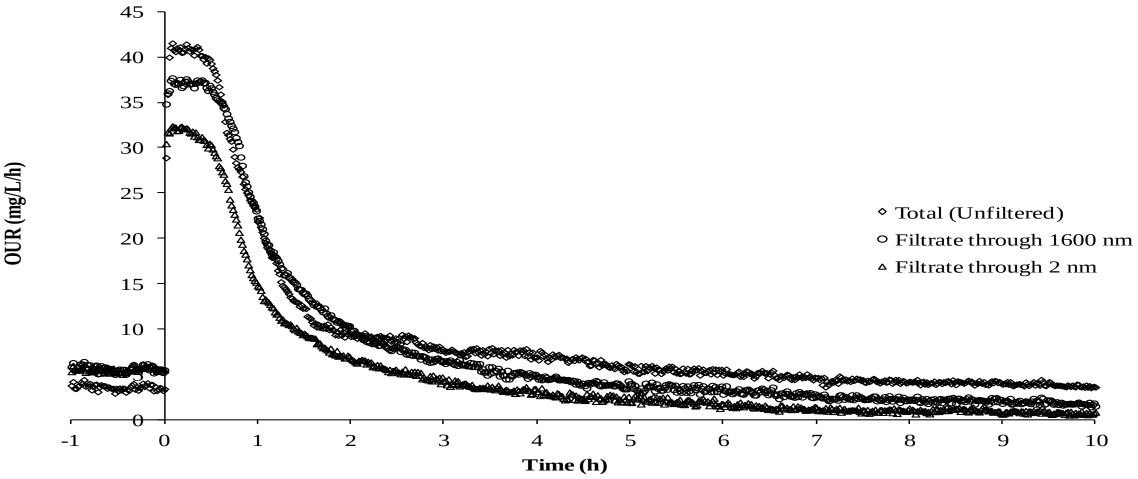
(d)

Figure 4.3 (contunity) : Impact of sludge disintegration on the PSD-based COD fractionation, (c) sonication E_S=100000 kJ/kg TS and (d) microwave irradiation T=175°C, t=10'.

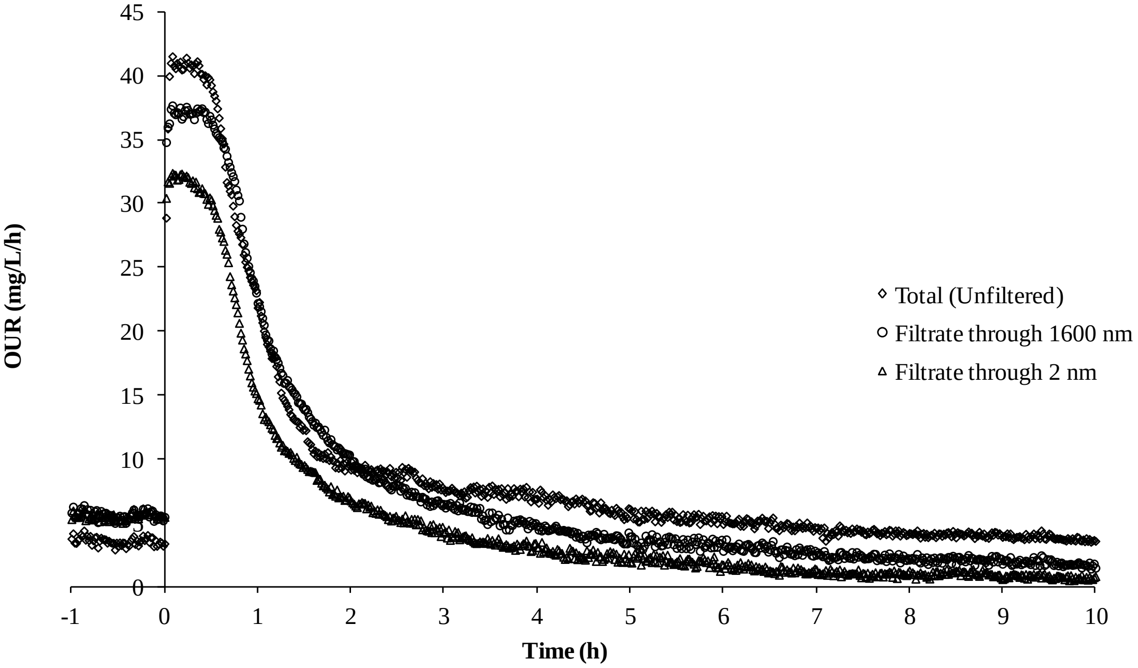
As apparent from the figure, in spite of different sampling times, physical categorization of the COD fractions into nine sequential size intervals ranging from 1600 down to 2 nm demonstrated similar trends for the two WAS samples studied. COD fingerprints after sonication at the specific energy input of 5000 kJ/kg TS indicated that the particulate size range (>1600 nm) was the predominant fraction with a 93% contribution; while the colloidal (2–1600 nm) and soluble (<2 nm) portions accounted for 4 and 3% of the TCOD level, respectively. When WAS samples were treated ultrasonically at the specific energy input of 30000 kJ/kg TS, 72% of the total organic content was in the form of particulate matter where the remaining 28% was distributed in the colloidal and soluble portions, each constituting 14% of the TCOD concentration. Extending the specific energy input to 100000 kJ/kg TS decreased the COD fraction at the particle size interval of >1600 nm to 46%; whereas colloidal and soluble size ranges corresponded to 25 and 29% of the TCOD content, respectively. The experimental results depicted in Figure 3 revealed that the most apparent impact of ultrasonic disintegration on WAS samples was the shifting of the COD peak at the particulate fraction (>1600 nm) towards the lowest size range (<2 nm), which was not surprising, since the conversion of organic matter with high molecular weight into smaller species (i.e. transformation of complex organics into simpler compounds through solubilization) was expected to be the dominant mechanism. These observations were quite compatible with the results of Koroglu et al. (Koroglu S, Zengin GE, Yagci N, Artan N.; 2012;33:1505–1510) who experimentally showed that the change in ultrasonic power had a significant effect on COD fractionation of sonicated WAS liquids and higher specific energy input increased the COD fraction at the soluble size range. Experimental data shown in Figure 4.3, on the other hand, confirmed that the WAS samples irradiated at the treatment temperature of 175^{o}C and exposure time of 10 minutes exhibited COD distribution characteristics very similar to those of their sonicated counterparts at 30000 kJ/kg TS. Unfortunately, detailed information about the influence of microwave irradiation on the PSD-based COD profile of WAS sample is not available in the literature. However, COD fingerprints of the irradiated WAS samples were in agreement with the one obtained for domestic wastewater reported by Dülekgürgen et al. (Dülekgürgen E, Doğruel S, Karahan Ö, Orhon D.; 2006;40:273–282.) where 65% of the initial COD level was determined to accumulate at the particulate range and the soluble portion was found to constitute 14% of the total organic content.

4.5 OUR Measurement

The biodegradability characteristics of disintegrated WAS samples were examined by means of respirometric measurements evaluating the generated OUR profiles for the assessment of COD fractions. The OUR curves obtained for sonicated and irradiated WAS samples are illustrated in Figure 4.4. The results of COD fractionation and the percentages of each fraction in TCOD are outlined in Table 4.5. According to the figures given in the table, the experimental data were quite consistent and did not exhibit significant differences between the two WAS samples tested. COD fractionation after sonication at the specific energy input of 5000 kJ/kg TS revealed that the disintegrated WAS samples could be characterized with a total biodegradable COD (CS) fraction of 88%, containing only 3% of readily biodegradable COD (SS) on average where the remaining 85% was classified as hydrolysable COD, almost entirely of particulate nature (XS). An increase in both concentrations and relative magnitudes of soluble COD components was observed for extended specific energy input values. When 30000 kJ/kg TS of specific energy input was applied to the WAS samples, the readily biodegradable COD fraction (SS) accounted for 10% of the TCOD. For the same pretreatment scheme, the slowly hydrolysable COD (XS) was observed as the major COD fraction, representing 65% of the TCOD; whereas the same ratio for the soluble part of the slowly biodegradable (rapidly hydrolysable) COD (SH) remained at 14%.

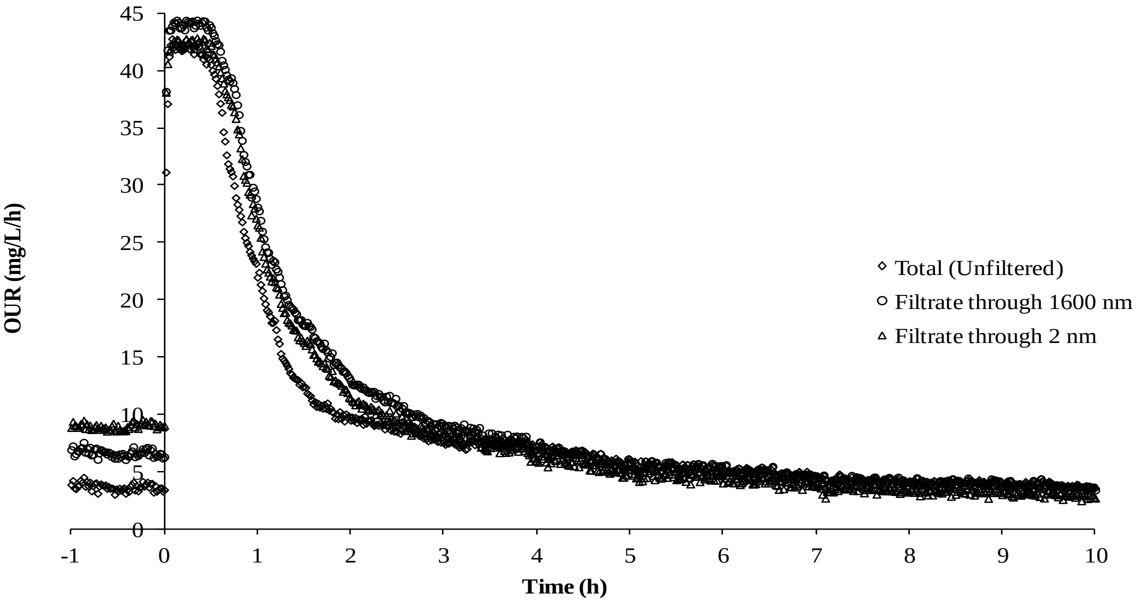


(a)

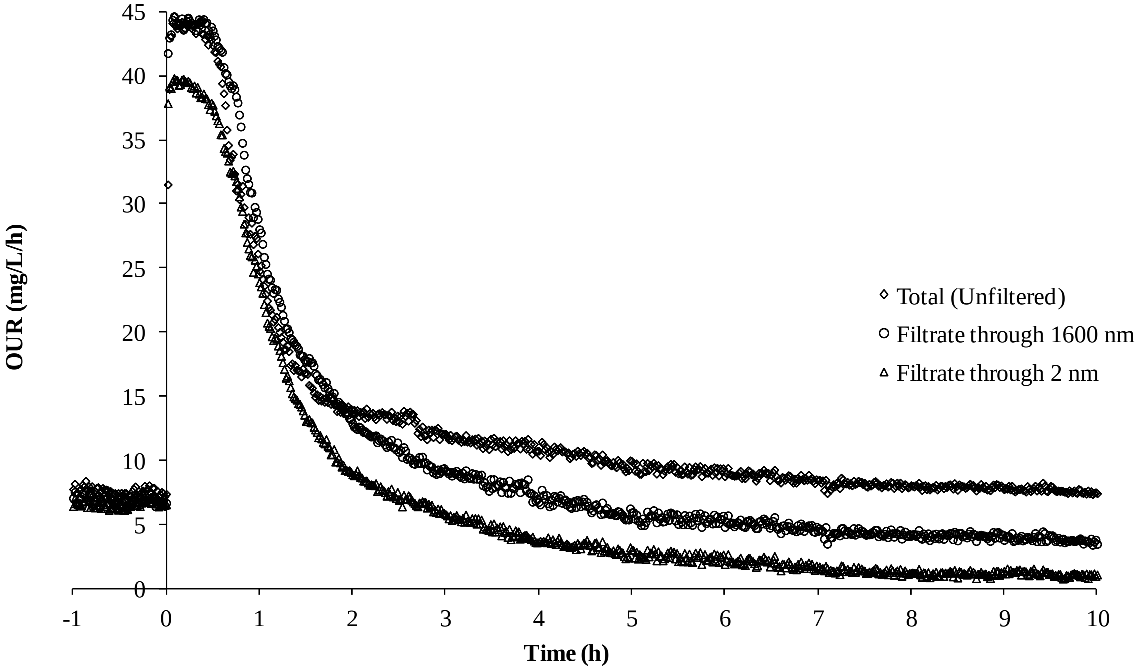


(b)

Figure 4.4: Respirogram for disintegrated WAS portions – Sample 1: (a) sonication E_S=5000 kJ/kg TS, (b) sonication E_S=30000 kJ/kg TS.



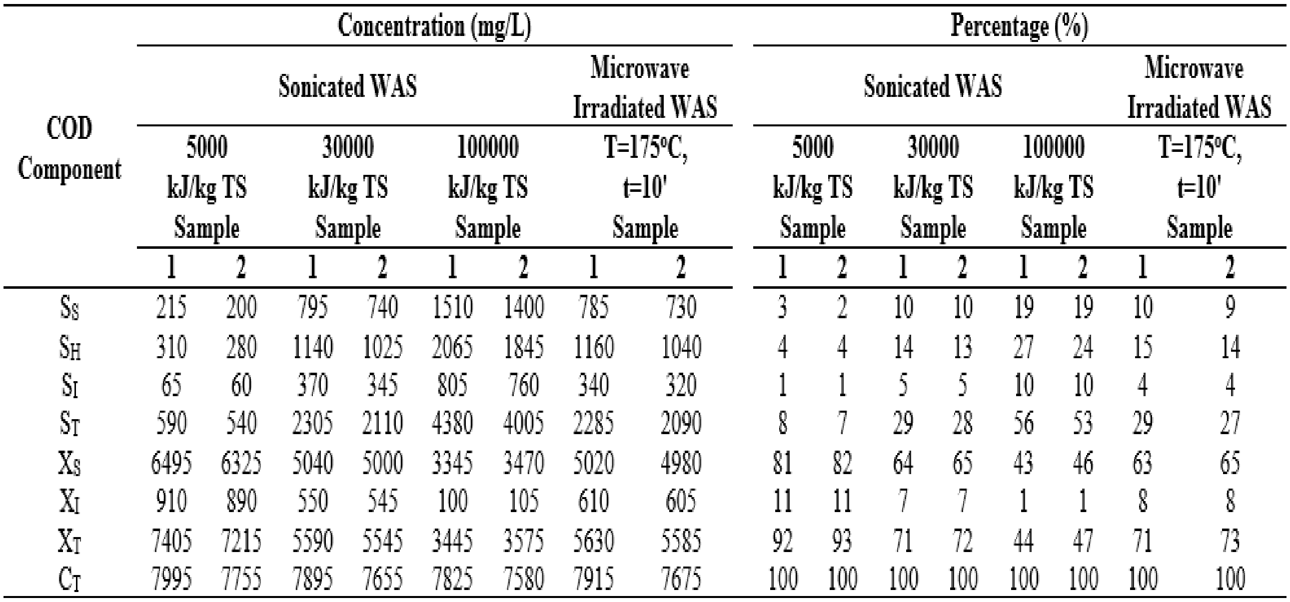
(c)



(d)

Figure 4.4 (contunity): Respirogram for disintegrated WAS portions – Sample 1: (c) sonication E_S=100000 kJ/kg TS and (d) microwave irradiation T=175^{o}C, t=10'.

Table 4.5 Results of COD fractionation for WAS samples after disintegration at optimum experimental condition.



COD Component	Concentration (mg/L)								Percentage (%)							
	Sonicated WAS						Microwave Irradiated WAS		Sonicated WAS						Microwave Irradiated WAS	
	5000 kJ/kg TS Sample		30000 kJ/kg TS Sample		100000 kJ/kg TS Sample		T=175°C, t=10' Sample		5000 kJ/kg TS Sample		30000 kJ/kg TS Sample		100000 kJ/kg TS Sample		T=175°C, t=10' Sample	
	1	2	1	2	1	2	1	2	1	2	1	2	1	2	1	2
S_S	215	200	795	740	1510	1400	785	730	3	2	10	10	19	19	10	9
S_H	310	280	1140	1025	2065	1845	1160	1040	4	4	14	13	27	24	15	14
S_I	65	60	370	345	805	760	340	320	1	1	5	5	10	10	4	4
S_T	590	540	2305	2110	4380	4005	2285	2090	8	7	29	28	56	53	29	27
X_S	6495	6325	5040	5000	3345	3470	5020	4980	81	82	64	65	43	46	63	65
X_I	910	890	550	545	100	105	610	605	11	11	7	7	1	1	8	8
X_T	7405	7215	5590	5545	3445	3575	5630	5585	92	93	71	72	44	47	71	73
C_T	7995	7755	7895	7655	7825	7580	7915	7675	100	100	100	100	100	100	100	100

Comparative evaluation of the values summarized in Table 4.5 indicated that microwave irradiation at optimum operating conditions (T=175^{o}C, t=10') and ultrasonic treatment at the specific energy input of 30000 kJ/kg TS demonstrated striking similarities in terms of their fractionation patterns which could be associated with a typical domestic sewage composition .The investigated WAS samples initially included 99% particulate COD and 1% soluble COD; at the specific energy input of 100000 kJ/kg TS, this ratio changed to 46/54% in favor of soluble COD components because of the transformation of complex high-molecular-weight organic compounds into simpler more biodegradable substances. As shown in Table 4.5, prolonged ultrasonic pretreatment at 100000 kJ/kg TS reflected a totally different COD structure than the domestic wastewater since it resulted in 19% of readily biodegradable COD (SS), 25% of rapidly hydrolysable COD (SH) and 10% of soluble inert (SI) COD fractions.

Eskicioglu et al. (2008) conducted his studies at such temperatures as 50, 75, 96, 120, 150 and 175^{0}C. SCOD/TCOD ratios increased to 9%, 12%, 21%, 24%, 28% and 35%. This ratio increases as the temperature goes up.

Eskicioglu et al. (2008) conducted his studies at such temperatures as 50,75 and 96^{0}C. SCOD / TCOD ratios increased from 0.06 to 0.14, 0.19 and 0.22. This ratio increases as the temperature goes up.

Qiang Yu et al,2010 in agreement with those of(Eskicioglu et al., 2007; Kennedy et al., 2007; Park et al., 2009). Energy has a significant effect on the SCOD/TCOD ratios. Because when the sludge was irradiated for the same contact time under different microwave energies, the sludge temperature was different, and at larger microwave energy, a higher sludge temperature was generated

Hang et al. (2006) conducted his studies at 72.5^{0}C. SCOD / TCOD ratios increased from 8% to 18%. This ratio increases as the temperature goes up.

Park et al. (2004)conducted his studies at 91^{0}C. SCOD/TCOD ratios increased from 19% to 21%. This ratio increases as the temperature goes up as shown in Figure 4.5 and 4.6

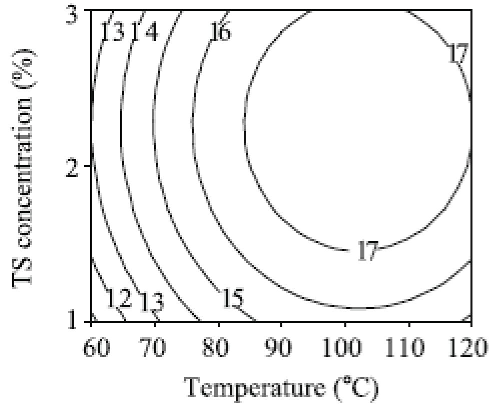


Figure 4.5: Two-dimensional contour plots of the quadratic model for solubilization degree of waste activated sludge with respect to pretreatment conditions of output power, target temperature, and solid concentration within the design boundaries.(Park et al,2009).

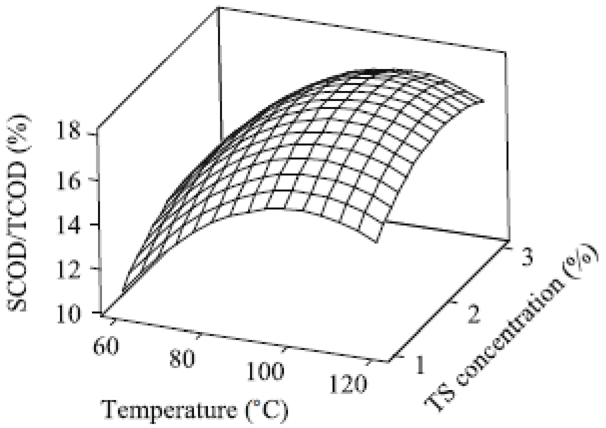


Figure 4.6: Three-dimensional contour plots of the quadratic model for solubilization degree of waste activated sludge with respect to pretreatment conditions of output power, target temperature, and solid concentration within the design boundaries. (Park et al,2009).

Two- and three-dimensional response surfaces of the quadratic model for the solubilization degree of waste activated sludge (Figures 4.5, 4.6) showed that the optimum condition was inside the design boundary only for temperature and TS concentration. At all temperatures and TS concentrations within the design boundaries solubilization degree increased constantly as power decreased.

C. Bougrier et al. (2004) conducted his studies 135^0C and $190\ ^0$C. According to his study, thermal treatment at 190 ◦C was more efficient than treatment at 135 ◦C in terms of total COD, lipids, carbohydrates and proteinvremovals and methane production. After treatment COD solubilisation was 34% and 46% at 135 ◦C and 190 ◦C. Li and Noike showed that solubilisation of 60% after a 170 ◦C pre-treatment. Valo et al. was reported in his study, soluble COD was initially 7% of total COD and reached 32% after 75 days of storage. Refloculation of treated sludge as soluble COD was around 44% (135 ◦C) and 60% (190 ◦C).

Saha et al.2011, investigate the effect of pretreatment intensity (MW temperature). For MW 50, MW 75, MW 100, MW 125, MW 150, and MW 175 samples, SCOD/TCOD ratios of WAS samples increased from 5.0 ± 0.3% to 11 ± 0.6%, 16 ± 0.8%, 26 ± 1.3%, 31 ± 1.6%, 35 ± 1.8% and 41 ± 2.1%. For MW temperatures 50, 75, 96, 120, 150,175

°C, these results corresponded to 2.2 ± 0.1, 3.2 ± 0.3, 5.2 ± 0.2, 6.2 ± 0.2, 7.0 ± 0.1 and, 8.2 ± 0.4 fold increases in the SCOD/TCOD ratios.

Thermal treatment at 190 ◦C was more efficient than treatment at 135 ◦C in terms of total COD, lipids, carbohydrates and protein removals and methane production. COD solubilisation was 34% and 46% after treatment at 135 ◦C and 190 ◦C, respectively, whereas, for example, a solubilisation of 60% after a 170 ◦C pre-treatment was reported by Li and Noike and Valo et al. . Soluble COD was initially 7% of total COD and reached 32% after 75 days of storage. In the same time, treated sludge underwent "refloculation" as soluble COD was around 44% (135 ◦C) and 60% (190 ◦C) as shown in Figure 4.7.

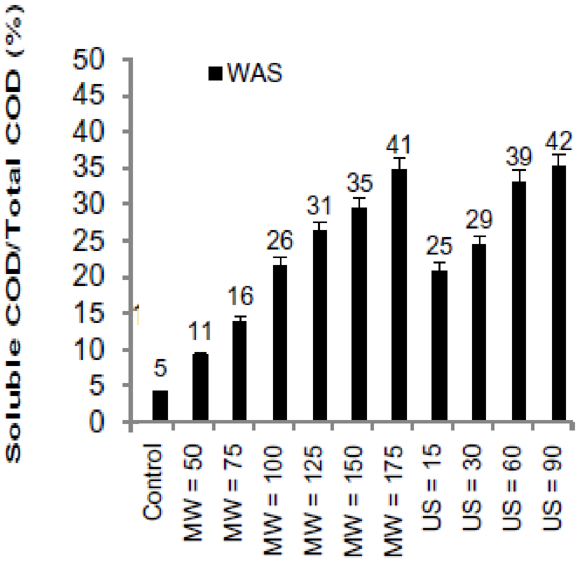
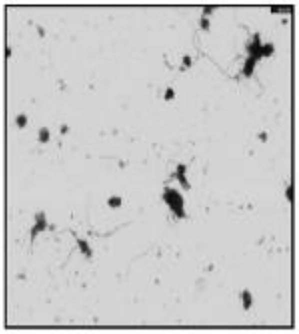
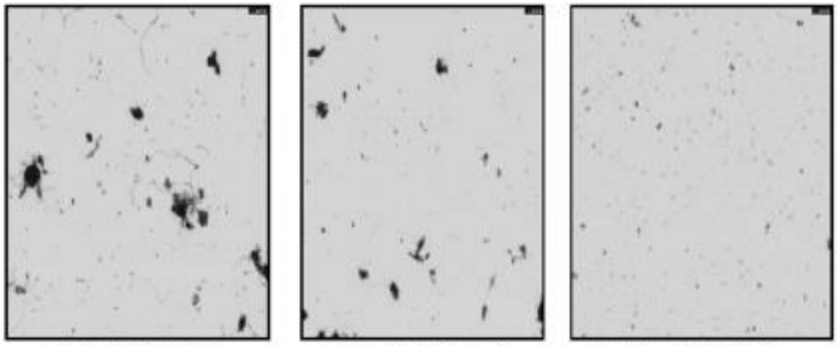


Fig. 4.7 Solubilization of MW, US pre-treated WAS samples (data represent the mean and error bars represent absolute difference between mean and duplicates).

As seen in in the figure 4.7., when the MW temperature is increasing, SCOD/TCOD ratio increases.



Control (WAS)



MW 50 (WAS) MW 100 (WAS) MW 175 (WAS)

Fig. 4.8 Images of sludge flocs in WAS before, after MW pretreatment.

As seen in Figure 4.8 above, MW pretreatment has significant efficiency on the sludge flocks solubilisation. According to pictures, flocks seems more solubiliz.ed during the temperature increasing. Also, the pictures explain the effect of MW pretreatment. Disintegration of flocks can easily observed. Cells are broken and the more solubilized.

All investigations are compared to my study, the same results are observed. MW pretreatment has significant effect on the floc disintegration. Also, when the temperature and time increase, the SCOD/TCOD ratio, SCOD, DD value increase. These results are very positive for pretreatment of sludge.

5. CONCLUSION

This study experimentally investigated the individual effects of ultrasonication and microwave irradiation processes on the disintegration of municipal WAS. In the light of the observations presented and discussed in the previous sections, the concluding remarks of the study may be outlined as follows:

(i) The results of sonication experiments pointed out that the increase in SCOD release (i.e. sludge disintegration degree) exposed an increasing trend with prolonging the specific energy input and ultrasonic density at all TS levels tested. The disintegration of WAS by ultrasonic pretreatment involved two stages where the initial rapid phase at relatively low specific energy input values was followed by a subsequent slower one for energy dosages higher than 30000 kJ/kg TS. A value of 1.5 W/mL was determined as the optimum ultrasonic density since the incremental disintegration rates were negligible. Sonication exhibited similar disintegration efficiencies for the studied WAS samples, regardless of different sampling periods.

(ii) Raising up to the temperature higher than the boiling point enhanced the disintegration degree of microwave pretreatment throughout the investigated TS range; whereas at a constant temperature, microwave heating of WAS at three different TS concentrations yielded almost similar disintegration performances. The improvement in the microwave irradiation efficiency declined by elevating the treatment temperature from 175 to 190^{o}C. For all TS contents applied, no significant difference in solubilization degree was obtained at the exposure times above 10 minutes. The disintegration rates of the examined WAS samples remained consistent despite different sampling dates.

(iii) Both ultrasonication and microwave irradiation achieved SS and VSS removal efficiencies in the range of 22–37% coupled with lower TS and VS reductions of only up to 5%, generating totally different profiles in terms of solid particles as compared with raw WAS samples. The initial COD levels did not appreciably change during the applied pretreatment processes. Sonicated WAS at the specific energy input of 30000 kJ/kg TS provided a COD solubilization rate (25–26%) very similar to that of the irradiated counterpart at the microwave temperature and contact time of 175^{o}C and 10 minutes, respectively. Variations in DOC release under selected operating conditions revealed similar patterns as those of SCOD. Disintegration by ultrasonication and microwave irradiation increased the concentrations of nitrogen and phosphorus species in the liquid phase.

(iv) PSD-based COD fractionation by sequential filtration / ultrafiltration proved to be a useful tool for a better interpretation of the impact of ultrasonication and microwave irradiation processes on WAS, as contrasted to the black-box type of evaluation based only on influent and effluent levels. The most pronounced effect of ultrasonic pretreatment on WAS samples was the partial dissipation of the COD peak at the particulate range (>1600 nm) and the shifting of some of the organic constituents for this interval towards the soluble size portion (<2 nm). Sonication at higher specific energy values led to a gradual increase in the COD content at the soluble size interval of <2 nm (soluble range). The PSD-based COD profiles of the WAS liquids irradiated at the optimum temperature of 175^{o}C and exposure time of 10 minutes revealed similar size distribution characteristics as those of their sonicated counterparts at 30000 kJ/kg TS.

(v) The OUR profiles obtained from respirometric analyses indicated that both concentrations and percentage contributions from soluble COD components increased with specific energy input during the ultrasonic treatment of WAS samples. COD fractionation patterns of sonicated (ES=30000 kJ/kg TS) and irradiated (T=175^{o}C, t=10') WAS liquids were quite similar to those of domestic sewage as they included basically the same COD fractions with different biodegradation characteristics.

(vi) An interesting issue for further research would be to evaluate the impact of ultrasonication and microwave irradiation processes on the PSD of other significant parameters reflecting the extracellular and intracellular constituents of disintegrated WAS portions; namely, proteins, carbohydrates and lipids. Performing a comprehensive study at pilot scale and conducting a techno-economic feasibility analysis may provide a deeper insight both in the interpretation and scaling up of the results.

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- Tuzla Foods Factory(BESAN)
- Çorlu Foods Factory
- Rize Lipton Tea Factories (DOSAN)
- HPC Factory
- Logistic Areas

- For 3rd Party Manufacturing

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  - Main responsibilities of work for Safety Programs:

- Supporting developing a behavioral safety system (Be Safe program) in all factories and logistic areas at Turkey. Providing required support and doing regular controls.

- Doing audits and inspections to act as Corporate SHE auditor for manufacturing sites within Turkey to check compliance with Unilever Standards and Turkish Regulations.

- Following and checking implementation and status of safety programs in all factories and logistic areas

- Following and checking SHE performance indicators and reports in all areas.

- Supporting the investigation and reporting of safety incident reports, conduct incident investigations and to check completion necessary corrective actions

- Supporting maintaining full compliance with all Unilever framework standards and Legal requirements about SHE issue.

- Participating external and internal audits, coordinating necessary activities and informing relevant people in the organization
- Supporting WCM (World Class Manufacturing) Program within sites

- Following and checking Global Unilever Safety Program within sites aligned with Be Safe & WCM in sites.

- Following and checking Risk Analysis Status Update, Best Practice & Lessons Learnt Sharing for all Turkey sites.

- In order to increase the SHE awareness among the employees to conduct Safety communication campaigns for all Turkey sites using all visual or written communication channels.

- To Deploy and develop the global/cluster SHE strategy, policy and standards in all sites to achieve excellent sustainable results

- Drive safety risk assessment tools and develop/implement appropriate controls

- Develop and deploy internal SHE auditing and inspection systems , participate in audits of other Unilever organizations as required

- Determining of dust explosion risk and to conduct/support proactive actions against Dust Explosion to compliance with ATEX necessities.

- Following /checking /supporting Risk analyses& safety programs of 3rd Party Manufacturers

- Doing audits and inspections to act as Unilever Corporate SHE auditor for 3rd Party Manufacturing sites within Turkey to check compliance with Unilever Standards and Turkish Regulations.

- Following and checking safety performance indicators and reports for 3rd Party Manufacturing sites.

  - Main responsibilities of work for Safe Travel Program:

- Developing Safe Travel Program in all Turkey. Providing required support and doing regular controls within sites.

- Doing audits and inspections to act as Corporate SHE auditor for manufacturing and logistic sites within Turkey to check compliance with Unilever Safe Travel Standards and Turkish Regulations.

- Following and checking implementation and status of Safe Travel Program in all factories and logistic areas

- Supporting the investigation and reporting of safety incident reports related to safe travel issues to conduct incident investigations and to check completion necessary corrective actions

- In order to increase the Safe Travel awareness among the employees to conduct Safety communication campaigns for all Turkey sites using all visual or written communication channels.

- Conducting and Checking training programs for the employees and ensure the completion of trainings for all drivers.

PUBLICATIONS/PRESENTATIONS ON THE THESIS

Dogruel S., Ozgen Asli S., 2016: Effect of ultrasonic and microwave disintegration on physico-chemical and biodegradation characteristics of waste-activated sludge *Taylor and Francis June 13,2016*